

On the second electronic state near the S_1 state in dimethyldiazirine

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I. INTRODUCTION

Diazirines contain a highly strained, three-membered, heterocyclic CN_2 ring, and generate a carbene radical and N_2 molecule when photolyzed by ultraviolet (UV) wavelength light.^{1,2} Since Pierce and Dobyns first established the ring structure of the CN_2 group,³ spectroscopic properties of diazirines have been extensively investigated in the gas phase. While the infrared spectrum of diazirine was first analyzed by Ettinger,⁴ most of the early spectroscopic studies on diazirine and substituted diazirines have been performed by Merritt and co-workers.⁵⁻¹³ They determined the structures of methyl- and dimethyldiazirines with microwave spectroscopy^{10,11} and analyzed the infrared spectra of methyl- and dimethyldiazirines, confirming the cyclic structure.^{12,13} Robertson and Merritt have reported the electronic spectra for the $n-\pi^*$ transition of various diazirines.⁶⁻⁹ For diazirine, the simplest member of the group, the strongest band system in the UV was assigned to the $\bar{A}^1B_1-X^1A_1$ transition and the band origin was determined to be located at $31\,187\text{ cm}^{-1}$.⁶ A long progression of the C-N symmetric stretching vibration (ν_3) has been observed. Substituted diazirines such as methyl-, dimethyl-, bromomethyl-, and chloromethyldiazirines show similar spectra to the unsubstituted counterpart except that the transition frequencies exhibit a significant red shift upon substitution.⁷⁻⁹ The electronic spectroscopy of difluorodiazirine was first investigated by Lombardi *et al.*¹⁴ and later by Hepburn and Hollas.¹⁵

A controversy lying in the electronic spectroscopy of diazirines is whether there really exists an electronic state within a few hundred cm^{-1} from the $^1(n\pi^*)$ state. Lombardi *et al.* first proposed the existence of the second electronic state in their analysis of the UV spectrum of difluorodiazirine and assigned it to a $^3(\pi\pi^*)$ state.¹⁴ Later, Merritt and co-workers reported the observation of the transition to the triplet $\pi\pi^*$ state in close proximity to the $^1(n\pi^*)$ state in the electronic spectra of diazirine⁶ and several substituted diazirines.⁷⁻⁹ For difluorodiazirine, however, Hepburn and Hollas later suggested that the alleged origin of the second electronic system is the perturbed $5_1^17_0$ band of the $\bar{A}^1B_1-X^1A_1$ transition.¹⁵ This controversy has been left unresolved yet mainly because diazirines are thermally unstable at elevated temperatures and most of them have too low vapor pressure at dry ice temperature, which makes it difficult to investigate the temperature dependence of the spectra.

Recently, fluorescence from the $^1(n\pi^*)$ state of several

alkyldiazirines has been observed both in solution^{16,17} and in the gas phase.¹⁸ The fluorescence provides a simple and sensitive tool of laser-induced fluorescence for electronic spectroscopy, which enables one to obtain rotationally and vibrationally cold spectra of diazirines in supersonic jet expansions. The spectra of molecules cooled in jet expansions make the vibrational analysis simple and get rid of possible complications due to hot band transitions.

In this paper, we report the fluorescence excitation spectra of the S_1-S_0 transition of dimethyldiazirine (DMD) obtained both in cold supersonic jet expansions and in a static cell at room temperature. Comparison of the fluorescence excitation spectra obtained in a jet and in a cell at room temperature confirms that the band which was previously assigned to the origin of the second electronic state is really a hot band transition of the ($n-\pi^*$) transition.

II. EXPERIMENT

About 3% premixtures of dimethyldiazirine in He were prepared in a stainless steel cylinder of internal volume of 4 l at least 12 h prior to each experiment. The mixture, kept at the pressure of 1 atm, was expanded through a 0.5 mm diameter nozzle which was driven with a homemade driver. The output beam from a pulsed dye laser (Lambda Physik SCANmate 2E) pumped with a Q-switched Nd:YAG laser (Spectra-Physics GCR-150) was frequency doubled in a KDP crystal. The phase-matching angle of the crystal was set by an autotracker (Inrad I) controlled by a personal computer. The second harmonic output, which was separated from the fundamental with three dichroic mirrors, was directed through the side arms, exciting the cooled DMD molecules in the jet expansions. The distance from the nozzle to the excitation laser beam was set 25 mm. Fluorescence from the excited DMD was collected with a 2 in. diameter $f/2$ quartz lens, filtered with a color filter (Schott GG-380) and a slit aperture, and then detected with a PMT (Hamamatsu H928). The PMT output signal was integrated in a gated integrator (SRS 250) and stored in the PC with the corresponding laser wavelength. The shot-to-shot fluctuation of the excitation laser pulses was monitored with a pyroelectric joulemeter (Molelectron P5-01). The energy of the excitation pulse was kept ≤ 1.0 mJ/pulse and the laser beam was unfocused to avoid saturation of transitions. The optogalvanic spectrum of a Ne hollow cathode lamp provided a frequency calibration for the dye laser with an accuracy of $\pm 0.2\text{ cm}^{-1}$. The fluorescence excitation (FE) spectrum at room tempera-

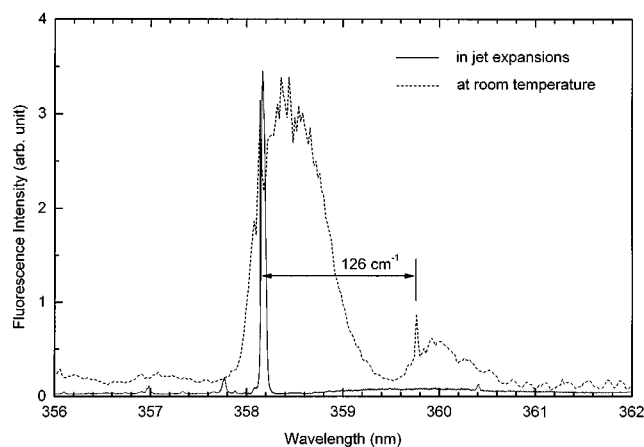


FIG. 1. The origin band region of the fluorescence excitation spectra of dimethyldiazirine obtained in a cell at room temperature (a) and in supersonic jet expansions (b). The band which appears 126 cm^{-1} red from the origin band at room temperature disappears in the spectrum obtained in jet expansions, confirming that it is a hot band of the $S_1 \leftarrow S_0$ transition.

ture was obtained with the fluorescence cell employed in the previous study.¹⁸ The DMD sample was synthesized following the procedure described previously.¹⁹

III. RESULTS AND DISCUSSION

Figure 1 shows two FE spectra which are obtained in a room-temperature cell and in supersonic jet expansions, respectively, for the wavelength region near the S_1 origin. As mentioned above, Merritt *et al.* have proposed the existence of another electronic state within less than a few hundred cm^{-1} from the S_1 state in all diazirines.^{6–9} They assigned the “second” electronic state to the ${}^3(\pi\pi^*)$ state. In DMD, the “second” electronic state was allegedly located 126 cm^{-1} red from the S_1 origin. It is demonstrated below, however, that the alleged “second” electronic state does not really exist and is a hot band transition of the $S_1 \leftarrow S_0$ system.

In the FE spectrum at room temperature, a band appears 126 cm^{-1} red from the S_1 origin, at exactly the same position where Robertson and Merritt reportedly observed the origin of the second state. In the jet spectrum, however, the band completely disappears, which confirms that the band is not the origin of another electronic transition but a hot band of the $S_1 \leftarrow S_0$ transition.

Further evidence supporting our conclusion comes from the vibrational frequencies⁹ that Robertson and Merritt reported for the second electronic state. All of the eight fundamental frequencies of the second electronic state are in perfect agreement with those of the S_1 state within 2 cm^{-1} , which, we suppose, is the uncertainty of frequency measurement in their work. If the second electronic state is the ${}^3(\pi\pi^*)$ state as they suggested, the fundamental frequencies of at least a few vibrational modes, in particular, the N=N stretching, should be different from those of the S_1 state, which is the ${}^1(n\pi^*)$, by a larger extent than the 2 cm^{-1} .

Possibly the experimental difficulty, which prevented Robertson and Merritt from trying the temperature dependence study, might lead them to the wrong conclusion; DMD is unstable at higher temperature than the room temperature and gives too low vapor pressure at the dry ice temperature, at which low-temperature spectra are usually obtained. They should have arrived at same conclusion as ours on the -126 cm^{-1} feature if they had investigated the temperature dependence of the spectrum.

The fact that the -126 cm^{-1} band, which was previously assigned to the origin of the second electronic state, turns out to be a hot band of the $S_1 \leftarrow S_0$ transition, invokes a question on the alleged observation of the second electronic state near the S_1 state in other diazirines such as diazirine, chloro- and bromomethyldiazirines, difluorodiazirine, and methyldiazirine. In fact, for difluorodiazirine, Hepburn and Hollas have questioned the existence of the second electronic state and suggested that the alleged origin of the second electronic system may be the perturbed $5_1^1 7_0^1$ of the $\tilde{A}^1 B_1 - X^1 A_1$ system.¹⁵ Our observation along with the suggestion of Hepburn and Hollas implies that the existence of the “second” excited electronic state within a few hundred wave numbers from the S_1 origins of various diazirines is questionable and should be subject to re-examination. Work is under way along this line.

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