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A theoretical study on vibrational levels of photoelectron spectra by the harmonic oscillator approximation method. (Handbook)

Kouichi Takeshita
Faculty of Bioindustry, Tokyo University of Agriculture, Abashiri, Hokkaido 099-24, Japan

Introduction

The photoelectron (PE) spectrum provide us the information such as the ionization energies and the the vibrational levels of the ionic states. The experimental investigation of the ionic states by the photoelectron (PE) spectrum had been done by many workers from 1860's to 1970's. A large number of data of PE spectra and handbooks have been published (Turner et al. 1970, Cvitas et al. 1977, Kimura et al. 1981, Bieri et al. 1981, Niessen et al. 1982, Bieri et al. 1980, Klasinc et al 1982, Niessen et al. 1980, Bieri et al. 1980, and Åsbrink et al. 1980). The assignment of the electronic states of PE spectrum have been assisted by a theoretical calculation of the vertical ionization energy using the Koopmans theorem, SCF or configuration interaction (CI) method (Turner et al. 1970, Kimura et al. 1981, Bieri et al. 1981, Niessen et al. 1982, Bieri et al. 1980, Niessen et al. 1980, and Bieri et al. 1980). In those calculations, the molecular structure has been used that of the ground state. Some PE spectra show well resolved vibrational structure. Many workers had been attempted to assign the vibrational modes. The assignment of the vibrational levels have been done by the use of the information of the vibrational frequencies of the ground state or the comparison with the spectrum of the deuterated spaces.

As a molecule is ionized, the equilibrium molecular structure, the vibrational frequencies and the character of the vibrational modes are changed from those of the ground state. The PE spectrum reflects these change. It is, therefore, interesting to investigate the PE spectrum associated with the change in the equilibrium molecular structure and

vibrational mode by ionization. In 1860's and early 1870's, it is not so easy to calculate the optimized molecular structure of polyatomic molecules by means of theoretical method. From the last 1970's, the development of the gradient technique have made possible to calculate the optimized molecular structure and the vibrational frequencies easily (Pulay 1977). However, no systematic ab initio investigation of the equilibrium molecular structure and the vibrational levels of the ionic states has been reported.

In this work, we calculated the equilibrium molecular structure of the ground and ionic states of the thirty organic compounds: Methylene fluoride (CH_2F_2), Methylene cloride (CH_2Cl_2), Dichlorodifluoromethane (CF_2Cl_2), Methylene bromide (CH_2Br_2), Ethylene

Table 1.1 Symmetry and electronic configuration of the ground state.

Molecule	Point group	Electronic configuration
CH_2F_2	C_{2v}	$\ldots(1a_2)^2(4b_1)^2(6a_1)^2(2b_2)^2$
CH_2Cl_2	C_{2v}	$\ldots(2a_2)^2(9a_1)^2(7b_1)^2(3b_2)^2$
CF_2Cl_2	C_{2v}	$\ldots(12a_1)^2(6b_1)^2(3a_2)^2(8b_2)^2$
CH_2Br_2	C_{2v}	$\ldots(15a_1)^2(5a_2)^2(6b_1)^2(13b_2)^2$
C_2H_4	D_{2h}	$\ldots(2b_{1u})^2(1b_{3u})^2(3a_g)^2(1b_{2g})^2(1b_{2u})^2$
C_2F_4	D_{2h}	$\ldots(1b_{3g})^2(5b_{1u})^2(1b_{1g})^2(1a_u)^2(4b_{3u})^2(4b_{2g})^2(6a_g)^2(2b_{2u})^2$
C_2Cl_4	D_{2h}	$\ldots(2b_{3g})^2(9a_g)^2(8b_{1u})^2(2b_{1g})^2(7b_{3u})^2(2a_u)^2(7b_{2g})^2(3b_{2u})^2$
trans-$C_2H_2F_2$	C_{2h}	$\ldots(6a_g)^2(6b_u)^2(7a_g)^2(2a_u)^2$
cis-$C_2H_2F_2$	C_{2v}	$\ldots(1a_2)^2(6b_2)^2(7a_1)^2(2b_1)^2$
1,1-$C_2H_2F_2$	C_{2v}	$\ldots(4b_2)^2(8a_1)^2(5b_2)^2(2b_1)^2$
trans-$C_2H_2Cl_2$	C_{2h}	$\ldots(2b_g)^2(9b_u)^2(10a_g)^2(3a_u)^2$
cis-$C_2H_2Cl_2$	C_{2v}	$\ldots(2a_2)^2(10a_1)^2(9b_2)^2(3b_1)^2$
1,1-$C_2H_2Cl_2$	C_{2v}	$\ldots(11a_1)^2(2a_2)^2(8b_2)^2(3b_1)^2$
trans-C_4H_6	C_{2h}	$\ldots(6b_u)^2(7a_g)^2(1a_u)^2(1b_g)^2$
cis-C_4H_6	C_{2v}	$\ldots(6b_2)^2(7a_1)^2(1b_1)^2(1a_2)^2$
C_6H_6	D_{6h}	$\ldots(3a_{1g})^2(2b_{1u})^2(1b_{2u})^2(3e_{1u})^4(1a_{2u})^2(3e_{2g})^4(1e_{1g})^4$
C_4H_5N	C_{2v}	$\ldots(6b_2)^2(9a_1)^2(2b_1)^2(1a_2)^2$
C_4H_4O	C_{2v}	$\ldots(6b_2)^2(8a_1)^2(9a_1)^2(2b_1)^2(1a_2)^2$
C_4H_4S	C_{2v}	$\ldots(2b_1)^2(11a_1)^2(3b_1)^2(1a_2)^2$
CH_2O	C_{2v}	$\ldots(1b_2)^2(5a_1)^2(1b_1)^2(2b_2)^2$
CH_2O_2	C_s	$\ldots(2a'')^2(10a')^2$
C_2H_2O	C_{2v}	$\ldots(7a_1)^2(1b_2)^2(1b_1)^2(2b_2)^2(2b_1)^2$
$C_2H_2O_2$	C_{2h}	$\ldots(1a_u)^2(1b_g)^2(6b_u)^2(7a_g)^2$
C_2H_2	$D_{\infty h}$	$\ldots(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4$
C_4H_2	$D_{\infty h}$	$\ldots(4\sigma_u)^2(5\sigma_g)^2(1\pi_u)^4(1\pi_g)^4$
C_6H_2	$D_{\infty h}$	$\ldots(6\sigma_u)^2(7\sigma_g)^2(1\pi_u)^4(1\pi_g)^4(2\pi_u)^4$
C_2N_2	$D_{\infty h}$	$\ldots(4\sigma_u)^2(5\sigma_g)^2(1\pi_u)^4(1\pi_g)^4$
C_4N_2	$D_{\infty h}$	$\ldots(7\sigma_g)^2(1\pi_u)^4(1\pi_g)^4(2\pi_u)^4$
HCN	$C_{\infty h}$	$\ldots(5\sigma)^2(1\pi)^4$
HC_3N	$C_{\infty h}$	$\ldots(9\sigma)^2(1\pi)^4(2\pi)^4$

(C_2H_4), Tetrafluoroethylene (C_2F_4), Tetrachloroethylene (C_2Cl_4), trans-1,2-Difluoroethylene (trans-$C_2H_2F_2$), cis-1,2-Difluoroethylene (cis-$C_2H_2F_2$), 1,1-Difluoroethylene (1,1-$C_2H_2F_2$), trans-1,2-Dichloroethylene (trans-$C_2H_2Cl_2$), cis-1,2-Dichloroethylene (cis-$C_2H_2Cl_2$), 1,1-Dichloroethylene (1,1-$C_2H_2Cl_2$), trans-Butadiene (trans-C_4H_6), cis-Butadiene (cis-C_4H_6), Benzene (C_6H_6), Pyrrole (C_4H_5N), Furan (C_4H_4O), Thiophen (C_4SH_4), Formaldehyde (CH_2O), Formic acid (CH_2O_2), Ketene (C_2H_2O), Glyoxal ($C_2H_2O_2$), Acetylene (C_2H_2), Diacetylene (C_4H_2), Triacetylene (C_6H_2), Cyanogen (C_2N_2), Dicyanoacetylene (C_4N_2), Hydrogen cyanide (HCN) and Cyanoacetylene (C_3HN). Within the framework of the adiabatic approximation and the harmonic oscillator approximation, we calculated the harmonic force constant matrix elements over variables of totally symmetric distortion and vibrational frequencies of the totally symmetric modes. The intensity of the vibrational transitions are governed by the Franck-Condon factor (FCF). The FCF is a square of the overlap integrals between the vibrational wavefunction of the ground state and that of the ionic state. The technique of the calculation of the FCF have been developed (Duschinsky 1937, Sharp et al. 1964, Warshel et al. 1972, Faulkner et al. 1979, and Olbrich et al. 1983). We obtained the approximate theoretical intensity curve using the FCF.

Table 1.2 Correlation tables

D_{6h}	D_{2h}
a_{1g}	a_g
b_{1u}	b_{2u}
b_{2u}	b_{3u}
a_{2u}	b_{1u}
e_{1g}	$b_{2g} + b_{3g}$
e_{1u}	$b_{2u} + b_{3u}$
e_{2g}	$a_g + b_{1g}$

Molecule: C_6H_6

$D_{\infty h}$	D_{2h}
π_u	$b_{2u} + b_{3u}$
σ_g	a_g
σ_u	a_{1u}
π_g	$b_{2g} + b_{3g}$

Molecules: C_2H_2, C_4H_2, C_6H_2, C_2N_2 and C_4N_2

$C_{\infty h}$	C_{2v}
π	$b_1 + b_2$
σ	a_1

Molecules: HCN and HC_3N

1. Method of calculations

1.1 Electronic states and molecular structure

Table 1.1 shows the point group and the electronic configuration of the ground state for each molecule. For

Table 1.3 Electronic configuration of the ground state with the lower symmetric point group.

Molecule	Point group	Electronic configuration
C_6H_6	D_{2h}	$\ldots(3b_{3u})^2(5b_{2u})^2(4b_{3u})^2(1b_{1u})^2(6a_g)^2(3b_{1g})^2(1b_{2g})^2(1b_{3g})^2$
C_2H_2	D_{2h}	$\ldots(2b_{1u})^2(3a_g)^2(1b_{2u})^2(1b_{3u})^2$
C_4H_2	D_{2h}	$\ldots(4b_{1u})^2(5a_g)^2(1b_{2u})^2(1b_{3u})^2(1b_{2g})^2(1b_{3g})^2$
C_6H_2	D_{2h}	$\ldots(6b_{1u})^2(7a_g)^2(1b_{2u})^2(1b_{3u})^2(1b_{2g})^2(1b_{3g})^2(2b_{2u})^2(2b_{3u})^2$
C_2N_2	D_{2h}	$\ldots(4b_{1u})^2(5a_g)^2(1b_{2u})^2(1b_{3u})^2(1b_{2g})^2(1b_{3g})^2$
C_4N_2	D_{2h}	$\ldots(7a_g)^2(1b_{2u})^2(1b_{3u})^2(1b_{2g})^2(1b_{3g})^2(2b_{2u})^2(2b_{3u})^2$
HCN	C_{2v}	$\ldots(5a_1)^2(1b_1)^2(1b_2)^2$
HC_3N	C_{2v}	$\ldots(9a_1)^2(1b_1)^2(1b_2)^2(2b_1)^2(2b_2)^2$

Table 1.4 0-0 ionization energy of the first ionic state.

Molecule	State	SCF	SDCI	Obs.	SCF-Obs.	SDCI-Obs.
C_2H_4	$^2B_{3u}$	8.80	9.86	10.51[a]	-1.71	-0.65
C_2F_4	$^2B_{2u}$	8.99	9.33	10.14[b]	-1.15	-0.81
Trans-$C_2H_2F_2$	^2A_u	8.83	9.40	10.21[b]	-1.38	-0.81
Cis-$C_2H_2F_2$	$^2B_1$	8.84	9.41	10.22[b]	-1.38	-0.81
1,1-$C_2H_2F_2$	$^2B_1$	8.87	9.51	10.29[b]	-1.42	-0.78
C_2Cl_4	$^2B_{2u}$	8.59	8.79	9.34[c]	-0.75	-0.55
Trans-$C_2H_2Cl_2$	^2A_u	8.68	9.09	9.64[c]	-0.96	-0.55
Cis-$C_2H_2Cl_2$	$^2B_1$	8.69	9.10	9.65[c]	-0.96	-0.55
1,1-$C_2H_2Cl_2$	$^2B_1$	8.69	9.21	9.83[c]	-1.14	-0.62
Trans-C_4H_6	^2B_g	7.75	8.41	9.08[a]	-1.33	-0.67
C_6H_6	$^2B_{2g}$	8.09	8.69	9.24[a]	-1.15	-0.55
C_4H_5N	$^2A_2$	6.91	7.54	8.02[d]	-1.11	-0.48
C_4H_4O	$^2A_2$	7.61	8.24	8.83[d]	-1.22	-0.59
C_4H_4S	$^2A_2$	7.79	8.34	8.85[d]	-1.06	-0.51
CH_2O	$^2B_2$	9.51	10.33	10.88[a]	-1.37	-0.55
CH_2O_2	$^2A'$	9.61	10.47	11.33[a]	-1.72	-0.86
C_2H_2O	$^2B_1$	8.31	8.93	9.64[a]	-1.33	-0.71
C_2H_2	$^2\Pi_u$	9.79	10.72	11.40[a]	-1.61	-0.68
C_4H_2	$^2\Pi_g$	9.22	9.70	10.17[a]	-0.95	-0.47
C_2N_2	$^2\Pi_g$	12.74	13.06	13.36[a]	-0.62	-0.30
C_4N_2	$^2\Pi_u$	11.20	11.57	11.81[a]	-0.61	-0.24
HCN	$^2\Pi$	11.99	12.91	13.60[a]	-1.61	-0.69
HC_3N	$^2\Pi$	10.59	11.17	11.60[a]	-1.01	-0.43

[a]Reference 1. [b]Reference 4. [c]Reference 5. [d]Reference 7.

ionic states, we have interested in the lowest ionic states which belong to each symmetry type of the point group. In a case of the non-degenerate electronic states, we assume that the point group of the ionic state is the same as that of the ground state. For the degenerate

electronic states, we must consider the Jhan-Tellar effect for the non-linear molecules and the Renner-Teller effect for the linear molecules. The $^2E_{1g}$, $^2E_{1u}$ and $^2E_{2g}$ states of Benzen are degenerate electronic states. In this case, we took the lower D_{2h} symmetry point group in account. Table 1.2 gives the correlation table between the D_{6h} and D_{2h} symmetry. Table 1.3 shows the electronic configuration of the ground state with the D_{2h} point group. The $^2\Pi_u$ or $^2\Pi_g$ states of the linear molecules like as C_2H_2, C_4H_2, C_6H_2, C_2N_2, C_4N_2, HCN and C_3HN are degenerate electronic states. In this case, we must check the stability of the molecular structure of a linear molecule. However, we have not yet done at present. We can not use the $D_{\infty h}$ and $C_{\infty h}$ point groups for the linear molecules because of the restriction of our programing system. In stead of the $D_{\infty h}$ and $C_{\infty h}$ point groups, we use the D_{2h} and C_{2v} lower point group, respectively. Table 1.2 is the correlation tables of these groups. Table 1.3 shows the electronic configuration of the ground state with the D_{2h} or C_{2v} point groups.

1.2 Basis sets.

We used the basis sets of the MIDI-4-type prepared by Tatewaki and Huzinaga (Tatewaki et al. 1980, Sakai et al. 1981, and Sakai et al. 1982). These are augmented by one p-type polarization function for H and one d-type polarization function for C, N, O, F, S, Cl and Br. The exponents of the polarization function for H, C, N, O, F, S, Cl and Br are 0.68, 0.61 0.87, 1.16, 1.50, 0.46, 0.56 and 0.43, respectively.

1.3 Optimization of molecular structure

The gradient technique for the Roothaan's restricted Hartree - Fock (RHF) method was employed to determine the optimum molecular structure of the ground state and the lowest species of ion. We have also interested in the second $^2B_2$ state of CH_2O, and the $^2B_1$ and $^2B_2$ states of C_2H_2O. In this case, we determined the optimum molecular structure by the use of the Newton-Raphson method in which the force and force constant matrix elements were obtained numerically from the total energy. The total energy was calculated by means of a multi-reference single excitation configuration interaction (MRSCI) method.

1.4 Calculation of ionization energies

The single and double excitation configuration interaction (SDCI) method was employed to obtain more accurate ionization energies for the

estimation of VIEs and AIEs. For the ground state and the lowest species of ion, a single reference configuration of an SCF wavefunction of the respective state were employed. For the 2^2B_1 and 2^2B_2 states, the multi-reference configurations were used. In the SDCI method, singly and doubly excited configuration state functions (CSFs) were generated where the inner shells (K shell of C, N, O and F, K and L shells of S and Cl, and K, L and M shells of Br) were kept frozen. The generated CSFs were then restricted to the first order interacting space (Mclean et al. 1973). If the dimensions of the CI were too large, we have adopted a CSF selection process by the use of second-order perturbation theory. The threshold for the selection was 5 or 8 μ hartree. We have estimated the total energy including the contribution from the rejected CSFs by a second-order perturbation theory (Shoda et al. 1986) .

1.5 Various kinds of ionization energies

The vertical ionization energy (VIE) and adiabatic ionization energy (AIE) are defined, respectively:

$$VIE = E_V - E_G$$
$$AIE = E_I - E_G.$$

Figure 1 illustrates potential energy curves of the ground state and the ionized states of a diatomic molecule. The internal coordinates of S_G and S_I are defined as the optimized bond length of the ground and ionic states, respectively. The total electronic energies of E_G and E_I are those at S_G and S_I, respectively. The total energy of E_V is that of the ionic state at S_G.

The figure also indicates the various kinds of inonzation energies and the relation between the vibrational levels of the ionic state and observed spectrum. The observed VIE is usually determined from the position of the maximum intensity of spectrum. We describe the vibrational frequencies of the ground and ionic states as ν_G and ν_I, respectively. The zero-point vibrational energies of the ground state (VE_{Go}) and the ionic state (VE_{Io}) are, respectively:

$$VE_{Go} = 1/2 * h * \nu_G$$
$$VE_{Io} = 1/2 * h * \nu_I .$$

The ionization energy between the zero-point vibrational levels (0-0 IE) is corrected by VE_{Io} and VE_{Go} :

$$0\text{-}0\ IE = AIE + (VE_{Io} - VE_{Go}).$$

The transition energy from the zero-point vibrational level of the ground state to the k-th vibrational level of the ionic state (IE_K) is written as follows:

$$IE_K = 0\text{-}0\ IE + k * h * \nu_I .$$

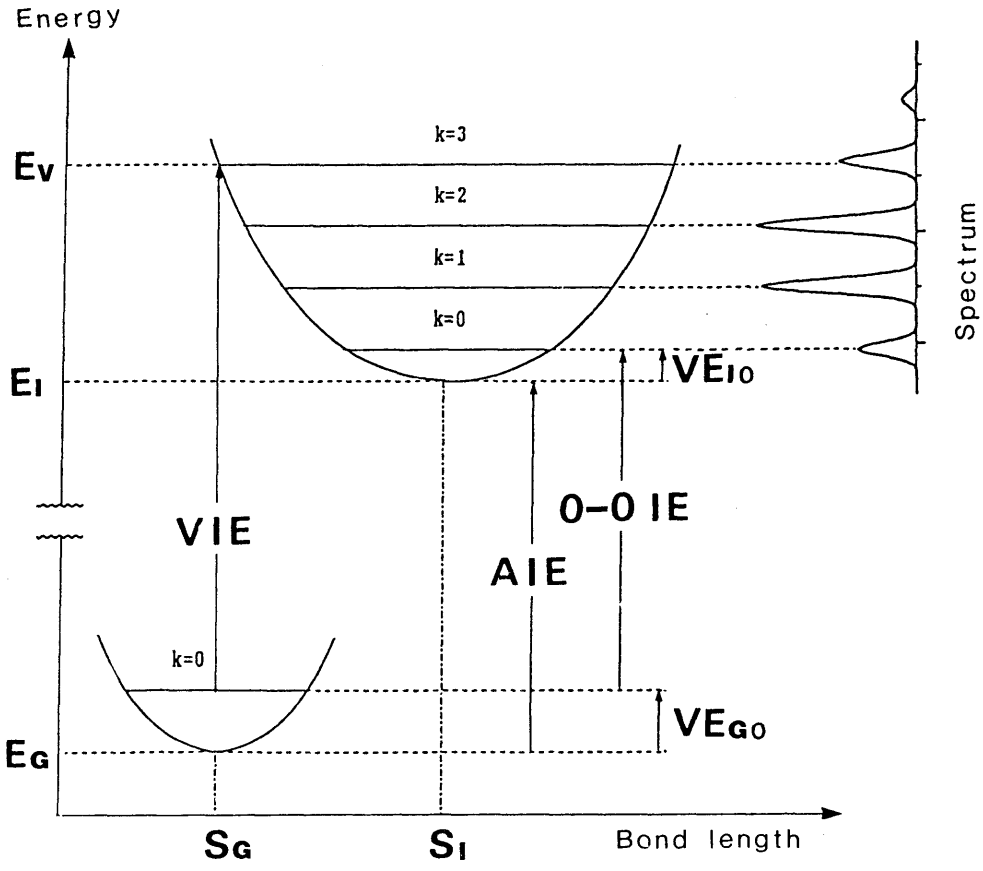

Fig. 1 Harmonic potential curve of a diatomic molecule and various kinds of ionization energies.

S_G and S_I : The internal coordinates of the optimized bond length of the ground and ionic states, respectively.

E_G : The total electronic energy of the ground state at S_G.

E_I : The total electronic energy of the ionic state at S_I.

E_V : The total electronic energy of the ionic state at S_G.

VIE : The vertical ionization energy.

AIE : The adiabatic ionizationn energy.

0-0 IE : The ionization energy between the zero-point vibrational levels.

VE_{GO} : The zero-point vibrational energy of the ground state.

VE_{IO} : The zero-point vibrational energy of the ionic state.

In a case of a polyatomic molecule, there are several vibrational modes. We denote the vibrational frequencies of the m-th mode of the ground and ionic states as ν_{Gm} and ν_{Im}, respectively. The zero-point vibrational energies (VE_{Go}, VE_{Io}) are

$$VE_{Go} = 1/2 * h \Sigma \nu_{Gm}$$
$$VE_{Io} = 1/2 * h \Sigma \nu_{Im} .$$

The K-th vibrational level is described by the set of the vibrational quantum numbers ($N_1, N_2, \ldots, N_n$). The vibrational energy of the K-th vibrational level (VE_K) from the zero-point vibrational level is

$$VE_K = h \Sigma N_m * \nu_{Im} .$$

The transition energy from the zero-point vibrational level of the ground state to the k-th vibrational level of the ionic state (IE_K) is

$$IE_K = 0\text{-}0\ IE + VE_K .$$

1.6 Totally symmetric internal coordinate and totally symmetric vibrational mode

The j-th totally symmetric internal coordinate (S_j) is defined by the use of the equivalent internal coordinates (q_i). If there are n equivalent internal coordinates, the totally symmetric internal coordinate is given by

$$S_j = n^{-1/2} * \Sigma q_i .$$

The totally symmetric vibrational mode is calculated by the use of the totally symmetric internal coordinates and totally symmetric force constant matrix elements.

1.7 Calculation of the vibrational frequency and Franck-Condon factor(FCF)

Within the framework of the harmonic oscillator approximation and by the use of the totally symmetric internal coordinate, the vibrational frequencies are obtained from the solution of the following secular equation:

$$| F - G^{-1}\lambda | = 0$$

where F is a totally symmetric force constant matrix and G is so called Willson's G matrix (Wilson et al. 1955). The totally symmetric harmonic force constant matrix elements of the ground state and the lowest species of ion were calculated by means of the gradient technique within the framework of the RHF method. The second derivative was estimated by numerical differentiation of the first derivative. For the second $^2B_2$ state of CH_2O, and the second $^2B_1$ and $^2B_2$ states of C_2H_2O, we estimated the totally symmetric

harmonic force constant matrix elements from a pointwise calculation of the energy obtained by the MRSCI method. The totally symmetric vibrational frequency (ν_m) is obtained from an eigenvalue (λ_m)

$$\nu_m = \lambda_m^{1/2} / (2\pi).$$

The relation between the vector of the totally symmetric normal coordinate (Q) and the vector of the geometrical distortion from the equilibrium structure (ΔS) is described by the use of the eigenvecter (L) of the secular equation

$$Q = L^{-1}\Delta S \quad .$$

The Franck-Condon factor of the transition from the zero-point vibrational level of the ground state to the K-th vibrational level of the ionic state ($FCF_{0\to K}$) is

$$FCF_{0\to K} = |\int \psi_G(Q_G,\lambda_G)\psi_I(Q_I,\lambda_I)d\tau|^2$$

where ψ_G and ψ_I are the vibrational wave functions of the ground and ionic states, Q_G and Q_I are the totally symmetric normal coordinates of the ground and ionic states, and λ_G and λ_I are the eigenvalues of the secular equations of the ground and ionic states, respectively.

This integral is estimated by means of Quasi-Random Number (QRN) method (Tanaka et al. 1974). In the estimation, we need the relational equation between the Q_I and Q_G. The relational equation is given by

$$Q_I = L_G^{-1}L_I Q_I + L_I^{-1}(S_I - S_G),$$

where S_G and S_I are the vectors of the equilibrium structure of the ground and ionic states by the use of the totally symmetric internal coordinate, and the L_G and L_I are the eigenvectors of the ground and ionic states, respectively. We calculated the FCFs only for the totally symmetric modes. The method of calculation of the FCF was the same as the one used in our previous study (Takeshita 1987).

1.8 Conventional potential energy distribution(%) and Classical half amplitude of the zero-point vibration

In order to characterize each normal mode, we calculated a conventional potential energy distribution(%) (Morino et al. 1952) and a classical half amplitude of the zero-point vibration. The conventional potential energy distribution(%) gives the relative contribution of each internal coordinate Sj to the normal coordinate Qi and is calculated by the following equation:

$$(F_{jj}^2 L_{ji} / \Sigma_j F_{jj}^2 L_{ji}) * 100 \quad .$$

The classical half amplitude of the zero-point vibration of the i-th

normal mode is obtained by

$$| Q_i | = (h\nu_i/\lambda_i)^{1/2} .$$

This is expanded by the use of the internal coordinate. The component of the j-th internal coordinate q_{ij} is

$$q_{ij} = n_j^{-1/2} * L_{ij} Q_i$$

where n_j is the number of the equivalent internal coordinates which compose the j-th totally symmetric internal coordinate.

1.9 Theoretical intensity curve

The theoretical intensity curve (TIC) is obtained by plotting the transition energy(TE_K) at X-axis and the Franck-Condon factor of the transition ($FCF_{0\to K}$) at Y-axis. In order to compare the theoretical intensity curve with observed spectrum, we use

2. Methylene fluoride CH_2F_2

Table 2.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C-H(ΔC-H)	C-F(ΔC-F)	H-C-H(ΔH-C-H)	F-C-F(ΔF-C-F)
$^1A_1$	1.087	1.335	112.45	108.47
Exp.[a]	1.091	1.358	112.1	108.23
$^2B_2$	1.185(+0.098)	1.246(-0.089)	77.66(-30.55)	117.00(+ 8.53)
$^2B_1$	1.082(-0.005)	1.382(-0.047)	121.66(+ 9.21)	83.53(-24.94)
$^2A_1$	1.119(+0.032)	1.335(0.000)	128.50(+16.05)	118.95(+10.48)
$^2A_2$	1.084(-0.003)	1.392(+0.057)	118.74(+ 6.29)	95.10(-13.37)

[a]Lide (1952).
Bond lengths are in angstroms, angles in degrees.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 2.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2B_2$	13.56	13.25	12.37	12.52	1.19	0.73
$^2B_1$	15.15	14.98	14.19	14.14	0.96	0.84
$^2A_1$	15.61	15.31	15.28	15.01	0.33	0.30
$^2A_2$	16.34	15.86	15.98	15.52	0.36	0.34

Total energies (a.u.) of $^1A_1$: -237.655549(SCF) and -238.134090(SDCI)

the Gaussian function of which area is determined by the Franck-Condon factor and band-width. A total intensity curve was obtained by using the assumption that the transition probability of the electronic part is the same for each ionic state.

1.10 Programming system

This work has been carried out by the use of the computer program system GRAMOL (Takeshita et al. 1981) for the gradient technique and the calculation of normal modes. GRAMOL includes the Program JAMOL3 of the RHF calculation part written by Kashiwagi et al (Kashiwagi et al. 1977). The calculations of the FCF and the theoretical intensity curve have done by the use of the program system FCF&TIC (Takeshita et al. 1990). The program MICA3 (Murakami et al. 1986) was used for the CI calculations.

2. Result

We show the optimized molecular structures of the ground and ionic states for each molecule (see tables 2.1 - 31.1). We also show the magnitude of the change in the geometry by ionization.

The ionization energies of VIE and AIE by the SCF and SDCI calculations are shown in tables from 2.2 to 31.2. The difference between VIE and AIE (Δ(VIE-AIE)) is also shown in the same

Table 2.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2B_2$	12.48	0.001
$^2B_1$	14.14	0.000
$^2A_1$	14.95	0.038
$^2A_2$	15.51	0.017

Table 2.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3	ν_4
$^1A_1$	3258	1659	1224	580
Obs.[a]	2963	1508	1079	532
$^2B_2$	2650	1288	1412	659
$^2B_1$	3336	1605	1192	608
$^2A_1$	2835	1449	984	479
$^2A_2$	3318	1624	1122	544

[a]Pace (1950).

Table 2.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3	ν_4
$^1A_1$	ΔC-H	99.4	0.1	0.0	0.1
	ΔC-F	0.3	2.3	84.9	11.2
	ΔH-C-H	0.1	96.3	0.0	0.1
	ΔF-C-F	0.2	1.3	15.1	88.6
$^2B_2$	ΔC-H	99.2	0.0	0.4	0.0
	ΔC-F	0.5	2.9	89.5	0.1
	ΔH-C-H	0.1	96.2	0.3	0.1
	ΔF-C-F	0.2	0.9	9.8	99.7
$^2B_1$	ΔC-H	96.8	1.5	0.0	0.4
	ΔC-F	2.0	73.4	8.9	8.0
	ΔH-C-H	0.3	14.0	90.3	1.3
	ΔF-C-F	1.0	11.3	0.8	90.4
$^2A_1$	ΔC-H	99.7	0.1	2.6	0.6
	ΔC-F	0.1	2.7	88.7	0.9
	ΔH-C-H	0.2	95.7	0.0	1.3
	ΔF-C-F	0.1	1.6	8.7	97.2
$^2A_2$	ΔC-H	99.3	0.0	0.2	0.0
	ΔC-F	0.4	1.3	86.5	2.2
	ΔH-C-H	0.1	98.0	1.4	0.0
	ΔF-C-F	0.1	0.7	11.9	97.8

Table 2.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3	ν_4
	ΔC-H	0.074	-0.002	0.000	-0.001
$^1A_1$	ΔC-F	-0.004	0.007	0.037	0.009
	ΔH-C-H	-0.4	11.2	0.1	0.2
	ΔF-C-F	0.5	-0.9	-2.6	4.1
	ΔC-H	0.083	-0.001	0.008	-0.003
$^2B_2$	ΔC-F	-0.007	-0.010	0.031	0.007
	ΔH-C-H	-0.8	10.2	4.6	-0.9
	ΔF-C-F	0.9	0.6	-2.5	4.5
	ΔC-H	0.072	0.001	0.003	-0.001
$^2B_1$	ΔC-F	-0.005	0.008	0.044	-0.001
	ΔH-C-H	-0.6	11.4	0.6	-0.3
	ΔF-C-F	0.3	-0.6	-1.9	3.9
	ΔC-H	0.078	0.002	-0.008	0.002
$^2A_1$	ΔC-F	-0.002	0.008	0.040	0.003
	ΔH-C-H	-0.6	11.7	-0.0	0.8
	ΔF-C-F	0.3	-1.2	-2.5	5.2
	ΔC-H	0.073	0.000	0.002	-0.001
$^2A_2$	ΔC-F	-0.005	0.006	0.043	0.004
	ΔH-C-H	-0.6	11.3	1.2	-0.0
	ΔF-C-F	0.4	-0.6	-2.3	4.0

Bond lengths are in angstroms, angles in degrees.

Table 2.7 Vibrational levels of the $^2B_1$ state.

IE	Vibrational levels				
12.81-12.83	(0 1 1 0),				(0 0 2 0)
12.97-13.00	(0 1 2 0),	(0 2 1 0),			(0 0 3 0)
13.14-13.18	(0 1 3 0),	(0 2 2 0),	(1 1 1 0),	(1 0 2 0),	(0 0 4 0)
13.32-13.35	(0 1 4 0),	(0 2 3 0),	(1 1 2 0),	(1 0 3 0),	(0 0 5 0)
13.48-13.51	(0 1 5 0),	(0 2 4 0),	(1 1 3 0),	(1 2 2 0),	(1 0 4 0)
13.65-13.69	(0 1 6 0),	(0 2 5 0),	(1 1 4 0),	(1 2 3 0),	(1 0 5 0)
13.81-13.85		(0 2 6 0),	(1 1 5 0),	(1 2 4 0),	(1 3 3 0)
13.99-14.02	(2 1 4 0),		(1 1 6 0),	(1 2 5 0),	(1 3 4 0)
14.16-14.19	(2 1 5 0),	(2 2 4 0),	(1 1 7 0),	(1 2 6 0),	(1 3 5 0)
14.33-14.35	(2 1 6 0),	(2 2 5 0),		(1 2 7 0),	(1 3 6 0)
14.49-14.53	(2 1 7 0),	(2 2 6 0),	(2 3 5 0),	(1 2 8 0),	(1 3 7 0)
14.67-14.70	(2 1 8 0),	(2 2 7 0),	(2 3 6 0),	(1 2 9 0),	(1 3 8 0)

0.005<FCF<0.022.

Table 2.8 Vibrational levels of the $^2B_2$ state.

IE	Vibrational levels
14.89	W(0 0 0 10)
14.97	W(0 0 0 11)
15.05	W(0 0 0 12)
15.12	W(0 0 0 13)
15.19	M(0 0 0 14), W(0 0 1 12)
15.27	M(0 0 0 15), W(0 0 1 13)
15.34	M(0 0 0 16), W(0 0 1 14)
15.40	M(0 0 0 17), W(0 0 1 15)
15.47	M(0 0 0 18), W(0 0 1 16)
15.55	M(0 0 0 19), W(0 0 1 17)
15.62	M(0 0 0 20), W(0 0 1 18)
15.70	M(0 0 0 21), W(0 0 1 19)
15.77	M(0 0 0 22), W(0 0 1 20)
15.87	W(0 0 0 23), W(0 0 1 21)
15.95	W(0 0 0 24), W(0 0 1 22)
16.02	W(0 0 0 25), W(0 0 1 23)
16.10	W(0 0 0 26)
16.17	W(0 0 0 27)

M:0.03<FCF<0.05 and W:0.01<FCF<0.03.

Table 2.9 Vibrational levels of the $^2A_1$ state.

IE	Vibrational levels			
14.95	M(0 0 0 0)			
15.01	S(0 0 0 1)			
15.07	S(0 0 0 2)			
15.13	S(0 0 0 3),	W(0 0 1 1),	M(0 1 0 0)	
15.19	M(0 0 0 4),		S(0 1 0 1)	
15.25	W(0 0 0 5),		S(0 1 0 2)	
15.31			M(0 1 0 3),	W(0 2 0 0)
15.37			M(0 1 0 4),	M(0 2 0 1)
15.43				M(0 2 0 2)
15.49				W(0 2 0 3)
15.55				W(0 2 0 4)

S:0.08<FCF<0.13, M:0.03<FCF<0.08 and W:0.01<FCF<0.03.

Table 2.10 Vibrational levels of the $^2A_2$ state.

IE	Vibrational levels
15.51	W(0 0 0 0)
15.58	M(0 0 0 1)
15.64-15.65	M(0 0 0 2), W(0 0 1 0)
15.71-15.72	M(0 0 0 3), M(0 0 1 1)
15.78	M(0 0 0 4), M(0 0 1 2), W(0 0 2 0)
15.85-15.86	W(0 0 0 5), M(0 0 1 3), M(0 0 2 1)
15.91-15.92	W(0 0 0 6), M(0 0 1 4), M(0 0 2 2)
15.99	M(0 0 1 5), M(0 0 2 3), W(0 0 3 1)
16.05-16.06	W(0 0 1 6), M(0 0 2 4), W(0 0 3 2)
16.12-16.13	W(0 0 1 7), W(0 0 2 5), W(0 0 3 3)
16.19-16.20	W(0 0 2 6), W(0 0 3 4)
16.26	W(0 0 2 7), W(0 0 3 5)
16.26	

M:0.03<FCF<0.08 and W:0.01<FCF<0.03.

3. Methylene cloride CH_2Cl_2

Table 3.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C-H (ΔC-H)	C-Cl (ΔC-Cl)	H-C-H(ΔH-C-H)	Cl-C-Cl(ΔCl-C-Cl)
$^1A_1$	1.082	1.775	111.74	112.55
Exp.[a]	1.085	1.767	112.1	112.2
$^2B_2$	1.083(+0.001)	1.780(+0.005)	117.25(+5.51)	90.84(-21.71)
$^2B_1$	1.113(+0.031)	1.707(-0.068)	102.24(-9.50)	118.58(+ 6.03)
$^2A_1$	1.092(+0.010)	1.765(-0.010)	119.01(+7.27)	121.10(+ 8.55)
$^2A_2$	1.083(+0.001)	1.794(+0.019)	114.05(+2.31)	103.79(- 8.76)

[a]Harmony et al. (1979).
Bond lengths are in angstroms, angles in degrees.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 3.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2B_2$	11.30	11.30	10.73	10.79	0.57	0.51
$^2B_1$	11.49	11.34	11.36	11.20	0.13	0.13
$^2A_1$	12.04	11.95	11.91	11.81	0.13	0.14
$^2A_2$	12.11	11.98	12.01	11.91	0.10	0.07

Total energies (a.u.) of $^1A_1$: -956.968094(SCF) and -957.364785(SDCI).

Table 3.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2B_2$	10.80	0.000
$^2B_1$	11.16	0.200
$^2A_1$	11.78	0.096
$^2A_2$	11.90	0.108

Table 3.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3	ν_4
$^1A_1$	3305	1572	755	304
Obs.[a]	2990	1424	706	286
$^2B_2$	3312	1547	807	330
$^2B_1$	2963	1186	721	337
$^2A_1$	3171	1458	640	310
$^2A_2$	3301	1566	744	303

[a]The Chemical Society of Japan (1966).

Table 3.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3	ν_4
$^1A_1$	ΔC-H	99.7	0.3	0.0	0.1
	ΔC-Cl	0.2	0.8	79.7	14.0
	ΔH-C-H	0.1	98.4	1.3	0.0
	ΔCl-C-Cl	0.1	0.5	19.0	86.0
$^2B_2$	ΔC-H	99.6	0.1	0.2	0.0
	ΔC-Cl	0.3	1.4	83.5	1.6
	ΔH-C-H	0.1	98.1	1.3	0.3
	ΔCl-C-Cl	0.1	0.5	15.0	98.1
$^2B_1$	ΔC-H	99.7	3.3	1.1	0.1
	ΔC-Cl	0.2	0.1	66.9	10.2
	ΔH-C-H	0.0	96.6	14.9	0.2
	ΔCl-C-Cl	0.1	0.0	17.2	89.6
$^2A_1$	ΔC-H	99.7	0.0	0.1	0.0
	ΔC-Cl	0.1	0.9	80.4	7.2
	ΔH-C-H	0.1	98.5	0.5	0.1
	ΔCl-C-Cl	0.1	0.7	19.0	92.7
$^2A_2$	ΔC-H	99.7	0.2	0.1	0.0
	ΔC-Cl	0.2	0.8	80.3	7.7
	ΔH-C-H	0.1	98.7	2.4	0.1
	ΔCl-C-Cl	0.1	0.4	17.3	92.2

Table 3.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3	ν_4
	ΔC-H	0.073	-0.003	0.001	-0.001
$^1A_1$	ΔC-Cl	-0.004	0.006	0.040	0.010
	ΔH-C-H	-0.4	11.5	0.9	-0.0
	ΔCl-C-Cl	0.4	-0.6	-2.8	3.4
	ΔC-H	0.073	-0.001	0.002	-0.000
$^2B_2$	ΔC-Cl	-0.004	0.007	0.046	0.003
	ΔH-C-H	-0.5	11.6	1.1	-0.3
	ΔCl-C-Cl	0.3	-0.5	-2.3	3.1
	ΔC-H	0.077	-0.009	-0.005	-0.001
$^2B_1$	ΔC-Cl	-0.003	-0.002	0.040	0.008
	ΔH-C-H	0.0	12.3	4.8	-0.2
	ΔCl-C-Cl	0.4	-0.1	-3.1	3.5
	ΔC-H	0.074	-0.000	-0.001	0.000
$^2A_1$	ΔC-Cl	-0.003	0.006	0.041	0.007
	ΔH-C-H	-0.5	11.9	0.6	0.1
	ΔCl-C-Cl	0.3	-0.7	-2.9	3.8
	ΔC-H	0.073	-0.002	0.001	-0.000
$^2A_2$	ΔC-Cl	-0.004	0.006	0.044	0.007
	ΔH-C-H	-0.4	11.5	1.3	-0.1
	ΔCl-C-Cl	0.3	-0.5	-2.6	3.3

Bond lengths are in angstroms, angles in degrees.

Table 3.7 Vibrational levels of the $^2B_2$ state.

IE	Vibrational levels
11.29	W(0 0 0 12)
11.33	W(0 0 0 13)
11.37	W(0 0 0 14)
11.41	M(0 0 0 15)
11.45	M(0 0 0 16)
11.49	M(0 0 0 17)
11.54	M(0 0 0 18)
11.58	M(0 0 0 19)
11.62	M(0 0 0 20)
11.66-11.68	M(0 0 0 21), W(0 0 1 19)
11.70-11.72	M(0 0 0 22), W(0 0 1 20)
11.74-11.76	M(0 0 0 23), W(0 0 1 21)
11.78-11.80	M(0 0 0 24), W(0 0 1 22)
11.82-11.84	M(0 0 0 25), W(0 0 1 23)
11.86-11.88	M(0 0 0 26), W(0 0 1 24)
11.90	M(0 0 0 27)
11.95	W(0 0 0 28)
11.99	W(0 0 0 29)
12.03	W(0 0 0 30)

M:0.03<FCF<0.06 and W:0.01<FCF<0.03.

Table 3.8 Vibrational levels of the $^2B_1$ state.

IE	Vibrational levels
11.16	S(0 0 0 0)
11.25	S(0 0 1 0)
11.34	S(0 0 2 0)
11.43	S(0 0 3 0)
11.52-11.53	M(0 0 4 0), W(1 0 0 0)
11.61-11.62	W(0 0 5 0), W(1 0 1 0)
11.71	W(1 0 2 0)

S:0.10<FCF<0.31, M:0.03<FCF<0.05 and W:0.009<FCF<0.03.

Table 3.9 Vibrational levels of the $^2A_1$ state.

IE	Vibrational levels			
11.78	S(0 0 0 0)			
11.82	S(0 0 0 1)			
11.86	S(0 0 0 2),	W(0 0 1 0)		
11.89-11.90	S(0 0 0 3),	M(0 0 1 1)		
11.93-11.94	M(0 0 0 4),	M(0 0 1 2)		
11.96-11.98		W(0 0 1 3),	W(0 1 0 0)	
12.00			M(0 1 0 1)	
12.04			M(0 1 0 2)	
12.08			W(0 1 0 3)	

S:0.09<FCF<0.20, M:0.03<FCF<0.05 and W:0.01<FCF<0.03.

Table 3.10 Vibrational levels of the $^2A_2$ state.

IE	Vibrational levels	
11.90	S(0 0 0 0)	
11.94	S(0 0 0 1)	
11.97	S(0 0 0 2)	
11.99		M(0 0 1 0)
12.01	S(0 0 0 3)	
12.03		M(0 0 1 1)
12.05	M(0 0 0 4)	
12.07		M(0 0 1 2)
12.09	M(0 0 0 5)	
12.10		M(0 0 1 3)
12.13	W(0 0 0 6)	
12.14		W(0 0 1 4)
12.18		W(0 0 1 5)

S:0.10<FCF<0.20, M:0.03<FCF<0.07 and W:0.01<FCF<0.03.

4. Dichlorodifluoromethane CF_2Cl_2

Table 4.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C-F (ΔC-F)	C-Cl (ΔC-Cl)	F-C-F (ΔF-C-F)	Cl-C-Cl(ΔCl-C-Cl)
$^1A_1$	1.309	1.759	107.96	111.69
Exp.[a]	1.345	1.745	106.3	112.5
$^2B_2$	1.266(-0.043)	1.785(+0.026)	113.17(+5.21)	91.32(-20.37)
$^2A_2$	1.275(-0.034)	1.789(+0.030)	112.54(+4.58)	104.54(- 7.15)
$^2B_1$	1.277(-0.032)	1.807(+0.048)	113.32(+5.36)	111.37(- 0.32)
$^2A_1$	1.281(-0.028)	1.819(+0.060)	112.17(+4.21)	113.68(+ 1.99)

[a]Takeo et al. (1977).
Bond lengths are in angstroms, angles in degrees.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 4.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2B_2$	12.12	12.06	11.61	11.66	0.51	0.40
$^2A_2$	12.70	12.55	12.56	12.47	0.14	0.08
$^2B_1$	13.26	13.08	13.15	13.00	0.11	0.08
$^2A_1$	13.58	13.44	13.45	13.31	0.13	0.13

Total energies (a.u.) of $^1A_1$: -1154.471619(SCF) and -1155.156970(SDCI).

Table 4.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2B_2$	11.67	0.000
$^2A_2$	12.47	0.198
$^2B_1$	13.00	0.309
$^2A_1$	13.31	0.120

Table 4.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3	ν_4
$^1A_1$	1266	730	497	285
Obs.	1102	667	469	262
$^2B_2$	1322	753	498	303
$^2A_2$	1301	731	477	268
$^2B_1$	1271	712	454	276
$^2A_1$	1253	702	453	282

[a]Giorgianni et al. (1979).

Table 4.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3	ν_4
	ΔC-F	65.7	13.6	0.4	0.1
$^1A_1$	ΔC-Cl	12.4	34.6	61.6	2.3
	ΔF-C-F	15.7	43.5	38.0	6.8
	ΔCl-C-Cl	6.2	8.4	0.0	90.8
	ΔC-F	66.7	8.5	0.5	0.2
$^2B_2$	ΔC-Cl	14.6	40.8	60.7	1.3
	ΔF-C-F	13.9	43.1	38.7	3.0
	ΔCl-C-Cl	4.8	7.6	0.1	95.6
	ΔC-F	70.2	8.0	1.0	0.1
$^2A_2$	ΔC-Cl	11.3	34.8	68.6	0.0
	ΔF-C-F	14.1	49.5	30.4	4.5
	ΔCl-C-Cl	4.4	7.7	0.1	95.4
	ΔC-F	72.2	6.6	1.8	0.2
$^2B_1$	ΔC-Cl	8.8	30.1	73.9	0.1
	ΔF-C-F	14.0	53.6	24.0	5.0
	ΔCl-C-Cl	5.0	9.7	0.3	94.8
	ΔC-F	73.4	5.0	2.4	0.1
$^2A_1$	ΔC-Cl	7.3	24.4	81.4	0.5
	ΔF-C-F	14.1	59.7	15.1	6.4
	ΔCl-C-Cl	5.3	10.9	1.1	93.0

Table 4.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3	ν_4
	ΔC-F	-0.038	0.010	0.002	-0.000
$^1A_1$	ΔC-Cl	0.023	0.023	-0.025	0.004
	ΔF-C-F	3.0	3.1	2.3	0.8
	ΔCl-C-Cl	-2.1	-1.5	0.1	3.1
	ΔC-F	-0.036	0.008	0.002	0.001
$^2B_2$	ΔC-Cl	0.026	0.029	-0.025	-0.003
	ΔF-C-F	3.0	3.4	2.3	0.6
	ΔCl-C-Cl	-1.7	-1.4	-0.1	3.0
	ΔC-F	-0.036	0.008	0.002	0.001
$^2A_2$	ΔC-Cl	0.023	0.026	-0.028	-0.000
	ΔF-C-F	3.0	3.6	2.1	0.6
	ΔCl-C-Cl	-1.8	-1.6	0.1	3.2
	ΔC-F	-0.037	0.007	0.003	0.001
$^2B_1$	ΔC-Cl	0.021	0.025	-0.030	0.001
	ΔF-C-F	3.0	3.8	1.9	0.7
	ΔCl-C-Cl	-1.9	-1.7	0.2	3.2
	ΔC-F	-0.037	0.006	0.003	0.000
$^2A_1$	ΔC-Cl	0.019	0.023	-0.032	0.002
	ΔF-C-F	2.9	3.9	1.5	0.8
	ΔCl-C-Cl	-1.9	-1.8	0.4	3.1

Bond lengths are in angstroms, angles in degrees.

Table 4.7 Vibrational levels of the $^2B_2$ state.

IE	Vibrational levels				
12.05	(0 0 0 10)				
12.08	(0 0 0 11)				
12.11		(0 0 1 10)			
12.12	(0 0 0 12)				
12.14		(0 0 1 11)			
12.16	(0 0 0 13)				
12.18		(0 0 1 12)			
12.20	(0 0 0 14)				
12.22		(0 0 1 13)			
12.23	(0 0 0 15)				
12.26		(0 0 1 14)			
12.25			(1 0 0 11)		
12.27	(0 0 0 16)				
12.28			(1 0 0 12)		
12.30		(0 0 1 15)			
12.31	(0 0 0 17)				
12.32			(1 0 0 13),	(0 0 2 14)	
12.33		(0 0 1 16)			
12.35	(0 0 0 18),				(1 0 1 12)
12.36			(1 0 0 14),	(0 0 2 15)	
12.37		(0 0 1 17)			
12.38	(0 0 0 19)				(1 0 1 13)
12.39				(0 0 2 16)	
12.40			(1 0 0 15)		
12.41		(0 0 1 18)			
12.42	(0 0 0 20),				(1 0 1 14)
12.43			(1 0 0 16),	(0 0 2 17)	
12.45		(0 0 1 19)			
12.46	(0 0 0 21),				(1 0 1 15)
12.47			(1 0 0 17),	(0 0 2 18)	
12.48		(0 0 1 20),			(1 0 1 16)
12.50	(0 0 0 22)				
12.51			(1 0 0 18),	(0 0 2 19)	
12.52		(0 0 1 21)			
12.53					(1 0 1 17)
12.55			(1 0 0 19)		
12.56	(1 0 2 16),	(0 0 1 22)			
12.57					(1 0 1 18)
12.59			(1 0 0 20)		
12.60	(1 0 2 17)				
12.61					(1 0 1 19)
12.62			(1 0 0 21)		
12.63	(1 0 2 18)				
12.65					(1 0 1 20)
12.69					(1 0 1 21)

0.005<FCF<0.015.

Table 4.8 Vibrational levels of the $^2A_2$ state.

IE	Vibrational levels
12.47	S(0 0 0 0)
12.50	S(0 0 0 1)
12.54	S(0 0 0 2)
12.56	M(0 1 0 0)
12.57	W(0 0 0 3)
12.59	M(0 1 0 1)
12.63	W(0 1 0 2), S(1 0 0 0)
12.66	S(1 0 0 1)
12.70	M(1 0 0 2)
12.72	W(1 1 0 0)
12.73	W(1 0 0 3)
12.76	W(1 1 0 1)
12.79	W(2 0 0 0)
12.83	W(2 0 0 1)
12.86	W(2 0 0 2)

S:0.07<FCF<0.20, M:0.03<FCF<0.05 and W:0.01<0.03.

Table 4.9 Vibrational levels of the $^2B_1$ state.

IE	Vibrational levels
13.00	S(0 0 0 0)
13.03	S(0 0 0 1)
13.06	W(0 0 1 0)
13.07	W(0 0 0 2)
13.09	S(0 1 0 0)
13.12	M(0 1 0 1)
13.16	S(1 0 0 0)
13.19	M(1 0 0 1)
13.23	W(1 0 0 2)
13.25	M(1 1 0 0)
13.28	W(1 1 0 1)
13.31	M(2 0 0 0)
13.35	W(2 0 0 1)

S:0.07<FCF<0.20, M:0.03<FCF<0.05 and W:0.01<0.03.

Table 4.10 Vibrational levels of the $^2A_1$ state.

IE	Vibrational levels				
13.31	S(0 0 0 0)				
13.35	S(0 0 0 1)				
13.37		M(0 0 1 0)			
13.38	S(0 0 0 2)				
13.40		M(0 0 1 1),	W(0 1 0 0)		
13.41	W(0 0 0 3)				
13.42				W(0 0 2 0)	
13.43			W(0 1 0 1)		
13.44		M(0 0 1 2)			
13.45	W(0 0 0 4),				W(0 1 1 0)
13.46				W(0 0 2 1)	
13.47	M(1 0 0 0),	W(0 0 1 3),	W(0 1 0 2)		
13.49					W(0 1 1 1)
13.50	M(1 0 0 1)				
13.52		W(1 0 1 0)			
13.53	W(1 0 0 2)				
13.56		W(1 0 1 1)			
13.57	W(1 0 0 3)				
13.59		W(1 0 1 2)			

S:0.07<FCF<0.20, M:0.03<FCF<0.05 and W:0.01<0.03.

5. Methylene bromide CH_2Br_2

Table 5.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C-H (ΔC-H)	C-Br (ΔC-Br)	H-C-H(ΔH-C-H)	Br-C-Br(ΔBr-C-Br)
$^1A_1$	1.082	1.919	111.59	113.79
Exp.[a]	1.080	1.931	113.8	112.5
$^2B_2$	1.083(+0.001)	1.918(-0.001)	116.39(+4.80)	92.98(-20.81)
$^2B_1$	1.101(+0.019)	1.871(-0.048)	106.64(-4.95)	118.79(+5.00)
$^2A_1$	1.090(+0.008)	1.906(-0.013)	116.98(+5.39)	122.63(+8.84)
$^2A_2$	1.084(+0.002)	1.931(+0.013)	113.05(+1.46)	106.00(-7.79)

[a] Tamagawa (1981).
Bond lengths are in angstroms, angles in degrees.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 5.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2B_2$	10.42	10.43	9.95	10.01	0.47	0.42
$^2B_1$	10.79	10.67	10.72	10.59	0.07	0.08
$^2A_1$	11.17	11.10	11.05	10.97	0.12	0.13
$^2A_2$	11.13	11.04	11.06	10.99	0.07	0.05

Total energies (a.u.) of $^1A_1$: -5174.289323(SCF) and -5174.648300(SDCI).

Table 5.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2B_2$	10.01	0.000
$^2B_1$	10.56	0.475
$^2A_1$	10.95	0.063
$^2A_2$	10.99	0.104

Table 5.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3	ν_4
$^1A_1$	3307	1543	651	215
Obs.[a]	2988	1388	576	174
$^2B_2$	3304	1522	692	201
$^2B_1$	3107	1333	597	207
$^2A_1$	3202	1455	551	230
$^2A_2$	3296	1542	657	215

[a]The Chemical Society of Japan (1986).

Table 5.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3	ν_4
$^1A_1$	ΔC-H	99.8	0.4	0.1	0.0
	ΔC-Br	0.1	0.8	77.7	15.2
	ΔH-C-H	0.0	98.5	1.4	0.1
	ΔBr-C-Br	0.1	0.4	20.9	84.7
$^2B_2$	ΔC-H	99.7	0.1	0.1	0.0
	ΔC-Br	0.2	1.4	80.3	4.2
	ΔH-C-H	0.1	98.1	1.2	0.4
	ΔBr-C-Br	0.1	0.4	18.4	95.5
$^2B_1$	ΔC-H	99.8	1.1	0.2	0.1
	ΔC-Br	0.2	0.5	69.0	17.1
	ΔH-C-H	0.0	98.2	5.9	0.1
	ΔBr-C-Br	0.1	0.3	24.9	82.8
$^2A_1$	ΔC-H	99.8	0.1	0.0	0.0
	ΔC-Br	0.1	0.8	75.0	13.2
	ΔH-C-H	0.1	98.7	0.7	0.0
	ΔBr-C-Br	0.1	0.5	24.3	86.8
$^2A_2$	ΔC-H	99.7	0.3	0.1	0.0
	ΔC-Br	0.2	0.8	78.9	9.3
	ΔH-C-H	0.1	98.6	2.2	0.2
	ΔBr-C-Br	0.1	0.3	18.8	90.5

Table 5.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3	ν_4
	ΔC-H	0.073	-0.003	0.001	-0.000
$^1A_1$	ΔC-Br	-0.004	0.006	0.040	0.009
	ΔH-C-H	-0.4	11.6	0.9	-0.1
	ΔBr-C-Br	0.3	-0.6	-2.9	2.9
	ΔC-H	0.073	-0.002	0.001	-0.000
$^2B_2$	ΔC-Br	-0.004	0.008	0.044	0.004
	ΔH-C-H	-0.4	11.7	1.0	-0.2
	ΔBr-C-Br	0.3	-0.5	-2.5	2.5
	ΔC-H	0.075	-0.005	0.002	-0.000
$^2B_1$	ΔC-Br	-0.003	0.004	-0.039	0.009
	ΔH-C-H	-0.2	12.2	-2.3	-0.1
	ΔBr-C-Br	0.3	-0.5	3.3	2.7
	ΔC-H	0.074	-0.001	0.000	-0.000
$^2A_1$	ΔC-Br	-0.003	0.006	-0.039	0.009
	ΔH-C-H	-0.5	11.9	-0.7	0.0
	ΔBr-C-Br	0.3	-0.7	3.2	3.2
	ΔC-H	0.073	-0.003	0.001	-0.000
$^2A_2$	ΔC-Br	-0.004	0.006	0.043	0.007
	ΔH-C-H	-0.4	11.6	1.2	-0.2
	ΔBr-C-Br	0.3	-0.5	-2.7	2.9

Bond lengths are in angstroms, angles in degrees.

Table 5.7 Vibrational levels of the $^2B_2$ state.

IE	Vibrational levels
10.38	W(0 0 0 15)
10.41	W(0 0 0 16)
10.43	W(0 0 0 17)
10.46	W(0 0 0 18)
10.48	W(0 0 0 19)
10.51	W(0 0 0 20)
10.53	W(0 0 0 21)
10.56	M(0 0 0 22)
10.58-10.59	M(0 0 0 23), W(0 0 1 20)
10.61-10.62	M(0 0 0 24), W(0 0 1 21)
10.63-10.64	M(0 0 0 25), W(0 0 1 22)
10.66-10.67	M(0 0 0 26), W(0 0 1 23)
10.68-10.69	M(0 0 0 27), W(0 0 1 24)
10.71-10.72	M(0 0 0 28), W(0 0 1 25)
10.73-10.74	M(0 0 0 29), W(0 0 1 26)
10.76-10.77	M(0 0 0 30), W(0 0 1 27)
10.79	W(0 0 1 28)
10.82	W(0 0 1 29)
10.84	W(0 0 1 30)

M:0.03<FCF<0.05 and W:0.005<FCF<0.03.

Table 5.8 Vibrational levels of the $^2B_1$ state.

IE	Vibrational levels
10.56	S(0 0 0 0)
10.59	W(0 0 0 1)
10.63	S(0 0 1 0)
10.66	W(0 0 1 1)
10.71	S(0 0 2 0)
10.73	W(0 1 0 0)
10.78	M(0 0 3 0)
10.86	W(0 0 4 0)
10.94	W(1 0 0 0)

S:0.16<FCF<0.48, M:0.03<FCF<0.05 and W:0.01<FCF<0.03.

Table 5.9 Vibrational levels of the $^2A_1$ state.

IE	Vibrational levels
10.95	M(0 0 0 0)
10.98	S(0 0 0 1)
11.01-11.02	S(0 0 0 2), M(0 0 1 0)
11.04-11.05	S(0 0 0 3), M(0 0 1 1)
11.06-11.07	M(0 0 0 4), M(0 0 1 2)
11.09-11.11	W(0 0 0 5), M(0 0 1 3), W(0 0 2 1)
11.13-11.14	W(0 0 1 4), W(0 0 2 2)
11.16	W(0 1 0 1)
11.19	W(0 1 0 2)
11.22	W(0 1 0 3)

S:0.12<FCF<0.17, M:0.03<FCF<0.07 and W:0.01<FCF<0.03.

Table 5.10 Vibrational levels of the $^2A_2$ state.

IE	Vibrational levels
10.99	S(0 0 0 0)
11.02	S(0 0 0 1)
11.04	S(0 0 0 2)
11.07	S(0 0 0 3), W(0 0 1 0)
11.10	S(0 0 0 4), M(0 0 1 1)
11.12	M(0 0 0 5), M(0 0 1 2)
11.15	W(0 0 0 6), M(0 0 1 3)
11.18	W(0 0 1 4)
11.20	W(0 0 1 5)

S:0.08<FCF<0.2, M:0.03<FCF<0.05 and W:0.01<FCF<0.03.

6. Ethylene C_2H_4

Table 6.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C=C (ΔC=C)	C-H (ΔC-H)	H-C=C (ΔH-C=C)
^1A_g	1.320	1.084	121.68
Exp.[a]	1.339	1.086	121.2
$^2B_{3u}$	1.404(+0.084)	1.085(+0.001)	120.74(-0.941)
$^2B_{3g}$	1.255(-0.065)	1.135(+0.051)	129.72(+8.033)
^2A_g	1.429(+0.109)	1.090(+0.006)	109.72(-11.962)
$^2B_{2u}$	1.340(+0.020)	1.142(+0.058)	130.08(+8.395)
$^2B_{1u}$	1.278(-0.042)	1.160(+0.075)	116.61(-5.073)

[a] Herzberg (1966).
Bond lengths are in angstroms, angles in degrees.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 6.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2B_{3u}$	9.03	10.15	8.82	9.88	0.21	0.27
$^2B_{3g}$	13.00	12.97	12.40	12.48	0.60	0.49
^2A_g	14.46	14.72	13.47	13.74	0.99	0.98
$^2B_{2u}$	16.64	16.40	15.96	15.68	0.68	0.72
$^2B_{1u}$	20.70	19.88	20.06	19.35	0.64	0.53

Total energies (a.u.) of ^1A_g: -77.946601(SCF) and -78.227357(SDCI).

Table 6.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2B_{3u}$	9.86	0.341
$^2B_{3g}$	12.45	0.082
^2A_g	13.70	0.007
$^2B_{2u}$	15.65	0.043
$^2B_{1u}$	19.32	0.101

Table 6.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3
^1A_g	3310	1834	1466
Obs.[a]	3026	1623	1342
$^2B_{3u}$	3317	1683	1368
$^2B_{3g}$	3075	1930	1201
^2B_g	3188	1562	1235
$^2B_{2u}$	2970	1723	1385
$^2B_{1u}$	2782	1981	1348

[a] Herzberg (1966).

Table 6.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3
	ΔC=C	2.1	64.7	29.6
^1A_g	ΔC-H	97.7	0.7	0.8
	ΔH-C=C	0.2	34.6	69.7
	ΔC=C	1.4	31.6	72.6
$^2B_{3u}$	ΔC-H	98.5	0.3	1.0
	ΔH-C=C	0.2	68.2	26.5
	ΔC=C	9.2	85.3	2.0
$^2B_{3g}$	ΔC-H	90.4	10.0	0.0
	ΔH-C=C	0.4	4.8	98.0
	ΔC=C	0.3	15.2	95.3
^2A_g	ΔC-H	99.7	0.7	0.2
	ΔH-C=C	0.0	84.2	4.5
	ΔC=C	4.8	74.9	15.4
$^2B_{2u}$	ΔC-H	94.7	4.0	0.1
	ΔH-C=C	0.4	21.2	84.5
	ΔC=C	4.4	82.5	9.9
$^2B_{1u}$	ΔC-H	95.5	2.2	1.5
	ΔH-C=C	0.2	15.3	88.6

Table 6.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3
	ΔC=C	-0.011	-0.048	0.026
^1A_g	ΔC-H	0.051	-0.004	0.003
	ΔH-C=C	0.2	2.6	3.0
	ΔC=C	-0.010	-0.038	0.046
$^2B_{3u}$	ΔC-H	0.051	-0.002	0.003
	ΔH-C=C	0.2	3.6	1.8
	ΔC=C	-0.019	0.048	0.006
$^2B_{2g}$	ΔC-H	0.053	0.014	-0.001
	ΔH-C=C	0.4	-1.2	4.1
	ΔC=C	-0.006	-0.030	0.058
^2A_g	ΔC-H	0.052	0.003	0.001
	ΔH-C=C	0.0	4.1	0.7
	ΔC=C	-0.016	-0.050	0.019
$^2B_{2u}$	ΔC-H	0.054	-0.009	0.001
	ΔH-C=C	0.4	2.0	3.3
	ΔC=C	-0.013	-0.050	0.014
$^2B_{1u}$	ΔC-H	0.055	-0.007	0.005
	ΔH-C=C	0.2	1.8	3.5

Bond lengths are in angstroms, angles in degrees.

Table 6.7 Vibrational levels of the $^2B_{3g}$ state.

IE	Progressions		
	A	B	C
12.45	S(0 0 0)		
12.60	S(0 0 1)		
12.69		M(0 1 0)	
12.75	M(0 0 2)		
12.83-12.84		M(0 1 1), M(1 0 0)	
12.90	W(0 0 3)		
12.93			W(0 2 0)
12.98-12.99		W(0 1 2), S(1 0 1)	
13.07-13.08			W(0 2 1), M(1 1 0)
13.13-13.14		M(1 0 2)	
13.21-13.22			W(2 0 0), M(1 1 1)
13.28-13.31		W(1 0 3), W(1 2 0)	
13.36-13.37			M(2 0 1), W(1 1 2)
13.51-13.52			W(2 0 2), W(1 1 3)

IE	D
13.45-13.46	W(2 1 0), W(1 2 1)
13.60-13.61	W(2 1 1)
13.75	W(2 1 2)

S:0.08<FCF<0.11, M:0.03<FCF<0.07 and W:0.01<0.03.

Table 6.8 Vibrational levels of the ^2A_g state.

IE	Progressions	
	A	B
13.70	W(0 0 0)	
13.89	M(0 1 0)	
14.09	S(0 2 0)	
14.24		W(0 2 1)
14.28	S(0 3 0)	
14.43		W(0 3 1)
14.47	S(0 4 0)	
14.63		W(0 4 1)
14.67	S(0 5 0)	
14.82		W(0 5 1)
14.86	S(0 6 0)	
15.01		W(0 6 1)
15.05	S(0 7 0)	
15.25	M(0 8 0)	
15.44	W(0 9 0)	
15.64	W(0 10 0)	

S:0.07<FCF<0.17, M:0.03<FCF<0.04 and W:0.007<0.03.

Table 6.9 Vibrational levels of the $^2B_{2u}$ state.

IE	Progressions		
	A	B	C
15.65	M(0 0 0)		
15.82	S(0 0 1)		
15.99	S(0 0 2)		
16.02		W(1 0 0)	
16.16	S(0 0 3)		
16.19		M(1 0 1)	
16.34	S(0 0 4)		
16.36		S(1 0 2)	
16.51	M(0 0 5)		
16.53		S(1 0 3)	
16.56			W(2 0 1)
16.68	M(0 0 6)		
16.70		M(1 0 4)	
16.73			W(2 0 2)
16.85	W(0 0 7)		
16.88		W(1 0 5)	
16.90			W(2 0 3)
17.05		W(1 0 6)	
17.07			W(2 0 4)
17.24			W(2 0 5)

S:0.07<FCF<0.15, M:0.03<FCF<0.07 and W:0.007<FCF<0.03.

Table 6.10 Vibrational levels of the $^2B_{1u}$ state.

IE	Vibrational levels				
19.32	S(0 0 0)				
19.49	S(0 0 1)				
19.65-19.66	M(0 0 2),	S(1 0 0)			
19.82-19.83	W(0 0 3),	S(1 0 1)			
20.00-20.01	W(0 0 4)	S(1 0 2),	M(2 0 0)		
20.17-20.18		M(1 0 3),	S(2 0 1)		
20.33-20.35		W(1 0 4),	M(2 0 2),	W(3 0 0)	
20.51-20.52			W(2 0 3),	W(3 0 1)	
20.69				W(3 0 2)	
20.86				W(3 0 3)	

S:0.08<FCF<0.15, M:0.03<FCF<0.07 and W:0.008<FCF<0.03.

7. Tetrafluoroethylene C_2F_4

Table 7.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C=C (ΔC=C)	C-F (ΔC-F)	C=C-F (ΔC=C-F)
^1A_g	1.303	1.297	123.54
Obs.[a]	1.311	1.319	123.76
$^2B_{2u}$	1.400(+0.097)	1.241(-0.056)	120.84(-2.70)
^2A_g	1.386(+0.083)	1.265(-0.032)	118.06(-5.48)
$^2B_{2g}$	1.288(-0.015)	1.294(-0.003)	125.73(+2.19)
$^2B_{3u}$	1.295(-0.008)	1.302(+0.005)	127.36(+3.82)
^2A_u	1.295(-0.008)	1.302(+0.005)	124.47(+0.93)
$^2B_{1g}$	1.299(-0.004)	1.304(+0.007)	125.05(+1.51)
$^2B_{1u}$	1.279(-0.024)	1.316(+0.019)	121.01(-2.53)
$^2B_{3g}$	1.288(-0.015)	1.325(+0.028)	122.67(-0.87)

[a]Carlos et al. (1974).
Bond lengths are in angstroms, angles in degrees.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 7.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2B_{2u}$	9.74	9.96	8.99	9.33	0.75	0.63
$^2B_{2g}$	17.61	16.66	17.55	16.64	0.06	0.02
^2A_g	17.53	16.81	17.09	16.51	0.44	0.30
$^2B_{3u}$	18.07	17.18	17.88	16.99	0.19	0.19
^2A_u	18.57	17.52	18.56	17.51	0.01	0.01
$^2B_{1g}$	18.77	17.71	18.73	17.68	0.04	0.03
$^2B_{1u}$	19.46	18.44	19.31	18.26	0.15	0.18
$^2B_{3g}$	20.26	19.23	20.14	19.05	0.12	0.18

Total energies (a.u.) of ^1A_g : -472.930060(SCF) and -473.777039(SDCI).

Table 7.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2B_{2u}$	9.33	0.031
^2A_g	16.48	0.006
$^2B_{2g}$	16.65	0.362
$^2B_{3u}$	17.00	0.031
^2A_u	17.51	0.841
$^2B_{1g}$	17.68	0.580
$^2B_{1u}$	18.27	0.092
$^2B_{3g}$	19.05	0.378

Table 7.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3
^1A_g	2145	874	433
Obs.[a]	1872	778	398
$^2B_{2u}$	1958	914	443
^2A_g	1528	878	411
$^2B_{2g}$	2243	858	374
$^2B_{3u}$	2218	849	426
^2A_u	2196	858	404
$^2B_{1g}$	2177	855	418
$^2B_{1u}$	2238	853	380
$^2B_{3g}$	2194	840	395

[a]Carlos et al. (1974).

Table 7.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3
^1A_g	ΔC=C	67.5	17.7	9.4
	ΔC-F	23.5	77.7	0.9
	ΔC=C-F	9.1	4.6	89.7
$^2B_{2u}$	ΔC=C	51.4	28.3	17.0
	ΔC-F	36.6	60.4	0.9
	ΔC=C-F	12.0	11.4	82.0
^2A_g	ΔC=C	55.2	32.4	2.9
	ΔC-F	33.4	58.4	1.5
	ΔC=C-F	11.3	9.2	95.6
$^2B_{2g}$	ΔC=C	68.8	20.8	7.4
	ΔC-F	25.3	76.0	1.2
	ΔC=C-F	5.9	3.2	91.5
$^2B_{3u}$	ΔC=C	66.6	21.0	7.7
	ΔC-F	26.1	74.4	1.5
	ΔC=C-F	7.3	4.7	90.8
^2A_u	ΔC=C	68.8	19.0	8.0
	ΔC-F	23.9	77.3	1.0
	ΔC=C-F	7.3	3.8	91.0
$^2B_{1g}$	ΔC=C	68.0	19.2	7.8
	ΔC-F	24.3	76.6	1.2
	ΔC=C-F	7.7	4.3	91.0
$^2B_{1u}$	ΔC=C	74.2	15.3	7.8
	ΔC-F	18.7	82.3	0.5
	ΔC=C-F	7.0	2.5	91.7
$^2B_{3g}$	ΔC=C	72.3	16.3	7.4
	ΔC-F	20.3	80.6	1.0
	ΔC=C-F	7.4	3.1	91.6

Table 7.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3
	ΔC=C	0.050	0.015	0.008
^1A_g	ΔC-F	-0.017	0.018	0.001
	ΔC=C-F	-1.0	-0.4	1.3
	ΔC=C	0.051	0.024	0.013
$^2B_{2u}$	ΔC-F	-0.018	0.015	0.001
	ΔC=C-F	-1.0	-0.6	1.2
	ΔC=C	0.057	0.026	0.005
^2A_g	ΔC-F	-0.019	0.015	0.002
	ΔC=C-F	-1.2	-0.6	1.4
	ΔC=C	0.049	0.016	0.006
$^2B_{2g}$	ΔC-F	-0.017	0.018	0.002
	ΔC=C-F	-0.9	-0.4	1.4
	ΔC=C	0.049	0.016	0.007
$^2B_{3u}$	ΔC-F	-0.018	0.017	0.002
	ΔC=C-F	-0.9	-0.4	1.3
	ΔC=C	0.050	0.015	0.007
^2A_u	ΔC-F	-0.017	0.018	0.001
	ΔC=C-F	-0.9	-0.4	1.3
	ΔC=C	0.050	0.015	0.007
$^2B_{1g}$	ΔC-F	-0.017	0.018	0.002
	ΔC=C-F	-0.9	-0.4	1.3
	ΔC=C	0.049	0.013	0.006
$^2B_{1u}$	ΔC-F	-0.015	0.019	0.001
	ΔC=C-F	-0.9	-0.3	1.4
	ΔC=C	0.050	0.014	0.007
$^2B_{3g}$	ΔC-F	-0.016	0.019	0.001
	ΔC=C-F	-0.9	-0.4	1.3

Bond lengths are in angstroms, angles in degrees.

Table 7.7 Vibrational levels of the $^2B_{2u}$ state.

IE	Progressions		
	A	B	C
9.33	M(0 0 0)		
9.38		W(0 0 1)	
9.44			W(0 1 0)
9.57	S(1 0 0)		
9.63		W(1 0 1)	
9.69			W(1 1 0)
9.81	S(2 0 0)		
9.87		W(2 0 1)	
9.93			M(2 1 0)
10.06	S(3 0 0)		
10.11		W(3 0 1)	
10.17			M(3 1 0)
10.30	S(4 0 0)		
10.36		W(4 0 1)	
10.41			M(4 1 0)
10.54	M(5 0 0)		
10.60		W(5 0 1)	
10.66			W(5 1 0)
10.79	W(6 0 0)		
10.90			W(6 1 0)

S:0.09<FCF<0.14, M:0.03<FCF<0.05 and W:0.005<FCF<0.03.

Table 7.7 Vibrational levels of the ^2A_g state.

IE	Progressions			
	A	B	C	D
16.48	W(0 0 0)			
16.53	W(0 0 1)			
16.58	M(0 0 2)			
16.63	M(0 0 3)			
16.67-16.68	M(0 0 4)	W(1 0 0)		
16.72-16.73	W(0 0 5)	M(1 0 1)		
16.77-16.79	W(0 0 6)	M(1 0 2)		
16.82-16.84	W(0 0 7)	S(1 0 3)		
16.86-16.87		M(1 0 4)	W(2 0 0)	
16.91-16.92		M(1 0 5)	M(2 0 1)	
16.96-16.97		W(1 0 6)	M(2 0 2)	
17.01-17.03		W(1 0 7)	M(2 0 3)	
17.05-17.06			M(2 0 4)	
17.10-17.11			M(2 0 5)	W(3 0 1)
17.15-17.16			W(2 0 6)	W(3 0 2)
17.20-17.22			W(2 0 7)	W(3 0 3)
17.25				W(3 0 4)
17.30				W(3 0 5)
17.35				W(3 0 6)

S:0.08<FCF<0.09, M:0.03<FCF<0.07 and W:0.005<FCF<0.03.

Table 7.8 Vibrational levels of the $^2B_{2g}$ state.

IE	Progressions		
	A	B	C
16.65	S(0 0 0)		
16.70	S(0 0 1)		
16.74-16.76	S(0 0 2)	M(0 1 0)	
16.79-16.80	W(0 0 3)	M(0 1 1)	
16.85		W(0 1 2)	
16.93			W(1 0 0)
16.97			W(1 0 1)

S:0.1<FCF<0.36, M:0.03<FCF<0.06 and W:0.01<FCF<0.03.

Table 7.9 Vibrational levels of the $^2B_{3u}$ state.

IE	Progressions		
	A	B	C
17.00	W(0 0 0)		
17.05	S(0 0 1)		
17.10-17.11	S(0 0 2)		
17.16	S(0 0 3)	W(0 1 1)	
17.21	S(0 0 4)	W(0 1 2)	
17.26	S(0 0 5)	W(0 1 3)	
17.32-17.33	M(0 0 6)	W(0 1 4)	W(1 0 1)
17.37-17.38	W(0 0 7)	W(0 1 5)	W(1 0 2)
17.42-17.43	W(0 0 8)		W(1 0 3)
17.49			W(1 0 4)
17.54			W(1 0 5)

S:0.1<FCF<0.2, M:0.03<FCF<0.06 and W:0.007<FCF<0.03.

Table 7.10 Vibrational levels of the $^2B_{1u}$ state.

IE	Progressions		
	A	B	C
18.27	S(0 0 0)		
18.32	S(0 0 1)		
18.36-18.38	S(0 0 2)	W(0 1 0)	
18.41-18.42	S(0 0 3)	M(0 1 1)	
18.46-18.47	M(0 0 4)	M(0 1 2)	
18.50-18.52	W(0 0 5)	M(0 1 3)	
18.55-18.56		W(0 1 4)	W(1 0 0)
18.60			W(1 0 1)
18.64			W(1 0 2)
18.69			W(1 0 3)

S:0.09<FCF<0.21, M:0.03<FCF<0.06 and W:0.006<FCF<0.03.

Table 7.11 Vibrational levels of the $^2B_{3g}$ state.

IE	Progressions				
	A	B	C	D	E
19.05	S(0 0 0)				
19.10		S(0 0 1)			
19.15	S(0 1 0)		W(0 0 2)		
19.20		M(0 1 1)			
19.25-19.26	M(0 2 0)		W(0 1 2)		
19.31-19.32		W(0 2 1)		M(1 0 0)	
19.36-19.37	W(0 3 0)				W(1 0 1)
19.43				W(1 1 0)	
19.47					W(1 1 1)
19.53				W(1 2 0)	

S:0.10<FCF<0.38, M:0.03<FCF<0.06 and W:0.007<FCF<0.03.

8. Tetrachloroethylene C_2Cl_4

Table 8.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C=C (ΔC=C)	C-Cl(ΔC-Cl)	C=C-Cl(ΔC=C-Cl)
^1A_g	1.324	1.724	122.68
Exp.[a]	1.354	1.718	122.15
$^2B_{2u}$	1.422(+0.098)	1.670(-0.054)	120.85(-1.83)
$^2B_{2g}$	1.309(-0.015)	1.702(-0.022)	122.54(-0.14)
$^2B_{3u}$	1.317(-0.007)	1.722(-0.002)	126.74(+4.06)
^2A_u	1.319(-0.005)	1.716(-0.008)	122.72(+0.04)
$^2B_{1u}$	1.309(-0.015)	1.730(+0.006)	118.67(-4.01)
$^2B_{1g}$	1.324(-0.000)	1.724(+0.001)	123.93(+1.25)
^2A_g	1.375(+0.051)	1.707(-0.017)	121.42(-1.26)
$^2B_{3g}$	1.311(-0.013)	1.750(+0.026)	121.54(-1.14)

[a]Strand (1967).
Bond lengths are in angstroms, angles in degrees.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 8.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2B_{2u}$	9.02	9.23	8.61	8.81	0.41	0.42
$^2B_{2g}$	11.83	11.49	11.79	11.48	0.04	0.01
$^2B_{3u}$	12.88	12.53	12.63	12.30	0.25	0.23
^2A_u	12.79	12.40	12.79	12.40	0.00	0.00
$^2B_{1u}$	13.26	12.88	12.99	12.61	0.27	0.27
$^2B_{1g}$	13.18	12.77	13.16	12.76	0.02	0.01
^2A_g	13.48	13.11	13.41	13.01	0.07	0.10
$^2B_{3g}$	14.12	13.72	14.04	13.64	0.08	0.08

Total energies (a.u.) of ^1A_g : -1911.569329(SCF) and -1912.238285(SDCI).

Table 8.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2B_{2u}$	8.79	0.072
$^2B_{2g}$	11.48	0.479
$^2B_{3u}$	12.30	0.000
^2A_u	12.40	0.915
$^2B_{1u}$	12.61	0.000
$^2B_{1g}$	12.76	0.475
^2A_g	12.99	0.573
$^2B_{3g}$	13.64	0.241

Table 8.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3
^1A_g	1825	477	254
Obs.[a]	1571	447	237
$^2B_{2u}$	1531	507	271
$^2B_{2g}$	1900	488	206
$^2B_{3u}$	1875	478	252
^2A_u	1848	481	242
$^2B_{1u}$	1893	476	254
$^2B_{1g}$	1824	477	252
^2A_g	1449	483	275
$^2B_{3g}$	1880	466	245

[a] Herzberg (1966).

Table 8.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3
^1A_g	ΔC=C	81.3	7.1	1.8
	ΔC-Cl	11.7	91.5	1.1
	ΔC=C-Cl	7.0	1.5	97.1
$^2B_{2u}$	ΔC=C	71.4	13.2	3.7
	ΔC-Cl	17.5	82.9	1.2
	ΔC=C-Cl	11.1	3.9	95.2
$^2B_{2g}$	ΔC=C	83.9	8.1	1.0
	ΔC-Cl	11.7	91.3	0.4
	ΔC=C-Cl	4.4	0.7	98.6
$^2B_{3u}$	ΔC=C	80.1	8.9	2.1
	ΔC-Cl	13.8	89.3	1.8
	ΔC=C-Cl	6.1	1.9	96.1
^2A_u	ΔC=C	81.9	7.4	1.6
	ΔC-Cl	11.9	91.3	0.9
	ΔC=C-Cl	6.2	1.2	97.5
$^2B_{1u}$	ΔC=C	84.4	5.7	1.1
	ΔC-Cl	8.6	93.6	0.1
	ΔC=C-Cl	7.1	0.7	98.8
$^2B_{1g}$	ΔC=C	81.1	7.2	1.7
	ΔC-Cl	12.2	91.3	1.3
	ΔC=C-Cl	6.8	1.5	97.0
^2A_g	ΔC=C	76.1	5.0	0.1
	ΔC-Cl	13.5	92.3	4.7
	ΔC=C-Cl	10.5	2.7	95.1
$^2B_{3g}$	ΔC=C	83.5	6.5	1.4
	ΔC-Cl	10.1	92.3	0.9
	ΔC=C-Cl	6.4	1.1	97.7

Table 8.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3
^1A_g	ΔC=C	0.055	0.007	0.003
	ΔC-Cl	-0.016	0.020	0.002
	ΔC=C-Cl	-0.8	-0.1	1.0
$^2B_{2u}$	ΔC=C	0.060	0.013	0.005
	ΔC-Cl	-0.017	0.018	0.002
	ΔC=C-Cl	-0.9	-0.3	0.9
$^2B_{2g}$	ΔC=C	0.054	0.008	0.002
	ΔC-Cl	-0.015	0.020	0.001
	ΔC=C-Cl	-0.8	-0.1	1.1
$^2B_{3u}$	ΔC=C	0.055	0.008	0.003
	ΔC-Cl	-0.017	0.020	0.002
	ΔC=C-Cl	-0.7	-0.2	1.0
^2A_u	ΔC=C	0.055	0.008	0.003
	ΔC-Cl	-0.016	0.020	0.001
	ΔC=C-Cl	-0.8	-0.2	1.0
$^2B_{1u}$	ΔC=C	0.054	0.006	0.002
	ΔC-Cl	-0.014	0.021	0.000
	ΔC=C-Cl	-0.8	-0.1	1.0
$^2B_{1g}$	ΔC=C	0.055	0.008	0.003
	ΔC-Cl	-0.016	0.020	0.002
	ΔC=C-Cl	-0.8	-0.2	1.0
^2A_g	ΔC=C	0.062	0.007	0.001
	ΔC-Cl	-0.017	0.020	0.004
	ΔC=C-Cl	-0.9	-0.2	1.0
$^2B_{3g}$	ΔC=C	0.055	0.007	0.002
	ΔC-Cl	-0.015	0.021	0.001
	ΔC=C-Cl	-0.8	-0.1	1.0

Bond lengths are in angstroms, angles in degrees.

Table 8.7 Vibrational levels of the $^2B_{2u}$ state.

IE	Progressions		
	A	B	C
8.79	M(0 0 0)		
8.85		M(0 1 0)	
8.92			W(0 2 0)
8.98	S(1 0 0)		
9.04		S(1 1 0)	
9.11			W(1 2 0)
9.17	S(2 0 0)		
9.23		S(2 1 0)	
9.29			W(2 2 0)
9.36	M(3 0 0)		
9.42		M(3 1 0)	
9.48			W(3 2 0)
9.55	W(4 0 0)		
9.61		W(4 1 0)	
9.67			W(4 2 0)
9.74	W(5 0 0)		
9.80		W(5 1 0)	

S:0.08<FCF<0.15, M:0.03<FCF<0.08 and W:0.007<FCF<0.03.

Table 8.8 Vibrational levels of the $^2B_{2g}$ state.

IE	Progressions	
	A	B
11.48	S(0 0 0)	
11.51		M(0 0 1)
11.54	S(0 1 0)	
11.57		W(0 1 1)
11.60	S(0 2 0)	
11.63		W(0 2 1)
11.66	W(0 3 0)	

S:0.10<FCF<0.48, M:0.03<FCF<0.04 and W:0.008<FCF<0.03.

Table 8.9 Vibrational levels of the $^2B_{3u}$ state.

IE	Progressions	
	A	B
12.33	W(0 0 1)	
12.36	W(0 0 2)	
12.39	M(0 0 3)	
12.43	M(0 0 4)	
12.45-12.46	S(0 0 5)	W(0 1 3)
12.48-12.49	S(0 0 6)	W(0 1 4)
12.51-12.52	S(0 0 7)	W(0 1 5)
12.55-12.55	S(0 0 8)	W(0 1 6)
12.58-12.58	S(0 0 9)	W(0 1 7)
12.61-12.61	M(0 0 10)	W(0 1 8)
12.64-12.64	M(0 0 11)	W(0 1 9)
12.67-12.68	W(0 0 12)	W(0 1 10)
12.70-12.71	W(0 0 13)	W(0 1 11)
12.73-12.74	W(0 0 14)	W(0 1 12)

S:0.08<FCF<0.11, M:0.03<FCF<0.07 and W:0.003<FCF<0.03.

Table 8.10 Vibrational levels of the $^2B_{1u}$ state.

IE	Progression A
12.64	W(0 0 1)
12.67	W(0 0 2)
12.70	W(0 0 3)
12.74	M(0 0 4)
12.77	M(0 0 5)
12.80	S(0 0 6)
12.83	S(0 0 7)
12.86	S(0 0 8)
12.89	S(0 0 9)
12.92	S(0 0 10)
12.96	S(0 0 11)
12.99	M(0 0 12)
13.02	M(0 0 13)
13.05	W(0 0 14)
13.08	W(0 0 15)
13.11	W(0 0 16)

S:0.08<FCF<0.13, M:0.03<FCF<0.07 and W:0.001<FCF<0.03.

Table 8.11 Vibrational levels of the $^2B_{3g}$ state.

IE	Progressions			
	A	B	C	D
13.64	S(0 0 0)			
13.67	S(0 0 1)			
13.70	M(0 0 2)	S(0 1 0)		
13.73	W(0 0 3)	S(0 1 1)		
13.76		M(0 1 2)	M(0 2 0)	
13.79		W(0 1 3)	M(0 2 1)	
13.82			W(0 2 2)	
13.87				W(1 0 0)
13.90				W(1 0 1)

S:0.08<FCF<0.24, M:0.03<FCF<0.08 and W:0.009<FCF<0.03.

9. trans-1,2-Difluoroethylene trans-$C_2H_2F_2$

Table 9.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C=C (ΔC=C)	C-F (ΔC-Cl)	C-H (ΔC-H)
^1A_g	1.310	1.324	1.079
Exp.[a]	1.329	1.344	1.080
^2A_u	1.400(+0.090)	1.254(-0.070)	1.086(+0.007)
^2A_g	1.321(+0.011)	1.248(-0.076)	1.153(+0.074)
^2B_u	1.289(-0.021)	1.350(+0.026)	1.100(+0.021)
^2B_g	1.297(-0.013)	1.418(+0.094)	1.079(0.000)

State	F-C=C(ΔF-C=C)	H-C=C (ΔH-C=C)
^1A_g	120.47	124.70
Exp.[a]	119.33	129.25
^2A_u	118.02(-2.45)	123.70(-1.0)
^2A_g	134.48(+14.01)	102.94(-21.76)
^2B_u	116.54(-3.93)	132.30(+7.60)
^2B_g	114.08(-6.39)	133.38(+8.68)

[a]Carlos et al. (1974).
Bond lengths are in angstroms, angles in degrees.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 9.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
^2A_u	9.38	9.91	8.84	9.41	0.54	0.50
^2A_g	14.60	14.13	13.55	13.47	1.05	0.66
^2B_u	16.13	15.48	15.99	15.35	0.14	0.13
^2B_g	17.37	16.76	16.98	16.31	0.39	0.45

Total energies (a.u.) of ^1A_g : -275.436996(SCF) and -276.009672(SDCI).

Table 9.3 0-0 ionization levels.

State	0-0 IE	FCF
^2A_u	9.40	0.063
^2A_g	13.40	0.000
^2B_u	15.31	0.063
^2B_g	16.29	0.076

Table 9.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3	ν_4	ν_5
^1A_g	3423	1949	1404	1257	602
Obs.[a]	3111	1694	1286	1123	548
^2A_u	3384	1840	1336	1382	596
^2A_g	2742	1912	1141	1119	589
^2B_u	3174	1998	1277	1026	563
^2B_g	3467	1930	1345	1048	541

[a]Craig et al. (1969).

Table 9.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5
	ΔC=C	1.5	66.8	10.6	2.7	6.7
	ΔC-F	0.1	15.7	0.8	59.3	16.2
^1A_g	ΔC-H	97.6	1.2	0.0	0.1	0.0
	ΔF-C=C	0.8	0.2	7.9	36.8	70.7
	ΔH-C=C	0.1	16.1	80.7	1.1	6.4
	ΔC=C	0.7	33.7	31.2	2.3	11.6
	ΔC-F	0.3	36.2	4.5	51.8	9.3
^2A_u	ΔC-H	97.9	0.1	0.6	0.4	0.0
	ΔF-C=C	0.9	0.4	22.1	18.7	70.9
	ΔH-C=C	0.2	29.6	41.6	26.9	8.1
	ΔC=C	0.5	43.7	30.3	18.8	0.2
	ΔC-F	2.7	42.1	7.8	23.9	11.9
^2A_g	ΔC-H	94.7	6.6	0.0	1.2	0.8
	ΔF-C=C	0.9	0.3	18.6	13.2	80.1
	ΔH-C=C	1.2	7.3	43.3	43.0	7.1
	ΔC=C	3.6	78.4	5.6	1.1	6.8
	ΔC-F	0.0	8.2	2.9	61.9	13.9
^2B_u	ΔC-H	95.7	4.5	0.0	0.6	0.1
	ΔF-C=C	0.7	0.6	8.7	35.1	74.4
	ΔH-C=C	0.0	8.2	82.9	1.3	4.9
	ΔC=C	2.2	80.3	6.4	0.6	4.2
	ΔC-F	0.1	6.2	0.3	52.8	20.1
^2B_g	ΔC-H	96.9	2.0	0.1	0.2	0.0
	ΔF-C=C	0.7	0.9	4.4	36.9	70.4
	ΔH-C=C	0.1	10.6	88.7	9.5	5.3

Table 9.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5
	ΔC=C	-0.009	-0.049	0.018	-0.008	0.008
	ΔC-F	-0.002	0.021	0.004	-0.033	0.011
^1A_g	ΔC-H	0.073	-0.006	0.001	-0.001	0.000
	ΔF-C=C	0.7	0.3	-1.5	3.0	2.7
	ΔH-C=C	-0.3	3.0	6.0	-0.6	-1.0
	ΔC=C	-0.008	-0.043	0.038	-0.008	0.014
	ΔC-F	-0.003	0.027	0.009	-0.023	0.008
^2A_u	ΔC-H	0.073	-0.002	0.004	-0.003	-0.000
	ΔF-C=C	0.7	-0.4	-2.5	1.8	2.7
	ΔH-C=C	-0.4	4.0	4.4	2.7	-1.1
	ΔC=C	0.005	-0.046	0.032	-0.020	0.002
	ΔC-F	-0.008	0.030	0.011	-0.015	0.009
^2A_g	ΔC-H	0.080	0.019	0.001	0.005	0.004
	ΔF-C=C	0.8	-0.4	-2.8	1.9	3.8
	ΔH-C=C	-1.1	2.4	4.8	3.9	-1.3
	ΔC=C	-0.013	-0.049	0.012	-0.005	0.007
	ΔC-F	0.000	0.017	0.009	-0.039	0.011
^2B_u	ΔC-H	0.075	-0.013	0.001	0.004	-0.001
	ΔF-C=C	0.6	0.5	-1.7	3.1	2.8
	ΔH-C=C	-0.2	2.3	6.7	-0.8	-0.9
	ΔC=C	-0.011	-0.051	0.013	-0.004	0.006
	ΔC-F	-0.002	0.015	0.003	-0.041	0.014
^2B_g	ΔC-H	0.072	-0.008	0.002	-0.002	-0.000
	ΔF-C=C	0.7	0.5	-1.1	3.3	2.6
	ΔH-C=C	-0.3	2.4	6.4	-2.1	-0.9

Bond lengths are in angstroms, angles in degrees.

Table 9.7 Vibrational levels of the ^2A_u state.

IE	Progressions	
	A	B
9.40	M(0 0 0 0 0)	
9.47		W(0 0 0 0 1)
9.63-9.64	S(0 1 0 0 0), W(0 0 1 0 1), W(0 0 0 1 1)	
9.70		M(0 1 0 0 1)
9.86-9.87	S(0 2 0 0 0), W(0 1 1 0 1), W(0 1 0 1 1)	
9.93		M(0 2 0 0 1)
10.08-10.10	M(0 3 0 0 0), W(0 2 1 0 1), W(0 2 0 1 1)	
10.16		W(0 3 0 0 1)
10.31-10.33	W(0 4 0 0 0), W(0 3 1 0 1), W(0 3 0 1 1)	
10.39		W(0 4 0 0 1)
10.54	W(0 5 0 0 0)	
10.61		W(0 5 0 0 1)

IE	C	D
9.57	W(0 0 1 0 0), W(0 0 0 1 0)	
9.73-9.74		W(0 0 2 0 0), W(0 0 1 1 0)
9.79-9.80	M(0 1 1 0 0), W(0 1 0 1 0)	
9.96		W(0 1 2 0 0), W(0 1 1 1 0)
10.02-10.03	W(0 2 1 0 0), W(0 2 0 1 0)	
10.19		W(0 2 1 1 0)
10.25-10.26	W(0 3 1 0 0), W(0 3 0 1 0)	
10.48	W(0 4 1 0 0), W(0 4 0 1 0)	

S:0.09<FCF<0.11, M:0.03<FCF<0.07 and W:0.004<FCF<0.03.

Table 9.8 Vibrational levels of the ^2A_g state.

(0 0 1 0 0) - (0 0 6 0 0), (0 0 0 0 1) - (0 0 4 0 1),
(0 0 1 0 2) - (0 0 4 0 2),
(0 1 2 0 0) - (0 1 6 0 0), (0 2 2 0 0) - (0 2 5 0 0),
(0 1 1 0 1) - (0 1 6 0 1), (0 1 1 0 2) - (0 1 4 0 2),
(1 0 1 0 0) - (1 0 4 0 0), (1 0 1 0 1) - (1 0 4 0 1),
(1 1 1 0 0) - (1 1 5 0 0), (1 1 1 0 1) - (1 1 5 0 1),
(0 2 1 0 1) - (0 2 5 0 1), (1 2 1 0 1) - (1 2 4 0 1),
(1 2 2 0 0) - (1 2 4 0 0)

0.001<FCF<0.011

Table 9.9 Vibrational levels of the ^2B_u state.

IE	Progressions	
	A	B
15.31	M(0 0 0 0 0)	
15.38		W(0 0 0 0 1)
15.54-15.56	S(0 1 0 0 0), W(0 0 1 0 1), W(0 0 0 1 1)	
15.61		M(0 1 0 0 1)
15.77-15.78	S(0 2 0 0 0), W(0 1 1 0 1), W(0 1 0 1 1)	
15.84		M(0 2 0 0 1)
15.99-16.01	M(0 3 0 0 0), W(0 2 1 0 1), W(0 2 0 1 1)	
16.07		W(0 3 0 0 1)
16.22-16.24	W(0 4 0 0 0), W(0 3 1 0 1), W(0 3 0 1 1)	
16.30		W(0 4 0 0 1)
16.45	W(0 5 0 0 0)	

IE	C	D
15.46-15.48	W(0 0 1 0 0), W(0 0 0 1 0), W(0 0 0 0 2)	
15.65		W(0 0 1 1 0)
15.69-15.71	M(0 1 1 0 0), W(0 1 0 1 0), W(0 1 0 0 2)	
15.88		W(0 1 1 1 0)
15.91-15.94	W(0 2 1 0 0), W(0 2 0 1 0), W(0 2 0 0 2)	
16.10		W(0 2 1 1 0)
16.14-16.17	W(0 3 1 0 0), W(0 3 0 1 0), W(0 3 0 0 2)	
16.39	W(0 4 1 0 0), W(0 4 0 1 0)	

S:0.09<FCF<0.11, M:0.03<FCF<0.07 and W:0.005<FCF<0.03.

Table 9.10 Vibrational levels of the ^2B_g state.

IE	Progressions		
	A	B	C
16.29	M(0 0 0 0 0)		
16.42	S(0 0 0 1 0)		
16.46		W(0 0 1 0 0)	
16.53			W(0 1 0 0 0)
16.55	S(0 0 0 2 0)		
16.59		M(0 0 1 1 0)	
16.66			M(0 1 0 1 0)
16.68	S(0 0 0 3 0)		
16.72		M(0 0 1 2 0)	
16.79			M(0 1 0 2 0)
16.81	M(0 0 0 4 0)		
16.85		W(0 0 1 3 0)	
16.92			W(0 1 0 3 0)
16.94	W(0 0 0 5 0)		
16.98		W(0 0 1 4 0)	
17.05			W(0 1 0 4 0)
17.07	W(0 0 0 6 0)		

S:0.15<FCF<0.22, M:0.03<FCF<0.08 and W:0.005<FCF<0.03.

10. cis-1,2-Difluoroethylene cis-$C_2H_2F_2$

Table 10.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C=C (ΔC=C)	C-F (ΔC-F)	C-H (ΔC-H)
$^1A_1$	1.310	1.320	1.079
Exp.[a]	1.331	1.335	1.084
$^2B_1$	1.402(+0.092)	1.252(-0.068)	1.085(+0.006)
$^2A_1$	1.387(+0.077)	1.247(-0.073)	1.110(+0.031)
$^2B_2$	1.295(-0.015)	1.421(+0.101)	1.079(0.000)
$^2A_2$	1.295(-0.015)	1.428(+0.108)	1.078(-0.001)

State	F-C=C (ΔF-C=C)	H-C=C (ΔH-C=C)
$^1A_1$	122.98	122.35
Exp.[a]	123.72	121.56
$^2B_1$	119.15(-3.83)	122.85(+0.50)
$^2A_1$	121.61(-1.37)	113.18(-9.17)
$^2B_2$	101.25(-21.73)	142.97(+20.62)
$^2A_2$	110.04(-12.94)	135.74(+13.39)

[a]Carlos et al. (1974).
Bond lengths are in angstroms, angles in degrees.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 10.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2B_1$	9.38	9.91	8.85	9.42	0.53	0.49
$^2A_1$	14.71	14.13	14.23	13.91	0.48	0.22
$^2B_2$	15.80	15.23	14.49	14.34	1.31	0.89
$^2A_2$	17.02	16.54	16.35	15.93	0.67	0.61

Total energies (a.u.) of $^1A_1$: -275.436797(SCF) and -276.009715(SDCI).

Table 10.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2B_1$	9.41	0.058
$^2A_1$	13.86	0.054
$^2B_2$	14.34	0.000
$^2A_2$	15.91	0.000

Table 10.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3	ν_4	ν_5
$^1A_1$	3435	1967	1387	1113	252
Obs.[a]	3122	1716	1263	1015	237
$^2B_1$	3398	1832	1437	1140	269
$^2A_1$	3090	1686	1209	1150	293
$^2B_2$	3483	1911	1183	1020	563
$^2A_2$	3485	1934	1230	989	303

[a]Craig et al. (1969).

Table 10.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5
$^1A_1$	ΔC=C	1.2	70.6	2.0	17.8	0.4
	ΔC-F	0.1	17.4	20.2	57.9	0.0
	ΔC-H	98.6	0.9	0.1	0.1	0.0
	ΔF-C=C	0.1	1.6	0.2	2.7	70.3
	ΔH-C=C	0.0	9.4	77.6	21.5	29.3
$^2B_1$	ΔC=C	0.7	43.6	1.3	43.6	0.6
	ΔC-F	0.2	41.3	37.8	21.4	0.0
	ΔC-H	98.9	0.1	0.4	0.4	0.0
	ΔF-C=C	0.1	1.5	1.3	4.2	70.2
	ΔH-C=C	0.0	13.5	59.2	30.4	29.2
$^2A_1$	ΔC=C	0.1	33.8	12.3	59.8	0.7
	ΔC-F	0.9	64.2	0.3	27.4	0.0
	ΔC-H	98.9	0.6	1.4	0.7	0.0
	ΔF-C=C	0.1	0.5	1.2	5.7	87.1
	ΔH-C=C	0.1	0.9	84.9	6.4	12.2
$^2B_2$	ΔC=C	3.6	81.3	9.4	1.4	0.1
	ΔC-F	0.1	1.8	0.1	97.0	3.0
	ΔC-H	95.8	2.6	0.1	0.3	0.0
	ΔF-C=C	0.5	10.0	0.2	0.8	87.6
	ΔH-C=C	0.0	4.3	90.2	0.5	9.4
$^2A_2$	ΔC=C	2.5	83.7	6.3	5.2	0.0
	ΔC-F	0.1	4.6	5.3	80.7	1.5
	ΔC-H	97.3	2.2	0.0	0.4	0.0
	ΔF-C=C	0.2	3.4	0.0	1.5	77.1
	ΔH-C=C	0.0	6.1	88.4	12.2	21.4

Table 10.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5
	ΔC=C	-0.008	-0.050	0.006	0.019	0.002
	ΔC-F	-0.002	0.021	-0.017	0.030	-0.000
$^1A_1$	ΔC-H	0.073	-0.006	-0.001	0.002	0.001
	ΔF-C=C	0.3	0.8	0.2	-0.8	2.8
	ΔH-C=C	0.1	2.3	4.8	2.6	-2.1
	ΔC=C	-0.008	-0.046	-0.006	0.037	0.003
	ΔC-F	-0.003	0.028	-0.020	0.016	-0.000
$^2B_1$	ΔC-H	0.073	-0.002	-0.003	0.003	0.000
	ΔF-C=C	0.3	0.7	0.5	-1.0	2.8
	ΔH-C=C	0.1	2.6	4.2	3.2	-2.1
	ΔC=C	-0.003	-0.042	-0.022	0.042	0.003
	ΔC-F	-0.005	0.034	-0.002	0.017	-0.000
$^2A_1$	ΔC-H	0.076	0.005	0.006	0.004	0.001
	ΔF-C=C	0.2	0.5	0.6	-1.2	2.7
	ΔH-C=C	-0.2	0.7	6.1	1.5	-1.2
	ΔC=C	-0.014	0.050	0.012	0.005	-0.001
	ΔC-F	-0.002	-0.009	0.002	0.045	-0.007
$^2B_2$	ΔC-H	0.072	0.010	0.001	0.002	0.000
	ΔF-C=C	0.3	-1.0	-0.1	-0.2	1.6
	ΔH-C=C	0.1	-1.8	6.0	0.4	-1.5
	ΔC=C	-0.011	0.051	0.010	0.010	0.000
	ΔC-F	-0.002	-0.013	-0.011	0.043	-0.004
$^2A_2$	ΔC-H	0.072	0.008	-0.000	0.003	-0.000
	ΔF-C=C	0.3	-0.9	-0.0	-0.5	2.3
	ΔH-C=C	0.1	-2.0	5.6	2.1	-1.9

Bond lengths are in angstroms, angles in degrees.

Table 10.7 Vibrational levels of the $^2B_1$ state.

IE	Progressions			
	A	B	C	D
9.41	M(0 0 0 0 0)			
9.44		W(0 0 0 0 1)		
9.48			W(0 0 0 0 2)	
9.59				W(0 0 0 1 C
9.64	S(0 1 0 0 0)			
9.67		M(0 1 0 0 1)		
9.70			W(0 1 0 0 2)	
9.81				M(0 1 0 1 C
9.85-9.86	S(0 2 0 0 0),W(0 1 0 1 1)			
9.90		M(0 2 0 0 1)		
9.93			W(0 2 0 0 2)	
10.08-10.09	S(0 3 0 0 0),W(0 2 0 1 1)			
10.04				M(0 2 0 1 C
10.12		M(0 3 0 0 1)		
10.16			W(0 3 0 0 2)	
10.27				W(0 3 0 1 C
10.30-10.32	M(0 4 0 0 0),W(0 3 0 1 1)			
10.35		W(0 4 0 0 1)		
10.50				W(0 4 0 1 C
10.55	W(0 5 0 0 0)			
10.58		W(0 5 0 0 1)		

S:0.08<FCF<0.12, M:0.03<FCF<0.06 and W:0.005<FCF<0.03.

Table 10.8 Vibrational levels of the $^2A_1$ state.

IE	Progressions				
	A	B	C	D	E
13.86	M(C 0 0 0 0)				
14.01		M(0 0 0 1 0)			
14.07	S(0 1 0 0 0)				
14.16			W(0 0 0 2 0)		
14.22		M(0 1 0 1 0)			
14.24				W(1 0 0 0 0)	
14.28	S(0 2 0 0 0)				
14.37			W(0 1 0 2 0)		
14.39					W(1 0 0 1 0)
14.43		M(0 2 0 1 0)			
14.45				W(1 1 0 0 0)	
14.49	M(0 3 0 0 0)				
14.58			W(0 2 0 2 0)		
14.60					W(1 1 0 1 0)
14.64		M(0 3 0 1 0)			
14.66				W(1 2 0 0 0)	
14.70	W(0 4 0 0 0)				
14.81					W(1 2 0 1 0)
14.85		W(0 4 0 1 0)			
14.87				W(1 3 0 0 0)	

S:0.08<FCF<0.10, M:0.03<FCF<0.06 and W:0.01<FCF<0.03.

11. 1,1-Difluoroethylene $1,1\text{-}C_2H_2F_2$

Table 11.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C=C (ΔC=C)	C-F (ΔC-F)	C-H (ΔC-H)
$^1A_1$	1.307	1.299	1.078
Exp.[a]	1.316	1.324	1.075
$^2B_1$	1.408(+0.101)	1.236(-0.063)	1.082(+0.004)
$^2B_2$	1.321(+0.014)	1.254(-0.045)	1.161(+0.083)
$^2A_1$	1.394(+0.087)	1.249(-0.050)	1.108(+0.030)
$^2A_2$	1.287(-0.020)	1.358(+0.059)	1.083(+0.005)

State	F-C=C (ΔF-C=C)	H-C=C (ΔH-C=C)
$^1A_1$	125.25	119.63
Exp.[a]	125.34	120.37
$^2B_1$	122.38(-2.87)	118.72(-0.91)
$^2B_2$	122.27(-2.98)	142.13(+22.50)
$^2A_1$	120.69(-4.56)	102.52(-17.11)
$^2A_2$	131.24(+5.99)	119.51(-0.12)

[a]Carlos et al. (1974).
Bond lengths are in angstroms, angles in degrees.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 11.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2B_1$	9.41	9.99	8.88	9.52	0.53	0.47
$^2B_2$	14.66	15.00	13.14	13.61	1.52	1.39
$^2A_1$	16.17	15.95	15.08	15.13	1.09	0.82
$^2A_2$	16.75	16.34	16.39	15.99	0.36	0.35

Total energies (a.u.) of $^1A_1$: -275.454949(SCF) and -276.028413(SDCI).

Table 11.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2B_1$	9.51	0.083
$^2B_2$	13.57	0.000
$^2A_1$	15.06	0.002
$^2A_2$	15.98	0.027

Table 11.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3	ν_4	ν_5
$^1A_1$	3361	1948	1510	1026	601
Obs.[a]	3060	1734	1359	926	550
$^2B_1$	3318	1718	1528	1046	639
$^2B_2$	2890	1858	1292	1089	609
$^2A_1$	2948	1561	1267	981	600
$^2A_2$	3324	1979	1482	938	546

[a]Freeman et al. (1969).

Table 11.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5
$^1A_1$	ΔC=C	1.2	69.1	0.8	18.9	2.1
	ΔC-F	0.0	17.0	7.0	76.2	3.4
	ΔC-H	98.7	0.8	0.0	0.2	0.0
	ΔF-C=C	0.0	7.1	2.1	2.3	94.4
	ΔH-C=C	0.1	6.0	90.1	2.4	0.0
$^2B_1$	ΔC=C	0.5	44.9	0.0	45.0	7.8
	ΔC-F	0.0	37.5	7.2	52.6	2.0
	ΔC-H	99.4	0.1	0.0	0.3	0.0
	ΔF-C=C	0.0	12.0	1.6	0.5	90.1
	ΔH-C=C	0.1	5.5	91.1	1.6	0.0
$^2B_2$	ΔC=C	4.3	62.1	0.5	23.1	3.7
	ΔC-F	0.1	24.8	7.3	68.3	3.9
	ΔC-H	95.1	2.7	3.1	0.5	0.0
	ΔF-C=C	0.0	9.5	1.1	0.6	92.0
	ΔH-C=C	0.6	0.9	88.0	7.5	0.4
$^2A_1$	ΔC=C	0.0	45.9	0.6	56.8	0.3
	ΔC-F	0.1	28.1	34.8	27.3	3.5
	ΔC-H	99.9	1.6	0.1	0.1	0.5
	ΔF-C=C	0.0	8.9	4.5	0.5	94.1
	ΔH-C=C	0.0	15.5	60.1	15.3	1.7
$^2A_2$	ΔC=C	1.2	73.2	0.5	15.6	1.0
	ΔC-F	0.0	16.3	5.1	81.0	0.0
	ΔC-H	98.6	0.8	0.0	0.2	0.0
	ΔF-C=C	0.0	5.0	1.2	2.0	99.0
	ΔH-C=C	0.2	4.8	93.2	1.1	0.0

Table 11.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5
	ΔC=C	-0.008	0.051	0.005	0.018	0.005
	ΔC-F	0.001	-0.020	-0.011	0.028	-0.005
$^1A_1$	ΔC-H	0.072	0.005	0.000	0.002	0.000
	ΔF-C=C	0.0	-1.1	-0.5	0.4	2.0
	ΔH-C=C	0.3	-1.7	5.5	0.7	0.1
	ΔC=C	-0.007	0.050	-0.001	0.033	0.011
	ΔC-F	0.000	-0.026	-0.010	0.020	-0.003
$^2B_1$	ΔC-H	0.072	0.002	-0.001	0.002	0.001
	ΔF-C=C	0.0	-1.4	-0.4	-0.2	2.0
	ΔH-C=C	0.3	-1.6	5.6	0.6	0.0
	ΔC=C	-0.015	0.049	-0.004	0.020	0.006
	ΔC-F	0.001	-0.022	-0.009	0.025	-0.005
$^2B_2$	ΔC-H	0.079	0.012	-0.010	0.003	0.001
	ΔF-C=C	0.1	-1.3	-0.4	0.2	2.1
	ΔH-C=C	0.6	-0.7	5.5	1.4	0.2
	ΔC=C	0.001	-0.052	0.005	0.038	0.002
	ΔC-F	-0.001	0.023	-0.022	0.015	-0.004
$^2A_1$	ΔC-H	0.075	0.008	-0.001	-0.001	0.002
	ΔF-C=C	-0.1	1.3	-0.8	-0.2	2.2
	ΔH-C=C	0.0	3.1	5.1	2.0	-0.5
	ΔC=C	-0.008	0.051	0.004	0.015	0.003
	ΔC-F	0.001	-0.022	-0.010	0.032	-0.000
$^2A_2$	ΔC-H	0.072	0.005	-0.000	0.002	0.001
	ΔF-C=C	0.0	-0.9	-0.4	0.4	2.0
	ΔH-C=C	0.3	-1.6	5.7	0.5	0.0

Bond lengths are in angstroms, angles in degrees.

Table 11.7 Vibrational levels of the $^2B_1$ state.

IE	Progressions	
	A	B
9.51	S(0 0 0 0 0)	
9.72	S(0 1 0 0 0)	
9.91		W(0 1 0 0 1)
9.94	S(0 2 0 0 0)	
10.13		W(0 2 0 0 1)
10.15	S(0 3 0 0 0)	
10.34		W(0 3 0 0 1)
10.36	S(0 4 0 0 0)	
10.55		W(0 4 0 0 1)
10.57	M(0 5 0 0 0)	
10.79	W(0 6 0 0 0)	

S:0.08<FCF<0.23, M:0.03<FCF<0.04 and W:0.01<FCF<0.03.

Table 11.8 Vibrational levels of the $^2B_2$ state.

IE	Progressions		
	A	B	C
14.05	W(0 0 0 0 3)		
14.21	W(0 0 0 0 4)		
14.37	W(0 0 0 0 5)		
14.41		W(1 0 0 0 3)	
14.44			W(0 1 0 0 4)
14.53	W(0 0 0 0 6)		
14.57		W(1 0 0 0 4)	
14.60			W(0 1 0 0 5)
14.69	W(0 0 0 0 7)		
14.73		W(1 0 0 0 5)	
14.76			W(0 1 0 0 6)
14.85	W(0 0 0 0 8)		
14.89		M(1 0 0 0 6)	
14.92-14.93			W(0 1 0 0 7), W(2 0 0 0 4)
15.01	W(0 0 0 0 9)		
15.05		M(1 0 0 0 7)	
15.08-15.09			W(0 1 0 0 8), W(2 0 0 0 5)
15.17	W(0 0 0 0 10)		
15.21		M(1 0 0 0 8)	
15.24-15.25			W(0 1 0 0 9), W(2 0 0 0 6)
15.33	W(0 0 0 0 11)		
15.37		W(1 0 0 0 9)	
15.40-15.41			W(0 1 0 0 10), W(2 0 0 0 7)
15.49	W(0 0 0 0 12)		
15.53		W(1 0 0 0 10)	
15.56-15.57			W(0 1 0 0 11), W(2 0 0 0 8)
15.65	W(0 0 0 0 13)		
15.69		W(1 0 0 0 11)	
15.73			W(2 0 0 0 9)
15.85		W(1 0 0 0 12)	
15.89			W(2 0 0 0 10)
16.01		W(1 0 0 0 13)	
16.05			W(2 0 0 0 11)
16.21			W(2 0 0 0 12)

IE	D
14.80	W(1 1 0 0 4)
14.96	W(1 1 0 0 5)
15.12	W(1 1 0 0 6)
15.28	W(1 1 0 0 7)
15.44	W(1 1 0 0 8)
15.60	W(1 1 0 0 9)
15.76	W(1 1 0 0 10)
15.92	W(1 1 0 0 11)

M:0.03<FCF<0.04 and W:0.005<FCF<0.03.

Table 11.9 Vibrational levels of the $^2A_1$ state.

IE	Progressions				
	A	B	C	D	E
15.25	(0 1 0 0 0)				
15.41		(0 1 0 1 0)			
15.45	(0 2 0 0 0)				
15.57			(0 2 1 0 0)		
15.60		(0 2 0 1 0)			
15.64	(0 3 0 0 0)				
15.68					(0 2 0 1 1
15.73				(0 2 1 1 0)	
15.76			(0 3 1 0 0)		
15.80		(0 3 0 1 0)			
15.83	(0 4 0 0 0)				
15.87					(0 3 0 1 1
15.92				(0 3 1 1 0)	
15.96			(0 4 1 0 0)		
15.99		(0 4 0 1 0)			
16.03	(0 5 0 0 0)				
16.06					(0 4 0 1 1
16.11				(0 4 1 1 0)	
16.15			(0 5 1 0 0)		
16.18		(0 5 0 1 0)			
16.22	(0 6 0 0 0)				
16.31				(0 5 1 1 0)	
16.34			(0 6 1 0 0)		
16.38		(0 6 0 1 0)			

0.005<FCF<0.018.

Table 11.10 Vibrational levels of the $^2A_2$ state.

IE	Progressions
15.98	W(0 0 0 0 0)
16.05	M(0 0 0 0 1)
16.10-16.11	M(0 0 0 0 2),W(0 0 0 1 0)
16.16-16.18	M(0 0 0 0 3),M(0 0 0 1 1)
16.21-16.25	M(0 0 0 0 4),M(0 0 0 1 2),W(0 0 0 2 0),W(0 1 0 0 0)
16.28-16.32	W(0 0 0 0 5),M(0 0 0 1 3),W(0 0 0 2 1),W(0 1 0 0 1)
16.34-16.37	M(0 0 0 1 4),W(0 0 0 2 2),M(0 1 0 0 2),W(0 1 0 1 0)
16.41-16.43	W(0 0 0 1 5),W(0 0 0 2 3),W(0 1 0 0 3),W(0 1 0 1 1)
16.48-16.50	W(0 0 0 2 4),W(0 1 0 0 4),W(0 1 0 1 2)
16.54-16.56	W(0 0 0 2 5),W(0 1 0 0 5),W(0 1 0 1 3)
16.61	W(0 1 0 1 4)
16.68	W(0 1 0 1 5)

M:0.03<FCF<0.04 and W:0.006<FCF<0.03.

12. trans-1,2-Dichloroethylene trans-$C_2H_2Cl_2$

Table 12.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C=C (ΔC=C)	C-Cl(ΔC-Cl)	C-H (ΔC-H)
^1A_g	1.314	1.736	1.079
Exp.[a]	1.332	1.725	1.092
^2A_u	1.399(+0.085)	1.653(-0.083)	1.085(+0.006)
^2A_g	1.326(+0.012)	1.719(-0.017)	1.082(+0.003)
^2B_u	1.302(-0.012)	1.741(+0.005)	1.088(+0.009)
^2B_g	1.304(-0.010)	1.791(+0.055)	1.080(+0.001)

State	Cl-C=C(ΔCl-C=C)	H-C=C (ΔH-C=C)
^1A_g	121.49	123.89
Exp.[a]	120.83	124.0
^2A_u	120.94(-0.55)	121.19(-2.70)
^2A_g	119.89(-1.60)	126.12(+2.23)
^2B_u	118.72(-2.77)	127.97(+4.08)
^2B_g	117.78(-3.71)	128.76(+4.87)

[a]Schafer et al. (1986).
Bond lengths are in angstroms, angles in degrees.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 12.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
^{2}Au	9.10	9.53	8.69	9.10	0.41	0.43
^{2}Ag	12.09	11.87	12.07	11.84	0.02	0.03
^{2}Bu	12.19	12.00	12.15	11.97	0.04	0.03
^{2}Bg	12.85	12.66	12.75	12.57	0.10	0.09

Total energies (a.u.) of $^1A_1$: -994.769687(SCF) and -995.260158(SDCI).

Table 12.3 0-0 ionization levels.

State	0-0 IE	FCF
^2A_u	9.09	0.064
^2A_g	11.81	0.718
^2B_u	11.97	0.670
^2B_g	12.57	0.456

Table 12.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3	ν_4	ν_5
^1A_g	3414	1823	1385	911	376
Obs.[a]	3071	1576	1270	844	349
^2A_u	3371	1639	1363	1001	384
^2A_g	3372	1680	1372	723	324
^2B_u	3330	1871	1338	856	365
^2B_g	3433	1838	1365	850	355

[a]Herzberg (1966).

Table 12.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5
	ΔC=C	1.3	80.2	5.2	0.1	3.6
	ΔC-Cl	0.0	6.7	0.9	44.2	40.6
^1A_g	ΔC-H	98.0	1.2	0.0	0.0	0.0
	ΔCl-C=C	0.5	0.3	5.3	50.7	52.7
	ΔH-C=C	0.1	11.6	88.6	5.1	3.1
	ΔC=C	0.7	46.6	29.8	2.6	7.4
	ΔC-Cl	0.1	13.7	0.2	49.7	27.2
^2A_u	ΔC-H	98.5	0.3	0.2	0.3	0.0
	ΔCl-C=C	0.6	0.1	6.6	46.3	59.3
	ΔH-C=C	0.2	39.3	63.3	1.0	6.2
	ΔC=C	1.3	82.2	3.7	0.2	0.4
	ΔC-Cl	0.0	5.8	0.4	52.6	9.1
^2A_g	ΔC-H	98.3	1.0	0.1	0.1	0.4
	ΔCl-C=C	0.3	0.4	2.2	32.8	76.4
	ΔH-C=C	0.1	10.7	93.6	14.3	13.7
	ΔC=C	2.0	84.1	3.5	0.1	3.7
	ΔC-Cl	0.0	5.2	1.5	44.6	41.5
^2B_u	ΔC-H	97.4	2.0	0.0	0.0	0.0
	ΔCl-C=C	0.5	0.4	5.6	50.2	52.4
	ΔH-C=C	0.1	8.3	89.4	5.0	2.4
	ΔC=C	1.8	84.7	3.3	0.0	2.6
	ΔC-Cl	0.0	4.4	0.9	40.0	46.0
^2B_g	ΔC-H	97.5	1.7	0.0	0.1	0.0
	ΔCl-C=C	0.5	0.5	4.5	50.8	49.4
	ΔH-C=C	0.1	8.7	91.3	9.1	2.0

Table 12.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5
	ΔC=C	-0.009	-0.053	0.012	-0.002	0.005
	ΔC-Cl	-0.002	0.018	0.006	-0.035	0.018
^1A_g	ΔC-H	0.073	-0.006	-0.000	-0.001	0.000
	ΔCl-C=C	0.6	0.4	-1.3	3.6	1.9
	ΔH-C=C	-0.3	2.5	6.3	-1.3	-0.5
	ΔC=C	-0.007	-0.048	0.033	-0.009	0.008
	ΔC-Cl	-0.002	0.022	-0.002	-0.032	0.014
^2A_u	ΔC-H	0.073	-0.003	0.002	-0.002	0.000
	ΔCl-C=C	0.6	-0.2	-1.4	3.2	2.1
	ΔH-C=C	-0.4	4.5	4.9	-0.6	-0.8
	ΔC=C	-0.009	-0.056	0.011	-0.002	0.002
	ΔC-Cl	-0.001	0.017	0.004	-0.043	0.009
^2A_g	ΔC-H	0.073	-0.006	0.002	0.002	0.002
	ΔCl-C=C	0.6	0.5	-1.0	3.8	3.1
	ΔH-C=C	-0.3	2.4	6.3	-2.4	-1.2
	ΔC=C	-0.010	-0.052	0.010	-0.002	0.004
	ΔC-Cl	-0.001	0.016	0.008	-0.037	0.018
^2B_u	ΔC-H	0.074	-0.008	0.000	-0.000	-0.000
	ΔCl-C=C	0.6	0.4	-1.4	3.6	1.9
	ΔH-C=C	-0.3	2.2	6.6	-1.3	-0.5
	ΔC=C	-0.010	-0.053	0.010	-0.001	0.004
	ΔC-Cl	-0.002	0.015	0.006	-0.038	0.020
^2B_g	ΔC-H	0.072	-0.007	0.001	-0.001	0.000
	ΔCl-C=C	0.6	0.4	-1.2	3.7	1.8
	ΔH-C=C	-0.3	2.2	6.5	-1.8	-0.4

Bond lengths are in angstroms, angles in degrees.

Table 12.7 Vibrational levels of the ^2A_u state.

IE	Progressions			
	A	B	C	D
9.09	M(0 0 0 0 0)			
9.14		M(0 0 0 0 1)		
9.18			W(0 0 0 0 2)	
9.21				W(0 0 0 1 0)
9.29	S(0 1 0 0 0)			
9.31-9.34		W(0 1 0 0 1),W(0 0 1 0 1)		
9.39			W(0 1 0 0 2)	
9.42				M(0 1 0 1 0)
9.50	M(0 2 0 0 0)			
9.51-9.54		M(0 2 0 0 1),W(0 1 1 0 1)		
9.59			W(0 2 0 0 2)	
9.62				W(0 2 0 1 0)
9.70	W(0 3 0 0 0)			
9.71-9.75		W(0 3 0 0 1),W(0 2 1 0 1)		
9.80			W(0 3 0 0 2)	
9.82				W(0 3 0 1 0)
9.90	W(0 4 0 0 0)			
9.95		W(0 4 0 0 1)		

IE	E
9.26	W(0 0 1 0 0), W(0 0 0 1 1)
9.46-9.47	W(0 1 1 0 0), W(0 1 0 1 1)
9.66-9.67	W(0 2 1 0 0), W(0 2 0 1 1)
9.87	W(0 3 0 1 1)

S:0.08<FCF<0.09, M:0.03<FCF<0.07 and W:0.006<FCF<0.03.

13. cis-1,2-Dichloroethylene cis-$C_2H_2Cl_2$

Table 13.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C=C (ΔC=C)	C-Cl(ΔC-Cl)	C-H (ΔC-H)
$^1A_1$	1.316	1.727	1.080
Exp.[a]	1.337	1.717	1.096
$^2B_1$	1.403(+0.087)	1.649(-0.078)	1.085(+0.005)
$^2B_2$	1.306(-0.009)	1.766(+0.039)	1.080(+0.001)
$^2A_1$	1.326(+0.011)	1.708(-0.019)	1.087(+0.007)
$^2A_2$	1.304(-0.012)	1.787(+0.061)	1.080(+0.001)

State	Cl-C=C(ΔCl-C=C)	H-C=C (ΔH-C=C)
$^1A_1$	125.16	120.56
Exp.[a]	123.95	120.3
$^2B_1$	123.96(-1.20)	118.77(-1.79)
$^2B_2$	111.11(-14.05)	131.39(+10.83)
$^2A_1$	129.24(+4.08)	118.23(-2.33)
$^2A_2$	118.73(-6.43)	126.55(+5.99)

[a]Schafer et al. (1986).
Bond lengths are in angstroms, angles in degrees.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 13.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2B_1$	9.09	9.52	8.70	9.11	0.39	0.41
$^2B_2$	11.64	11.56	10.82	10.86	0.82	0.70
$^2A_1$	12.13	11.96	12.06	11.86	0.07	0.10
$^2A_2$	12.52	12.42	12.32	12.25	0.20	0.17

Total energies (a.u.) of $^1A_1$: -994.769160(SCF) and -995.259975(SDCI).

Table 13.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2B_1$	9.10	0.102
$^2B_2$	10.86	0.000
$^2A_1$	11.84	0.113
$^2A_2$	12.25	0.003

Table 13.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3	ν_4	ν_5
$^1A_1$	3411	1830	1297	760	180
Obs.[a]	3086	1591	1179	711	173
$^2B_1$	3378	1616	1303	843	193
$^2B_2$	3435	1835	1179	756	312
$^2A_1$	3334	1697	1286	696	205
$^2A_2$	3433	1853	1231	717	204

[a]Herzberg (1966).

Table 13.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5
$^1A_1$	ΔC=C	1.0	82.0	4.7	4.6	0.2
	ΔC-Cl	0.0	7.9	1.1	84.8	0.2
	ΔC-H	98.9	0.8	0.0	0.1	0.0
	ΔCl-C=C	0.1	1.3	0.0	4.1	81.5
	ΔH-C=C	0.0	7.9	94.1	6.4	18.1
$^2B_1$	ΔC=C	0.5	62.6	13.6	16.0	0.4
	ΔC-Cl	0.1	14.7	6.3	73.5	0.2
	ΔC-H	99.3	0.3	0.0	0.3	0.0
	ΔCl-C=C	0.1	1.6	0.2	5.4	81.2
	ΔH-C=C	0.0	20.8	79.9	4.8	18.2
$^2B_2$	ΔC=C	2.0	85.2	6.1	1.3	0.0
	ΔC-Cl	0.1	2.8	0.1	91.0	0.4
	ΔC-H	97.7	1.6	0.0	0.2	0.0
	ΔCl-C=C	0.2	5.2	0.3	4.3	92.6
	ΔH-C=C	0.0	5.3	93.5	3.2	6.9
$^2A_1$	ΔC=C	0.9	84.3	0.7	2.0	0.3
	ΔC-Cl	0.0	8.4	0.7	82.9	0.4
	ΔC-H	99.0	0.8	0.0	0.0	0.0
	ΔCl-C=C	0.1	1.5	0.0	5.3	85.7
	ΔH-C=C	0.0	5.1	98.6	9.7	13.6
$^2A_2$	ΔC=C	1.6	86.1	4.4	2.5	0.0
	ΔC-Cl	0.0	4.6	0.6	86.5	0.0
	ΔC-H	98.3	1.4	0.0	0.2	0.0
	ΔCl-C=C	0.1	2.1	0.0	3.8	85.3
	ΔH-C=C	0.0	6.0	95.0	7.1	14.6

Table 13.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5
	ΔC=C	-0.008	0.054	0.010	0.008	0.001
	ΔC-Cl	-0.002	-0.019	-0.006	0.040	0.001
$^1A_1$	ΔC-H	0.073	0.005	-0.001	0.001	0.000
	ΔCl-C=C	0.2	-0.7	-0.1	-0.8	1.9
	ΔH-C=C	0.1	-2.1	5.7	1.2	-1.2
	ΔC=C	-0.007	-0.054	0.020	0.019	0.002
	ΔC-Cl	-0.002	0.022	-0.011	0.034	0.001
$^2B_1$	ΔC-H	0.073	-0.003	-0.000	0.002	0.000
	ΔCl-C=C	0.2	0.7	-0.2	-0.9	1.9
	ΔH-C=C	0.1	3.2	5.0	1.1	-1.2
	ΔC=C	-0.010	0.053	0.011	0.004	-0.000
	ΔC-Cl	-0.002	-0.013	-0.002	0.046	-0.002
$^2B_2$	ΔC-H	0.072	0.007	0.000	0.002	0.000
	ΔCl-C=C	0.2	-0.8	-0.1	-0.5	1.4
	ΔH-C=C	0.1	-1.9	6.0	1.0	-0.9
	ΔC=C	-0.007	0.056	0.004	0.006	0.001
	ΔC-Cl	-0.001	-0.020	-0.004	0.041	0.002
$^2A_1$	ΔC-H	0.074	0.005	0.001	0.001	-0.000
	ΔCl-C=C	0.2	-0.7	0.0	-0.8	1.9
	ΔH-C=C	0.0	-1.7	5.8	1.5	-1.0
	ΔC=C	-0.009	0.053	0.009	0.006	0.000
	ΔC-Cl	-0.002	-0.016	-0.004	0.044	-0.000
$^2A_2$	ΔC-H	0.073	0.007	-0.001	0.002	0.000
	ΔCl-C=C	0.2	-0.7	-0.1	-0.6	1.7
	ΔH-C=C	0.1	-1.9	5.9	1.4	-1.1

Bond lengths are in angstroms, angles in degrees.

Table 13.7 Vibrational levels of the $^2B_1$ state.

IE	Progressions			
	A	B	C	D
9.10	S(0 0 0 0 0)			
9.20		M(0 0 0 1 0)		
9.26			M(0 0 1 0 0)	
9.30	S(0 1 0 0 0)			
9.46			M(0 1 1 0 0)	
9.40		M(0 1 0 1 0)		
9.50-9.51	S(0 2 0 0 0),W(0 1 0 2 0)			
9.57				M(0 1 1 1 0)
9.60		M(0 2 0 1 0)		
9.66			M(0 2 1 0 0)	
9.70-9.71	M(0 3 0 0 0),W(0 2 0 2 0)			
9.77				W(0 2 1 1 0)
9.81		W(0 3 0 1 0)		
9.86			W(0 3 1 0 0)	
9.90	W(0 4 0 0 0)			
10.01		W(0 4 0 1 0)		

S:0.10<FCF<0.18, M:0.03<FCF<0.06 and W:0.008<FCF<0.03.

Table 13.8 Vibrational levels of the $^2A_1$ state.

IE	Progressions
11.84	S(0 0 0 0 0)
11.86	S(0 0 0 0 1)
11.89	S(0 0 0 0 2)
11.92-11.93	S(0 0 0 0 3), W(0 0 0 1 0)
11.94-11.95	S(0 0 0 0 4), W(0 0 0 1 1)
11.97-11.98	M(0 0 0 0 5), W(0 0 0 1 2)
11.99-12.00	W(0 0 0 0 6), W(0 0 0 1 3)

S:0.08<FCF<0.24, M:0.03<FCF<0.04 and W:0.01<FCF<0.03.

14. 1,1-Dichloroethylene $1,1\text{-}C_2H_2Cl_2$

Table 14.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C=C (ΔC=C)	C-Cl(ΔC-Cl)	C-H (ΔC-H)
$^1A_1$	1.314	1.734	1.080
Exp.[a]	1.324	1.721	1.079
$^2B_1$	1.410(+0.096)	1.662(-0.072)	1.082(+0.002)
$^2B_2$	1.302(-0.012)	1.738(+0.004)	1.083(+0.003)
$^2A_2$	1.308(-0.006)	1.750(+0.016)	1.082(+0.002)
$^2A_1$	1.324(+0.010)	1.740(+0.006)	1.081(+0.001)

State	Cl-C=C(ΔCl-C=C)	H-C=C (ΔH-C=C)
$^1A_1$	122.87	120.32
Exp.[a]	123.0	119.75
$^2B_1$	120.34(-2.53)	119.65(-0.67)
$^2B_2$	132.73(+9.86)	120.24(-0.08)
$^2A_2$	126.62(+3.75)	120.37(+0.05)
$^2A_1$	119.96(-2.91)	120.66(+0.34)

[a]Nakata et al. (1982)
Bond lengths are in angstroms, angles in degrees.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 14.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2B_1$	9.11	9.65	8.71	9.23	0.40	0.42
$^2B_2$	11.43	11.44	10.95	11.03	0.48	0.31
$^2A_2$	12.10	12.03	12.02	11.97	0.08	0.06
$^2A_1$	12.52	12.42	12.46	12.34	0.06	0.08

Total energies (a.u.) of $^1A_1$: -994.765626(SCF) and -995.257642(SDCI).

Table 14.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2B_1$	9.21	0.085
$^2B_2$	11.03	0.000
$^2A_2$	11.97	0.155
$^2A_1$	12.33	0.273

Table 14.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3	ν_4	ν_5
$^1A_1$	3335	1835	1500	641	316
Obs.[a]	3035	1616	1391	601	299
$^2B_1$	3316	1592	1435	682	346
$^2B_2$	3323	1868	1493	663	320
$^2A_2$	3327	1833	1496	631	308
$^2A_1$	3337	1704	1521	571	332

[a]Herzberg (1966).

Table 14.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5
$^1A_1$	ΔC=C	1.1	77.3	9.0	5.0	0.2
	ΔC-Cl	0.0	5.3	2.8	83.2	8.7
	ΔC-H	98.8	0.6	0.2	0.1	0.0
	ΔCl-C=C	0.0	2.7	1.3	11.6	91.1
	ΔH-C=C	0.1	14.2	86.7	0.1	0.0
$^2B_1$	ΔC=C	0.5	27.1	58.3	11.7	0.8
	ΔC-Cl	0.0	2.0	13.7	79.7	8.5
	ΔC-H	99.4	0.1	0.2	0.1	0.0
	ΔCl-C=C	0.0	1.0	6.8	8.4	90.7
	ΔH-C=C	0.1	69.8	21.1	0.1	0.0
$^2B_2$	ΔC=C	1.1	78.2	4.8	6.6	0.1
	ΔC-Cl	0.0	8.8	3.4	85.8	0.1
	ΔC-H	98.8	0.7	0.1	0.1	0.0
	ΔCl-C=C	0.0	2.5	0.9	7.3	99.8
	ΔH-C=C	0.1	9.8	90.8	0.2	0.0
$^2A_2$	ΔC=C	1.1	78.1	7.5	4.9	0.1
	ΔC-Cl	0.0	6.2	2.9	85.1	3.4
	ΔC-H	98.8	0.7	0.1	0.1	0.0
	ΔCl-C=C	0.0	2.5	1.1	9.8	96.5
	ΔH-C=C	0.1	12.7	88.4	0.1	0.0
$^2A_1$	ΔC=C	0.9	69.7	19.2	0.9	0.0
	ΔC-Cl	0.0	3.2	2.9	85.6	3.6
	ΔC-H	99.0	0.3	0.4	0.1	0.0
	ΔCl-C=C	0.0	2.3	2.0	13.4	96.2
	ΔH-C=C	0.1	24.4	75.6	0.1	0.2

Table 14.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5
	C=C	-0.009	-0.053	0.012	-0.002	0.005
	C-Cl	-0.002	0.018	0.006	-0.035	0.018
^1A_g	C-H	0.073	-0.006	-0.000	-0.001	0.000
	Cl-C=C	0.6	0.4	-1.3	3.6	1.9
	H-C=C	-0.3	2.5	6.3	-1.3	-0.5
	ΔC=C	-0.008	-0.052	0.015	0.007	0.001
	ΔC-Cl	0.001	0.015	-0.009	0.034	-0.007
$^1A_1$	ΔC-H	0.072	-0.004	0.002	0.001	0.000
	ΔCl-C=C	0.0	0.7	-0.4	0.9	1.7
	ΔH-C=C	0.3	2.5	5.2	0.1	-0.0
	ΔC=C	-0.007	-0.036	0.048	0.014	0.003
	ΔC-Cl	0.000	0.008	-0.018	0.030	-0.007
$^2B_1$	ΔC-H	0.072	-0.001	0.002	0.001	0.000
	ΔCl-C=C	0.0	0.4	-1.0	0.7	1.7
	ΔH-C=C	0.3	5.2	2.6	0.1	-0.0
	ΔC=C	-0.008	-0.053	0.011	0.009	0.001
	ΔC-Cl	0.001	0.020	-0.010	0.037	-0.001
$^2B_2$	ΔC-H	0.072	-0.005	0.001	0.001	0.000
	ΔCl-C=C	0.0	0.7	-0.3	0.7	1.6
	ΔH-C=C	0.3	2.1	5.4	0.2	-0.0
	ΔC=C	-0.008	-0.053	0.014	0.008	0.001
	ΔC-Cl	0.001	0.017	-0.010	0.036	-0.005
$^2A_2$	ΔC-H	0.072	-0.005	0.002	0.001	0.000
	ΔCl-C=C	0.0	0.7	-0.4	0.8	1.7
	ΔH-C=C	0.3	2.4	5.3	0.1	-0.0
	ΔC=C	-0.007	-0.052	0.023	0.003	0.000
	ΔC-Cl	0.000	0.013	-0.010	0.036	-0.005
$^2A_1$	ΔC-H	0.072	-0.003	0.003	0.001	0.000
	ΔCl-C=C	0.0	0.7	-0.5	0.9	1.7
	ΔH-C=C	0.3	3.3	4.8	0.1	-0.1

Bond lengths are in angstroms, angles in degrees.

Table 14.7 Vibrational levels of the $^2B_1$ state.

IE	Progressions	
	A	B
9.21	S(0 0 0 0 0)	
9.29		M(0 0 0 1 0)
9.38-9.41	S(0 0 1 0 0),W(0 0 0 2 0),M(0 1 0 0 0)	
9.47-9.49		M(0 0 1 1 0),W(0 1 0 1 0)
9.56-9.59	S(0 0 2 0 0),W(0 0 1 2 0),M(0 1 1 0 0)	
9.65-9.67		M(0 0 2 1 0),M(0 1 1 1 0)
9.73-9.76	M(0 0 3 0 0),W(0 0 2 2 0),M(0 1 2 0 0)	
9.83-9.85		W(0 0 3 1 0),W(0 1 2 1 0)
9.91-9.94	W(0 0 4 0 0),W(0 0 3 2 0),W(0 1 3 0 0)	
10.01-10.03		W(0 0 4 1 0),W(0 1 3 1 0)

S:0.08<FCF<0.12, M:0.03<FCF<0.07 and W:0.007<FCF<0.03.

Table 14.8 Vibrational levels of the $^2B_2$ state.

IE	Progressions
11.35	W(0 0 0 0 8)
11.39	W(0 0 0 0 9)
11.43	W(0 0 0 0 10)
11.47	M(0 0 0 0 11)
11.51	M(0 0 0 0 12)
11.55	M(0 0 0 0 13)
11.58	M(0 0 0 0 14)
11.62	M(0 0 0 0 15)
11.66	S(0 0 0 0 16)
11.70	S(0 0 0 0 17)
11.74	S(0 0 0 0 18)
11.78	M(0 0 0 0 19)
11.82	M(0 0 0 0 20)
11.86	M(0 0 0 0 21)
11.90	M(0 0 0 0 22)
11.94	M(0 0 0 0 23)
11.98	W(0 0 0 0 24)
12.02	W(0 0 0 0 25)
12.06	W(0 0 0 0 26)

S:0.08<FCF<0.09, M:0.03<FCF<0.08 and W: 0.008<FCF<0.03.

Table 14.9 Vibrational levels of the $^2A_2$ state.

IE	Progressions
11.97	S(0 0 0 0 0)
12.01	S(0 0 0 0 1)
12.05	S(0 0 0 0 2), W(0 0 0 1 0)
12.09	S(0 0 0 0 3), M(0 0 0 1 1)
12.12-12.13	M(0 0 0 0 4), M(0 0 0 1 2)
12.16	M(0 0 0 0 5), W(0 0 0 1 3)
12.20	W(0 0 0 1 4)

S:0.08<FCF<0.25, M:0.03<FCF<0.06 and W: 0.01<FCF<0.03.

Table 14.10 Vibrational levels of the $^2A_1$ state.

IE	Progression
12.33	S(0 0 0 0 0)
12.37	S(0 0 0 0 1)
12.41	S(0 0 0 0 2)
12.45	S(0 0 0 0 3)
12.49	W(0 0 0 0 4)

S:0.09<FCF<0.35 and W:0.02<FCF<0.03.

15. trans-Butadiene trans-C_4H_6

Table 15.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C-C (ΔC-C)	C=C (ΔC=C)	C_1-H_5(ΔC_1-H_5)	C_1-H_6(ΔC_1-H_6)	C_2-H_7(ΔC_2-H_7)
^1A_g	1.468	1.326	1.083	1.085	1.086
Exp.[a]	1.463	1.341	1.090		
^2B_g	1.402(-0.066)	1.378(+0.053)	1.083(+0.000)	1.084(-0.001)	1.084(-0.002)
^2A_u	1.538(+0.071)	1.366(+0.040)	1.082(-0.001)	1.083(-0.001)	1.084(-0.002)
^2A_g	1.828(+0.360)	1.293(-0.032)	1.090(+0.007)	1.082(-0.002)	1.083(-0.003)
^2B_u	1.450(-0.018)	1.307(-0.019)	1.089(+0.006)	1.179(+0.094)	1.110(+0.024)

State	C=C-C(ΔC=C-C)	H_5-C_1=C_2(ΔH_5-C_1=C_2)	H_6-C_1=C_2(ΔH_6-C_1=C_2)	H_7-C_2=C_1(ΔH_7-C_2=C:
^1A_g	124.14	121.49	121.64	119.49
Exp.[a]	123.3	121.8		
^2B_g	121.22(-2.92)	121.14(-0.35)	121.27(-0.37)	119.21(-0.28)
^2A_u	123.69(-0.45)	119.97(-1.52)	122.07(+0.43)	119.61(+0.12)
^2A_g	119.14(-5.00)	115.95(-5.54)	125.74(+4.10)	142.05(+22.56)
^2B_u	122.52(-1.62)	138.14(+16.65)	110.97(-10.67)	117.09(-2.40)

[a]Kuchitsu et al. (1968).
Bond lengths are in angstroms, angles in degrees.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 15.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
^2B_g	8.02	8.70	7.75	8.41	0.27	0.29
^2A_u	11.08	11.54	10.89	11.30	0.19	0.24
^2A_g	12.23	12.37	10.99	11.55	1.24	0.82
^2B_u	14.22	13.91	13.59	13.35	0.63	0.56

Total energies (a.u.) of ^1A_g: -154.747954(SCF) and -155.244041(SDCI)

Table 15.3 0-0 ionization levels.

State	0-0 IE	FCF
^2B_g	8.41	0.263
^2A_u	11.30	0.195
^2A_g	11.46	0.000
^2B_u	13.22	0.000

Table 15.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
^1A_g	3394	3316	3296	1883	1574	1409	1306	952	548
Obs.[a]	3101	3014	3014	1643	1442	1279	1205	890	513
^2B_g	3441	3359	3323	1805	1602	1386	1369	1001	553
^2A_u	3446	3361	3327	1769	1568	1393	1258	896	525
^2A_g	3406	3373	3269	1814	1455	1262	862	421	356
^2B_u	3283	3044	2512	1914	1392	1237	1067	785	482

[a]Herzberg (1966).

Table 15.5 Conventional potential energy distribution(%).

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
^1A_g									
$\Delta C-C$	0.0	0.1	0.1	13.2	9.1	1.4	25.8	32.1	4.1
$\Delta C=C$	0.0	1.1	0.3	65.3	0.1	14.5	0.2	4.2	3.3
ΔC_1-H_6	62.5	5.5	30.9	0.2	0.1	0.1	0.0	0.0	0.0
ΔC_1-H_8	35.7	22.5	40.7	0.2	0.1	0.1	0.0	0.0	0.0
ΔC_2-H_7	1.2	70.0	27.8	0.1	0.1	0.0	0.0	0.1	0.0
$\Delta C=C-C$	0.1	0.6	0.1	2.0	0.1	8.5	20.7	2.7	58.2
$\Delta H_6-C_1=C_2$	0.2	0.2	0.0	2.0	49.9	1.8	21.0	33.0	7.1
$\Delta H_8-C_1=C_2$	0.2	0.0	0.1	5.2	19.4	23.8	24.2	25.1	8.6
$\Delta H_7-C_2=C_1$	0.1	0.1	0.0	11.9	21.4	49.8	8.1	2.9	18.7
^2B_g									
$\Delta C-C$	0.0	0.4	0.0	25.6	12.2	9.0	26.6	17.8	2.2
$\Delta C=C$	0.0	0.4	0.6	42.6	1.2	19.6	9.5	7.8	4.5
ΔC_1-H_6	54.4	0.1	44.8	0.1	0.0	0.0	0.0	0.1	0.0
ΔC_1-H_8	44.6	1.9	52.8	0.1	0.0	0.1	0.1	0.0	0.0
ΔC_2-H_7	0.4	96.2	1.7	0.0	0.1	0.2	0.1	0.1	0.0
$\Delta C=C-C$	0.1	0.8	0.0	0.8	1.1	23.3	3.2	0.7	58.8
$\Delta H_6-C_1=C_2$	0.2	0.1	0.0	0.7	51.3	5.6	3.5	40.7	7.4
$\Delta H_8-C_1=C_2$	0.2	0.1	0.0	7.0	16.8	33.9	0.4	31.2	8.4
$\Delta H_7-C_2=C_1$	0.1	0.1	0.0	23.1	17.3	8.3	56.6	1.8	18.7
^2A_u									
$\Delta C-C$	0.0	0.2	0.0	9.8	6.8	0.0	19.4	39.7	4.9
$\Delta C=C$	0.0	0.5	0.6	58.8	1.1	21.2	0.8	3.5	4.3
ΔC_1-H_6	57.9	0.1	41.2	0.1	0.0	0.0	0.0	0.0	0.1
ΔC_1-H_8	41.0	2.4	55.9	0.1	0.0	0.2	0.0	0.0	0.0
ΔC_2-H_7	0.5	95.9	2.1	0.2	0.0	0.1	0.1	0.1	0.0
$\Delta C=C-C$	0.1	0.7	0.0	2.1	0.0	7.3	16.9	7.0	58.4
$\Delta H_6-C_1=C_2$	0.2	0.1	0.0	4.1	45.2	1.5	29.2	25.6	6.8
$\Delta H_8-C_1=C_2$	0.2	0.1	0.0	8.0	20.1	19.2	31.1	19.7	7.8
$\Delta H_7-C_2=C_1$	0.1	0.1	0.0	16.8	26.8	50.5	2.6	4.4	17.6
^2A_g									
$\Delta C-C$	0.0	0.0	0.0	1.2	0.8	1.4	0.7	70.7	0.1
$\Delta C=C$	0.4	1.7	0.5	86.6	8.1	1.0	0.5	0.1	1.0
ΔC_1-H_6	17.2	4.8	77.4	0.2	0.0	0.0	0.2	0.0	0.0
ΔC_1-H_8	81.0	0.0	17.7	0.4	0.2	0.0	0.0	0.0	0.0
ΔC_2-H_7	1.0	93.3	4.2	1.6	0.3	0.3	0.0	0.5	0.6
$\Delta C=C-C$	0.1	0.2	0.0	1.0	0.5	2.1	2.1	16.0	82.6
$\Delta H_6-C_1=C_2$	0.2	0.0	0.0	3.7	41.8	8.1	46.7	0.8	1.5
$\Delta H_8-C_1=C_2$	0.1	0.0	0.1	3.9	44.7	15.6	42.0	0.7	1.2
$\Delta H_7-C_2=C_1$	0.1	0.0	0.0	1.5	3.6	71.5	7.7	11.3	13.1
^2B_u									
$\Delta C-C$	0.0	0.5	0.1	18.6	15.7	34.2	12.5	13.4	2.0
$\Delta C=C$	1.3	0.2	0.8	68.8	10.0	0.1	8.0	4.4	0.4
ΔC_1-H_6	98.0	1.0	0.3	0.5	0.0	0.0	1.3	1.3	0.9
ΔC_1-H_8	0.0	0.8	96.6	0.6	0.1	0.5	0.1	0.1	0.2
ΔC_2-H_7	0.7	96.5	1.8	0.1	0.2	0.1	0.4	0.9	0.1
$\Delta C=C-C$	0.0	0.8	0.1	1.8	10.1	22.4	7.2	10.3	44.4
$\Delta H_6-C_1=C_2$	0.0	0.1	0.3	0.1	31.6	3.4	41.1	11.5	11.9
$\Delta H_8-C_1=C_2$	0.0	0.0	0.0	0.6	0.1	3.6	8.5	55.2	22.7
$\Delta H_7-C_2=C_1$	0.0	0.1	0.1	9.0	32.1	35.7	21.0	2.8	17.6

Table 15.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5
^1A_g	$\Delta C-C$	-0.001	-0.004	0.003	0.030	-0.020
	$\Delta C=C$	-0.001	-0.006	-0.003	-0.035	0.001
	ΔC_1-H_5	0.059	0.017	0.041	-0.003	0.001
	ΔC_1-H_6	-0.045	0.035	0.047	-0.003	0.001
	ΔC_2-H_7	0.008	0.062	-0.039	-0.002	-0.001
	$\Delta C=C-C$	-0.2	0.6	-0.3	0.9	0.1
	$\Delta H_5-C_1=C_2$	-0.4	0.4	0.0	1.1	4.4
	$\Delta H_6-C_1=C_2$	0.5	-0.1	0.2	1.8	2.7
	$\Delta H_7-C_2=C_1$	0.3	-0.2	0.1	2.5	-2.6
		ν_6	ν_7	ν_8	ν_9	
	$\Delta C-C$	0.009	0.035	0.038	0.011	
	$\Delta C=C$	0.015	-0.002	0.007	0.005	
	ΔC_1-H_5	0.002	0.001	0.000	0.001	
	ΔC_1-H_6	0.001	-0.001	0.001	0.000	
	ΔC_2-H_7	0.001	0.001	0.001	0.001	
	$\Delta C=C-C$	-1.6	-2.3	-0.8	3.0	
	$\Delta H_5-C_1=C_2$	-0.9	-2.9	3.6	-1.4	
	$\Delta H_6-C_1=C_2$	3.5	3.1	-3.2	1.5	
	$\Delta H_7-C_2=C_1$	4.6	-1.7	1.0	-2.0	
		ν_1	ν_2	ν_3	ν_4	ν_5
^2B_g	$\Delta C-C$	-0.000	-0.006	0.001	0.037	-0.021
	$\Delta C=C$	-0.000	-0.004	-0.005	-0.032	-0.004
	ΔC_1-H_5	0.055	0.003	0.049	-0.002	0.000
	ΔC_1-H_6	-0.050	0.010	0.053	-0.002	0.000
	ΔC_2-H_7	0.005	0.073	-0.010	-0.000	-0.001
	$\Delta C=C-C$	-0.2	0.7	-0.0	0.5	0.5
	$\Delta H_5-C_1=C_2$	-0.4	0.3	0.2	0.6	4.5
	$\Delta H_6-C_1=C_2$	0.5	-0.2	0.2	2.0	2.6
	$\Delta H_7-C_2=C_1$	0.3	-0.2	0.0	3.4	-2.4
		ν_6	ν_7	ν_8	ν_9	
	$\Delta C-C$	0.020	-0.028	0.026	0.007	
	$\Delta C=C$	0.020	0.011	0.011	0.007	
	ΔC_1-H_5	0.001	0.000	0.001	0.001	
	ΔC_1-H_6	0.002	0.001	0.000	0.000	
	ΔC_2-H_7	0.002	-0.001	0.001	0.001	
	$\Delta C=C-C$	-2.7	0.8	-0.4	3.1	
	$\Delta H_5-C_1=C_2$	-1.7	1.1	4.2	-1.4	
	$\Delta H_6-C_1=C_2$	4.2	-0.4	-3.6	1.5	
	$\Delta H_7-C_2=C_1$	1.9	3.9	0.8	-2.0	

Table 15.6 Condt.

		ν_1	ν_2	ν_3	ν_4	ν_5
^2A_u	$\Delta C-C$	-0.000	-0.005	0.001	0.028	-0.019
	$\Delta C=C$	-0.001	-0.004	-0.005	-0.034	0.004
	ΔC_1-H_5	0.056	0.003	0.047	-0.002	0.001
	ΔC_1-H_6	-0.048	0.011	0.055	-0.002	0.001
	ΔC_2-H_7	0.005	0.072	-0.011	-0.002	-0.000
	$\Delta C=C-C$	-0.2	0.7	-0.0	0.9	-0.0
	$\Delta H_5-C_1=C_2$	-0.4	0.3	0.2	1.5	4.1
	$\Delta H_6-C_1=C_2$	0.5	-0.2	0.2	2.1	2.8
	$\Delta H_7-C_2=C_1$	0.3	-0.2	0.0	2.8	-2.9

		ν_6	ν_7	ν_8	ν_9
	$\Delta C-C$	0.002	0.035	0.046	0.013
	$\Delta C=C$	0.019	-0.003	0.007	0.006
	ΔC_1-H_5	0.001	-0.000	0.001	0.001
	ΔC_1-H_6	0.002	-0.000	0.000	0.000
	ΔC_2-H_7	0.001	0.002	0.001	0.000
	$\Delta C=C-C$	-1.4	-2.2	-1.3	2.9
	$\Delta H_5-C_1=C_2$	-0.8	-3.6	3.1	-1.3
	$\Delta H_6-C_1=C_2$	3.0	3.8	-2.7	1.4
	$\Delta H_7-C_2=C_1$	4.4	-1.0	1.2	-1.9

		ν_1	ν_2	ν_3	ν_4	ν_5
^2A_g	$\Delta C-C$	0.000	0.000	0.000	-0.019	-0.012
	$\Delta C=C$	-0.003	-0.007	-0.004	0.037	0.008
	ΔC_1-H_5	-0.031	0.016	0.065	0.003	0.001
	ΔC_1-H_6	0.067	-0.001	0.030	0.004	0.002
	ΔC_2-H_7	0.007	0.071	-0.015	0.007	0.002
	$\Delta C=C-C$	0.3	0.5	-0.2	-0.8	-0.4
	$\Delta H_5-C_1=C_2$	0.5	0.1	0.0	-1.6	3.8
	$\Delta H_6-C_1=C_2$	-0.4	0.0	0.3	-1.6	3.8
	$\Delta H_7-C_2=C_1$	-0.3	0.1	0.2	-1.0	-1.1

		ν_6	ν_7	ν_8	ν_9
	$\Delta C-C$	0.019	-0.015	0.099	-0.002
	$\Delta C=C$	0.004	0.003	0.001	0.002
	ΔC_1-H_5	0.000	-0.003	0.000	0.000
	ΔC_1-H_6	0.001	0.001	0.000	0.000
	ΔC_2-H_7	-0.002	0.000	-0.002	0.002
	$\Delta C=C-C$	-1.2	1.3	-2.4	4.2
	$\Delta H_5-C_1=C_2$	-2.1	5.5	0.5	-0.5
	$\Delta H_6-C_1=C_2$	2.9	-5.1	-0.4	0.4
	$\Delta H_7-C_2=C_1$	6.4	2.2	1.8	-1.5

Table 5.6 Contd.

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5
	$\Delta C-C$	0.000	-0.007	0.003	0.034	-0.029
	$\Delta C=C$	-0.006	-0.002	-0.004	-0.035	-0.012
^2B_u	ΔC_1-H_8	0.074	-0.007	-0.004	-0.004	-0.001
	ΔC_1-H_9	0.002	0.009	0.084	-0.006	-0.002
	ΔC_2-H_7	0.007	0.076	-0.009	0.002	-0.003
	$\Delta C=C-C$	-0.0	0.7	0.2	0.8	1.8
	$\Delta H_8-C_1=C_2$	-0.1	0.4	0.6	0.2	4.7
	$\Delta H_9-C_1=C_2$	0.3	-0.2	-0.1	0.9	-0.3
	$\Delta H_7-C_2=C_1$	0.1	-0.3	-0.3	2.3	-4.0

	ν_6	ν_7	ν_8	ν_9
$\Delta C-C$	-0.032	0.021	-0.021	0.007
$\Delta C=C$	0.001	0.009	-0.006	0.002
ΔC_1-H_8	-0.000	0.005	0.005	0.004
ΔC_1-H_9	0.004	0.002	-0.002	-0.002
ΔC_2-H_7	-0.001	-0.003	-0.004	-0.001
$\Delta C=C-C$	2.0	-1.2	-1.4	2.8
$\Delta H_8-C_1=C_2$	1.2	4.3	-2.2	-2.1
$\Delta H_9-C_1=C_2$	-1.6	2.6	6.3	3.8
$\Delta H_7-C_2=C_1$	3.2	2.6	0.9	-2.2

Bond lengths are in angstroms, angles in degrees.

Table 15.7 Vibrational levels of the ^2B_g state.

IE	Progressions		
	A	B	The rest
8.41	S(0 0 0 0 0 0 0 0 0)		
8.48			W(0 0 0 0 0 0 0 0 1)
8.58		M(0 0 0 0 0 0 1 0 0),	M(0 0 0 0 0 1 0 0 0)
8.63	S(0 0 0 1 0 0 0 0 0)		
8.70			W(0 0 0 1 0 0 0 0 1)
8.80-8.81		M(0 0 0 1 0 0 1 0 0),	W(0 0 0 1 0 1 0 0 0)
8.86	S(0 0 0 2 0 0 0 0 0)		
9.03		W(0 0 0 2 0 0 1 0 0)	
9.08	W(0 0 0 3 0 0 0 0 0)		

S:0.08<FCF<0.26, M:0.03<FCF<0.6 and W:0.01<FCF<0.03.

Table 15.8 Vibrational levels of the ^2A_u state.

IE	Vibrational levels
11.30	S(0 0 0 0 0 0 0 0 0)
11.36	S(0 0 0 0 0 0 0 0 1)
11.41-11.43	S(0 0 0 0 0 0 0 1 0),M(0 0 0 0 0 0 0 0 2)
11.46-11.48	M(0 0 0 0 0 0 1 0 0),M(0 0 0 0 0 1 0 0 0),M(0 0 0 0 0 0 0 1 1)
11.52-11.54	W(0 0 0 1 0 0 0 0 0),W(0 0 0 0 0 0 1 0 1),M(0 0 0 0 0 0 0 2 0), W(0 0 0 0 0 1 0 0 1),W(0 0 0 0 0 0 0 1 2)
11.57-11.59	W(0 0 0 0 0 0 1 1 0),W(0 0 0 1 0 0 0 0 1),W(0 0 0 0 0 1 0 1 0), W(0 0 0 0 0 0 0 2 1)
11.63-11.65	W(0 0 0 1 0 0 0 1 0),W(0 0 0 0 0 1 0 1 1)
11.70	W(0 0 0 1 0 0 0 1 1)

S:0.12<FCF<0.20, M:0.03<FCF<0.8 and W:0.01<FCF<0.03.

16. cis-Butadiene cis-C_4H_6

Table 16.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C-C (ΔC-C)	C=C (ΔC=C)	C_1-H_6(ΔC_1-H_6)	C_1-H_8(ΔC_1-H_8)	C_2-H_7(ΔC_2-H_7)
$^1A_1$	1.480	1.325	1.083	1.084	1.085
$^2A_2$	1.410(-0.070)	1.377(+0.052)	1.083(0.0)	1.082(-0.002)	1.083(-0.002)
$^2B_1$	1.547(+0.067)	1.366(+0.041)	1.082(-0.001)	1.083(-0.001)	1.083(-0.002)
$^2A_1$	1.896(+0.416)	1.292(-0.033)	1.091(+0.008)	1.080(-0.004)	1.080(-0.005)
$^2B_2$	1.386(-0.094)	1.317(-0.008)	1.080(-0.003)	1.090(+0.006)	1.203(+0.118)

State	C=C-C(ΔC=C-C)	H_6-C_1=C_2(ΔH_6-C_1=C_2)	H_8-C_1=C_2(ΔH_8-C_1=C_2)	H_7-C_2=C_1(ΔH_7-C_2=(
$^1A_1$	127.27	120.74	122.72	118.00
$^2A_2$	125.07(-2.20)	120.06(-0.68)	123.27(+0.55)	117.83(-0.17)
$^2B_1$	127.31(+0.04)	119.43(-1.31)	123.06(+0.34)	118.72(+0.72)
$^2A_1$	119.76(-7.51)	114.89(-5.85)	126.98(+4.26)	141.80(+23.80)
$^2B_2$	149.07(+21.80)	123.71(+2.97)	117.20(-5.52)	110.08(-7.92)

Bond lengths are in angstroms, angles in degrees.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 16.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2A_2$	8.00	8.69	7.74	8.41	0.26	0.28
$^2B_1$	11.00	11.49	10.81	11.25	0.19	0.24
$^2A_1$	12.36	12.48	10.94	11.53	1.42	0.95
$^2B_2$	13.29	13.10	12.31	12.43	0.98	0.67

Total energies (a.u.) of $^1A_1$: -154.741534(SCF) and -155.237980(SDCI).

Table 16.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2A_2$	8.42	0.178
$^2B_1$	11.24	0.208
$^2A_1$	11.47	0.000
$^2B_2$	12.34	0.000

Table 16.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
$^1A_1$	3400	3331	3309	1841	1570	1455	1129	932	315
$^2A_2$	3451	3376	3339	1774	1610	1430	1164	995	335
$^2B_1$	3448	3380	3334	1721	1553	1437	1108	867	294
$^2A_1$	3431	3423	3268	1798	1456	1307	899	437	270
$^2B_2$	3428	3258	2434	1976	1531	1149	967	896	235

Table 16.5 Conventional potential energy distribution(%).

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
$^1A_1$									
$\Delta C-C$	0.0	0.1	0.1	15.4	13.0	0.8	11.4	47.3	0.4
$\Delta C=C$	0.0	0.9	0.4	65.3	2.1	12.9	2.8	5.8	0.2
ΔC_1-H_5	52.3	3.5	43.4	0.1	0.1	0.1	0.1	0.0	0.0
ΔC_1-H_6	45.4	15.2	38.7	0.2	0.1	0.1	0.0	0.0	0.1
ΔC_2-H_7	1.8	80.0	17.3	0.1	0.0	0.1	0.0	0.1	0.0
$\Delta C=C-C$	0.1	0.1	0.0	0.3	0.9	1.6	4.0	1.0	85.3
$\Delta H_5-C_1=C_2$	0.2	0.1	0.0	2.2	49.6	1.2	30.1	25.9	2.6
$\Delta H_6-C_1=C_2$	0.2	0.0	0.1	9.0	14.8	21.0	39.5	18.8	1.4
$\Delta H_7-C_2=C_1$	0.1	0.1	0.0	7.4	19.3	62.4	12.2	1.2	10.0
$^2A_2$									
$\Delta C-C$	0.0	0.4	0.0	28.4	17.0	1.2	18.4	22.2	0.2
$\Delta C=C$	0.0	0.3	0.6	40.7	0.0	27.8	13.1	6.9	0.2
ΔC_1-H_5	41.9	0.1	57.3	0.1	0.0	0.1	0.0	0.1	0.0
ΔC_1-H_6	56.8	1.7	40.8	0.0	0.1	0.3	0.1	0.0	0.2
ΔC_2-H_7	0.7	97.2	1.1	0.0	0.1	0.1	0.2	0.1	0.0
$\Delta C=C-C$	0.1	0.1	0.0	0.9	1.3	0.8	4.6	0.0	88.4
$\Delta H_5-C_1=C_2$	0.2	0.1	0.0	1.1	47.8	0.3	18.1	38.7	1.9
$\Delta H_6-C_1=C_2$	0.2	0.1	0.1	13.3	13.5	15.7	31.5	30.8	0.2
$\Delta H_7-C_2=C_1$	0.1	0.1	0.0	15.5	20.2	53.9	14.1	1.2	8.8
$\Delta C-C$	0.0	0.1	0.0	10.8	14.2	0.0	5.7	61.4	0.5
$\Delta C=C$	0.0	0.4	0.7	56.0	9.0	21.4	1.6	7.0	0.2
ΔC_1-H_5	52.2	0.0	47.1	0.1	0.1	0.0	0.0	0.1	0.0
ΔC_1-H_6	46.3	1.8	51.3	0.1	0.1	0.2	0.0	0.0	0.0
ΔC_2-H_7	0.9	97.4	0.9	0.1	0.0	0.1	0.0	0.1	0.0
$\Delta C=C-C$	0.1	0.1	0.0	0.2	0.9	1.0	3.1	2.4	84.4
$\Delta H_5-C_1=C_2$	0.2	0.1	0.0	6.8	39.7	0.9	36.7	16.6	3.1
$\Delta H_6-C_1=C_2$	0.2	0.1	0.0	17.5	8.0	17.5	43.6	11.1	1.5
$\Delta H_7-C_2=C_1$	0.1	0.1	0.0	8.6	28.2	58.8	9.4	1.3	10.4
$^2A_1$									
$\Delta C-C$	0.0	0.0	0.0	1.1	0.8	1.4	1.5	51.1	15.8
$\Delta C=C$	0.6	1.4	0.5	87.4	11.5	0.0	0.1	0.0	0.0
ΔC_1-H_5	87.5	5.5	6.6	0.2	0.0	0.0	0.2	0.0	0.0
ΔC_1-H_6	10.9	62.1	26.1	0.4	0.4	0.0	0.0	0.0	0.3
ΔC_2-H_7	0.9	30.6	66.7	1.5	0.2	0.4	0.1	0.0	0.0
$\Delta C=C-C$	0.0	0.1	0.0	0.0	0.0	1.9	3.1	18.8	79.7
$\Delta H_5-C_1=C_2$	0.0	0.2	0.0	4.3	37.3	8.9	45.3	6.1	0.4
$\Delta H_6-C_1=C_2$	0.1	0.1	0.0	4.4	49.4	9.8	43.8	4.7	0.0
$\Delta H_7-C_2=C_1$	0.0	0.0	0.0	0.7	0.5	77.5	6.0	19.3	3.6
$^2B_2$									
$\Delta C-C$	0.0	0.0	1.6	38.0	5.2	7.8	10.6	25.5	1.3
$\Delta C=C$	0.2	0.7	0.2	56.2	1.9	8.8	2.1	21.2	0.0
ΔC_1-H_5	84.5	14.6	0.0	0.2	0.0	0.0	0.0	0.1	0.0
ΔC_1-H_6	14.8	84.5	0.2	0.1	0.0	0.0	0.0	0.4	0.2
ΔC_2-H_7	0.0	0.1	95.9	2.5	0.0	3.1	2.7	4.5	1.7
$\Delta C=C-C$	0.1	0.0	0.2	0.1	0.1	2.5	0.0	0.1	79.1
$\Delta H_5-C_1=C_2$	0.1	0.1	0.2	0.1	58.9	24.9	24.9	6.1	5.4
$\Delta H_6-C_1=C_2$	0.2	0.0	0.5	1.5	33.6	37.3	25.4	1.7	6.9
$\Delta H_7-C_2=C_1$	0.1	0.0	1.2	1.5	0.3	15.6	34.3	40.4	5.3

Table 16.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5
$^1A_1$	$\Delta C-C$	-0.001	-0.004	0.003	0.033	-0.025
	$\Delta C=C$	-0.001	-0.005	-0.004	-0.035	0.005
	ΔC_1-H_5	0.054	0.014	0.048	-0.002	0.001
	ΔC_1-H_6	-0.050	0.029	0.045	-0.002	0.002
	ΔC_2-H_7	0.010	0.066	-0.031	-0.002	-0.001
	$\Delta C=C-C$	-0.3	0.2	-0.1	-0.3	0.5
	$\Delta H_5-C_1=C_2$	-0.4	0.4	0.0	1.2	4.5
	$\Delta H_6-C_1=C_2$	0.4	-0.2	0.3	2.3	2.4
	$\Delta H_7-C_2=C_1$	0.3	-0.2	0.1	2.0	-2.6
		ν_6	ν_7	ν_8	ν_9	
	$\Delta C-C$	0.006	0.025	0.044	0.002	
	$\Delta C=C$	0.013	0.006	0.008	0.001	
	ΔC_1-H_5	0.001	0.001	0.001	0.000	
	ΔC_1-H_6	0.001	0.000	0.001	0.001	
	ΔC_2-H_7	0.001	0.001	0.001	0.000	
	$\Delta C=C-C$	-0.7	-1.1	-0.5	2.5	
	$\Delta H_5-C_1=C_2$	-0.7	-3.7	3.0	-0.5	
	$\Delta H_6-C_1=C_2$	3.0	4.2	-2.5	0.4	
	$\Delta H_7-C_2=C_1$	4.9	-2.2	0.6	-1.0	
		ν_1	ν_2	ν_3	ν_4	ν_5
$^2A_2$	$\Delta C-C$	0.000	-0.006	0.001	0.040	-0.025
	$\Delta C=C$	-0.000	-0.004	-0.005	-0.031	0.000
	ΔC_1-H_5	-0.048	0.002	0.055	-0.002	0.001
	ΔC_1-H_6	0.056	0.010	0.046	-0.001	0.001
	ΔC_2-H_7	-0.006	0.073	-0.008	0.000	-0.001
	$\Delta C=C-C$	0.3	0.2	-0.1	-0.6	0.5
	$\Delta H_5-C_1=C_2$	0.5	0.3	0.1	0.8	4.5
	$\Delta H_6-C_1=C_2$	-0.5	-0.2	0.2	2.8	2.3
	$\Delta H_7-C_2=C_1$	-0.3	-0.3	0.1	2.9	-2.7
		ν_6	ν_7	ν_8	ν_9	
	$\Delta C-C$	-0.006	0.026	0.029	0.001	
	$\Delta C=C$	0.020	0.014	0.010	0.001	
	ΔC_1-H_5	0.001	0.001	0.001	0.000	
	ΔC_1-H_6	0.002	0.001	-0.000	0.001	
	ΔC_2-H_7	0.001	0.002	0.001	0.000	
	$\Delta C=C-C$	-0.4	-1.0	-0.1	2.4	
	$\Delta H_5-C_1=C_2$	-0.3	-2.7	4.0	-0.5	
	$\Delta H_6-C_1=C_2$	2.4	3.5	-3.5	0.2	
	$\Delta H_7-C_2=C_1$	4.2	-2.2	0.7	-0.9	

Table 16.6 Contd.

		ν_1	ν_2	ν_3	ν_4	ν_5
$^2B_1$	$\Delta C-C$	-0.000	-0.004	0.001	0.029	-0.030
	$\Delta C=C$	-0.000	-0.004	-0.005	-0.033	0.012
	ΔC_1-H_5	0.053	-0.001	0.050	-0.002	0.001
	ΔC_1-H_6	-0.050	0.010	0.052	-0.001	0.001
	ΔC_2-H_7	0.007	0.073	-0.007	-0.001	-0.000
	$\Delta C=C-C$	-0.3	0.2	-0.0	-0.3	0.5
	$\Delta H_5-C_1=C_2$	-0.4	0.3	0.2	1.9	4.1
	$\Delta H_6-C_1=C_2$	0.5	-0.2	0.2	3.1	1.8
	$\Delta H_7-C_2=C_1$	0.3	-0.2	0.0	2.0	-3.2

	ν_6	ν_7	ν_8	ν_9
$\Delta C-C$	-0.001	0.020	0.051	0.003
$\Delta C=C$	0.018	0.005	0.009	0.001
ΔC_1-H_5	0.001	0.000	0.001	0.000
ΔC_1-H_6	0.002	0.001	0.000	0.000
ΔC_2-H_7	0.002	0.001	0.001	0.000
$\Delta C=C-C$	-0.5	-1.0	-0.7	2.6
$\Delta H_5-C_1=C_2$	-0.6	-4.3	2.2	-0.6
$\Delta H_6-C_1=C_2$	2.7	4.6	-1.8	0.4
$\Delta H_7-C_2=C_1$	4.6	-2.0	0.6	-1.0

		ν_1	ν_2	ν_3	ν_4	ν_5
$^2A_1$	$\Delta C-C$	0.000	-0.001	0.000	-0.019	-0.011
	$\Delta C=C$	-0.006	-0.004	-0.004	0.037	0.010
	ΔC_1-H_5	-0.018	0.019	0.069	0.002	0.001
	ΔC_1-H_6	0.058	-0.037	0.024	0.003	0.002
	ΔC_2-H_7	0.041	0.060	-0.007	0.007	0.002
	$\Delta C=C-C$	0.3	-0.0	-0.2	0.0	-0.0
	$\Delta H_5-C_1=C_2$	0.5	-0.1	-0.0	-1.7	3.6
	$\Delta H_6-C_1=C_2$	-0.3	0.1	0.4	-1.7	4.0
	$\Delta H_7-C_2=C_1$	-0.2	0.2	0.2	-0.7	-0.4

	ν_6	ν_7	ν_8	ν_9
$\Delta C-C$	0.020	-0.022	0.091	0.028
$\Delta C=C$	-0.000	0.001	0.001	0.000
ΔC_1-H_5	0.000	-0.002	-0.001	0.000
ΔC_1-H_6	0.000	0.001	0.000	0.001
ΔC_2-H_7	-0.003	-0.001	-0.000	-0.000
$\Delta C=C-C$	-0.9	1.1	-2.0	2.2
$\Delta H_5-C_1=C_2$	-2.3	5.4	1.4	-0.2
$\Delta H_6-C_1=C_2$	2.3	-5.1	-1.2	-0.1
$\Delta H_7-C_2=C_1$	6.5	1.9	2.4	-0.6

Table 16.6 Contd.

		ν_1	ν_2	ν_3	ν_4	ν_5
	ΔC-C	0.001	0.001	-0.009	-0.045	-0.012
	ΔC=C	-0.002	-0.005	0.002	0.034	-0.005
$^2B_2$	ΔC_1-H_6	0.068	0.027	0.001	0.003	0.001
	ΔC_1-H_8	-0.029	0.068	-0.003	0.002	0.001
	ΔC_2-H_7	-0.001	0.003	0.084	-0.013	0.001
	ΔC=C-C	-0.3	0.1	0.4	0.3	0.2
	ΔH_6-C_1=C_2	-0.4	0.3	0.4	-0.2	4.6
	ΔH_8-C_1=C_2	0.5	-0.0	-0.6	-1.0	3.5
	ΔH_7-C_2=C_1	0.3	-0.1	-1.1	-1.2	-0.4

		ν_6	ν_7	ν_8	ν_9
	ΔC-C	0.018	0.018	-0.024	0.003
	ΔC=C	0.012	0.005	-0.014	-0.000
	ΔC_1-H_6	0.001	0.000	-0.001	0.000
	ΔC_1-H_8	-0.001	-0.000	-0.002	-0.001
	ΔC_2-H_7	0.013	0.011	0.012	0.004
	ΔC=C-C	-1.3	0.1	0.2	3.3
	ΔH_6-C_1=C_2	-3.6	3.2	-1.3	-0.8
	ΔH_8-C_1=C_2	4.6	-3.4	0.7	0.9
	ΔH_7-C_2=C_1	3.2	4.3	3.8	-0.8

Bond lengths are in angstroms, angles in degrees.

Table 16.7 Vibrational levels of the $^2A_2$ state.

IE	Progressions		
	A	B	the rest
8.42	S(0 0 0 0 0 0 0 0 0 0)		
8.46		S(0 0 0 0 0 0 0 0 0 1)	
8.50			M(0 0 0 0 0 0 0 0 0 2)
8.55			W(0 0 0 0 0 0 0 0 0 3)
8.60			M(0 0 0 0 0 1 0 0 0 0)
8.64	S(0 0 0 1 0 0 0 0 0 0)		M(0 0 0 0 0 1 0 0 0 1)
8.68		M(0 0 0 1 0 0 0 0 0 1)	W(0 0 0 0 0 1 0 0 0 2)
8.72			W(0 0 0 1 0 0 0 0 0 2)
8.77			W(0 0 0 0 0 2 0 0 0 0)
8.82			M(0 0 0 1 0 1 0 0 0 0)
8.86	M(0 0 0 2 0 0 0 0 0 0)		W(0 0 0 1 0 1 0 0 0 1)
8.90		W(0 0 0 2 0 0 0 0 0 1)	
9.04			W(0 0 0 2 0 1 0 0 0 0)
9.08	W(0 0 0 3 0 0 0 0 0 0)		

S:0.09<FCF<0.18, M:0.03<FCF<0.07 and W:0.008<FCF<0.03.

Table 16.8 Vibrational levels of the $^2B_1$ state.

IE	Progressions		
	A	B	the rest
11.24	S(0 0 0 0 0 0 0 0 0 0)		
11.28		M(0 0 0 0 0 0 0 0 0 1)	
11.35	S(0 0 0 0 0 0 0 0 1 0)		
11.38		M(0 0 0 0 0 0 0 0 1 1)	M(0 0 0 0 0 0 0 1 0 0)
11.42			M(0 0 0 0 0 0 1 0 0 0)
11.45	S(0 0 0 0 0 0 0 0 2 0)		W(0 0 0 1 0 0 0 0 0 0)
11.48 11.49		W(0 0 0 0 0 0 0 0 2 1)	W(0 0 0 0 0 0 0 1 1 0)
11.53			M(0 0 0 0 0 0 1 0 1 0)
11.56	W(0 0 0 0 0 0 0 0 3 0)		W(0 0 0 1 0 0 0 0 1 0)
11.59			W(0 0 0 0 0 0 0 1 2 0)
11.63			W(0 0 0 0 0 0 1 0 2 0)
11.67			W(0 0 0 1 0 0 0 0 2 0)

S:0.08<FCF<0.21, M:0.03<FCF<0.05 and W:0.01<FCF<0.03.

Table 16.9 Vibrational levels of the $^2A_1$ state.

IE	Vibrational levels		
11.90	(0 0 0 0 0 1 0 5 0)		
11.96	(0 0 0 0 0 1 0 6 0)		
12.01	(0 0 0 0 0 1 0 7 0),	(0 0 0 0 0 2 0 4 0)	
12.06	(0 0 0 0 0 1 0 8 0),	(0 0 0 0 0 2 0 5 0)	
12.10-12.12	(0 0 0 0 0 2 0 5 1),	(0 0 0 0 0 2 0 6 0)	
12.15-12.17	(0 0 0 0 0 2 0 6 1),	(0 0 0 0 0 2 0 7 0),	(0 0 0 0 0 3 0 4 0)
12.21-12.23	(0 0 0 0 0 2 0 7 1),	(0 0 0 0 0 2 0 8 0),	(0 0 0 0 0 3 0 5 0)
12.26-12.28	(0 0 0 0 0 3 0 5 1),		(0 0 0 0 0 3 0 6 0)
12.31-12.34	(0 0 0 0 0 3 0 6 1),		(0 0 0 0 0 3 0 7 0)
12.37-12.39	(0 0 0 0 0 3 0 7 1),	(0 0 0 0 0 4 0 5 0),	(0 0 0 0 0 3 0 8 0)
12.42-12.44	(0 0 0 0 0 3 0 8 1),	(0 0 0 0 0 4 0 6 0),	(0 0 0 0 0 3 0 9 0),
	(0 0 0 0 0 4 0 5 1)		
12.48-12.50	(0 0 0 0 0 4 0 6 1),	(0 0 0 0 0 4 0 7 0)	
12.53-12.55	(0 0 0 0 0 4 0 7 1),	(0 0 0 0 0 4 0 8 0),	(0 0 0 0 0 5 0 5 0)
12.61		(0 0 0 0 0 4 0 9 0),	(0 0 0 0 0 5 0 6 0)
12.66			(0 0 0 0 0 5 0 7 0)
12.71			(0 0 0 0 0 5 0 8 0)

0.05<FCF<0.022

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Table 17.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C_1-C_2(ΔC_1-C_2)	C_2-C_3(ΔC_2-C_3)	C_1-H(ΔC_1-H)	C_2-H(ΔC_2-H)
^1A_g	1.388	1.388	1.083	1.083
Exp.[a]	1.397	1.397	1.084	1.084
$^2B_{2g}$	1.425(+0.037)	1.357(-0.031)	1.083(0.000)	1.081(-0.002)
$^2B_{3g}$	1.380(-0.008)	1.446(+0.058)	1.080(-0.003)	1.082(-0.001)
^2A_g	1.360(-0.028)	1.440(+0.052)	1.119(+0.036)	1.084(+0.001)
$^2B_{1g}$	1.407(+0.019)	1.343(-0.045)	1.077(-0.006)	1.105(+0.022)
$^2B_{1u}$	1.420(+0.031)	1.420(+0.032)	1.081(-0.002)	1.081(-0.002)
$^2B_{3u}$	1.402(+0.014)	1.368(-0.020)	1.168(+0.085)	1.079(-0.004)
$^2B_{2u}$	1.370(-0.018)	1.468(+0.080)	1.080(-0.003)	1.102(+0.019)

State	C_6-C_1-C_2(ΔC_6-C_1-C_2)	C_3-C_2-H(ΔC_3-C_2-H)
^1A_g	120.00	120.00
Exp.[a]	120.00	120.00
$^2B_{2g}$	121.81(+1.81)	121.56(+1.56)
$^2B_{3g}$	118.05(-1.95)	118.39(-1.61)
^2A_g	127.77(+7.77)	116.45(-3.55)
$^2B_{1g}$	112.32(-7.68)	123.68(+3.68)
$^2B_{1u}$	120.00(0.00)	120.00(0.00)
$^2B_{3u}$	132.84(+12.84)	125.36(+5.36)
$^2B_{2u}$	113.32(-6.68)	110.58(-9.42)

[a]Herzberg (1966).

The $^2B_{2g}$, $^2B_{3g}$, ^2A_g, $^2B_{1g}$, $^2B_{1u}$, $^2B_{3u}$ and $^2B_{2u}$ states of point group D_{2h} correlate to the $^2E_{1g}$, $^2E_{1g}$, $^2E_{2g}$, $^2E_{2g}$, $^2A_{1g}$, $^2E_{1u}$ and $^2E_{1u}$ states of D_{6h}, respectively.

Bond lengths are in angstroms, angles in degrees.

The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 17.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2B_{2g}$	8.28	8.88	8.08	8.68	0.20	0.20
$^2B_{3g}$	8.30	8.89	8.11	8.69	0.19	0.20
^2A_g	12.69	12.35	12.15	11.84	0.54	0.51
$^2B_{1g}$	12.69	12.36	12.17	11.85	0.52	0.51
$^2B_{1u}$	12.90	12.94	12.73	12.74	0.17	0.20
$^2B_{2u}$	15.18	14.81	14.35	14.10	0.83	0.71
$^2B_{3u}$	15.14	14.80	14.61	14.30	0.53	0.50

Total energies (a.u.) of ^1A_g: -230.442437(SCF) and -231.118882(SDCI).

Table 17.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2B_{2g}$	8.69	0.225
$^2B_{3g}$	8.69	0.233
^2A_g	11.81	0.043
$^2B_{1g}$	11.84	0.040
$^2B_{1u}$	12.73	0.289
$^2B_{2u}$	14.05	0.003
$^2B_{3u}$	14.24	0.000

Table 17.4 Vibrational frequencies (cm^{-1}) of the totally symmetric modes of point group D_{2h}.

State	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
^1A_g	3369	3339	1788	1271	1079	660
Obs.[a]	3073	3056	1599	1178	995	608
$^2B_{2g}$	3401	3377	1828	1293	1041	637
$^2B_{3g}$	3401	3381	1731	1280	1042	641
^2A_g	3358	2961	1602	1224	1048	704
$^2B_{1g}$	3441	3150	1842	1164	1057	602
$^2B_{1u}$	3408				1026	
$^2B_{2u}$	3397	3138	1534	1173	914	535
$^2B_{3u}$	3412	2518	1723	595	1258	1042

[a]Herzberg (1966).
The a_g modes of ν_1, ν_2, ν_3, ν_4, ν_5 and ν_6 (point group D_{2h}) correlate to the a_{1g}, e_{2g}, e_{2g}, e_{2g}, a_{1g} and e_{2g} modes(point group D_{6h}), respectively.

Table 17.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
	ΔC_1-C_2	0.7	0.1	24.9	7.0	67.1	1.1
	ΔC_2-C_3	0.3	0.2	49.1	13.8	32.1	2.0
^1A_g	ΔC_1-H	33.4	65.5	0.1	0.0	0.3	0.0
	ΔC_2-H	65.6	33.6	0.0	0.0	0.5	0.0
	$\Delta C_6-C_1-C_2$	0.0	0.6	10.6	0.5	0.0	76.5
	ΔC_3-C_2-H	0.0	0.0	15.2	78.6	0.0	20.4
	ΔC_1-C_2	0.4	0.2	17.1	1.6	79.9	1.6
	ΔC_2-C_3	0.6	0.1	59.3	17.3	17.9	1.3
$^2B_{2g}$	ΔC_1-H	11.4	87.5	0.1	0.0	0.3	0.0
	ΔC_2-H	87.5	11.6	0.2	0.0	0.5	0.0
	$\Delta C_6-C_1-C_2$	0.1	0.6	9.2	0.3	0.7	77.0
	ΔC_3-C_2-H	0.0	0.0	14.0	80.8	0.7	20.1
	ΔC_1-C_2	0.9	0.0	32.2	17.7	47.8	0.7
	ΔC_2-C_3	0.1	0.3	36.9	9.2	49.5	3.1
$^2B_{3g}$	ΔC_1-H	67.5	31.8	0.2	0.0	0.3	0.0
	ΔC_2-H	31.5	67.4	0.0	0.0	0.6	0.0
	$\Delta C_6-C_1-C_2$	0.1	0.5	10.7	0.9	0.9	75.3
	ΔC_3-C_2-H	0.0	0.0	20.0	72.1	0.9	20.9
	ΔC_1-C_2	0.5	0.7	32.3	19.5	43.3	0.1
	ΔC_2-C_3	0.2	0.1	36.0	7.1	52.0	3.1
^2A_g	ΔC_1-H	0.2	98.2	1.0	0.1	0.0	0.0
	ΔC_2-H	98.9	0.3	0.1	0.0	0.3	0.0
	$\Delta C_6-C_1-C_2$	0.1	0.8	12.4	0.5	2.7	78.2
	ΔC_3-C_2-H	0.0	0.0	18.2	72.9	1.3	18.6
	ΔC_1-C_2	0.6	0.0	22.3	0.3	75.7	1.7
	ΔC_2-C_3	0.0	1.5	61.5	9.3	22.1	1.0
$^2B_{1g}$	ΔC_1-H	99.0	0.0	0.2	0.0	0.5	0.0
	ΔC_2-H	0.0	98.0	1.9	0.3	0.2	0.0
	$\Delta C_6-C_1-C_2$	0.4	0.4	8.0	0.2	0.7	73.3
	ΔC_3-C_2-H	0.0	0.0	6.1	89.9	0.9	24.0
	ΔC_1-C_2	0.8	0.7	60.0	3.2	15.2	2.6
	ΔC_2-C_3	0.0	0.0	29.4	3.0	59.3	1.2
$^2B_{2u}$	ΔC_1-H	98.5	0.7	0.2	0.0	0.3	0.0
	ΔC_2-H	0.5	98.3	2.2	4.5	1.5	0.1
	$\Delta C_6-C_1-C_2$	0.2	0.1	6.7	0.0	1.7	91.6
	ΔC_3-C_2-H	0.0	0.2	1.5	89.3	22.1	4.6
	ΔC_1-C_2	0.2	0.1	13.9	1.0	86.5	1.7
	ΔC_2-C_3	0.8	0.3	60.1	20.1	11.7	1.2
$^2B_{3u}$	ΔC_1-H	0.0	99.0	1.5	0.0	0.1	1.1
	ΔC_2-H	98.7	0.1	0.3	0.0	0.8	0.0
	$\Delta C_6-C_1-C_2$	0.2	0.4	9.4	0.3	0.7	74.3
	ΔC_3-C_2-H	0.0	0.1	14.9	78.6	0.3	21.6

State	Component	ν_1	ν_6
$^2B_{1u}$	ΔC_1-C_2	0.9	99.1
	ΔC_1-H	99.1	0.9

Table 17.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
	ΔC_1-C_2	-0.004	-0.001	0.017	-0.007	0.020	0.002
	ΔC_2-C_3	-0.004	0.003	-0.034	0.014	0.020	-0.005
^1A_g	ΔC_1-H	0.043	0.060	0.002	-0.000	0.002	0.000
	ΔC_2-H	0.042	-0.030	-0.001	0.000	0.002	-0.000
	ΔC_6-C_1-C_2	0.0	0.5	-1.7	0.3	-0.0	3.0
	ΔC_3-C_2-H	-0.0	-0.0	2.0	3.6	-0.0	1.6
	ΔC_1-C_2	-0.003	-0.002	0.015	-0.004	0.023	0.003
	ΔC_2-C_3	-0.005	0.002	-0.035	0.015	0.014	-0.004
$^2B_{2g}$	ΔC_1-H	0.025	0.069	0.002	0.000	0.002	-0.000
	ΔC_2-H	0.049	-0.018	-0.002	0.001	0.002	0.000
	ΔC_6-C_1-C_2	-0.1	0.5	-1.6	0.2	-0.3	3.0
	ΔC_3-C_2-H	0.0	-0.0	1.9	3.6	-0.3	1.6
	ΔC_1-C_2	-0.004	0.000	0.018	-0.011	0.016	0.002
	ΔC_2-C_3	-0.002	-0.004	-0.032	0.013	0.027	-0.006
$^2B_{3g}$	ΔC_1-H	0.060	-0.041	0.003	-0.001	0.002	-0.000
	ΔC_2-H	0.029	0.043	-0.000	-0.001	0.002	0.000
	ΔC_6-C_1-C_2	0.2	-0.5	-1.7	0.4	0.3	3.0
	ΔC_3-C_2-H	-0.0	0.0	2.2	3.4	0.3	1.6
	ΔC_1-C_2	-0.003	-0.003	0.018	-0.011	0.015	0.001
	ΔC_2-C_3	-0.004	0.002	-0.033	0.011	0.029	-0.007
^2A_g	ΔC_1-H	0.003	0.078	0.007	0.001	0.001	0.000
	ΔC_2-H	0.052	-0.003	0.001	-0.000	0.002	0.001
	ΔC_6-C_1-C_2	-0.2	-0.5	-1.8	0.3	0.6	3.0
	ΔC_3-C_2-H	-0.0	-0.1	2.3	3.5	0.4	1.6
	ΔC_1-C_2	-0.004	-0.001	0.017	-0.002	0.022	0.003
	ΔC_2-C_3	0.001	-0.007	-0.035	0.010	0.015	-0.003
$^2B_{1g}$	ΔC_1-H	0.073	0.000	0.003	0.001	0.003	-0.001
	ΔC_2-H	0.000	0.053	-0.006	-0.002	0.002	-0.001
	ΔC_6-C_1-C_2	0.4	-0.4	-1.5	-0.1	-0.3	3.1
	ΔC_3-C_2-H	-0.0	0.1	1.4	3.9	-0.3	1.9
	ΔC_1-C_2	-0.004	-0.004	0.024	0.004	-0.010	0.003
	ΔC_2-C_3	0.000	-0.001	-0.031	0.008	-0.037	-0.003
$^2B_{2u}$	ΔC_1-H	0.073	-0.006	0.003	0.000	-0.002	0.000
	ΔC_2-H	0.004	0.053	0.006	0.007	0.004	-0.001
	ΔC_6-C_1-C_2	0.4	-0.2	-1.7	-0.0	-0.7	3.4
	ΔC_3-C_2-H	-0.0	-0.3	0.7	4.0	2.2	0.6
	ΔC_1-C_2	-0.002	-0.001	0.013	0.003	-0.003	0.024
	ΔC_2-C_3	-0.006	-0.003	-0.036	-0.004	0.016	0.011
$^2B_{3u}$	ΔC_1-H	0.002	0.085	-0.009	-0.005	0.001	-0.002
	ΔC_2-H	0.052	-0.002	-0.002	0.000	0.000	0.002
	ΔC_6-C_1-C_2	-0.3	0.4	-1.7	3.3	0.2	-0.3
	ΔC_3-C_2-H	0.0	0.2	2.0	1.7	3.6	-0.2

State	Component	ν_1	ν_6
$^2B_{1u}$	ΔC_1-C_2	-0.004	0.020
	ΔC_1-H	0.042	0.002

Bond lengths are in angstroms, angles in degrees.

Table 17.7 Vibrational levels of the $^2B_{2g}$ state.

IE	Vibrational levels			
8.69	S(0 0 0 0 0 0)			
8.77	S(0 0 0 0 0 1)			
8.82-8.85	M(0 0 0 0 0 2),	S(0 0 0 0 1 0)		W(0 0 0 1 0 0)
8.90-8.95	W(0 0 0 0 0 3),	M(0 0 0 0 1 1),	S(0 0 1 0 0 0),	W(0 0 0 1 0 1),
		W(0 0 0 0 2 0)		
8.98-9.01		W(0 0 0 0 1 2),	M(0 0 1 0 0 1),	W(0 0 0 1 0 2)
9.05-9.08	W(0 0 1 0 1 0),		W(0 0 1 0 0 2),	W(0 0 1 1 0 0)
9.12-9.14	W(0 0 1 0 1 1),	W(0 0 2 0 0 0)		
9.22		W(0 0 2 0 0 1)		

S:0.08<FCF<0.23, M:0.03<FCF<0.07 and W:0.008<FCF<0.03.

Table 17.8 Vibrational levels of the $^2B_{3g}$ state.

IE	Vibrational levels			
8.69	S(0 0 0 0 0 0)			
8.77	S(0 0 0 0 0 1)			
8.82-8.85	M(0 0 0 0 0 2),	S(0 0 0 0 1 0),	W(0 0 0 1 0 0)	
8.90-8.95	W(0 0 0 0 0 3),	M(0 0 0 0 1 1),	W(0 0 0 1 0 1),	M(0 0 1 0 0 0),
		W(0 0 0 0 2 0)		
8.98-9.03		W(0 0 0 0 1 2),	W(0 0 0 1 0 2),	M(0 0 1 0 0 1),
				W(0 0 1 0 1 0)
9.06				W(0 0 1 0 0 2)
9.11				W(0 0 1 0 1 1)

S:0.08<FCF<0.24, M:0.03<FCF<0.07 and W:0.007<FCF<0.03.

Table 17.9 Vibrational levels of the ^2A_g state.

IE	Vibrational levels				
11.81	M(0 0 0 0 0 0)				
11.90	M(0 0 0 0 0 1)				
11.98-12.01	W(0 0 0 0 0 2),	S(0 0 1 0 0 0)			
12.07-12.10		S(0 0 1 0 0 1)			
12.18-12.21		M(0 0 1 0 0 2),	S(0 0 2 0 0 0)		
12.27-12.30		W(0 0 1 0 0 3),	S(0 0 2 0 0 1)		
12.38-12.41		W(0 1 1 0 0 0),	M(0 0 2 0 0 2),	M(0 0 3 0 0 0)	
12.46-12.49		W(0 1 1 0 0 1),	W(0 0 2 0 0 3),	M(0 0 3 0 0 1)	
12.57-12.60	W(0 0 4 0 0 0),	W(0 1 2 0 0 0),		W(0 0 3 0 0 2)	
12.66-12.69	W(0 0 4 0 0 1),	W(0 1 2 0 0 1),			
12.77-12.78		W(0 1 3 0 0 0)			

S:0.08<FCF<0.09, M:0.03<FCF<0.05 and W:0.01<FCF<0.03.

Table 17.10 Vibrational levels of the $^2B_{1g}$ state.

IE	Vibrational levels
11.84	M(0 0 0 0 0 0)
11.92	M(0 0 0 0 0 1)
11.98-11.99	W(0 0 0 0 0 2), W(0 0 0 1 0 0)
12.06-12.07	W(0 0 0 0 0 3), M(0 0 0 1 0 1), M(0 0 1 0 0 0)
12.13-12.14	W(0 0 0 1 0 2), M(0 0 1 0 0 1)
12.21-12.22	M(0 0 1 0 0 2), W(0 0 1 1 0 0)
12.29-12.30	W(0 0 1 0 0 3), M(0 0 1 1 0 1), W(0 0 2 0 0 0)
12.36-12.37	M(0 0 2 0 0 1), W(0 0 1 1 0 2)
12.43-12.45	W(0 0 2 0 0 2), W(0 0 1 2 0 1) W(0 0 2 1 0 0)
12.52-12.53	W(0 0 3 0 0 0), W(0 0 2 1 0 1), W(0 1 1 0 0 1)
12.59-12.60	W(0 0 3 0 0 1), W(0 0 2 1 0 2)
12.67	W(0 0 3 0 0 2)
12.74	W(0 0 3 1 0 1)

M:0.03<FCF<0.06 and W:0.01<FCF<0.03.

Table 17.11 Vibrational levels of the $^2B_{2u}$ state.

IE	Vibrational levels
14.12	W(0 0 0 0 0 1)
14.18	W(0 0 0 0 0 2)
14.23-14.25	W(0 0 0 0 0 3), W(0 0 0 0 1 1)
14.30-14.31	W(0 0 0 0 0 4), W(0 0 0 0 1 2)
14.34-14.39	W(0 0 0 0 0 5), M(0 0 0 0 1 3), W(0 0 0 0 2 1), W(0 0 0 1 0 3)
14.41-14.46	W(0 0 0 1 0 4), W(0 0 0 0 1 4), W(0 0 0 0 2 2), W(0 0 1 0 0 3), W(0 0 0 1 1 2)
14.48-14.51	W(0 0 0 0 1 5), W(0 0 0 0 2 3), W(0 0 1 0 1 2), W(0 0 0 1 1 3)
14.54-14.57	W(0 0 0 1 1 4), W(0 0 0 0 2 4), W(0 0 1 0 1 3)
14.61-14.64	W(0 0 0 1 1 5), W(0 0 0 0 2 5), W(0 0 1 0 1 4)

M:0.03<FCF<0.04 and W:0.01<FCF<0.03.

Table 17.12 Vibrational levels of the $^2B_{3u}$ state.

IE	Vibrational levels
14.47	W(0 0 0 0 0 3)
14.54	M(0 0 0 0 0 4)
14.62	M(0 0 0 0 0 5)
14.69	M(0 0 0 0 0 6)
14.77-14.78	M(0 0 0 0 0 7), W(0 1 0 0 0 3)
14.84-14.86	M(0 0 0 0 0 8), M(0 1 0 0 0 4)
14.91-14.93	M(0 0 0 0 0 9), M(0 1 0 0 0 5)
14.99-15.00	W(0 0 0 0 0 10), M(0 1 0 0 0 6)
15.06-15.08	W(0 0 0 0 0 11), M(0 1 0 0 0 7)
15.15-15.17	M(0 1 0 0 0 8), W(0 2 0 0 0 4)
15.23-15.24	M(0 1 0 0 0 9), W(0 2 0 0 0 5)
15.30-15.32	M(0 1 0 0 0 10), W(0 2 0 0 0 6)
15.37-15.39	W(0 1 0 0 0 11), W(0 2 0 0 0 7)
15.45	W(0 1 0 0 0 12)
15.54	W(0 2 0 0 0 9)
15.61	W(0 2 0 0 0 10)

M:0.03<FCF<0.07 and W:0.01<FCF<0.03.

18. Pyrrole C_4H_5N

Table 18.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	N-C_2(ΔN-C_2)	C_2-C_3(ΔC_2-C_3)	C_2-H(ΔC_2-H)	C_3-H(ΔC_3-H)	N-H(ΔN-H)
$^1A_1$	1.362	1.362	1.078	1.079	0.996
Exp.[a]	1.370	1.382	1.076	1.077	0.996
$^2A_2$	1.345(-0.017)	1.424(+0.062)	1.080(+0.002)	1.078(-0.001)	1.004(+0.008)
$^2B_1$	1.365(-0.007)	1.363(+0.001)	1.077(-0.001)	1.079(+0.0)	1.009(+0.013)
$^2A_1$	1.352(-0.010)	1.329(-0.033)	1.083(+0.005)	1.078(-0.001)	1.001(+0.005)
$^2B_2$	1.340(-0.022)	1.431(+0.069)	1.078(+0.0)	1.120(+0.041)	1.005(+0.009)

State	C_2-N-C_5(ΔC_2-N-C_5)	N-C_2-C_3(ΔN-C_2-C_3)	N-C_2-H(ΔN-C_2-H)	C_2-C_3-H(ΔC_2-C_3-H)
$^1A_1$	109.58	108.17	121.22	125.92
Exp.[a]	109.8	107.7	121.5	125.5
$^2A_2$	109.16(-0.42)	108.48(+0.31)	121.88(+0.66)	124.81(- 1.11)
$^2B_1$	113.96(+4.38)	106.54(-1.63)	122.04(+0.82)	127.43(+ 1.51)
$^2A_1$	111.29(+1.71)	114.30(+6.13)	122.82(+1.60)	149.68(+23.76)
$^2B_2$	110.78(+1.20)	106.74(-1.43)	127.76(+6.54)	111.88(-14.04)

[a]Kuchitsu et al. (1968).
Bond lengths are in angstroms, angles in degrees.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 18.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2A_2$	7.17	7.82	6.90	7.53	0.27	0.29
$^2B_1$	8.29	8.74	8.14	8.57	0.15	0.17
$^2A_1$	12.45	12.76	11.00	11.64	1.44	1.12
$^2B_2$	13.80	14.47	13.14	12.95	0.66	1.52

Total energies (a.u.) of $^1A_1$: -208.579316(SCF) and -209.197273(SDCI).

Table 18.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2A_2$	7.54	0.211
$^2B_1$	8.54	0.330
$^2A_1$	11.59	0.000
$^2B_2$	12.88	0.022

Table 18.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
$^1A_1$	3914	3429	3405	1634	1537	1255	1150	1095	961
Obs.[a]	3400	3133	3100	1467	1384	1237	1144	1076	711
$^2A_2$	3824	3442	3426	1689	1581	1266	1166	1146	956
$^2B_1$	3768	3457	3431	1532	1517	1236	1118	1031	944
$^2A_1$	3856	3448	3384	1751	1394	1168	1135	873	539
$^2B_2$	3802	3423	2937	1645	1396	1214	1099	956	720

[a]Herzberg (1966).

Table 18.5 Conventional potential energy distribution(%).

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
$^1A_1$									
$\Delta N-C_2$	0.7	0.3	0.2	18.5	2.4	37.9	57.0	17.4	0.0
ΔC_2-C_3	0.0	0.9	0.0	14.8	19.3	18.4	6.1	0.0	0.0
ΔC_2-H	0.0	63.7	32.5	0.0	0.1	0.3	0.1	0.0	0.0
ΔC_3-H	0.0	32.1	63.3	0.1	0.0	0.4	0.0	0.1	0.0
$\Delta N-H$	96.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0
ΔC_2-N-C_5	2.4	1.9	0.7	44.5	11.0	7.1	1.8	40.7	52.4
$\Delta N-C_2-C_3$	0.8	1.0	3.2	1.3	48.9	14.0	6.8	7.2	46.8
$\Delta N-C_2-H$	0.1	0.0	0.0	19.6	0.0	11.9	21.9	6.8	0.0
ΔC_2-C_3-H	0.0	0.0	0.1	1.2	18.3	10.1	6.3	27.7	0.8
$^2A_2$									
$\Delta N-C_2$	1.0	0.1	0.5	26.3	10.5	54.6	19.8	16.7	0.0
ΔC_2-C_3	0.0	0.6	0.1	0.1	9.5	13.9	8.7	24.8	0.1
ΔC_2-H	0.0	20.3	71.6	0.0	0.0	0.4	0.0	0.0	0.0
ΔC_3-H	0.0	78.0	18.7	0.4	0.0	0.3	0.0	0.1	0.0
$\Delta N-H$	93.8	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.0
ΔC_2-N-C_5	3.8	0.9	2.7	22.9	40.8	7.9	23.5	35.1	50.2
$\Delta N-C_2-C_3$	1.3	0.0	6.2	22.6	28.0	14.2	0.1	0.3	49.3
$\Delta N-C_2-H$	0.1	0.0	0.0	12.9	9.1	3.0	0.1	22.8	0.0
ΔC_2-C_3-H	0.0	0.0	0.1	14.8	2.2	5.7	47.7	0.1	0.4
$^2B_1$									
$\Delta N-C_2$	0.7	0.4	0.1	30.1	2.6	24.6	53.5	19.4	0.4
ΔC_2-C_3	0.0	0.8	0.1	17.7	22.9	1.5	7.5	2.6	0.3
ΔC_2-H	0.0	81.8	14.0	0.2	0.1	0.1	0.1	0.0	0.0
ΔC_3-H	0.0	13.4	83.6	0.4	0.0	0.0	0.0	0.2	0.0
$\Delta N-H$	96.1	0.1	0.0	0.1	0.0	0.1	0.1	0.0	0.0
ΔC_2-N-C_5	2.3	1.9	0.3	8.7	37.2	6.1	21.8	26.3	50.7
$\Delta N-C_2-C_3$	0.8	1.7	2.0	12.2	21.8	19.0	0.7	33.6	48.1
$\Delta N-C_2-H$	0.1	0.1	0.0	5.9	12.5	23.6	9.0	7.6	0.0
ΔC_2-C_3-H	0.0	0.0	0.1	24.8	2.8	25.1	7.3	10.3	0.5
$^2A_1$									
$\Delta N-C_2$	0.5	0.0	0.3	15.7	25.7	20.8	26.4	0.2	1.5
ΔC_2-C_3	0.0	1.5	0.2	43.3	30.3	2.6	0.8	0.0	4.4
ΔC_2-H	0.0	3.9	93.7	0.1	0.3	0.2	0.0	0.0	0.0
ΔC_3-H	0.0	94.6	4.1	0.6	0.7	0.0	0.0	0.0	0.0
$\Delta N-H$	98.6	0.0	0.0	0.0	0.1	0.0	0.2	0.0	0.0
ΔC_2-N-C_5	0.7	0.1	0.6	18.5	0.0	2.3	23.5	45.2	42.0
$\Delta N-C_2-C_3$	0.2	0.0	1.0	2.6	9.8	18.2	15.3	45.6	42.3
$\Delta N-C_2-H$	0.1	0.0	0.1	19.1	16.5	41.3	0.5	0.3	6.7
ΔC_2-C_3-H	0.0	0.0	0.1	0.2	16.7	14.6	33.4	8.7	3.2
$^2B_2$									
$\Delta N-C_2$	1.0	0.8	0.0	19.8	20.6	20.6	4.5	1.4	1.7
ΔC_2-C_3	0.0	0.2	0.0	0.6	1.1	6.3	9.9	8.5	3.3
ΔC_2-H	0.1	91.0	0.8	0.0	0.0	0.2	0.0	0.2	0.0
ΔC_3-H	0.0	0.4	94.0	1.8	0.9	0.3	0.0	0.0	0.6
$\Delta N-H$	93.5	0.1	0.0	0.1	0.0	0.0	0.0	0.0	0.0
ΔC_2-N-C_5	4.0	3.2	0.3	23.9	48.0	20.6	65.6	0.6	35.5
$\Delta N-C_2-C_3$	1.4	4.2	4.6	39.0	21.3	39.4	17.8	0.2	58.2
$\Delta N-C_2-H$	0.1	0.0	0.1	7.6	8.0	10.5	2.0	3.3	0.4
ΔC_2-C_3-H	0.0	0.0	0.2	7.1	0.1	2.1	0.1	85.8	0.3

Table 18.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5
$^1A_1$	$\Delta N-C_2$	-0.004	-0.003	0.002	-0.022	-0.004
	ΔC_2-C_3	-0.000	-0.006	-0.001	0.023	-0.029
	ΔC_2-H	0.002	0.062	-0.038	0.000	-0.002
	ΔC_3-H	0.000	0.038	0.062	0.003	-0.000
	$\Delta N-H$	0.097	-0.002	0.001	-0.001	-0.002
	ΔC_2-N-C_5	0.5	-0.4	0.2	1.8	-1.1
	$\Delta N-C_2-C_3$	-0.2	0.2	-0.4	-0.1	1.5
	$\Delta N-C_2-H$	0.2	-0.2	0.1	4.8	-0.6
	ΔC_2-C_3-H	0.0	0.1	-0.3	1.7	4.4
		ν_6	ν_7	ν_8	ν_9	
	$\Delta N-C_2$	0.021	0.022	0.013	0.002	
	ΔC_2-C_3	0.018	-0.012	-0.001	0.001	
	ΔC_2-H	0.003	0.001	-0.000	-0.001	
	ΔC_3-H	0.003	0.000	-0.001	0.000	
	$\Delta N-H$	0.002	0.001	0.001	0.001	
	ΔC_2-N-C_5	-0.4	-0.1	-1.0	-3.4	
	$\Delta N-C_2-C_3$	0.5	-0.4	-0.4	2.6	
	$\Delta N-C_2-H$	-2.0	3.4	1.8	0.3	
	ΔC_2-C_3-H	2.0	-2.2	3.3	-1.6	
		ν_1	ν_2	ν_3	ν_4	ν_5
$^2A_2$	$\Delta N-C_2$	-0.004	-0.001	-0.003	-0.017	-0.019
	ΔC_2-C_3	-0.000	-0.005	-0.002	0.000	0.028
	ΔC_2-H	0.002	0.034	0.064	-0.001	0.001
	ΔC_3-H	0.000	0.064	-0.034	0.004	-0.001
	$\Delta N-H$	0.098	-0.002	-0.002	-0.002	-0.001
	ΔC_2-N-C_5	0.5	-0.2	-0.4	0.8	2.0
	$\Delta N-C_2-C_3$	0.3	-0.1	-0.2	2.8	4.1
	$\Delta N-C_2-H$	-0.2	0.0	0.5	0.8	-1.2
	ΔC_2-C_3-H	0.0	-0.1	0.3	3.6	-1.9
		ν_6	ν_7	ν_8	ν_9	
	$\Delta N-C_2$	-0.023	0.012	0.012	0.000	
	ΔC_2-C_3	-0.019	0.012	-0.027	0.005	
	ΔC_2-H	-0.004	0.001	-0.000	-0.001	
	ΔC_3-H	-0.003	-0.000	-0.002	0.001	
	$\Delta N-H$	-0.002	0.002	0.000	0.002	
	ΔC_2-N-C_5	-0.5	-0.6	-1.0	-3.3	
	$\Delta N-C_2-C_3$	0.6	-0.1	-0.1	2.6	
	$\Delta N-C_2-H$	-1.5	0.2	3.7	0.0	
	ΔC_2-C_3-H	2.1	4.5	-0.3	-1.3	

Table 18.6 Condt.

		ν_1	ν_2	ν_3	ν_4	ν_5
	$\Delta N-C_2$	-0.004	-0.003	0.001	-0.010	-0.014
	ΔC_2-C_3	-0.000	-0.006	-0.002	-0.026	0.024
$^2B_1$	ΔC_2-H	0.002	0.068	-0.024	-0.003	0.002
	ΔC_3-H	0.000	0.024	0.069	-0.000	0.002
	$\Delta N-H$	0.099	-0.003	0.001	-0.001	-0.001
	ΔC_2-N-C_5	0.5	-0.4	0.1	-0.8	2.0
	$\Delta N-C_2-C_3$	-0.2	0.3	-0.3	1.4	-0.6
	$\Delta N-C_2-H$	0.3	-0.2	0.1	0.6	5.9
	ΔC_2-C_3-H	0.0	0.1	-0.3	4.6	0.8

		ν_6	ν_7	ν_8	ν_9
	$\Delta N-C_2$	0.017	-0.019	0.027	-0.012
	ΔC_2-C_3	0.017	0.011	-0.015	0.010
	ΔC_2-H	0.002	-0.001	0.000	-0.002
	ΔC_3-H	0.003	-0.002	-0.001	0.000
	$\Delta N-H$	0.002	-0.001	0.003	0.001
	ΔC_2-N-C_5	-0.6	1.0	-2.3	-2.7
	$\Delta N-C_2-C_3$	0.6	-0.9	-0.0	2.5
	$\Delta N-C_2-H_2$	3.6	2.9	0.3	-1.0
	ΔC_2-C_3-H	-1.9	-0.5	1.8	-0.1

		ν_1	ν_2	ν_3	ν_4	ν_5
	$\Delta N-C_2$	-0.004	-0.000	-0.003	-0.020	-0.020
	ΔC_2-C_3	-0.000	-0.007	-0.002	0.033	-0.022
$^2A_1$	ΔC_2-H	0.001	0.014	0.072	0.002	-0.003
	ΔC_3-H	0.001	0.071	-0.014	0.005	-0.004
	$\Delta N-H$	0.097	-0.002	-0.002	-0.001	-0.002
	ΔC_2-N-C_5	0.5	-0.1	-0.4	2.0	-0.1
	$\Delta N-C_2-C_3$	-0.2	-0.0	0.5	-0.6	1.0
	$\Delta N-C_2-H$	0.3	-0.1	-0.2	3.8	2.6
	ΔC_2-C_3-H	0.0	-0.0	0.3	0.5	3.4

		ν_6	ν_7	ν_8	ν_9
	$\Delta N-C_2$	0.016	0.021	0.001	0.002
	ΔC_2-C_3	-0.007	0.003	-0.001	-0.004
	ΔC_2-H	0.002	0.001	0.000	0.001
	ΔC_3-H	-0.000	0.000	-0.001	-0.000
	$\Delta N-H$	0.000	0.002	-0.001	-0.001
	ΔC_2-N-C_5	0.7	-1.7	3.1	1.2
	$\Delta N-C_2-C_3$	-1.3	1.1	-2.6	0.9
	$\Delta N-C_2-H$	4.4	0.7	-0.5	-0.9
	ΔC_2-C_3-H	-3.3	4.7	2.9	0.7

Table 18.6 Condt.

		ν_1	ν_2	ν_3	ν_4	ν_5
$^2B_2$	$\Delta N-C_2$	-0.004	-0.004	-0.001	-0.013	-0.028
	ΔC_2-C_3	-0.000	-0.004	0.001	-0.005	0.011
	ΔC_2-H	0.003	0.072	-0.005	-0.000	-0.001
	ΔC_3-H	0.000	0.005	0.078	0.010	-0.012
	$\Delta N-H$	0.098	-0.004	-0.000	-0.002	-0.002
	ΔC_2-N-C_5	0.5	-0.4	0.1	0.7	2.2
	$\Delta N-C_2-C_3$	-0.2	0.4	-0.4	0.9	-1.1
	$\Delta N-C_2-H$	0.3	-0.2	0.3	2.1	4.4
	ΔC_2-C_3-H	0.0	0.2	-0.6	2.5	-0.4

	ν_6	ν_7	ν_8	ν_9
$\Delta N-C_2$	0.020	0.012	0.002	-0.010
ΔC_2-C_3	0.021	-0.035	0.012	0.027
ΔC_2-H	0.004	-0.001	0.001	0.001
ΔC_3-H	-0.006	0.002	0.001	-0.012
$\Delta N-H$	0.002	0.000	0.001	0.001
ΔC_2-N-C_5	1.2	-2.5	-0.2	-2.3
$\Delta N-C_2-C_3$	-1.3	1.1	0.1	2.4
$\Delta N-C_2-H$	3.9	2.0	1.0	1.3
ΔC_2-C_3-H	-2.0	0.6	6.0	-1.6

Bond lengths are in angstroms, angles in degrees.

Table 18.7 Vibrational levels of the $^2A_2$ state.

IE	Vibrational levels
7.54	S(0 0 0 0 0 0 0 0 0)
7.66-7.68	M(0 0 0 0 0 0 0 0 1), M(0 0 0 0 0 0 0 1 0), M(0 0 0 0 0 0 1 0 0)
7.74-7.75	S(0 0 0 0 1 0 0 0 0), W(0 0 0 1 0 0 0 0 0)
7.78-7.83	W(0 0 0 0 0 0 0 0 2), W(0 0 0 0 0 0 0 2 0), W(0 0 0 0 0 0 1 0 1), W(0 0 0 0 0 0 0 1 1), W(0 0 0 0 0 0 1 1 0)
7.85-7.88	M(0 0 0 0 1 0 0 0 1), M(0 0 0 0 1 0 0 1 0), M(0 0 0 0 1 0 1 0 0)
7.93	M(0 0 0 0 2 0 0 0 0)
8.00	W(0 0 0 0 1 0 0 1 1), W(0 0 0 0 1 0 1 0 1)
8.05-8.08	W(0 0 0 0 2 0 0 0 1), W(0 0 0 0 2 0 0 1 0), W(0 0 0 0 2 0 1 0 0)
8.13	W(0 0 0 0 3 0 0 0 0)

S:0.13<FCF<0.21, M:0.03<FCF<0.07 and W:0.01<FCF<0.03.

Table 18.8 Vibrational levels of the $^2B_1$ state.

IE	Vibrational levels
8.54	S(0 0 0 0 0 0 0 0 0)
8.66-8.67	S(0 0 0 0 0 0 0 0 1), S(0 0 0 0 0 0 0 1 0)
8.73	M(0 0 0 0 1 0 0 0 0)
8.77-8.80	M(0 0 0 0 0 0 0 0 2), M(0 0 0 0 0 0 0 1 1), W(0 0 0 0 0 0 0 2 0)
8.84-8.86	W(0 0 0 0 1 0 0 0 1), W(0 0 0 0 1 0 0 1 0)
8.90-8.91	W(0 0 0 0 0 0 0 1 2), W(0 0 0 0 0 0 0 2 1)

S:0.13<FCF<0.33, M:0.03<FCF<0.08 and W:0.01<FCF<0.03.

19. Furan C_4H_4O

Table 19.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	O-C₂(ΔO-C₂)	C₂-C₃(ΔC₂-C₃)	C₂-H(ΔC₂-H)	C₃-H(ΔC₃-H)
$^1A_1$	1.342	1.343	1.076	1.078
Exp.[a]	1.362	1.361	1.075	1.077
$^2A_2$	1.321(-0.020)	1.404(+0.061)	1.080(+0.004)	1.079(+0.001)
$^2B_1$	1.316(-0.026)	1.366(+0.023)	1.076(+0.000)	1.080(+0.002)
$^2A_1$	1.326(-0.016)	1.318(-0.025)	1.082(+0.006)	1.079(+0.002)
$^2B_2$	1.315(-0.026)	1.402(+0.059)	1.079(+0.003)	1.128(+0.050)

State	C₅-O-C₂(ΔC₅-O-C₂)	O-C₂-C₃(ΔO-C₂-C₃)	O-C₂-H(ΔO-C₂-H)	C₂-C₃-H(ΔC₂-C₃-H)
$^1A_1$	107.30	110.83	116.33	126.65
Exp.[a]	106.56	110.65	115.98	127.83
$^2A_2$	107.57(+0.27)	110.54(-0.29)	117.18(+0.85)	125.49(-1.16)
$^2B_1$	113.56(+6.26)	108.54(-2.29)	117.83(+1.50)	128.20(+1.55)
$^2A_1$	110.10(+2.80)	116.86(+6.03)	118.13(+1.80)	150.70(+24.05)
$^2B_2$	108.34(+1.04)	109.47(-1.36)	122.32(+5.99)	112.70(-13.95)

[a]Hata et al. (1978).
Bond lengths are in angstroms, angles in degrees.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 19.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2A_2$	7.88	8.53	7.60	8.23	0.28	0.30
$^2B_1$	10.03	10.37	9.51	9.88	0.52	0.49
$^2A_1$	13.08	13.22	11.61	12.28	1.47	0.94
$^2B_2$	14.72	14.74	14.06	13.82	0.66	0.92

Total energies (a.u.) of $^1A_1$: -228.3753081(SCF) and -229.001064(SDCI).

Table 19.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2A_2$	8.24	0.211
$^2B_1$	9.87	0.205
$^2A_1$	12.28	0.000
$^2B_2$	13.82	0.025

Table 19.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8
$^1A_1$	3456	3421	1671	1537	1249	1160	1076	955
Obs.[a]	3121	3089	1483	1380	1138	1061	986	724
$^2A_2$	3448	3432	1659	1578	1265	1187	1146	953
$^2B_1$	3472	3431	1589	1498	1222	1185	1026	935
$^2A_1$	3445	3391	1765	1379	1196	1089	847	517
$^2B_2$	3408	2844	1600	1373	1253	1153	941	717

[a]Herzberg (1966).

Table 19.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8
$^1A_1$	$\Delta O-C_2$	0.3	0.1	9.2	12.1	7.0	82.6	18.8	0.4
	ΔC_2-C_3	1.0	0.1	27.3	8.6	16.0	0.8	0.2	0.0
	ΔC_2-H	79.7	15.5	0.1	0.1	0.1	0.1	0.0	0.0
	ΔC_3-H	14.6	81.6	0.2	0.0	0.3	0.1	0.1	0.0
	ΔC_5-O-C_2	2.6	0.3	40.9	0.6	4.4	1.4	31.8	55.3
	$\Delta O-C_2-C_3$	1.8	2.3	8.2	47.7	25.9	6.1	12.7	43.4
	$\Delta O-C_2-H$	0.1	0.0	14.2	6.8	31.7	8.0	2.7	0.0
	$\Delta C_2-C_3-H_2$	0.0	0.1	0.1	24.1	14.8	1.0	33.8	0.8
$^2A_2$	$\Delta O-C_2$	0.3	0.2	25.2	6.5	62.1	18.2	30.8	0.2
	ΔC_2-C_3	0.8	0.0	0.5	12.6	13.3	30.8	0.8	0.1
	ΔC_2-H	65.5	28.9	0.0	0.1	0.5	0.0	0.0	0.0
	ΔC_3-H	28.8	64.9	0.3	0.0	0.4	0.1	0.0	0.0
	ΔC_5-O-C_2	3.0	1.1	20.4	38.3	7.8	10.9	30.0	52.9
	$\Delta O-C_2-C_3$	1.6	4.8	23.2	30.5	12.1	4.9	1.9	46.3
	$\Delta O-C_2-H$	0.1	0.0	15.6	9.2	0.0	29.9	1.7	0.0
	$\Delta C_2-C_3-H_2$	0.0	0.1	14.8	2.9	3.7	5.3	34.7	0.4
$^2B_1$	$\Delta O-C_2$	0.4	0.0	11.1	12.9	23.8	65.1	3.7	0.0
	ΔC_2-C_3	0.8	0.2	19.7	11.7	20.5	4.4	0.0	0.2
	ΔC_2-H	87.5	7.4	0.1	0.2	0.2	0.1	0.0	0.0
	ΔC_3-H	6.9	90.7	0.1	0.0	0.4	0.0	0.3	0.0
	ΔC_5-O-C_2	2.2	0.1	40.9	1.9	4.0	8.3	2.1	56.2
	$\Delta O-C_2-C_3$	2.1	1.5	9.5	41.7	11.9	3.5	67.8	43.0
	$\Delta O-C_2-H$	0.1	0.0	18.7	5.8	10.8	16.8	3.3	0.0
	$\Delta C_2-C_3-H_2$	0.0	0.1	0.1	25.7	28.4	1.8	22.8	0.5
$^2A_1$	$\Delta O-C_2$	0.0	0.2	12.3	23.2	28.4	27.4	0.0	0.9
	ΔC_2-C_3	1.8	0.1	52.0	21.9	1.4	0.8	0.1	3.5
	ΔC_2-H	8.5	89.2	0.2	0.2	0.2	0.0	0.0	0.0
	ΔC_3-H	89.6	8.8	0.8	0.5	0.0	0.0	0.0	0.0
	ΔC_5-O-C_2	0.1	0.6	15.1	0.0	2.1	24.6	45.7	46.3
	$\Delta O-C_2-C_3$	0.0	0.9	2.7	8.4	19.6	16.0	43.4	40.8
	$\Delta O-C_2-H$	0.0	0.1	17.0	30.1	35.4	0.1	0.4	5.8
	$\Delta C_2-C_3-H_2$	0.0	0.0	0.0	15.7	13.0	31.1	10.4	2.7
$^2B_2$	$\Delta O-C_2$	0.6	0.1	20.7	11.0	26.9	23.3	2.0	0.9
	ΔC_2-C_3	0.3	0.1	0.5	3.4	15.1	11.3	3.1	2.1
	ΔC_2-H	90.9	1.5	0.0	0.0	0.4	0.0	0.1	0.0
	ΔC_3-H	0.7	93.2	1.2	1.1	0.0	0.0	0.0	0.7
	ΔC_5-O-C_2	3.5	0.3	20.2	47.4	23.8	54.7	25.4	40.5
	$\Delta O-C_2-C_3$	4.0	4.4	40.3	26.8	30.7	2.9	9.8	55.1
	$\Delta O-C_2-H$	0.1	0.2	10.1	10.1	1.6	7.6	1.4	0.3
	$\Delta C_2-C_3-H_2$	0.0	0.3	7.0	0.2	1.4	0.2	58.2	0.5

Table 19.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5
$^1A_1$	$\Delta O\text{-}C_2$	-0.002	0.001	-0.016	-0.014	-0.008
	$\Delta C_2\text{-}C_3$	-0.006	-0.002	0.034	-0.015	-0.016
	$\Delta C_2\text{-}H$	0.066	-0.029	0.003	-0.002	-0.001
	$\Delta C_3\text{-}H$	0.029	0.067	0.003	0.001	-0.003
	$\Delta C_5\text{-}O\text{-}C_2$	-0.5	0.2	2.0	-0.2	0.4
	$\Delta O\text{-}C_2\text{-}C_3$	0.3	-0.4	-0.7	1.4	-0.8
	$\Delta O\text{-}C_2\text{-}H$	-0.3	0.1	4.1	2.2	3.7
	$\Delta C_2\text{-}C_3\text{-}H_2$	0.1	-0.3	-0.3	4.6	-2.8
		ν_6	ν_7	ν_8		
	$\Delta O\text{-}C_2$	0.031	0.012	0.005		
	$\Delta C_2\text{-}C_3$	-0.004	0.002	0.002		
	$\Delta C_2\text{-}H$	0.002	-0.000	-0.001		
	$\Delta C_3\text{-}H$	0.001	-0.001	0.000		
	$\Delta C_5\text{-}O\text{-}C_2$	-0.2	-0.9	-3.5		
	$\Delta O\text{-}C_2\text{-}C_3$	-0.4	-0.5	2.6		
	$\Delta O\text{-}C_2\text{-}H$	2.0	0.9	0.3		
	$\Delta C_2\text{-}C_3\text{-}H_2$	-0.8	3.6	-1.6		
		ν_1	ν_2	ν_3	ν_4	ν_5
$^2A_2$	$\Delta O\text{-}C_2$	-0.002	0.002	-0.018	-0.014	-0.024
	$\Delta C_2\text{-}C_3$	-0.006	-0.001	0.004	0.031	-0.018
	$\Delta C_2\text{-}H$	0.060	-0.040	-0.001	0.002	-0.004
	$\Delta C_3\text{-}H$	0.040	0.060	0.004	-0.001	-0.003
	$\Delta C_5\text{-}O\text{-}C_2$	-0.4	0.3	0.9	1.9	-0.5
	$\Delta O\text{-}C_2\text{-}C_3$	0.2	-0.4	0.8	-1.4	0.5
	$\Delta O\text{-}C_2\text{-}H$	-0.2	0.1	3.3	3.9	-0.1
	$\Delta C_2\text{-}C_3\text{-}H_2$	0.1	-0.3	3.5	-2.4	1.5
		ν_6	ν_7	ν_8		
	$\Delta O\text{-}C_2$	0.012	0.016	0.004		
	$\Delta C_2\text{-}C_3$	-0.025	0.004	0.004		
	$\Delta C_2\text{-}H$	-0.000	0.001	-0.001		
	$\Delta C_3\text{-}H$	-0.002	-0.001	0.001		
	$\Delta C_5\text{-}O\text{-}C_2$	-0.5	-0.9	-3.5		
	$\Delta O\text{-}C_2\text{-}C_3$	-0.3	-0.2	2.6		
	$\Delta O\text{-}C_2\text{-}H$	3.7	0.9	0.2		
	$\Delta C_2\text{-}C_3\text{-}H_2$	-1.7	4.3	-1.4		
		ν_1	ν_2	ν_3	ν_4	ν_5
$^2B_1$	$\Delta O\text{-}C_2$	-0.003	0.001	-0.018	-0.014	0.014
	$\Delta C_2\text{-}C_3$	-0.006	-0.003	0.032	-0.019	0.018
	$\Delta C_2\text{-}H$	0.069	-0.020	0.002	-0.003	0.002
	$\Delta C_3\text{-}H$	0.020	0.070	0.002	-0.000	0.003
	$\Delta C_5\text{-}O\text{-}C_2$	-0.5	0.1	2.3	-0.4	-0.4
	$\Delta O\text{-}C_2\text{-}C_3$	0.4	-0.3	-0.9	1.4	0.5
	$\Delta O\text{-}C_2\text{-}H$	-0.3	0.0	4.8	2.0	-2.0
	$\Delta C_2\text{-}C_3\text{-}H_2$	0.2	-0.3	-0.3	4.7	3.7

Table 19.6 Contd.

		ν_6	ν_7	ν_8		
	$\Delta O-C_2$	0.028	0.005	-0.001		
	ΔC_2-C_3	-0.010	-0.001	-0.005		
	ΔC_2-H	0.002	-0.000	0.001		
	ΔC_3-H	0.000	-0.002	-0.000		
	ΔC_5-O-C_2	-0.7	-0.2	3.6		
	$\Delta O-C_2-C_3$	-0.3	-1.0	-2.5		
	$\Delta O-C_2-H$	3.0	0.9	-0.3		
	$\Delta C_2-C_3-H_2$	-1.1	2.7	1.2		
		ν_1	ν_2	ν_3	ν_4	ν_5
	$\Delta O-C_2$	-0.001	-0.003	-0.018	-0.019	0.021
	ΔC_2-C_3	-0.008	-0.002	0.035	-0.017	-0.004
$^2A_1$	ΔC_2-H	0.021	0.070	0.003	-0.002	0.002
	ΔC_3-H	0.069	-0.022	0.006	-0.003	0.000
	ΔC_5-O-C_2	-0.2	-0.4	1.9	0.0	0.5
	$\Delta O-C_2-C_3$	0.0	0.5	-0.7	0.9	-1.4
	$\Delta O-C_2-H$	-0.2	-0.3	3.5	3.6	3.9
	$\Delta C_2-C_3-H_2$	0.0	0.3	0.2	3.3	-3.0
		ν_6	ν_7	ν_8		
	$\Delta O-C_2$	0.021	0.001	0.002		
	ΔC_2-C_3	0.004	-0.001	-0.003		
	ΔC_2-H	0.001	0.000	0.000		
	ΔC_3-H	0.000	-0.001	-0.000		
	ΔC_5-O-C_2	-2.0	3.2	1.3		
	$\Delta O-C_2-C_3$	1.3	-2.6	1.0		
	$\Delta O-C_2-H$	-0.2	-0.5	-0.8		
	$\Delta C_2-C_3-H_2$	4.9	3.4	0.7		
		ν_1	ν_2	ν_3	ν_4	ν_5
	$\Delta O-C_2$	-0.003	-0.001	-0.014	-0.022	0.021
	ΔC_2-C_3	-0.004	0.002	-0.004	0.021	0.028
$^2B_2$	ΔC_2-H	0.073	-0.008	0.000	0.001	0.004
	ΔC_3-H	0.008	0.078	0.007	-0.015	-0.002
	ΔC_5-O-C_2	-0.4	0.1	0.8	2.5	1.1
	$\Delta O-C_2-C_3$	0.4	-0.4	0.9	-1.5	-1.0
	$\Delta O-C_2-H$	-0.2	0.4	2.5	5.1	1.3
	$\Delta C_2-C_3-H_2$	0.1	-0.6	2.6	-1.0	-1.5
		ν_6	ν_7	ν_8		
	$\Delta O-C_2$	0.021	0.004	-0.008		
	ΔC_2-C_3	-0.026	0.008	0.021		
	ΔC_2-H	-0.001	0.002	0.002		
	ΔC_3-H	0.001	0.001	-0.014		
	ΔC_5-O-C_2	-1.7	-0.7	-2.8		
	$\Delta O-C_2-C_3$	0.3	0.4	2.7		
	$\Delta O-C_2-H$	2.9	0.8	1.0		
	$\Delta C_2-C_3-H_2$	-0.6	6.1	-1.8		

Bond lengths are in angstroms, angles in degrees.

Table 19.7 Vibrational levels of the $^2A_2$ state.

IE	Vibrational levels
8.24	S(0 0 0 0 0 0 0 0)
8.36-8.39	M(0 0 0 0 0 0 0 1), W(0 0 0 0 0 0 1 0), S(0 0 0 0 0 1 0 0)
8.44	S(0 0 0 1 0 0 0 0)
8.50-8.58	W(0 0 0 0 0 1 0 1), M(0 0 0 0 0 2 0 0), M(0 0 0 1 0 0 0 1), W(0 0 0 1 0 0 1 0), M(0 0 0 1 0 1 0 0)
8.63	M(0 0 0 2 0 0 0 0)
8.70-8.73	W(0 0 0 1 0 1 0 1), W(0 0 0 1 0 2 0 0)
8.75-8.78	W(0 0 0 2 0 0 0 1), M(0 0 0 2 0 1 0 0)
8.83	W(0 0 0 3 0 0 0 0)
8.90-8.93	W(0 0 0 2 0 1 0 1), W(0 0 0 2 0 2 0 0)
8.97-9.02	W(0 0 0 3 0 1 0 0), W(0 0 0 4 0 0 0 0)

S:0.10<FCF<0.22, M:0.03<FCF<0.08 and W:0.004<FCF<0.03.

Table 19.8 Vibrational levels of the $^2B_1$ state.

IE	Vibrational levels
9.87	S(0 0 0 0 0 0 0 0)
9.99-10.02	S(0 0 0 0 0 0 0 1), M(0 0 0 0 0 0 1 0), W(0 0 0 0 1 0 0 0)
10.07-10.12	M(0 0 1 0 0 0 0 0), M(0 0 0 0 0 0 0 2), M(0 0 0 0 0 0 1 1), W(0 0 0 0 0 0 2 0)
10.18-10.23	M(0 0 1 0 0 0 0 1), W(0 0 1 0 0 0 1 0), W(0 0 0 0 0 0 0 3), W(0 0 0 0 0 0 1 2)
10.30-10.31	W(0 0 1 0 0 0 0 2), W(0 0 1 0 0 0 1 1)

S:0.18<FCF<0.21, M:0.05<FCF<0.08 and W:0.01<FCF<0.03.

20. Thiophen C_4SH_4

Table 20.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	$S-C_2$($\Delta S-C_2$)	C_2-C_3(ΔC_2-C_3)	C_2-H(ΔC_2-H)	C_3-H(ΔC_3-H)
$^1A_1$	1.729	1.349	1.079	1.081
Exp.[a]	1.714	1.370	1.078	1.081
$^2A_2$	1.716(-0.012)	1.411(+0.061)	1.083(+0.004)	1.081(-0.001)
$^2B_1$	1.744(+0.016)	1.335(-0.014)	1.079(+0.000)	1.082(+0.001)
$^2A_1$	1.781(+0.052)	1.333(-0.016)	1.078(-0.001)	1.084(+0.003)
$^2B_2$	1.905(+0.176)	1.317(-0.032)	1.093(+0.014)	1.083(+0.002)

State	C_5-S-C_2(ΔC_5-S-C_2)	$S-C_2-C_3$($\Delta S-C_2-C_3$)	$S-C_2-H$($\Delta S-C_2-H$)	C_2-C_3-H(ΔC_2-C_3-H)
$^1A_1$	91.26	111.81	120.39	123.58
Exp.[a]	92.2	111.5	119.8	123.3
$^2A_2$	89.70(-1.56)	113.31(+1.50)	120.67(+0.28)	122.68(-0.90)
$^2B_1$	93.63(+2.37)	109.88(-1.93)	120.03(-0.36)	123.89(+0.31)
$^2A_1$	98.50(+7.24)	103.01(-8.80)	120.80(+0.41)	120.38(-3.20)
$^2B_2$	80.68(-10.58)	116.88(+5.07)	100.73(-19.66)	121.81(-1.77)

[a] Bak et al. (1961).
Bond lengths are in angstroms, angles in degrees.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 20.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2A_2$	8.06	8.65	7.78	8.33	0.28	0.32
$^2B_1$	8.52	8.98	8.42	8.91	0.10	0.07
$^2A_1$	11.42	11.77	10.89	11.32	0.53	0.45
$^2B_2$	13.23	13.32	12.08	12.48	1.15	0.84

Total energies (a.u.) of $^1A_1$: -550.687022(SCF) and -551.277283(SDCI).

Table 20.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2A_2$	8.34	0.155
$^2B_1$	8.90	0.425
$^2A_1$	11.32	0.003
$^2B_2$	12.48	0.000

Table 20.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8
$^1A_1$	3415	3381	1586	1509	1179	1101	880	654
Obs.[a]	3108	3084	1404	1358	1079	1032	832	604
$^2A_2$	3415	3396	1643	1459	1204	1145	911	661
$^2B_1$	3429	3400	1681	1429	1198	1037	810	614
$^2A_1$	3457	3366	1597	1409	1156	1053	738	552
$^2B_2$	3377	3268	1724	1417	1120	1088	573	470

[a]Herzberg (1966).

Table 20.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8
	ΔS-C_2	0.2	0.0	0.5	11.0	0.4	1.6	38.3	6.6
	ΔC_2-C_3	0.8	0.1	43.7	7.1	12.5	4.0	0.3	0.0
$^1A_1$	ΔC_2-H	84.3	11.8	0.2	0.0	0.0	0.1	0.0	0.0
	ΔC_3-H	11.2	85.8	0.0	0.2	0.0	0.4	0.0	0.0
	ΔC_5-S-C_2	2.0	0.2	23.6	12.6	1.2	22.1	7.7	61.1
	ΔS-C_2-C_3	1.4	2.0	20.9	19.6	0.0	29.6	52.1	32.2
	ΔS-C_2-H	0.0	0.0	2.9	24.9	47.5	18.7	1.4	0.1
	ΔC_2-C_3-H	0.0	0.1	8.1	24.5	38.4	23.5	0.2	0.0
	ΔS-C_2	0.0	0.3	2.6	8.4	2.2	0.3	42.3	3.5
	ΔC_2-C_3	0.5	0.1	6.0	27.9	0.0	35.2	0.1	0.0
$^2A_2$	ΔC_2-H	13.4	79.6	0.0	0.1	0.1	0.1	0.1	0.0
	ΔC_3-H	85.3	12.6	0.4	0.0	0.2	0.2	0.0	0.0
	ΔC_5-S-C_2	0.5	2.5	0.3	36.4	9.7	37.9	4.1	58.9
	ΔS-C_2-C_3	0.1	4.7	61.3	3.8	1.3	1.0	51.6	37.6
	ΔS-C_2-H	0.0	0.0	2.5	23.3	2.6	24.0	1.7	0.1
	ΔC_2-C_3-H	0.0	0.1	27.0	0.0	84.0	1.2	0.2	0.0
	ΔS-C_2	0.2	0.0	0.6	6.7	0.1	3.0	30.7	13.3
	ΔC_2-C_3	1.1	0.1	52.6	6.0	7.4	9.3	0.4	0.0
$^2B_1$	ΔC_2-H	82.8	13.6	0.3	0.0	0.0	0.2	0.0	0.0
	ΔC_3-H	13.0	84.4	0.1	0.2	0.0	0.6	0.0	0.0
	ΔC_5-S-C_2	1.8	0.2	20.9	7.5	0.1	20.0	9.7	64.6
	ΔS-C_2-C_3	1.2	1.7	16.5	14.3	0.2	44.3	58.8	21.9
	ΔS-C_2-H	0.0	0.0	2.5	31.7	47.7	15.4	0.4	0.2
	ΔC_2-C_3-H	0.0	0.1	6.6	33.8	44.5	7.4	0.0	0.1
	ΔS-C_2	0.2	0.0	0.0	5.4	0.1	0.2	22.6	20.5
	ΔC_2-C_3	0.9	0.3	53.0	7.4	1.8	8.2	0.6	0.2
$^2A_1$	ΔC_2-H	94.4	1.0	0.4	0.1	0.0	0.1	0.0	0.0
	ΔC_3-H	0.8	97.7	0.0	0.1	0.0	0.5	0.0	0.0
	ΔC_5-S-C_2	1.8	0.0	20.3	10.7	0.9	15.5	16.1	63.9
	ΔS-C_2-C_3	1.7	1.0	19.1	17.2	0.2	38.8	60.4	14.9
	ΔS-C_2-H	0.0	0.0	1.5	23.5	49.1	33.4	0.0	0.5
	ΔC_2-C_3-H	0.0	0.1	5.7	35.7	48.0	3.3	0.1	0.0
	ΔS-C_2	0.0	0.0	1.2	5.3	0.9	1.4	4.0	42.6
	ΔC_2-C_3	0.8	1.2	58.5	5.2	3.8	6.7	0.1	0.1
$^2B_2$	ΔC_2-H	2.3	90.8	0.9	0.5	0.0	0.1	0.0	0.1
	ΔC_3-H	96.4	2.5	0.1	0.1	0.0	0.5	0.0	0.0
	ΔC_5-S-C_2	0.2	3.2	20.9	7.4	0.7	26.8	35.2	55.0
	ΔS-C_2-C_3	0.4	2.2	12.3	28.2	7.5	18.9	60.0	2.1
	ΔS-C_2-H	0.0	0.1	1.6	20.9	43.6	34.4	0.6	0.0
	ΔC_2-C_3-H	0.0	0.0	4.6	32.4	48.5	11.4	0.1	0.1

Table 20.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5
	$\Delta S-C_2$	-0.003	0.001	0.004	-0.015	-0.002
	ΔC_2-C_3	-0.005	-0.002	-0.038	0.012	-0.012
	ΔC_2-H	0.068	-0.025	-0.003	0.001	-0.001
$^1A_1$	ΔC_3-H	0.025	0.069	-0.001	0.003	-0.001
	ΔC_5-S-C_2	-0.3	0.1	-1.1	0.6	-0.2
	$\Delta S-C_2-C_3$	0.3	-0.3	1.0	0.8	-0.0
	$\Delta S-C_2-H$	-0.2	0.0	-1.7	3.9	4.3
	ΔC_2-C_3-H	0.1	-0.3	2.9	3.9	-3.8

		ν_6	ν_7	ν_8
	$\Delta S-C_2$	-0.003	0.037	0.023
	ΔC_2-C_3	-0.005	-0.003	-0.000
	ΔC_2-H	-0.001	0.001	0.000
	ΔC_3-H	-0.002	0.001	0.000
	ΔC_5-S-C_2	-0.5	0.7	-2.7
	$\Delta S-C_2-C_3$	-0.6	-1.7	2.0
	$\Delta S-C_2-H$	2.0	1.2	-0.5
	ΔC_2-C_3-H	2.2	0.5	-0.2

		ν_1	ν_2	ν_3	ν_4	ν_5
	$\Delta S-C_2$	-0.001	-0.003	-0.007	-0.015	-0.004
	ΔC_2-C_3	-0.005	-0.002	-0.012	0.034	0.000
	ΔC_2-H	0.027	0.068	-0.001	0.002	-0.001
$^2A_2$	ΔC_3-H	0.068	-0.027	0.004	0.001	-0.001
	ΔC_5-S-C_2	-0.1	-0.3	-0.1	1.2	-0.3
	$\Delta S-C_2-C_3$	-0.1	0.4	1.2	-0.4	-0.1
	$\Delta S-C_2-H$	-0.1	-0.2	1.3	4.9	-0.9
	ΔC_2-C_3-H	-0.2	0.3	4.2	-0.0	4.9

		ν_6	ν_7	ν_8
	$\Delta S-C_2$	-0.002	0.037	0.018
	ΔC_2-C_3	-0.027	-0.002	0.002
	ΔC_2-H	-0.002	0.002	-0.000
	ΔC_3-H	-0.002	0.000	0.001
	ΔC_5-S-C_2	-0.9	0.4	-2.7
	$\Delta S-C_2-C_3$	0.1	-1.5	2.1
	$\Delta S-C_2-H$	3.6	1.4	-0.5
	ΔC_2-C_3-H	-0.8	0.5	-0.1

		ν_1	ν_2	ν_3	ν_4	ν_5
	$\Delta S-C_2$	-0.003	0.001	0.004	-0.011	-0.001
	ΔC_2-C_3	-0.006	-0.002	-0.038	0.010	-0.009
	ΔC_2-H	0.067	-0.027	-0.004	0.001	-0.000
$^2B_1$	ΔC_3-H	0.027	0.068	-0.002	0.002	-0.001
	ΔC_5-S-C_2	-0.3	0.1	-1.1	0.5	-0.0
	$\Delta S-C_2-C_3$	0.3	-0.3	1.0	0.7	-0.1
	$\Delta S-C_2-H$	-0.2	0.0	-1.5	4.3	4.3
	ΔC_2-C_3-H	0.1	-0.3	2.5	4.4	-4.1

Table 20.6 Cont'd.

		ν_6	ν_7	ν_8		
	$\Delta S-C_2$	-0.004	-0.037	-0.030		
	ΔC_2-C_3	-0.007	0.004	0.001		
	ΔC_2-H	-0.001	-0.002	0.000		
	ΔC_3-H	-0.002	-0.000	-0.000		
	ΔC_5-S-C_2	-0.5	-0.9	2.8		
	$\Delta S-C_2-C_3$	-0.7	2.1	-1.6		
	$\Delta S-C_2-H$	1.7	-0.7	0.6		
	ΔC_2-C_3-H	1.2	-0.1	0.4		
		ν_1	ν_2	ν_3	ν_4	ν_5
	$\Delta S-C_2$	-0.003	0.000	0.000	-0.011	-0.001
	ΔC_2-C_3	-0.006	-0.003	-0.039	0.011	-0.004
	ΔC_2-H	0.072	-0.007	-0.004	0.001	0.000
$^2A_1$	ΔC_3-H	0.007	0.073	-0.001	0.002	0.000
	ΔC_5-S-C_2	-0.4	0.0	-1.1	0.6	0.1
	$\Delta S-C_2-C_3$	0.3	-0.3	1.0	0.8	0.1
	$\Delta S-C_2-H$	-0.2	-0.0	-1.2	3.8	4.4
	ΔC_2-C_3-H	0.2	-0.2	2.4	4.5	-4.2
		ν_6	ν_7	ν_8		
	$\Delta S-C_2$	-0.001	-0.034	0.038		
	ΔC_2-C_3	-0.008	0.005	-0.004		
	ΔC_2-H	-0.001	-0.002	-0.000		
	ΔC_3-H	-0.002	-0.000	0.001		
	ΔC_5-S-C_2	-0.5	-1.2	-2.7		
	$\Delta S-C_2-C_3$	-0.7	2.2	1.3		
	$\Delta S-C_2-H$	3.0	-0.3	-1.0		
	ΔC_2-C_3-H	0.9	-0.4	-0.2		
		ν_1	ν_2	ν_3	ν_4	ν_5
	$\Delta S-C_2$	0.000	-0.000	-0.007	-0.012	0.004
	ΔC_2-C_3	-0.005	-0.006	0.038	0.009	0.006
	ΔC_2-H	0.011	0.073	0.006	0.004	0.000
$^2B_2$	ΔC_3-H	0.072	-0.012	0.002	0.002	-0.001
	ΔC_5-S-C_2	-0.1	-0.4	0.9	0.4	0.1
	$\Delta S-C_2-C_3$	-0.2	0.5	-0.8	0.9	-0.2
	$\Delta S-C_2-H$	-0.1	-0.3	1.3	3.6	-4.2
	ΔC_2-C_3-H	-0.2	0.2	-2.1	4.4	4.4
		ν_6	ν_7	ν_8		
	$\Delta S-C_2$	-0.004	-0.024	0.053		
	ΔC_2-C_3	-0.006	0.002	-0.001		
	ΔC_2-H	-0.001	0.001	-0.003		
	ΔC_3-H	-0.002	-0.001	0.001		
	ΔC_5-S-C_2	-0.5	-2.2	-1.8		
	$\Delta S-C_2-C_3$	-0.5	3.1	0.4		
	$\Delta S-C_2-H$	2.9	-1.5	0.0		
	ΔC_2-C_3-H	1.7	0.6	-0.4		

Bond lengths are in angstroms, angles in degrees.

Table 20.7 Vibrational levels of the $^2A_2$ state.

IE	Vibrational levels
7.77	S(0 0 0 0 0 0 0 0)
7.85-7.88	S(0 0 0 0 0 0 0 1), W(0 0 0 0 0 0 1 0)
7.91-8.00	W(0 0 0 0 0 1 0 0), W(0 0 0 0 1 0 0 0), W(0 0 0 0 0 0 0 2),
	S(0 0 0 1 0 0 0 0), M(0 0 1 0 0 0 0 0), W(0 0 0 0 0 0 1 1),
	W(0 0 0 0 0 1 0 1), W(0 0 0 0 1 0 0 1)
8.03-8.06	M(0 0 0 1 0 0 0 1), W(0 0 1 0 0 0 0 1), W(0 0 0 1 0 0 1 0)
8.09-8.18	W(0 0 0 1 0 1 0 0), W(0 0 0 1 1 0 0 0), W(0 0 0 1 0 0 0 2),
	W(0 0 1 0 1 0 0 0), W(0 0 0 2 0 0 0 0), W(0 0 1 1 0 0 0 0),
	W(0 0 2 0 0 0 0 0)
8.21-8.24	W(0 0 0 2 0 0 0 1), W(0 0 1 1 0 0 0 1)

S:0.08<FCF<0.16, M:0.04<FCF<0.06 and W:0.01<FCF<0.03.

Table 20.8 Vibrational levels of the $^2B_1$ state.

IE	Vibrational levels
8.42	S(0 0 0 0 0 0 0 0)
8.50-8.55	S(0 0 0 0 0 0 0 1), S(0 0 0 0 0 0 1 0), S(0 0 0 0 0 1 0 0)
8.60-8.65	M(0 0 0 0 0 0 1 1), W(0 0 0 0 0 0 2 0), M(0 0 1 0 0 0 0 0),
	W(0 0 0 0 0 1 0 1), M(0 0 0 0 0 1 1 0)
8.73	W(0 0 1 0 0 0 1 0)

S:0.09<FCF<0.43, M:0.03<FCF<0.04 and W:0.01<FCF<0.02.

21. Formaldehyde CH_2O

Table 21.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C=O (ΔC=O)	C-H (ΔC-H)	H-C=O (ΔH-C=O)
$^1A_1$	1.181	1.103	122.22
Exp.[a]	1.210	1.102	119.5
1^2B_2	1.209(+0.028)	1.097(-0.006)	117.71(-4.51)
$^2B_1$	1.325(+0.144)	1.093(-0.010)	118.81(-3.41)
$^2A_1$	1.264(+0.083)	1.093(-0.010)	115.05(-7.17)
2^2B_2	1.253(+0.072)	1.201(+0.098)	132.29(+10.07)

[a]Brown et al. (1988).
Bond lengths are in angstroms, angles in degrees.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 21.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SD-CI
1^2B_2	9.61	10.40	9.53	10.35	0.08	0.05
$^2B_1$	12.68	14.15	11.93	13.28	0.75	0.87
$^2A_1$	14.90	15.79	14.56	15.35	0.47	0.44
2^2B_2	---	16.75	---	15.79	--	0.96

Total energies (a.u.) of $^1A_1$: -113.747398(SCF) and -114.053771(SDCI).

Table 21.3 0-0 ionization levels.

State	0-0 IE	FCF
1^2B_2	10.33	0.667
$^2B_1$	13.25	0.028
$^2A_1$	15.33	0.185
2^2B_2	15.73	0.016

Table 21.4 Vibrational frequencies (cm^{-1})

State	ν_1	ν_2	ν_3
$^1A_1$	3104	2021	1639
Obs.[a]	2766	1746	1500
1^2B_2	3184	1765	1442
$^2B_1$	3238	1366	1633
$^2A_1$	3206	1539	1528
2^2B_2	2632	1846	1394

[a]Brown et al. (1989).

Table 21.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3
$^1A_1$	ΔC=O	1.1	88.5	5.3
	ΔC-H	98.9	0.0	0.4
	ΔH-C=O	0.0	11.5	94.3
1^2B_2	ΔC=O	0.9	82.7	11.6
	ΔC-H	99.0	0.2	0.0
	ΔH-C=O	0.2	17.1	88.4
$^2B_1$	ΔC=O	0.6	90.1	16.1
	ΔC-H	99.3	0.2	0.1
	ΔH-C=O	0.1	9.7	83.8
$^2A_1$	ΔC=O	0.6	99.4	4.2
	ΔC-H	99.3	0.4	0.0
	ΔH-C=O	0.1	0.3	95.8
2^2B_2	ΔC=O	8.4	66.3	25.1
	ΔC-H	88.7	14.4	1.5
	ΔH-C=O	2.9	19.3	73.4

Table 21.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3
$^1A_1$	ΔC=O	-0.006	-0.048	0.010
	ΔC-H	0.075	0.001	0.004
	ΔH-C=O	0.1	2.1	5.0
1^2B_2	ΔC=O	-0.007	-0.050	0.016
	ΔC-H	0.074	-0.003	-0.001
	ΔH-C=O	0.3	2.7	5.2
$^2B_1$	ΔC=O	-0.007	-0.052	-0.026
	ΔC-H	0.073	-0.002	-0.002
	ΔH-C=O	0.3	-1.5	5.4
$^2A_1$	ΔC=O	-0.006	-0.055	-0.012
	ΔC-H	0.073	-0.003	-0.001
	ΔH-C=O	0.3	0.3	5.8
2^2B_2	ΔC=O	-0.018	-0.042	0.024
	ΔC-H	0.079	-0.027	-0.008
	ΔH-C=O	1.1	2.5	4.4

Bond lengths are in angstroms, angles in degrees.

Table 21.7 Vibrational levels of the $^2B_1$ state.

IE	Progressions		
	A	B	C
13.25	W(0 0 0)		
13.42	W(0 1 0)		
13.45		S(0 0 1)	
13.59	W(0 2 0)		
13.62		S(0 1 1)	
13.65			W(0 0 2)
13.76	W(0 3 0)		
13.79		S(0 2 1)	
13.82			M(0 1 2)
13.86			
13.93	M(0 4 0)		
13.96		S(0 3 1)	
13.99			M(0 2 2)
14.03			
14.10	W(0 5 0)		
14.13		M(0 4 1)	
14.16			W(0 3 2)
14.20			
14.30		W(0 5 1)	
14.33			W(0 4 2)
14.36			

S:0.08<FCF<0.13, M:0.03<FCF<0.06 and W:0.01<FCF<0.03.

Table 21.8 Vibrational levels of the $^2A_1$ state.

IE	Progressions
	A
15.32	S(0 0 0)
15.51	S(0 0 1), S(0 1 0)
15.70	M(0 0 2), S(0 1 1), S(0 2 0)
15.89	W(0 0 3), M(0 1 2), M(0 2 1),W(0 3 0)
16.08	W(0 1 3), W(0 2 2),W(0 3 1)

S:0.08<FCF<0.20 M:0.04<FCF<0.06 and W:0.007<FCF<0.02.

Table 21.9 Vibrational levels of the 2^2B_2 state.

IE	Progressions	
	B	C
15.73	W(0 0 0)	
15.90	M(0 0 1)	
15.96		W(0 1 0)
16.06-16.08	M(0 0 2), W(1 0 0)	
16.13		W(0 1 1)
16.23-16.25	M(0 0 3), M(1 0 1)	
16.28-16.30		M(0 1 2)
16.40-16.42	M(0 0 4), M(1 0 2)	
16.46-16.48		M(0 1 3), W(1 1 1)
16.55-16.59	M(0 0 5), M(1 0 3), W(2 0 1)	
16.63-16.65		W(0 1 4), W(1 1 2)
16.73-16.77	W(0 0 6), M(1 0 4), W(2 0 2)	
16.80-16.82		W(0 1 5), W(1 1 3)
16.90-16.94	M(1 0 5), W(2 0 3)	
16.98-17.00		W(1 1 4)
17.07-17.09	W(1 0 6), W(2 0 4)	
17.15		W(1 1 5)
17.25-17.27	W(2 0 5)	
17.42	W(2 0 6)	

M:0.03<FCF<0.08 and W:0.008<FCF<0.03.

22. Formic acid CH_2O_2

Table 22.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C-H (ΔC-H)	C-O_1 (ΔC-O_1)	C-O_2 (ΔC-O_2)	O-H (ΔO_2-H)
^{1}A'	1.094	1.179	1.321	0.952
Exp.[a]	1.097	1.202	1.343	0.972
^{2}A'	1.091(-0.003)	1.257(+0.078)	1.243(-0.078)	0.964(+0.012)
^{2}A"	1.088(-0.006)	1.327(+0.148)	1.224(-0.097)	0.969(+0.018)

State	O_1-C-H(ΔO_1-C-H)	O_1-C-O_2(ΔO_1-C-O_2)	C-O_2-H(ΔC-O_2-H)
^{1}A'	124.76	124.91	108.41
Exp.[a]	124.1	124.9	106.3
^{2}A'	116.61(-8.15)	123.86(+1.05)	117.22(+8.81)
^{2}A"	121.35(-3.41)	120.36(-4.55)	115.67(+7.26)

[a]Herzberg (1966).

Bond lengths are in angstroms, angles in degrees.

The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 22.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2A'$	10.11	10.88	9.66	10.52	0.45	0.36
$^2A''$	11.70	12.44	10.70	11.63	1.00	0.81

Total energies (a.u.) of $^1A'$: -188.570787 (SCF) and -189.027513 (SDCI).

Table 22.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2A'$	10.47	0.123
$^2A''$	11.56	0.009

Table 22.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7
$^1A'$	4082	3269	2033	1528	1435	1276	697
Obs.[a]	3570	2943	1770	1387	1229	1105	625
$^2A'$	3918	3335	1796	1527	1326	1281	605
$^2A''$	3841	3380	1844	1527	1363	1226	642

[a]Herzberg (1966).

Table 22.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7
	ΔC-H	0.0	98.3	0.2	0.1	0.1	0.0	0.0
	ΔC-O_1	0.0	0.8	83.1	5.3	0.7	2.3	0.2
$^1A'$	ΔC-O_2	0.0	0.1	7.7	2.3	21.5	61.9	4.3
	ΔO-H	99.9	0.0	0.0	0.0	0.3	0.1	0.0
	ΔO_1-C-H	0.0	0.1	5.0	86.7	14.8	2.8	7.5
	ΔO_1-C-O_2	0.0	0.6	1.4	0.5	16.3	3.2	76.3
	ΔC-O_2-H	0.0	0.1	2.6	5.0	46.4	29.6	11.8
	ΔC-H	0.0	98.8	0.0	0.8	0.0	0.0	0.0
	ΔC-O_1	0.0	0.2	31.9	18.2	40.1	4.1	0.3
$^2A'$	ΔC-O_2	0.1	0.5	50.2	37.3	1.7	9.0	0.5
	ΔO-H	99.8	0.0	0.0	0.0	0.0	0.1	0.0
	ΔO_1-C-H	0.0	0.1	16.2	8.9	55.6	15.6	19.2
	ΔO_1-C-O_2	0.0	0.4	0.0	13.0	2.1	0.5	77.1
	ΔC-O_2-H	0.0	0.1	1.6	21.8	0.6	70.7	3.0
	ΔC-H	0.0	98.9	0.2	0.2	0.1	0.1	0.1
	ΔC-O_1	0.0	0.3	9.1	6.0	10.7	52.3	3.7
$^2A''$	ΔC-O_2	0.1	0.6	60.1	3.4	0.2	4.7	2.3
	ΔO-H	99.8	0.0	0.0	0.0	0.0	0.1	0.0
	ΔO_1-C-H	0.0	0.1	17.5	25.3	47.8	0.3	41.9
	ΔO_1-C-O_2	0.1	0.1	12.2	53.7	26.6	2.3	36.4
	ΔC-O_2-H	0.0	0.1	0.8	11.3	14.6	40.2	15.5

Table 22.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7
	ΔC-H	-0.001	0.105	0.004	0.003	0.002	0.000	0.000
	ΔC-O_1	0.000	-0.006	0.048	0.010	-0.004	-0.006	0.001
$^1A'$	ΔC-O_2	-0.002	-0.003	-0.021	0.009	0.029	-0.045	0.010
	ΔO-H	0.093	0.002	-0.000	0.001	-0.003	-0.002	-0.000
	ΔO_1-C-H	0.0	-0.4	-2.2	7.7	3.2	1.3	-1.7
	ΔO_1-C-O_2	0.2	0.7	-0.9	-0.4	-2.6	1.1	4.3
	ΔC-O_2-H	-0.1	-0.4	2.1	-2.4	7.4	5.5	2.9
	ΔC-H	-0.000	0.104	0.001	0.006	0.000	-0.001	0.000
	ΔC-O_1	-0.000	-0.004	-0.038	0.020	0.034	-0.011	0.002
$^2A'$	ΔC-O_2	-0.003	-0.005	0.043	0.027	0.006	-0.014	0.003
	ΔO-H	0.095	0.000	0.000	0.001	0.001	-0.002	-0.000
	ΔO_1-C-H	0.0	-0.3	4.4	-2.3	6.4	3.4	-3.1
	ΔO_1-C-O_2	0.2	0.7	-0.1	-2.3	-1.0	-0.5	5.1
	ΔC-O_2-H	-0.2	-0.4	-1.7	4.5	-0.8	8.9	1.5
	ΔC-H	-0.001	0.103	0.004	0.004	0.003	-0.002	0.001
	ΔC-O_1	0.000	0.005	-0.025	0.021	0.026	-0.041	-0.006
$^2A''$	ΔC-O_2	-0.003	0.005	0.049	0.012	-0.003	-0.009	-0.004
	ΔO-H	0.096	0.001	0.001	0.000	-0.001	-0.002	0.000
	ΔO_1-C-H	0.0	-0.4	3.8	-4.7	6.1	0.3	2.3
	ΔO_1-C-O_2	-0.3	-0.3	-3.1	6.7	-4.5	-0.9	2.1
	ΔC-O_2-H	-0.2	-0.4	-1.4	5.1	5.5	6.5	-2.3

Bond lengths are in angstroms, angles in degrees.

Table 22.7 Assignment of the vibrational levels of the $^2A'$ state of CH_2O_2.

Progression	Vibrational levels
10.47	S(0 0 0 0 0 0 0)
10.66-10.69	S(0 0 1 0 0 0 0), W(0 0 0 1 0 0 0), W(0 0 0 0 0 1 0)
10.85-10.91	S(0 0 2 0 0 0 0), M(0 0 1 1 0 0 0), W(0 0 1 0 0 1 0)
11.07-11.14	S(0 0 3 0 0 0 0), W(0 0 2 1 0 0 0), W(0 0 2 0 0 1 0)
11.30-11.36	M(0 0 4 0 0 0 0), W(0 0 3 1 0 0 0), W(0 0 3 0 0 1 0)
11.52-11.58	W(0 0 5 0 0 0 0), W(0 0 4 0 0 1 0)

S:0.012<FCF<0.23, M:0.03<FCF<0.07 and W:0.005<FCF<0.03.

Table 22.8 Assignment of the vibrational levels of the $^2A''$ state of CH_2O_2.

Progression	Vibrational levels
A	W(0 0 0 0 0 0 0) W(0 0 1 0 0 0 0) M(0 0 2 0 0 0 0) M(0 0 3 0 0 0 0) W(0 0 4 0 0 0 0) W(0 0 5 0 0 0 0) W(0 0 6 0 0 0 0)
B	W(0 0 0 0 0 1 0), W(0 0 0 0 1 0 0), W(0 0 0 1 0 0 0) W(0 0 1 0 0 1 0), M(0 0 1 0 1 0 0), W(0 0 1 1 0 0 0) W(0 0 2 0 0 1 0), M(0 0 2 0 1 0 0), W(0 0 2 1 0 0 0) W(0 0 3 0 0 1 0), M(0 0 3 0 1 0 0), W(0 0 3 1 0 0 0) W(0 0 4 0 0 1 0), W(0 0 4 0 1 0 0), W(0 0 4 1 0 0 0) W(0 0 5 0 0 1 0), W(0 0 5 0 1 0 0) W(0 0 6 0 1 0 0)
C	W(0 0 0 0 1 1 0), W(0 0 0 0 2 0 0), W(0 0 0 1 1 0 0) W(0 0 1 0 1 1 0), W(0 0 1 0 2 0 0), W(0 0 1 1 1 0 0) W(0 0 2 0 1 1 0), W(0 0 2 0 2 0 0), W(0 0 2 1 1 0 0) W(0 0 3 0 1 1 0), W(0 0 3 0 2 0 0), W(0 0 3 1 1 0 0) W(0 0 4 0 1 1 0), W(0 0 4 0 2 0 0), W(0 0 4 1 1 0 0) W(0 0 5 0 1 1 0), W(0 0 5 0 2 0 0)

M:0.025<FCF<0.04 and W:0.005<FCF<0.025.

23. Ketene C_2H_2O

Table 23.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C=C (ΔC=C)	C=O (ΔC=O)	C-H (ΔC-H)	H-C=C (ΔH-C=C)
$^1A_1$	1.310	1.140	1.079	118.99
Exp.[a]	1.315	1.16	1.079	118.85
1^2B_1	1.406(+0.096)	1.095(-0.045)	1.085(+0.006)	117.69(-1.30)
1^2B_2	1.257(-0.052)	1.296(+0.155)	1.096(+0.017)	119.58(+0.59)
2^2B_1	1.351(+0.041)	1.276(+0.135)	1.081(+0.003)	117.37(-1.62)
2^2B_2	1.318(+0.008)	1.234(+0.094)	1.128(+0.049)	127.91(+8.92)
$^2A_1$	1.339(+0.029)	1.116(-0.025)	1.138(+0.060)	96.29(-22.70)

[a]Herzberg (1966).
Bond lengths are in angstroms, angles in degrees.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 23.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SD-CI
1^2B_1	8.66	9.14	8.32	8.94	0.34	0.20
1^2B_2	13.43	14.45	12.40	13.41	0.03	0.04
2^2B_1	---	15.80	---	14.89	---	0.91
2^2B_2	---	16.82	---	15.92	---	0.90
$^2A_1$	16.98	16.98	15.77	15.93	1.21	1.05

Total energies (a.u.) of $^1A_1$: -151.564055(SCF) and -151.968518(SDCI).

Table 23.3 0-0 ionization levels.

State	0-0 IE	FCF
1^2B_1	8.93	0.231
1^2B_2	13.36	0.011
2^2B_1	14.86	0.007
2^2B_2	15.92	0.024
$^2A_1$	15.87	0.000

Table 23.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3	ν_4
$^1A_1$	3349	2372	1523	1253
Obs.[a]	3070	2152	1388	1118
1^2B_1	3288	2596	1471	1049
1^2B_2	3182	2135	1337	1057
2^2B_1	3343	2125	1474	1033
2^2B_2	3215	2692	1503	1127
$^2A_1$	2737	2439	1335	992

[a]Herzberg (1966).

Table 23.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3	ν_4
$^1A_1$	ΔC=C	0.9	27.9	19.0	58.1
	ΔC=O	0.0	71.9	4.6	20.1
	ΔC-H	99.0	0.1	0.1	0.3
	ΔH-C=C	0.1	0.1	76.3	21.5
1^2B_1	ΔC=C	0.3	9.8	4.8	93.0
	ΔC=O	0.0	90.2	0.0	6.8
	ΔC-H	99.6	0.0	0.0	0.1
	ΔH-C=C	0.1	0.0	95.2	0.1
1^2B_2	ΔC=C	1.3	70.6	2.9	26.8
	ΔC=O	0.0	27.6	8.3	65.8
	ΔC-H	98.6	0.6	0.0	0.1
	ΔH-C=C	0.1	1.2	88.8	7.3
2^2B_1	ΔC=C	0.5	45.4	6.0	51.4
	ΔC=O	0.0	54.4	1.2	46.2
	ΔC-H	99.3	0.0	0.4	0.2
	ΔH-C=C	0.2	0.2	92.4	2.2
2^2B_2	ΔC=C	0.9	30.0	28.0	31.5
	ΔC=O	9.8	42.3	0.1	51.1
	ΔC-H	88.2	27.3	1.4	0.7
	ΔH-C=C	1.1	0.4	70.4	16.7
$^2A_1$	ΔC=C	0.6	17.6	59.4	22.1
	ΔC=O	2.6	77.8	10.6	2.6
	ΔC-H	96.8	4.6	1.2	0.2
	ΔH-C=C	0.0	0.1	28.9	75.1

Table 23.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3	ν_4
$^1A_1$	ΔC=C	-0.007	-0.036	-0.024	0.034
	ΔC=O	0.001	0.044	-0.009	0.015
	ΔC-H	0.072	-0.002	-0.002	0.002
	ΔH-C=C	0.3	0.3	5.5	2.4
1^2B_1	ΔC=C	-0.006	-0.029	-0.015	0.054
	ΔC=O	-0.001	0.043	0.000	0.007
	ΔC-H	0.073	0.001	-0.001	0.001
	ΔH-C=C	0.3	-0.0	6.0	0.2
1^2B_2	ΔC=C	-0.008	0.048	-0.008	0.020
	ΔC=O	0.001	-0.037	-0.016	0.039
	ΔC-H	0.074	0.005	-0.001	0.001
	ΔH-C=C	0.3	-0.9	6.0	1.5
2^2B_1	ΔC=C	-0.006	0.043	-0.014	0.034
	ΔC=O	-0.000	-0.043	-0.006	0.030
	ΔC-H	0.072	0.000	-0.003	0.002
	ΔH-C=C	0.4	-0.3	5.9	0.8
2^2B_2	ΔC=C	0.006	-0.035	-0.030	0.027
	ΔC=O	-0.016	0.034	0.002	0.028
	ΔC-H	0.066	0.037	-0.007	0.004
	ΔH-C=C	0.7	-0.4	5.2	2.1
$^2A_1$	ΔC=C	0.006	-0.033	-0.043	0.022
	ΔC=O	-0.008	0.043	-0.011	0.005
	ΔC-H	0.077	0.017	0.006	0.002
	ΔH-C=C	-0.2	0.3	4.0	5.3

Bond lengths are in angstroms, angles in degrees. 2.10

Table 23.7 Vibrational levels of the 1^2B_2 state.

IE	Progressions A
13.36	W(0 0 0 0)
13.62-13.66	W(0 1 0 0), M(0 0 0 2)
13.88-13.92	W(0 2 0 0), M(0 1 0 2), W(0 0 0 4), W(0 1 1 1), W(0 0 1 3)
14.15-14.19	W(0 3 0 0), M(0 2 0 2), W(0 1 0 4), W(0 2 1 1), W(0 1 1 3)
14.41-14.45	W(0 4 0 0), M(0 3 0 2), W(0 2 0 4), W(0 3 1 1), W(0 2 1 3)
14.68-14.72	W(0 5 0 0), W(0 4 0 2), W(0 3 0 4)
14.95	W(0 5 0 2)

IE	Progressions B
13.49	W(0 0 0 1)
13.76-13.79	M(0 1 0 1), W(0 0 0 3), W(0 1 1 0), W(0 0 1 2)
14.02-14.05	M(0 2 0 1), M(0 1 0 3), W(0 2 1 0), W(0 1 1 2)
14.28-14.32	M(0 3 0 1), M(0 2 0 3), W(0 3 1 0), W(0 2 1 2)
14.55-14.58	W(0 4 0 1), W(0 3 0 3) W(0 3 1 2)
14.81	W(0 5 0 1), W(0 4 0 3)

M:0.03<FCF<0.07 and W:0.005<FCF<0.03.

Table 23.8 Vibrational levels of the 2^2B_1 state

IE	Progressions A
14.86	W(0 0 0 0)
14.99	W(0 0 0 1)
15.12-15.12	M(0 0 0 2), W(0 1 0 0)
15.24-15.25	M(0 0 0 3), M(0 1 0 1)
15.37-15.38	M(0 0 0 4), M(0 1 0 2)
15.50-15.51	M(0 0 0 5), M(0 1 0 3), W(0 2 0 1)
15.63-15.64	W(0 0 0 6), M(0 1 0 4), W(0 2 0 2)
15.76-15.78	W(0 0 0 7), M(0 1 0 5), M(0 2 0 3)
15.91	W(0 1 0 6), W(0 2 0 4), W(0 3 0 2)
16.03	W(0 1 0 7), W(0 2 0 5), W(0 3 0 3)
16.16	W(0 2 0 6), W(0 3 0 4)

IE	Progressions B
15.17	W(0 0 1 1)
15.30	W(0 0 1 2)
15.43	W(0 0 1 3), W(0 1 1 1)
15.55-15.56	W(0 0 1 4), W(0 1 1 2)
15.68-15.69	W(0 0 1 5), W(0 1 1 3)
15.81-15.83	W(0 1 1 4), W(0 2 1 2)
15.95	W(0 1 1 5), W(0 2 1 3)
16.08	W(0 2 1 4)

M:0.03<FCF<0.08 and W:0.005<FCF<0.03.

Table 23.9 Vibrational levels of the 2^2B_2 state.

IE	Progressions			
	A			
15.92	W(0 0 0 0)			
16.06	M(0 0 0 1)			
16.20	S(0 0 0 2)			
16.34	S(0 0 0 3)			
16.43-16.48	S(0 0 0 4)			
16.57-16.62	M(0 0 0 5),	W(0 1 1 1),		W(0 0 2 2)
16.71-16.76	W(0 0 0 6),	W(0 1 1 2),	W(0 2 0 1),	W(0 0 2 3)
16.85-16.90	W(0 0 0 7),	W(0 1 1 3),	W(0 2 0 2),	W(0 0 2 4)
17.00-17.01		W(0 1 1 4),	W(0 2 0 3)	
17.15			W(0 2 0 4)	

IE	Progressions	
	B	
16.11	W(0 0 1 0)	
16.25-16.25	W(0 0 1 1),	W(0 1 0 0)
16.39-16.39	M(0 0 1 2),	M(0 1 0 1)
16.53-16.53	M(0 0 1 3),	M(0 1 0 2)
16.66-16.67	M(0 0 1 4),	M(0 1 0 3)
16.80-16.81	W(0 0 1 5),	W(0 1 0 4)
16.94-16.95	W(0 0 1 6),	W(0 1 0 5)
17.09		W(0 1 0 6)

S:0.08<FCF<0.12 M:0.03<FCF<0.08 and W:0.005<FCF<0.03.

Table 23.10 Vibrational levels of the $^2A_1$ state.

IE	Progressions				
16.12	W(0 0 0 2)				
16.16		W(0 0 1 1)			
16.24	W(0 0 0 3)				
16.28		W(0 0 1 2)			
16.36	W(0 0 0 4)				
16.40		M(0 0 1 3)			
16.45			W(0 0 2 2)		
16.48	W(0 0 0 5)				
16.53		M(0 0 1 4)			
16.57-16.58			W(0 0 2 3),	W(1 0 0 3)	
16.61-16.62	W(0 0 0 6),			W(0 0 3 2),	W(1 0 1 2)
16.65		M(0 0 1 5)			
16.69-16.70			W(0 0 2 4),	W(1 0 0 4)	
16.73 16.74	W(0 0 0 7),			W(0 0 3 3),	W(1 0 1 3)
16.77		W(0 0 1 6)			
16.79	W(1 0 2 2)				
16.82			W(0 0 2 5),	W(1 0 0 5)	
16.86-16.87				W(0 0 3 4),	W(1 0 1 4)
16.90-16.91	W(1 0 2 3),	W(0 0 1 7)			
16.94-16.95			W(0 0 2 6),	W(1 0 0 6)	
16.98-16.99				W(0 0 3 5),	W(1 0 1 5)
17.02-17.03	W(1 0 2 4),	W(0 0 1 8)			
17.06			W(0 0 2 7)		
17.10-17.11				W(0 0 3 6)	W(1 0 1 6)
17.15	W(1 0 2 5)				
17.23					W(1 0 1 7)
17.28	W(1 0 2 6)				

M:0.03<FCF<0.04 and W:0.006<FCF<0.03.

24. Glyoxal $C_2H_2O_2$

Table 24.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C=C (ΔC=C)	C-H (ΔC-H)	C=O (ΔC=O)
^1A_g	1.517	1.101	1.182
Exp.[a]	1.526	1.132	1.212
^2A_g	2.036(+0.519)	1.102(+0.001)	1.122(-0.060)
^2A_u	1.585(+0.068)	1.095(-0.006)	1.228(+0.046)
^2B_g	1.445(-0.072)	1.091(-0.010)	1.245(+0.063)
^2B_u	1.464(-0.053)	1.113(+0.012)	1.195(+0.013)
	H-C=C(ΔH-C=C)	O-C=C(ΔO-C=C)	
^1A_g	114.90	121.27	
Exp.[a]	112.2	121.2	
^2A_g	103.90(-11.00)	113.76(-7.51)	
^2A_u	117.57(+2.67)	118.97(-2.30)	
^2B_g	121.17(+6.27)	116.34(-4.93)	
^2B_u	120.18(+5.28)	118.92(-2.35)	

[a]Kuchitsu et al. (1969).
Bond lengths are in angstroms, angles in degrees.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 24.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
^2A_g	10.79	10.40	9.80	9.92	0.99	0.48
^2B_u	13.10	12.63	12.98	12.47	0.12	0.16
^2B_g	13.64	14.11	13.18	13.57	0.46	0.54
^2A_u	15.56	15.87	15.26	15.43	0.30	0.44

Total energies (a.u.) of ^1A_g : -226.352259(SCF) and -226.899522(SDCI).

Table 24.3 0-0 ionization levels.

State	0-0 IE	FCF
^2A_g	9.85	0.000
^2B_u	12.46	0.449
^2B_g	13.57	0.101
^2A_u	15.41	0.165

Table 24.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3	ν_4	ν_5
^1A_g	3180	2050	1483	1183	612
Obs.[a]	2844	1742	1338	1060	553
^2A_g	3204	2280	1135	573	245
^2A_u	3283	1885	1438	1078	568
^2B_g	3327	1826	1275	1457	627
^2B_u	3062	2071	1367	1229	617

[a]Herzberg (1966).

Table 24.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5
	ΔC=C	0.3	5.4	6.3	41.6	33.6
^1A_g	ΔC-H	98.2	0.1	0.5	0.1	0.0
	ΔC=O	0.5	76.8	5.3	0.1	2.4
	ΔH-C=C	0.1	14.0	82.9	19.4	7.8
	ΔO-C=C	0.9	3.8	5.0	38.8	56.2
	ΔC=C	0.0	0.3	1.0	12.9	71.8
^2A_g	ΔC-H	93.9	4.4	0.1	0.0	0.0
	ΔC=O	5.4	92.0	0.0	0.5	1.4
	ΔH-C=C	0.3	2.3	96.9	13.9	18.7
	ΔO-C=C	0.4	1.0	2.0	72.8	8.1
	ΔC=C	0.2	5.2	3.0	43.7	34.2
^2A_u	ΔC-H	98.1	0.1	0.2	0.5	0.0
	ΔC=O	0.6	72.0	9.8	0.1	3.1
	ΔH-C=C	0.2	19.0	82.8	14.7	7.8
	ΔO-C=C	0.9	3.8	4.1	41.0	55.0
	ΔC=C	0.5	11.3	45.4	12.1	17.8
^2B_g	ΔC-H	97.9	0.0	0.6	0.6	0.0
	ΔC=O	0.4	60.9	0.0	21.1	3.7
	ΔH-C=C	0.2	24.6	30.1	53.6	8.7
	ΔO-C=C	1.0	3.3	23.9	12.6	69.8
	ΔC=C	0.7	12.0	24.0	29.5	24.2
^2B_u	ΔC-H	98.3	0.6	0.4	0.0	0.0
	ΔC=O	0.1	71.2	19.2	0.4	3.4
	ΔH-C=C	0.1	14.1	38.4	47.7	5.1
	ΔO-C=C	0.9	2.1	18.0	22.4	67.3

Table 24.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5
	ΔC=C	-0.006	-0.024	-0.019	-0.052	0.031
^1A_g	ΔC-H	0.075	-0.002	-0.003	-0.002	0.001
	ΔC=O	-0.003	0.034	-0.006	0.001	0.003
	ΔH-C=C	-0.3	2.9	4.9	-2.6	-1.1
	ΔO-C=C	0.7	-1.2	1.0	2.9	2.3
	ΔC=C	-0.001	-0.015	-0.019	-0.066	0.095
^2A_g	ΔC-H	0.074	0.014	0.002	0.000	0.000
	ΔC=O	-0.009	0.031	-0.000	0.001	-0.001
	ΔH-C=C	-0.6	1.5	6.4	-2.2	-1.6
	ΔO-C=C	0.6	-0.8	0.8	4.3	0.9
	ΔC=C	-0.006	-0.025	-0.014	-0.056	0.033
^2A_u	ΔC-H	0.074	0.002	-0.002	-0.003	-0.000
	ΔC=O	-0.004	0.035	-0.009	0.001	0.004
	ΔH-C=C	-0.4	3.3	4.9	-2.2	-1.1
	ΔO-C=C	0.7	-1.2	0.9	3.0	2.2
	ΔC=C	-0.007	-0.030	0.048	-0.021	0.020
^2B_g	ΔC-H	0.074	-0.000	0.004	-0.003	0.000
	ΔC=O	-0.003	0.034	0.000	-0.014	0.004
	ΔH-C=C	-0.4	3.8	3.4	3.9	-1.2
	ΔO-C=C	0.7	-1.1	-2.4	1.5	2.7
	ΔC=C	-0.008	-0.031	-0.031	0.039	0.023
^2B_u	ΔC-H	0.077	-0.005	-0.003	0.001	-0.000
	ΔC=O	-0.002	0.033	-0.012	0.002	0.004
	ΔH-C=C	-0.2	3.0	3.5	4.6	-0.9
	ΔO-C=C	0.7	-0.9	1.9	-2.4	2.7

Bond lengths are in angstroms, angles in degrees.

Table 24.7 Vibrational levels of the ^2B_u state.

IE	Progressions			
	A	B	C	the rest
12.46	S(0 0 0 0 0)			
12.54	S(0 0 0 0 1)			
12.61-12.63	M(0 0 0 0 2)	M(0 0 1 0 0)		
12.71-12.72		W(0 0 1 0 1)	S(0 1 0 0 0)	
12 79			M(0 1 0 0 1)	
12.84				W(1 0 0 0 0)
12.89				W(0 1 1 0 0)
12.97				W(0 2 0 0 0)

S:0.09<FCF<0.45, M:0.03<FCF<0.05 and W:0.01<FCF<0.03.

Table 24.8 Vibrational levels of the ^2B_g state.

IE	Progressions		
	A	B	the rest
13.57	S(0 0 0 0 0)		
13.65		M(0 0 0 0 1)	
13.72-13.75			W(0 0 0 0 2), W(0 0 0 1 0)
13.80	S(0 1 0 0 0)		
13.87		S(0 1 0 0 1)	
13.95-13.98			W(0 1 0 0 2), W(0 1 0 1 0)
14.02	S(0 2 0 0 0)		
14.10		M(0 2 0 0 1)	
14.18-14.20			W(0 2 0 0 2), W(0 2 0 1 0)
14.25	S(0 3 0 0 0)		
14.33		M(0 3 0 0 1)	
14.40			W(0 3 0 0 2)
14.48	M(0 4 0 0 0)		
14.55		W(0 4 0 0 1)	

S:0.08<FCF<0.18, M:0.03<FCF<0.08 and W:0.009<FCF<0.03.

Table 24.9 Vibrational levels of the ^2A_u state.

IE	Progressions			
	A	B	C	the rest
15.41	S(0 0 0 0 0)			
15.48	S(0 0 0 0 1)			
15.54-15.55	M(0 0 0 0 2)	S(0 0 0 1 0)		
15.59-15.64		M(0 0 0 1 1)	S(0 1 0 0 0)	W(0 0 1 0 0)
15.68-15.71		W(0 0 0 1 2)	M(0 1 0 0 1)	W(0 0 0 2 0)
15.75-15.78			W(0 1 0 0 2)	W(0 0 0 2 1), M(0 1 0 1 0)
15.82-15.85				W(0 1 1 0 0), M(0 1 0 1 1)
15.88-15.91				M(0 2 0 0 0), W(0 1 0 2 0)
15.95				W(0 2 0 0 1)
16.01				W(0 2 0 1 0)

S:0.08<FCF<0.17, M:0.03<FCF<0.07 and W:0.01<FCF<0.03.

25. Acetylene C_2H_2

Table 25.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C≡C (ΔC≡C)	C-H (ΔC-H)
$^1\Sigma_g$	1.191	1.065
Exp.[a]	1.208	1.058
$^2\Pi_u$	1.234(+0.043)	1.080(+0.015)
$^2\Sigma_g$	1.194(+0.003)	1.189(+0.124)
$^2\Sigma_u$	1.161(-0.030)	1.220(+0.155)

[a]Herzberg (1966).
Bond lengths are in angstroms.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 25.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2\Pi_u$	9.93	10.98	9.81	10.74	0.12	0.24
$^2\Sigma_g$	17.41	17.14	16.94	16.67	0.47	0.47
$^2\Sigma_u$	20.04	19.30	19.26	18.74	0.78	0.56

Total energies (a.u.) of $^1\Sigma_g$: -76.732685(SCF) and -76.985277(SDCI).

Table 25.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2\Pi_u$	10.72	0.645
$^2\Sigma_g$	16.61	0.259
$^2\Sigma_u$	18.69	0.125

Table 25.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2
$^1\Sigma_g$	3687	2226
Obs.[a]	3373	1974
$^2\Pi_u$	3535	2056
$^2\Sigma_g$	2795	2052
$^2\Sigma_u$	2912	2146

[a]Herzberg (1966).

Table 25.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2
$^1\Sigma_g$	ΔC≡C	8.8	90.6
	ΔC-H	91.2	9.4
$^2\Pi_u$	ΔC≡C	7.9	91.0
	ΔC-H	92.1	9.0
$^2\Sigma_g$	ΔC≡C	25.8	74.9
	ΔC-H	74.2	25.1
$^2\Sigma_u$	ΔC≡C	50.2	49.8
	ΔC-H	49.8	50.2

Table 25.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2
$^1\Sigma_g$	ΔC≡C	-0.018	0.045
	ΔC-H	0.069	0.017
$^2\Pi_u$	ΔC≡C	-0.018	0.047
	ΔC-H	0.070	0.017
$^2\Sigma_g$	ΔC≡C	-0.028	0.041
	ΔC-H	0.074	0.037
$^2\Sigma_u$	ΔC≡C	-0.035	0.031
	ΔC-H	0.063	0.055

Bond lengths are in angstroms.

Table 25.7 Vibrational levels of the $^2\Sigma_g$ state.

IE	Progressions		
	A	B	C
16.61	S(0 0)		
16.86		S(0 1)	
16.96	S(1 0)		
17,12			W(0 2)
17.21		S(1 1)	
17.30	S(2 0)		
17.46			W(1 2)
17.56		M(2 1)	
17.65	W(3 0)		

S:0.10<FCF<0.27, M:0.03<FCF<0.04 and W: 0.01<FCF<0.03.

Table 25.8 Vibrational levels of the $^2\Sigma_u$ state.

IE	Progressions		
	A	B	C
18.69	S(0 0)		
18.96		S(0 1)	
19.05	S(1 0)		
19.22			W(0 2)
19.32		S(1 1)	
19.41	S(2 0)		
19.58			W(1 2)
19.68		M(2 1)	
19.77	S(3 0)		
19.94			W(2 2)
20.04		W(3 1)	
20.13	W(4 0)		

S:0.08<FCF<0.22, M:0.03<FCF<0.08 and W: 0.01<FCF<0.03.

26. Diacetylene C_4H_2

Table 26.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C-C (ΔC-C)	C≡C (ΔC≡C)	C-H (ΔC-H)
$^1\Sigma_g$	1.391	1.192	1.064
Exp.[a]	1.376	1.205	1.446
$^2\Pi_g$	1.335(-0.056)	1.220(+0.028)	1.075(+0.011)
$^2\Pi_u$	1.439(+0.048)	1.213(+0.021)	1.074(+0.010)
$^2\Sigma_g$	1.674(+0.283)	1.182(-0.010)	1.078(+0.014)
$^2\Sigma_u$	1.386(-0.005)	1.183(-0.009)	1.205(+0.141)

[a]Herzberg (1966).
Bond lengths are in angstroms.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 26.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2\Pi_g$	9.38	9.94	9.22	9.70	0.16	0.24
$^2\Pi_u$	12.39	12.70	12.28	12.50	0.11	0.20
$^2\Sigma_g$	18.29	17.93	17.57	17.88	0.72	0.05
$^2\Sigma_u$	19.13	18.48	18.52	18.01	0.61	0.47

Total energies (a.u.) of $^1\Sigma_g$: -152.323528(SCF) and -152.768964(SDCI).

Table 26.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2\Pi_g$	9.70	0.549
$^2\Pi_u$	12.48	0.386
$^2\Sigma_g$	17.83	0.0
$^2\Sigma_u$	18.95	0.186

Table 26.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3
$^1\Sigma_g$	3636	2496	942
Obs.[a]	3329	2184	874
$^2\Pi_g$	3537	2449	1010
$^2\Pi_u$	3548	2387	884
$^2\Sigma_g$	3503	2295	509
$^2\Sigma_u$	2798	2392	953

[a]Herzberg (1966).

Table 26.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3
$^1\Sigma_g$	ΔC-C	0.2	23.5	78.8
	ΔCΞC	5.1	71.8	20.7
	ΔC-H	94.7	4.8	0.6
$^2\Pi_g$	ΔC-C	0.3	32.7	69.0
	ΔCΞC	4.7	63.0	30.2
	ΔC-H	95.0	4.4	0.8
$^2\Pi_u$	ΔC-C	0.2	22.1	80.1
	ΔCΞC	5.0	73.0	19.4
	ΔC-H	94.8	4.9	0.6
$^2\Sigma_g$	ΔC-C	0.1	5.3	97.5
	ΔCΞC	7.0	86.5	2.6
	ΔC-H	92.9	8.2	0.0
$^2\Sigma_u$	ΔC-C	7.4	17.4	78.5
	ΔCΞC	41.1	37.8	20.4
	ΔC-H	51.5	44.9	1.2

Table 26.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3
$^1\Sigma_g$	ΔC-C	0.005	-0.039	0.042
	ΔCΞC	-0.010	0.031	0.010
	ΔC-H	0.070	0.013	0.003
$^2\Pi_g$	ΔC-C	0.005	-0.041	0.036
	ΔCΞC	-0.010	0.031	0.013
	ΔC-H	0.071	0.013	0.003
$^2\Pi_u$	ΔC-C	0.005	-0.040	0.044
	ΔCΞC	-0.010	0.032	0.009
	ΔC-H	0.071	0.014	0.003
$^2\Sigma_g$	ΔC-C	0.006	-0.036	0.070
	ΔCΞC	-0.011	0.032	0.003
	ΔC-H	0.071	0.018	-0.000
$^2\Sigma_u$	ΔC-C	0.023	-0.032	0.042
	ΔCΞC	-0.024	0.021	0.010
	ΔC-H	0.063	0.054	0.005

Bond lengths are in angstroms.

Table 26.7 Vibrational levels of the $^2\Sigma_u$ state.

IE	Progressions		
	A	B	C
17.95	S(0 0 0)		
18.25		S(0 1 0)	
18.30	S(1 0 0)		
18.54			M(0 2 0)
18.59		S(1 1 0)	
18.64	S(2 0 0)		
18.89			M(1 2 0)
18.94		M(2 1 0)	
18.99	W(3 0 0)		
19.24			W(2 2 0)
19.29		W(3 1 0)	

S:0.10<FCF<0.22, M:0.03<FCF<0.06 and W:0.01<FCF<0.03.

Table 26.8 Vibrational levels of the $^2\Sigma_g$ state.

IE	Progressions
18.02	W(0 0 3)
18.08	M(0 0 4)
18.15	S(0 0 5)
18.21	S(0 0 6)
18.27	S(0 0 7)
18.33	S(0 0 8)
18.40-18.43	S(0 0 9), W(0 1 5)
18.46-18.49	M(0 0 10), W(0 1 6)
18.52-18.56	M(0 0 11), W(0 1 7)
18.59-18.62	W(0 0 12), W(0 1 8)
18.68-18.71	W(0 1 9)

S:0.08<FCF<0.17, M:0.03<FCF<0.07 and W: 0.01<FCF<0.03.

27. Triacetylene C_6H_2

Table 27.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	CΞC (ΔCΞC)	C-C (ΔC-C)	CΞC (ΔCΞC)	C-H (ΔC-H)
$^1\Sigma_g$	1.196	1.386	1.194	1.065
$^2\Pi_u$	1.233(+0.037)	1.343(-0.043)	1.206(+0.012)	1.073(+0.008)
$^2\Pi_g$	1.188(-0.008)	1.399(+0.013)	1.216(+0.022)	1.073(+0.008)
$^2\Sigma_g$	1.192(-0.004)	1.388(+0.002)	1.189(-0.005)	1.193(+0.128)
$^2\Sigma_u$	1.191(-0.005)	1.386(+0.0)	1.188(-0.006)	1.198(+0.133)

Bond lengths are in angstroms.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 27.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2\Pi_u$	8.91	9.38	8.73	8.06	0.18	1.32
$^2\Pi_g$	11.64	11.81	11.56	10.64	0.08	1.17
$^2\Sigma_g$	18.75	18.13	18.27	17.80	0.48	0.33
$^2\Sigma_u$	18.86	18.31	18.33	17.89	0.53	0.42

Total energies (a.u.) of $^1\Sigma_g$: -227.912786(SCF) and -228.527152(SDCI).

Table 27.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2\Pi_u$	8.04	0.518
$^2\Pi_g$	10.63	0.659
$^2\Sigma_g$	17.74	0.249
$^2\Sigma_u$	17.83	0.222

Table 27.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3	ν_4
$^1\Sigma_g$	3637	2579	2313	655
$^2\Pi_u$	3566	2493	2138	675
$^2\Pi_g$	3567	2617	2247	647
$^2\Sigma_g$	2763	2560	2252	647
$^2\Sigma_u$	2778	2573	2256	655

Table 27.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3	ν_4
$^1\Sigma_g$	ΔC≡C	0.0	58.2	22.7	15.7
	ΔC-C	0.1	26.3	0.7	75.8
	ΔC≡C	5.0	14.5	72.5	8.3
	ΔC-H	94.9	1.0	4.2	0.2
$^2\Pi_u$	ΔC≡C	0.0	46.6	27.8	23.3
	ΔC-C	0.1	33.7	0.1	69.5
	ΔC≡C	4.3	18.5	68.9	7.0
	ΔC-H	95.6	1.2	3.2	0.3
$^2\Pi_g$	ΔC≡C	0.0	68.3	13.4	15.1
	ΔC-C	0.1	24.2	2.8	75.4
	ΔC≡C	4.7	7.0	79.2	9.3
	ΔC-H	95.2	0.5	4.6	0.3
$^2\Sigma_g$	ΔC≡C	4.2	66.6	11.8	15.0
	ΔC-C	5.8	19.2	2.2	76.4
	ΔC≡C	30.1	0.6	61.7	8.5
	ΔC-H	59.9	13.6	24.3	0.1
$^2\Sigma_u$	ΔC≡C	3.3	15.2	12.3	66.7
	ΔC-C	5.3	76.1	2.1	20.3
	ΔC≡C	30.0	8.3	61.4	0.9
	ΔC-H	61.4	0.3	24.2	12.1

Table 27.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3	ν_4
$^1\Sigma_g$	ΔCΞC	-0.000	-0.041	-0.023	0.010
	ΔC-C	0.002	0.030	-0.004	0.024
	ΔCΞC	-0.010	-0.014	0.029	0.005
	ΔC-H	0.070	-0.006	0.012	0.001
$^2\Pi_u$	ΔCΞC	-0.000	-0.039	-0.027	0.013
	ΔC-C	0.002	0.031	-0.002	0.022
	ΔCΞC	-0.009	-0.017	0.029	0.005
	ΔC-H	0.071	-0.007	0.010	0.002
$^2\Pi_g$	ΔCΞC	-0.000	0.043	-0.017	0.010
	ΔC-C	0.002	-0.029	-0.009	0.024
	ΔCΞC	-0.010	0.010	0.031	0.006
	ΔC-H	0.071	0.005	0.012	0.002
$^2\Sigma_g$	ΔCΞC	-0.011	0.043	-0.016	0.010
	ΔC-C	0.015	-0.026	-0.008	0.024
	ΔCΞC	-0.021	0.003	0.026	0.005
	ΔC-H	0.067	0.031	0.038	0.001
$^2\Sigma_u$	ΔCΞC	-0.010	0.043	-0.017	0.010
	ΔC-C	0.014	-0.026	-0.008	0.024
	ΔCΞC	-0.021	0.004	0.026	0.005
	ΔC-H	0.068	0.029	0.038	0.002

Bond lengths are in angstroms.

Table 27.7 Vibrational levels of the $^2\Sigma_g$ state.

IE	Progressions		
	A	B	C
17.74	S(0 0 0 0)		
18.02		S(0 0 1 0)	
18.06-18.08	S(1 0 0 0), M(0 1 0 0)		
18.30			W(0 0 2 0)
18.34-18.36		S(1 0 1 0), W(0 1 1 0)	
18.40-18.43	S(2 0 0 0), M(1 1 0 0)		
18.64			W(1 0 2 0)
18.68-18.70		W(2 0 1 0)	
18.74-18.77	W(3 0 0 0), W(2 1 0 0)		

S:0.07<FCF<0.27, M:0.03<FCF<0.05 and W:0.009<FCF<0.03.

Table 27.8 Vibrational levels of the $^2\Sigma_u$ state.

IE	Progressions		
	A	B	C
17.83	S(0 0 0 0)		
18.11		S(0 0 1 0)	
18.15-18.17	S(1 0 0 0), M(0 1 0 0)		
18.39			W(0 0 2 0)
18.43-18.45		S(1 0 1 0), W(0 1 1 0)	
18.49-18.52	S(2 0 0 0), M(1 1 0 0)		
18.73			W(1 0 2 0)
18.77-18.80		M(2 0 1 0)	
18.84-18.86	M(3 0 0 0), W(2 1 0 0)		

S:0.08<FCF<0.27, M:0.03<FCF<0.04 and W:0.01<FCF<0.03.

28. Cyanogen C_2N_2

Table 28.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C-C (ΔC-C)	C≡N (ΔC≡N)
$^1\Sigma_g$	1.398	1.134
Exp.[a]	1.389	1.15
$^2\Pi_g$	1.347(-0.051)	1.166(+0.032)
$^2\Sigma_g$	1.414(+0.016)	1.127(-0.007)
$^2\Sigma_u$	1.399(+0.001)	1.120(-0.014)
$^2\Pi_u$	1.452(+0.054)	1.159(+0.025)

[a]Herzberg (1966).
Bond lengths are in angstroms, angles in degrees.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 28.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2\Pi_g$	12.94	13.41	12.74	13.06	0.20	0.35
$^2\Sigma_g$	15.86	14.99	15.84	15.03	0.02	-0.04
$^2\Sigma_u$	16.26	15.40	16.23	15.46	0.03	-0.06
$^2\Pi_u$	15.68	15.88	15.52	15.56	0.16	0.32

Total energies (a.u.) of $^1\Sigma_g$: -184.385757(SCF) and -184.866681(SDCI).

Table 28.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2\Pi_g$	13.06	0.532
$^2\Sigma_g$	15.03	0.956
$^2\Sigma_u$	15.46	0.888
$^2\Pi_u$	15.55	0.277

Table 28.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2
$^1\Sigma_g$	2737	930
Obs.[a]	2330	854
$^2\Pi_g$	2604	987
$^2\Sigma_g$	2744	893
$^2\Sigma_u$	2799	942
$^2\Pi_u$	2570	857

[a]Herzberg (1966).

Table 28.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2
$^1\Sigma_g$	ΔC-C	20.2	81.3
	ΔC≡N	79.8	18.7
$^2\Pi_g$	ΔC-C	28.3	73.6
	ΔC≡N	71.7	26.4
$^2\Sigma_g$	ΔC-C	18.6	81.9
	ΔC≡N	81.4	18.1
$^2\Sigma_u$	ΔC-C	19.1	82.8
	ΔC≡N	80.9	17.2
$^2\Pi_u$	ΔC-C	19.1	82.3
	ΔC≡N	80.9	17.7

Table 28.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2
$^1\Sigma_g$	ΔC-C	-0.038	0.043
	ΔC≡N	0.031	0.009
$^2\Pi_g$	ΔC-C	-0.041	0.037
	ΔC≡N	0.031	0.012
$^2\Sigma_g$	ΔC-C	-0.038	0.044
	ΔC≡N	0.031	0.009
$^2\Sigma_u$	ΔC-C	-0.038	0.043
	ΔC≡N	0.030	0.008
$^2\Pi_u$	ΔC-C	-0.039	0.045
	ΔC≡N	0.032	0.009

Bond lengths are in angstroms, angles in degrees.

Table 28.7 Vibrational levels of the $^2\Pi_u$ state.

IE	Progression
15.55	S(0 0)
15.66	S(0 1)
15.76	S(0 2)
15.87	S(0 3), W(1 0)
15.97	W(0 4), M(1 1)
16.08	M(1 2)

S:0.08<FCF<0.31, M:0.03<FCF<0.05 and W: 0.01<FCF<0.03.

29. Dicyanoacetylene C_4N_2

Table 29.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C-C (ΔC-C)	C≡C (ΔC≡C)	C≡N (ΔC≡N)
$^1\Sigma_g$	1.391	1.189	1.136
Exp.[a]	1.367	1.198	1.161
$^2\Pi_u$	1.363(-0.028)	1.232(+0.043)	1.143(+0.007)
$^2\Pi_g$	1.405(+0.014)	1.182(-0.007)	1.163(+0.027)
$^2\Sigma_u$	1.393(+0.002)	1.184(-0.005)	1.127(-0.009)
$^2\Sigma_g$	1.394(+0.003)	1.186(-0.003)	1.127(-0.009)

[a]Brown et al (1989)..
Bond lengths are in angstroms.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 29.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2\Pi_u$	11.45	12.00	11.22	11.59	0.23	0.41
$^2\Pi_g$	14.43	14.64	14.23	13.83	0.20	0.81
$^2\Sigma_u$	15.56	14.94	15.46	14.82	0.10	0.12
$^2\Sigma_g$	15.51	14.89	15.50	14.94	0.01	-0.05

Total energies (a.u.) of $^1\Sigma_g$: -259.978293(SCF) and -260.599992(SDCI).

Table 29.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2\Pi_u$	11.57	0.386
$^2\Pi_g$	13.82	0.549
$^2\Sigma_u$	14.82	0.186
$^2\Sigma_g$	14.94	0.0

Table 29.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3
$^1\Sigma_g$	2696	2467	640
Obs.[a]	2267	2119	692
$^2\Pi_u$	2568	2292	637
$^2\Pi_g$	2673	2390	631
$^2\Sigma_u$	2724	2494	642
$^2\Sigma_g$	2727	2494	641

[a]Herzberg (1866).

Table 29.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3
$^1\Sigma_g$	ΔC-C	23.8	1.4	77.1
	ΔCΞC	31.9	52.2	15.5
	ΔCΞN	44.3	46.4	7.5
$^2\Pi_u$	ΔC-C	27.1	1.9	73.6
	ΔCΞC	28.5	49.1	21.6
	ΔCΞN	44.4	49.0	4.8
$^2\Pi_g$	ΔC-C	24.7	0.5	76.6
	ΔCΞC	57.8	25.2	14.8
	ΔCΞN	17.5	74.3	8.6
$^2\Sigma_u$	ΔC-C	23.1	1.6	77.7
	ΔCΞC	30.7	53.7	15.1
	ΔCΞN	46.2	44.7	7.2
$^2\Sigma_g$	ΔC-C	23.1	1.7	77.3
	ΔCΞC	30.4	54.0	15.4
	ΔCΞN	46.5	44.4	7.3

Table 29.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3
$^1\Sigma_g$	ΔC-C	0.029	-0.007	0.024
	ΔCΞC	-0.030	0.035	0.010
	ΔCΞN	-0.023	-0.022	0.004
$^2\Pi_u$	ΔC-C	0.030	-0.007	0.023
	ΔCΞC	-0.031	0.037	0.013
	ΔCΞN	-0.024	-0.023	0.004
$^2\Pi_g$	ΔC-C	0.030	-0.004	0.024
	ΔCΞC	-0.040	-0.024	0.009
	ΔCΞN	-0.015	0.029	0.005
$^2\Sigma_u$	ΔC-C	0.029	-0.007	0.025
	ΔCΞC	-0.029	0.036	0.009
	ΔCΞN	-0.023	-0.021	0.004
$^2\Sigma_g$	ΔC-C	0.029	-0.007	0.024
	ΔCΞC	-0.029	0.036	0.010
	ΔCΞN	-0.023	-0.021	0.004

Bond lengths are in angstroms.

Table 29.7 Vibrational levels of the $^2\Pi_u$ state.

IE	Progressions
11.57	S(0 0 0)
11.85-11.89	S(1 0 0), S(0 1 0)
12.17-12.21	W(2 0 0), W(1 1 0)

S:0.08<FCF<0.63 and W:0.02<FCF<0.03.

Table 29.8 Vibrational levels of the $^2\Pi_g$ state.

IE	Progressions		
13.82	S(0 0 0)		
13.90		S(0 0 1)	
13.98			W(0 0 2)
14.12	S(0 1 0)		
14.19		M(0 1 1)	
14.41	W(0 2 0)		

S:0.16<FCF<0.54, M:0.05<FCF<0.06 and W: 0.02<FCF<0.03.

30. Hydrogen cyanide HCN

Table 30.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C-H (ΔC-H)	CΞN (ΔCΞN)
$^1\Sigma$	1.068	1.133
Exp.[a]	1.064	1.156
$^2\Pi$	1.093(+0.025)	1.187(+0.054)
$^2\Sigma$	1.089(+0.021)	1.119(-0.014)

[a]Herzberg (1966).
Bond lengths are in angstroms.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 30.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2\Pi$	12.22	13.33	12.02	12.94	0.20	0.39
$^2\Sigma$	12.84	13.45	12.82	13.47	0.02	-0.02

Total energies (a.u.) of $^1\Sigma$: -92.773544(SCF) and -93.044101(SDCI).

Table 30.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2\Pi$	12.91	0.479
$^2\Sigma$	13.46	0.937

Table 30.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2
$^1\Sigma$	3643	2424
Obs.[a]	3311	2097
$^2\Pi$	3375	2148
$^2\Sigma$	3468	2468

[a]Herzberg (1966).

Table 30.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2
$^1\Sigma$	ΔC-H	92.5	8.2
	ΔCΞN	7.5	91.8
$^2\Pi$	ΔC-H	94.0	6.8
	ΔCΞN	6.0	93.2
$^2\Sigma$	ΔC-H	87.3	14.0
	ΔCΞN	12.7	86.0

Table 30.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2
$^1\Sigma$	ΔC-H	0.098	0.024
	ΔCΞN	-0.015	0.043
$^2\Pi$	ΔC-H	0.102	0.022
	ΔCΞN	-0.014	0.046
$^2\Sigma$	ΔC-H	0.098	0.034
	ΔCΞN	-0.018	0.041

Bond lengths are in angstroms.

31. Cyanoacetylene C_3HN

Table 31.1 Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C-H(ΔC-H)	CΞC(ΔCΞC)	C-C(ΔC-C)	CΞN(ΔCΞN)
$^1\Sigma$	1.065	1.190	1.393	1.136
Exp.[a]	1.058	1.205	1.378	1.159
$^2\Pi$	1.081(+0.016)	1.234(+0.044)	1.366(-0.027)	1.143(+0.007)
$^2\Sigma$	1.074(+0.009)	1.193(+0.003)	1.366(-0.027)	1.128(-0.008)

[a]Herzberg (1966).
Bond lengths are in angstroms.
The values in parenthesis are the magnitude of the change in geometry by ionization.

Table 31.2 Ionization energies(eV).

State	VIE		AIE		Δ(VIE-AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2\Pi$	10.75	11.44	10.62	11.20	0.13	0.24
$^2\Sigma$	12.47	13.05	12.44	13.04	0.03	0.01

Total energies (a.u.) of $^1\Sigma$: -168.359035(SCF) and -168.820731(SDCI).

Table 31.3 0-0 ionization levels.

State	0-0 IE	FCF
$^2\Pi$	11.17	0.630
$^2\Sigma$	13.04	0.835

Table 31.4 Vibrational frequencies (cm^{-1}).

State	ν_1	ν_2	ν_3	ν_4
$^1\Sigma$	3631	2651	2375	936
Obs.[a]	3327	2271	2077	876
$^2\Pi$	3473	2514	2208	943
$^2\Sigma$	3559	2653	2361	975

[a]Herzberg (1966).

Table 31.5 Conventional potential energy distribution(%).

State	Component	ν_1	ν_2	ν_3	ν_4
$^1\Sigma$	ΔC-H	94.5	0.9	4.7	0.3
	ΔC≡C	5.4	10.0	73.9	10.8
	ΔC-C	0.2	18.3	3.7	79.8
	ΔC≡N	0.0	70.9	17.7	9.1
$^2\Pi$	ΔC-H	93.8	0.6	5.9	0.3
	ΔC≡C	6.0	4.9	77.3	11.9
	ΔC-C	0.2	17.3	6.7	79.2
	ΔC≡N	0.0	77.2	10.1	8.6
$^2\Sigma$	ΔC-H	95.3	0.7	4.2	0.5
	ΔC≡C	4.6	9.8	70.1	15.9
	ΔC-C	0.1	20.7	4.8	77.3
	ΔC≡N	0.0	68.8	20.9	6.4

Table 31.6 Classical half amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3	ν_4
	ΔC-H	0.099	0.008	0.018	0.003
$^1\Sigma$	ΔC≡C	-0.014	0.016	0.042	0.010
	ΔC-C	0.004	-0.036	-0.015	0.043
	ΔC≡N	-0.000	0.040	-0.019	0.008
	ΔC-H	0.101	0.008	0.017	0.004
$^2\Pi$	ΔC≡C	-0.014	0.018	0.043	0.013
	ΔC-C	0.003	-0.037	-0.016	0.041
	ΔC≡N	-0.000	0.041	-0.020	0.007
	ΔC-H	0.099	0.007	0.020	0.003
$^2\Sigma$	ΔC≡C	-0.015	0.012	0.043	0.011
	ΔC-C	0.004	-0.034	-0.019	0.041
	ΔC≡N	-0.000	0.042	-0.014	0.008

Bond lengths are in angstroms.

table. This value gives the magnitude of the change in the energy. In the SDCI calculations, the weight of a reference configuration beyonds about 80% for all cases and the each weight of another CSF is smaller than 1 %. The weight of a reference configurations of the ground state and ionic state is almost the same value in a few percentage. This result shows that the RHF approximation method for the ionic state is the same level as that for the ground state. Tables 2.3 - 31.3 give the 0-0 IE's and the FCF of the 0-0 vibrational transition. In most cases, the correction of the zero-point vibrational energy is smaller than 0.1 eV. We compare the calculated 0-0 IE's of the first ionic states with the observed values in table 1.4. This table shows that the calculated 0-0 IE's by the RHF and SDCI methods are underestimated compared with the observed values, and that the SDCI method gives better 0-0 IE's than the RHF method.

Tables 2.4 - 31.4 give the calculated vibrational frequencies and the observed values of the ground state. The calculated vibrational frequencies of the ground state are overestimated about 10% compared with the observed values. Tables 2.5 - 31.5 give the conventional potential energy distribution(%). Tables 2.6 - 31.6 give the classical half amplitude of the zero-point vibrational levels. We characterize each normal mode by the use of the conventional potential energy distribution and the classical half amplitude of the zero-point vibrational levels. For example, Table 4.5 shows that the conventional potential energy distribution of the

ν_2 and ν_3 modes of the $^2B_2$ state of CF_2Cl_2 are mixture of the C-Cl stretching motion and the F-C-F bending motion. Table 4.6 of the classical half amplitude of the zero-point vibrational levels shows that the phase of the linear combination of the C-Cl stretching motion and the F-C-F bending motion is in-phase for the ν_2 mode and out-of-phase for ν_3 mode. Information on the magnitude of the change in the equilibrium molecular structure and the classical half amplitude of the zero-point vibrational level helps us to understand which vibrational level of excitation contributes to the intensity. For example, the equilibrium molecular structure of the $^2A_2$ state of CH_2F_2 changes appreciably in the C-F distance (+0.057Å), the H-C-H angle (+6.29°) and the F-C-F angle (-13.37°) (see Table 2.1). The magnitude of the change in the H-C-H angle is within the classical half amplitude of the zero-point vibrational levels of the ν_2 mode (ΔH-C-H : ±11.3°, see Table 2.6). The magnitude of the change in the C-F distance and the H-C-H angle are beyond the classical half amplitude of the zero-point vibrational levels of the ν_3 mode (ΔC-F : ± 0.043Å) and the ν_4 mode (ΔF-C-F : ±4.0°), respectively. Thus, the higher vibrational excitation of the ν_3 and ν_4 modes contribute to intensity (see Table 2.10).

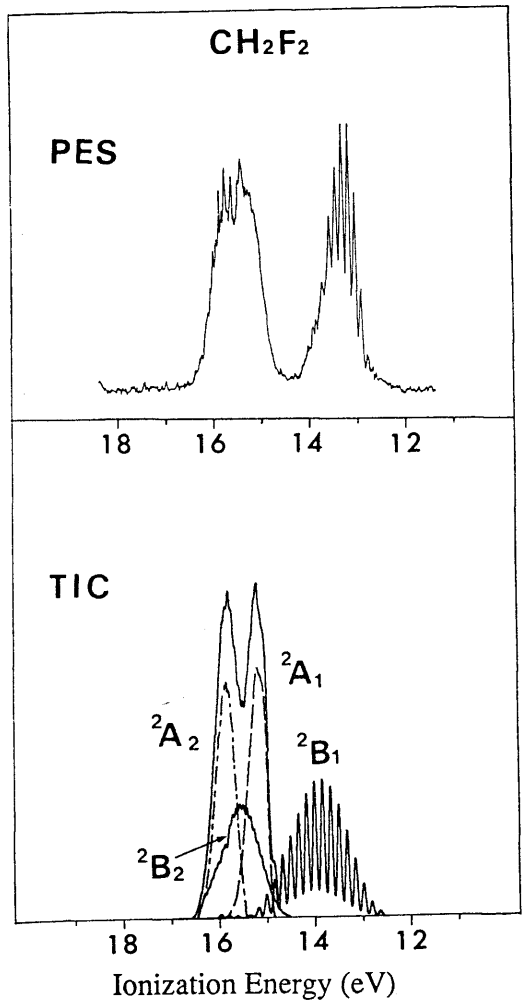

Fig. 2.1 Theoretical intensity curve and Photoelectron spectrum (From Turner et al. 1970) of Methylene fluoride. Band-width : 0.04 eV.

Figures 2.1 - 31.1 give the overall feature of the theoretical intensity curve compared with the observed PES. The band-width of the TIC is 0.08 eV.

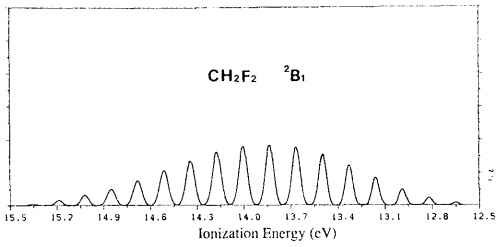

Fig. 2.2 Theoretical intensity curve of the $^2B_1$ state of Methylene fluoride.
Band-width : 0.04 eV.

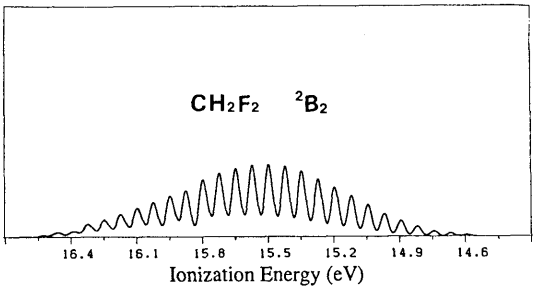

Fig. 2.3 Theoretical intensity curve of the $^2B_2$ state of Methylene fluoride.
Band-width : 0.04 eV.

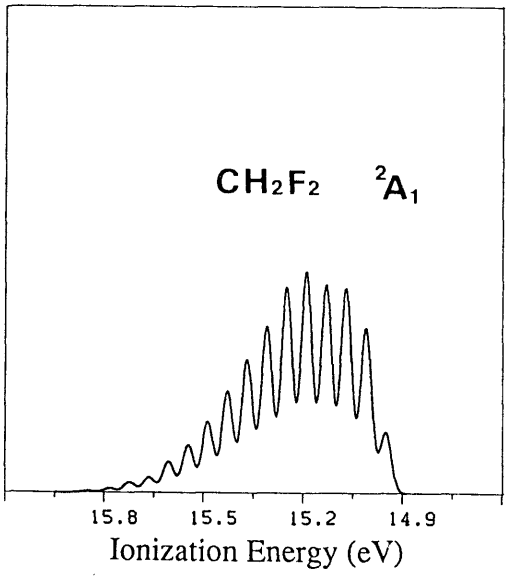

Fig. 2.4 Theoretical intensity curve of the $^2A_1$ state of Methylene fluoride.
Band-width : 0.04 eV.

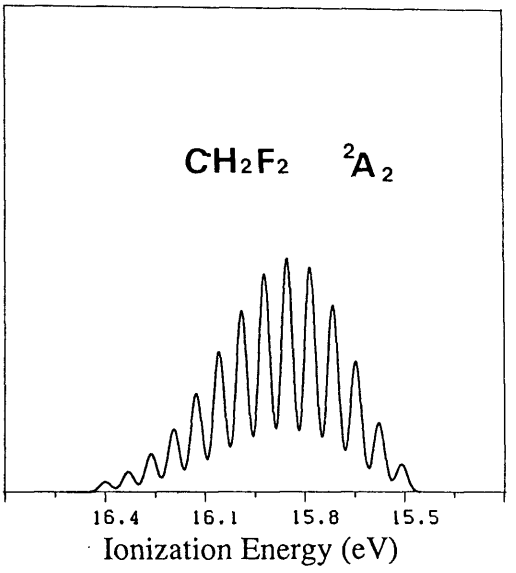

Fig. 2.5 Theoretical intensity curve of the $^2A_2$ state of Methylene fluoride.
Band-width : 0.04 eV.

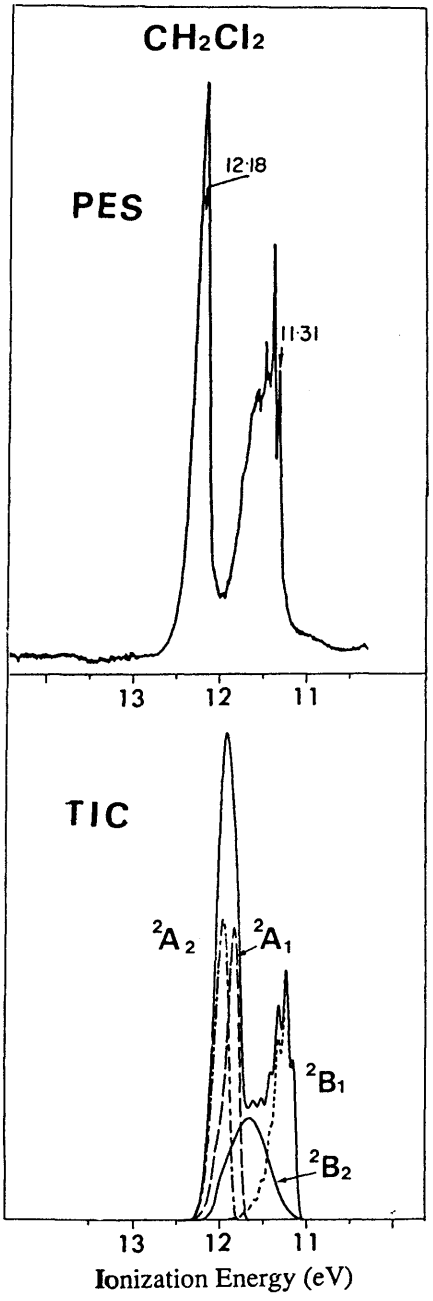

Fig. 3.1 Theoretical intensity curve and Photo electron spectrum (From Turner et al. 1970) of Methylene cloride. Band-width : 0.08 eV.

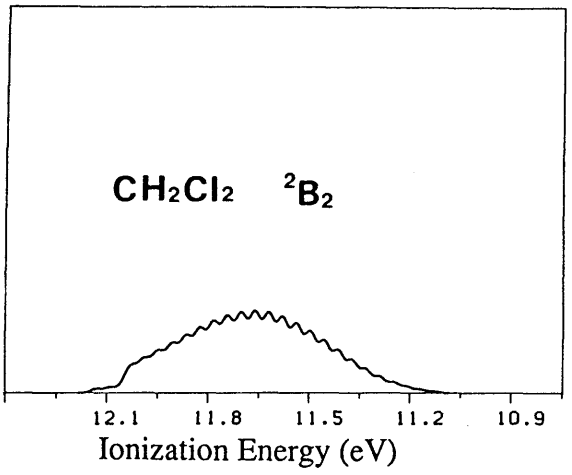

Fig. 3.2 Theoretical intensity curve of the $^2B_2$ state of Methylene cloride. Band-width : 0.04 eV.

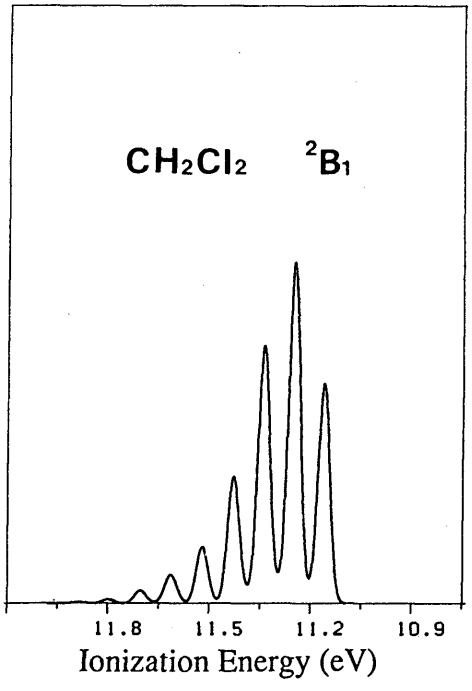

Fig. 3.3 Theoretical intensity curve of the $^2B_1$ state of Methylene cloride. Band-width : 0.04 eV.

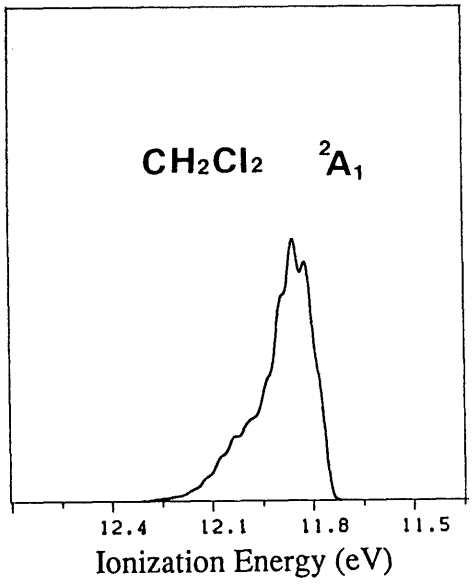

Fig. 3.4 Theoretical intensity curve of the $^2A_1$ state of Methylene cloride.
Band-width : 0.04 eV.

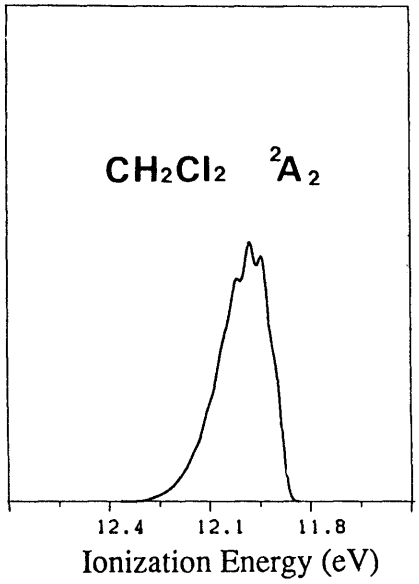

Fig. 3.5 Theoretical intensity curve of the $^2A_2$ state of Methylene cloride.
Band-width : 0.04 eV.

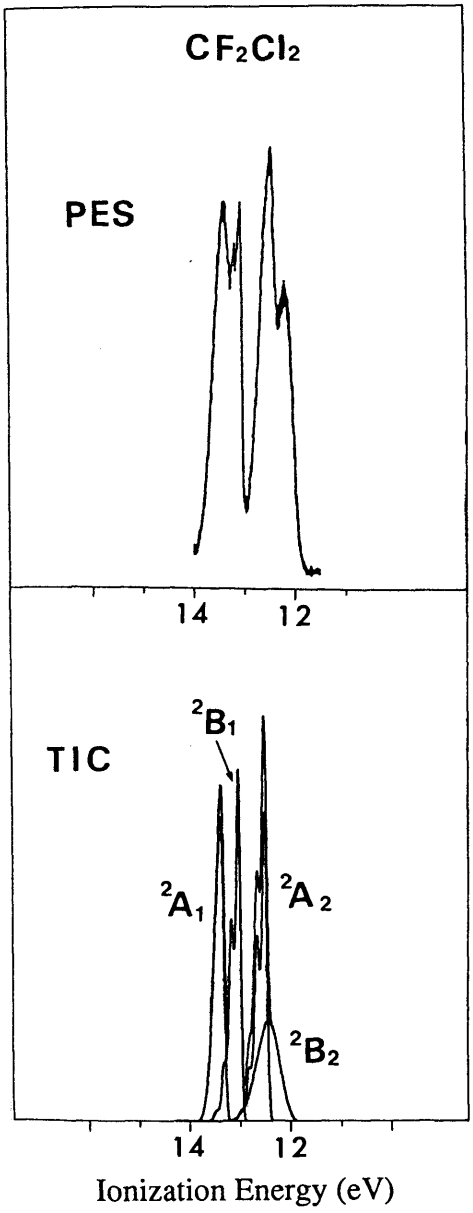

Fig. 4.1 Theoretical intensity curve and Photo-electron spectrum of Dichlorodifluoromethane.
Band-width : 0.08 eV.

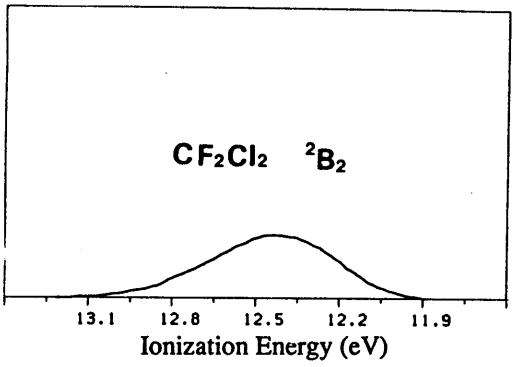

Fig. 4.2 Theoretical intensity curve of the $^2B_2$ state of Dichlorodifluoromethane. Band-width : 0.04 eV.

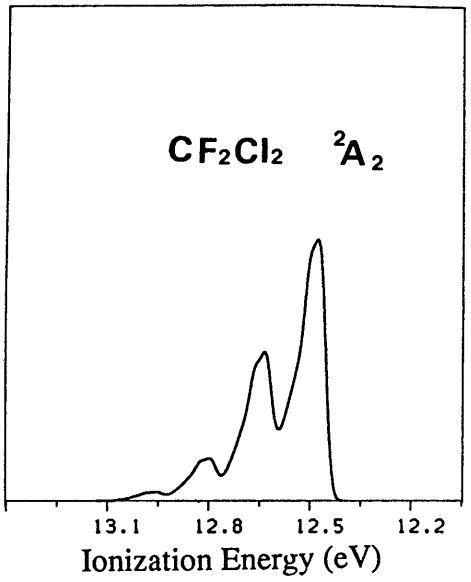

Fig. 4.3 Theoretical intensity curve of the $^2A_2$ state of Dichlorodifluoromethane. Band-width : 0.04 eV.

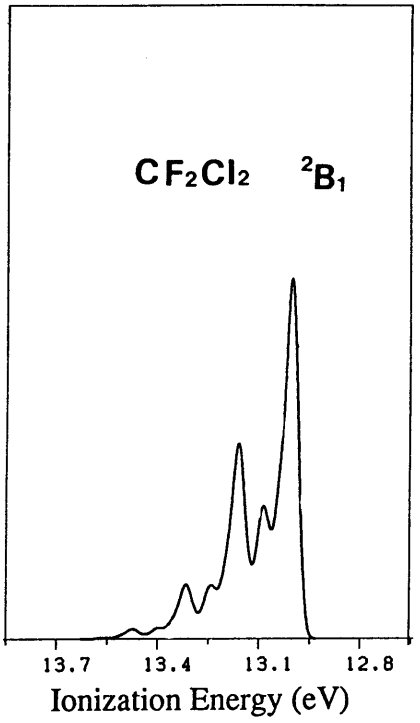

Fig. 4.4 Theoretical intensity curve of the $^2B_1$ state of Dichlorodifluoromethane. Band-width : 0.04 eV.

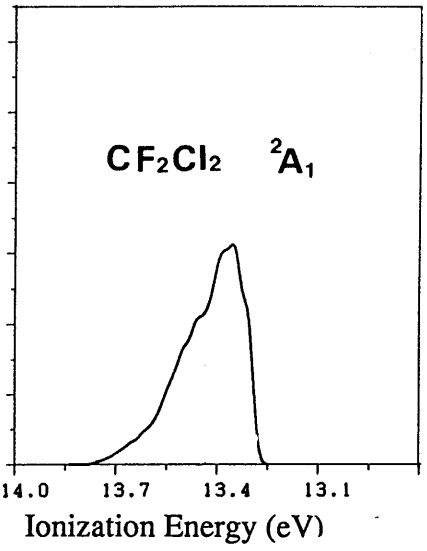

Fig. 4.5 Theoretical intensity curve of the $^2A_1$ state of Dichlorodifluoromethane. Band-width : 0.04 eV.

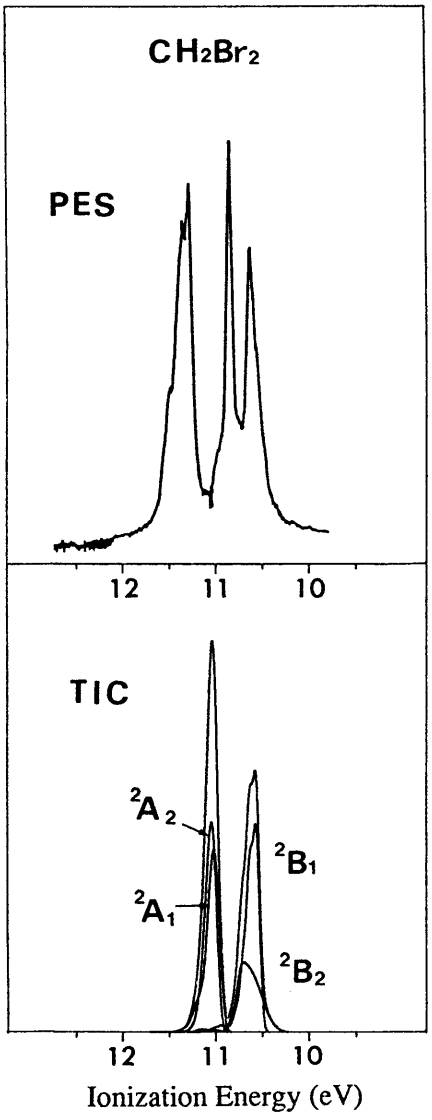

Fig. 5.1 Theoretical intensity curve and Photoelectron spectrum (From Turner et al. 1970) of Methylene bromide. Band-width : 0.08 eV.

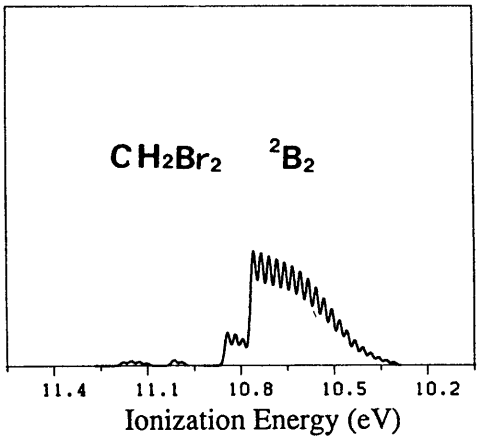

Fig. 5.2 Theoretical intensity curve of the $^2B_2$ state of Methylene bromide. Band-width : 0.02 eV. Disapperarance of spectrum beyond 10.8 eV is due to neglecting the vibrational levels higher than (0 0 0 30) and (0 0 1 30) levels.

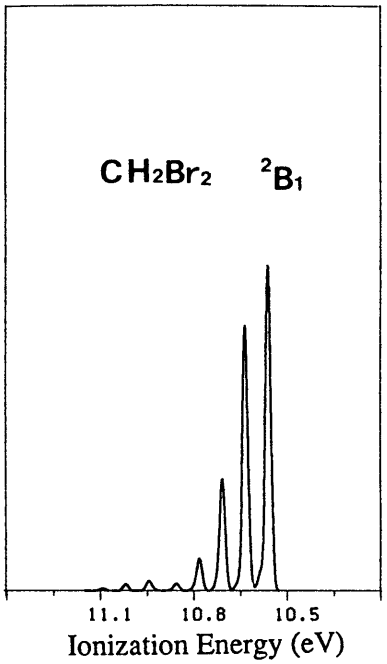

Fig. 5.3 Theoretical intensity curve of the $^2B_1$ state of Methylene bromide. Band-width : 0.02 eV.

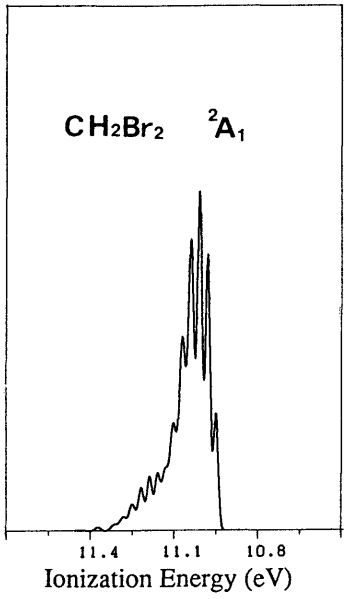

Fig. 5.4 Theoretical intensity curve of the $^2A_1$ state of Methylene bromide. Band-width : 0.02 eV.

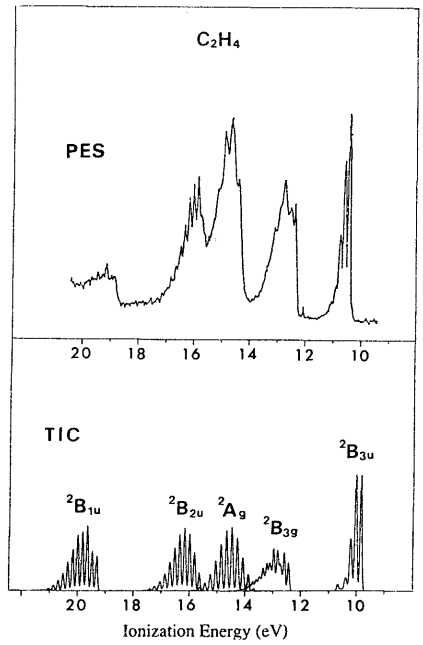

Fig. 6.1 Theoretical intensity curve and Photoelectron spectrum (From Kimura et al. 1981) of Ethylene. Band-width : 0.08 eV.

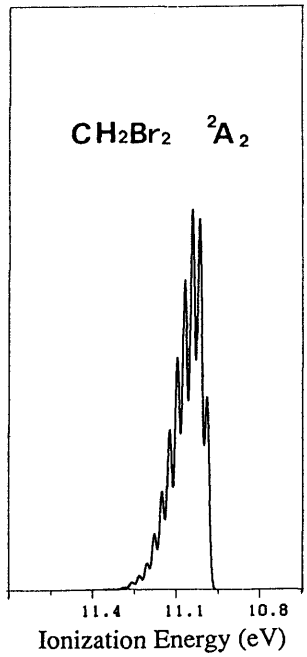

Fig. 5.5 Theoretical intensity curve of the $^2A_2$ state of Methylene bromide. Band-width : 0.02 eV.

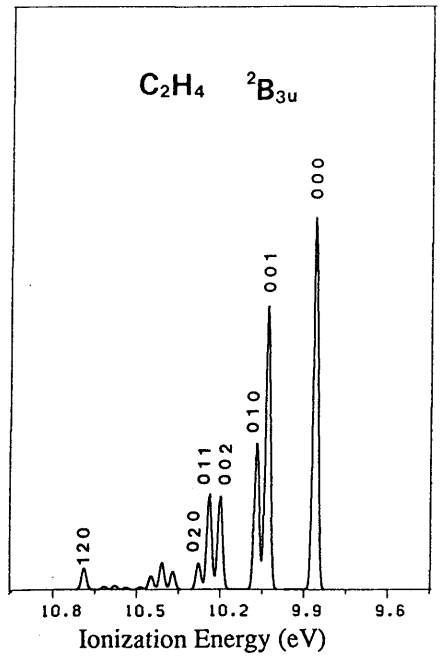

Fig. 6.2 Theoretical intensity curve of the $^2B_{3u}$ state of Ethylene. Band-width : 0.02 eV.

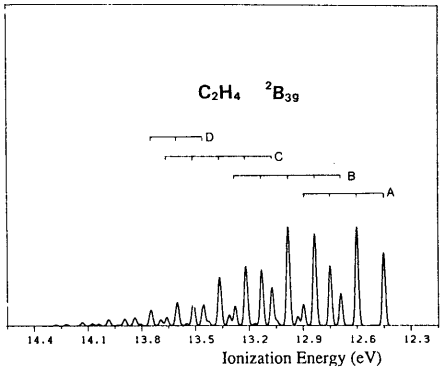

Fig. 6.3 Theoretical intensity curve of the $^2B_{3g}$ state of Ethylene. Band-width : 0.02 eV.

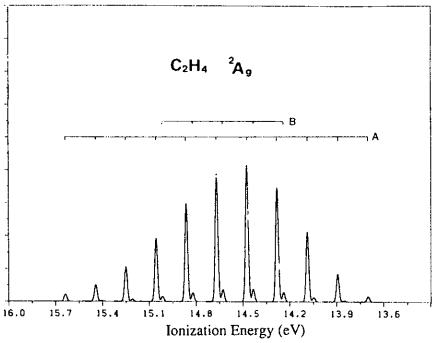

Fig. 6.4 Theoretical intensity curve of the ^2A_g state of Ethylene. Band-width : 0.02 eV.

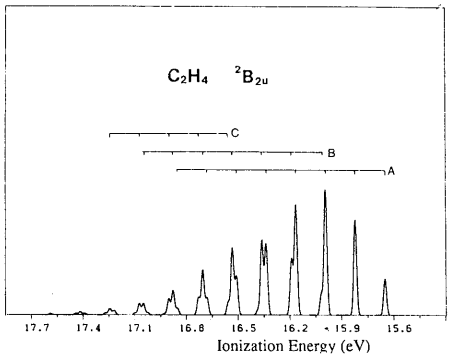

Fig. 6.5 Theoretical intensity curve of the $^2B_{2u}$ state of Ethylene. Band-width : 0.02 eV.

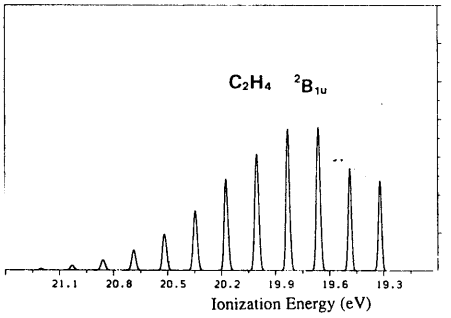

Fig. 6.6 Theoretical intensity curve of the $^2B_{1u}$ state of Ethylene. Band-width : 0.02 eV.

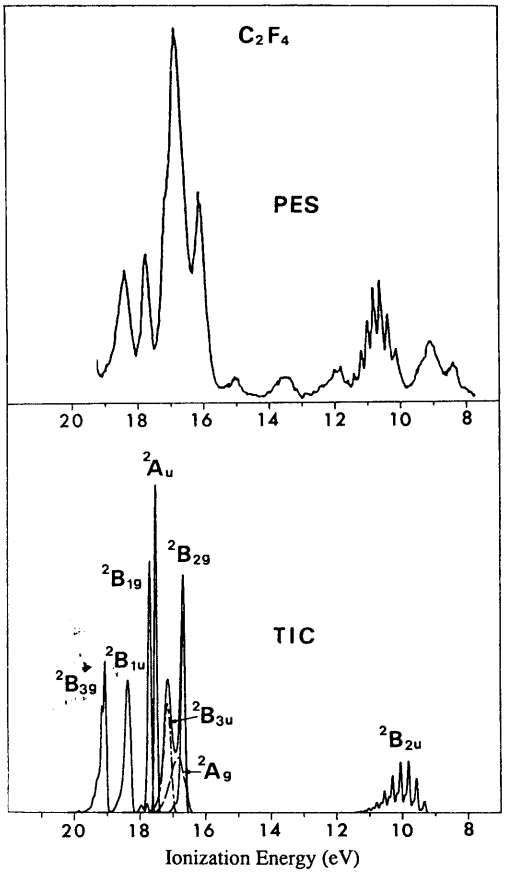

Fig. 7.1 Theoretical intensity curve and Photoelectron spectrum (From Bieri et al. 1981) of Tetrafluoroethylene. Band-width : 0.08 eV.

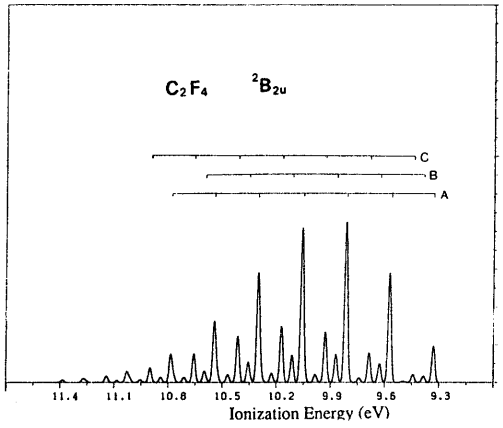

Fig. 7.2 Theoretical intensity curve of the $^2B_{2u}$ state of Tetrafluoroethylene.
Band-width : 0.02 eV.

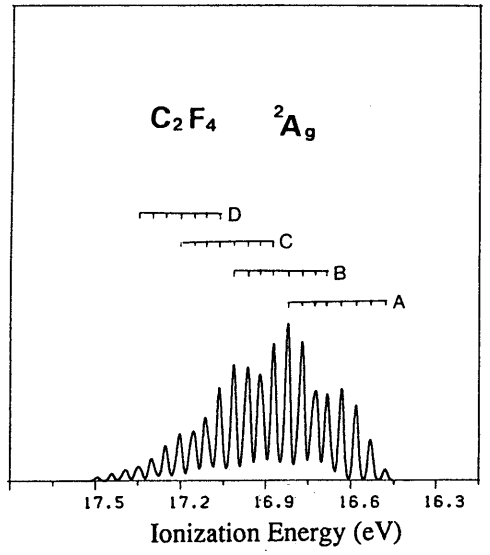

Fig. 7.3 Theoretical intensity curve of the ^2A_g state of Tetrafluoroethylene.
Band-width : 0.02 eV.

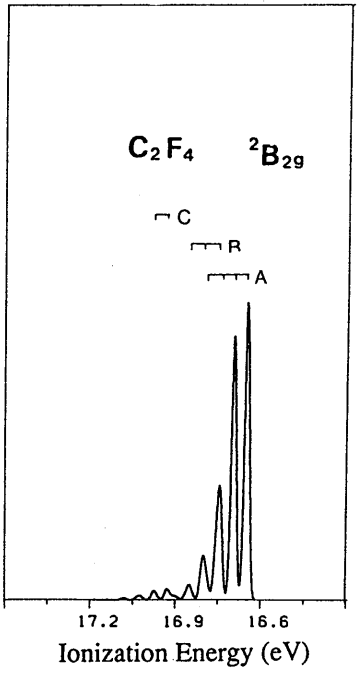

Fig. 7.4 Theoretical intensity curve of the $^2B_{2g}$ state of Tetrafluoroethylene.
Band-width : 0.02 eV.

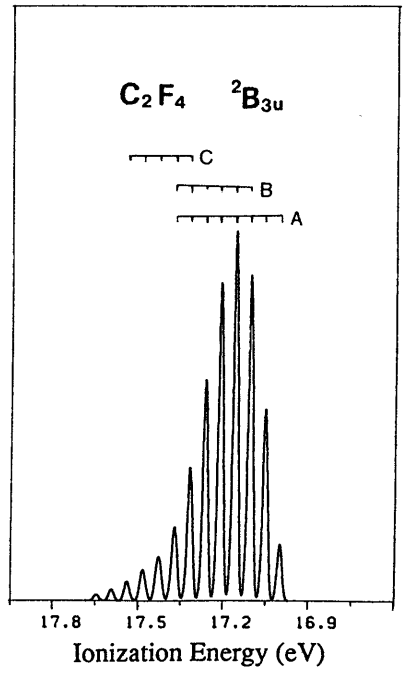

Fig. 7.5 Theoretical intensity curve of the $^2B_{3u}$ state of Tetrafluoroethylene.
Band-width : 0.02 eV.

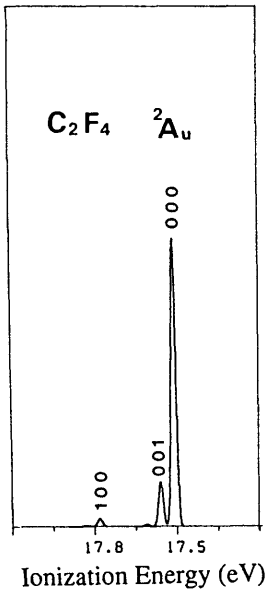

Fig. 7.6 Theoretical intensity curve of the ^2A_u state of .Tetrafluoroethylene.
Band-width : 0.02 eV.

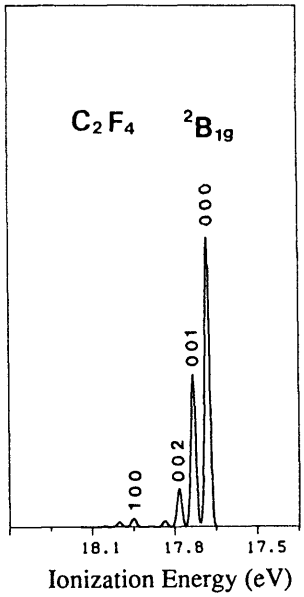

Fig. 7.7 Theoretical intensity curve of the $^2B_{1g}$ state of Tetrafluoroethylene.
Band-width : 0.02 eV.

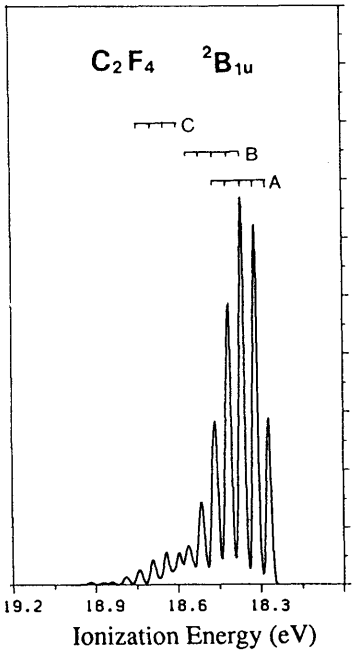

Fig. 7.8 Theoretical intensity curve of the $^2B_{1u}$ state of Tetrafluoroethylene.
Band-width : 0.02 eV.

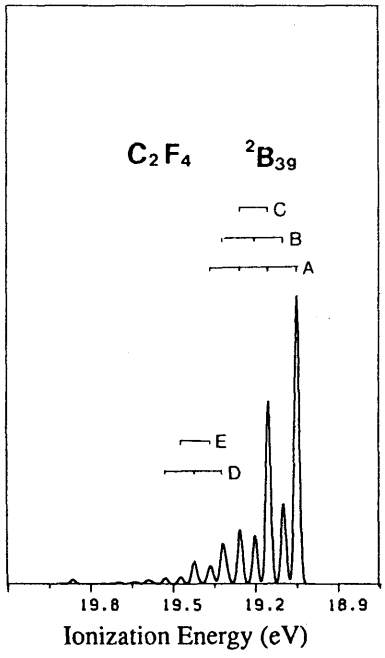

Fig. 7.9 Theoretical intensity curve of the $^2B_{3g}$ state of Tetrafluoroethylene.
Band-width : 0.02 eV.

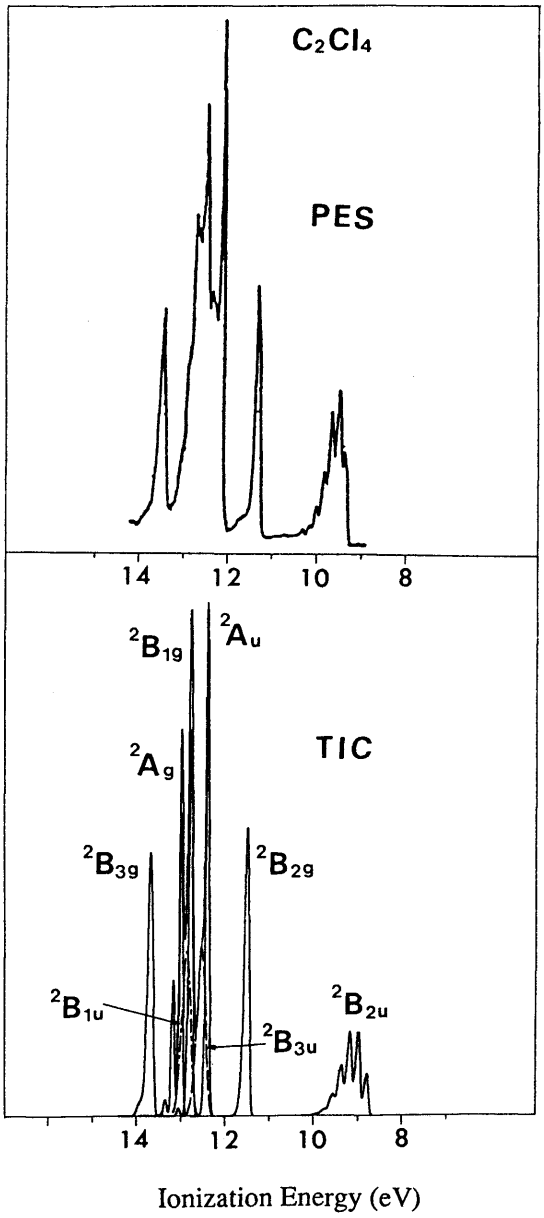

Fig. 8.1 Theoretical intensity curve and Photoelectron spectrum (From Niessen et al. 1982) of Tetrachloroethylene. Band-width : 0.08 eV.

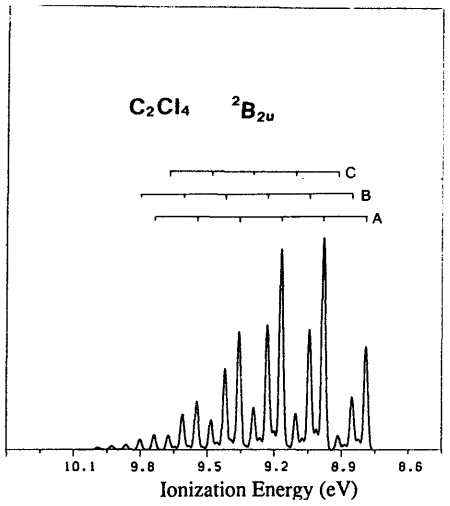

Fig. 8.2 Theoretical intensity curve of the $^2B_{2u}$ state of Tetrachloroethylene. Band-width : 0.02 eV.

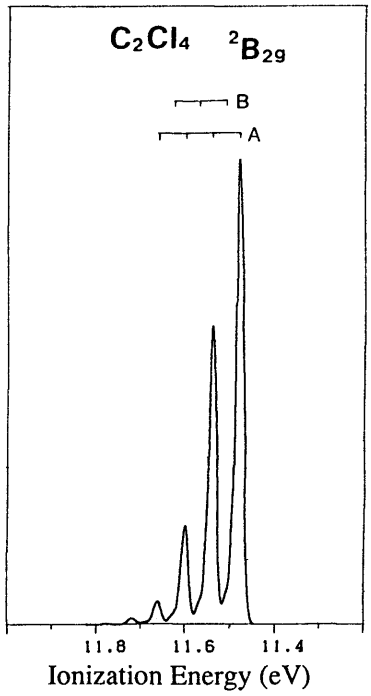

Fig. 8.3 Theoretical intensity curve of the $^2B_{2g}$ state of Tetrachloroethylene. Band-width : 0.02 eV.

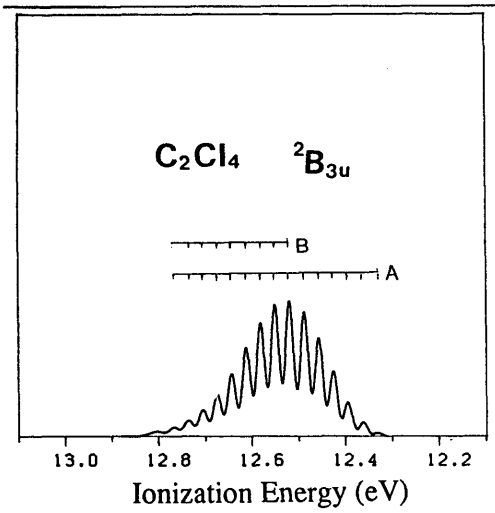

Fig. 8.4 Theoretical intensity curve of the $^2B_{3u}$ state of Tetrachloroethylene. Band-width : 0.02 eV.

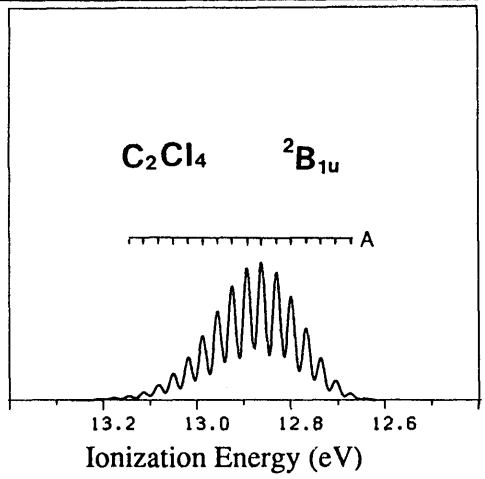

Fig. 8.6 Theoretical intensity curve of the $^2B_{1u}$ state of Tetrachloroethylene. Band-width : 0.02 eV.

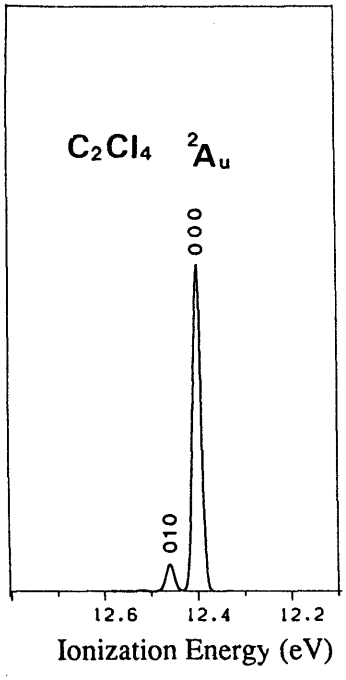

Fig. 8.5 Theoretical intensity curve of the ^2A_u state of Tetrachloroethylene. Band-width : 0.02 eV.

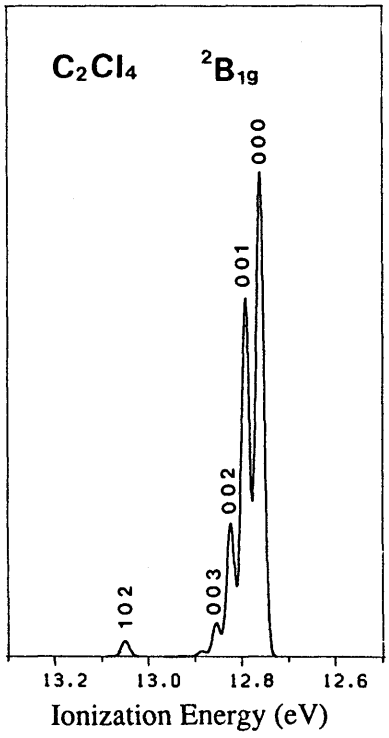

Fig. 8.7 Theoretical intensity curve of the $^2B_{1g}$ state of Tetrachloroethylene. Band-width : 0.02 eV.

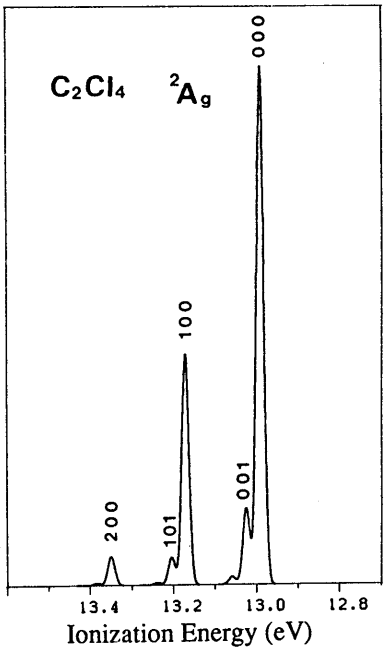

Fig. 8.8 Theoretical intensity curve of the ^2A_g state of Tetrachloroethylene. Band-width : 0.02 eV.

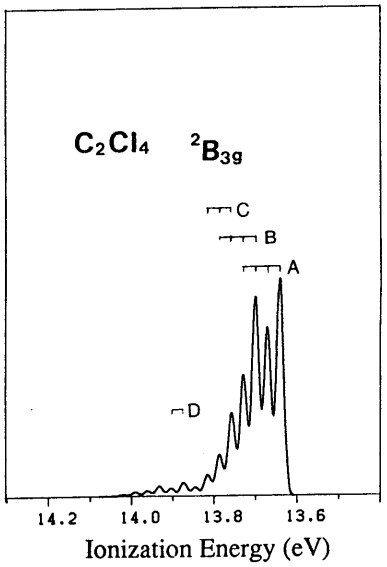

Fig. 8.9 Theoretical intensity curve of the $^2B_{3g}$ state of Tetrachloroethylene. Band-width : 0.02 eV.

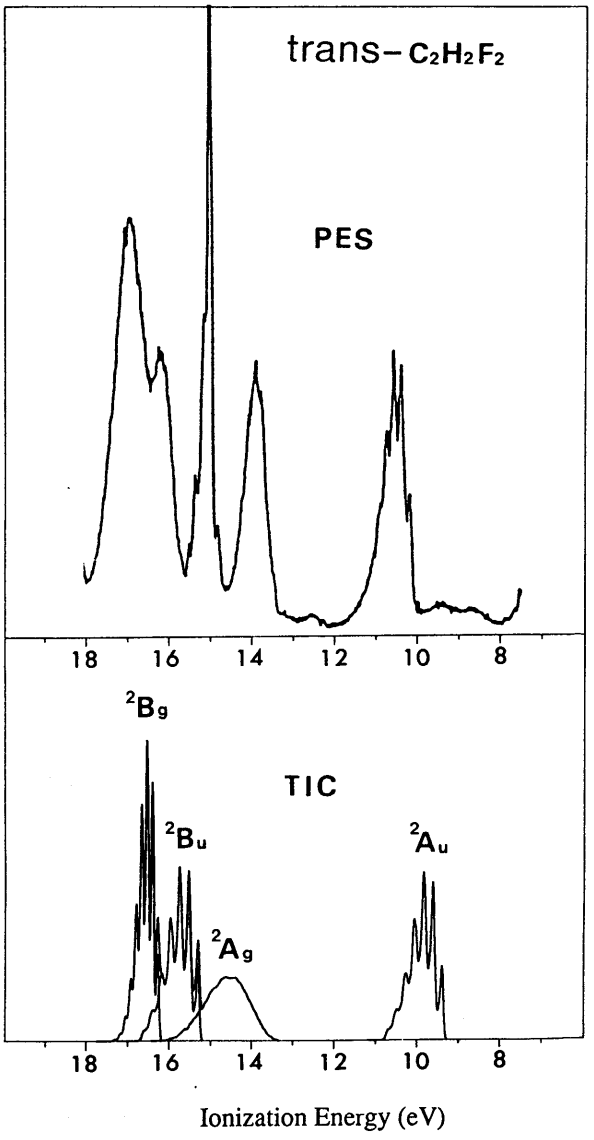

Fig. 9.1 Theoretical intensity curve and Photoelectron spectrum (From Bieri et al. 1981) of trans-1,2-Difluoroethylene. Band-width : 0.08 eV.

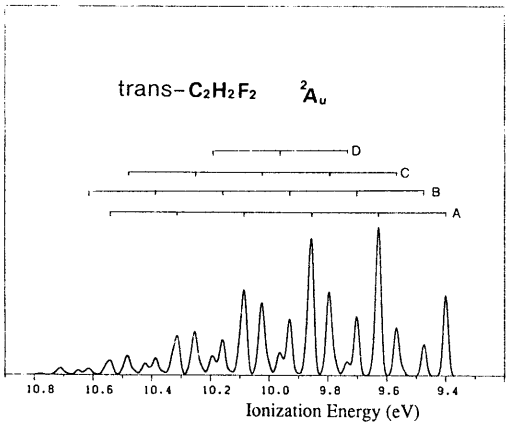

Fig. 9.2 Theoretical intensity curve of the ^2A_u state of trans-1,2-Difluoroethylene. Band-width : 0.02 eV.

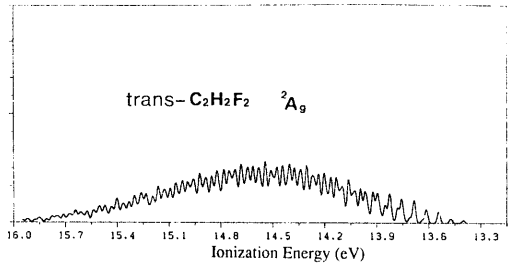

Fig. 9.3 Theoretical intensity curve of the ^2A_g state of trans-1,2-Difluoroethylene. Band-width : 0.02 eV.

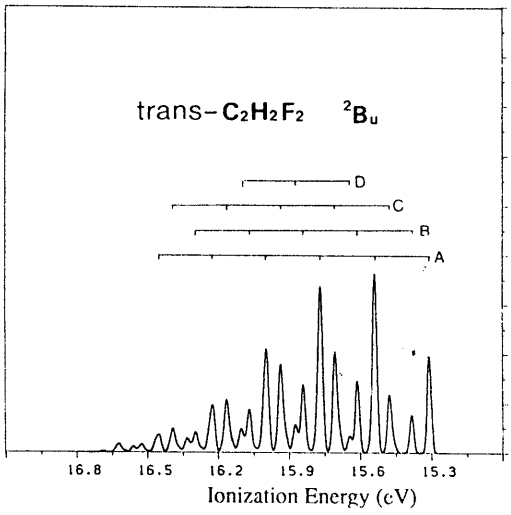

Fig. 9.4 Theoretical intensity curve of the ^2B_u state of trans-1,2-Difluoroethylene. Band-width : 0.02 eV.

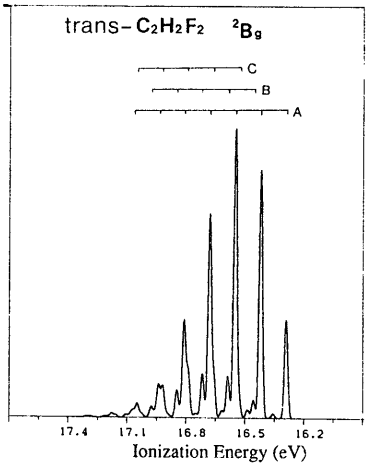

Fig. 9.5 Theoretical intensity curve of the ^2B_g state of trans-1,2-Difluoroethylene. Band-width : 0.02 eV.

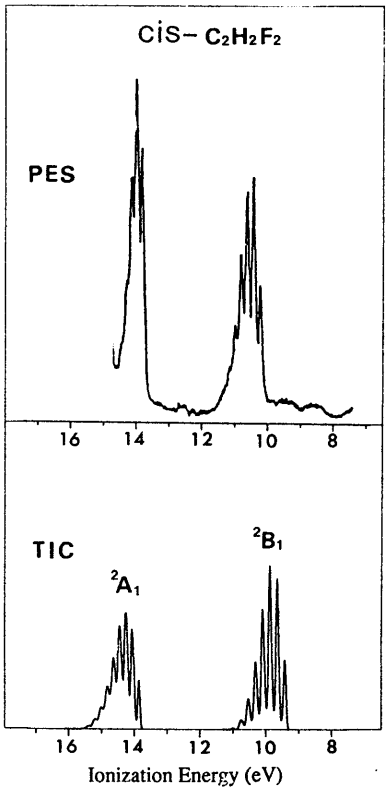

Fig. 10.1 Theoretical intensity curve and Photoelectron spectrum (From Bieri et al. 1981) of cis-1,2-Difluoroethylene. Band-width : 0.08 eV. Theoretical intensity curves of the ^2B_g (0-0 IE : 14.34 eV) and ^2A_g (0-0 IE : 15.91 eV) states are omitted.

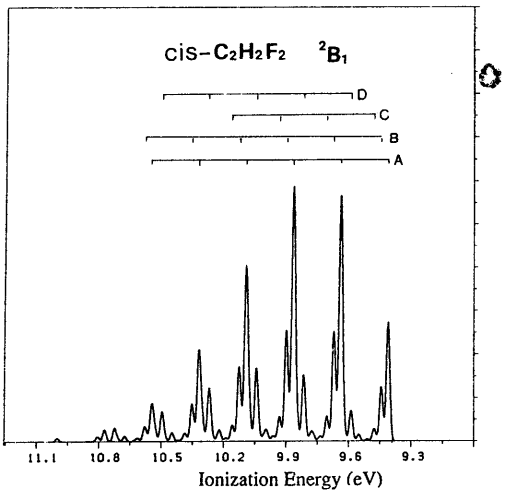

Fig. 10.2 Theoretical intensity curve of the $^2B_1$ state of cis-1,2-Difluoroethylene. Band-width : 0.02 eV.

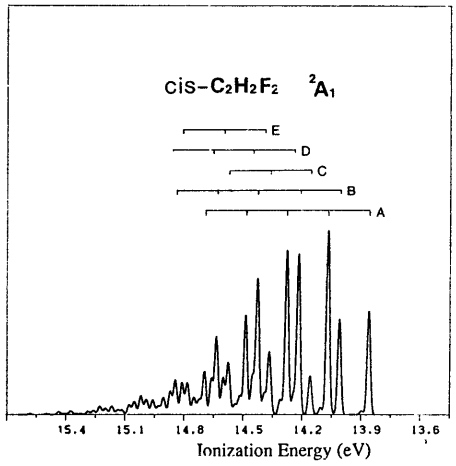

Fig. 10.3 Theoretical intensity curve of the $^2A_1$ state of cis-1,2-Difluoroethylene. Band-width : 0.02 eV.

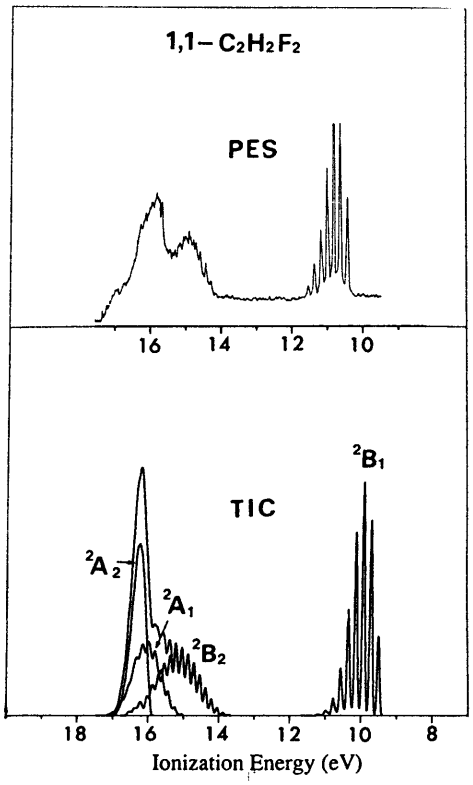

Fig. 11.1 Theoretical intensity curve and Photoelectron spectrum(From Turner et al. 1970) of 1,1-Difluoroethylene. Band-width : 0.08 eV.

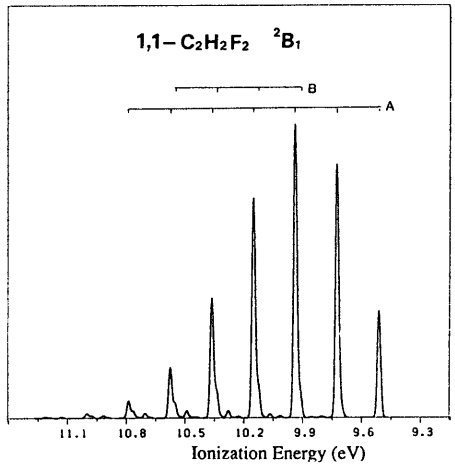

Fig. 11.2 Theoretical intensity curve of the $^2B_1$ state of 1,1-Difluoroethylene. Band-width : 0.02 eV.

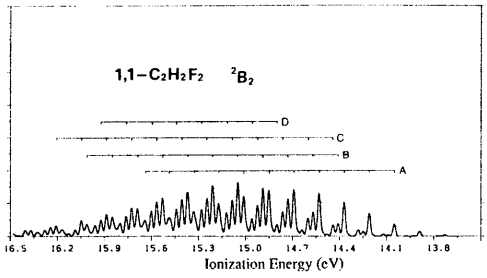

Fig. 11.3 Theoretical intensity curve of the $^2B_2$ state of 1,1-Difluoroethylene. Band-width : 0.02 eV.

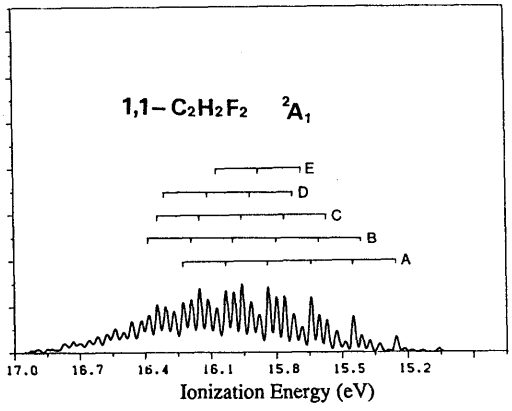

Fig. 11.4 Theoretical intensity curve of the $^2A_1$ state of 1,1- Difluoroethylene. Band-width : 0.02 eV.

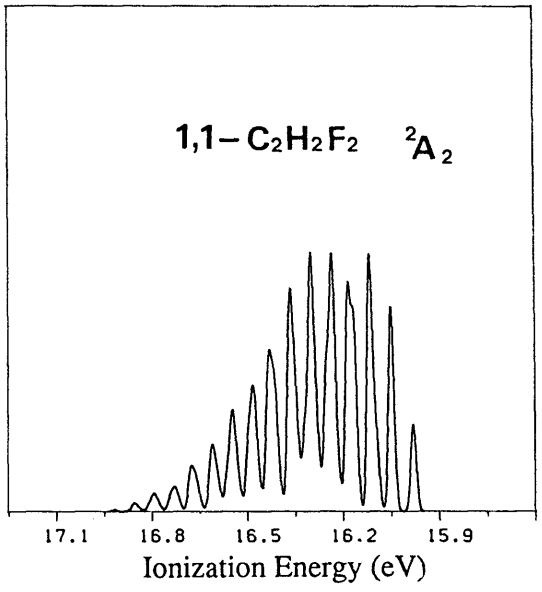

Fig. 11.5 Theoretical intensity curve of the $^2A_2$ state of 1,1- Difluoroethylene. Band-width : 0.02 eV.

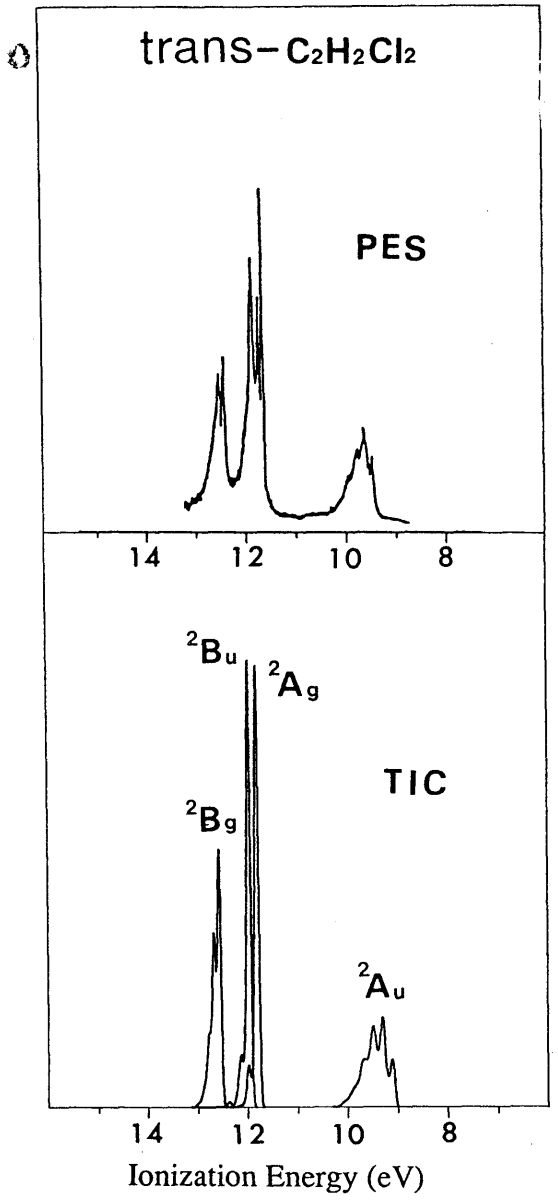

Fig. 12.1 Theoretical intensity curve and Photoelectron spectrum (From Niessen et al. 1982) of trans-1,2-Dichloroethylene. Band-width : 0.08 eV.

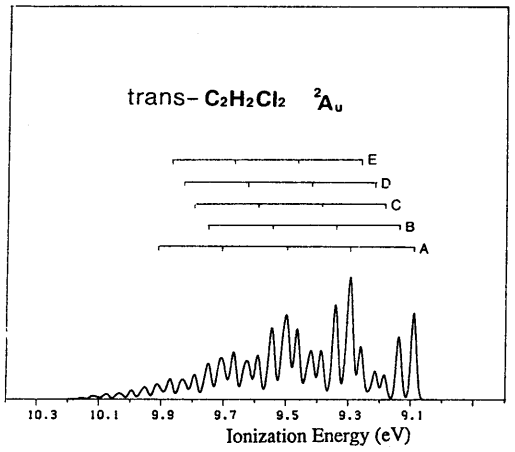

Fig. 12.2 Theoretical intensity curve of the ^2A_u state of trans-1,2- Dichloroethylene. Band-width : 0.02 eV.

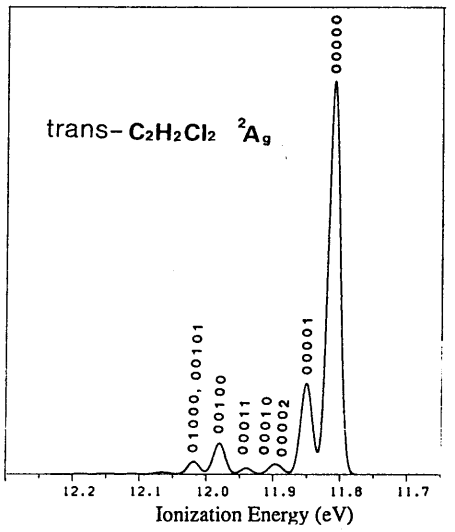

Fig. 12.3 Theoretical intensity curve of the ^2A_g state of trans-1,2- Dichloroethylene. Band-width : 0.02 eV.

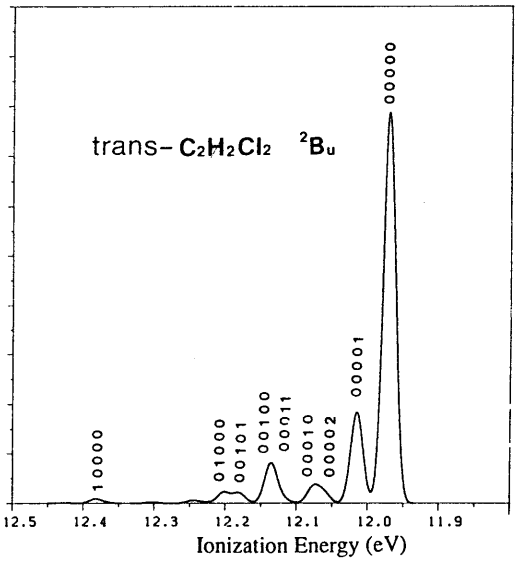

Fig. 12.4 Theoretical intensity curve of the ^2B_u state of trans-1,2- Dichloroethylene. Band-width : 0.02 eV.

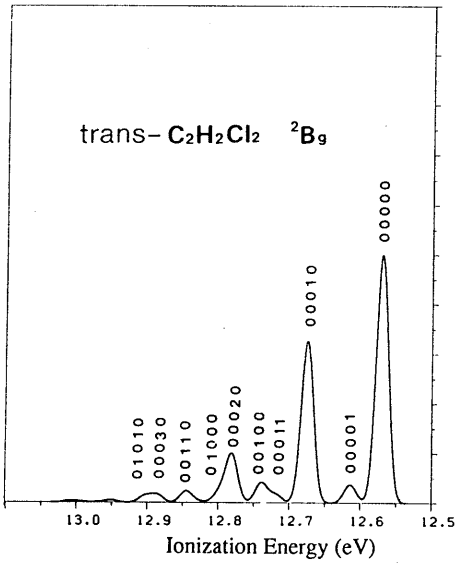

Fig. 12.5 Theoretical intensity curve of the ^2B_g state of trans-1,2- Dichloroethylene. Band-width : 0.02 eV.

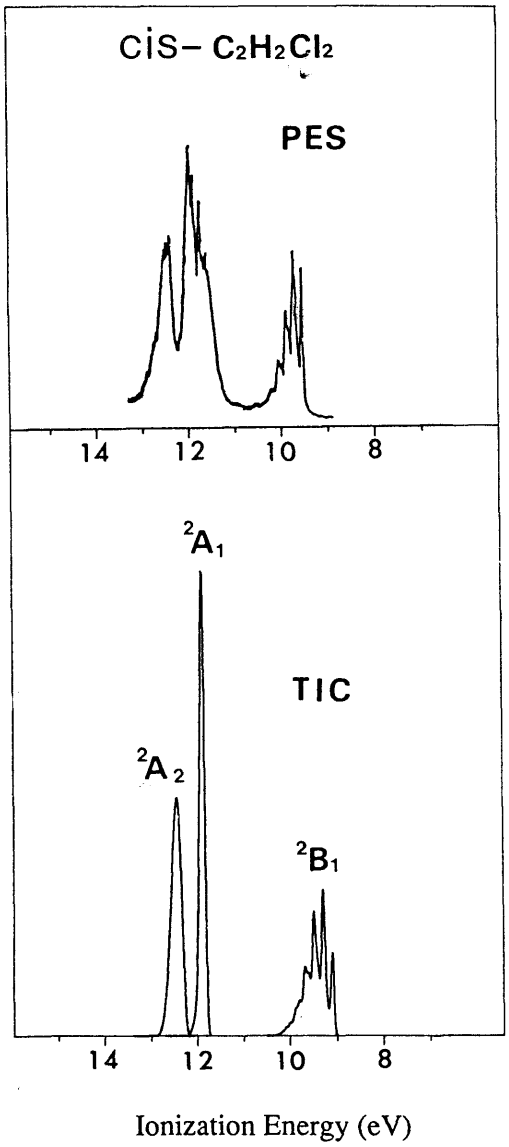

Fig. 13.1 Theoretical intensity curve and Photo-electron spectrum (From Niessen et al. 1982) of cis-1,2-Dichloroethylene. Band-width : 0.08 eV. Theoretical intensity curve of the $^2B_2$ (0-0 IE : 10.86 eV) is omitted.

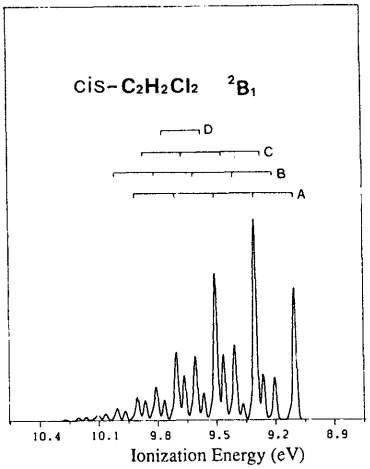

Fig. 13.2 Theoretical intensity curve of the $^2B_1$ state of cis-1,2-Dichloroethylene. Band-width : 0.02 eV.

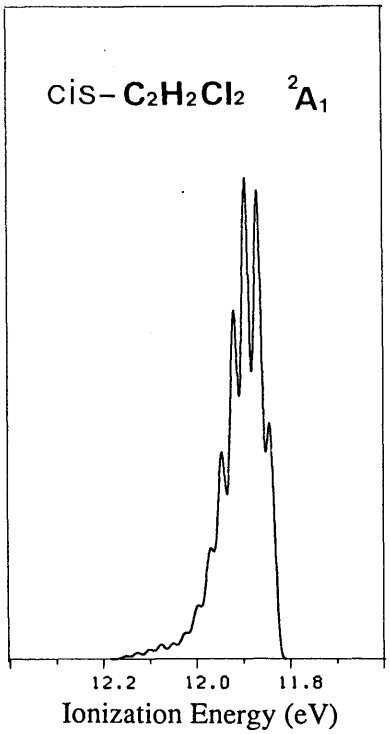

Fig. 13.3 Theoretical intensity curve of the $^2A_1$ state of cis-1,2-Dichloroethylene. Band-width : 0.02 eV.

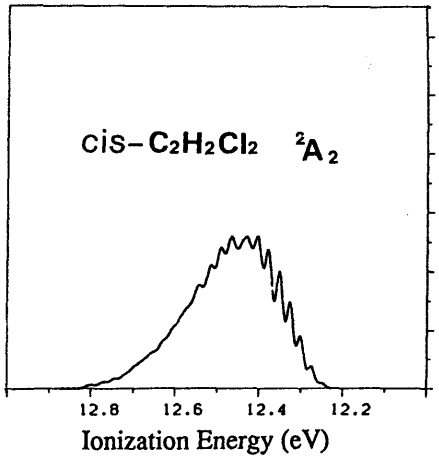

Fig. 13.4 Theoretical intensity curve of the $^2A_2$ state of cis-1,2-Dichloroethylene.

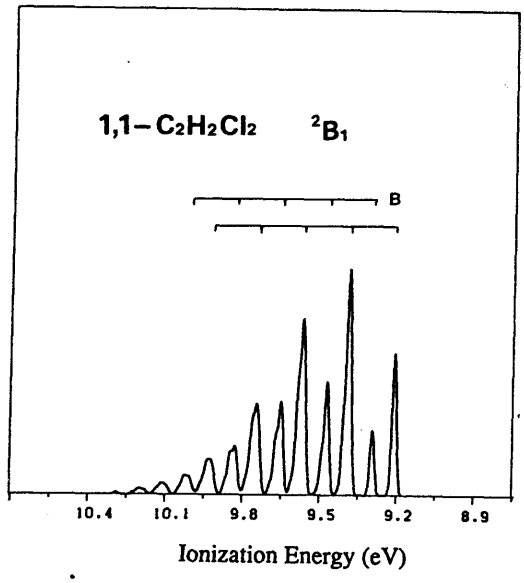

Fig. 14.2 Theoretical intensity curve of the $^2B_1$ state of 1,1-Dichloroethylene. Band-width : 0.02 eV.

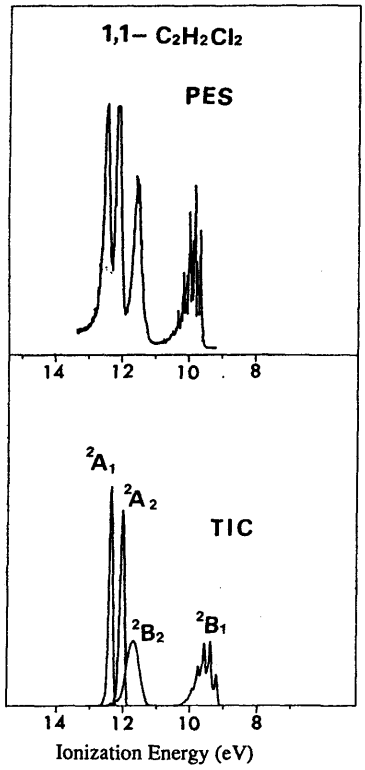

Fig. 14.1 Theoretical intensity curve Photoelectron spectrum (From Niessen et al. 1982) of 1,1-Dichloroethylene. Band-width : 0.08 eV.

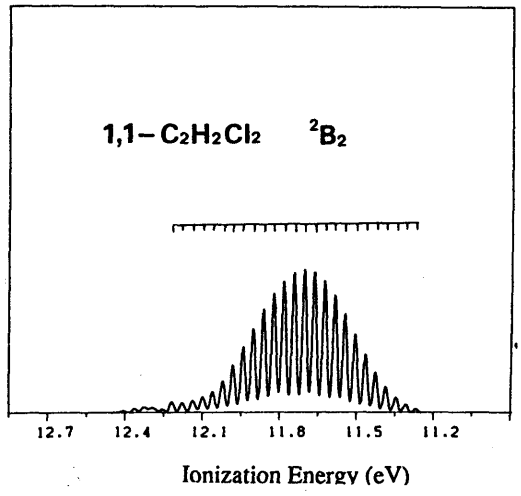

Fig. 14.3 Theoretical intensity curve of the $^2B_2$ state of 1,1-Dichloroethylene. Band-width : 0.02 eV.

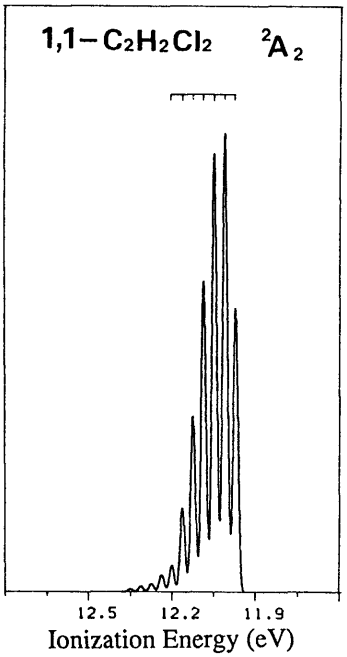

Fig. 14.4 Theoretical intensity curve of the $^2A_2$ state of 1,1- Dichloroethylene. Band-width : 0.02 eV.

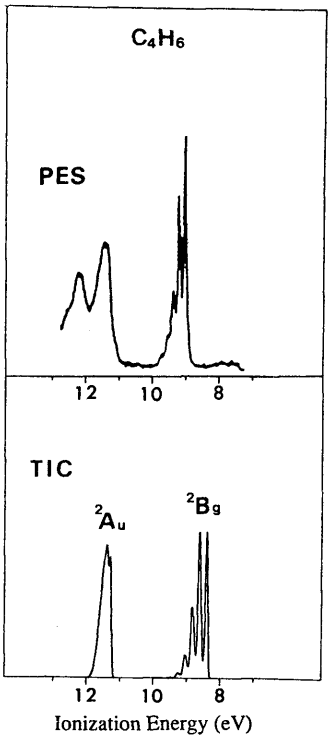

Fig. 15.1 Theoretical intensity curve and Photoelectron spectrum (From Bieri et al. 1980) of trans-Butadiene. Band-width : 0.08 eV. Theoretical intensity curves of the ^2A_u (0-0 IE : 11.46 eV) and ^2B_u (0-0 IE : 13.22 eV) states are omitted.

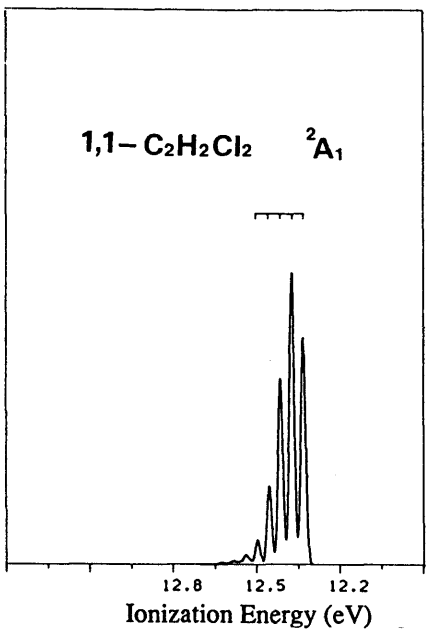

Fig. 14.5 Theoretical intensity curve of the $^2A_1$ state of 1,1- Dichloroethylene. Band-width : 0.02 eV.

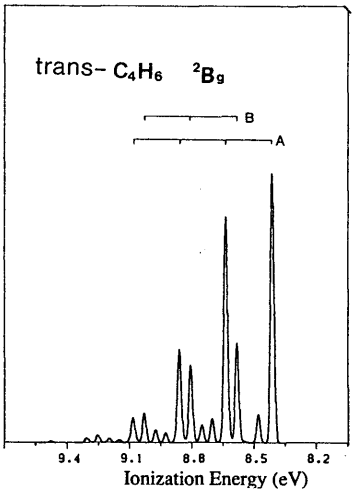

Fig. 15.2 Theoretical intensity curve of the ^2B_u state of trans-Butadiene. Band-width : 0.02 eV.

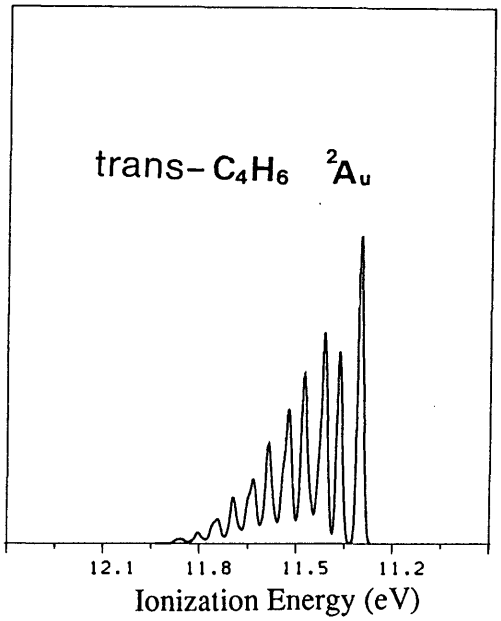

Fig. 15.3 Theoretical intensity curve of the ^2A_u state of trans- Butadiene. Band-width : 0.02 eV.

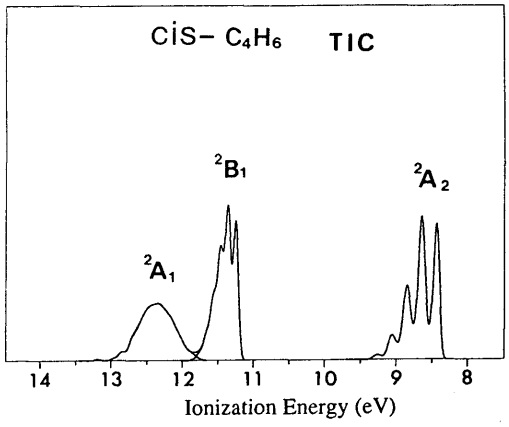

Fig. 16.1 Theoretical intensity curve of cis- Butadiene. Band-width : 0.08 eV. Theoretical intensity curve of the $^2B_2$ (0-0 IE : 12.34 eV) is omitted.

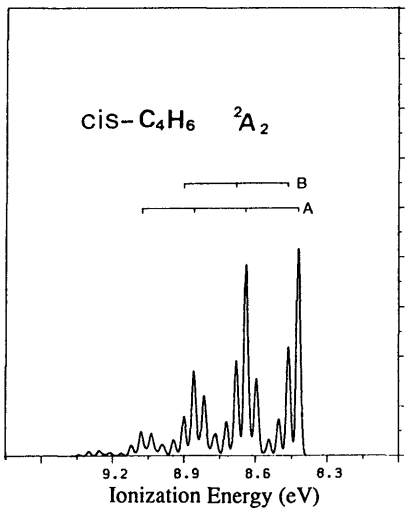

Fig. 16.2 Theoretical intensity curve of the $^2A_2$ state of cis- Butadiene. Band-width : 0.02 eV.

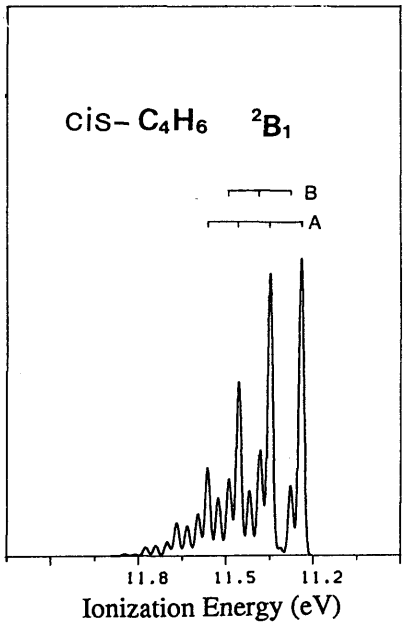

Fig. 16.3 Theoretical intensity curve of the $^2B_1$ state of cis Butadiene. Band-width : 0.02 eV.

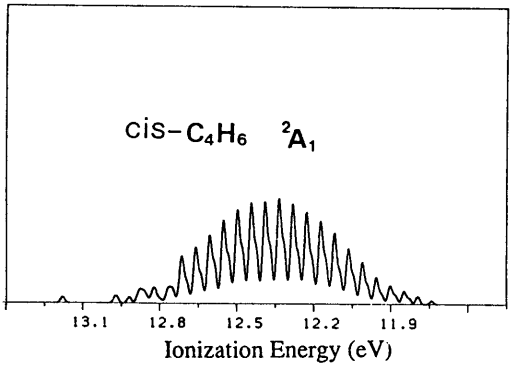

Fig. 16.4 Theoretical intensity curve of the $^2A_1$ state of cis-Butadiene. Band-width : 0.02 eV.

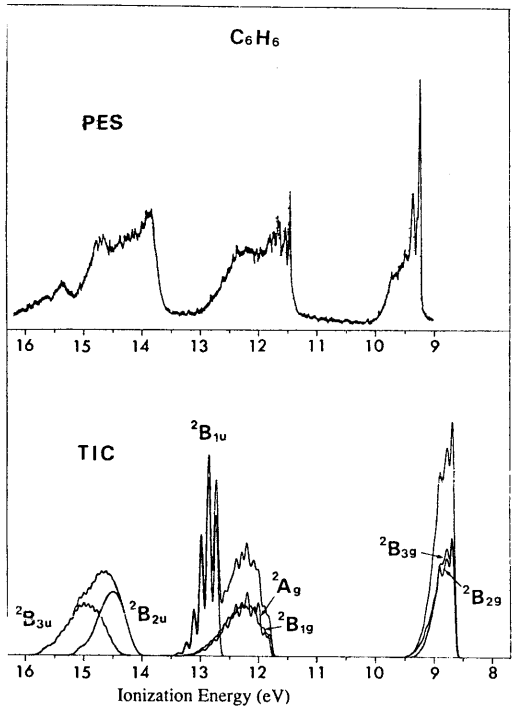

Fig. 17.1 Theoretical intensity curve and Photoelectron spectrum (From Turner et al. 1970) of Benzene. Band-width : 0.08 eV.

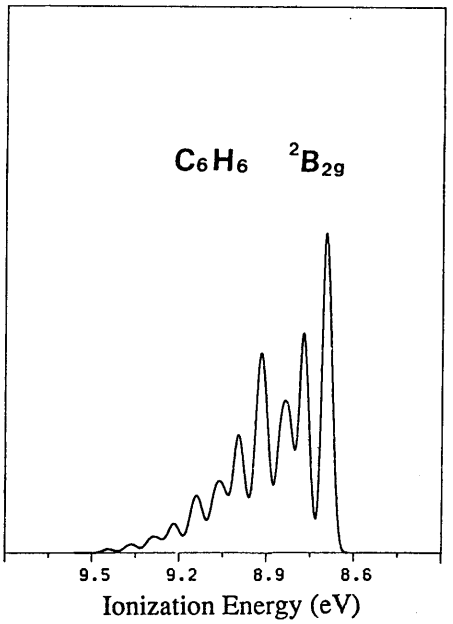

Fig. 17.2 Theoretical intensity curve of the $^2B_{2g}$ state of Benzene. Band-width : 0.04 eV.

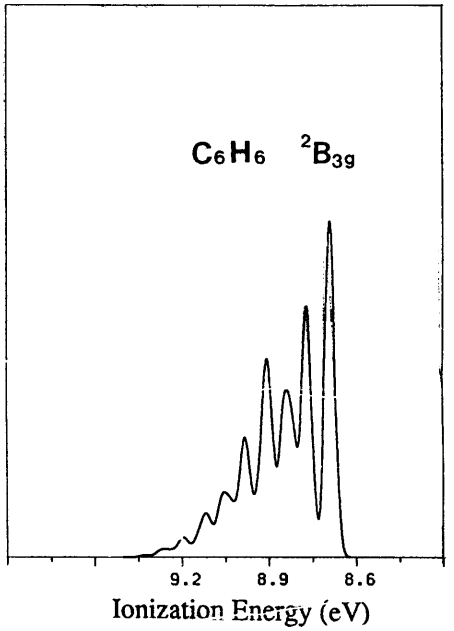

Fig. 17.3 Theoretical intensity curve of the $^2B_{3g}$ state of Benzene. Band-width : 0.04 eV.

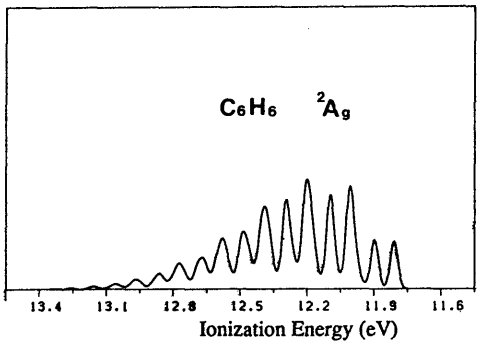

Fig. 17.4 Theoretical intensity curve of the ^2A_g state of Benzene. Band-width : 0.04 eV.

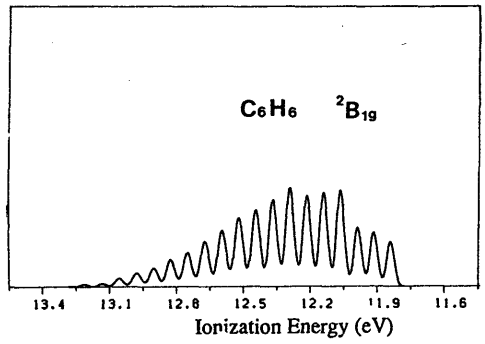

Fig. 17.5 Theoretical intensity curve of the $^2B_{1g}$ state of Benzene. Band-width : 0.04 eV.

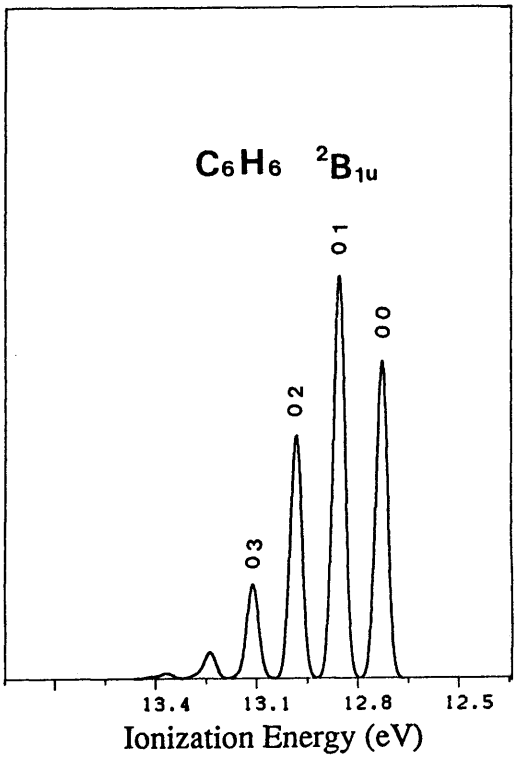

Fig. 17.6 Theoretical intensity curve of the $^2B_{1u}$ state of Benzene. Band-width : 0.04 eV.

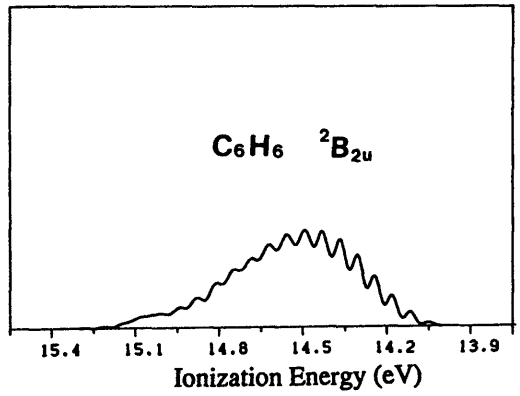

Fig. 17.7 Theoretical intensity curve of the $^2B_{2u}$ state of Benzene. Band-width : 0.04 eV.

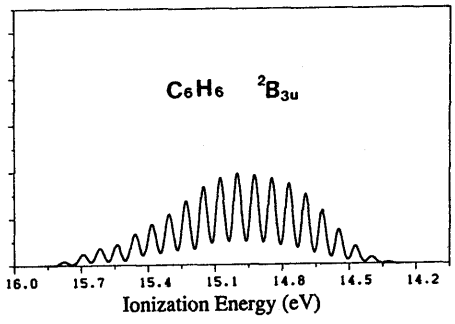

Fig. 17.8 Theoretical intensity curve of the $^2B_{3u}$ state of Benzene. Band-width : 0.04 eV.

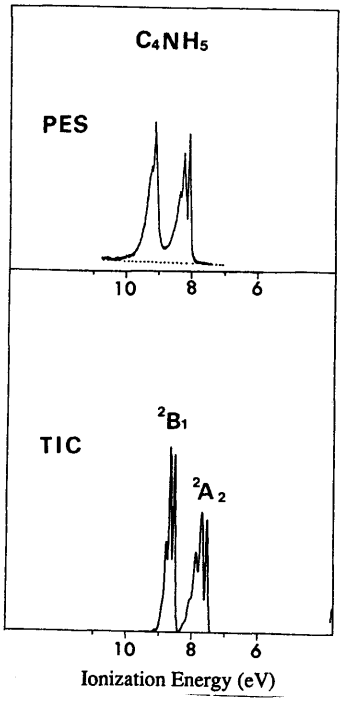

Fig. 18.1 Theoretical intensity curve and Photoelectron spectrum (From Klasinc et al.1982) of Pyrrole. Band-width : 0.08 eV. Theoretical intensity curves of the $^2A_1$ (0-0 IE : 11.59 eV) and $^2B_2$ (0-0 IE : 12.88 eV) states are omitted.

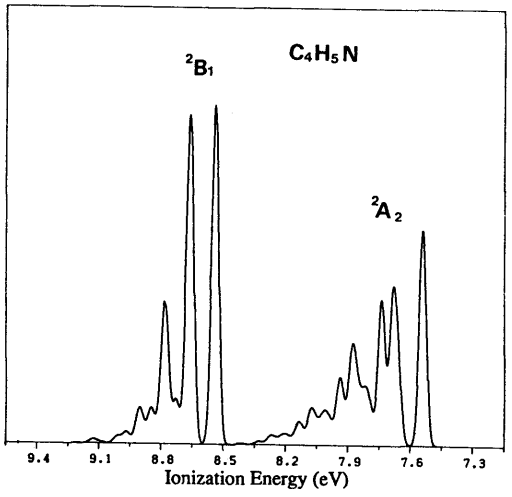

Fig. 18.2 Theoretical intensity curve of the $^2A_2$ and $^2B_1$ states of Pyrrole. Band-width : 0.04 eV.

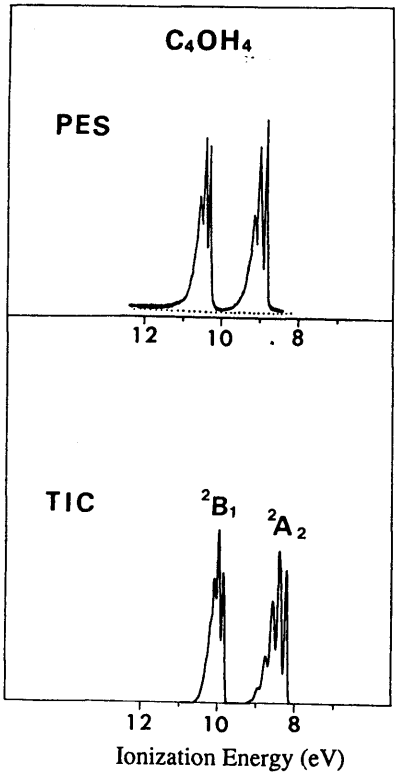

Fig. 19.1 Theoretical intensity curve and Photoelectron spectrum (From Klasinc et al.1982) of Furan. Band-width : 0.08 eV. Theoretical intensity curves of the $^2A_1$ (0-0 IE : 12.28 eV) and $^2B_2$ (0-0 IE 13.82 eV) states are omitted.

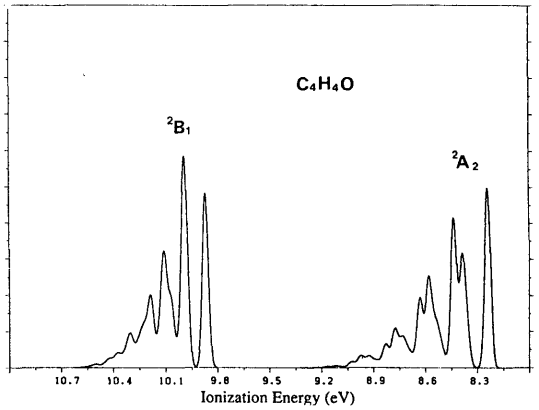

Fig. 19.2 Theoretical intensity curve of the $^2A_2$ and $^2B_1$ states of Furan. Band-width : 0.04 eV.

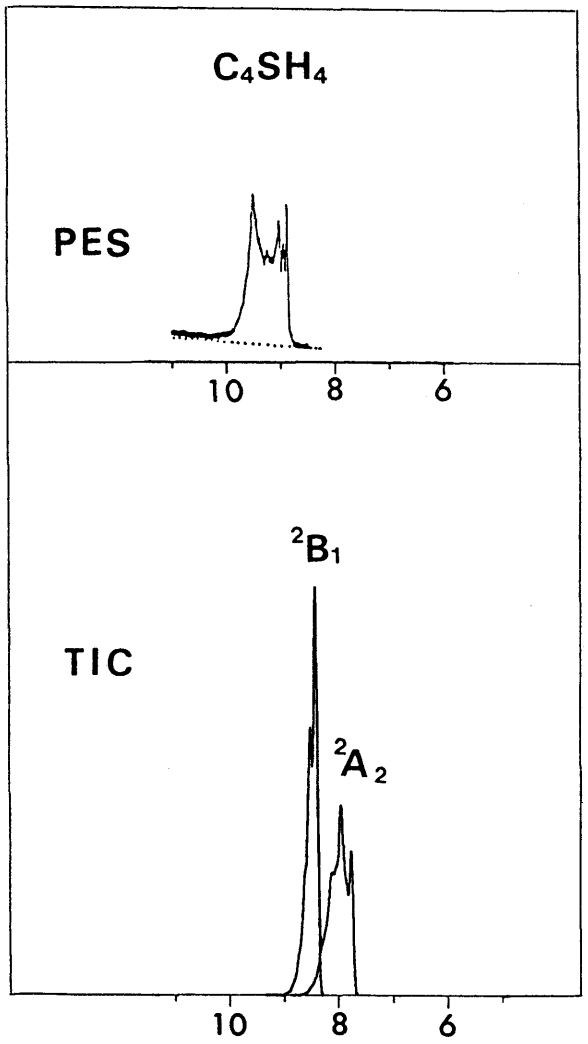

Fig. 20.1

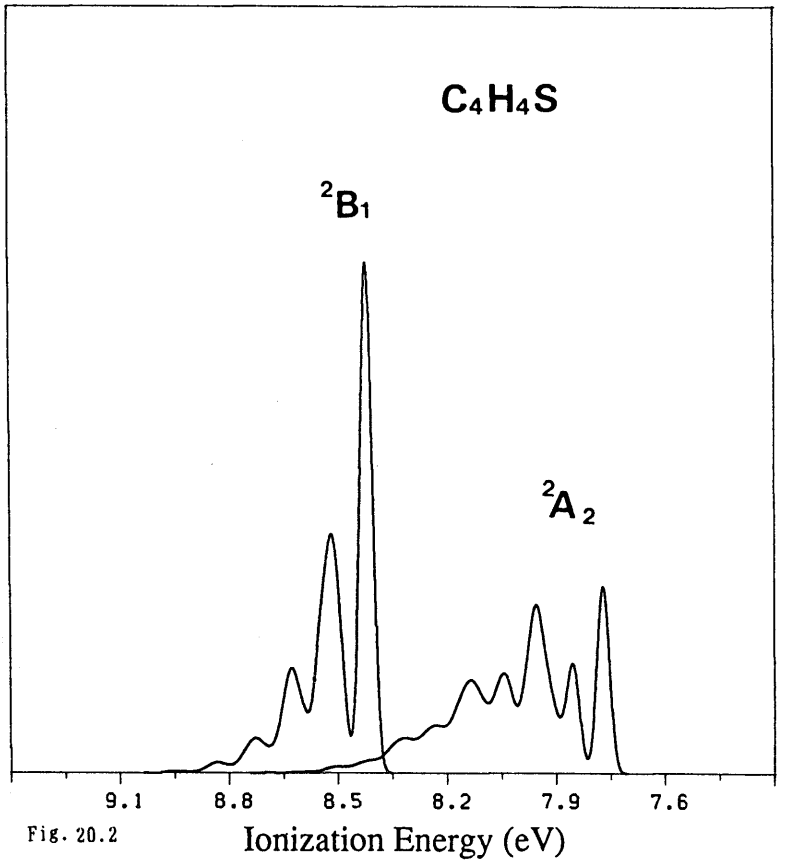

Fig. 20.2

Fig. 20.1 Theoretical intensity curve and Photoelectron spectrum (From Klasinc et al.[1882]) of Thiophen. Band-width : 0.08 eV. Theoretical intensity curves of the $^2A_1$ (0-0 IE : 11.32 eV) and $^2B_2$ (0-0 IE : 12.48 eV) states are omitted.

Fig. 20.2 Theoretical intensity curve of the $^2A_2$ and $^2B_1$ states of Thiophen. Band-width : 0.04 eV.

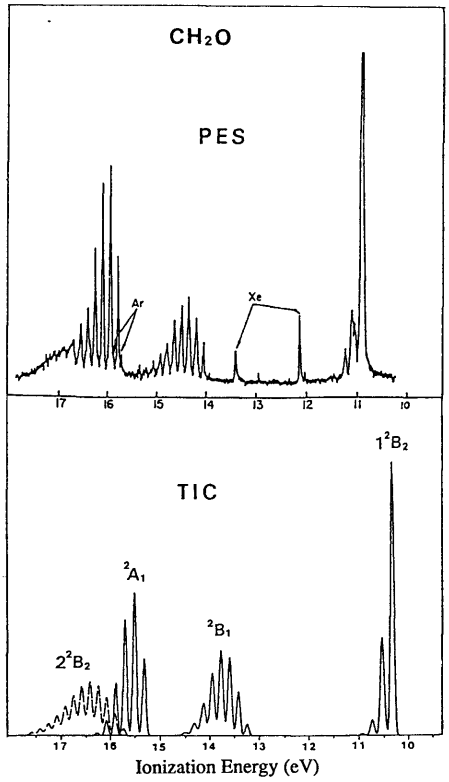

Fig. 21.1 Theoretical intensity curve and Photoelectron spectrum (From Turner et al. 1970) of Formaldehyde. Band-width : 0.08 eV.

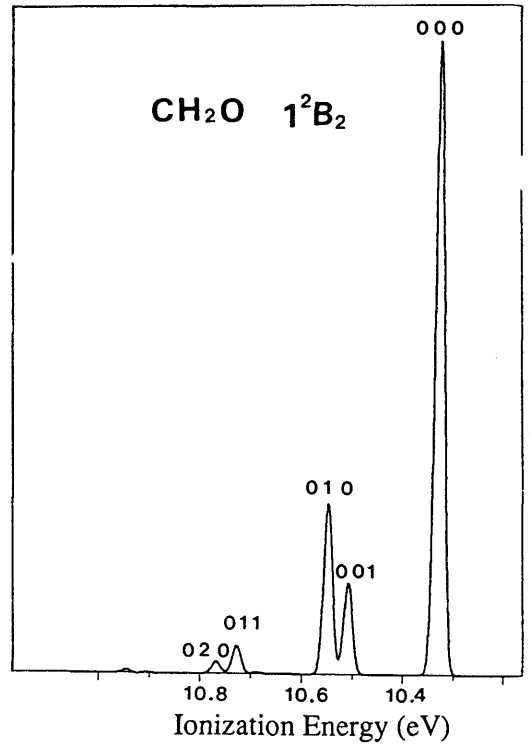

Fig. 21.2 Theoretical intensity curve of the 1^2B_2 state of Formaldehyde. Band-width: 0.04 eV.

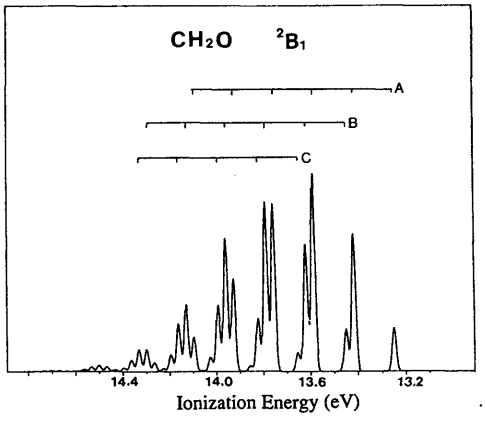

Fig. 21.3 Theoretical intensity curve of the $^2B_1$ state of Formaldehyde. Band-width : 0.04 eV.

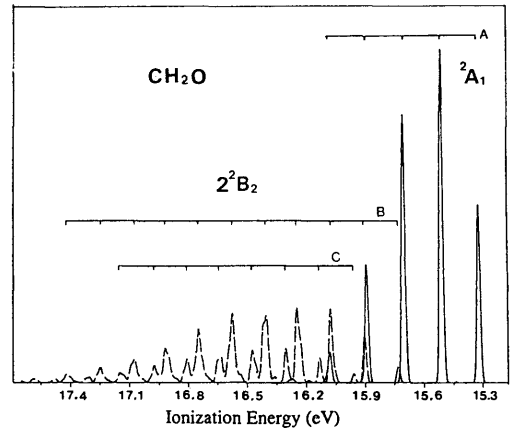

Fig. 21.4 Theoretical intensity curve of the $^2A_1$ and 2^2B_2 states of Formaldehyde. Band-width : 0.04 eV.

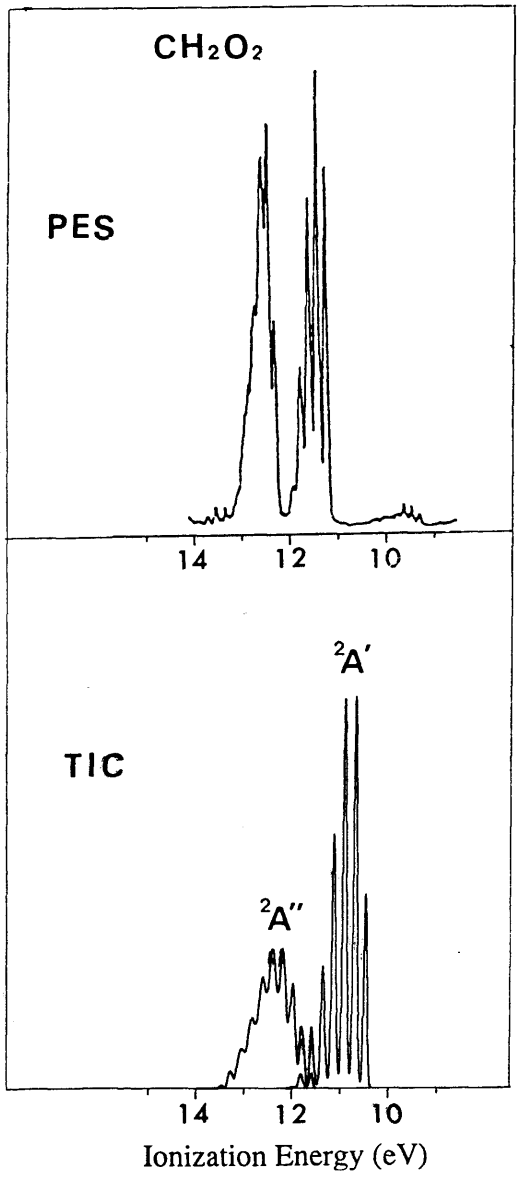

Fig. 22.1 Theoretical intensity curve and Photoelectron spectrum (From Niessen et al.1980) of Formic acid. Band-width: 0.08 eV.

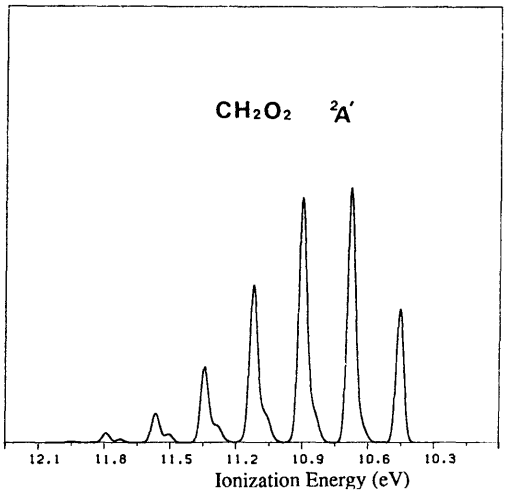

Fig. 22.2 Theoretical intensity curve of the $^2A'$ state of Formic acid. Band-width : 0.04 eV.

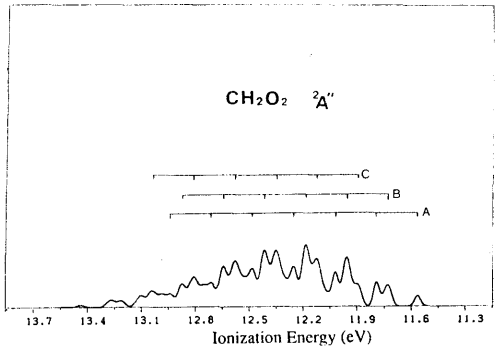

Fig. 22.3 Theoretical intensity curve of the $^2A''$ state of Formic acid. Band-width : 0.04 eV.

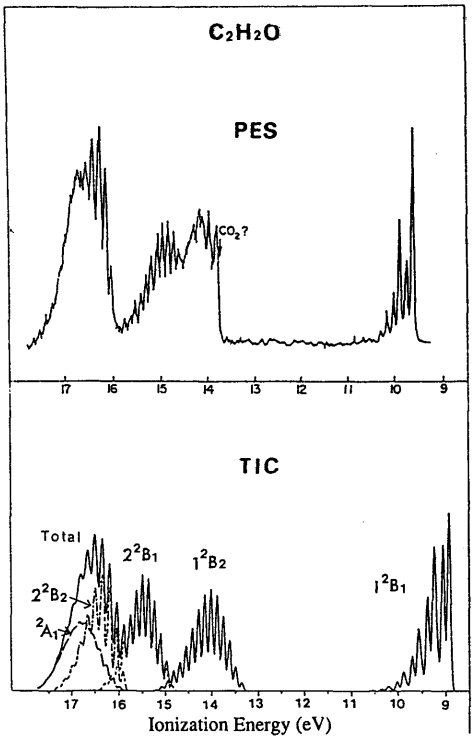

Fig. 23.1 Theoretical intensity curve and Photoelectron spectrum (From Turner et al.1970) of Ketene. Band-width : 0.08 eV.

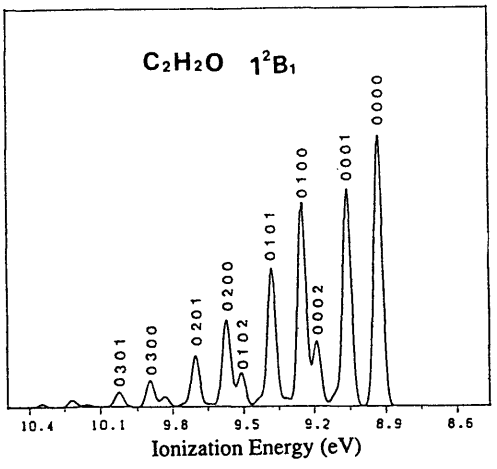

Fig. 23.2 Theoretical intensity curve of the 1^2B_1 state of Ketene. Band-width : 0.04 eV.

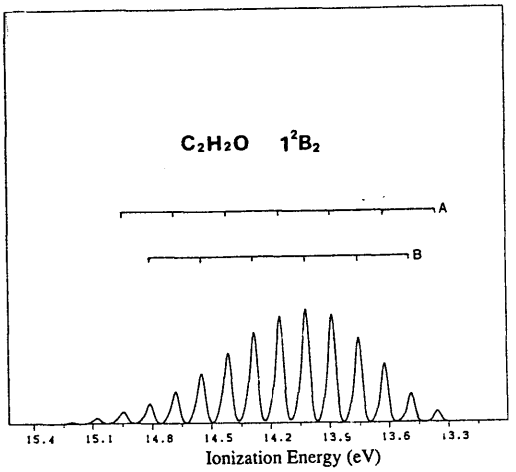

Fig. 23.3 Theoretical intensity curve of the 1^2B_2 state of Ketene. Band-width : 0.04 eV.

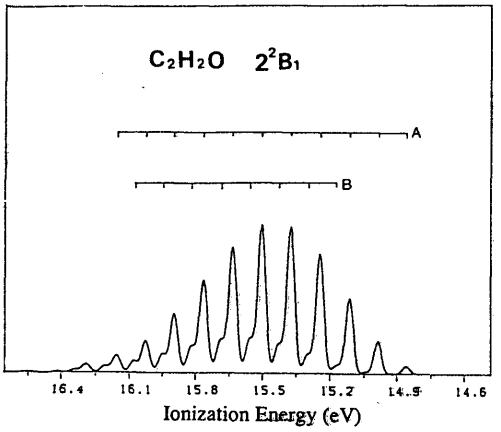

Fig. 23.4 Theoretical intensity curve of the 2^2B_1 state of Ketene. Band-width : 0.04 eV.

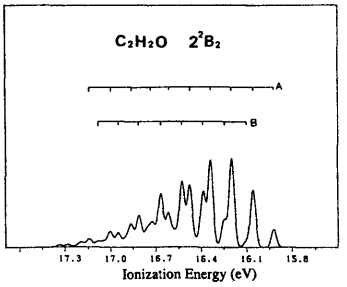

Fig. 23.5 Theoretical intensity curve of the 2^2B_2 state of Ketene. Band-width : 0.04 eV.

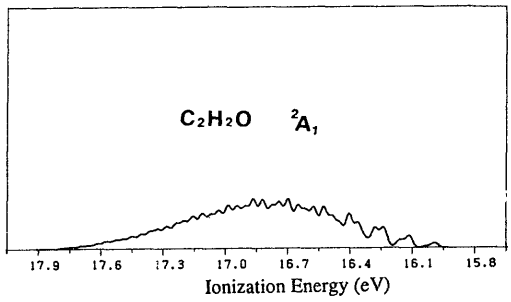

Fig. 23.6 Theoretical intensity curve of the $^2A_1$ state of Ketene. Band-width : 0.04 eV.

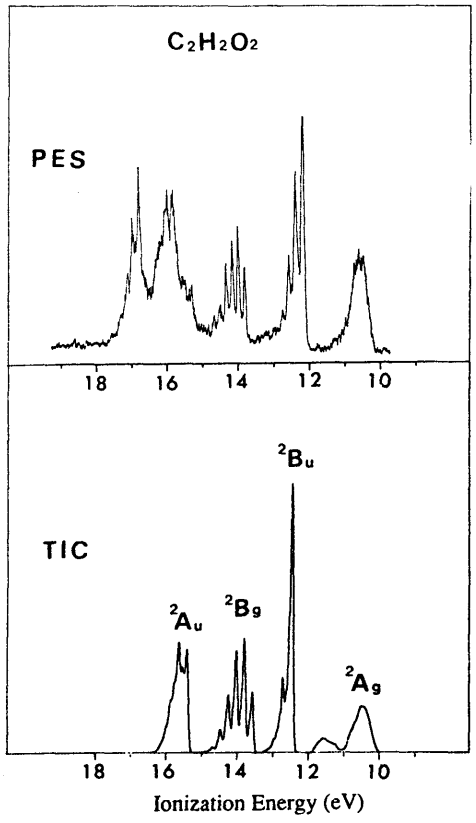

Fig. 24.1 Theoretical intensity curve and Photoelectron spectrum (From Turner et al. 1970)of Glyoxal. Band-width : 0.08 eV.

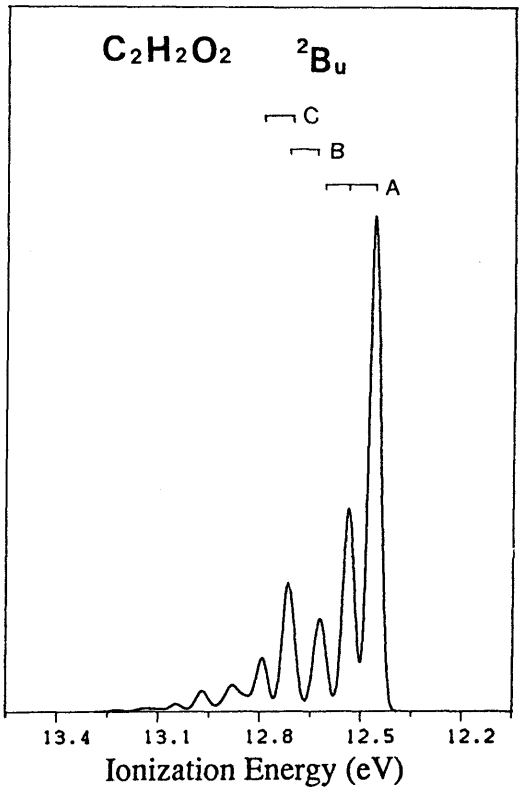

Fig. 24.2 Theoretical intensity curve of the ^2B_u state of Glyoxal. Band-width : 0.04 eV.

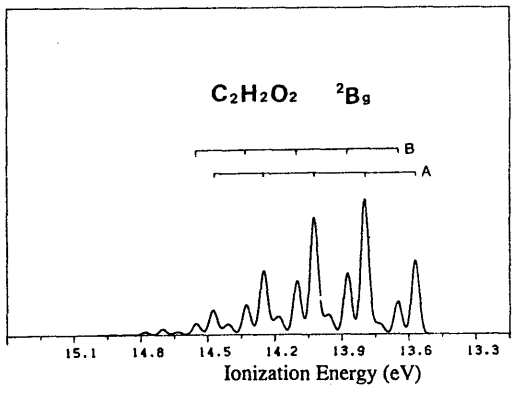

Fig. 24.3 Theoretical intensity curve of the ^2B_g state of Glyoxal. Band-width : 0.04 eV.

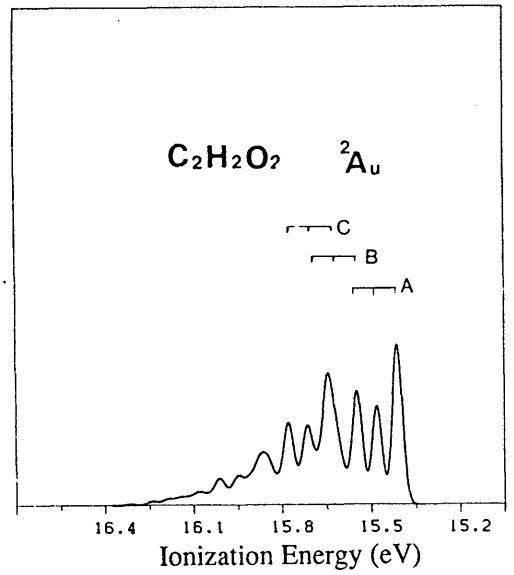

Fig. 24.4 Theoretical intensity curve of the ^2A_u state of Glyoxal. Band-width : 0.04 eV.

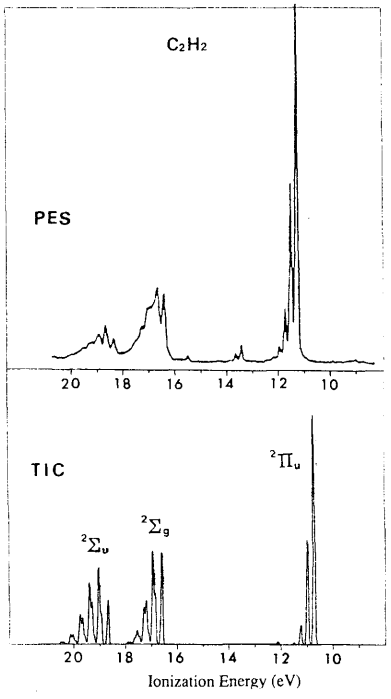

Fig. 25.1 Theoretical intensity curve and Photoelectron spectrum (From Bieri et al. 1980) of Acetylene. Band-width : 0.08 eV.

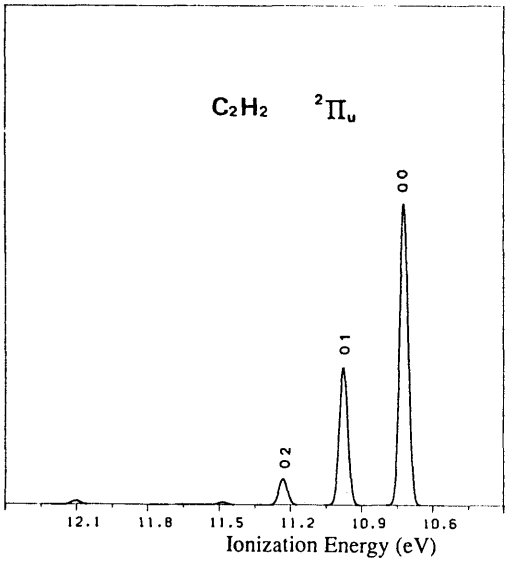

Fig. 25.2 Theoretical intensity curve of the $^2\Pi_u$ state of Acetylene. Band-width : 0.04 eV.

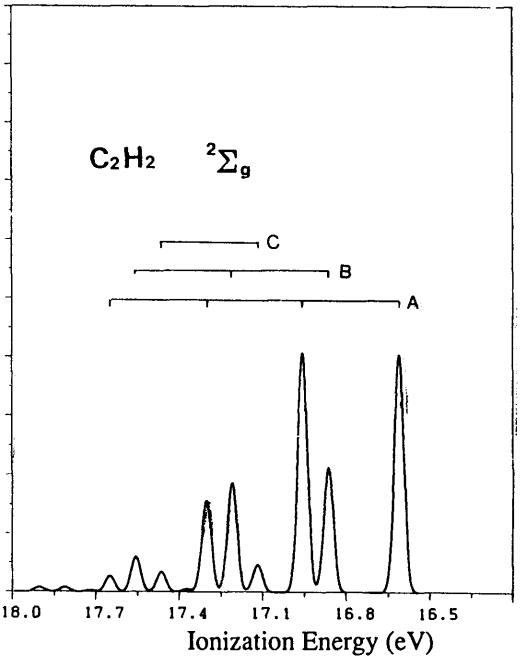

Fig. 25.3 Theoretical intensity curve of the $^2\Sigma_g$ state of Acetylene. Band-width : 0.04 eV.

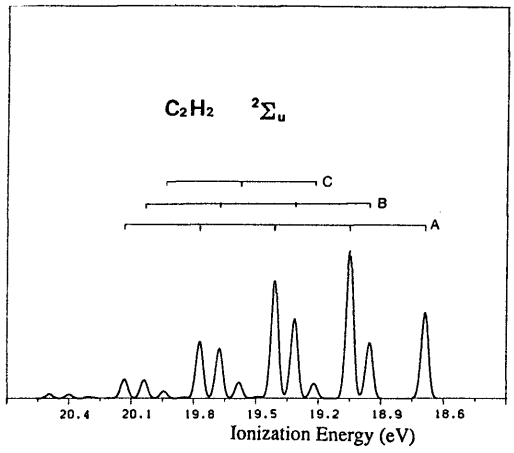

Fig. 25.4 Theoretical intensity curve of the $^2\Sigma_u$ state of Acetylene. Band-width : 0.04 eV.

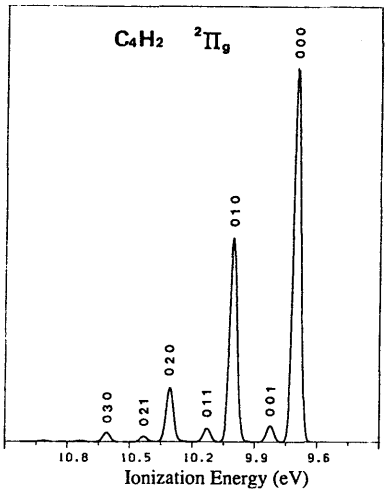

Fig. 26.2 Theoretical intensity curve of the $^2\Pi_g$ state of Diacetylene. Band-width : 0.04 eV.

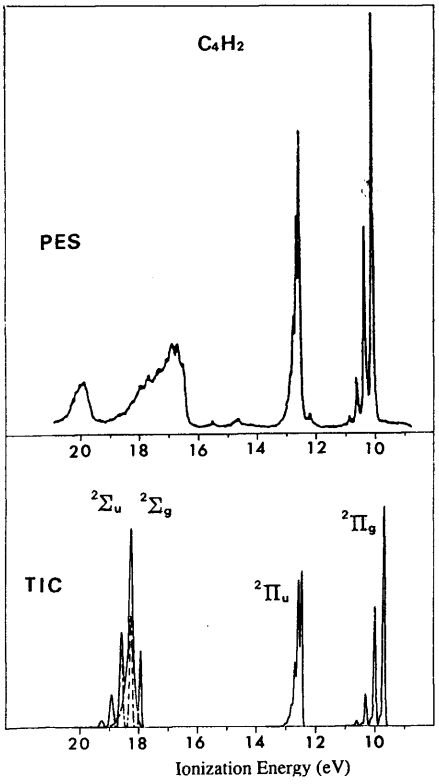

Fig. 26.1 Theoretical intensity curve and Photoelectron spectrum (From Bieriet al. 1980) of Diacetylene. Band-width : 0.08 eV.

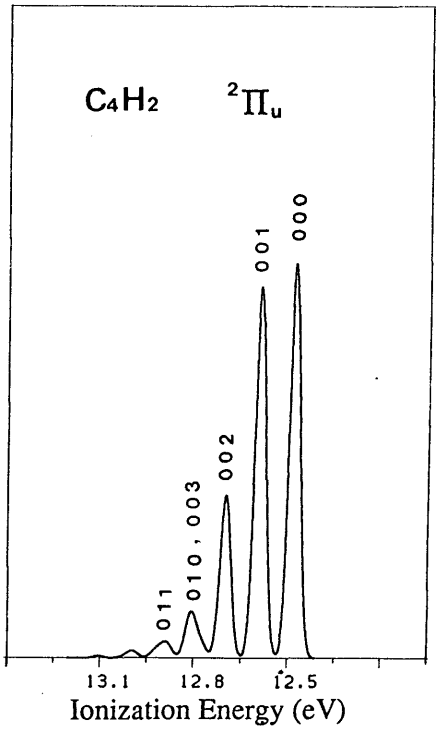

Fig. 26.3 Theoretical intensity curve of the $^2\Pi_u$ state of Diacetylene. Band-width : 0.04 eV.

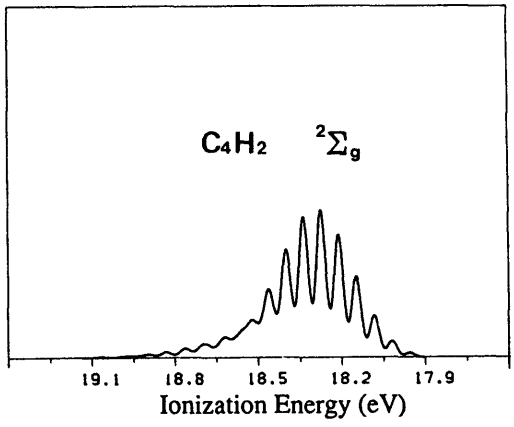

Fig. 26.4 Theoretical intensity curve of the $^2\Sigma_g$ state of Diacetylene. Band-width: 0.04eV.

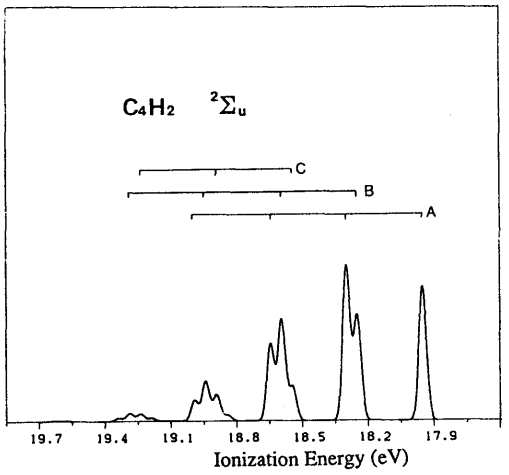

Fig. 26.5 Theoretical intensity curve of the $^2\Sigma_u$ state of Diacetylene. Band-width: 0.04eV.

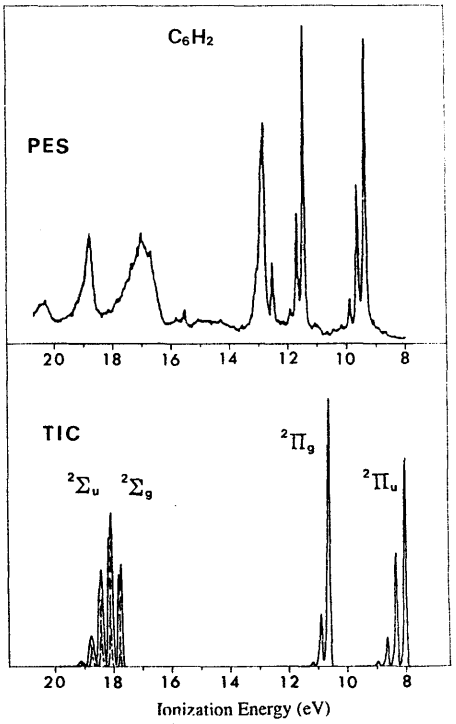

Fig. 27.1 Theoretical intensity curve and Photoelectron spectrum (From Bieriet al. 1980) of Triacetylene. Band-width: 0.08eV.

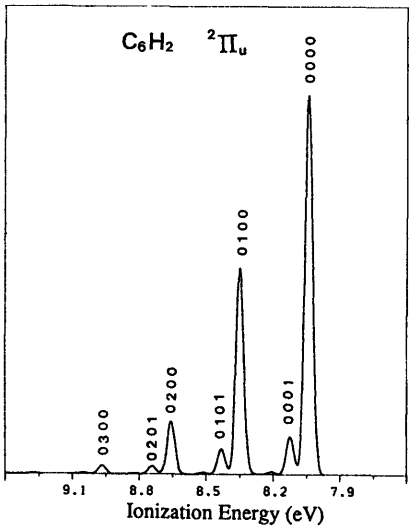

Fig. 27.2 Theoretical intensity curve of the $^2\Pi_u$ state of Triacetylene. Band-width : 0.04 eV.

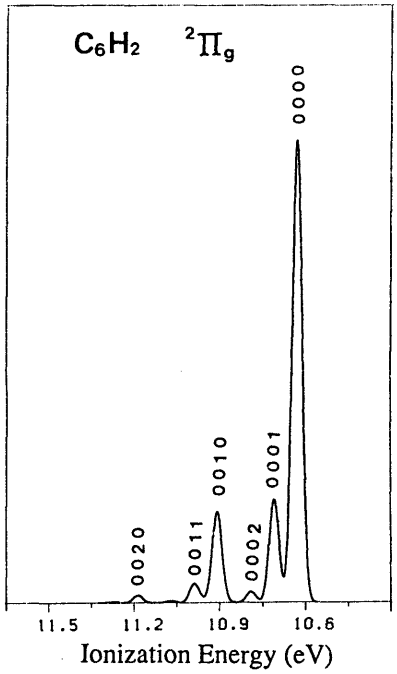

Fig. 27.3 Theoretical intensity curve of the $^2\Pi_u$ state of Triacetylene. Band-width : 0.04 eV.

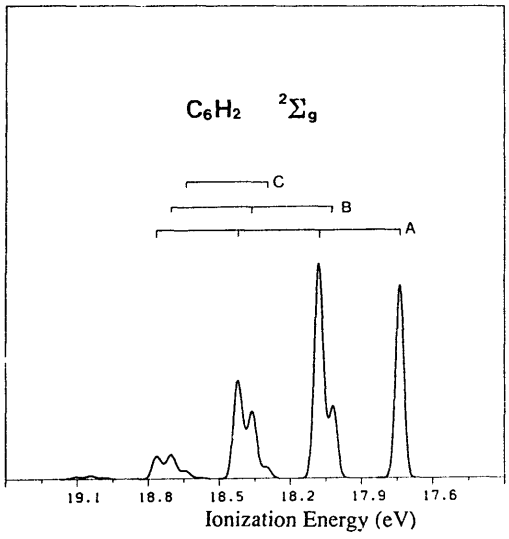

Fig. 27.4 Theoretical intensity curve of the $^2\Sigma_u$ state of Triacetylene. Band-width : 0.04 eV.

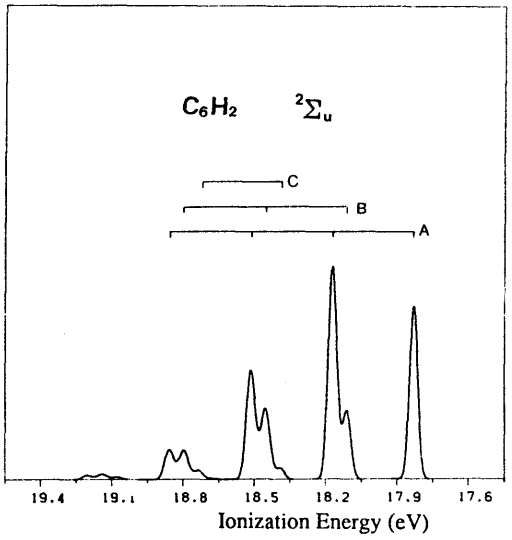

Fig. 27.5 Theoretical intensity curve of the $^2\Sigma_u$ state of Triacetylene. Band-width : 0.04 eV.

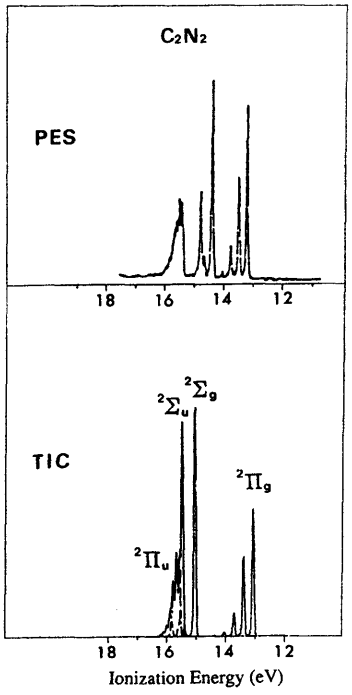

Fig. 28.1 Theoretical intensity curve and Photoelectron spectrum (From Åstrand et al.1980) of Cyanogen Band-width : 0.08 eV.

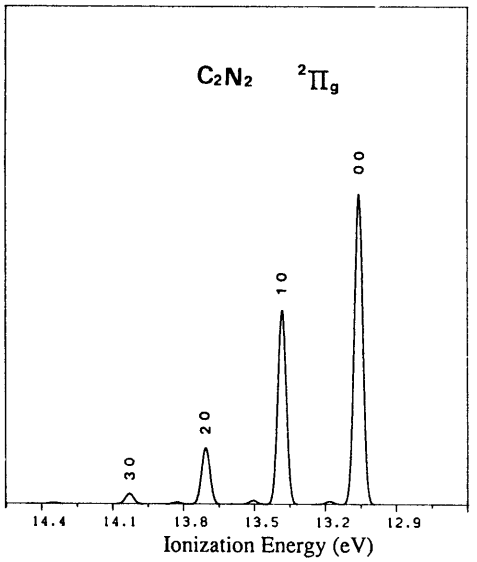

Fig. 28.2 Theoretical intensity curve of the $^2\Pi_g$ state of Cyanogen. Band-width : 0.04 eV.

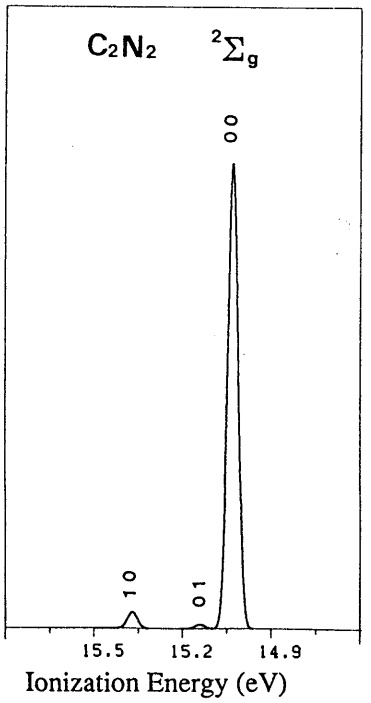

Fig. 28.3 Theoretical intensity curve of the $^2\Sigma_g$ state of Cyanogen. Band-width : 0.04 eV.

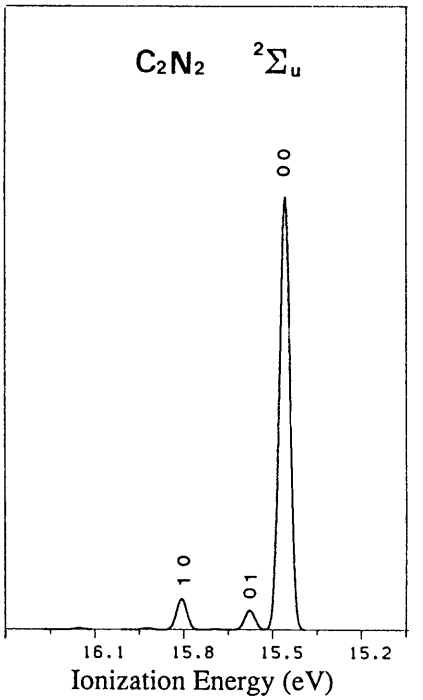

Fig. 28.4 Theoretical intensity curve of the $^2\Sigma_u$ state of Cyanogen. Band-width : 0.04 eV.

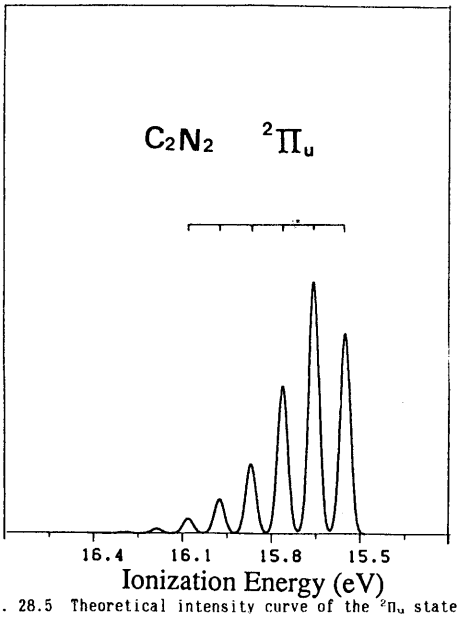

Fig. 28.5 Theoretical intensity curve of the $^2\Pi_u$ state of Cyanogen. Band-width : 0.04 eV.

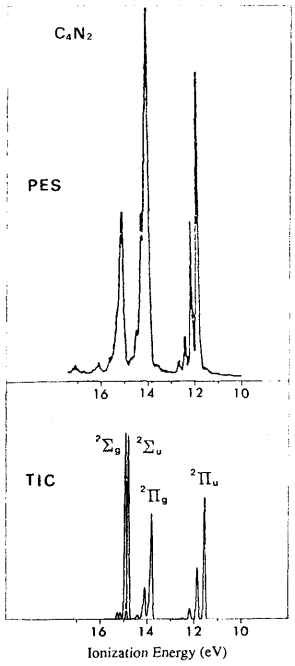

Fig. 29.1 Theoretical intensity curve and Photoelectron spectrum (From Åsbrink et al. 1980) of Dicyanoacetylene. Band-width : 0.08 eV.

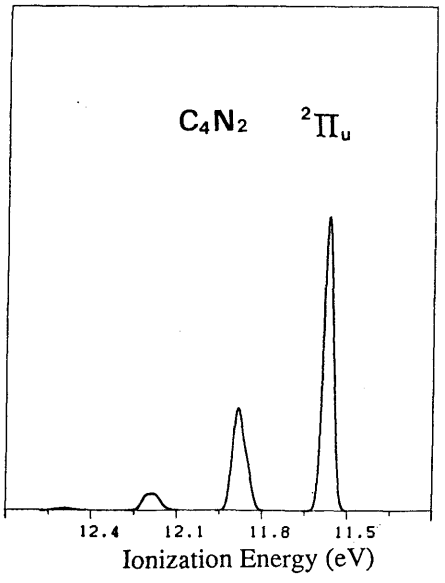

Fig. 29.2 Theoretical intensity curve of the $^2\Pi_u$ state of Dicyanoacetylene. Band-width : 0.04 eV.

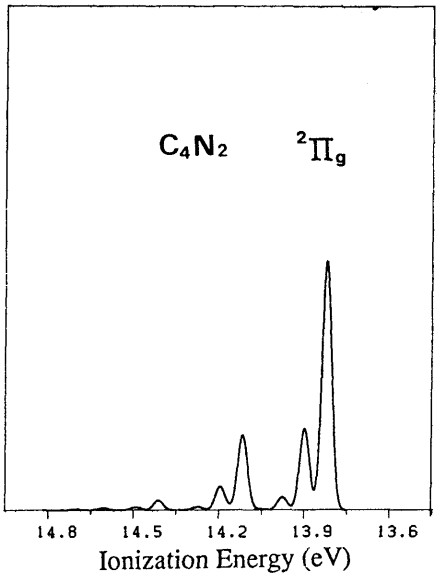

Fig. 29.3 Theoretical intensity curve of the $^2\Pi_g$ state of Dicyanoacetylene. Band-width : 0.04 eV.

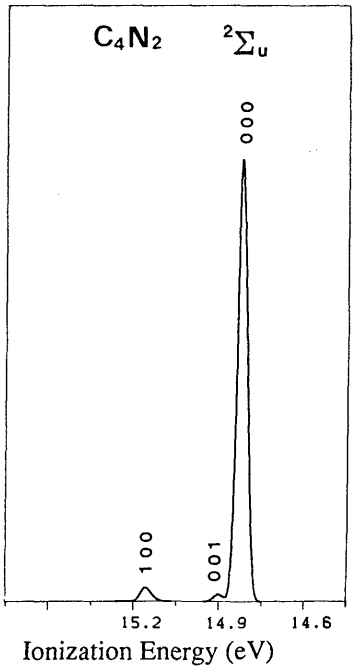

Fig. 29.4 Theoretical intensity curve of the $^2\Sigma_u$ state of Dicyanoacetylene. Band-width : 0.04 eV.

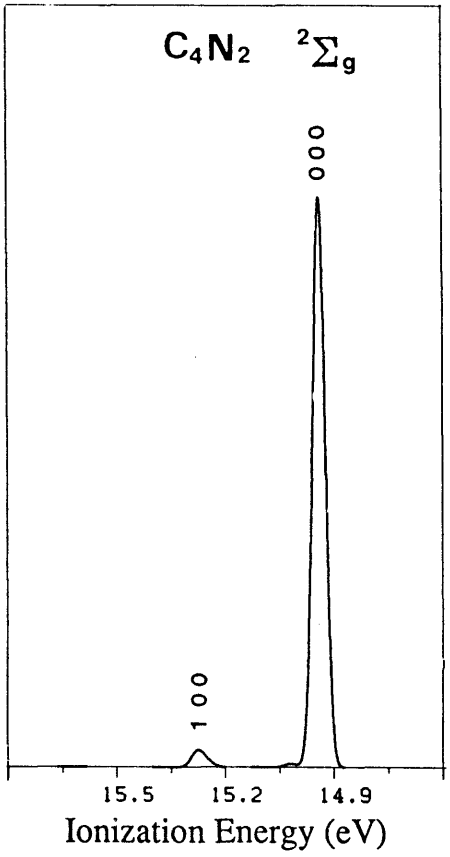

Fig. 29.5 Theoretical intensity curve of the $^2\Sigma_g$ state of Dicyanoacetylene. Band-width : 0.04 eV.

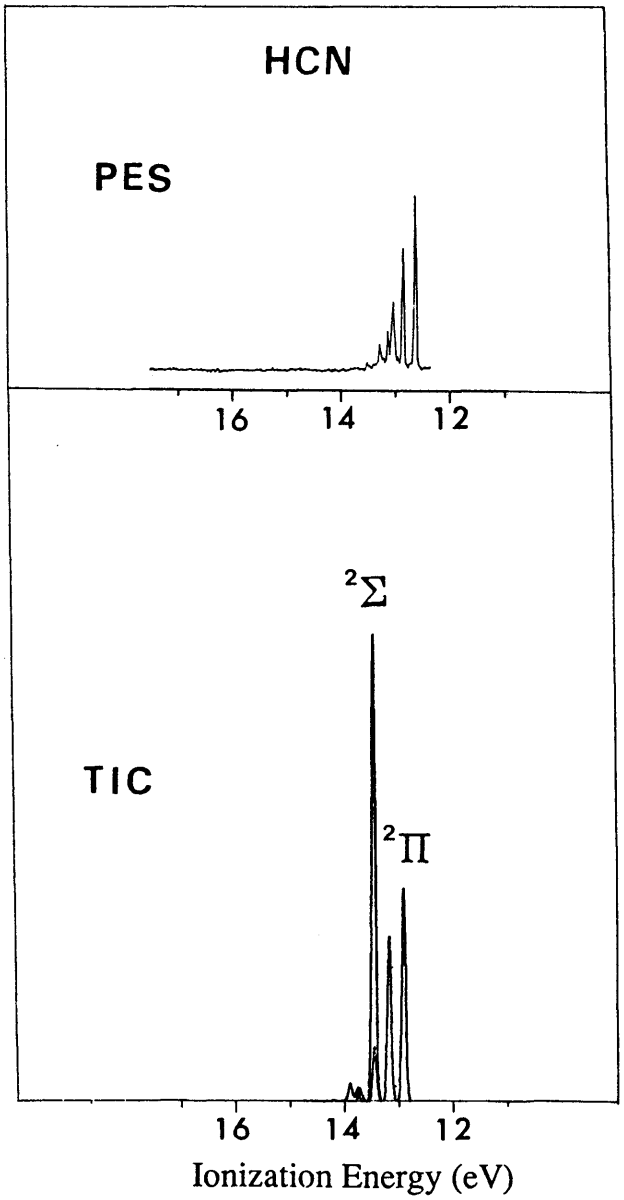

Fig. 30.1 Theoretical intensity curve and Photoelectron spectrum (From Turner et al. 1970) of Hydrogen cyanide. Band-width : 0.08 eV.

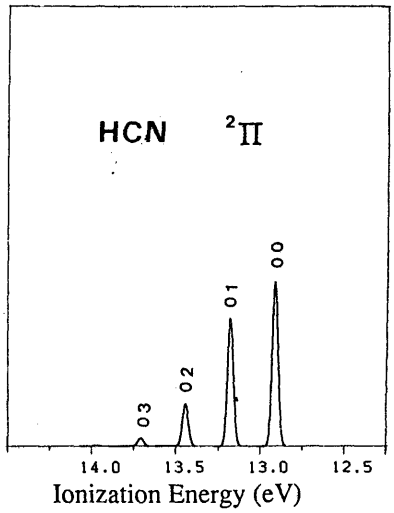

Fig. 30.2 Theoretical intensity curve of the $^2\Pi$ state of Hydrogen cyanide. Band-width : 0.04 eV.

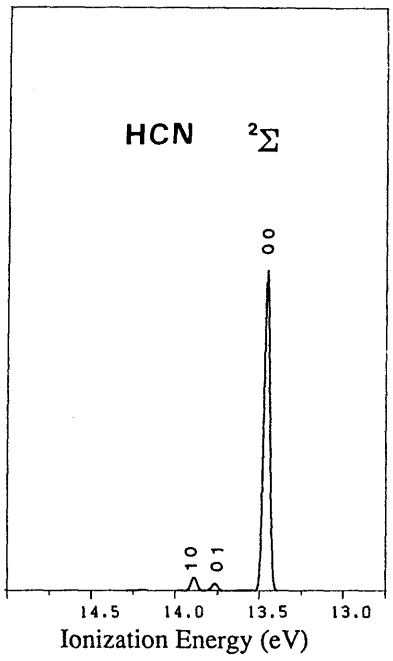

Fig. 30.3 Theoretical intensity curve of the $^2\Sigma$ state of Hydrogen cyanide. Band-width : 0.04 eV.

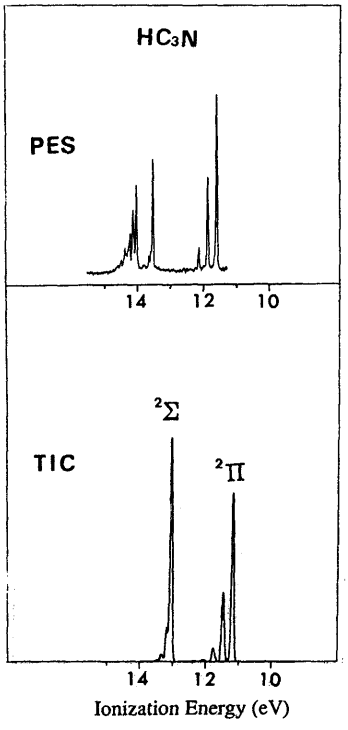

Fig. 31.1 Theoretical intensity curve and Photoelectron spectrum(From Turner et al 1970) of Cyanoacetylene. Band-width : 0.084 eV.

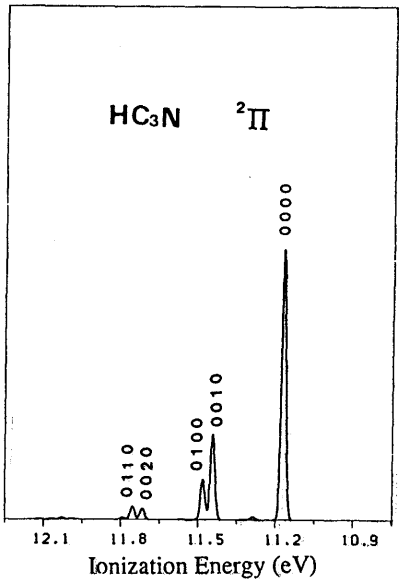

Fig. 31.2 Theoretical intensity curve of the $^2\Pi$ state of Cyanoacetylene. Band-width : 0.02 eV.

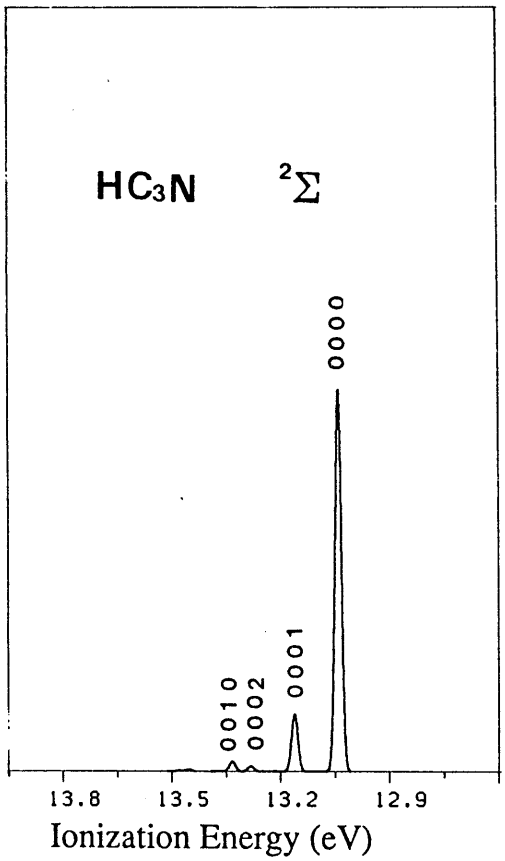

Fig. 31.3 Theoretical intensity curve of the $^2\Sigma$ -state of Cyanoacetylene. Band-width : 0.02 eV.

Figures 2.n - 31.n (n ≧ 2) give the theoretical intensity curve of each ionic state where the band-width is 0.04 eV or 0.02 eV, and show the vibrational levels. The assignment of the vibrational levels is given in the same figure or in tables 2.n - 31.n (n ≧ 7). We omit the theoretical intensity curves of the $^2B_2$ and $^2A_2$ states of cis-1,2-Difluoroethyleneare, the $^2B_2$ state of cis-1,2-Dichloroethylene, the ^2A_g and ^2B_u states of trans-Butadiene, the $^2B_2$ of cis-Butadiene, the $^2A_1$ and $^2B_2$ states of Pyrrole, the $^2A_1$ and $^2B_2$ states of Furan, and the $^2A_1$ and $^2B_2$ states of Thiophen. The magnitude of the change in the equilibrium molecular structure of these states is very large compared with the classical half amplitude of the zero-point vibrational level. We bave not succeeded in obtaining a reasonable theoretical intensity curve because of restriction of the program system FCF&TIC where an available maximum vibrational quantum number is below 30.

We have published papers on Methylene fluoride (Takeshita 1990), Methylene cloride (Takeshita 1990), Dichlorodifluoromethane (Takeshita 1990), Formaldehyde (Takeshita 1991), Ethylene (Takeshita 1991) and Ketene (Takeshita 1992). Discussion on each molecule and new assignment of PES based on this calculation should be found in these papers. We are preparing papers on the other molecules.

Acknowledgement

The computations have been performed on the HITAC-M280H computer at the Center for Information Processing Education of Hokkaido University.

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