

Photodissociation of CH_3N_3 —Spectral Evidences for the Formation of Triplet CH_3N Radical*

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Organic azides and nitrenes play significant roles in many organic reactions. Methyl azide CH_3N_3 and methyl nitrene CH_3N are their simplest forms respectively. Theoretical calculations^[1,2] predicted that the rearrangement of CH_3N via 1,2-hydrogen shift to CH_2NH on its singlet surface has little or no barrier, which implies that the isomerization would be very fast. As a result, it would be very difficult to observe the singlet CH_3N radical. It was generally accepted that in the photolysis of CH_3N_3 , no CH_3N could be produced. However, the triplet CH_3N radical is stable and can be produced in corona discharge^[3] as well as in the reaction of metastable nitrogen with CH_3N_3 ^[4]. Recently, Shang *et al.*^[5] suggested that the photodissociation of CH_3N_3 on its first excited singlet surface is a concerted process, that is to say, the 1,2-hydrogen shift and N_2 split-off occur synchronously. In this short communication, new spectral evidences for the existence of the triplet CH_3N radical in photodissociation of CH_3N_3 will be presented.

Methyl azide was prepared by the reaction of dimethyl sulfate and sodium azide^[6]. The photodissociation of CH_3N_3 was investigated in the UV region from 292 nm to 315 nm in a flowing gas cell. This wavelength region locates at the long wavelength side of the first electronic absorption band ($n \rightarrow \pi^*$ transition) of CH_3N_3 . The experimental setup was essentially the same as that in Ref. 5. The sample pressures were around 4×10^3 Pa. Briefly, a GCR-4 YAG laser-pumped PDL-3 dye laser (Spectra Physics) was used as the light source. R610, R640 and DCM (Exiton) dyes were used and the dye laser was frequency doubled in a BBO (Cstech) crystal to obtain the desired wavelengths. UV laser went into the cell through a quartz window with Brewster angle to reduce the scattered light. Side emissions were collected through a monochromator (WDP500-2A, the Second Optical Factory of Beijing). The output of the R955 photomultiplier tube was amplified and then averaged by the 4100 Boxcar system (EG & G). Both the 286 computer and the recorder were used to record the spectra. In lifetime measurements, the HP54510A digital

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oscilloscope was employed to record the realtime signal and the data were transferred to the 386SX-25 computer via GPIB bus.

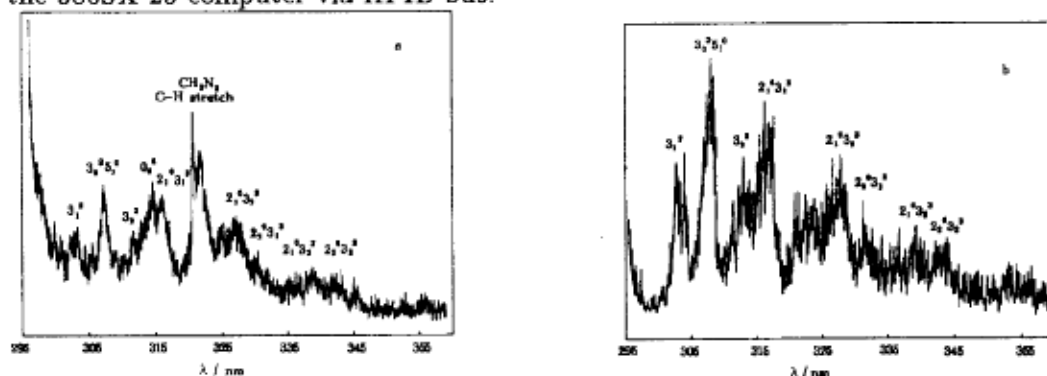
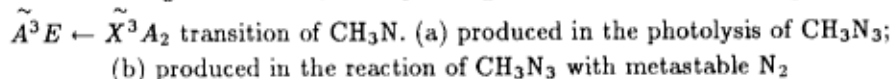


Fig.1 Comparison of the laser induced emission spectra showing the existence of the triplet CH_3N radical

The laser wavelength is 294 nm, corresponding to the excitation of the 3_0^3 band of the



The emission spectra were obtained at different wavelengths. It was found that some emission features track with the photolysis laser wavelengths and are Raman-like, while others fix at definite emission wavelengths and are fluorescence-like. The Raman-like emission has been analyzed already^[5]. The fluorescence-like emission was assigned to the emission from triplet CH_3N radical based on three experimental evidences: the dispersed spectra, the excitation spectra and the extrapolated lifetime. Fig.1a shows the emission spectrum in the photodissociation of CH_3N_3 at 294 nm which also exactly matches to the excitation of 3_0^3 band of the $\tilde{A}^3E \leftarrow \tilde{X}^3A_2$ transition of CH_3N . Fig.1b is the dispersed spectrum of the 3_0^3 band of the triplet CH_3N obtained previously in our laboratory^[4]. It can be seen clearly that the fluorescence part of Fig.1a fits the pure fluorescence spectrum of Fig. 1b very well in both the position and the relative intensity of the peaks. If the photodissociation wavelengths deviated to the absorption band of the radical, emissions from the excited triplet electronic states can still be observed though the intensities are weaker. These observations indicate that both the electronically excited and ground triplet CH_3N radical exist. The branching ratio of initially produced excited radical to the ground state radical is difficult to obtain because of the relatively high pressure used in our experiments. It is estimated that three collisions per molecule can occur within the laser pulse width (ca. 6 ns) at 4×10^3 Pa bulk CH_3N_3 .

The excitation spectra were obtained when the photolysis laser was scanned while the monochromator was set at 324.9 nm and 327.7 nm, corresponding to collecting the fluorescence of 0_0^0 band and 3_0^1 band of the $\tilde{A}-\tilde{X}$ system of CH_3N respectively. As shown in Fig. 2, the distinct peaks at about 314 nm and 307 nm fit well to our previously reported fluorescence excitation spectrum^[4].

The fluorescence decay profiles were recorded at various pressures. The time profile of scattered laser light was convoluted with the exponential decay of the fluorescence. Raman emission and background fluorescence or both were considered when necessary. Fig.3 shows the measured results. The extrapolated lifetime of the \tilde{A}^3E CH_3N at its ground vibration state is about 500 ns and the lifetime at $2.3 \times 10^2 \text{ Pa}$ read from the curve is 155 ns, consistent with the value measured previously^[4].

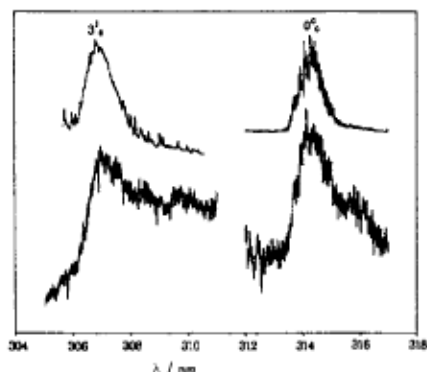


Fig.2 Fluorescence excitation spectra of the triplet CH_3N radical

Upper Curve: radical produced in the reaction of CH_3N_3 with metastable N_2 ; lower curve: radical produced in the photodissociation of CH_3N_3

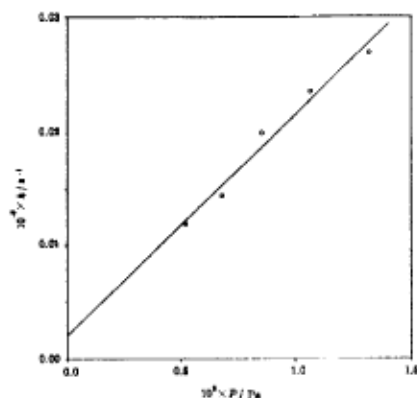
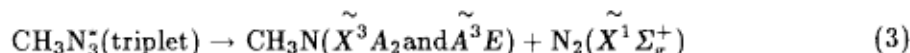
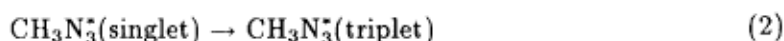
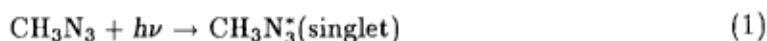


Fig.3 Emission decay rates of the excited triplet CH_3N at its ground vibration state as a function of CH_3N_3 pressure

It is too early to be sure of the mechanism about the formation of CH_3N radical, but one of the most plausible mechanisms could be



The key step of the above scheme is the singlet and triplet interaction of excited CH_3N_3 . According to the *ab initio* SCF-CI study of the photochemical behavior of HN_3 ^[7], the first triplet state, the first excited singlet state and the second triplet state lie on 5.11 eV, 5.53 eV and 5.59 eV respectively. These states are so close that the coupling among them could be intense. Experiments showed that photolysis of HN_3 can produce triplet NH radical in absence of collisions^[8]. Since the electronic structure of CH_3N_3 is similar to that of HN_3 , it is reasonable to assume that there exists strong interaction between the singlet and triplet state of the excited CH_3N_3 . The role of collision played in the reaction is not clear yet. It will be very desirable to explore the excited potential surface of CH_3N_3 and we are planning to make such theoretical investigations. Moreover, the

two-color photolysis-probe experiments will be helpful for a better understanding on the photochemical behaviour of CH_3N_3 . We have done such experiment, which confirms the observation of CH_3N in photodissociation of CH_3N_3 . The full account will be reported in the future.

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CH_3N_3 的光解 — 生成三线态 CH_3N 自由基的光谱证据

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摘要 研究了 CH_3N_3 在第一电子吸收带的光解, 获得了生成三线态 CH_3N 自由基的重要证据并对可能的反应机制进行了讨论. 其机理以激发态 CH_3N_3 经单线态三线态相互作用后解离生成三线态自由基的可能性较大.

关键词: 光解, 自由基, 发射谱, 荧光