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Photoelectron Angular Distribution for Jahn-Teller Split Bands of Some Molecules in VUV Photoelectron Spectroscopy

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Measurements of photoelectron angular distribution were carried out with NeI and HeI resonance lines for Jahn-Teller split bands of methane, ethane, cyclopropane, neopentane, tetramethylsilane, carbon tetrachloride, and ammonia. The variation of an asymmetry parameter β across the band is presented. Significant β variations across the Jahn-Teller split bands due to the 1^2T_2 states of $C(CH_3)_4^+$ and CCl_4^+ could not be explained in terms of photoelectron energy dependence of β. These abnormal variations will be discussed on the basis of characteristics of the degenerate molecular orbitals split by the Jahn-Teller effect.

Ejection of an electron from a fully occupied degenerate orbital in a molecule induces an orbitally degenerate doublet state of the corresponding ion. The degeneracy of such a state can be removed by a spin-orbit coupling and/or the Jahn-Teller (J-T) effect. The Jahn-Teller effect means that a molecule in a degenerate electronic state is unstable toward distortions that lower the molecular symmetry, thereby removing the electronic degeneracy. The J-T split bands in molecular photoelectron spectroscopy are well known and we can see some typical examples in fundamental molecules as summarized by Rabalais.[1] Interestingly two evidences called the static and dynamic Jahn-Teller effects are distinguished for convenience. The static Jahn-Teller effect means that the distorted molecule has a permanent distortion that lowers its symmetry and that the interaction between the electronic and vibrational motions may be very small. The dynamic Jahn-Teller effect refers to the coupling of the electronic and vibrational motions. The difference between these Jahn-Teller effects should be discriminated by analyzing the appearance of the J-T active vibrational modes and the magnitude of the J-T energy splitting.

On the other hand, measurement of photoelectron angular distribution gives important and valuable information on the electronic structure of a molecule and on the coupling between electronic and vibrational motions. The former information gives correlation between the nature (σ or π types) of ionized molecular orbital and the value of β, an asymmetry parameter,[2-10] and has so far been used to confirm the orbital assignments of photoelectron (PE) spectra for many large molecules by several workers.[11-25] The latter information mainly associated with shape resonances has demonstrated several aspects of photoionization processes.[26-29] Photoelectron vibrational structures obtained with line sources such as NeI and HeI resonance lines are typically well represented by the Franck-Condon (F-C) factors between vibrational wavefunctions of the ground and ionic states, and generally give the same photoelectron angular distribution. Deviations are the exception and are usually attributed to many-electron interactions with an intermediate and autoionizing state. However shape resonances which lead to the temporary trapping of photoelectrons by a centrifugal barrier enhance the coupling between electronic and nuclear motions and the effects are large in both vibrational intensities and angular distributions. Therefore, when there is no autoionization process in the vicinity of shape resonances, the effects of shape resonance on PE bands induce non-Franck-Condon vibrational intensity distribution and the vibration-dependent angular distribution. Experimental confirmation of non-F-C intensity distribution was reported for the 5σ levels of CO[26] and for the $3\sigma_g$ level of N_2.[28] Experimental confirmation of the v-dependent angular distribution has also been reported for N_2,[27,30,31,33,35-38] CO,[29,34-37,39] O_2[31,35,37] and CO_2.[32,35,36,40] Most measurements of vibrationally resolved angular distributions have been restricted to the single HeI wavelength,[30-36] so that energy-dependence effects could not be confirmed.

In relation to the dependence of β on vibrational structures, it is of interest to know how β values for J-T split bands depend on geometrical distortions of individual components of the final state. Photoelectron angular distribution measurements have been so far reported for J-T split bands of some molecules.[11,12,18,19,41] Carlson and White reported for the first time that the HeI β values of components for each of J-T split bands in halomethanes are essentially equal to one another.[11] Leng and Nyberg pointed out that this fact is also true in cases of cyclopropane and allene.[18,19] Sell and Kuppermann have found the monotonic change of β across band II in SF_6[41] but concluded that the β variation is typical of general photoelectron energy dependence.[7]

Focusing on the problem about the β variation across the J-T split band, we carefully measured photoelectron angular distributions for various J-T split bands of several molecules.

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. Therefore, the β values of individual bands were calculated from PE spectral data obtained at two angles of 90° and 135° with the following expression derived from Eq. 1

$$\beta = 8(R-1)/(R+2) \tag{2}$$

where $R=J\,(90°)/J\,(135°)$.

Measurements of photoelectron angular distribution were carried out with a photoelectron spectrometer (VG Scientific Ltd., model ADES-400), as previously described elsewhere.[24] The PE spectrometer was connected to a microcomputer (NEC COMPO BS/80) system, in order to automatically control a scan voltage, a sample pressure and rotation of a turn table putting an analyzer. The PE spectra obtained were stored temporarily in a multichannel scaler (16bits×4K channels) and preserved in a floppy disk for calculating β values later. The multichannel scaler and controllers were home-made. Each β value of the spectral data was evaluated with Eq. 2 after subtracting the background and correcting the energy shift between the data obtained at 90° and 135°.

Since the β values obtained by an angular-dispersive PE spectrometer often contain a systematic error because of the various experimental problems, the systematic error must always be assessed in order to determine the most accurate values. Therefore we measured the β values for the PE bands of Ar, Xe, N_2, O_2, and CO_2 as a check on a calibration before and after measurements of samples in question. For these calibration gases, plots of our experimental raw β values against the corresponding ones taken from Ref. 36 exhibit a linear relationship in the range between -1 and 2, as shown in Fig. 1. Therefore all β values presented in this work were corrected by using such linear relationship. Furtheremore, standard deviations of the β values were found to be less than 0.03 under our experimental conditions. Energy resolutions used here were about 55 and 120 meV in a full width at half maximum of the peak ($^2P_{3/2}$) of Ar.

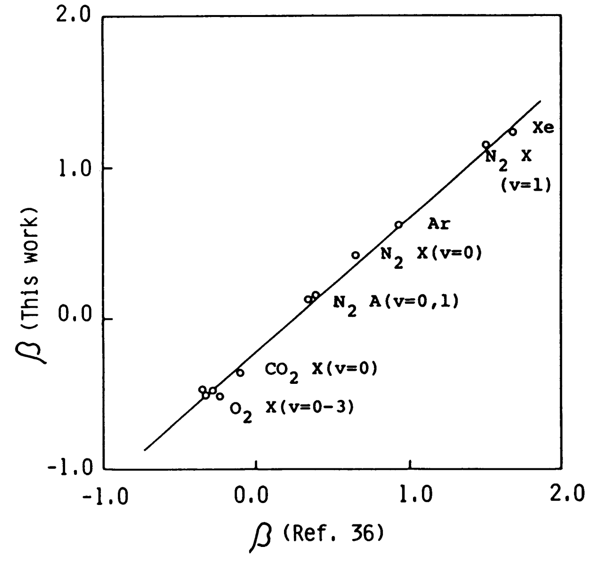

Fig. 1. Plot of our experimental raw β values of PE bands for calibration gases against those taken from Ref. 36.

The samples used here are methane, ethane, cyclopropane, neopentane, tetramethylsilane, carbon tetrachloride and ammonia. Methane and ethane were purchased from Gascro Kogyo K. K., neopentane and tetramethylsilane from Tokyo Kasei K. K., and cyclopropane from Takachiho Kagaku Cogyo K. K. All gaseous chemicals were about 99.5% pure. Ammonia was dehydrated by use of the drying agent of CaO, and the others were used without further purification.

Results

Plots of β values against ionization energies are shown in Figs. 2—8 for the PE spectra of the molecules mentioned above, together with the HeI spectra obtained at θ=90°. Each value of β is the mean value for eleven channels' and the error bar indicates the standard deviation. The experimental NeI and HeI β values for various bands are summarized in Table 1, together with assignments of the ionic states and the available data.

The PE spectrum of methane (Fig. 2) consists of three components of the 1^2T_2 state split by the J-T effect.[42] The HeI β value for each of the components is found to be almost the same. On the other hand, the NeI β values decreases monotonically above 15 eV. However, considering the vicinity to the threshold and the background of slow electrons, this variation of the NeI β value cannot be verified definitely. Our NeI and HeI β values are slightly larger than those of Carlson *et al.*[43] and Marr and Holmes.[44] However, it may be concluded that no significant variation of the HeI β across the J-T split band was observed in agreement with the result of Carlson *et al.*[43]

The PE spectrum of ethane (Fig. 3) consists of the 1^2E_g, 1^2A_{1g}, and 1^2E_u ionic states.[42] There are three band maxima in the 11.5—14.5 eV region which were assigned to the 1^2E_g and 1^2A_{1g} states although the order of their states has been controversial. To our knowledge, no data of β values for these bands have ever been published. It has been expected that the order of the 1^2A_g and 1^2E_g states might be determined from photoelectron angular distribution measurements. However, the order could not be identified clearly since, as can be seen from Fig. 3, no definite difference among β values for these maxima was observed at both NeI and HeI radiations. Nevertheless it may be concluded that there is no variation of β across the J-T split band of the 1^2E_g state. The PE band assigned to the 1^2E_u state in the region of 14.5 to 16.5 eV exhibits two maxima due to the J-T splitting. The HeI β variation across the band seems to slightly decrease toward higher ionization energy (*ca.* 0.05/eV) while the NeI β variation is steep but it is not certain owing to the vicinity to the threshold.

The PE spectrum of neopentane (Fig. 4) in the 10-17 eV region consists of four bands due to ionization from the $4t_2$, $1t_1$, 1e, and $3t_2$ orbital.[42] All these bands display the J-T splittings as discussed by Jonas *et al.*[12] Concerning the β variation across each of the

Table 1. Experimental asymmetry parameters for Jahn-Teller split bands of various molecules

Molecule	Ionic State[a]	I_v/eV[a]	NeI photon[b] E_e/eV	NeI photon[b] β	HeI photon[b] E_e/eV	HeI photon[b] β
CH_4		13.6[c]	3.25	0.59	7.62	0.72
$[T_d]$	1^2T_2	14.5	2.35	0.57	6.72	0.71 (0.6)[d]
		15.2	1.65	0.44	6.02	0.74
C_2H_6	1^2E_g	11.99	4.86	0.14	9.23	0.22
$[D_{3d}]$		12.70	4.15	0.10	8.52	0.21
	1^2A_g	13.5	3.35	0.11	7.72	0.21
	1^2E_u	15.15	1.70	0.36	6.07	0.57
		15.9	0.95	0.16	5.32	0.54
C_3H_6	$1^2E'$	10.60	6.25	(0.35)[e]	10.62	0.42 (0.60)[e]
$[D_{3h}]$		11.30	5.55	(0.40)	9.92	0.33 (0.50)
	$1^2E''$	13.0	3.85	(0.28)	8.22	0.23 (0.43)
$C(CH_3)_4$	1^2T_2	10.90	5.95	0.29	10.32	0.27
$[T_d]$		11.41	5.44	0.33	9.81	0.34 (0.7)[d]
		11.9	4.95	0.27	9.32	0.42
	1^2T_1	12.55	4.30	−0.12	8.67	0.36
		12.9	3.95	−0.15	8.32	0.37 (0.7)
		13.2	3.65	—	8.02	—
	1^2E	13.93			7.29	0.71 (0.9)
		14.3			6.92	0.72
	2^2T_2	15.24			5.98	0.56
		15.6			5.62	0.52 (0.9)
		15.9			5.32	—
$Si(CH_3)_4$	1^2T_2	10.29[f]	6.56	−0.02	10.93	0.33
$[T_d]$		10.62	6.23	−0.06	10.60	0.33 (0.4)[d]
		10.9	5.95	−0.08	10.32	0.34
	1^2T_1	12.7	4.15	−0.02	8.52	0.39 (0.4)
		12.9	3.95	—	8.32	—
	2^2T_2	13.8			7.42	—
		14.1			7.12	0.59 (0.6)
	1^2A_1	14.5			6.72	—
	1^2E	15.6			5.62	0.64 (0.8)
CCl_4	1^2T_1	11.69[g]	5.16	(0.28)[h]	9.53	0.42 (0.54)[h]
$[T_d]$	1^2T_2	12.44	4.41		8.78	0.71
		12.65	4.20	(0.65)	8.57	0.79 (0.74)
		12.78	4.07		8.44	0.82
	1^2E	13.37	3.48	(0.50)	7.85	0.57 (0.55)
		13.50	3.35		7.72	0.57
	2^2T_2	16.58			4.64	0.00 (0.00)
NH_3	$1^2A'$	10.85			10.37	1.18 (0.82)[i]
$[C_{3v}]$	$1^2E'$	15.8			5.42	0.47 (0.21)
		16.5			4.72	0.44

a) Taken from Ref. 42 unless other comments are made. I_v indicates the ionization energy for each peak in the band. b) E_e is the photoelectron kinetic energy. NeI and HeI photon energies are 16.85 and 21.22 eV, respectively. c) Ref. 48. d) Ref. 43. e) Ref. 19. f) Ref. 12. g) Ref. 49. h) Ref. 45. i) Ref. 35.

four bands, significant variations were observed for the first and fourth bands but no variations for the second and third bands, as can be seen in Fig. 4. The HeI β variation across the first band (1^2T_2) (Fig. 5) was found to increase monotonically toward higher ionization energy (*ca.* 0.15/eV). This variation seems to be also realized even in the NeI β variation. In Fig. 4, NeI β plots for the first and second components for the 1^2T_2 band split by the J-T effect increase gradually, but that for the third component decreases suddenly by the overlap effect of the small β value of the second band (1^2T_1). The HeI β variation across the fourth band (2^2T_2) is seen to decrease in contrast with that for the first band. The NeI β variation across the 2^2T_2 band is uncertain as well as that of the third band (1^2E) owing to the vicinity of the threshold and the background of slow electrons. Our HeI β values obtained here are considerably small in comparison with those of Jonas *et al.*[12] It may be concluded that the first and fourth bands show the significant β variations.

Figure 6 shows the PE spectrum of $Si(CH_3)_4$ and NeI and HeI β plots for PE bands in the region of 10 to 16eV. The HeI β values are in good agreement with those reported by Jonas *et al.*[12] This molecule is interesting by virtue of the similarity to $C(CH_3)_4$. Concerning the variation of β across the first band due

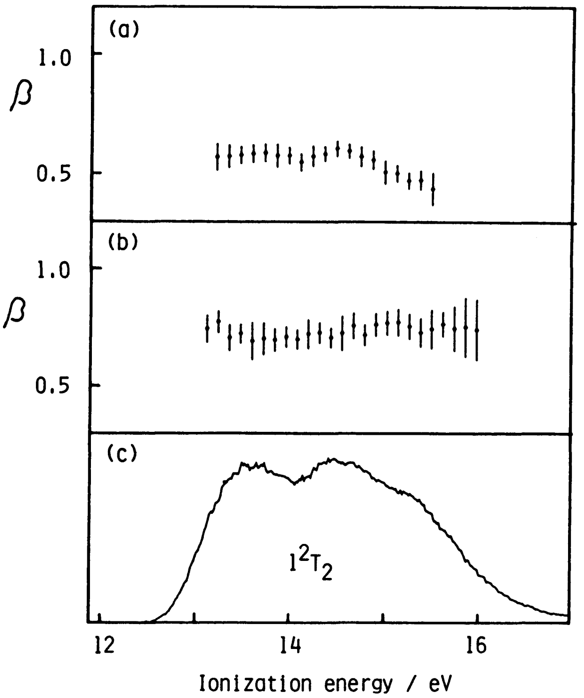

Fig. 2. Plots of β values of methane obtained with (a) NeI and (b) HeI photons and (c) HeI PE spectrum at θ=90°.

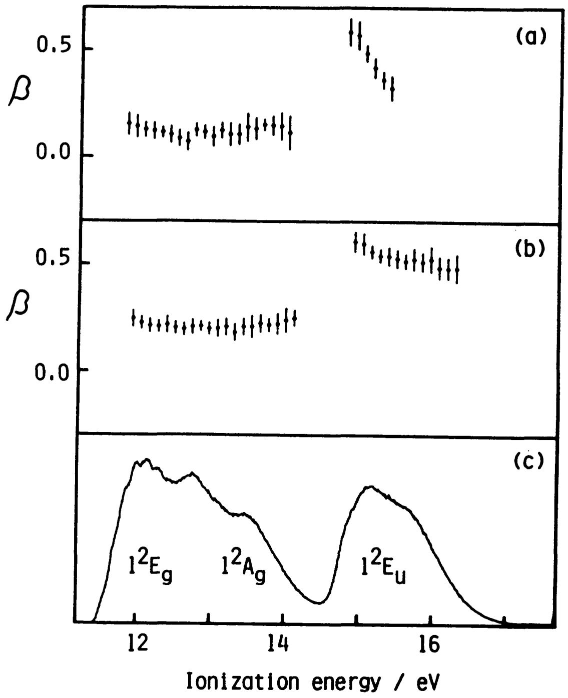

Fig. 3. Plots of β values of ethane obtained with (a) NeI and (b) HeI photons and (c) HeI PE spectrum at θ=90°.

to the 1^2T_2 state, the HeI β plot shows no variation but the NeI β plot a significant variation. Variations of β for the other bands were uncertain because the PE bands are heavily overlapped with each other.

Carbon tetrachloride has the same valence electronic structure as neopentane. Orbital assignments of the PE spectra (Figs. 7A and 7B) are well known and the first four bands are assigned to the 1^2T_1, 1^2T_2, 1^2E, and 2^2T_2 states, respectively.[42] The second (1^2T_2) and third (1^2E) bands show the J-T splittings. The HeI β values for these four bands have so far been reported by Carlson and White[11] and Carlson *et al.*[45] who have not taken account of β variation across each of the bands. Our HeI β values for the four bands are in good agreement with those of Carlson *et al.*[45] It is found from Figs. 7A and 7B that the β variations exist definitely for the 1^2T_2 and 2^2T_2 bands but no significant variation for the other bands. Carbon dioxide and argon shown in Figs. 7A and 7B, respectively, were used as an internal standard to check and correct energy shifts between the spectra obtained at 90° and 135°. The correction was performed by making the β values for the peak of the the internal standard flat.

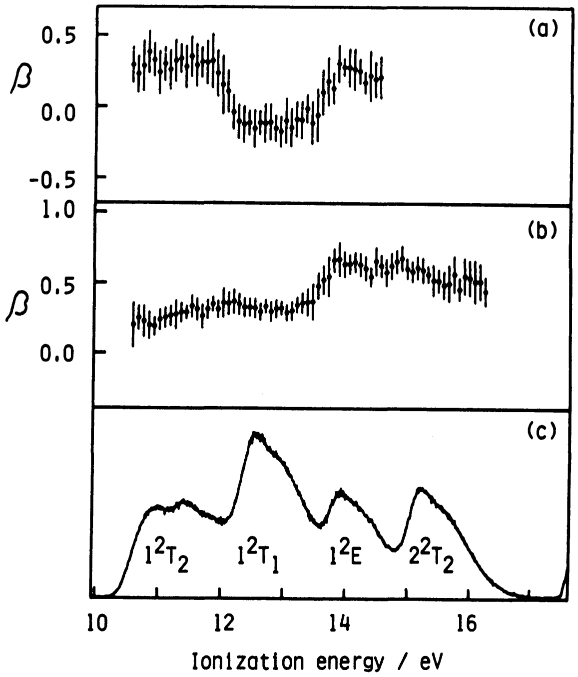

Fig. 4. Plots of β values of neopentane obtained with (a) NeI and (b) HeI photons and (c) HeI PE spectrum at θ=90°.

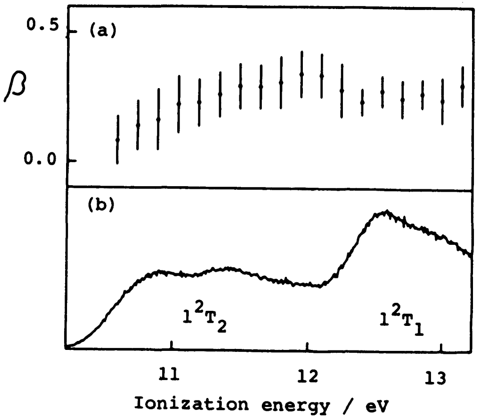

Fig. 5. Plot of HeI β values of the first band of neopentane and HeI PE spectrum obtained at θ=90°.

For the PE spectrum of ammonia, the second band assigned to the $1^2E'$ ionic state exhibits the J-T splitting

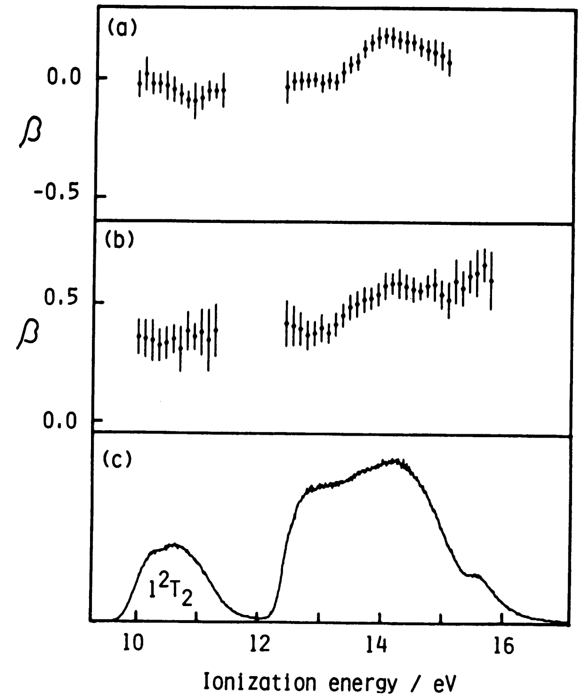

Fig. 6. Plots of β values of $Si(CH_3)_4$ obtained with (a) NeI and (b) HeI photons and (c) HeI PE spectrum at $\theta=90°$.

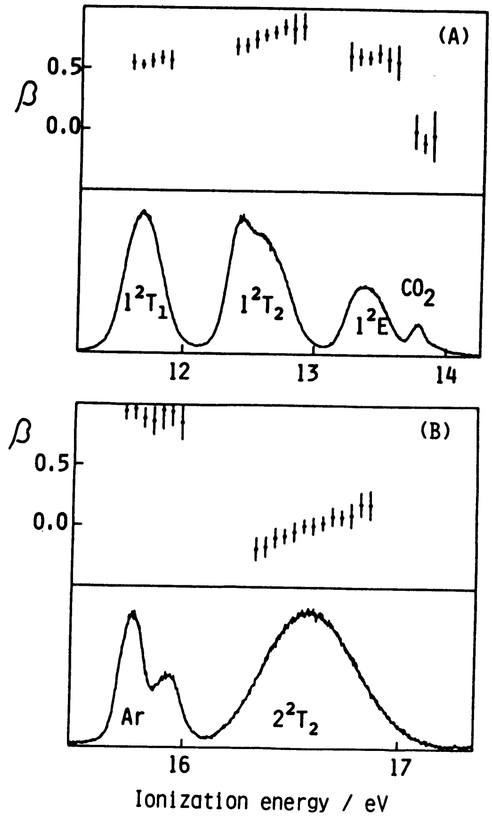

Fig. 7. Plots of HeI β values and HeI PE spectra obtained at $\theta=90°$ for (A) the first three bands of CCl_4 and (B) the fourth band of CCl_4.

of about 0.7 eV.[42] The HeI β variation across the band is flat as shown in Fig. 8A. Our HeI β values obtained here are higher by about 0.3 than those of Hancock and Samson.[35]

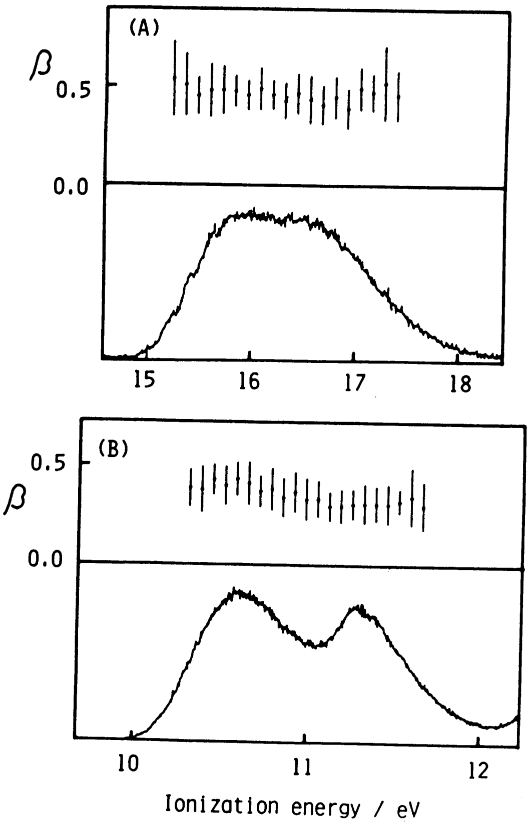

Fig. 8. Plots of HeI β values and HeI PE spectra obtained at $\theta=90°$ for (A) the second band of ammonia and (B) the first band of cyclopropane.

For the PE spectrum of cyclopropane (Fig. 8B), the first band ($1^2E'$) having two peaks shows the relatively large splitting (0.7 eV) by the J-T effect.[42] Leng and Nyberg[19] have reported a significant variation of β across the band. We also confirmed the same variation although our HeI β values obtained here are slightly lower than those of Leng and Nyberg, as listed in Table 1.

Discussion

The asymmetry parameter basically depends on two factors; the kinetic energy of the photoelectron and the nature of the molecular orbital from which the photoelectron is ejected. When considering variation of β across a band, it must be checked whether the variation is analogous to the photoelectron energy dependence. The energy dependence of β for various bands is shown in Fig. 9 by using the experimental NeI and HeI β values. Here, the energy dependence was assumed to be linear in the region of NeI to HeI photon energies. This assumption seems to be valid from the fact that the energy separation between the two photon energies is relatively small. For example, the energy dependence of β obtained with synchrotron radiation[45] is nearly linear for each of the four bands of CCl_4, as shown in Fig. 9. Consequently it may be noted from Fig. 9 that the energy dependence of β for

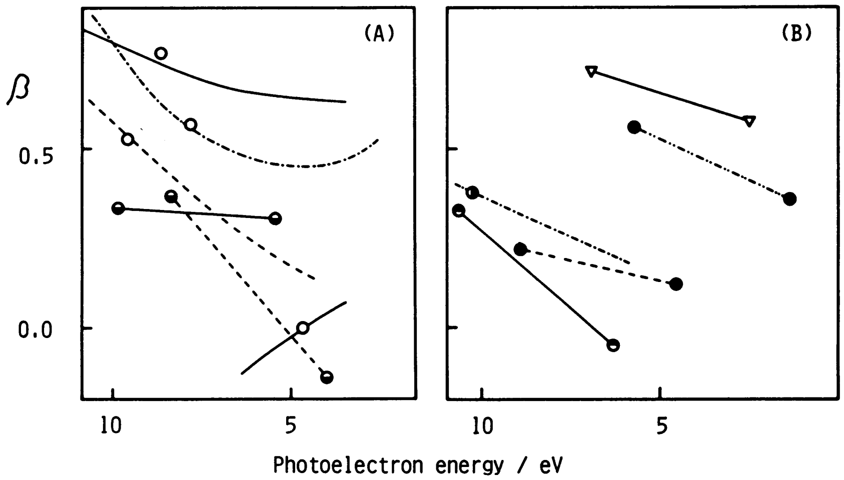

Fig. 9. Photoelectron energy dependence of β in the region of NeI and HeI photons for (A) CCl_4 (○) and neopentane (◒); $^2T_2$ (——), $^2T_1$ (----), and ^2E (-·-·-·), and (B) 1^2T_2 (—▽—) of methane, $1^2E'$ (-·-◑-·-) of cyclopropane 1^2E_{1g} (--●--) and 1^2E_{1u} (-··-●-··-) of ethane, and 1^2T_2 (—◓—) of TMS.

each of the bands discussed in this work decreases commonly toward lower photoelectron energy, except for that of the 2^2T_2 band of CCl_4.

Figure 10 shows the degree of variation of HeI β with the J-T splitting for each of the J-T split bands in question. Then, it is found that the trend of β variations for the 1^2T_2 band of CCl_4 and the 1^2T_2 band of $C(CH_3)_4$ is certainly different from the energy dependence of β as shown in Fig. 9. The β variations for the other bands are very small or similar to the tendency of the energy dependence. The variations of β across the vibrational envelopes of π bands for various unsaturated hydrocarbons[2,7,8] and across the J-T split bands of some molecules[11,19,41] have been so far reported. Most of the β variations were interpreted in terms of the photoelectron energy dependence. In this sense, β variations for the 1^2T_2 bands of CCl_4 and $C(CH_3)_4$ cannot be explained in terms of the energy dependence. Here we tried to consider the abnormal β variation on the basis of characteristics of the ionized molecular orbitals.

The asymmetry parameter for an atom is given as a function of the quantum number (l) of an orbital angular momentum of an ionized orbital,[46] and it may be generally recognized that the larger the value of l is, the lower the β value. For molecular orbitals (MOs), the value of l is usually a poor quantum number. An MO (ψ_j) is expanded in terms of the spherical harmonics Y_{lm} (θ,ϕ),[13,47]

$$\Psi_j(r,\theta,\phi) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} C_{lm}(r)Y_{lm}(\theta,\phi), \tag{3}$$

$$C_{lm}(r) = \iint Y_{lm}^{*}(\theta,\phi)\Psi_j(r,\theta,\phi)\sin\theta \mathrm{d}\theta \mathrm{d}\phi, \tag{4}$$

where C_{lm} (r) is the expansion coefficient, depending on the character of the MO and on a position of the origin of the one-center expansion. If the molecule has a center of symmetry, it is reasonable to select the center as the origin. The most probable value of l is that one corresponding to the maximum value of $|C_{lm}|^2$ integrated over r. We abbreviate $|C_{lm}|^2$ to C_{lm}^2 hereafter. The C_{lm}^2 value for each component of the degenerate MO in the ionic state is the same but the values for the individual MOs lifted by the J-T effect should be different from each other. A significant variation of β across the J-T split band should be attributed to the value of l or the value of C_{lm}^2 for the corresponding MO.

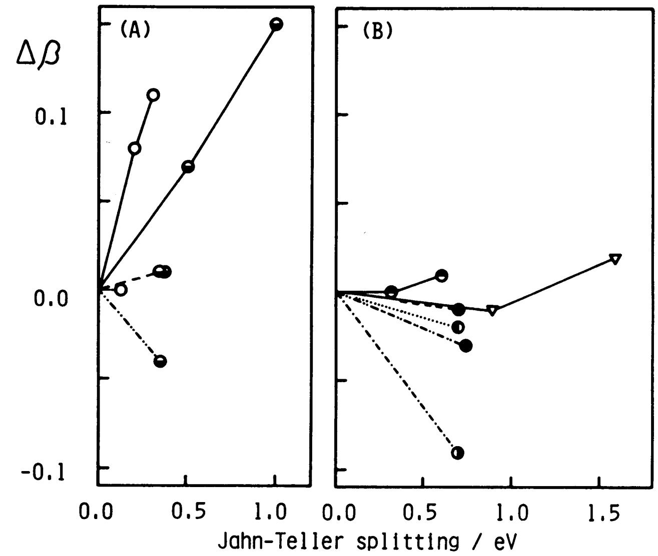

Fig. 10. Degree of β variations against Jahn-Teller splittings for (A) 1^2T_2 (—○—) and 1^2E (····○····) of CCl_4^+ and 1^2T_2 (—◒—), 1^2T_1 (--◒--), 1^2E (---◒---), and 2^2T_2 (-··-◒-··-) of $C(CH_3)_4^+$, and (B) 1^2T_2 (—▽—) of methane, 1^2T_2 (—◓—) of TMS, $1^2E'$ (-·-◑-·-) of cyclopropane, $1^2E'$ (····◐····) of ammonia, and 1^2E_{1g} (--●--) and 1^2E_{1u} (-··-●-··-) of ethane.

In this sense, we calculated the values of C_{lm}^2 integrated over r to determine the most probable values

Table 2. The largest two values of C_{lm}^2 for MO of the individual components in the J-T split 1^2T_2 state of CH_4^{+}[a)]

MO level[b)]	Td		Type I		Type I′		Type IV	
/eV	$l=1$	$l=2$	$l=1$	$l=2$	$l=1$	$l=2$	$l=1$	$l=2$
I_1 13.6	0.892	0.077	0.870	0.094	0.870	0.089	0.876	0.090
I_2 14.5	0.892	0.077	0.896	0.071	0.896	0.071	0.885	0.080
I_3 15.2	0.892	0.077	0.908	0.064	0.901	0.070	0.908	0.060

a) Concerning Types I, I′, and IV, see text. b) The values are the experimental ionization energies.

Table 3. The values of C_{lm}^2 for MOs of individual components in various J-T split states of CCl_4^+

Ionic state	MO level[a)] /eV	Theoretical values of C_{lm}^2 $l=1$	$l=2$	$l=3$	$l=4$	$l=5$
	I_1			0.590	0.212	
1^2T_1	I_2 11.69			0.610	0.203	
	I_3			0.617	0.203	
	I_1 12.44	0.267	0.208	0.071	0.260	
1^2T_2	I_2 12.65	0.272	0.188	0.065	0.273	
	I_3 12.78	0.277	0.177	0.058	0.288	
1^2E	I_1 13.37		0.589		0.107	0.199
	I_2 13.50		0.597		0.094	0.202
	I_1	0.477	0.252	0.103		
2^2T_2	I_2 16.58	0.469	0.261	0.106		
	I_3	0.468	0.272	0.108		

a) The values are the experimental ionization energies.

of l for the MOs corresponding to the J-T split components in the $^2T_2$ state of CH_4^+. The values of l and m used for this expansion were from 0 to 6 and 0 to 4, respectively. The normalized condition was completely satisfied within these limitations of l and m. The calculated results are listed in Table 2. We used the MOs obtained in Types I, I′, and IV described in Ref. 48 as the J-T distorted geometries of CH_4^+. It is found from Table 2 that the most probable l value for each of the MOs is 1. Concerning the values of C_{lm}^2 for $l=1$, those of the degenerate MOs (Td) are equal to one another whereas each of the split MOs' is not the same and increases with increase of the ionization energy. The variation of β may be attributed to this slight variation of C_{lm}^2 (about 0.03).

The calculation of the MO expansion for CCl_4^+ was also carried out. The molecular orbitals obtained in Type I were used for CCl_4^+.[50)] The calculated results are listed in Table 3. The normalized condition was almost completely (90%) satisfied. It is found that the most probable l values for the 1^2T_1, 1^2E, and 2^2T_2 states are 3, 2, and 1, respectively. However, the most probable value for the second state (1^2T_2) cannot be determined because the C_{lm}^2 values for $l=1$, 2, and 4 are close to one another. The difference of the C_{lm}^2 values among the J-T split MOs in the individual ionic states is commonly slight (0.03) as shown in Table 3. If experimental β values can be estimated on the basis of the weighted average on the theoretical β values for the quantum numbers (ls) obtained from the one-center expansion method, it may be noted that the more the number of ls inducing significant variations of the C_{lm}^2 values is, the larger the variation of β. Considering that the abnormal variation of β appears only in the second PE band of CCl_4, the interpretation in terms of the variation of the C_{lm}^2 value seems to be consistent with the experimental results.

As another appraoch, we calculated radial distributions ($4\pi r^2\psi^2$) of the degenerate MOs of neutral molecules to predict the β variations in the approximation of Koopmans' theorem. This is to compare distribution patterns of the MOs for the bands showing β variations with those of the MOs for the bands showing no β variation. This comparison is more useful for the intramolecular bands than the intermolecular bands. Figure 11 shows the radial distributions of the degenerate orbitals for CH_4, NH_3, and $C(CH_3)_4$, the centers of the molecules being taken at C and N atoms. The β variations for the 1^2T_2 state of CH_4^+ and for the $1^2E'$ state of NH_3^+ are very small although the magnitude of the J-T splittings are considerably large. The β variations for the 1^2T_1 and 1^2E states for $C(CH_3)_4^+$ are also very small. The radial distributions for these states exhibit the pattern which consists of a single peak. On the other hand, the β variation for the 1^2T_2 state of $C(CH_3)_4^+$ is abnormal, and the radial distribution for this state shows the pattern which consists of two peaks. This pattern is quite different from those for the $^2T_1$ and ^2E states of this molecule. The radial distribution pattern for the 2^2T_2 state, which consists of one shoulder and one peak, is closer to that for the 1^2T_2 rather than those for the $^2T_1$ and ^2E states although the variation of β for the 2^2T_2 band is not so remarkable.

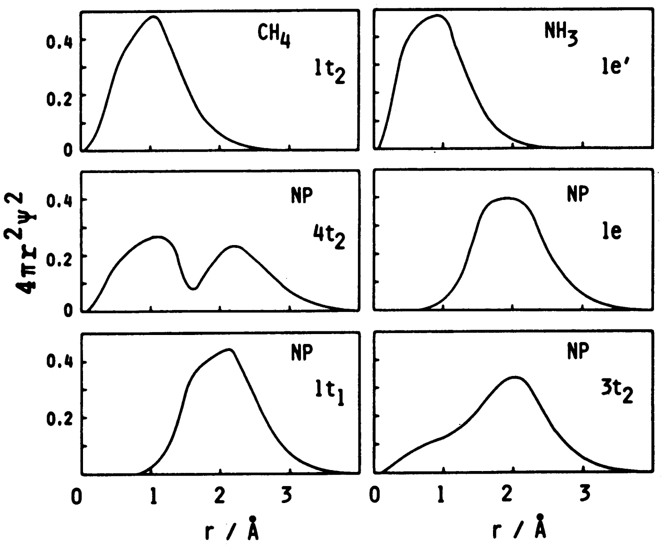

Fig. 11. Radial distributions of various MOs for methane, ammonia and neopentane (NP).

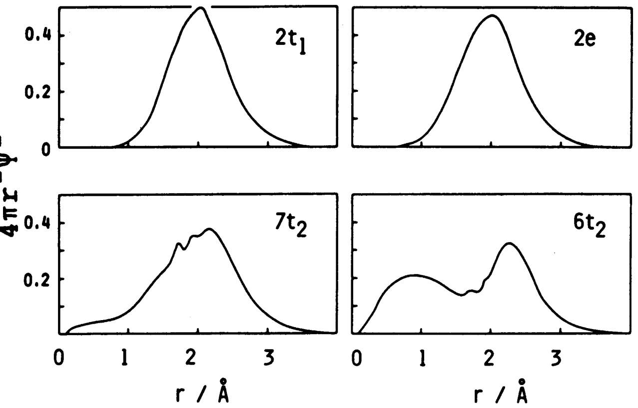

Fig. 12. Radial distributions of various MOs for CCl_4.

Concerning the radial distributions in CCl_4 shown in Fig. 12, the distribution patterns for the 1^2T_2 and 2^2T_2 states in CCl_4^+ are very similar to those for the 2^2T_2 and 1^2T_2 states in $C(CH_3)_4^+$, respectively. For CCl_4, the β variation for the 1^2T_2 state is abnormal. The β variation for the 2^2T_2 state shows the change of about 0.7 per 1 eV (Fig. 7B) which is quite large in comparison with the energy dependence of β (about 0.06 per 1 eV).[44]

In addition to the above considerations, we suggest that the effects of the shape resonance and the vibronic interaction on the β variation across the J-T split band should be investigated for these molecules.

The *ab initio* SCF MO calculations and the calculations of the one-center expansion of the MOs and the radial distributions of the MOs were carried out at the Hokkaido University Computing Center. The *ab initio* SCF MO calculations were performed with IMS version of GAUSSIAN 70 using 4-31 G basis set.

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