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Direct formation of CH_2 ($\tilde{b}\,^1B_1$) in the near-UV photodissociation of diazirine

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Abstract

A prompt, long-lived, and red fluorescence has been observed in the photodissociation of the jet-cooled diazirine (H_2CN_2) excited at the origin (322.96 nm) of the $S_1 \leftarrow S_0$ transition. The fluorescence decays (~ 16 μs) and range (> 575 nm) indicate that the emitting species is the electronically excited singlet methylene, CH_2 ($\tilde{b}\,^1B_1$). The linear dependence of the fluorescence intensity on the photolysis laser power strongly supports that the fluorescing CH_2 ($\tilde{b}\,^1B_1$) is produced directly from the first excited singlet state of diazirine. The observation that the fluorescence appears in the visible wavelength region indicates that the CH_2 ($\tilde{b}\,^1B_1$) fragments are highly vibrationally excited. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Diazirine (H_2CN_2), which contains a three-membered CN_2 ring, has a strong $\pi^* \leftarrow n$ transition in the near-ultraviolet (UV) wavelength region, followed by the decomposition into CH_2 and N_2 products [1]. Due to its structural uniqueness and the strong absorption band, the photochemistry of diazirine has been both extensively and intensively studied [1] since its first preparation [2,3].

However, diazirine has not drawn that much attention of recent state-resolved studies [4] on the photodissociation dynamics despite that its photochemistry brings some interesting dynamical features; it produces easily detectable simple fragments whose spectroscopic data are well documented and the photochemical decomposition involves the breakage of a highly strained three-membered ring. In addition, it is small enough to be tractable with the state-of-the-art theoretical methods. It seems like that the explosive nature of diazirine has prevented it from becoming the topic of recent experimental studies.

Recently Platz and coworkers [5,6] investigated the photochemistry of several substituted diazirine compounds in liquid solutions. They observed fluorescence and found that its intensity decreases as the temperature increases, showing that electronically excited diazirines decay through non-radiative processes with an activation barrier. In contrast to many recent experimental studies for the substituted diazirines, only a few theoretical studies [7–9] have been reported. In 1978, Bigot et al. first studied potential energy surfaces of the ground and low-lying excited states with the SCF method using STO-3G basis set [7]. Later, Müller–Remmers and Jug inves-

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tigated the photochemical reaction mechanism of the electronically excited diazirine with a SINDO1 method [8]. Yamamoto et al. has reported the most detailed theoretical study on the photodissociation process of diazirine [9]. By using the MC-SCF method with a 6-31G* basis set, they predicted that the diazirine molecule excited to the S_1 state decomposes into $N_2 + {}^1CH_2$ via two different singlet paths with little barriers.

Here, we synthesized the diazirine molecule and investigated its photochemistry in the collisionless condition. In an attempt to detect the ${}^1CH_2$ ($\tilde{a}\,{}^1A_1$) photofragments, which was expected from the known photochemistry [1,7–9], we observed a long-lived and red fluorescence in the absence of the probe laser tuned to the $\tilde{b}\,{}^1B_1 \leftarrow \tilde{a}\,{}^1A_1$ transition of the ${}^1CH_2$. A temporal and spectral characterization of the fluorescence has led to the conclusion that the electronically excited CH_2 ($\tilde{b}\,{}^1B_1$) is formed in one-photon photodissociation of diazirine with the near-UV light.

2. Experimental

The diazirine sample was synthesized following the procedure reported previously [10]. The diazirine gas was mixed with He gas in a 4-l stainless steel cylinder. The diazirine was about 3% in the total pressure of 6 atm. Diazirine in the mixture was fairly stable and did not show any sign of decomposition after the storage for 1 month at room temperature.

The mixture, kept at the pressure of 1 atm, was expanded through a 0.5 mm diameter nozzle, which was driven with a home-made 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 diazirine molecules in the jet expansions. The distance from the nozzle to the excitation laser beam was 25 mm. Fluorescence from the photofragments was collected with a 2″ diameter $f/2$ quartz lens, filtered with a color filter (Schott OG-530), and then detected with a PMT. Two kinds of PMT were employed; for the spectral distribution measurement, a red-sensitive side-view PMT (Hamamastu R928) was used and a 2″ diameter head-on-type PMT (Hamamatsu H1161), which provides much larger viewing area, was used for the lifetime measurement. The time evolution of the fluorescence signal was obtained by accumulating the PMT signal with a 300 MHz digital oscilloscope (LeCroy 9450A). The lifetime was deduced by fitting the decay curve with a least-squares fitting routine. Since the lifetime of the fluorescence was very long (vide infra), it was not possible to obtain the dispersed fluorescence spectrum with a monochromator equipped with a PMT and a gated integrator. Instead, the spectral distribution was roughly estimated from the intensity change of the PMT signal by varying the kind of the color filters in front of the PMT.

The shot-to-shot fluctuation of the excitation laser pulses was monitored with a pyroelectric joule meter (Molectron P5-01). The energy of the excitation pulse was kept at approximately 1.0 mJ/pulse and the laser beam was mildly collimated to 1.0 mm in diameter at the interaction region with a 1-m focal length quartz lens. The optogalvanic spectrum of a Ne hollow cathode lamp provided a frequency calibration for the dye laser with an accuracy of ± 0.2 cm^{-1}.

3. Results and discussion

As expected from the broad absorption spectrum for the $S_1 \leftarrow S_0$ transition [11], no fluorescence from the electronically excited diazirine (S_1) was observed, which should appear in the UV or blue visible region as in other diazirines [5,6,12,13]. Instead, a prompt and long-lived emission in the red was observed when diazirine was exited at the origin band (322.96 nm) of the $S_1 \leftarrow S_0$ transition in collisionless supersonic jet expansions.

In order to identify the species giving the prompt fluorescence, the temporal decay of the total emission was measured. Fig. 1 shows the decay curve obtained with an OG 530 color filter in front of the PMT, which transmits most of the fluorescence while blocking the scattered light of the excitation. The

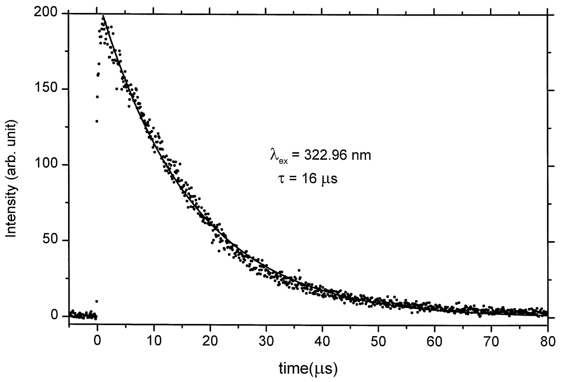

Fig. 1. The temporal decay of the prompt and red fluorescence observed in the photodissociation of diazirine in the near-UV wavelength (322.96 nm). The lifetime was estimated to be 16 μs. Some deviation from the single-exponential decay is noticeable, which is expected for the species with long lifetimes; a large portion of the emitting species travels out of the viewing zone.

decay curve follows a single-exponential function in general but shows some deviation at the long delay time. The deviation is likely due to the fact that the emitting species travels out of the viewing zone of the PMT with a rate faster than the inverse of its lifetime. A least-squares fit to the experiment gives a lifetime of 16 μs with an uncertainty of ±0.2 μs. The second key information required for the identification of the emitting species is the spectral distribution of the emission. As stated in Section 2, we failed to disperse the emission with a monochromator and our current detection system. As an alternative, we measured the intensity of the PMT signal with varying the cut-off wavelength by using several long-pass color filters in front of the PMT. The dispersed spectrum was then roughly estimated from the intensity variation with the cut-off wavelength change (Fig. 2). The broken line is the estimated spectral distribution of the emission. In spite of the low resolution of this method, it is clear that the emission is most intense at the wavelengths longer than 575 nm. It should be mentioned here that the spectral sensitivity of the PMT (Hamamatsu R928) significantly decreases at the wavelength longer than 750 nm and thus the intensities at these wavelengths are underestimated.

The fluorescence lifetimes of CH_2 ($\tilde{b}\,^1B_1$) have been measured by many groups, but exact times are still controversial [14]. Recently, Moore and coworkers have carefully measured the lifetimes of CH_2 ($\tilde{b}\,^1B_1$) in a collisionless condition. The lifetime strongly depends on the excited quantum state and varies from 4 to 10 μs for the (0,14,0), (0,15,0), (0,16,0) and (0,17,0) vibrational levels [14]. In general, the lower vibrational levels tend to have the longer lifetimes. Therefore, the observed lifetime of 16 μs is consistent with that of CH_2 ($\tilde{b}\,^1B_1$) in the case where most of the fragments are populated in the (0,14,0) and/or in the lower levels (vide infra). The red spectral distribution of the fluorescence is also in a good agreement with the emission spectrum of the laser-excited CH_2 ($\tilde{b}\,^1B_1$) [15] and that of the photochemically generated CH_2 ($\tilde{b}\,^1B_1$) in the 193 nm photodissociation of ketene [16].

There are two possible mechanisms for the generation of CH_2 ($\tilde{b}\,^1B_1$) in the photodissociation of CH_2N_2: one is the direct formation of CH_2 ($\tilde{b}\,^1B_1$) from the one-photon excited CH_2N_2 (S_1) and the other from the highly excited CH_2N_2 (S_n, $n \geqslant 2$) by two- or three-photon absorption.

$$CH_2N_2(S_0) + h\nu \to CH_2N_2(S_1) \to CH_2\left(\tilde{b}\,^1B_1\right) + N_2\left(X^1\Sigma_g^+\right) \quad (1)$$

$$CH_2N_2(S_0) + nh\nu(n = 2 \text{ or } 3) \to CH_2N_2(S_n) \to CH_2\left(\tilde{b}\,^1B_1\right) + N_2\left(X\,^1\Sigma_g^+\right) \quad (2)$$

The simplest way to distinguish these two mecha-

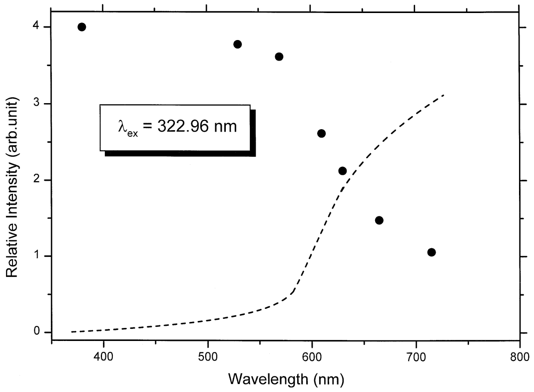

Fig. 2. The spectral distribution of the prompt emission in the photodissociation of diazirine in the near-UV wavelength. The broken line shows an estimated spectrum and the procedure to obtain this spectrum is described in the text. The spectrum is very similar to that of the CH_2 ($\tilde{b}\,^1B_1$) fragments generated in the 193 nm photodissociation of ketene [16].

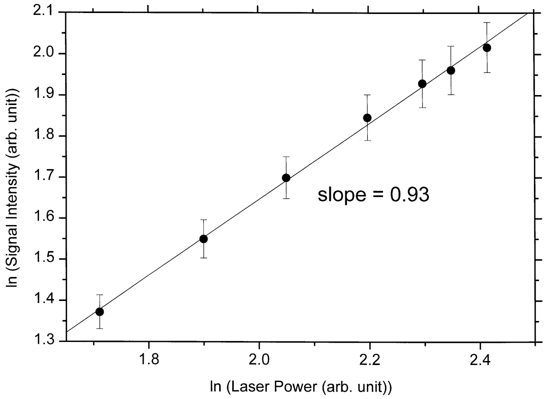

Fig. 3. The laser power dependence of the CH_2 ($\tilde{b}\,^1B_1$) fluorescence intensity. The fluorescence intensity linearly depends upon the laser power, confirming that the formation of CH_2 ($\tilde{b}\,^1B_1$) is the one-photon process.

nisms is to measure the laser power dependence of the fluorescence signal intensity. The first Scheme (1) would give a linear dependence of the fluorescence on the laser power, while the second Scheme (2) would give a quadratic or cubic dependence with two or three photons absorbed, respectively. As shown in Fig. 3, the ln(fluorescence intensity) – ln(laser power) plot gives a slope of 0.93, and this strongly supports the Scheme (1). That is, the formation of CH_2 ($\tilde{b}\,^1B_1$) is from the one-photon process. Another possibility is the excitation of the CH_2 ($\tilde{a}\,^1A_1$) formed in one-photon photodissociation of diazirine to the $\tilde{c}\,^1A_1$ state by the photolysis laser light. Even in this case, however, the power dependence should be quadratic, which is contrary to the observation. Furthermore no fluorescence has been reported from the $\tilde{c}\,^1A_1$ state. It is convincing, therefore, that the electronically excited singlet methylene radical, CH_2 ($\tilde{b}\,^1B_1$) is directly formed in the decomposition of CH_2N_2 excited to its first singlet excited state (S_1).

The significant generation of CH_2 ($\tilde{b}\,^1B_1$) in the photodissociation of diazirine in the near-UV has not been expected in the former studies [1,7–9]. In a recent ab initio study, Yamamoto et al. [9] have mentioned the possibility of the existence of the reaction pathway from $CH_2N_2(S_1)$ to CH_2 ($\tilde{b}\,^1B_1$) and N_2 products. However, they concluded that the contribution of this channel would be minor because there is a well-defined reaction pathway leading the system toward the singlet diazomethane conical intersection exclusively. It is interesting to note that the formation of CH_2 ($\tilde{b}\,^1B_1$) has been postulated before on the photochemical reactions of $^1CH_2$ to explain the higher reactivity of photochemically generated carbene compared to the thermally generated carbene [17]. Our observation suggests that this postulate may be true, but more data for other diazirines would be needed to confirm this postulate.

The observation that the emission spectrum of the CH_2 ($\tilde{b}\,^1B_1$) fragments appears in the visible region indicates that the CH_2 ($\tilde{b}\,^1B_1$) fragments are produced with a significant vibrational excitation. The (0,14,0)–(0,0,0,) band of the $\tilde{b}\,^1B_1 \leftrightarrow \tilde{a}\,^1A_1$ transition spans from 588 to 615 nm for the rotational levels up to $J = 8$ [14]. Hence the short wavelength limit of 575 nm of the emission indicates that the CH_2 ($\tilde{b}\,^1B_1$) fragments are populated at least up to the (0,14,0) level. Such a high vibrational energy content might come from the large difference in the H–C–H bond angles of the CH_2N_2 (S_1) and CH_2 ($\tilde{b}\,^1B_1$) radicals, about 125° [9] and 180° [18], respectively. That is, as the dissociation proceeds, the bending potential experiences a strong torque along the bending angle, and this gives highly vibrational excitation of the fragment. A quantitative measurement of the vibrational energy content requires a high-resolution dispersed fluorescence spectrum, which is under progress with a photon counting detection system in this group, and thus detailed discussion on the dynamical implication of the vibrational energy excitation is deferred to the forthcoming paper.

The existence of the CH_2 ($\tilde{a}\,^1A_1$) fragment has been also checked since energetically CH_2 ($\tilde{a}\,^1A_1$) can be surely formed in the photodissociation of diazirine. We tried to detect the CH_2 ($\tilde{a}\,^1A_1$) fragment by exciting its (0,15,0)–(0,0,0) band with a probe laser light, but have failed because it was impossible to distinguish the emission due to laser-induced fluorescence by the probe laser from the prompt emission obtained with the photolysis laser only. Furthermore, the broad quantum state distribution of the CH_2 ($\tilde{a}\,^1A_1$) fragments would give very weak signal in the laser-induced fluorescence technique, in which only a single quantum state is probed at a given excitation wavelength. Therefore, this observation does not exclude the non-negligible yield of the CH_2 ($\tilde{a}\,^1A_1$) fragment. An ingenious method which can simultaneously measure the CH_2 ($\tilde{a}\,^1A_1$) and CH_2 ($\tilde{b}\,^1B_1$) fragments should be devised to give an unambiguous answer to this question.

In conclusion, we experimentally found that the electronically excited singlet methylene, CH_2 ($\tilde{b}\,^1B_1$) is generated in the photodissociation of diazirine (H_2CN_2) by the $S_1 \leftarrow S_0$ transition. The long lifetime and red spectral range of the fluorescence strongly suggest that the CH_2 ($\tilde{b}\,^1B_1$) fragment is highly vibrationally excited. High-resolution dispersed spectrum of the fluorescence from CH_2 ($\tilde{b}\,^1B_1$) fragments, as well as measurements of dynamical quantities such as the translational and internal energy contents of N_2 fragments or branching ratios of the CH_2 ($\tilde{a}\,^1A_1$) and CH_2 ($\tilde{b}\,^1B_1$) channels would be helpful for the better understanding of the dissociation dynamics of diazirine in the S_1 state. Work is underway along this direction.

Acknowledgements

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