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THEORETICAL STUDY ON THE FIRST BROAD BAND OF THE PHOTOELECTRON SPECTRUM OF H_2O_2 WITH INCLUSION OF THE VIBRATIONAL STRUCTURE

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1. Introduction

Hydrogen peroxide is an important molecule in photochemical processes [1,2] in atmospheric observations. The ground state has been studied extensively [3] and is found to have a skew conformation having C_2 symmetry with an H–O–O–H dihedral angle of about 120°. The electronic configuration is $...(5a)^2(4b)^2$. A detailed discussion of the stability of the ground state was given by Cremer [3]. The photoelectron (PE) spectrum of H_2O_2 was reported [4–6] and the entire ultraviolet spectrum given [7]. The PE spectrum between 10 and 14 eV appears to originate from two distinct ionization processes with a clear vibrational structure on the rise of the first band. This strongly suggests a non-dissociative nature for the first two ionic states of H_2O_2. The vertical ionization potential (VIP) has been analyzed [4,5,8]. Detailed investigations on the low-lying excited and ionic states of H_2O_2 are scarce and are mostly concerned with accurate estimation of VIP and excitation energies [9–11]. Recently, Schinke and Staemmler [12] considered the photodissociation of H_2O_2 by the use of ab initio potential energy surfaces of the lowest two excited states [13].

In the present communication we confine our attention to the lowest two ionic states of H_2O_2 which appear as the first two broad bands between 10 and 14 eV in the PE spectrum. Detailed investigations on the equilibrium geometries of the two states have been performed. We have analysed the vibrational structure associated with the transitions and estimated the Franck–Condon factors (FCF) to provide an understanding of the intensity distribution of the PE bands.

2. Basis sets and method of calculation

We have used two distinct basis sets. The first set is based on the MIDI-4 basis set of Tatewaki and Huzinaga [14] for O. This is augmented by one d-type polarization function of exponent 1.16 [14]. For H we have used the MINI-3 basis set. This is augmented by a p-type polarization function with exponent 0.68 [14]. We call this set I. The second set for O is the extended basis (11s7p) contracted to [7s4p] by Salez and Veillard [15]. Their contraction scheme 13 is used for the s-type functions and scheme 8 for the p-type functions. This gave the best energy for H_2O among their various contraction

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schemes [15]. The polarization functions are the same as in set I. For H we choose the same basis as in set I but a scale factor 1.2 [16] is used. This is set II.

We have used both self-consistent field (SCF) and configuration interaction (CI) methods for the ground state and the lowest two ionized states. The SCF method is used to obtain the optimized geometries, potential energy surface and harmonic force constants. The bond distances O–O and O–H, the bond angle ∠O–O–H and the dihedral angle ∠H–O–O–H are used as variable parameters.

The CI method is used for the calculation of the ionization energies. The CI calculation is confined to single and double substitutions (SDCI) from an SCF wavefunction of the respective state. The total numbers of generated configuration state functions (CSF) of the ^{1}A, ^{2}A and ^{2}B state are 10506, 10893 and 10893, respectively with basis set I. For basis set II the total numbers are 25122 for the ^{1}A state and 25541 for the ^{2}A and ^{2}B states. As the dimension of the CI with set II is too large, we have adopted a CSF selection process by the use of second-order perturbation theory. The threshold for the selection is 5 μhartree. The dimension of the Hamiltonian matrix is then reduced to 9485 , 6555 and 6758 for the ^{1}A, ^{2}A and ^{2}B states, respectively. We have estimated the total energy including the contribution from the rejected CSFs by second-order perturbation theory [17].

3. Results and discussion

The potential energy is calculated as a function of dihedral angle with basis set I and the SCF method. For each dihedral angle the bond distances and bond angle are optimized. Fig. 1 shows the potential energy diagrams for the ^{1}A, ^{2}B and ^{2}A states as a function of the dihedral angle. It is clear that the trans conformation has the lowest energy in the ^{2}B state whereas the cis conformation has the lowest energy in the ^{2}A state. The calculated barrier height for the ^{2}B state is 3.69 eV and that of the ^{2}A state 2.24 eV. The calculated cis and trans barrier heights of the ground state are 0.35 and 0.04 eV, respectively. Those compare favorably with more accurate estimates of cis and trans barrier heights of 0.38 and 0.03 eV obtained by Cremer [3]. The rotational barrier heights appear to be much greater in the ionic states than in the ground state.

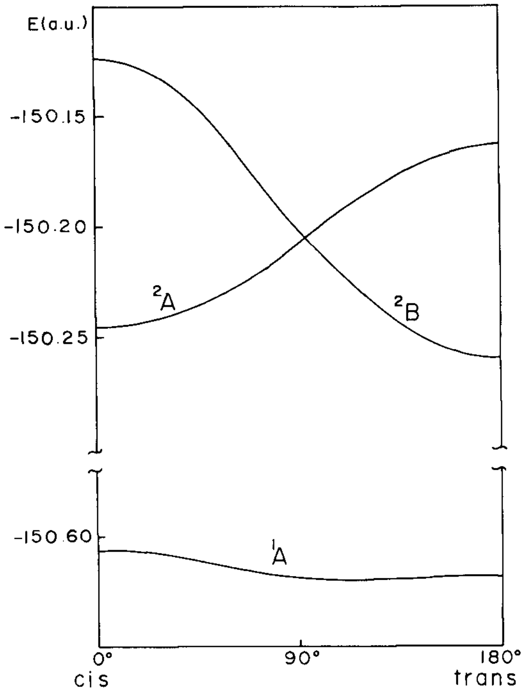

Fig. 1. The potential energy diagrams for the ^{2}B and ^{2}A states as a function of the H–O–O–H dihedral angle by use of the SCF method with basis set I.

Table 1 shows the optimized geometry parameters for the ground and two ionic states in both cis and trans conformations. For comparison the experimental and theoretical geometry parameters for the ground state [3] are also listed. We notice that the error of the optimized geometry parameter is largest for the O–O bond distance. Other parameters, particularly the dihedral angle, agree well with experiment.

Comparing the geometry of the ionized states with the ground state, we notice the following considerable changes. For the ^{2}B state the dihedral angle changes about 62° whereas that of the ^{2}A state changes about 118° from the ground state. The O–O bond distance becomes shorter by 0.14 Å in both ionic states. The ∠O–O–H bond angle of the ^{2}A state becomes larger by 10°.

Table 2 contains the SCF and CI energies of the

Table 1
Equilibrium geometry parameters for the ground and ionic states of H_2O_2 by the SCF method

State		Equilibrium geometry parameters			
		R(O–O) (Å)	R(O–H) (Å)	A($\angle$O–O–H) (deg)	dihedral angle ($\angle$H–O–O–H) (deg)
^{1}A	set I [a]	1.391	0.948	102.4	115.0
	set II	1.390	0.947	102.6	118.4
	Cremer-1	1.390	0.943	102.9	111.2
	Cremer-2	1.451	0.967	99.3	119.3
	exp.	1.463	0.967	99.3	120.2
trans ^{2}B	set I	1.244	0.977	106.8	180.0
	set II	1.250	0.976	106.8	180.0
cis ^{2}B	set I	1.235	0.993	129.8	0.0
cis ^{2}A	set I	1.243	0.975	113.2	0.0
	set II	1.249	0.975	113.2	0.0
trans ^{2}A	set I	1.309	0.985	117.7	180.0

[a] Set I: present result with basis set I. set II: present result with basis set II. Cremer-1: Best SCF result listed in ref. [3]. Cremer-2: Best RS-MP result listed in ref. [3]. Exp.: experimental result shown in ref. [3].

Table 2
SCF and CI energies of the ground and two lowest ionic states of H_2O_2

State	Energy values (au)				
	present calculation				other values
	basis I		basis II		
	SCF	CI	SCF	CI	
^{1}A [a]	−150.6197	−150.9853	−150.8264	−151.2138	−150.8242 [b] −150.8455 [c] −151.2803 [d]
^{2}B [a]	−150.2063	−150.5785	−150.4102	−150.8012	
^{2}A [a]	−150.1706	−150.5322	−150.3707	−150.7486	
trans ^{2}B	−150.2595	−150.6167	−150.4596	−150.8346	
cis ^{2}A	−150.2450	−150.6023	−150.4443	−150.8190	

[a] Geometry of the ground state by the SCF method.
[b] SCF result of ref. [3] with [4s3p1d/2s2p] basis.
[c] SCF result of ref. [3] with (11s6p2d/6s2p) basis.
[d] Rescaled RS-MP result of ref. [3] with [4s3p1d/2s1p] basis.

ground and ionic states. In the CI calculation with basis set I at the optimized geometry, the weight of the main configuration is 91.5% for the ^{1}A state and 91.7% for the ^{2}A and ^{2}B state, respectively. The weight of other configurations is less than 0.42% for each state. This result means that a single reference approximation method is appropriate in these cases. Table 3 contains the VIP and 0–0 transition energies calculated by using the SCF and CI methods. In order to estimate the 0–0 transition energies, we use the zero-point vibrational energy based on the harmonic oscillator potential model.

Table 3
Vertical ionization potentials and 0–0 transition energies for the first two ionic states of H_2O_2

State	Ionization potential (eV)						
	vertical				0–0 transition		
	present calculation		other values		present calculation		other values obs.
	SCF	CI	obs.	cal.	SCF	CI	
^2B	11.25 a)	11.07 a)	11.69 c),	11.7 g)	9.85 a)	10.08 a)	10.54 d)
	11.33 b)	11.23 b)	11.51 d)		10.02 b)	10.36 b)	
			11.7 e)				
			11.15 f)				
^2A	12.22 a)	12.33 a)	12.69 c),	12.8 g)	10.22 a)	10.44 a)	
	12.40 b)	12.66 b)	12.56 d)		10.42 b)	10.76 b)	
			12.0 e)				
			12.34 f)				

a) Result with basis set I. b) Result with basis set II. c) Ref. [4]. d) Ref. [5]. e) Ref. [6]. f) Ref. [8]. g) Ref. [11].

As mentioned before, the PE spectrum of H_2O_2 between 10 and 14 eV is composed of two distinct ionizations with vibrational structure on the rise of the first band. Using the harmonic oscillator model, we have calculated the vibrational frequencies for the four symmetric modes for the ground and two ionic states; the ν_1 mode of the O–H stretching, the ν_2 mode of the O–O–H bending, the ν_3 mode of the O–O stretching and the ν_4 mode of the H–O–O–H torsion. The results are listed in table 4. Some experimental results are also listed. As is expected from the calculated rotational barrier height in the ionic state, the calculated vibrational frequency for the torsional oscillator modes is appreciably larger for the ionic states than that for the ground state. The calculated O–O stretching frequency of the ionic states is large compared with that of the ground state. This may be related to the shortening of the O–O bond distance with ionization. We calculated the FCFs for the respective ionic states and the theoretical intensity

Table 4
Vibrational frequencies for the ground and ionic states of H_2O_2 by the SCF method

State	Vibrational frequency (cm^{-1})				
	^1A		trans ^2B		cis ^2A present calculation
	present calculation	other values	present calculation	other values	
ν_1 (O–H)	4125 a)	3614 c)	3772 a)		3806 a)
	4144 b)		3792 b)		3826 b)
ν_2(∠O–O–H)	1615 a)	1315 c)	1737 a)		1578 a)
	1611 b)		1720 b)		1499 b)
ν_3 (O–O)	1137 a)	890 c)	1579 a)	1080±50 e)	1511 a)
	1172 b)	880 d)	1568 b)		1575 b)
ν_4 (∠H–O–O–H)	378 a)	465 c)	961 a)		762 a)
	386 b)		951 b)		749 b)

a) Result with basis set I. b) Result with basis set II. c) Ref. [18]. d) Ref. [19]. e) Ref. [5].

curve [20]. The FCFs for the torsional mode are estimated for vibrational levels which are below the top of the rotational barrier. Fig. 2 shows the profile. A total intensity curve is obtained with the assumption that the transition probability of the electronic part is equal in weight for both ^{2}B and ^{2}A states. This is compared with the PE profile due to Osafune and Kimura [4]. The theoretical curve agrees with experiment quite well.

The calculated 0–0 transition energies for the ^{2}B and ^{2}A states are 10.36 and 10.76 eV, respectively, by the SD-CI calculation with the basis set II. In the theoretical curve of fig. 2, the first peak at 10.36 eV is due to the 0–0 transition of the ^{2}B state. On the other hand, since the value of the FCF of the ^{2}A state is negligibly small, we cannot find any peak near 10.76 eV corresponding to the 0–0 transition energy of the ^{2}A state.

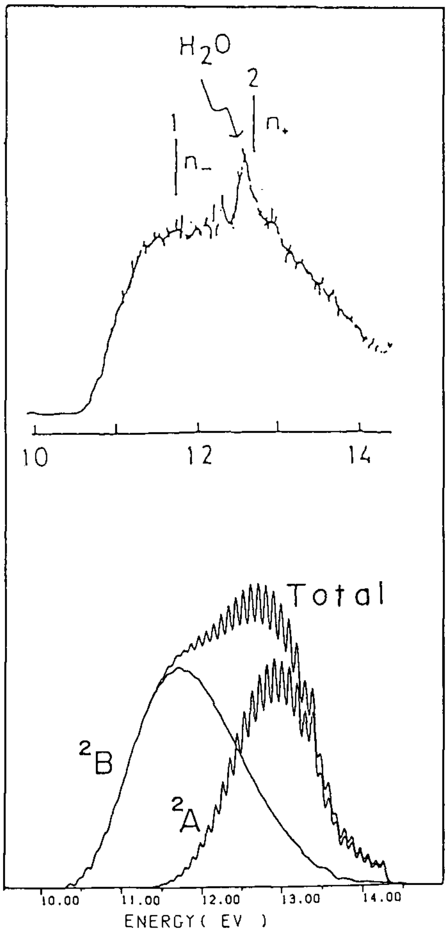

Fig. 2. The theoretical ionization pattern compared with the PE profile due to Osafune and Kimura [4]. Adiabatic ionization energies are calculated using the SD-CI calculation with basis set II. A harmonic force field for the calculation of the Franck–Condon factor is obtained by the SCF method with basis set II.

It is also apparent that the intensity contribution due to the ^{2}B state is distributed from 10.5 to 13.5 eV. The maximum peak is located near 11.6 eV which is in good agreement with the observed vertical ionization energy. On the other hand, the theoretical curve of the ^{2}A states starts from 11.5 eV and the maximum peak is around 13.0 eV.

Tables 5 and 6 contain the energy levels in order of the magnitude of FCFs for the ^{2}B and ^{2}A states. We find that the higher vibrational excitations of the

Table 5
Franck–Condon factors for the ^{2}B state

Quantum number (v_1 v_2 v_3 v_4)	Ionization energy (eV)	Franck–Condon factor
(0 0 3 5)	11.53	0.0168
(0 0 3 6)	11.65	0.0164
(0 0 3 4)	11.41	0.0162
(0 0 2 5)	11.34	0.0159
(0 0 2 4)	11.22	0.0154
(0 0 2 6)	11.46	0.0153
(0 0 3 7)	11.77	0.0151
(0 0 4 5)	11.73	0.0146
(0 0 3 3)	11.30	0.0143
(0 0 4 6)	11.84	0.0142
(0 0 2 7)	11.57	0.0140
(0 0 4 4)	11.61	0.0139
(0 0 2 3)	11.10	0.0137
(0 0 3 8)	11.89	0.0133
(0 0 4 7)	11.96	0.0132
(0 0 2 8)	11.69	0.0123
(0 0 4 3)	11.49	0.0122
(0 0 4 8)	12.08	0.0117
(0 0 3 9)	12.00	0.0113
(0 0 3 2)	11.18	0.0112
(0 0 1 5)	11.14	0.0109
(0 0 2 2)	10.98	0.0109
(0 0 5 5)	11.92	0.0108
(0 0 1 4)	11.03	0.0107
(0 0 5 6)	12.04	0.0107
(0 0 1 6)	11.26	0.0104
(0 0 2 9)	11.81	0.0104
(0 0 5 4)	11.80	0.0103
(0 0 4 9)	12.20	0.0100

Table 6
Franck–Condon factors for the ^2A state

Quantum number (ν_1 ν_2 ν_3 ν_4)	Ionization energy (eV)	Franck–Condon factor
(0 0 2 16)	12.64	0.0053
(0 0 2 17)	12.73	0.0053
(0 0 2 15)	12.54	0.0052
(0 0 3 16)	12.83	0.0052
(0 0 3 17)	12.92	0.0051
(0 0 2 18)	12.82	0.0051
(0 0 3 15)	12.74	0.0050
(0 0 3 18)	13.02	0.0049
(0 0 2 14)	12.45	0.0049
(0 0 2 19)	12.91	0.0047
(0 0 3 14)	12.65	0.0047
(0 1 2 16)	12.82	0.0046
(0 1 2 15)	12.73	0.0046
(0 0 3 19)	13.11	0.0046
(0 1 3 16)	13.02	0.0045
(0 1 3 15)	12.92	0.0045
(0 1 2 17)	12.91	0.0045
(0 1 2 14)	12.64	0.0044
(0 1 3 17)	13.11	0.0044
(0 1 3 14)	12.83	0.0044
(0 0 2 13)	12.36	0.0044
(0 0 2 20)	13.01	0.0043
(0 0 3 13)	12.55	0.0043
(0 1 2 18)	13.01	0.0042
(0 1 3 18)	13.20	0.0041
(0 0 3 20)	13.20	0.0041
(0 1 2 13)	12.54	0.0041
(0 0 4 16)	13.03	0.0041
(0 1 3 13)	12.74	0.0040
(0 0 4 17)	13.12	0.0040
(0 0 1 16)	12.44	0.0040
(0 0 1 17)	12.53	0.0040
(0 0 4 15)	12.93	0.0040

H–O–O–H torsional mode (ν_4) and the O–O stretching mode (ν_3) contribute to the intensities. This is connected with the large geometry change of the H–O–O–H dihedral angle and the O–O bond distance with ionization.

We observe distinct vibrational structure in the theoretical curve of the ^2B state. This is because of the relation among the frequencies of the ν_2, ν_3 and ν_4 modes where the frequencies of the ν_2 and ν_3 modes are almost same and twice that of ν_4.

4. Conclusion

The lowest ionic state ^2B is found to be most stable in the trans conformation. The second lowest is ^2A and is stable in the cis conformation. The estimated rotational barrier heights are 3.69 and 2.24 eV for the ^2B and ^2A states, respectively. These barriers are much greater than that of the ground state.

By the use of the Franck–Condon factors, the intensity curve of ionization is calculated theoretically. The theoretical intensity curve agrees quite well with the PE spectrum. The intensity distribution in the PE spectrum is interpreted as follows: The ionization due to the ^2B state contributes in the region from 10.5 to 13.5 eV and the maximum peak is near 11.6 eV. On the other hand, the ionization to ^2A starts near 11.5 eV and the maximum peak is around 13.0 eV. The calculated 0–0 transition energies for the ^2B and ^2A state are 10.36 and 10.76 eV, respectively. The higher vibrational excitations of the H–O–O–H torsional mode (ν_4) and the O–O stretching mode (ν_3) contribute to the intensities.

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