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One-photon and Two-photon Electronic Spectra of Two Caged Amines

Narishi GONOHE, Norio YATSUDA, Naohiko MIKAMI, and Mitsuo ITO*

Department of Chemistry, Faculty of Science, Tohoku University, Sendai, 980

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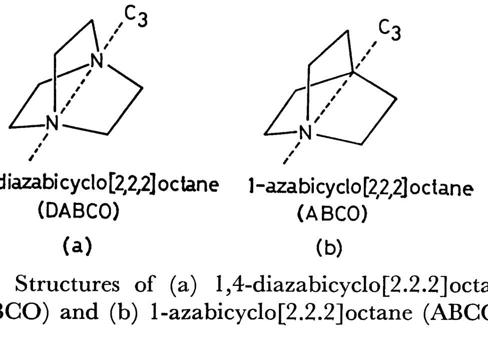
The one-photon fluorescence excitation and two-photon resonant multiphoton ionization spectra of the $S_1 \leftarrow S_0$ transition of 1,4-diazabicyclo[2.2.2]octane (DABCO) in a supersonic free jet have been obtained and analyzed. It was found from the vibrational analysis that the $S_1 \leftarrow S_0$ transition is one-photon forbidden, two-photon allowed and the one-photon absorption appears by the vibronic interaction between the S_1 and S_2 states through the e′ vibrations. In addition, from the fluorescence spectrum and the polarization studies of the two-photon spectrum using the two linearly polarized laser beams of different wavelengths, it was concluded that the S_1 state is ${}^1A_1'$. The sequence structure involving the low-frequency cage torsional vibration has been observed in the two-photon resonant multiphoton ionization spectra of DABCO and 1-azabicyclo[2.2.2]octane (ABCO). The potential functions with respect to the torsional motion for both ground and excited states have been determined by utilizing the observed vibrational levels. It was found that the torsional potential has a broad minimum near the D_{3h} (for DABCO) and C_{3v} (for ABCO) conformations.

The electronic spectra of 1,4-diazabicyclo[2.2.2]octane (DABCO) and 1-azabicyclo[2.2.2]octane (ABCO) (Fig. 1) have been studied by many workers[1–6] with special interest in their cage structures. The spectra of these molecules with the rigid structure generally show a well-resolved vibrational structure compared with the broad and structureless spectra of non-rigid saturated amines such as trimethylamine and triethylamine. However, the one-photon absorption spectra of DABCO and ABCO due to the $S_1 \leftarrow S_0$ transition (280—260 nm for DABCO and 250—230 nm for ABCO) are still broad and show only a faint vibrational structure. Recently, Parker and Avouris[7] have observed the corresponding two-photon absorption spectra by means of fluorescence excitation (FE) and multiphoton ionization (MPI) techniques and found a rich vibronic structure. They concluded from their laser polarization studies that the S_1 state is a totally symmetric Rydberg state which is one-photon forbidden and two-photon allowed in the transition from the S_0 state. The two-photon absorption spectrum of DABCO is characteristic of extensive sequence bands involving the low-frequency torsional vibration in which the two N pyramids are twisted in the opposite sense about the C_3 symmetry axis. Although the potential of the torsional motion has been discussed by several workers[8–10] for DABCO, no conclusive result is obtained yet. The corresponding potential for ABCO has never been studied.

In the present paper, we report the one-photon fluorescence excitation spectra and the two-photon resonant multiphoton ionization spectra of the $S_1 \leftarrow S_0$ transition of DABCO seeded in a supersonic free jet. On account of temperature cooling effect through the free expansion, most of the hot bands in the room temperature spectrum disappeared and a well resolved vibrational structure showed up. Vibrational analysis of the one-photon and two-photon absorption spectra thus obtained and the $S_1 \leftarrow S_0$ fluorescence spectrum as well as the laser polarization studies of the two-photon absorption spectrum led us to a definite assignment of the S_1 state of DABCO. The torsional potential was also obtained for both S_0 and S_1 states of DABCO and ABCO from the two-photon resonant multiphoton ionization spectra of the vapor and the supersonic free jets.



1,4-diazabicyclo[2,2,2]octane (DABCO) (a)   1-azabicyclo[2,2,2]octane (ABCO) (b)

Fig. 1. Structures of (a) 1,4-diazabicyclo[2.2.2]octane (DABCO) and (b) 1-azabicyclo[2.2.2]octane (ABCO).

Experimental

The experimental setup for measurements of the FE and MPI spectra of a supersonic free jet was already described elsewhere.[11,12] A Molectron scanning dye laser (DL-14) pumped by a nitrogen laser (UV-22) was used as an exciting light source for measurements of the two-photon resonant MPI spectrum and the second harmonic of the dye laser for the one-photon resonant FE spectrum. The FWHM of the dye laser light was about 0.5 cm^{-1}. Coumarin 540 (Exciton) was used to cover the spectral region of the $S_1 \leftarrow S_0$ transition. The MPI spectra of the vapor at room temperature were measured with a metal gas cell equipped with windows and a pair of electrodes instead of the supersonic jet cell. The fluorescence spectrum of DABCO vapor at room temperature excited by the frequency-doubled dye laser was obtained with a Nikon grating monochromator having reciprocal dispersion of 3 nm/mm in the second order and recorded by photon counting method. The fluorescence decay was also measured by the use of a boxcar integrator (Brookdeal 9415).

In polarization studies of the two-photon resonant MPI spectrum of DABCO at room temperature, two linearly polarized laser beams of different wavelengths were used; the second harmonic of the Nd:YAG laser (Quanta-Ray) and dye laser pumped by the same second harmonic. The laser beam was depolarized by passing through a polarization scrambler and then the linear polarization was achieved by a polaroid sheet. The two linearly polarized light beams thus obtained were focussed from opposit directions into the center of the metal gas cell described above. The ions produced by MPI process were detected by biassed parallel electrodes equipped inside the cell. In order to avoid the MPI process by the single beam, the laser power was sup-

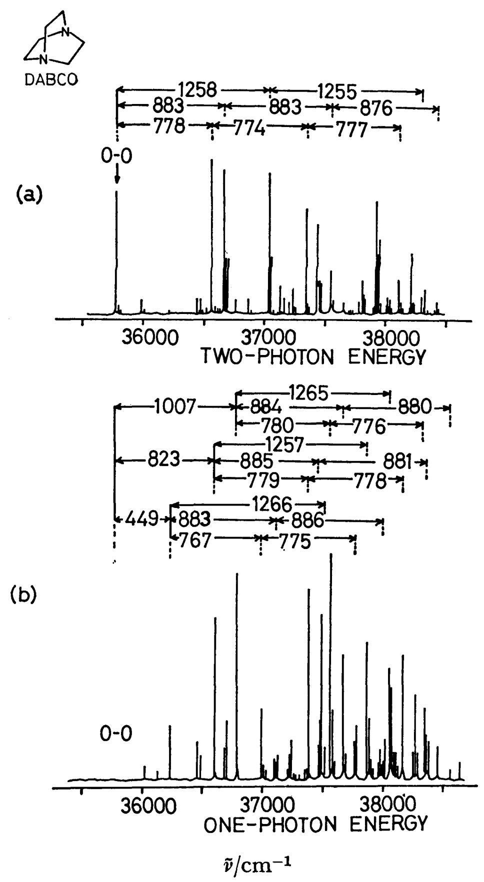


Fig. 2. (a) Two-photon resonant MPI and (b) one-photon fluorescence excitation spectra of the $S_1 \leftarrow S_0$ transition of DABCO in a supersonic free jet. The spectra are corrected for laser intensity variation.

pressed to such an extent that the ions are not produced by the signle beam.

The samples used were obtained from Tokyo-kasei Co. Ltd. DABCO was sublimed several times in vacuum. ABCO was prepared from its hydrochloride and purified by sublimation in vacuum.

Results and Discussion

One-photon and Two-photon Absorption Spectra of DABCO in a Supersonic Free Jet. The two-photon resonant MPI spectrum of DABCO in a supersonic free jet of He carrier gas at 2.5 atm. is shown in Fig. 2a. First ionization potential of DABCO is 7.2 eV. Therefore, using the dye laser in the visible region ($\approx$540 nm), four photons are necessary to excite the molecule into the ionization continuum. Since the S_1 state of DABCO is located at around 270 nm, the spectrum shown in Fig. 2a is due to two-photon resonant four-photon ionization process. It is seen from the figure that the spectrum exhibits a well-resolved vibrational structure. Comparing with the two-photon spectrum of the vapor at room temperature reported by Parker and Avouris,7) the individual vibronic bands become extremely sharp (with FWHM of 4 cm^{-1}) and most of the vibrational hot bands are swept out in the supersonic jet spectrum, indicating very low rotational and vibrational temperatures of the jet. The observed main vibronic bands are listed in Table 1 together with their assignments. The overall spectral pattern is rather simple. The longest wavelength band at 35783 cm^{-1} 13) is readily assigned to the 0-0 band and most of other intense bands are interpreted as the vibronic bands involving the fundamentals, overtones and combinations of three excited-state totally symmetric vibrations of 778, 883, and 1258 cm^{-1}.

Table 1. Vibrational assignments of the main bands in the two-photon resonant MPI spectrum for the $S_1 \leftarrow S_0$ transition of DABCO in a supersonic free jet

$\tilde{\nu}$ / cm^{-1}	$\Delta\tilde{\nu}$ / cm^{-1} a)	Intensity	Analysis	Assignment
35783	0	vs		0-0
36561	778	vs	$0+778$	ν_3' b)
36666	883	vs	$0+883$	ν_2' b)
36672	889	m	$0+889$	ν_α' c)
36685	902	m	$0+902$	ν_β' c)
37041	1258	vs	$0+1258$	ν_1' b)
37052	1269	m	$0+1269$	ν_γ' c)
37335	1552	s	$0+778\times2=1556$	$2\nu_3'$
37439	1656	s-m	$0+778+883=1661$	$\nu_3'+\nu_2'$
37447	1664	m-w	$0+889+778=1667$	$\nu_\alpha'+\nu_3'$
37459	1676	m-w	$0+902+778=1680$	$\nu_\beta'+\nu_3'$
37549	1766	m-w	$0+883\times2=1766$	$2\nu_2'$
37553	1770	w(sh)	$0+889+883=1772$	$\nu_\alpha'+\nu_2'$
37567	1784	w	$0+902+883=1785$	$\nu_\beta'+\nu_2'$
37822	2039	m-w	$0+778+1258=2036$	$\nu_3'+\nu_1'$
37830	2047	w	$0+1269+778=2047$	$\nu_\gamma'+\nu_3'$
37921	2138	s	$0+883+1258=2141$	$\nu_2'+\nu_1'$
37927	2144	m(sh)	$0+889+1258=2147$	$\nu_\alpha'+\nu_1'$
37932	2149	m	$0+1269+883=2152$	$\nu_\gamma'+\nu_2'$
37943	2160	m-w	$0+902+1258=2160$	$\nu_\beta'+\nu_1'$
38112	2329	w	$0+778\times3=2334$	$3\nu_3'$
38215	2432	m	$0+778\times2+883=2439$	$2\nu_3'+\nu_2'$
38222	2439	w	$0+889+2\times778=2445$	$\nu_\alpha'+2\nu_3'$
38238	2455	w	$0+902+2\times778=2458$	$\nu_\beta'+2\nu_3'$
38296	2513	w	$0+1258\times2=2516$	$2\nu_1'$
38312	2529	w	$0+1269+1258=2527$	$\nu_\gamma'+\nu_1'$
38322	2539	w	$0+778+2\times883=2544$	$\nu_3'+2\nu_2'$
38425	2642	w	$0+883\times3=2649$	$3\nu_2'$

a) Frequency difference from the 0-0 transition at 35783 cm^{-1}. b) We follow the notations given in Ref. 7. c) We tentatively designate these vibrations as ν_α' (889 cm^{-1}), ν_β'(902 cm^{-1}), and ν_γ'(1269 cm^{-1}), respectively.

The one-photon absorption spectrum of the same $S_1 \leftarrow S_0$ transition of DABCO in a supersonic free jet is shown in Fig. 2b, which was taken by FE method. In contrast with the broad spectrum in vapor at room temperature, the supersonic jet spectrum exhibits a well-resolved vibrational structure. The vibrational structure is similar to that of the two-photon absorption spectrum with respect to repeated appearance of the excited-state vibrations of 778, 883, and 1258 cm^{-1}. A great difference between the two spectra is that the 0-0 band at 35783 cm^{-1} appearing strongly in the two-photon spectrum is completely missing in the one-photon spectrum. Moreover, in the one-photon spectrum, the progressions and combinations of

TABLE 2. VIBRATIONAL ASSIGNMENT OF THE MAIN BANDS IN THE ONE-PHOTON FLUORESCENCE EXCITATION SPFCTRUM FOR THE $S_1\leftarrow S_0$ TRANSITION OF DABCO IN A SUPERSONIC FREE JET

$\tilde{\nu}$ / cm^{-1}	$\Delta\tilde{\nu}$ / cm^{-1} a)	Intensity	Analysis	Assignment
(35783)				0-0
36232	449	w-m	0+449	$\nu'_{27}(e')$ b)
36606	823	s	0+823	$\nu'_{26}(e')$ b)
36704	921	w-m	0+921	ν'_{ω} c)
36792	1007	vs	0+1007	$\nu'_{20}(e')$ b)
37000	1217	m	0+449+778=1227	$\nu'_{27}+\nu'_3$
37116	1333	w	0+449+883=1332	$\nu'_{27}+\nu'_2$
37388	1605	vs	0+823+778=1601	$\nu'_{26}+\nu'_3$
37482	1699	w	0+921+778=1699	$\nu'_{\omega}+\nu'_3$
37492	1709	s	0+823+883=1706	$\nu'_{26}+\nu'_2$
37498	1715	w	0+449+1258=1707	$\nu'_{27}+\nu'_1$
37573	1790	vs	0+1007+778=1785	$\nu'_{20}+\nu'_3$
37584	1801	w-m	0+921+883=1804	$\nu'_{\omega}+\nu'_2$
37674	1892	m	0+1007+883=1890	$\nu'_{20}+\nu'_2$
37774	1991	w	0+449+778×2=2005	$\nu'_{27}+2\nu'_3$
37867	2084	m-s	0+823+1258=2081	$\nu'_{26}+\nu'_1$
37962	2179	w	0+921+1258=2179	$\nu'_{\omega}+\nu'_1$
38001	2218	w	0+449+883×2=2215	$\nu'_{27}+2\nu'_2$
38049	2266	m	0+1007+1258=2265	$\nu'_{20}+\nu'_1$
38159	2376	m	0+823+778×2=2379	$\nu'_{26}+2\nu'_3$
38261	2478	m	0+921+778×2=2477	$\nu'_{\omega}+2\nu'_3$
38349	2566	m	0+1007+778×2=2563	$\nu'_{20}+2\nu'_3$
38374	2591	w	0+823+883×2=2589	$\nu'_{26}+2\nu'_2$
38556	2773	w	0+1007+883×2=2773	$\nu'_{20}+2\nu'_2$

a) Frequency difference from the 0-0 transition at 35783 cm^{-1} (which is observed in the two-photon spectrum). b) The assignments of these vibrations were carried out on the basis of the fluorescence spectrum in Fig. 3. The numbering of the vibbration is in accord with that in Ref. 15. c) The assignment of this vibration is not established yet. We designate this vibration as ν'_{ω}.

the totally symmetric vibrations start from the bands at 36232, 36606, and 36792 cm^{-1}, which act as false origins of the spectrum. The detailed vibrational analysis is listed in Table 2.

The vibrational structures of the one-photon and two-photon spectra mentioned above are typical for one-photon forbidden and two-photon allowed transition. It is concluded, therefore, that the S_1 state of DABCO should be of either A_1' or E'' symmetry from the optical selection rule for D_{3h} point group. Based on this conclusion, the frequency differences between the 0-0 band and the three false origins of the one-photon spectrum (449, 823, and 1007 cm^{-1}) must represent some non-totally symmetric vibrations in the excited state which make the one-photon forbidden transition allowed by vibronic coupling. Determination of the symmetry species of these excited state vibrations will lead to unambiguous assignment of the S_1 state. With this aim in mind, we measured the fluorescence spectrum of DABCO in vapor, which will be described in the next section.

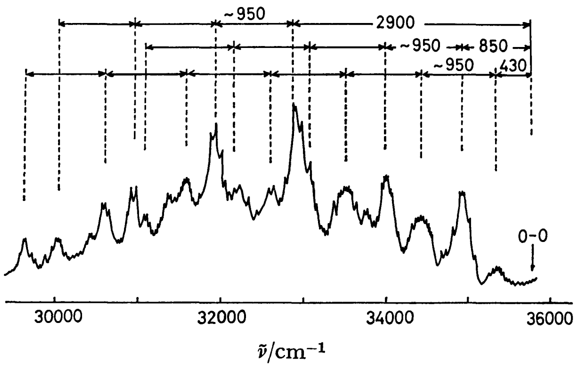


Fig. 3. Fluorescence spectrum of DABCO vapor at room temperature.

Fluorescence Spectrum of DABCO. The fluorescence spectrum of DABCO vapor was excited by frequency-doubled dye laser light at 271.7 nm, which coincides with the strongest band at 36792 cm^{-1} of the one-photon absorption spectrum. In order to obtain the fluorescence spectrum originating from the vibrationless level of the S_1 state, 2-methylbutane vapor ($\approx$5300 Pa) was added to DABCO vapor to accelerate vibrational relaxation. The fluorescence spectrum thus obtained is shown in Fig. 3. The effective vibrational relaxation is proved by absence of band in the region of shorter wavelength than 0-0 band position.

As is seen from the figure, the 0-0 band does not appear as in the case of the one-photon absorption spectrum. There are long progressions of 950 cm^{-1} starting from 0—430, 0—850, and 0—2900 cm^{-1} bands.[14] Assignments of the ground state vibrations of DABCO are fairly well established from the IR and Raman studies.[9,15,16] According to their assignments, the ground-state frequencies of 430, 850, and 2900 cm^{-1} may be identified as ν_{27}(e', NC_3 deformation mode), ν_{26}(e', NC_3 stretching mode), and ν_{20}(e', C–H stretching mode), respectively. The frequency of 950 cm^{-1} should be a totally symmetric vibration and assigned to $\nu_4(a_1')$ of a cage squashing mode in which the two N pyramids move along the C_3 axis in the opposite directions. The corresponding excited-state vibrational frequency is 882 cm^{-1}. Thus, the bands at 0—430, 0—850, and 0—2900 cm^{-1} are assigned as the false origins involving the ground-state e' vibrations. The vibrations of 430 and 850 cm^{-1} correspond to the excited-state vibrations of 449 and 823 cm^{-1}, respectively, which make the false origins in the one-photon absorption spectrum. The excited-state vibration corresponding to the ν_{20}(e') of 2900 cm^{-1} is hard to find in the one-photon absorption spectrum. Remained excited-state vibration forming the false origin in the absorption spectrum is of 1007 cm^{-1}. This suggests that the 1007 cm^{-1} vibration corresponds to the ground-state vibration of 2900 cm^{-1}. If it would be the case, a drastic frequency decrease should occur for ν_{20}(e') in the transition from the ground state to the excited state.

It is established from the above results that the perturbing vibrations of the one-photon forbidden $S_1\leftarrow S_0$ transition are of e' symmetry. Taking into account the results obtained in a previous section, this leads

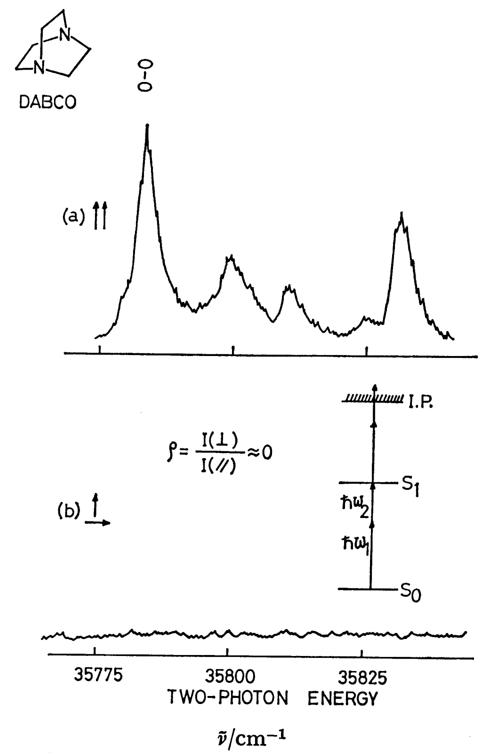


Fig. 4. Polarized two-photon resonant MPI spectrum of the $S_1 \leftarrow S_0$ transition of DABCO in the region around the 0-0 band at room temperature.
(a): Parallel polarization, (b): perpendicular polarization.

to the conclusion that the S_1 state is A_1'. The $S_1(A_1') \leftarrow S_0(A_1')$ transition should appear in the one-photon spectrum by borrowing intensity from the one-photon allowed $S_n(E') \leftarrow S_0(A')$ transition through vibronic coupling between $S_1(A_1')$ and $S_n(E')$. The $S_n(E')$ state is probably the second excited state (S_2) around 39813 cm^{-1}, which has been assigned to E' symmetry by Parker *et al.*[5,7]

Laser Polarization Studies. It was found from the vibrational analysis described in a previous section that the S_1 state is A_1'. This result is in agreement with the conclusion derived by Parker and Avouris[7] from their laser polarization studies of the two-photon absorption spectrum. In their polarization studies, they used two identical photons and measured the ratio of the two-photon absorption signal from a circularly polarized source to that from a linearly polarized source of the same intensity. We carried out a different polarization measurement. In our measurement, two linearly polarized laser beams of different frequencies were used; the frequency of one laser beam was fixed at 530 nm (second harmonic of YAG laser) and that of another beam was varied between 590 and 583 nm to observe the 0-0 band region. Two-photon resonant MPI spectrum of DABCO at room temperature was taken for both parallel and perpendicular polarizations of the two laser beams. The results obtained is shown in Fig. 4. It is seen from the figure that the spectrum appears strongly in the parallel polarization while it is extremely weak in the perpendicular polarization. The ratio ρ of the intensity of perpendicular polarization to that of parallel one (which corresponds to depolarization ratio in Raman scattering) is nearly zero. Since ρ should be 3/4 for non-totally symmetric state and less than 3/4 for totally symmetric state,[17,18] it is concluded that the S_1 state is A_1' in agreement with the result derived from the vibrational analysis.

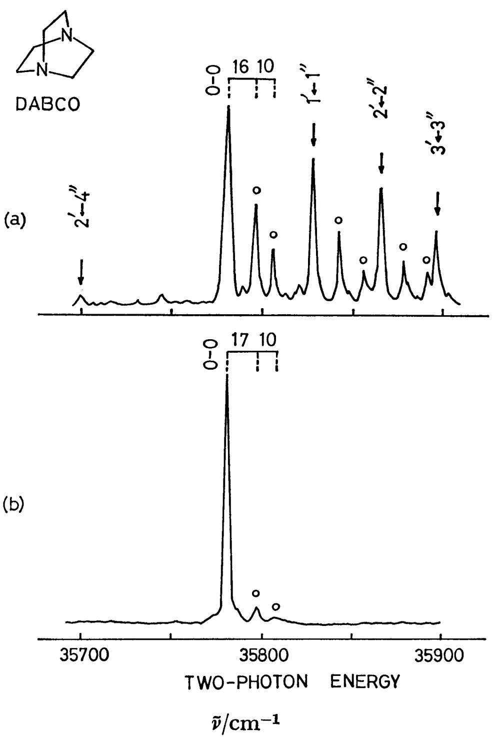


Fig. 5. Sequence structures for the 0-0 band region of DABCO in the two-photon resonant MPI spectrum.
(a): At room temperature, (b): in a supersonic free jet.

Low Frequency Torsional Motion of DABCO and ABCO. The two-photon absorption spectrum of DABCO vapor at room temperature has been studied in detail by Parker and Avouris.[7] They found the presence of extensive sequence structure in the spectrum. The sequence structure was attributed by them to the $\Delta v=0$ and ± 2 transitions of the $\nu_{13}(a_1'')$ low-frequency torsional motion in which the two N pyramids are twisted in the opposite sense about the C_3 symmetry axis. We also observed the identical sequence structure which is shown in Fig. 5a for the 0-0 band region. In order to confirm the assignments given by Parker and Avouris, the two-photon resonant MPI spectrum was measured for DABCO in a supersonic free jet. The result is shown in Fig. 5b. It is seen that the bands assigned to the torsional motion (which are indicated by arrows in Fig. 5a) completely disappear in the supersonic jet spectrum, supporting their assignment. Our supersonic jet spectrum adds nothing more than the results obtained by Parker and Avouris about the sequence of the a_1'' torsional vibration.

In the two-photon absorption spectrum of DABCO vapor at room temperature, Parker and Avouris also noted the presence of a minor sequence in addition to the major sequence described above. The bands belonging to the minor sequence are indicated by

TABLE 3. OBSERVED AND CALCULATED TRANSITION ENERGIES ASSOCIATED WITH THE TORSIONAL VIBRATION IN THE TWO-PHOTON RESONANT MPI SPECTRUM OF DABCO AND THE CALCULATED VIBRATIONAL LEVELS

Transition	Observed $\tilde{\nu}$/cm^{-1}	Calculated $\tilde{\nu}$/cm^{-1}	v	Ground state $\tilde{\nu}$/cm^{-1}	Excited state $\tilde{\nu}$/cm^{-1}
0-0	35780		1	54	99
$1'\leftarrow1''$	35826	35825	2	119$^{a)}$	204$^{a)}$
$2'\leftarrow2''$	35865	35865	3	196	315
$3'\leftarrow3''$	35897	35899	4	284$^{a)}$	431$^{a)}$
$4'\leftarrow4''$	35927	35927	5	384	553
$5'\leftarrow5''$	35952	35949	6	479	681
$2'\leftarrow0$	35984	35984			
$3'\leftarrow1''$	36043	36041	ν_0	42	93
$4'\leftarrow2''$	36092	36092			
$5'\leftarrow3''$	36134	36137			
$0\leftarrow2''$	35661	35661			
$1'\leftarrow3''$	35681	35683			

a) These are the observed values.

TABLE 4. OBSERVED AND CALCULATED TRANSITION ENERGIES ASSOCIATED WITH THE TORSIONAL VIBRATION IN THE TWO-PHOTON RESONANT MPI SPECTRUM OF ABCO AND THE CALCULATED VIBRATIONAL LEVELS

Transition	Observed $\tilde{\nu}$/cm^{-1}	Calculated $\tilde{\nu}$/cm^{-1}	v	Ground state $\tilde{\nu}$/cm^{-1}	Excited state $\tilde{\nu}$/cm^{-1}
0-0	39095		1	37	63
$1'\leftarrow1''$	39125	39121	2	87$^{a)}$	134$^{a)}$
$2'\leftarrow2''$	39142	39142	3	150	215
$3'\leftarrow3''$	39159	39159	4	227$^{a)}$	304$^{a)}$
$4'\leftarrow4''$	39172	39172	5	317	403
$5'\leftarrow5''$	39188	39181	6	420	510
$2'\leftarrow0$	39229	39229			
$3'\leftarrow1''$	39282	39273	ν_0	24	54
$4'\leftarrow2''$	39312	39312			
$5'\leftarrow3''$	39346	39347			
$0\leftarrow2''$	39008	39008			
$1'\leftarrow3''$	39006	39007			

a) These are the observed values.

open circles in Fig. 5a. Most of these bands disappear or appear weakly in the supersonic jet spectrum, indicating that they are also hot bands. These bands may be assigned to the $\Delta v=0$ transitions of a low-frequency vibration. By assuming same Franck-Condon factor for these bands as that for the 0-0 band, the frequency of the ground-state vibration involved is estimated to be about ≈ 150 cm^{-1} for a non-degenerate vibration and about ≈ 300 cm^{-1} for a degenerate vibration from the intensities of these bands relative to that of the 0-0 band of the room temperature spectrum. It is known from the vibrational spectra that the lowest-frequency fundamental vibration except the torsional vibration $\nu_{13}(a_1'')$ is $\nu_{36}(e'')$ of the rocking mode of N pyramids with the frequency of 332 cm^{-1}. Therefore, we assign the minor sequence as the $\Delta v=0$ transitions of $\nu_{36}(e'')$. It is noticed in Fig. 5 that in the supersonic jet spectrum $1'\leftarrow1''$ and $2'\leftarrow2''$ bands of $\nu_{36}(e'')$ still remain with weak intensity, while the $\Delta v=0$ and ±2 bands of $\nu_{13}(a_1'')$ are absent. Since the ground-state vibrational frequency of $\nu_{36}(e'')$ is higher than that of $\nu_{13}(a_1'')$, the above result indicates a non-Boltzmann distribution between the levels of $\nu_{13}(a_1'')$ and $\nu_{36}(e'')$ in a supersonic free jet.

Table 3 summarizes the observed transitions of DABCO associated with $\nu_{13}(a_1'')$, which will be used later for determination of the potentials of the torsional mode in the ground and excited states.

The two-photon resonant MPI spectrum of ABCO was also observed for the vapor at room temperature as well as for the supersonic jet and they are shown in Fig. 6 for the 0-0 band region. An extensive sequence structure similar to that of DABCO was found in the room temperature spectrum. The bands of the major sequence indicated by arrows in the figure are assigned to the $\Delta v=0$ and ±2 transitions of the torsional motion corresponding to $\nu_{13}(a_1'')$ of DABCO. The band indicated by the open circle is probably due to the $1'\leftarrow1''$ transition of the rocking motion similar to $\nu_{36}(e'')$ of DABCO. The observed transitions are summarized in Table 4. In a supersonic free jet, the intensities of all these sequence bands greatly decrease, but the $1'\leftarrow1''$, $2'\leftarrow2''$, and $3'\leftarrow3''$ transitions for the torsional mode and the $1'\leftarrow1''$ transition for the rocking mode still seen with weak intensities. This suggests that ABCO is less efficient in the vibrational cooling than DABCO.

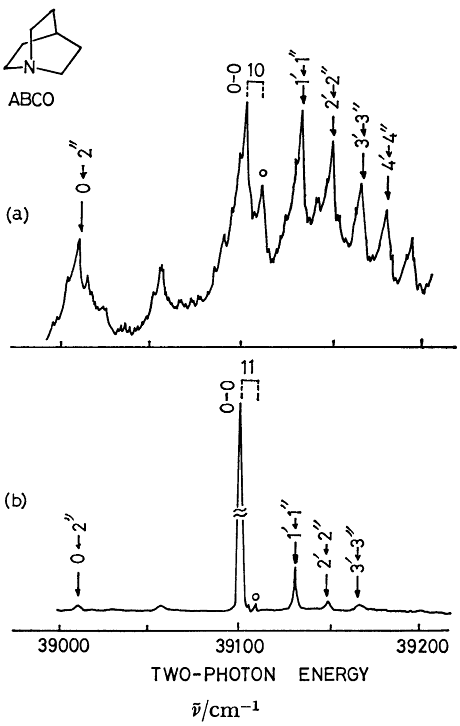


Fig. 6. Sequence structures for the 0-0 band region of ABCO in the two-photon resonant MPI spectrum. (a): At room temperature, (b): in a supersonic free jet.

By utilizing the observed transitions associated with the torsional motion given in Tables 3 and 4, we can obtain the potentials and the vibrational levels for

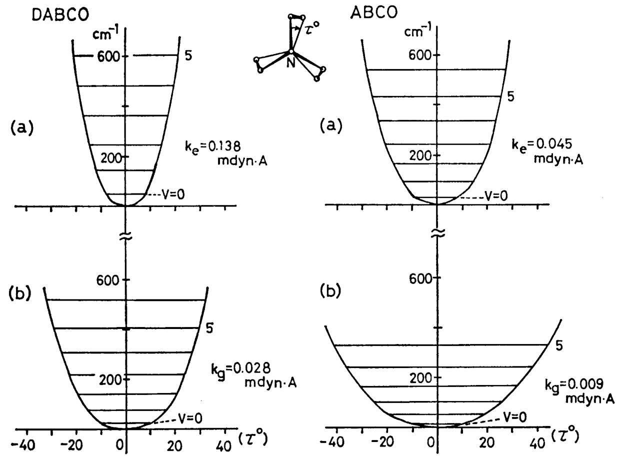


Fig. 7. The calculated potential function of the torsional vibration (a) in the excited state and (b) in the ground state of DABCO (left side) and ABCO (right side). The observed values for $v=2$ and $v=4$ are used as a reference of the calculation for the other levels.

both ground and excited states. Since only the transitions accompanying with even quantum changes are allowed in the two-photon absorption spectrum, the vibrational levels of even quantum number states are directly obtained from the experiment. We attempted to determine the torsional potentials and energy levels by assuming an anharmonic potential of $V(Q)=(1/2)kQ^2+bQ^4$, where Q is the normal coordinate of the torsional motion, $k(=4\pi^2\nu_0^2m)$ is the force constant, ν_0 and m being the zeroth-order harmonic frequency and reduced mass, respectively. Applying the first-order perturbation theory, the vibrational energy[19] is given by

$$w=\left(v+\frac{1}{2}\right)h\nu_0+\frac{3}{64\pi^4}(2v^2+2v+1)\frac{h^2b}{m^2\nu_0^2},$$

where v is the vibrational quantum number. The calculation was carried out by using the observed values of $v=2$ and $v=4$ levels for the ground and excited states with the effective reduced mass of 26.8 amu A^2/rad^2 [10] for both ground and excited states. The calculated transition energies are compared with the observed ones in Tables 3 and 4, where the values of the vibrational levels and ν_0 obtained from the calculation are also given. It is found that the calculated transition energies agree very well with the observed energies. Figure 7 shows the potential energies as a function of the "twist angle" τ about the C_3 axis. The ground-state potential is considerably flat and has a broad minimum near D_{3h} or C_{3v} conformation. Yokozeki and Kuchitsu[10] determined the ground-state potential of DABCO from their electron diffraction studies and obtained a double minimum potential with the barrier of ≈ 35 cm^{-1}. Since our potential without the barrier reproduces the observed energies very well, the deviation from D_{3h} or C_{3v} conformation seems to be not significant.

As is seen from Fig. 7, the torsional potential becomes sharp in the excited state. In fact, the force constant for the excited state is five times larger than that for the ground state. The sharpening may qualitatively be explained from the electronic character of the S_1 state. According to Parker and Avouris, the S_1 state of DABCO or ABCO is a totally symmetric Rydberg state arising through the excitation of a non-bonding electron localized on the nitrogen atom to the 3s nitrogen atomic orbital. Thus, the s character of the nitrogen atom increases in the S_1 state compared with that in the ground state, leading to a more rigid cage.

Conclusion

We have obtained and analyzed the one-photon FE and two-photon resonant MPI spectra due to the $S_1 \leftarrow S_0$ transition of DABCO in a supersonic free jet. It was found from the vibrational analysis that the $S_1 \leftarrow S_0$ transition is one-photon forbidden, two-photon allowed and the one-photon absorption appears by the vibronic interaction between the S_1 and S_2 states through the e′ vibrations. The S_1 state was definitely assigned to A_1' from the vibrational analyses of the absorption and fluorescence spectra as well as from the laser polarization studies. The sequence structures appearing in the two-photon absorption spectra of DABCO and ABCO have been analyzed and the potentials of the torsional motion have been determined for both ground and excited states. It has been found that the torsional potential has a broad minimum in the ground state and it becomes sharp in the excited state.

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13) The wavenumber of the 0-0 band (35783 cm^{-1}) does not agree with that (35794 cm^{-1}) reported by Parker and Avouris (Table 1 in Ref. 7), latter being the value uncorrected for vacuum.
14) The strong intensities of 0—2900 cm^{-1} band and the long progression of 950 cm^{-1} starting from 0—2900 cm^{-1} band suggested that they are due to the phosphorescence. We observed the lifetime for these bands and found that

it is about 200 ns at the vapor pressure of *ca*. 67 Pa, which is same for the other bands. It was concluded that the emission is almost certainly fluorescence.

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