ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 108 (1997) 123–128

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A: CHEMISTRY

Fluorescence and radiationless decay pathways of dimethyldiazirine (S_1) in the gas phase

Taek-Soo Kim [a], Young S. Choi [a,*], Ilhwan Kwak [b]

[a] *Department of Chemistry, Inha University, Incheon 402-751, South Korea*
[b] *Bolak Company Limited, Technical Research Institute, Hwasung-gun, Kyungki-do, South Korea*

Received 10 July 1996; revised 2 December 1996; accepted 6 February 1997

Abstract

Fluorescence emission was observed from dimethyldiazirine (DMD) excited at 350–360 nm, and the fluorescence excitation spectrum was obtained in the gas phase. The emitting state was identified as the first excited singlet state, $S_1(^1B_2)$, based on the dispersed fluorescence spectrum and a comparison of the excitation spectrum with the absorption spectrum reported previously. The S_1 state efficiently decayed through radiationless processes. An analysis of the relative decay rates, deduced from the intensity ratios of the fluorescence excitation and photoacoustic spectra, led to the conclusion that DMD in the S_1 state decays via two radiationless decay pathways: one was energy dependent with a barrier of 300 ± 50 cm^{-1} and the other was almost energy independent. The former was attributed to vibrational predissociation to dimethylcarbene and N_2, and the latter to internal conversion to highly vibrationally excited levels of S_0. The fluorescence quantum yield was estimated to be 0.002 or less at the electronic origin of the S_1 state. © 1997 Elsevier Science S.A.

Keywords: Dimethyldiazirine; Fluorescence; Photochemistry; Radiationless processes

1. Introduction

Diazirines are a group of molecules containing a three-membered ring of carbon and two double-bonded nitrogen atoms. Since identification [1], much has been learned of the electronic spectroscopy [2–5], photochemistry [6,7] and thermal decomposition [6] of various diazirines. On photolysis in the ultraviolet (UV) or thermolysis, diazirines generate a molecule of nitrogen and a carbene [6,7]. If the carbene has an α-hydrogen atom, it will rapidly transform into an alkene through H migration. Although a variety of studies have revealed many aspects of diazirine photochemistry, controversies still exist regarding the concerted nature of the breaking of the two C–N bonds during decomposition and the primary decay pathways of electronically excited diazirines [6,7].

Dimethyldiazirine (DMD), in which the CN_2 ring plane is perpendicular to the plane containing the three C atoms, has C_{2v} symmetry [8]. Its long-wavelength band extends from approximately 295 to 359 nm in the gas phase [5]. The gas phase photolysis of DMD, excited in this band, generates mostly propene and N_2, suggesting that the primary dissociation channel is to $(CH_3)_2C\!: + N_2$ [9]. Recently, Modarelli et al. [10,11] have observed fluorescence from electronically excited DMD in solution; the intensity of emission decreases as the temperature increases, indicating that electronically excited DMD decays through a non-radiative decay process with an activation barrier. The triplet states play only a minor role in the photodecomposition of alkyldiazirines. Seburg and McMahon [12] have photolysed 3-methyldiazirine isolated in various low-temperature matrices. They reported that the [1,2] H shift in ethylidene is very fast and that triplet states are not involved in the photochemistry of diazirines even in an Xe matrix.

Theoretical studies have been conducted on the photochemical processes of diazirines in the S_1 state [13–15]. Most recently, Yamamoto et al. [15] have investigated the potential energy surface and minimum energy paths for the photochemical decomposition of diazirine (S_1) by employing a higher level method and a larger basis set than in previous studies. They noticed that diazirine excited in its S_1 state decays through two almost barrierless paths; one leads to ground state diazomethane and the other yields directly $N_2 + {}^1CH_2$. Furthermore, the efficiency of intersystem crossing is predicted to be so low that it barely contributes to the photochemistry of diazirine.

---

* Corresponding author. Tel.: +82 32 860 7672; fax: +82 32 867 5604; e-mail: yschoi@dragon.inha.ac.kr

1010-6030/97/$17.00 © 1997 Elsevier Science S.A. All rights reserved
PII S1010-6030(97)00078-6

Stimulated by these recent studies in solution and the theoretical predictions, a series of investigations on the spectroscopy and photochemical processes in electronically excited diazirines has been initiated in our group. In this paper, we report the observation of fluorescence from gaseous DMD molecules excited in the first singlet excited state (S_1). The emitting state is unambiguously identified to be the $S_1(^1B_2)$ state. The intensity variation of the fluorescence excitation spectrum as a function of energy suggests that, in the gas phase, DMD (S_1) decays via two major non-radiative channels: energy-independent internal conversion and vibrational predissociation over a small potential barrier which is formed by the avoided crossing of the $n\pi^*$ and $n\sigma^*$ potential energy surfaces [13–15].

2. Experimental details

The experimental apparatus employed in this work has been described in detail elsewhere [16]. Briefly, gaseous DMD is passed slowly through a fluorescence cell (Pyrex tube; length, 50 cm; diameter, 1 in) with two quartz windows on both sides. In the middle of the cell, a viewport with a quartz window is attached to monitor the fluorescence. The output beam from a pulsed dye laser (Lambda Physik SCANmate 2E), pumped with a *Q*-switched Nd:YAG laser (Spectra-Physics GCR-150), is frequency doubled in a KDP crystal. The second harmonic, which is separated from the fundamental with three dichroic mirrors, is directed through the fluorescence cell at room temperature. Fluorescence from excited DMD is collected with a quartz lens (diameter, 2 in), filtered with a colour filter and an aperture, and then detected with a photomultiplier tube (PMT) (Hamamatsu H928). The PMT output signal is integrated with a gated integrator (SRS 250) and stored in a personal computer. The shot-to-shot fluctuation of the laser power is monitored with a pyroelectric joulemeter (Molectron P5-01). The energy of the excitation pulse is maintained at 1.0 mJ per pulse and the laser beam is unfocused to avoid saturation of transitions. The optogalvanic spectrum of an Ne hollow cathode lamp provides frequency calibration for the dye laser with an accuracy of $\pm 0.5\ \mathrm{cm}^{-1}$.

The simple photoacoustic cell employed for photoacoustic spectroscopy is a Pyrex tube (diameter, 1 in; length, 10 cm) with two quartz windows at both ends and an electric microphone in the middle. The laser beam is passed unfocused through the cell and the acoustic signal from the microphone is processed in the same manner as in the fluorescence excitation experiment. The dispersed fluorescence spectrum is obtained with a scanning monochromator (focal length 25 cm). The fluorescence from excited DMD is imaged on the entrance slit of the monochromator and the dispersed light is detected with a PMT. The wavelength of the monochromator is calibrated with the emission lines of an Ne hollow cathode lamp.

The DMD sample was synthesized following the procedure described previously [17].

3. Results and discussion

3.1. Observation of fluorescence and identification of the emitting state

Fluorescence is observed from DMD in the gas phase on irradiation in the wavelength region 350–360 nm. The intensity is relatively weak, implying a low fluorescence quantum yield. In order to identify the emitting molecule and electronic state, the fluorescence excitation and dispersed fluorescence spectra were taken. The fluorescence excitation spectrum (5 Torr DMD, 25 °C) is shown in Fig. 1 (full curve). The prominent bands in the excitation spectrum are listed in Table 1, together with the corresponding bands observed in the absorption spectrum of DMD [5] and their assignments. The positions of the bands observed in the fluorescence excitation spectrum are in excellent agreement with those in the absorption spectrum, confirming that the fluorescence carrier is the DMD molecule. This agreement indicates that the upper electronic state is the $\tilde{A}^1B_2$ state identified in the absorption spectrum [5]. This is the first excited singlet state (S_1) of DMD, which originates from the $n\pi^*$ configuration [5,13–15].

The agreement between the excitation and absorption spectra does not necessarily prove that the $S_1(^1B_2)$ state is the emitting state, because the initially excited DMD may relax to a nearby electronic state through an intramolecular process. such as internal conversion or intersystem crossing. Since this ambiguity can be clearly resolved by the examination of the frequency distribution of the emission spectrum, the dispersed emission spectrum from the origin band was obtained and is shown in Fig. 2. Although the resolution and signal-to-noise ratio of the spectrum are not outstanding, the resonance fluorescence band corresponding to the 0_0^0 transition is discernible, establishing that the emission is the fluorescence accompanying the transition from the S_1 state to the ground state (S_0), $\tilde{X}^1A_1$.

The existence of fluorescence, although fairly weak, enables the simple but sensitive spectroscopic tool of laser-induced fluorescence (LIF) to be employed to determine the structure and vibrational frequencies in the S_1 state. Therefore extensive studies on the high-resolution spectroscopy and state-resolved photodissociation dynamics of DMD and other diazirines in general are expected to follow this work. The fluorescence lifetime of the DMD molecules excited to the S_1 state is much shorter than the estimated radiative lifetime of DMD (S_1) from the absorption spectrum (see below). This discrepancy implies that intramolecular electronic relaxation processes, such as predissociation, internal conversion and/or intersystem crossing, occur in DMD (S_1), which are discussed in the next section.

3.2. Radiationless decay pathways

The most noticeable characteristic of the fluorescence excitation spectrum in Fig. 1 is that the band intensity strongly decreases with increasing vibrational energy in the S_1 state. As a result, the bands are too weak to be identified below 346

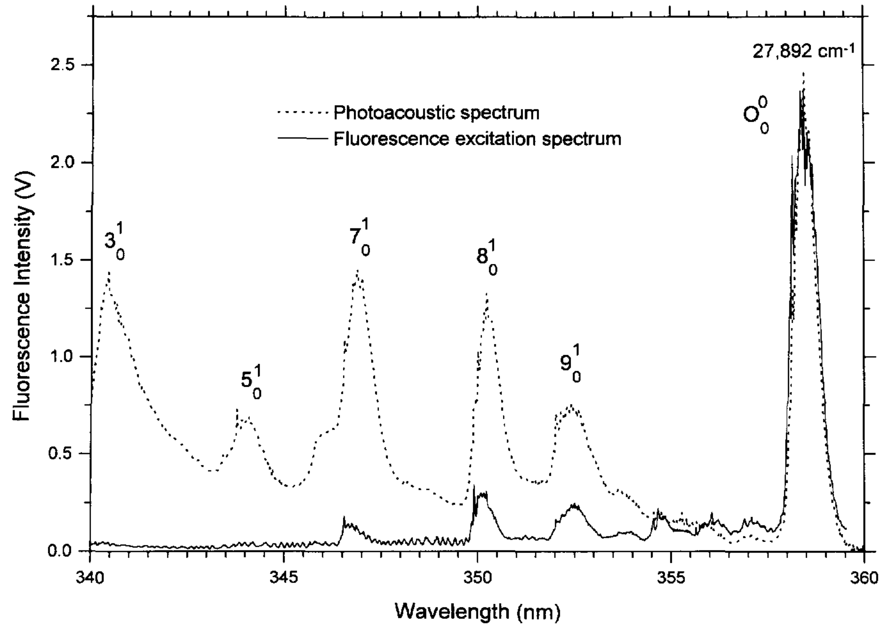

Fig. 1. Fluorescence excitation (FE) and photoacoustic (PA) spectra of the $S_1 \leftarrow S_0$ transition of dimethyldiazirine in the gas phase. Vibronic assignments are given for the prominent bands of totally symmetric (a_1) vibrations following Ref. [5]. ν_3, ν_5, ν_7, ν_8 and ν_9 are the N=N stretch, symmetric CH_3 deformation, CH_3 rock, C–C stretch and CCC deformation respectively. The intensity of the FE spectrum decreases strongly with increasing energy, but the PA signal persists, indicating the manifestation of an energy-dependent non-radiative decay pathway.

Table 1
Positions of the observed bands in the fluorescence excitation and absorption spectra of dimethyldiazirine in the gas phase

Fluorescence excitation spectrum [a]	Absorption spectrum [b]	Assignments [b]
358.14 nm	358.03 nm	0^0_0
352.02 nm	351.91 nm	9^1_0
349.90 nm	349.79 nm	8^1_0
346.54 nm	346.45 nm	7^1_0
343.78 nm	343.66 nm	5^1_0
340.14 nm	340.04 nm	3^1_0

[a] From this work. Vacuum wavelengths.
[b] From Ref. [5]. Air wavelengths.

nm in the spectrum. The strong decrease in the fluorescence quantum yield indicates a rapid increase in radiationless decay process(es) with increasing energy. The measurement of the fluorescence lifetimes of excited DMD in various vibronic levels should provide quantitative information on the decay rates and pathways in the excited state.

In DMD, however, even the origin band, which is expected to have the longest lifetime, is too short lived to be measured directly with our current time resolution of approximately 5–6 ns, limited by the pulse duration of the Nd:YAG laser. Hence, instead of measuring the decay rates directly, a semi-quantitative approach is attempted in this work; relative decay rates as a function of vibronic energy are deduced by calculating the ratios of the band intensities of the absorption and fluorescence excitation spectra. Since the band intensities measured in the photoacoustic spectrum are proportional to the number of photons absorbed, the photoacoustic spectrum gives the same information as the absorption spectrum. Since photoacoustic spectra are easily obtained, we used these intensities to calculate the relative band intensities. The fluorescence quantum yield ϕ_{fl} for a given vibronic level is proportional to the fluorescence intensity (I_{fl}) from the level divided by the photoacoustic signal intensity (I_{PA}) for the vibronic band

$$\phi_{fl} \propto I_{fl}/I_{PA} \tag{1}$$

It can also be defined in terms of the radiative and non-radiative rates, which are represented as k_r and k_{nr} respectively

$$\phi_{fl} = k_r/(k_r + k_{nr}) = k_r/k_{tot} \tag{2}$$

where $k_{tot} = k_r + k_{nr}$. Assuming that the radiative lifetime does not vary significantly with energy

$$k_{tot} \propto I_{PA}/I_{fl} \tag{3}$$

Eq. (3) implies that the I_{PA}/I_{fl} values for various vibronic bands give the relative decay rates.

The photoacoustic spectrum of DMD, taken for the same wavelength range as the fluorescence excitation spectrum, is plotted as the broken trace in Fig. 1. In contrast with the fluorescence excitation spectrum, the band intensity persists up to the highest energy measured in this work. The quantities I_{PA} and I_{fl} in the ratio I_{PA}/I_{fl} were obtained by integrating a range of approximately 1 nm around each absorption band. The resultant I_{PA}/I_{fl} ratios, which represent the relative decay rates, are plotted in Fig. 3.

Fig. 3 shows that the decay rate does not vary significantly up to 300 cm^{-1} above the band origin, but rapidly increases above that energy. This observation implies that a non-radi-

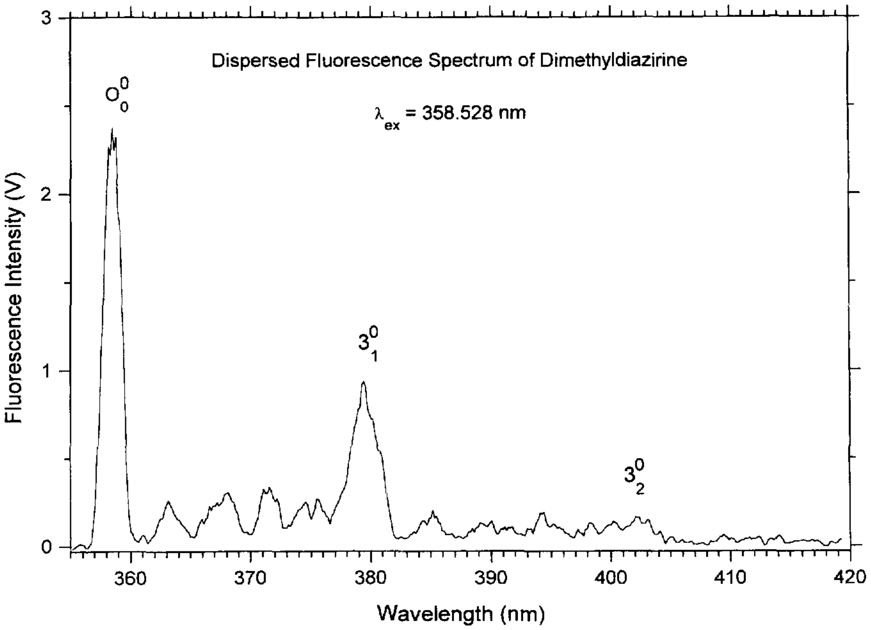

Fig. 2. Dispersed fluorescence spectrum of dimethyldiazirine excited to the electronic origin of the S_1 state. The resonance fluorescence band is the strongest and a short progression of the N=N stretching vibration (ν_3) is noticeable.

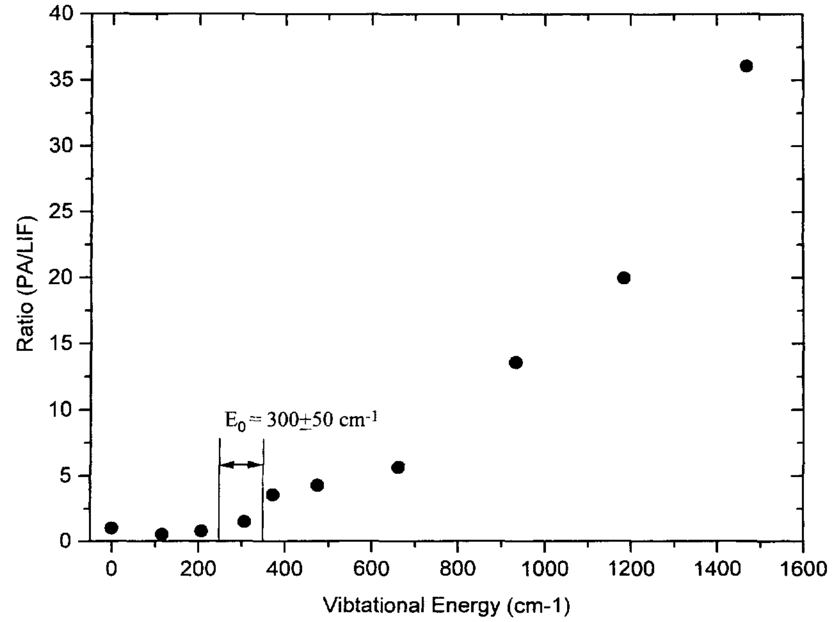

Fig. 3. Intensity ratios of the photoacoustic signal to the fluorescence excitation spectrum as a function of the vibrational energy in the S_1 state.

ative decay channel with an activation barrier opens up in this energy range. The height of the barrier was determined to be 300 ± 50 cm^{-1} from Fig. 3. This decay route is tentatively ascribed to the dissociation to a carbene radical and an N_2 molecule over the barrier on the S_1 potential energy surface.

According to the prediction of Yamamoto et al. [15], the primary photochemical pathway of diazirines (S_1) is the crossing of the barrier formed by the conical intersection of the $n\pi^*$ and $n\sigma^*$ potential energy surfaces. Recently, Modarelli et al. [10] have observed that the fluorescence intensity from various alkyldiazirines excited in the S_1 state in pentane solution decreases with increasing temperature. This temperature dependence supports the existence of a barrier on the S_1 potential energy surface of diazirines.

The *ab initio* study [15] on unsubstituted diazirine predicts a barrier height of 0.3 kcal mol^{-1} (105 cm^{-1}). This value is in reasonable agreement with our own, considering the fact that DMD has two methyl groups on the ring carbon atom. Better agreement comes from the temperature dependence of fluorescence of DMD (S_1) in pentane solution; Modarelli et al. [10] have obtained an activation energy of −0.964 kcal mol^{-1} (340 cm^{-1}). This agreement is so close that it seems somewhat fortuitous considering the fact that their work was performed in pentane solution.

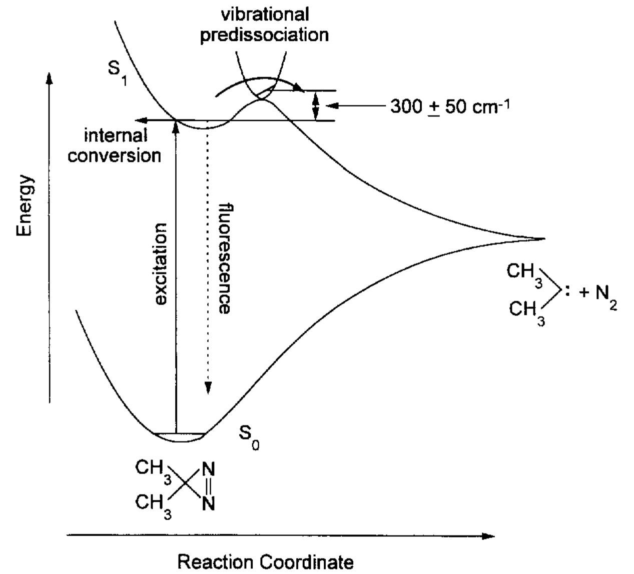

Fig. 4. Schematic potential energy diagram representing the photophysics and photochemistry of dimethyldiazirine excited in the S_1 state. The vibrational predissociation over the barrier becomes dominant as the excitation energy increases.

Even at energies lower than the barrier for predissociation, the fluorescence of DMD is quite weak. The fluorescence signal has an identical time response to the scattered light from our excitation laser (approximately 5 ns), indicating a fluorescence lifetime of less than 5 ns. From the absorption spectrum [18], the radiative lifetime (τ_0) was roughly estimated to be 2.3 μs [19]. The ratio of these two values gives a fluorescence quantum yield of less than 0.2% for the electronic origin and other bands below 300 cm^{-1}. The fact that the fluorescence quantum yield of the levels below the barrier for predissociation is much smaller than unity indicates that another efficient non-radiative decay pathway exists responsible for the decay of the DMD molecules excited to the levels below the predissociation barrier. This radiationless decay pathway, which is nearly energy independent and dominant in the decay of the levels below the barrier, is assigned to internal conversion from the S_1 to S_0 state. Intersystem crossing to the T_1 state is also a candidate, but recent experimental and theoretical studies exclude this possibility. Modarelli et al. [10] have failed to detect triplet–triplet transient absorption in the laser flash photolysis of DMD in pentane solution, and no triplet signal was detected in the matrix-isolated photochemistry of 3-methyldiazirine [12]. Yamamoto et al. [15] have also predicted, in their *ab initio* study, that the efficiency of intersystem crossing is very low in diazirine.

Combining all the results from this and previous studies, the potential energy surface and photophysics of DMD (S_1) may be summarized as shown in Fig. 4. The DMD molecule excited to the S_1 state decays via two radiationless pathways: internal conversion and vibrational predissociation. Below the barrier for vibrational predissociation, internal conversion dominates the decay. The vibrational predissociation channel becomes predominant as the energy increases above the barrier. Fluorescence emission is only a minor channel at all levels of excitation.

In pentane solution, the photodecomposition of DMD is known to proceed via two primary pathways: carbene formation and direct production of alkene through [1,2] hydrogen migration in the excited state [10]. Frey [6] found that gas phase photolysis of methyldiazirine gives ethylidene in 60% yield and ethylene in 40% yield. These previous results suggest that both of these pathways may be responsible for the predissociation of DMD in the S_1 state. Modarelli et al. [10,11] have observed that, on deuteration, the activation energy for predissociation increases from 0.964 kcal mol^{-1} to 1.509 kcal mol^{-1}, implying that direct alkene formation is the major channel for predissociation. Since deuteration may also change the barrier for the carbene formation pathway, it is premature to conclude that alkene formation is the dominant channel in the dissociation along the S_1 surface. Since the excess energy, which will be distributed among various degrees of freedom of the fragments, is significantly larger for the alkene formation channel than for the carbene pathway, the N_2 fragments formed in the alkene channel will have significantly more kinetic energy than those in the carbene channel. Hence the relative amounts of fast and slow N_2 fragments may be measured using time-of-flight mass spectrometry following the photolysis of DMD to provide a quantitative insight into the relative importance of the competing channels and their dependence on the photolysis wavelength. An experimental investigation along these lines is presently under way in our laboratory.

Acknowledgements

This work was supported by the Korean Science and Engineering Foundation (Project No. 95-0501-04-01-3) and the Ministry of Education of Korea through the 1995–1996 Basic Science Research Institute Program (Project No. BSRI-95-3432). The authors thank Dr. Charles Pibel for critical reading of the manuscript.

References

[1] L. Pierce, V. Dobyns, J. Am. Chem. Soc. 84 (1962) 2651.
[2] J.A. Merritt, Can. J. Phys. 40 (1992) 1683. L.C. Robertson, J.A. Merritt, J. Mol. Spectrosc. 19 (1966) 372.
[3] L.C. Robertson, J.A. Merritt, J. Mol. Spectrosc. 24 (1967) 44.
[4] L.C. Robertson, J.A. Merritt, J. Chem. Phys. 57 (1972) 941.
[5] L.C. Robertson, J.A. Merritt, J. Chem. Phys. 56 (1972) 2919.
[6] H.M. Frey, Adv. Photochem. 4 (1966) 225.
[7] M.T.H Liu, Chem. Soc. Rev. 11 (1982) 136.
[8] J.E. Wollrab, L.H. Schrpen, D.P. Ames, J.A. Merritt, J. Chem. Phys. 49 (1968) 2405.
[9] H.M. Frey, I.D.R. Stevens, J. Chem. Soc. (1963) 3514.
[10] D.A. Modarelli, S. Morgan, M.S. Platz, J. Am. Chem. Soc. 114 (1992) 7034.
[11] D.A. Modarelli, M.S. Platz, J. Am. Chem. Soc. 115 (1993) 470.

[12] R.A. Seburg, R.J. McMahon, J. Am. Chem. Soc. 114 (1992) 7183.

[13] B. Bigot, R. Ponec, A. Sevin, A. Devaquet, J. Am. Chem. Soc. 100 (1978) 8575.

[14] P.L. Müller-Remmers, K. Jug, J. Am. Chem. Soc. 107 (1985) 7275.

[15] N. Yamamoto, F. Bernardi, A. Bottoni, M. Olivucci, M. Robb, S. Wilsey, J. Am. Chem. Soc. 116 (1994) 2064.

[16] T.-S. Kim, Y.S. Choi, Bull. Korean Chem. Soc. 17 (1996) 745.

[17] E. Schmitz, R. Ohme, Chem. Ber. 94 (1961) 2166.

[18] T.-S. Kim, Y.S. Choi, A low-resolution absorption spectrum of the gaseous dimethyldiazirine obtained with a UV–visible spectrometer, unpublished results, (1995).

[19] S.J. Strickler, R.A. Berg, J. Chem. Phys. 37 (1962) 814.