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A theoretical study on the ionic states of difluoroethylene with an analysis of the vibrational structure of the photoelectron spectra

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A theoretical study on the ionic states of difluoroethylene with an analysis of the vibrational structure of the photoelectron spectra

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Abstract

Ab initio calculations have been performed to study the molecular structures and vibrational levels of the low-lying ionic states of difluoroethylene. The equilibrium molecular structures and vibrational modes of these states are presented. The theoretical ionization intensity curves including the vibrational structures of the ionic states are also presented and compared with the photoelectron spectra. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

There are three isomers of difluoroethylene: *trans*, *cis*, and 1:1 difluoroethylene. The electronic configuration of the ground state of the *trans* isomer is represented by $\ldots(1a_u)^2\ (1b_g)^2\ (6a_g)^2\ (6b_u)^2\ (7a_g)^2\ (2a_u)^2$ with the C_{2h} symmetry point group. The electronic configurations of the ground states of the *cis* and 1:1 isomers are represented by respectively $\ldots(5b_2)^2\ (1a_2)^2\ (6b_2)^2\ (7a_1)^2\ (2b_1)^2$ and $\ldots(1a_2)^2\ (4b_2)^2\ (8a_1)^2\ (5b_2)^2\ (2b_1)^2$ with the C_{2v} symmetry point group.

Several photoelectron spectroscopy investigations of difluoroethylene have been published by quite a few researchers [1–4]. It has been shown that the first band has an well-resolved vibrational structure and the upper bands have more complicated forms.

Theoretical studies of the photoelectron spectrum have been reported by some researchers [4,5]. Bieri et al. [4] have obtained the vertical ionization energies from semiempirical HAM/3 calculations and many-body Green's function calculations. Heaton and El-Talbi [5] have obtained the molecular structure of the ground state. They have calculated the vertical ionization energies by using the Koopmans' theorem and ΔSCF method.

As far as we are aware, there is no theoretical study of the molecular structures and vibrational analysis of the ionic states. There is also no theoretical study on the vibrational structures of photoelectron spectra. In this paper, we examine theoretically the molecular structures and the vibrational structure of the photoelectron spectra.

Within the framework of the adiabatic approximation and the harmonic oscillator approximation, we calculated the harmonic force constant matrix elements with variables of the totally symmetric distortion and the vibrational frequencies of the totally symmetric modes. We had restriction that the symmetry of the ionic state is the same as that of the ground state. We used the single configuration RHF wavefunction to calculate the optimum molecular structures and the harmonic force constant matrix elements. We obtained approximate theoretical intensity curves using the Franck–Condon factor (FCF), which is calculated by taking the square of the

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Table 1
Optimized molecular structure of *trans*-$C_2H_2F_2$. Bond lengths are in ångström, angles in degree

State	C=C	C–F	C–H	C=C–F	C=C–H
^1A_g	1.310	1.324	1.079	120.47	124.70
Exp.[a]	1.329	1.344	1.080	119.33	129.25
^2A_u	1.400	1.254	1.086	118.02	123.70
^2A_g	1.321	1.248	1.153	134.48	102.94
^2B_u	1.289	1.350	1.100	116.54	132.30
^2B_g	1.297	1.418	1.079	114.08	133.38

[a] Ref. [12].

overlap integrals between the vibrational wavefunction of the ground state and that of the ionic state. Based on these calculations, we discuss the form of spectra of the low-lying ionic states. We also discuss the effect of vibrational excitation of each mode on the spectrum in connection with the geometrical change by ionization.

2. Method of calculations

We have used the split valence type basis sets of the MIDI-4-type prepared by Tatewaki and Huzinaga [6]. These are augmented by one p-type polarization function for H and one d-type polarization function for C and F. The exponents of the polarization functions of H, C, and F are 0.68, 0.61, and 1.50, respectively.

The gradient technique for the Roothaan's restricted Hartree–Fock (RHF) method was applied to find the optimum molecular structures of the ground and ionic states.

The normal vibrational calculation of the totally symmetric modes was done by means of the gradient technique with the RHF wavefunction. We imposed some restrictions on the calculation of the Franck–Condon factor which are as follows: only the vibrational transitions between the zero-point vibrational level of the ground state and the totally symmetric modes of the ionic state were allowed. The method of calculation of the Franck–Condon factor was the same as we used in a previous paper [7].

The single and double excitation configuration interaction (SDCI) method was used to obtain more accurate ionization energies. We used a single reference configuration of the RHF wavefunction of the respective state. In the SDCI method, singly and doubly excited configuration state functions (CSFs) were generated where the inner shells were kept frozen.

In the calculation of the theoretical intensity curve, we used the 0–0 ionization energy which was obtained from the adiabatic ionization energy at the SDCI level corrected by the zero-point vibrational energy of the totally symmetric modes.

This work was carried out by using the computer program system GRAMOL [8] for the gradient technique and the calculation of normal modes, and ALCKEMY [9–11] for the CI calculations.

3. Results and discussion

3.1. Trans-difluoroethylene

The optimized geometrical parameters of the ground and four ionic states (^2A_u, ^2A_g, ^2B_u, and ^2B_g) are listed in Table 1.

Table 2 gives the vertical and adiabatic ionization energies at the SCF and SDCI levels. It also gives

Table 2
Ionization energies (eV) of *trans*-$C_2H_2F_2$. VIE: vertical ionization energy; AIE: adiabatic ionization energy. Total energies of ^1A_g: −275.436996 (SCF) and −276.009072 (SDCI)

State	VIE		AIE		Δ(VIE − AIE)		0–0 transition	
	SCF	SDCI	SCF	SDCI	SCF	SDCI	0–0 IE	FCF
^2A_u	9.38	9.90	8.84	9.41	0.54	0.49	9.40	0.063
^2A_g	14.60	14.13	13.55	13.48	1.05	0.65	13.41	0.000
^2B_u	16.13	15.47	15.99	15.35	0.14	0.12	15.31	0.438
^2B_g	17.37	16.75	16.98	16.29	0.39	0.46	16.27	0.076

the energy lowering of the adiabatic ionization energy compared with the vertical ionization energy. The 0–0 ionization energies and the Franck–Condon factors of the 0–0 transitions are listed in Table 2. In the SDCI calculations, the weights of the reference function are 86–89% at the optimized geometry. The weight of another reference function is $< 1\%$. This result suggests that the single configuration RHF method is a reasonable approximation method for those states.

Bieri et al. have reported that the 0–0 ionization energies of the ^2A_u, ^2A_g, and ^2B_u states are 10.21, 13.51, and 15.09 eV, respectively. Table 2 reveals that the Franck–Condon factors of the 0–0 transitions of the ^2A_u and ^2B_u states are large enough to observed the 0–0 transition. The ^2A_g state however has so negligibly small value that the peak of the 0–0 transition should be impossible to observe.

The vibrational frequencies of the ground and ionic states are shown in Table 3. The frequencies are arranged in order of magnitude.

A overall feature of the theoretical intensity curve with a half-width of 0.08 eV is indicated in Fig. 1 compared with the observed photoelectron spectrum. The theoretical intensity curve except the fourth band reproduces well the vibrational structure of the photoelectron spectrum.

The vibrational structure of the theoretical intensity curve of the first ionic state (^2A_u) reproduces well that of the photoelectron spectrum. There are found four or five peaks in both the theoretical intensity curve and photoelectron spectrum. The first peak at 9.40 eV is the 0–0 transition. Fig. 2 shows a more resolved vibrational structure with a half-width of 0.02 eV. We find four vibrational progressions: progressions A, B, C, and D. Progression A has strong intensity and progressions B and C have medium intensity. Progression A is mainly a vibrational transition of $n\nu_2$ ($n = 1$–5). Progression B is the transition of $\nu_5 + n\nu_2$ ($n = 1$–5). Progression C is the transitions of $\nu_3 + n\nu_2$ ($n = 1$–4) and $\nu_4 + n\nu_2$ ($n = 1$–4). The ν_2 mode contributes to all progressions. The character of ν_2 is a mixture of the C–F stretching, C=C stretching, and C=C–H bending motions. We calculated a classical half-amplitude of the zero-point vibrational level and compared it with the magnitude of the change in the geometry upon ionization. This result helps us to understand the contribution of each vibrational mode on the intensity in connection with the change in the geometry by ionization. The magnitude of the geometrical

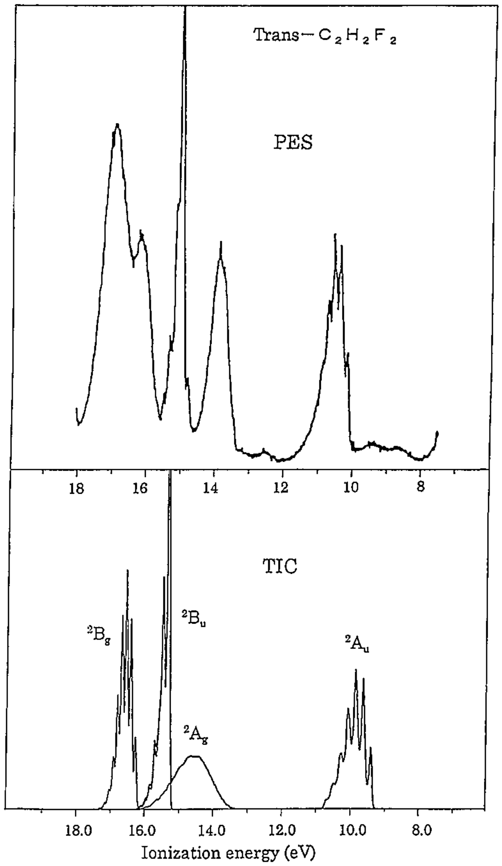

Fig. 1. Theoretical intensity curve and photoelectron spectrum by Niessen et al. [3] of *trans*-$C_2H_2F_2$. Band-width: 0.08 eV.

Table 3
Vibrational frequencies (cm^{-1}) of the totally symmetric modes of *trans*-$C_2H_2F_2$. Observed vibrational frequencies [13] of the ν_1, ν_2, ν_3, ν_4 and ν_5 modes of the ground state are 3111, 1694, 1286, 1123, and 548 cm^{-1}, respectively

Mode	^1A_g	^2A_u	^2A_g	^2B_u	^2B_g
ν_1	3423	3384	2742	3174	3467
ν_2	1949	1840	1912	1998	1930
ν_3	1404	1336	1141	1277	1345
ν_4	1257	1382	1119	1026	1048
ν_5	602	596	589	563	541

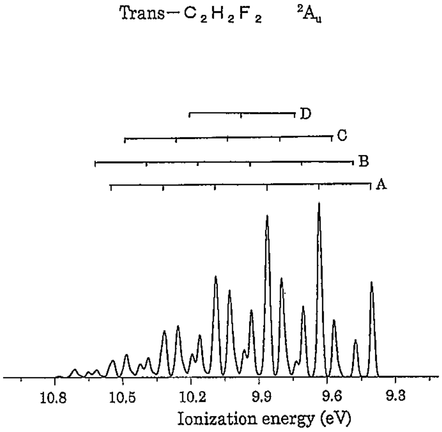

Fig. 2. Theoretical intensity curve of the ^2A_u state of *trans*-$C_2H_2F_2$. Band-width: 0.02 eV.

change in the C=C and C–F bond length is larger than the classical half-amplitude of the C=C and C–F stretching motions. Therefore, the vibrational excitation of the C–F stretching and C=C stretching modes contribute to the intensity. The character of ν_2 is a mixture of C–F and C=C stretching motions and the phase of the two stretching motions are consistent with the change of phase in the C=C and C–F bond length. Thus, the vibrational excitation of ν_2 mainly contributes to the intensity.

The second ionic state is the ^2A_g state. The theoretical intensity curve and the photoelectron spectrum show no vibrational structure (see Fig. 1). The vibrational excitations of the ν_1, ν_2, ν_3, and ν_5 modes contribute to the intensity. The ν_3 mode is excited especially to the higher vibrational level. The character of ν_1 is the C–H stretching mode. The character of ν_2 is the out-of-phase overlap of the C=C and C–F stretching motions. The ν_3 mode is a mixture of the C=C–H bending, C=C stretching, and C=C–F bending motions. The ν_5 mode is the C=C–F bending mode. The change in the geometry of the C–F, C–H, C=C–F, and C=C–H are larger than the classical half-amplitude of the C–F stretching, C–H stretching, C=C–F bending, and C=C–H bending motions. Especially the magnitude of the change in the C=C–F and C=C–H angles is larger than the classical half-amplitude (by four times). The ν_3 mode has a large amplitude in the C=C–F and C=C–H bending modes and the phase of these motions is consistent with the phase of change in the C=C–F and C=C–H angles. Thus, higher vibrational excitation of ν_3 contributes to the intensity.

The third ionic state is the ^2B_u state. The theoretical intensity curve in Fig. 1 reproduces well the photoelectron spectrum. The 0–0 transition at 15.31 eV has a maximum intensity. The second peak at 15.47 eV is the transition of the ν_3 mode. The geometrical changes in the C=C–F and C=C–H angles are slightly larger than the classical half-amplitude of the C=C–F and C=C–H bending modes. Thus the 0–0 transition should have maximum intensity. An excitation of ν_3 has some intensity because of large amplitude in the C=C–F and C=C–H motions.

The fourth band of the photoelectron spectrum is observed between 15.8 and 18.0 eV (see Fig. 1), where two maxima are found at 16.3 and 17.0 eV. Koopmans' theorem gives that the ordering of the vertical ionized states are 2^2A_g, ^2B_g, and 2^2A_u from the lower-energy side [5]. We calculated the vertical ionization energies of the second ionic states of ^2A_g and ^2A_u by means of the two-reference SDCI method. The result of the calculation is that the vertical ionization energies of the 2^2A_g and 2^2A_u states are 17.52 and 17.91 eV, respectively. The vertical ionization energy of the ^2B_g state is 16.75 eV (see Table 2). Therefore, the ordering of the vertical ionized states at the SDCI level is ^2B_g, 2^2A_g, and 2^2A_u. The 0–0 ionization energy of the ^2B_g state is 16.27 eV at the SDCI level. Comparing the observed spectrum with the theoretical intensity curve of the ^2B_g state, we propose that the first maximum at 16.3 eV may corresponds to the ^2B_g state, and the second maximum is due to the 2^2A_g and 2^2A_u states. This assignment is consistent with that by Bieri et al. [4].

Fig. 1 indicates the vibrational structure of the ^2B_g state. The first peak at 16.27 eV is assigned to the 0–0 transition. The vibrational progression of $n\nu_4$ ($n = 0$–6) has strong intensity. The character of ν_4 is a mixture of the C–F stretching and C=C–F bending motions. The geometrical changes in the C–F, C=C–F and C=C–H are larger than the classical half-amplitude of the C–F stretching, C=C–F bending, and C=C–H bending motions, and the phase of the C–F stretching, C=C–F bending and C=C–H bending motions of ν_4 are consistent with the phase of the change in the geometry.

Table 4
Optimized molecular structure of *cis*-$C_2H_2F_2$. Bond lengths are in ångström, angles in degree. The electronic configurations of the 1^2B_2 and 2^2B_2 states are $\ldots(5b_2)^1\ (1a_2)^2\ (6b_2)^2\ (7a_1)^2\ (2b_1)^2$ and $\ldots(5b_2)^2\ (1a_2)^2\ (6b_2)^1\ (7a_1)^2\ (2b_1)^2$, respectively

State	C=C	C–F	C–H	C=C–F	C=C–H
$^1A_1$	1.310	1.320	1.079	122.98	122.35
Exp.[a]	1.331	1.335	1.084	123.72	121.56
$^2B_1$	1.402	1.252	1.085	119.15	122.85
$^2A_1$	1.387	1.247	1.110	121.61	113.18
1^2B_2	1.276	1.329	1.121	123.88	127.77
2^2B_2	1.260	1.258	1.231	149.97	97.56
$^2A_2$	1.295	1.428	1.078	110.04	135.74

[a] Ref. [13].

3.2. *Cis-difluoroethylene*

The optimized geometrical parameters of the ground and five ionic states ($^2B_1$, $^2A_1$, 1^2B_2, 2^2B_2, and $^2A_2$) are collected in Table 4. We could fortuitously obtain the two different optimized molecular structures of the 1^2B_2 and 2^2B_2 states by the RHF method. The electronic configurations of the 1^2B_2 and 2^2B_2 states are $\ldots(5b_2)^1\ (1a_2)^2\ (6b_2)^2\ (7a_1)^2\ (2b1)^2$ and $\ldots(5b_2)^2\ (1a_2)^2\ (6b_2)^1\ (7a_1)^2\ (2b_1)^2$, respectively.

The vertical and adiabatic ionization energies at the SCF and SDCI levels are summarized in Table 5. It also shows the energy lowering of the adiabatic ionization energy compared with the vertical ionization energy. The 0–0 ionization energies and the Franck–Condon factors of the 0–0 transitions are given in Table 5. In the SDCI calculations, the weights of the reference function are 86–89% at the optimized geometry.

Table 6
Vibrational frequencies (cm^{-1}) of the totally symmetric modes of *cis*-$C_2H_2F_2$. Observed vibrational frequencies [13] of the ν_1, ν_2, ν_3, ν_4 and ν_5 modes of the ground state are 3122, 1716, 1263, 1015, and 237 cm^{-1}, respectively

State mode	$^1A_1$	$^2B_1$	$^2A_1$	1^2B_2	$2\,^2B_2$	$^2A_2$
ν_1	3435	3398	3090	3483	2466	3485
ν_2	1967	1832	1686	1911	2278	1934
ν_3	1387	1437	1209	1183	1233	1230
ν_4	1113	1140	1150	1020	972	989
ν_5	252	269	293	563	320	303

Bieri et al. have reported that the 0–0 ionization energies of the $^2B_1$, $^2A_1$, and $^2B_2$ states are 10.22, 13.79, and 14.89 eV, respectively. Table 5 indicates that the Franck–Condon factors of the 0–0 transitions of the $^2B_1$ and $^2A_1$ states are so large as to observe the 0–0 transition. The 1^2B_2 state however has so negligibly small value that the peak of the 0–0 transition should be impossible to observe.

The vibrational frequencies of the ground and ionic states are shown in Table 6.

Fig. 3 illustrates an overall form of the theoretical intensity curve of the $^2B_1$ and $^2A_1$ states with a half-width of 0.08 eV together with the observed photoelectron spectrum.

The first ionic state is the $^2B_1$ state. The vibrational structure of the theoretical intensity curve reproduces well that of the photoelectron spectrum (see Fig. 3). The first peak at 9.41 eV is the 0–0 transition. Fig. 4 shows a more resolved theoretical intensity curve. Four vibrational progressions of A, B, C, and D are found. Progression A has strong intensity and progression B has medium intensity.

Table 5
Ionization energies (eV) of *cis*-$C_2H_2F_2$. VIE: vertical ionization energy; AIE: adiabatic ionization energy. Total energies of $^1A_1$: −275.436797 (SCF) and −276.009025 (SDCI) Koopmans' theorem gives the VIEs of the 1^2B_2 and 2^2B_2 states 16.64 and 18.98 eV, respectively. The electronic configurations of the vertical ionization state of 1^2B_2 is $\ldots(5b_2)^1\ (1a_2)^2\ (6b_2)^2\ (7a_1)^2\ (2b_1)^2$

State	VIE		AIE		Δ(VIE − AIE)		0–0 transition	
	SCF	SDCI	SCF	SDCI	SCF	SDCI	0–0 IE	FCF
$^2B_1$	9.38	9.90	8.85	9.42	0.53	0.48	9.41	0.058
$^2A_1$	14.71	14.13	14.23	13.91	0.48	0.22	13.86	0.054
1^2B_2	15.80	15.22	14.49	14.33	1.31	0.89	14.49	0.000
2^2B_2	–	–	14.80	14.77	–	–	14.72	0.000
$^2A_2$	17.02	16.53	16.35	15.91	0.67	0.62	15.89	0.000

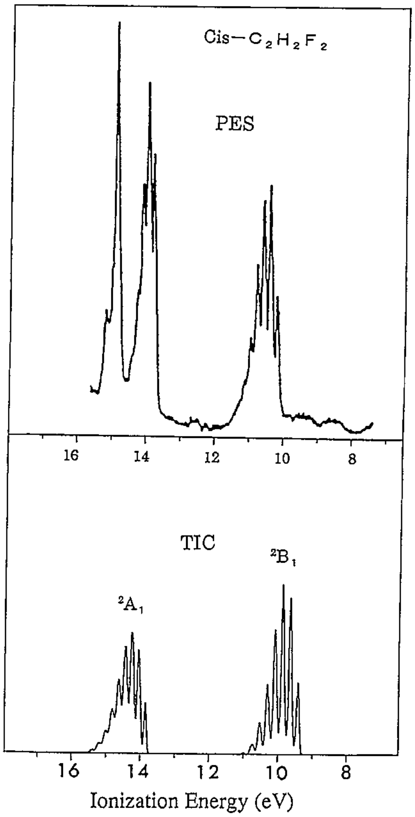

Fig. 3. Theoretical intensity curve of the $^2B_1$ state of 1:1-$C_2H_2F_2$. Band-width: 0.02 eV.

Progression A is mainly vibrational excitations of $n\nu_2$ ($n = 0$–5) and progression B is $n\nu_2 + \nu_5$ ($n =$ 1–5). Progressions C and D are $n\nu_2 + 2\nu_5$ ($n = 0$–3) and $n\nu_2 + \nu_4$ ($n = 0$–4), respectively. The character of ν_2 is the out-of-phase overlap of the C=C and C–F stretching motions. The character of ν_5 is the C=C–F bending mode. The C=C bond lengthens and the C–F bond shortens upon ionization. The magnitude of the geometrical change in the C=C and C–F bond length is larger than the classical half-amplitude of the C=C and C–F stretching motions, and the phase of the C–F and C=C stretching motions of ν_2 is consistent with the change of phase in the C=C and C–F bond length. Thus, the vibrational excitation of ν_2 mainly contributes to the intensity.

The second ionic state is the $^2A_1$ state. The vibrational structure of the theoretical intensity curve reproduces well that of the photoelectron spectrum (see Fig. 3). The first peak at 13.86 eV is the 0–0 transition. The vibrational progressions $n\nu_2$ ($n = 0$–4) and $n\nu_2 + \nu_3$ ($n = 1$–4) have strong intensity. The characters of ν_2 and ν_3 are the C–F stretching and C=C–H bending modes, respectively. The change in the geometry of the C=C, C–F, and C=C–H is larger than the classical half-amplitude of the C=C stretching, C–F stretching, and C=C–H bending motions. The ν_2, ν_3, and ν_4 modes are characterized mainly by the C–F stretching, C=C–H bending, and C=C stretching modes, respectively. However, the phase of the classical half-amplitude of the C=C stretching and C–F stretching motions of ν_4 is not consistent with the phase of the geometrical change in the C=C and C–F. Thus the vibrational excitation of ν_4 does not contribute to the intensity. The ν_2 mode has a large amplitude of the C–F stretching motion. The ν_3 mode has a large amplitude of the C=C stretching and C=C–H bending motions and the phase of those motions is consistent with the phase of the geometrical change in the C=C and C=C–H. Therefore, the vibrational excitations of ν_2 and ν_3 have strong intensity.

Fig. 3 shows that the third band of the photoelectron spectrum has a sharp peak at 15 eV. The third band indicates that the 0–0 transition has a strong intensity and the magnitude of the change in the geometry by ionization should be small. The

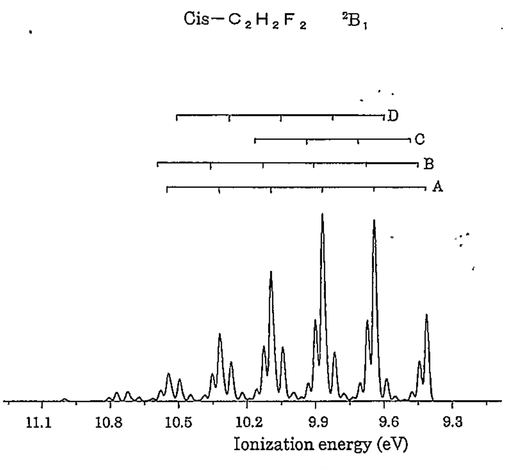

Fig. 4. Theoretical intensity curve of the $^2B_1$ state of *cis*-$C_2H_2F_2$. Band-width: 0.02 eV.

Table 7
Optimized molecular structure of 1:1-$C_2H_2F_2$. Bond lengths are in ångström, angles in degree

State	C=C	C–F	C–H	C=C–F	C=C–H
$^1A_1$	1.307	1.299	1.078	125.25	119.63
Exp.[a]	1.316	1.324	1.075	125.34	120.37
$^2B_1$	1.408	1.236	1.082	122.38	118.72
$^2B_2$	1.321	1.254	1.161	122.27	142.13
$^2A_1$	1.394	1.249	1.108	120.69	102.52
$^2A_2$	1.287	1.358	1.083	131.24	119.51

[a] Ref. [12].

result of the calculations of the 0–0 ionization energies suggests that the 1^2B_2, 2^2B_2 or $^2A_2$ states maybe correspond to this band (see Table 3). However, the table also indicates that the Franck–Condon factors of the 0–0 transitions of these states have negligibly small values. Therefore, we are not able to find a reasonable assignment of the electronic state of the third band.

For the 1^2B_2, 2^2B_2 and $^2A_2$ states, the change in the C–F bond length, C=C–F bond angle, and C=C–H bond angle are rather large compared with the classical half-amplitude. The ν_3, ν_4, and ν_5 modes are characterized by the C=C–H bending, C–F stretching, and C=C–F bending modes, respectively. The higher vibrational excitations of the ν_3, ν_4, and ν_5 modes should be contribute to the intensity and the shape of spectrum should be broad.

3.3. *1:1-difluoroethylene*

Table 7 collects the optimized geometrical parameters of the ground and ionic states.

Table 8 gives the vertical and adiabatic ionization energies at the SCF and SDCI levels. It also gives the energy lowering of the adiabatic ionization energy compared with the vertical ionization energy. The 0–0 ionization energies and the Franck–Condon factors of the 0–0 transitions are listed in Table 8. In the SDCI calculations, the weights of the reference function are 88% at the optimized geometry.

Bieri et al. have reported that the 0–0 ionization energies of the $^2B_1$ and $^2B_2$ states are 10.29 and 14.06 eV, respectively. Table 8 indicates that the Franck–Condon factors of the 0–0 transition of the $^2B_1$ is large enough to observe the 0–0 transition. The $^2B_2$ state however has so negligibly small value that the peak of the 0–0 transition should be impossible to observe.

The vibrational frequencies of the ground and ionic states are shown in Table 9.

A overall feature of the theoretical intensity curve with a half-width of 0.08 eV is illustrated in Fig. 5 compared with the observed photoelectron spectrum.

For the first ionic state of $^2B_1$, the vibrational structure of the theoretical intensity curve reproduces well that of the photoelectron spectrum. Fig. 6 illustrates a detail of the theoretical intensity curve. The first peak at 9.51 eV is the 0–0 transition. The vibrational progression of A with strong intensity is

Table 9
Vibrational frequencies (cm^{-1}) of the totally symmetric modes of 1:1-$C_2H_2F_2$. Observed vibrational frequencies [14] of the ν_1, ν_2, ν_3, ν_4 and ν_5 modes of the ground state are 3060, 1734, 1359, 926 and 550 cm^{-1}, respectively

Mode	$^1A_1$	$^2B_1$	$^2B_2$	$^2A_1$	$^2A_2$
ν_1	3361	3318	2890	2948	3324
ν_2	1948	1718	1858	1561	1979
ν_3	1510	1528	1292	1267	1482
ν_4	1026	1046	1089	981	938
ν_5	601	639	609	600	546

Table 8
Ionization energies (eV) of 1:1-$C_2H_2F_2$. VIE: vertical ionization energy; AIE: adiabatic ionization energy. Total energies of $^1A_1$: −275.454949 (SCF) and −276.027688 (SDCI)

State	VIE		AIE		Δ(VIE − AIE)		0–0 transition	
	SCF	SDCI	SCF	SDCI	SCF	SDCI	0–0 IE	FCF
$^2B_1$	9.41	9.99	8.88	9.52	0.53	0.47	9.51	0.083
$^2B_2$	14.66	14.99	13.14	13.61	1.52	1.38	13.57	0.000
$^2A_1$	16.17	15.94	15.08	15.13	1.09	0.81	15.06	0.002
$^2A_2$	16.75	16.33	16.39	15.97	0.36	0.36	15.96	0.027

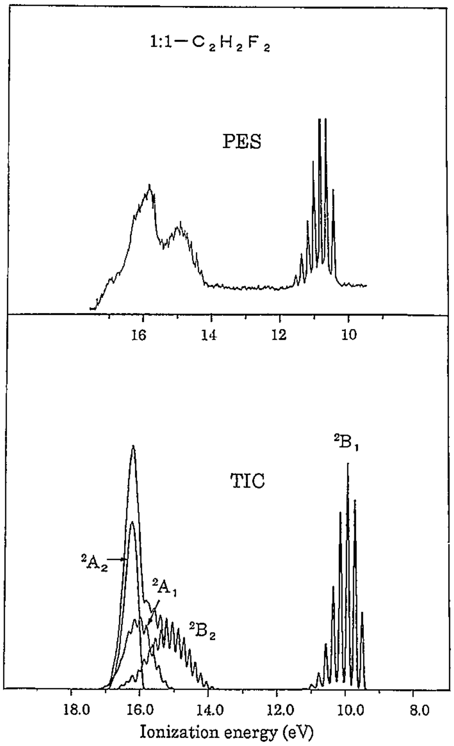

Fig. 5. Theoretical intensity curve and photoelectron spectrum by Turner et al. [1] of 1:1-$C_2H_2F_2$. Band-width: 0.08 eV.

the $n\nu_2$ $(n = 0–6)$ transition. The vibrational progression of B is the $n\nu_2 + \nu_5$ $(n = 0–4)$ transition. The character of ν_2 is the out-of-phase overlap of the C=C and C–F stretching motions. The magnitude of the change in the C=C bond length, C–F bond length, and C=C–F bond angle are larger than the classical half-amplitude of the C=C stretching, C–F stretching, and C=C–F bending motions. The phase of the C=C stretching, C–F stretching, and C=C–F bending motions of the ν_2 mode fairly is consistent with the phase of the geometrical change. Thus only the vibrational excitation of ν_2 contributes to the intensity.

The second ionic state is the $^2B_2$ state. Fig. 5 indicates that the second band of the photoelectron spectrum is observed above 14.2 eV. The maximum of the band is 14.9 eV. The band shows a vibrational structure. The theoretical intensity curve of the $^2B_2$ state reproduces well the vibrational structure of the photoelectron spectrum. The peak of the 0–0 transition is not recognized in this figure. The peak at 14.05 eV is assigned to the $3\nu_3$ level. The vibrational structure of the theoretical intensity curve seems to has a simple vibrational progression. However, the vibrational structure consists of overlapping of the four vibrational progressions. The first progression of $n\nu_3$ $(n = 3–13)$ has a strong intensity at the lower-energy side. The second progression of $\nu_1 + n\nu_3$ $(n = 3–13)$ has a strong intensity at the higher-energy side. The third progression of $\nu_2 + n\nu_3$ $(n = 4–11)$ and $2\nu_1 + n\nu_3$ $(n = 4–12)$ has also strong intensity. The fourth progression of $\nu_1 + \nu_2 + n\nu_3$ $(n = 4–11)$ has weak intensity. The character of ν_3 is the C=C–H bending mode. The ν_1 mode is the C–H stretching mode. The ν_2 mode is the C=C stretching mode. The change in the C=C–H bond angle is larger than the classical half-amplitude of the C=C–H bending motion by four times. Therefore, the higher vibrational excitation of the C=C–H bending mode (ν_3) contributes to the intensity. The change in the C–F and C–H bond length is larger than the classical half-amplitude of the C–F and C–H stretching motions. This situation is ascribed to the vibrational excitations of the ν_1 and ν_2 modes.

Fig. 5 indicates that the $^2A_1$ and $^2A_2$ states contribute to the band at 16 eV.

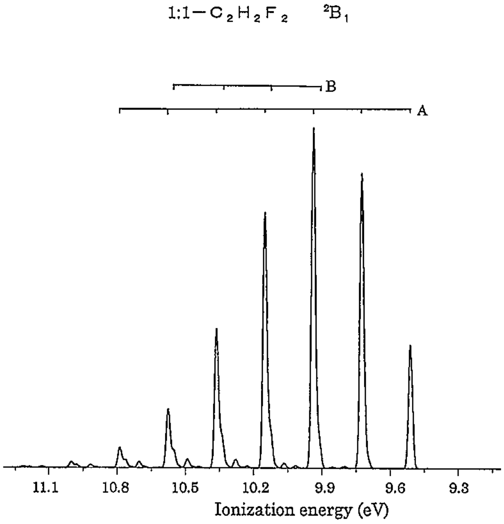

Fig. 6. Theoretical intensity curve of the $^2B_2$ state of 1:1-$C_2H_2F_2$. Band-width: 0.02 eV.

Fig. 5 shows the theoretical intensity curve of the $^2A_1$ state. The first peak at 15.05 eV with weak intensity is the 0–0 transition. The peak at 15.25 eV is assigned to the ν_2 excitation. There are found five vibrational progressions. The progressions of $n\nu_2$ ($n = 0$–6), $n\nu_2 + \nu_3$ ($n = 1$–6), $n\nu_2 + \nu_4$ ($n = 2$–6), $n\nu_2 + \nu_3 + \nu_4$ ($n = 2$–6), and $n\nu_2 + \nu_3 + \nu_5$ ($n = 2$–4) contribute to the intensity. For all progressions, the higher vibrational excitation of ν_2 contributes to the intensity. The magnitudes of the change in the C=C, C–F, C=C–F, and C=C–H are larger than the classical half-amplitude. The ν_2 mode has an perceptible amplitude in the C=C stretching, C–F stretching, C=C–F bending, and C=C–H bending motions. The phase of these motions is consistent with the phase of the geometrical change in the C=C, C–F, C=C–F, and C=C–H. Thus the higher vibrational excitation of ν_2 contributes mainly to the intensity.

The vibrational structure of the $^2A_2$ state is assigned to the five vibrational progressions overlapping each other. The progressions of $n\nu_5$ ($n = 0$–5), $\nu_4 + n\nu_5$ ($n = 0$–5), $2\nu_4 + n\nu_5$ ($n = 2$–5), $\nu_2 + n\nu_5$ ($n = 2$–5), and $\nu_2 + \nu_3 + n\nu_5$ ($n = 2$–5) contribute to the intensity. The higher vibrational excitations of ν_5 contribute to all progressions. The character of ν_5 is the C=C–F bending mode. The change in the C=C–F angle is larger than the classical half-amplitude of the C=C–F bending motion by three times. Therefore, higher vibrational excitation of ν_5 contributes mainly to the intensity.

Koopmans' theorem gives that the vertical ionization energy of the second $^2B_2$ state is lower than that of the first $^2A_2$ state. We have calculated the vertical ionization energy of the 2^2B_2 state by means of the MRSDCI calculation using the three reference functions as follows: $\ldots(1a_2)^2\ (4b_2)^2\ (8a_1)^2\ (5b_2)^1\ (2b_1)^2$, $\ldots(1a_2)^2\ (4b_2)^1\ (8a_1)^2\ (5b_2)^2\ (2b_1)^2$, and $\ldots(1a_2)^2\ (4b_2)^1\ (8a_1)^2\ (5b_2)^2\ (2b_1)^1\ (3b_1)^1$. The result of the calculation gives 16.13 eV as the vertical ionization energy, which is lower than that of the $^2A_2$ state (16.33 eV). Therefore, the 2^2B_2 state also contributes to the band near 16 eV.

4. Conclusions

Equilibrium molecular structures and vibrational frequencies were calculated for the ground and low-lying ionic states of the three isomers of difluoroethylene. We obtained the theoretical intensity curve by using Franck–Condon factors.

For the first band of all isomers, the theoretical intensity curves reproduce the vibrational structures of the photoelectron spectra closely. The theoretical intensity curves of the $^2A_1$ state of the *cis* isomer and the $^2B_2$ state of the 1:1 isomer reproduce the vibrational structures of the second band. The theoretical intensity curves of the ^2A_g and ^2B_u states of the *trans* isomer reproduce the second and third band of the photoelectron spectrum, respectively.

For the first band of all isomers, the vibrational excitation of the ν_2 mode contributes mainly to the intensity. The character of the ν_2 is the out-of-phase overlap mode of the C=C and C–F stretching motions. This situation is connected with the C=C bond lengthening and C–F bond shortening by ionization.

For the second band of the *cis* isomer, the vibrational excitations of the ν_2 (C–F stretching) mode and the ν_3 (C=C–H bending) mode contribute to the intensity. For the second band of the 1:1 isomer, higher vibrational excitation of the ν_3 (C=C–H bending) mode contributes to the intensity.

The second band of the *trans* isomer shows no vibrational structure. This situation originates from the vibrational structure which is complicated by the vibrational excitations of the ν_1, ν_2, ν_3, and ν_5 modes because of large change in the geometry of the C–F, C–H, C=C–F, and C=C–F by ionization.

The third band of the *cis* isomer at 15 eV shows a sharp form. The result of the calculation of the 0–0 ionization energies shows that the 1^2B_2 and 2^2B_2 states should contribute to this band. However, we could not obtain a reasonable theoretical intensity curve because of the large geometrical change in C–F, C=C–F, and C=C–H.

The $^2A_1$, 2^2B_2, and $^2A_2$ states of the 1:1 isomer contribute to the band at 16 eV. The present study reveals the apparent contribution of the $^2A_1$ and $^2A_2$ states to the intensity.

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