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Photoelectron Angular Distribution and Assignment of Photoelectron Spectrum of Ozone

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For the first three ionized states of ozone the ordering of $^2A_1$, $^2B_2$ and $^2A_2$ states has so far been controversial both experimentally and theoretically. The present work establishes assignment of the $^2A_2$ state by using the characteristic of electron energy dependence of an asymmetry parameter (β) of photoelectron angular distribution measured with NeI, HeI, and NeII resonance radiation. From measurements of photoelectron spectra of ozone with NeI, HeI, and HeII radiation, we newly find that two bands centered at 16.50 and 17.6 eV exhibit vibrational structures with the spacings of about 850 and about 1000 cm^{-1}, respectively. Furthermore abnormally weak bands are also confirmed at 22.7, 24.1, and 26.8 eV in the HeII spectrum.

Three studies of ozone by a high resolution VUV photoelectron (PE) spectroscopy have so far been reported in the literature,[1-3] except a work performed at a low resolution.[4] There appears disagreement concerning the identification of PE bands and vibrational spacings and orbital assignment of bands. For example, Frost *et al.*[1] and Brundle[2] reported four and five bands in the HeI spectrum, respectively, but Dyke *et al.*[3] identified eight bands including weak bands. Furthermore, Dyke *et al.* estimated the adiabatic ionization energy (IE) of the first band to be 12.44 eV, whereas other workers assigned it to 12.53,[1] 12.56[2] and 12.519 eV[5] as the corresponding value, respectively. For a vibrational structure of the third band at 13.57 eV, Frost *et al.* and Dyke *et al.* suggested that the bending mode is excited, but their values for the vibrational spacing are not equal. Brundle, on the other hand, concluded that the stretch mode is excited in the band.

We suppose that sources inducing the disagreement may be as follows; i) the sample of ozone was mainly contaminated with oxygen, ii) some PE bands due to ozone are weak and diffuse, and iii) the π biradical nature (predicted to be about 23% theoretically[6,7]) of the ground state of ozone makes the orbital assignment of bands difficult.

In order to explain the PE spectrum of ozone, various theoretical calculations[8-15] which go beyond the single-configuration SCF approximation have so far been carried out, but the calculated results are not always consistent, as described by Cederbaum *et al.*[13] Particularly for the first two PE bands at 12.75 and 13.02 eV,[3] the energy difference is so small that the assignment of the ionic states could not be deduced definitely even if the most reliable theoretical calculation is carried out. Therefore, Cederbaum *et al.*[13] and Maloquist *et al.*[15] calculated each vibrational structure of the first three PE bands to assign by comparison with the experimental PE bands. However, the calculated vibrational structures by them disagree for the $^2A_1$ and $^2B_2$ states and the proposed assignments also differ. In addition to the first three PE bands, observation of some shake-up or CI bands is predicted from the theoretical calculations taking account of configuration interaction (CI).

In the present study, we measured NeI, HeI, and HeII PE spectra at a high resolution using a very pure sample of ozone in order to establish the PE bands of ozone. For the first three PE bands, measurements of the photoelectron angular distribution parameter (β) were also carried out at NeI, HeI, and NeII radiation in order to determine the nature of their bands unambiguously by using the characteristics of the photon energy dependence of β.

Experimental

The photoelectron angular distribution of free molecules for unpolarized radiation is given by

$$J(\theta) \propto 1 + \frac{1}{2}\beta\left(\frac{3}{2}\sin^2\theta - 1\right) \tag{1}$$

where $J(\theta)$ is the photoelectron intensity, θ is the angle between the incoming photons and the outgoing photoelectrons, and β is the asymmetry parameter ranging between -1 and 2. In order to obtain β values, the photoelectron spectra were measured at θ=90° and 135° using NeI, HeI, and NeII radiation, with a photoelectron spectrometer (VG Scientific Ltd., model ADES-400), as described previously.[16,17] The energy resolution of about 120 meV was used to increase photoelectron counts and to measure in the short time for avoiding a variation of a sample pressure. On the other hand, NeI, HeI, and HeII spectra of ozone were recorded using a PE spectrometer (JASCO Ltd., model PE-1A) described elsewhere.[18] An energy resolution was about 25 meV for NeI and HeI spectra and about 70 meV for HeII spectrum. A full spectrum was usually measured with a scan voltage of 5 or 7 mV per one channel. Each of two PE spectrometers mentioned above was connected to a microcomputer system in order to control a scan voltage, a sample pressure and rotation of a turn table putting an analyzer for angular distribution measurement, automatically. Data were stored in a multichannel scaler and processed by use of a microcomputer (NEC COMPO BS/80) equipped with a floppy disk drive, an X-Y plotter and a printer. The multichannel scaler and the controller for driving pulse motors were home-made.

The ozone used in this work was produced from oxygen in a commercial ozonizer (NIPPON OZONE Ltd., type 0-1-2), stored by adsorbing on nonindicating silica gel at −196 °C (liq. N_2) and purified by pumping off oxygen. The glass vessel containing the adsorbed ozone, equipped with a teflon needle valve, was then connected to the spectrometer. The ozone was introduced into the spectrometer at the required pressure through the teflon needle valve, by raising the temperature of the vessel to about −80 °C by ethanol-liq. N_2. In the case of using the JASCO spectrometer, the ozone encounters no metal except for an ionization chamber coated by an aquadag, but little amount of the residual oxygen was measured all the time. In the case of using the VG spectrometer equipped with a stainless steel needle valve and a copper inlet tube, the decomposition of ozone was also found not to affect the value. Argon was used for the energy calibration.

Results

Figure 1A shows the HeI photoelectron spectrum of ozone obtained here which is partially contaminated by a little amount of the residual oxygen. The oxygen contamination was easily identified since more amount of oxygen was observed at early stage of measurement. Fig. 1C exhibits the PE spectrum of pure ozone obtained by subtracting the pure oxygen spectrum (Fig. 1B) from Fig. 1A. We tentatively classified the PE bands into two types by their intensities. Individual ionization bands in Fig. 1C are indicated by solid lines with the numerals or alphabet at their band maxima which correspond to vertical ionization energies. Numerals are used for the bands with normal intensity in the spectrum while alphabet is used for the abnormally weak band which must be shake-up or CI band.

The first three bands in the 12—14 eV region are known to exhibit complex vibrational structures. The interpretation of the vibrational spacing and the orbital assignmet for these bands have so far been controversial. Figure 2 shows the first three bands measured with a scan voltage of 1 mV per one channel. Then, analyses of the vibrational separations elucidate that there are three ionized states in the 12—14 eV region. Furthermore, the adiabatic IE value of the first ionized state is confirmed to be 12.43 eV as shown in Fig. 2, in agreement with the value of Dyke *et al.*3) The vibrational structures will be discussed in detail later.

It should be noted that the vibrational structure centered at 16.5 eV (band 4) is fairly resolved in this work, which was not reported in the previous papers.1—4) Figure 3 exhibits the expanded PE bands measured with a scan voltage of 1 mV, and there the two vibrational structures are identified with the spacings

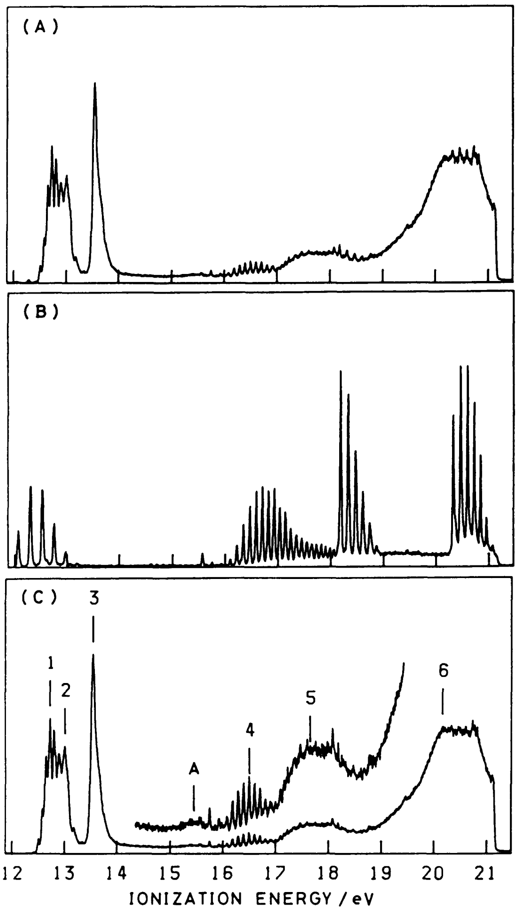

Fig. 1. HeI photoelectron spectrum of (A) ozone sample, (B) oxygen and (C) ozone obtaind by subtracting (B) from (A). Solid line indicates the maximum of the band.

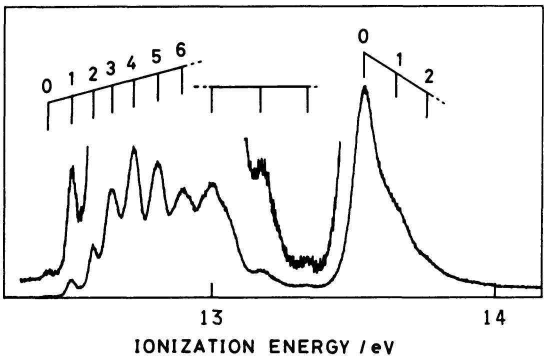

Fig. 2. Expanded scale spectrum of the first three bands 1 to 3 in the HeI spectrum of ozone.

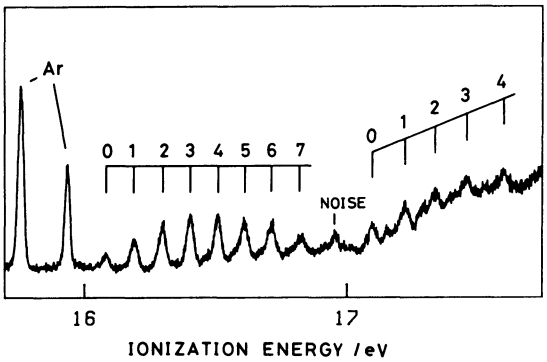

Fig. 3. Expanded scale spectrum of the bands 4 and 5 in the HeI spectrum of ozone.

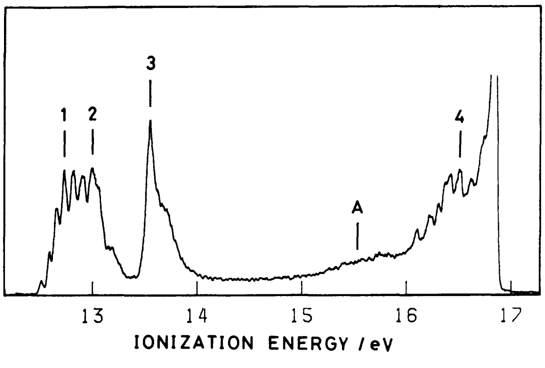

Fig. 4. NeI photoelectron spectrum of ozone.

TABLE 1. ASYMMETRY PARAMETER (β) AND ASSIGNMENT OF THE FIRST THREE PHOTOELECTRON BANDS OF OZONE

Experimental						Theoretical assignments		
				β value		References		
Band	I_v (eV)	Ionic state	NeI	HeI	NeII	[8,9,11,14]	[10,13]	[12,15]
1	12.73[a)]	1^2A_1	0.31	0.15	0.69	1^2A_1	1^2A_1	1^2B_2
2	13.00	1^2B_2	0.29	0.11	0.69	1^2B_2	1^2A_2	1^2A_1
3	13.54	1^2A_2	−0.31	0.10	0.87	1^2A_2	1^2B_2	1^2A_2

a) The adiabatic ionization energy is 12.43 eV.

TABLE 2. COMPARISON OF EXPERIMENTAL IONIZATION ENERGIES WITH THEORETICAL RESULTS FOR THE PE BANDS IN THE REGION BETWEEN 14 AND 28 eV

Experimental		Theoretical results[d)]	
Band	I_v (eV)	Ref. 14	Ref. 10
A	15.6	2^2B_2 15.19 (1.6)	$^2B_2$ 16.45 (1.2)
4	16.50[a)]	2^2B_1 17.17 (44.9)	$^2B_1$ 15.91 (44.4)
5	17.6[b)]	3^2A_1 18.20 (28.1)	$^2A_1$ 17.61 (39.3)
		4^2B_2 18.67 (15.6)	$^2B_2$ 19.02 (13.2)
			$^2B_2$ 19.40 (29.9)
6	19.4[c)]	5^2B_2 20.13 (6.4)	$^2A_1$ 20.34 (2.3)
		5^2A_1 20.35 (24.5)	$^2A_1$ 21.69 (6.2)
		6^2A_1 21.57 (2.5)	$^2B_2$ 22.08 (33.2)
	20.00	6^2B_2 21.65 (47.1)	$^2A_1$ 22.58 (14.4)
		5^2B_1 22.28 (42.6)	$^2B_1$ 22.95 (33.2)
	20.8[c)]	7^2B_2 22.42 (22.3)	$^2A_1$ 23.12 (22.9)
		7^2A_1 22.56 (31.9)	$^2A_1$ 23.84 (5.3)
B	22.7		
C	24.1		
D	26.8		

a) The adiabatic IE is 16.09 eV. b) The adiabatic IE is 17.10 eV. c) Shoulders of band 6. d) The ionic states and the I_v's (eV) are shown with the monopole intensities multiplied by one hundred in the parentheses.

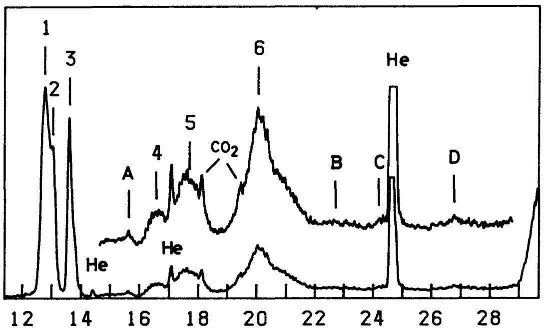

Fig. 5. HeII photoelectron spectrum of ozone.

of about 850 and 1000 cm^{-1}, respectively. The NeI spectrum shown in Fig. 4 also displays the vibrational structure near 16.5 eV although the spectrum is complicated by NeI (16.67 and 16.85 eV) resonance lines. The weak and diffuse band at 15.6 eV (band A) indicated by Dyke *et al.* could be also certified in the NeI and HeI spectra in this work. Concerning other bands, our HeI and NeI spectra are in good agreement with the previous ones.

The HeII spectrum of ozone shown in Fig. 5 is in fair agreement with that reported by Dyke *et al.*[3)] They however suggested only a very weak band at 24.7 eV (corresponding to the band C) in the region between 21 and 28 eV. As can be seen in Fig. 5, the bands B and D were found as well as the band C. The ionization energies determined in this work are listed in Tables 1 and 2.

Concerning photoelectron angular distribution, the experimental NeI and HeI β values for the first three bands are plotted against ionization energy in Fig. 6, together with the HeI spectrum obtained at θ=90°. The HeI β values for the three vertical IE peaks are commonly about 0.1, and the NeI β values for the first and second peaks are also about 0.3 similarly. However, the NeI β value (−0.31) for the third peak is quite different from those of them.

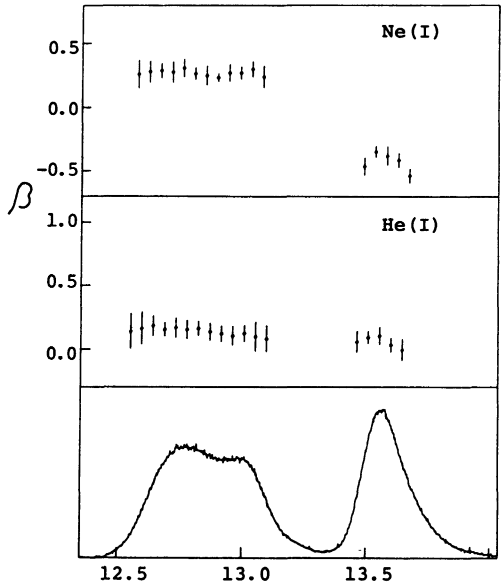

Fig. 6. Plots of experimental β values of ozone obtained for NeI and HeI radiation in the first three bands, and HeI photoelectron spectrum obtained at θ=90°.

Discussion

The PE Bands in the 12—14 eV Region. It is of no doubt from the PE spectra mentioned above that there are three bands in the 12—14 eV region. The assignment for the first three ionic states of ozone presents an interesting problem for theoretical

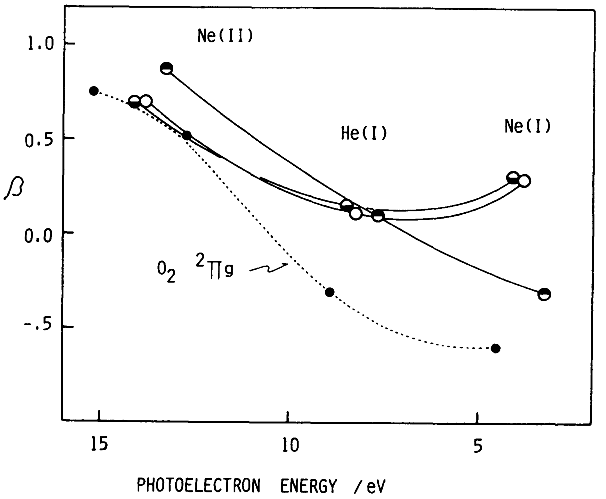

Fig. 7. Photoelectron energy dependence of β for (◒) band 1, (○) band 2 and (◓) band 3 of ozone and for (●) the $^2\Pi_g$ band of oxygen.

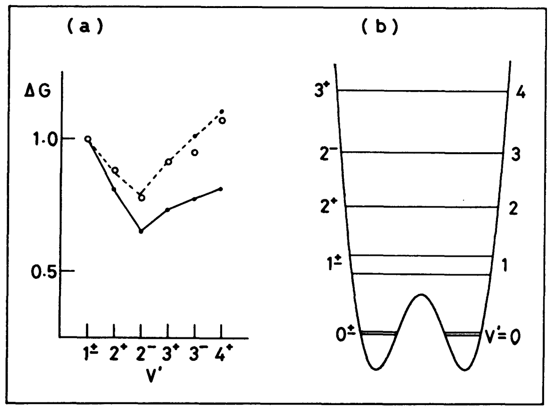

Fig. 8. (a) Plots of the relative vibrational spacing against vibrational quantum number for the first ionized state. Open circle shows the experimental value; solid line, the theoretical value taken from Ref. 23 in the case of $\rho=0.6$ and $B=1.2$; dotted line, corrected with anharmonicity. (b) Potential curve and vibrational levels in the case of solid line in (a).

treatments of correlation and/or reorganization effects. If Koopmans' theorem[19] is assumed, the order of increasing ionization energy would be $1a_2$ (13.24 eV), $6a_1$ (15.01 eV) and $4b_2$ (15.39 eV) from *ab initio* SCF MO calculation.[14] However, the order of the ionic states suggested previously by both experimental and theoretical studies is either the $^2A_1$, $^2B_2$, and $^2A_2$ state or the $^2A_1$, $^2A_2$, and $^2B_2$ state, predicting a breakdown of Koopmans' theorem because of the π biradical nature of the initial state.

The a_2 orbital of ozone consists of a simple combination of the p_π terminal oxygen orbitals and it is very similar to the $1\pi_g$ orbital of oxygen molecule. Our aim is to determine the a_2 orbital by using the characteristic of the photoelectron energy dependence of β. Fig. 7 shows plots of β values obtained at NeI, HeI, and NeII radiation for the three vertical IE peaks, together with that of β for the $v'=1$ peak of the $1\ ^2\Pi_g$ ionic state of oxygen molecule.[20,21] The peak of $v'=1$ for oxygen involves no autoionization effect at NeI radiation.[20] It is found from Fig. 7 that the β curve for the third peak of ozone has higher slope than those for others and is quite similar to that for the $^2\Pi_g$ state of oxygen molecule. Therefore, the third ionized state of ozone must be assigned to the $^2A_2$. Next problem is the order of the first two ionized states which should be either the $^2A_1$ and $^2B_2$ or the $^2B_2$ and $^2A_1$. It should be determined by analysis of the vibrational spacing.

Concerning the vibrational structure of the two bands in the 12—13.4 eV region, Fig. 2 exhibits easily distinguishable two vibrational progressions which consist of seven peaks in the low region of 12.43 up to 12.91 eV and three peaks in the high region of 13.00 to 13.34 eV. For the first progression, the relative vibrational spacing (ΔG) between the adjacent peaks from $v'=0$ up to 6 is irregular as shown by open circle in Fig. 8a, which exhibits the minimum value of 540 cm^{-1} at the third spacing and gradually increases toward higher quanta. The averaged separation is about 640 cm^{-1} and assigned to the bending mode, ν_2, which is 719 cm^{-1} in neutral ozone.[22] The irregular spacing obtained in this work is in good agreement with that reported by Dyke *et al.*[3] who suggested that the Renner-Teller effect contributes to the irregularity.

We investigated the irregular spacing on the basis of the double-minimum potential method proposed by Coon *et al.*[23] If parameters $\rho=0.6$ and $B=1.2$ are used, individual spacings are displayed by a solid line in Fig. 8a according to the notation of v' by Coon *et al.* Furthermore, the experimental spacings are better reproduced by taking account of an anharmonicity of $2X'h\nu(v'+1)$, as shown by dotted line in Fig. 8a. Then the estimated separation, $h\nu$, is 690 cm^{-1} and assigned to the bending mode ν_2. Figure 8b shows the double-minimum potential and the vibrational levels obtained here by use of $\rho=0.6$ and $B=1.2$. The barrier height at $\phi=180°$ (linear ozone) is about 830 cm^{-1} corresponding to about one vibrational energy. The positions of the minima give the angle of an equilibrium geometry of the ionized state of ozone. The angle was obtained as about 170° and is very different from that (116.8°) of the neutral ozone.[22] This fact clearly predicts that Franck-Condon factors between the ionized state and the neutral ground state do not reproduce the experimental results at all, in spite of the satisfactory reproducibility of vibrational spacing. As the result, we must conclude that the irregular spacing can not be explained by the model such as the Renner-Teller effect but possibly results from an anharmonicity such as some potential change near an equilibrium geometry of the cation.

For the second band, the peak at 13.00 eV displaying a shoulder in the high energy side allows us to predict the partial overlap of the progression belonging to the first band. The first two spacings between the adjacent peaks at 13.00 up to 13.34 eV are 1380 and 1330 cm^{-1}, respectively, and assigned to the symmetric stretch mode, ν_1 (1124 cm^{-1} in neutral[22]). The vertical IE value of the second ionic state is naturally assigned to be 13.00 eV. The adiabatic IE value however seems not to be the same as the vertical one because the spectral pattern of the first band exhibits such change as an increase of the background in the region above the peak of $v'=5$.

Concerning the third band at 13.54 eV, the vibrational structure is badly broadened but is still resolved as a faint structure. The broadening may be brought about by a predissociation5) as one of some possibilities. The averaged separation is about 900 cm^{-1}, being in better agreement with the value (900 cm^{-1}) of Brundle2) than that (800 cm^{-1}) of Dyke *et al.*3) The vibration may be assigned to the ν_1.

Considering the vibrational structure of the first three ionic states, the excitation of the bending mode must be due to ionization from the angle-determining a_1 orbital, so that the first band may be assigned to the $^2A_1$ state. Since the third band is assigned to the $^2A_2$ state from the result of the photoelectron angular distribution, the second band must be the $^2B_2$ state. Experimental asymmetry parameters and assignment for these bands are summarized in Table 1 in comparison with theoretical assignments.

The PE Bands in the 14—28 eV Region. The bands observed in the region above 14 eV can be classified into two types by their intensities. First, the bands 4—6 with normal intensity are obtained at 16.5, 17.6, and 20.0 eV, respectively, and secondly, the CI bands *A—D* with abnormally weak intensity appear at 15.6, 22.7, 24.1, and 26.8 eV, respectively. In order to interpret these bands, we consider it most useful to refer to available theoretical results calculated by *ab initio* CI methods.10,14) Their results are compared in Table 2. The theoretical calculations by Basch10) and Kosugi *et al.*14) presented both the ionization energies and the monopole intensities which wholly seem to be in good agreement with the experimental results.

Let's consider the bands 4 and 5. According to the calculated results by Refs. 10 and 14, the band 4 corresponds to the $^2B_1$ ionic state. As can be seen from Fig. 3, this band has the vibrational spacing of about 850 cm^{-1} of which value is almost constant over the eight vibrational peaks. Hence, the vibration may be predicted to be the stretch mode ν_1 weakened by ionization from the strong bonding orbital of $1b_1$, rather than a bending mode. The band 5 exhibits a faint vibrational structure of about 1000 cm^{-1} associated with stretch mode in the low energy region, as shown in Fig. 3. The band seems to consist of overlapping bands due to two ionized states at least since it is broad and intense. This expectation is in good agreement with the theoretical results, one of which predicts two ionized states of $^2A_1$ and $^2B_2$, as listed in Table 2.

The band 6 centered at 20.00 eV exhibits two shoulders at 19.4 and 20.8 eV. According to the theoretical results, this band must correspond to many ionized states. Two theoretical results available are not consistent with each other and definite assignment of this band will be also impossible experimentally.

Concerning the abnormally weak CI bands, the band A at 15.6 eV may be assigned to the $^2B_2$ state as predicted by the theoretical results.10,14) The other CI bands B—D must be interpreted by some theoretical calculations involving configuration interaction.

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