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Two-photon Excitation Spectra of 1-Azabicyclo[2.2.2]octane and Trimethylamine

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The two-photon fluorescence excitation spectra of 1-azabicyclo[2.2.2]octane (ABCO) and trimethylamine were measured in the excitation wavelength range of 410—520 nm. The effect of the polarization (linear or circular) indicates that the symmetries of the upper states are $\tilde{A}^1A_1$, $\tilde{B}^1A_1$, and $\tilde{C}^1E$ for ABCO while $\tilde{A}^1A_1$ and $\tilde{B}^1E$ for trimethylamine in C_{3v} point group approximation. Rotational envelopes for the sequence structures are calculated forcircularly and linearly polarized light excitation and are in good agreement with experiment.

The ultraviolet absorption bands of amines are considered as Rydberg transitions.[1)] The polarization measurements in two-photon absorption have assigned the lowest excited state of the open amines, *e.g.*, trimethylamine as A_1 in C_{3v} point group.[2)] In contrast to the open amine the caged one $N(C_2H_4)_3CH$ or ABCO has richly structured UV and multi-photon absorption spectra.[3)] All of the observed transitions are considered as two-photon allowed ones to low-lying Rydberg states (3p, 3s←n).[1—3)] Because the *ab initio* quantum chemical calculation predicts small core splitting for both trimethylamine and ABCO, the observed bands cannot be further classified as $^1E(3p_{xy})$, $^1A_1(3p_z)$ or the superposition of the two transitions.[4)] In this report we have studied two-photon absorption of ABCO by linearly and circularly polarized light in order to assign the symmetries of the low lying Rydberg states and to compare them with those of trimethylamine.

Experimental

The apparatus for the UV fluorescence excitation spectra is similar to that previously reported, except for a dye laser.[2)] Briefly, an 1 MW N_2 laser pumped dye laser light was focused into a quartz cell containing gases or solutions of amines with a lens (f=30 mm). The UV fluorescence was viewed through three UV transmitting filters (Toshiba UV-D33S) at 90° to the laser beam, and was detected by a solar blind photomultiplier (HTV-R166UH). The signal was averaged by a gated integrator. Linear polarization of the laser light was achieved by a polarizer which consists of ten quartz plates placed at Brewster's angle. Circularly polarized light was generated by passing the laser light through Fresnel rhombs.

The hydrochloride of ABCO was obtained from Tokyo Kasei Company. ABCO prepared from the hydrochloride solution was purified by sublimation through Molecular Sieves 13X. Trimethylamine was prepared from aq solution (30%, Nakarai Chemicals) with sodium hydroxide.

Results

ABCO. Figure 1 shows the two-photon fluorescence excitation spectra of ABCO in the vapor phase. Both the first and the second absorption bands show extensive progression and sequence structures. The origin of the first band was at 39097 cm^{-1} (511.55 nm). Since that of the second band was weak as has been reported by Parker and Avouris,[3b)] the measured value (43940 cm^{-1}) would not be quite accurate. The reported values for the first absorption bands are 39080 cm^{-1} obtained in one-photon absorption by Halpern *et al.*,[3a)] 39076 cm^{-1} and 39095 cm^{-1} reported in multiphoton ionization experiment by Halpern *et al.*[3d)] and Gonohe *et al.*,[5)] respectively.

The two-photon excitation spectrum of the pentane solution (10^{-3}—10^{-2} mol dm^{-3}) was also measured. The spectrum in solution appears blue shifted, compared to the spectrum in the vapor phase. The blue shift is expected for the Rydberg transitions.[1)] Since the electronic transitions are Rydberg ones of the lone-pair electron on the nitrogen atom, the repulsion between lone-pair and bonding-pair electrons decreases upon excitation. Because the pyramidal NC_3 skeleton tends to flatten, the cage squashing mode $\nu_{12}'(a_1)$ with frequency 650±10 cm^{-1} is observed up to several quanta, along with many combination bands. These vibrational structures are also observed in one-photon absorption[3a)] and multi-photon ionization[3b)] spectra. The progression with 625 cm^{-1}/618 cm^{-1} was assigned to this ν_{12} mode in one-photon/multi-photon reports of Halpern *et al.*[3a,d)] respectively. At wavelength longer than the 0-0 band, a hot band with frequency 603 cm^{-1} was identified as due to ν_{12}'' observed in one-photon absorption (600 cm^{-1}),[3a)] multi-photon ionization (602 cm^{-1}),[3d)] and infrared spectra (604 cm^{-1}).[6)]

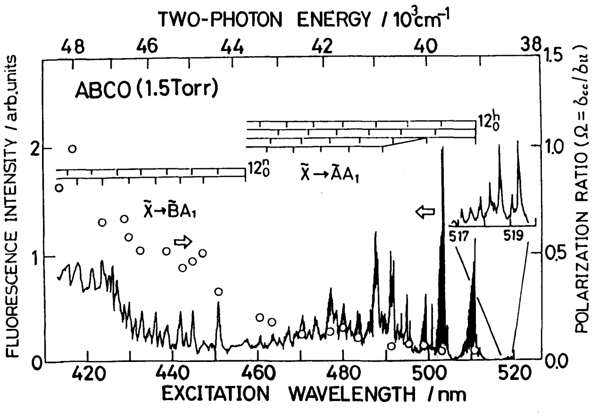

Fig. 1. Two-photon fluorescence excitation spectrum of ABCO in the vapor phase (recorded in linear polarization). The well resolved progressions are ν'_{12} (a_1) cage squashing mode built on the origin and on the ν'_{11} (a_1) and ν_{33}' (e) or ν_9' (a_1) modes after Halpern *et al.* (3a, d). Spectrum is corrected for the laser power. The pressure was a vapor pressure of ABCO at room temperature (1.5 Torr, 1 Torr ≈ 133.322 Pa).

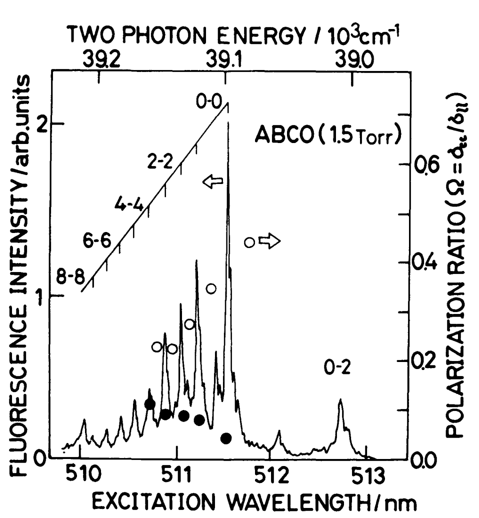

Fig. 2. The sequence structure of torsional motion built on the 0-0 band of ABCO (Ã–X̃) in the vapor phase (recorded in linear polarization) and polarization ratios (δ_{cc}/δ_{ll}) at the peaks (●) and the valleys (○). The origin (0-0) and the hot bands (v′-v″) are indicated in this figure.

The band structures were obtained at higher resolution. The detailed sequence structures of ν_{12} (0-0), (1-0), and (0-1) bands resemble each other (see Fig. 2 for example) while the spectral consequence of combination bands becomes highly conjunct and is different from that of the (0-0) bands. This is probably because of the different rovibronic selection rules *i.e.*, $\Delta K=0$ for A_1-A_1 (the 0-0 band) and $\Delta K=\pm 1$, ± 2 for E-A_1 transitions (the combination bands).[7]

Figure 2 shows the detailed structures of the first sequence bands. Similar sequence structures are observed in the multiphoton ionization spectrum of 1,4-diazabicyclo[2.2.2]octane.[8] They are assigned as due to the torsional motion about the z axis and the potential energy has a small hump at $\phi=0°$ and a double minimum around $\phi=10°$. Assuming a quartic-quadratic potential for the ground state of ABCO, Gonohe *et al.*[5] have assigned the strongest sequence structures to a cage torsional motion (ν_{19}) with low vibrational frequencies (54 cm^{-1} in the ground state). Actually, our studies show the increase of the hot bands in intensity with temperature from 20 °C to 90 °C.

The polarization ratio was measured to deduce the upper state symmetries (Figs. 1 and 2). According to McClain *et al.*[9] the intensity of two-photon absorption depends upon the polarizations of the two photons and so is different when using circularly and linearly polarized light sources. When the symmetry of the upper state is totally symmetric A_1 in C_{3v} point group, the ratios ($\Omega=\delta_{cc}/\delta_{ll}$) become less than 1.5 for the Q branches, where δ_{cc} is the absorptivity of two identical circularly polarized photons and δ_{ll} that by linearly polarized ones. For other cases, *i.e.*, O/P/R/S branches for A_1 and O/P/Q/R/S branches for E, the ratios are expected to be 1.5. The observed Ω values in Fig. 1 were less than 1.5 for all transitions, indicating two photon allowed A_1 symmetry of the excited states. Figure 2 shows the detailed excitation spectrum measured by the linearly polarized light and the polarization ratios. The Ω value for the peak at 511.55 nm is 0.04 which is in good agreement with $\Omega=0.030$—0.038 reported by Berg *et al.*[3c] The Ω values are larger at the positions between the peaks. This is because of the superposition of the branches other than the Q branches. These Ω values are well reproduced by calculation as will be discussed in the later section. The values at the peaks for the first absorption band were essentially constant while those increase with the excitation energy in the second absorption band (Fig. 1). In the second absorption band the Ω values at the peaks were not different from those for the valleys. The second band has a diffuse absorption structure compared to the first band. This diffuseness increases in the shorter wavelength region. Both the Ω values and the background intensity start increasing at $\lambda \simeq 440$ nm. These results indicate the superposition of two state in this region; one is a totally symmetric state and the other one at the shorter wavelength region is a non-totally symmetric one.

Trimethylamine The two-photon excitation spectrum of trimethylamine and the polarization ratios were also measured in the vapor phase and the pentane solution as shown in Fig. 3. The Ω values were obtained in the vapor phase and not in the solution phase. In solution phase solvent induced mixing of electronic states would occur and the measured Ω value is an averaged one of the mixed states.[10] The excitation spectrum was measured in pentane solution in order to suppress the decomposition of trimethylamine at shorter wavelength region. Actually, the increase of the fluorescence quantum yield have been reported by addition of third-body or buffer gases in the vapor phase.[11,12] The shape of the spectrum in solution resembles that of the one-photon absorption spectrum in the ultraviolet region, while the excitation spectrum obtained in the vapor phase is quite different from that in the solution phase. The "structures" observed in the vapor phase are in good agreement with those reported by Halpern *et al.*[3d] The disparities of the excitation spectrum between vapor and solution phases may be due to the photo-decomposition[11,12] and the multiphoton ionization processes,[3d] because both processes quench the fluorescence. Since the Ω values are less than 1.5 for the first absorption band ($\lambda=500$—440 nm), the symmetry of the upper state is assigned to a totally symmetric one.

Although the two-photon fluorescence excitation spectrum in Fig. 3 and the reported one-photon absorption spectra cannot be clearly resolved spectroscopically, the polarization measurement can reveal these overlapped bands. At shorter wavelength ($\lambda<440$ nm) a non-totally symmetric upper state appears, as indicated by increase in the Ω values with decreasing wavelengths. This decomposition of the absorption spectrum into two parts is in good agreement with that reported by Cureton *et al.*[12] According to them, in the fluorescence decay of trimethylamine, one-photon excitation at longer wavelength region produces almost single exponential decay but at $\lambda<230$ nm this becomes dual exponential. This is explained on the basis that there are two strongly overlapping absorption bands, resulting

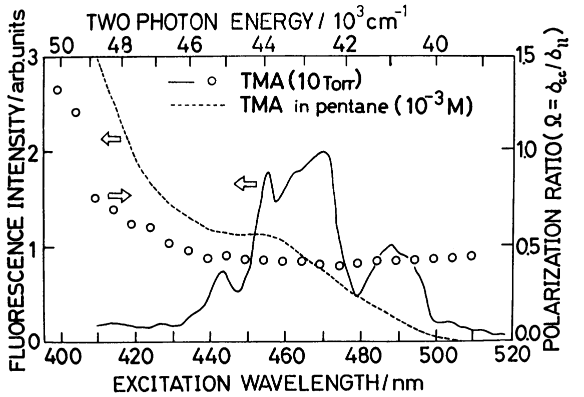

Fig. 3. Fluorescence excitation spectra of trimethylamine in pentane solution (1×10^{-3} mol dm^{-3}, broken line) and in the vapor phase (solid line: 10 Torr) recorded in linear polarization. Polarization ratios (δ_{cc}/δ_{ll}), were measured in the vapor phase (○). Spectrum is corrected for the laser power.

inevitably in simultaneous excitation of both S_2 and S_1 states. They observed no significant improvement in fitting to three exponentials than was obtained for two, and thus there has been no evidence for multi-exponential fluorescence. This has been the case for other open amines, triethyl- and tripropylamine.

Discussion

Electronic States. Prior to considering the electronic states of ABCO and trimethylamine it is useful to review the states for ammonia. The first few excited states of ammonia result from excitation of an a_1 lone pair electron of the nitrogen atom,[13]

$\cdots(e)^4(a_1)^2$	$\tilde{X}A_1$
$\cdots(e)^4(a_1)\,(3sa_1)$	$\tilde{A}A_1$
$\cdots(e)^4(a_1)\,(3p_{xy}e)$	$\tilde{B}E$
$\cdots(e)^4(a_1)\,(3p_za_1)$	$\tilde{C}A_1$.

Since alkyl substitution does not change the relative positions in energy of the $(3sa_1)$ and $(3p_{xy}e)$ orbitals, the first excited state of the open amines has A_1 symmetry, *i.e.* 3s←n. Actually, the Ω values for trimethylamine are less than 1.5 for $\lambda=500$—440 nm. Since the Ω values for trimethylamine increased from 0.5 to 1.4 with decreasing excitation wavelengths from 440 to 400 nm, the second absorption band can be assigned as E state.

The first absorption band of ABCO has A_1 symmetry as we saw from the polarization ratios. The observed Ω values in the region $\lambda<460$ nm increase from 0.2 to 1.0 with decreasing the wavelengths. Since the second band consists of two states, *i.e.*, totally and non-totally symmetric states, the second and third excited states have A_1 and E symmetries, respectively. The electronic states observed are $\tilde{A}A_1$, $\tilde{B}A_1$, and $\tilde{C}E$. The relative position of B and C states is reversed compared to ammonia and open amines. This may be explained by the variation of quantum defects caused by interaction between Rydberg orbitals and nuclei. The energy for the Rydberg orbitals is given by,

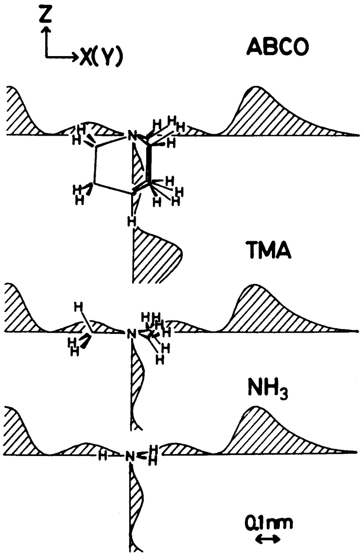

Fig. 4. Schematics for electron density $(r^2\psi(r)^2)$ of 3p Rydberg orbitals and molecular structures of ABCO, trimethylamine (TMA), and ammonia.

$$E_n = I_p - R/(n-\delta)^2,$$

where I_p is an ionization potential and R the Rydberg constant. The quantum defect δ will be large if the probability is high that the electron is near the nucleus, while δ will be small where the nuclei are situated on the nodal planes of the orbitals.[1,14] Actually for ammonia where the nuclei are three hydrogen atoms, δ_z for p_z is smaller than δ_{xy} for p_{xy}. The hydrogen atoms strongly interact with $3p_{xy}$ orbital, because ammonia has a planar structure in the excited state. For the $3p_z$ orbital this interaction is expected to be small. Schematics for these interactions are shown in Fig. 4, where radial populations $(r^2\psi(r)^2)$ of 3p orbitals are illustrated along with molecular structures of ammonia and the amines. These interactions would be the case for trimethylamine *i.e.*, $\delta_z<\delta_{xy}$. For ABCO the skeletal CH_2 group may interact strongly with $3p_z$ as with $3p_{xy}$ orbitals, then $\delta_z\approx\delta_{xy}$. This difference may change the relative position of A_1 and E electronic states.

The energy difference between $A_1(3p_z)$ and $E(3p_{xy})$ for vertical excitation may be obtained from the threshold wavelength of each states in Fig. 1. It is rather small ($\approx$0.3 eV) as predicted by quantum chemical calculation[4] compared with that for ammonia ($\approx$0.5 eV).

Calculation of Rovibronic Profiles. As previously observed, the rotational profiles in the excitation spectra are strongly dependent upon the polarization of the absorbed photons. The theoretical explanation of this dependence is given by McClain *et al.*[9] and Wunsch *et al.*[15] They computed the polarization dependence of vibronic bands in benzene. In this section we apply this theory to the rovibronic bands in ABCO.

The probability for an identical two-photon absorption is described in detail by Wunsch *et al.*[15] In brief, it is given by two independent contributions, $C_0M_0R_0$ and $C_2M_2R_2$. Geometrical factors C_J, which depend on the polarization of the photons absorbed, are given by $C_0=1/3$, $C_2=2/15$ for linearly polarized photons and by $C_0=0$, $C_2=1/5$ for circularly polarized photons.

The molecular parameters M_J are obtained from the two-photon tensor elements. For the $A_1 \leftarrow A_1$ transition, $M_0=(M_{xx}+M_{yy}+M_{zz})^2/3$ and $M_2=(M_{xx}+M_{yy}-2M_{zz})^2/6$. The rotational factors R_2 are given by the Placzek-Teller factors[16] $b_{J'K'}^{JK}$ and contribute to all branches in the transition of $J \rightarrow J'$ and $K \rightarrow K'$;

for

$$J' = J,\ b_{J'K'}^{JK} = [J(J+1)-3K^2]^2/J(J+1)(2J-1)(2J+3)$$

$$J' = J+1,\ b_{J'K'}^{JK} = 3K^2[(J+1)^2-K^2]^2/J(J+1)(J+2)(2J+1)$$

$$J' = J+2,\ b_{J'K'}^{JK} = 3[(J+1)^2-K^2][(J+2)^2-K^2]/2(J+1)(J+2)(2J+1)(2J+3)$$

and $(2J+1)b_{J'K'}^{JK} = (2J'+1)b_{JK}^{J'K'}$.

Since R_0 is given by $R_0=\delta_{JJ'}\times\delta_{KK'}$ the $C_0M_0R_0$ contributes only to Q branches, where $\delta_{JJ'}$ and $\delta_{KK'}$ are delta functions. The selection rule is $\Delta K=0$ for the $A_1 \leftarrow A_1$ transition. By assuming the symmetric top molecule, rotational energies of ABCO were estimated by the formula,

$$E = BJ(J+1) + (C-B)K^2.$$

To compute a two-photon excitation spectrum, one must assume values for the rotational constants B and C. We took $B'=0.092\ \text{cm}^{-1}$, $B''=0.091\ \text{cm}^{-1}$, $C'=0.093\ \text{cm}^{-1}$, and $C''=0.095\ \text{cm}^{-1}$, which correspond to C–N–C angles 111.0° for $\tilde{A}$ and 109.5° for $\tilde{X}$, respectively. The CH_2 group was considered as a mass point in calculation of these constants. The angle 109.5° was taken from the structure of trimethylamine.[17] The shape of the calculated spectrum was very sensitive to these constants. Concerning the vibrational energy levels, the values for the ground state are obtained from Gonohe *et al.*,[5] while those for the excited state are taken from the experimental values in Fig. 2.

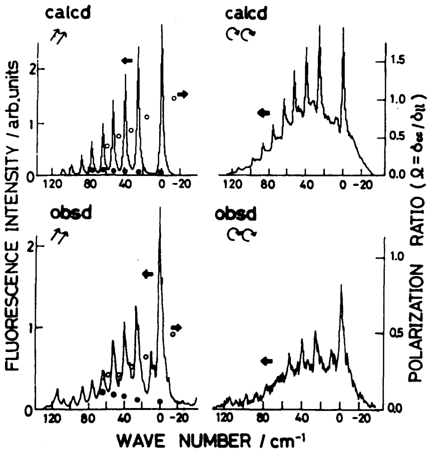

Fig. 5. The calculated and observed rovibronic structures of an A_1, $\Delta v=0$ transition in ABCO. ⇈ and ↻↻ for linearly and circularly polarized light, respectively. The band in circularly polarized light is enlarged by a factor of 20 (calculation) and 14 (experimental). Circles are polarization ratios (δ_{cc}/δ_{ll}) (See Fig. 2).

Comparison of calculated profiles with experimental band shapes shows good agreement (Fig. 5). To reproduce the observed spectrum for circularly polarized light, the Q branch must include a small contribution from $C_0M_0R_0$ since the polarization of the laser light was not perfect. *Ca.* 1% of the linearly polarized light was included in the calculation. The molecular parameter M_0/M_2 is assumed to be 11.6, that corresponds to $M_{xx}=M_{yy}=0.56\ M_{zz}$. As shown in Fig. 5, this values reproduces experimental Ω values for the peaks and for the valley.

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