

Fluorescence Excitation Spectroscopy of the Jet-cooled Dimethyldiazirine: the CH₃ Torsional Mode Assignment

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Dimethyldiazirine ((CH₃)₂CN₂) is an intriguing molecule in terms of the photophysical and photochemical properties due to its high-strained trigonal CN₂ ring. Spectroscopic studies have been carried out for this molecule in the ground electronic state, and it has been found that dimethyldiazirine belongs to the C_{2v} point group.^{1,2} Fluorescence excitation and dispersed fluorescence spectra of dimethyldiazirine for the S₁-S₀ (¹B₂-¹A₁) transition have been recently reported.^{3,4} The relatively strong bands in the fluorescence excitation spectrum have been assigned to the specific vibrational modes of the S₁ state.⁴ However, the low frequency bands observed in the 0-200 cm⁻¹ region above the origin (27,919 cm⁻¹) remain still unassigned. Here, these low-frequency bands are assigned to the modes associated with the CH₃ torsional motion. A simple sinusoidal function has been used to calculate energy levels of the CH₃ torsional mode of the S₁ state to be compared with the experiment, providing the potential barrier height for the internal rotation of the CH₃ moiety with respect to the rest of the molecule.

Experimental Section

The detailed experimental setup has been already published elsewhere.⁴ Briefly, the gas mixture of dimethyldiazirine (~3%) and He was expanded into a vacuum chamber through a nozzle orifice (d=0.5 mm, General Valve) with a home-made nozzle driver. The vacuum chamber was equipped with a 6"-diffusion pump and a liquid N₂ trap, and the background pressure was maintained below 10⁻⁵ Torr when the nozzle was operated with a repetition rate of 10 Hz. The second harmonic output of a Nd:YAG laser (GCR-150, Spectra-Physics) was used to pump a dye laser (Lambda Physik, Scanmate 2E) to generate the laser pulses in the 680-720 nm region. These laser pulses were then frequency-doubled to generate the UV laser pulses in the 340-360 nm region using a KDP crystal placed on an autotracker (Inrad I). The UV laser pulse was overlapped with the molecular beam at the position of ~25 mm downstream from the nozzle orifice. The fluorescence was detected by a PMT (Hamamatsu, H1161), gate-integrated by a boxcar (SR250), A/D converted *via* the interface (SR245), and stored in a PC using a data acquisition program which also controls the dye laser. The shot-to-shot fluctuation of the laser pulses were monitored by a pyroelectric joulemeter (Molelectron P5-01), and used for the normalization of the signal. The laser wavelength was calibrated with an accuracy of ±0.2 cm⁻¹ by mea-

suring the optogalvanic spectrum of a Ne hollow-cathode lamp.

Results and Discussion

The fluorescence excitation spectrum of dimethyldiazirine in the first 500 cm⁻¹ region from the origin is shown in Figure 1. The bands observed at 31, 65, 93, and 162 cm⁻¹ are labeled as 1, 2, 3, and 4, respectively in Figure 1, and assigned as the CH₃ torsional progression bands. The CH₃ torsional progressions combined with the 196.3 cm⁻¹ (14²), and 280.2 cm⁻¹ (9¹) bands are weakly observed, as indicated in Figure 1. The fluorescence excitation spectra taken at several different backing pressures show no difference in relative peak intensities, indicating that the observed bands are not from vibrationally excited states of the ground state. The unassigned bands in Figure 1 that are weakly observed might represent either the energy levels associated with the coupling of the CH₃ internal rotation to the overall rotation of the entire molecule or those coupled with other vibrational modes.

The CH₃ torsional mode is often treated as the hindered internal rotation, and corresponding vibrational frequencies provide the information about the potential shape along the CH₃ torsional angle. Here, we used a simple sinusoidal function for the potential as follows,

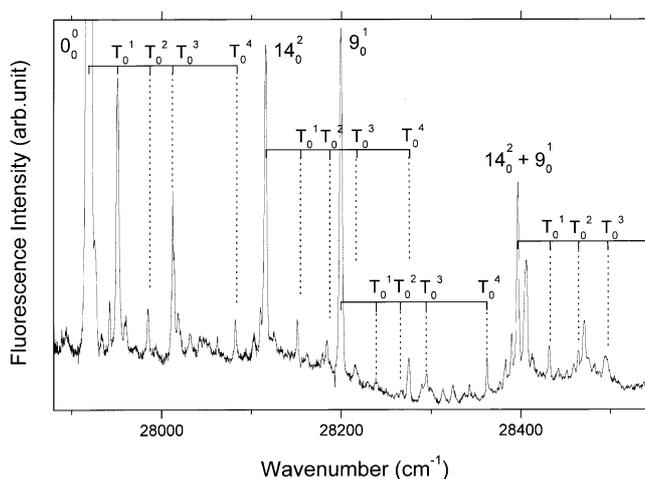


Figure 1. The first 500 cm⁻¹ region from the origin of the fluorescence excitation spectrum of the jet-cooled dimethyldiazirine. The CH₃ torsional progression bands are indicated as numbers, 1-4. See Ref. 4 for other assignments.

Table 1. Observed and calculated frequencies of the CH₃ torsional bands (in cm⁻¹)

| number ^a | observed | calculated ^b | symmetry |
|---------------------|----------|-------------------------|----------------|
| 1 | 31 | 36 | e |
| | - | 56 | a ₂ |
| 2 | 65 | 64 | a ₁ |
| 3 | 93 | 98 | e |
| 4 | 162 | 147 | e |

^aThe torsional progression number as indicated in Figure 1. ^bCalculated wavenumbers with $F=5.517$ cm⁻¹ and $V_3=60$ cm⁻¹.

$$V(\phi) = (V_3/2) \{1 - \cos(3\phi)\}$$

where ϕ and V_3 are the torsional angle and the barrier height of the potential, respectively. Actually, dimethyldiazirine has two identical CH₃ groups, and therefore, the kinetic energy term of the Hamiltonian should be the sum of two identical rotors and their interaction term. However, the interaction term contributes little to the energy levels, and is neglected in the calculation. Therefore, the Hamiltonian is simplified as follows,

$$H = -F(d^2/d\phi^2) + V(\phi)$$

where F is the internal rotational constant in cm⁻¹. The reduced moment of inertia, rI_α , can be calculated from the molecular structure using the relation of $rI_\alpha = I_\alpha \times (1 - \sum_i (I_\alpha/I_i) \lambda_i^2)$ where I_α represents the moment of inertia of the CH₃ top, $I_{i=a,b,c}$ represent the principal moments of inertia, and λ_i is the direction cosine between I_i and I_α , giving $F = h/(8\pi^2 \times rI_\alpha)$.⁵ Since the equilibrium molecular structure of the excited dimethyldiazirine is not known, the value of $F=5.517$ cm⁻¹, calculated from the molecular structure of the ground state,¹ has been used in the calculation. The nonzero matrix elements in the free rotor basis set, $|m\rangle = (2\pi)^{-1/2} \exp(-im\phi)$, are thus $\langle m|H|m\rangle = Fm^2 + (V_3/2)$ and $\langle m|H|m \pm 3\rangle = -V_3/4$. A 40×40 Hamiltonian matrix is diagonalized to give eigenvalues. In Table 1, the energy levels of the CH₃ torsional mode calculated with $V_3=60$ cm⁻¹ are listed with their symmetry species. Most of the calculated values are in good agreement with the experimental ones within ± 5 cm⁻¹. The 56 cm⁻¹ band (a₂) is symmetry-forbidden (only vibronically allowed), and thus is not observed in the spectrum. The barrier height is varied in the calculation, and it has been found that V_3 should be 60 ± 20 cm⁻¹ for reproducing the experiment reasonably well. The torsional potential height has been known to be ~ 400 cm⁻¹ in the ground state,¹ indicating that the torsional motion becomes almost free in the excited state, Figure 2. The decrease of the barrier height by the electronic excitation may be originated from the elongation of both C-N bonds induced by the electronic transition.⁶

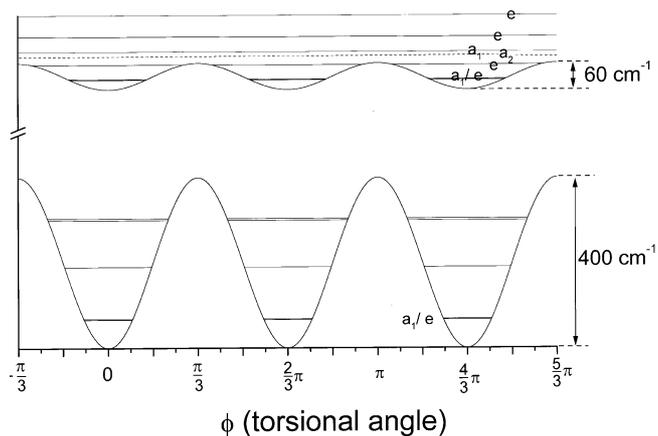


Figure 2. The torsional potential shapes assuming simple sinusoidal functions for both of the ground and excited states of dimethyldiazirine. The barrier height of the ground state is taken from Ref. 1.

In summary, the low frequency ($< \sim 200$ cm⁻¹ from the origin) bands observed in the fluorescence excitation spectrum of the jet-cooled dimethyldiazirine are assigned to vibrational modes associated with the CH₃ torsional motion. In the model calculation assuming a sinusoidal function for the potential shape along the CH₃ torsional angle, the barrier height of 60 ± 20 cm⁻¹ reproduces the experiment well. This suggests nearly free rotation of the CH₃ moiety with respect to the rest of the molecule in the electronically excited state of dimethyldiazirine.

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