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The CH_3N Diradical: Experimental and Theoretical Determinations of the Ionization Energies**

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Methylnitrene, the CH_3N diradical, is one of the most interesting of all organic free radicals, and it has drawn a lot of attention in both experiments[1–5] and theory.[6–11] As the simplest alkyl nitrene, the general class of molecules with the form RN, CH_3N is a dielectronic radical similar to carbene CH_2:, and is thought to be an important intermediate in many organic and inorganic reactions.[12–14] Berry suggests[1] that the alkyl nitrene should have electron states similar to NH which has been well characterized by spectroscopists. However, much less is known about alkyl nitrenes such as CH_3N, $CH_3CH_2{-}N$, $(CH_3)_2CH{-}N$, or $(CH_3)_3C{-}N$. There are no reports on the ionization energy of the nitrenes until now, but these ionization energies, especially the first ionization energy, are important physical and chemical data.

When combined with ab initio molecular orbital calculations, HeI photoelectron spectroscopy (PES) gives a lot of information on the electronic and vibrational structures, the configuration, the bonding characteristics, as well as the relative photoionization cross sections of different molecular orbitals. Of course, the most important information obtained from the PES study is the ionization energy of the different molecular orbitals. Pople[15]and Ng[16] and their co-workers pointed out that the ab initio Gaussian 2 (G2) calculation can correctly predict the first ionization energy.

We have shown how to generate a continuous flowing beam of short-lived species by the microwave discharge or pyrolysis of the parent species, allowing us to perform PES studies on reactive open-shell species such as NO_3,[17] $(CH_3)_2N$,[18] CH_3O,[19] CH_3S,[19] CH_3SS,[20] CH_3CH_2S,[21] $(CH_3)_3CO$[22] and further demonstrated that the G2 calculation can also predict the ionization energies of different ionic states. Herein, we present the experimental and theoretical determinations of the ionization energies of different ionic states for the CH_3N diradical; this is also the first report on ionization energy for the nitrenes.

Calculations on the CH_3N_3 molecule indicate that the bond between the CH_3N and N_2 units is the weakest present and therefore pyrolysis of the CH_3N_3 offers a simple route to the CH_3N diradical through loss of the N_2 unit.[23–26] However, in the pyrolysis study of CH_3N_3 carried out by Bock and co-workers,[24–26] no PES signals of the CH_3N diradical could be detected and PES signals attributed to CH_2NH appeared when CH_3N_3 was heated to 770 K.

Through careful analysis of the experimental process used by Bock et al.[24–26] it is clear that: 1) the distance from the point of pyrolyzation of the parent compound to the photoionized point for the new species generated is too far (maybe more than half meter); 2) the pyrolysis temperature (770 K) for maintaining the new species is also too high. Obviously, it is difficulty to record the PES signals of transient species which have a short life-time, such as the CH_3N diradical. In fact, mixed PE spectra showing CH_3N_3 and CH_2NH (these spectra are the same as Figure 1 reported by Bock and Ralph in ref. [26]) were always obtained from the pyrolysis of the CH_3N_3 at 650(±0.5) °C with the heater installed outside our PE spectrometer.[27] When the PES of the species generated by pyrolysis of CH_3N_3 are recorded in situ (see Experimental Section) a lot of the short-lived active species is detected at a lower temperature in our PE spectrometer.

Figure 1 gives the PE spectrum of the product obtained from the pyrolysis of CH_3N_3 at 145 (±0.5) °C, the spectrum is recorded in situ under protection of the NO species. Noteworthy is that the mixed PE spectra showing both CH_3N_3 and CH_2NH are also obtained at 215 (±0.5) °C if NO is not

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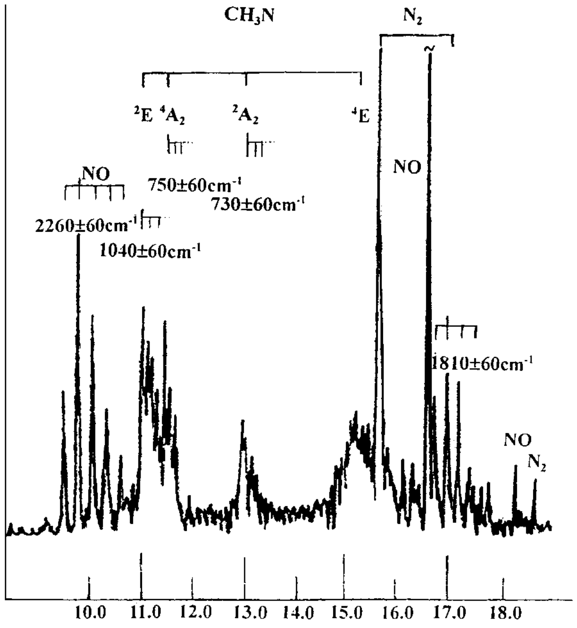

Figure 1. The PE spectrum (PES) of the CH_3N diradical obtained by pyrolysis of the CH_3N_3 at 145 (±0.5) °C.

present.[27] An expanded PE spectrum in which the fine vibrational structures could be clearly seen in the low ionization energy region (< 13.50 eV) is given in Figure 2.

For calibration purposes it is worth noting that the PES bands of the NO molecule (bands at 9.54 eV, with fine vibrational structure ($2260 \pm 60\,cm^{-1}$), at 16.56 eV (most intense band in Figure 1), and at 18.32 eV[28]), are clearly displayed in the PE spectra (Figures 1 and 2). The PES peaks at 15.60 eV, 16.98 eV with vibrational structure ($1810 \pm 60\,cm^{-1}$), and 18.78 eV are characteristic of the N_2 molecule.[28] Thus, the pyrolysis of the CH_3N_3 generates N_2.

$$CH_3N_3 \xrightarrow{145(\pm 0.5)\,^\circ C} CH_3N\!: + N_2 \qquad (1)$$

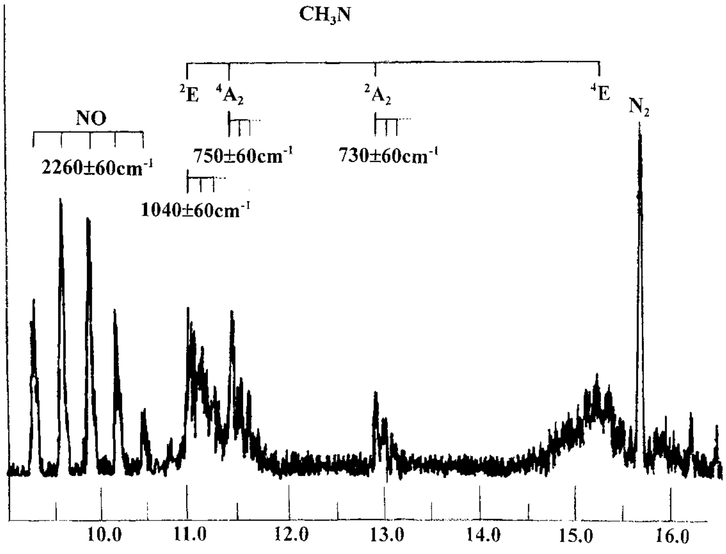

Figure 2. The expanded PE spectrum, in the lower ionization region (< 16.00 eV), of the CH_3N diradical obtained by pyrolysis of the CH_3N_3 at 145 (±0.5) °C.

The PES bands at 11.04, 11.40, 12.85, and 15.53 eV are assigned to the CH_3N diradical. The peaks at 11.04, 11.40, and 12.85 eV are sharp with some structure to the higher ionization-energy side. This peak form is characteristic of the ionization of slightly bonding or slightly antibonding orbitals, i.e. the "vertical" ionization energy is equivalent to the adiabatic ionization energy of the PES band.[28] The peak at 11.04 eV is assigned to the lowest energy PES peak of the CH_3N radical cation, because the vibrational spacing ($1040 \pm 60\,cm^{-1}$) is in excellent agreement with the reported vibrational frequency ($1040\,cm^{-1}$) of the neutral CH_3N diradical,[3, 11] and the vibrational spacing of the PES band resulting from electronic ionization of a nonbonding orbital should be close to the vibrational frequency of the neutral species. The position of the first CH_3N PES peak matches well with the results of both G2 and DFT calculations, and is assigned as the ^2E state of the CH_3N radical cation (see Table 1). According to the Frank–Condon principle, the energies of the ionic states are given using the vertical ionization energy (I_v), chosen as the maximum of the PES bands, and the computed ionization energy (E_v) should be obtained from the difference of the total energies of the resulting cation/neutral radical in C_{3v} symmetry.

Table 1. The experimental vertical ionization energies (I_v), calculated ionization energies (E_v) according to C_{3v} symmetry from the G2 and DFT methods, and relative intensities of the PES signals observed from different ionic states of the CH_3N diradical.

PES experimental I_v [eV][a]	G2 energies E [eV]	DFT energies E [eV]	Cationic states	Relative intensity this work[b]	statistical ratio
11.04	11.063	11.006	^2E[c]		
11.40	11.301	11.492	$^4A_2$[d]	1.95	2
12.85	12.880	13.263	$^2A_2$[d]	1.00	1
15.53	15.495	15.361	^4E[e]		

[a] ±0.02 eV. [b] Corrected for analyzer sensitivity ±0.02. [c] Ionic states come from electron ionization of the HOMO(2e) for CH_3N radical. [d] Ionic states come from electron ionization of the SHOMO($5a_1$) for the CH_3N diradical. [e] Ionic states come from electron ionization of the 1e orbital of the CH_3N diradical.

The assignment of the PES bands for a new species can be supported by theoretical analysis. According to C_{3v} symmetry and a $^3A_2$ ground state for the CH_3N diradical the molecular orbitals would be, in the order of increasing energy:

$$(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(1e)^4(5a_1)^2(2e)^2$$

The removal of an electron from the HOMO will leave the ion in the singlet state ^2E, whereas removal of an electron from each of the other valence shell orbitals in turn can leave both quartet and doublet states of the cation.

The HOMO(2e) of the CH_3N diradical has a dominant contribution from the lone-pair electrons of the nitrogen atom with a small degree of the C–N antibonding character. This means that removal of an electron from the HOMO(2e) of CH_3N, leading to the cation in the singlet state ^2E, should gives a sharp PES peak with fine structure of $1040 \pm 60\ cm^{-1}$ which is in excellent agreement with the reported vibrational frequency $1040\ cm^{-1}$ of the C–N stretch mode of the neutral CH_3N diradical.[3, 11]

The orbital character of the $5a_1$ of the CH_3N diradical is essentially that of a lone-pair orbital of the nitrogen atom. This means that the removal of the electrons of the $5a_1$ orbital should lead to two sharp peaks corresponding to $^4A_2$ and $^2A_2$ ionic states of the CH_3N radical cation, and the intensity of the PES band for the $^4A_2$ ionic state should be two times that of the $^2A_2$ ionic state, because the intensity of the PES band represents the relative ionic statistical weights.

A careful analysis of the intensities of the two peaks at 11.40 and 12.85 eV for the PE spectrum of the pyrolyzed CH_3N_3 shows that the intensity of the peak at 11.40 eV is about 1.95 times that of the peak at 12.85 eV. That is to say, the intensity ratio of the two peaks is in good agreement with the ratio of relative ionic statistical weight led by electron ionization of the $5a_1$ orbital for the CH_3N diradical, that is, they correspond to the $^4A_2$ and $^2A_2$ ionic states of the CH_3N radical cation. The vibrational spacing ($750 \pm 60\ cm^{-1}$) of the peak at 11.40 eV is very close to the vibrational spacing ($730 \pm 60\ cm^{-1}$) of the peak at 12.85 eV. This fact also shows that the two PES peaks should arise from the result of electron ionization of the same orbital. The PES band centered near 15.53 eV could be attributed to removal of the electrons from the 1e orbital or maybe also includes the contribution of more orbitals in the deep valence shell of CH_3N, because the band is very broad. As indicated in Table 1, PES experimental and both G2 and DFT theoretical results agree reasonably well.

Experimental Section

Methyl azide CH_3N_3 was prepared according to the methods reported in refs. [26, 29]. The purity of CH_3N_3 was checked by mass spectrometry and NMR spectroscopy. The PE spectrum of the CH_3N_3 obtained is the same as that reported[26] and did not vary from day to day before each experiment.

The PES experiment was performed in a double-chamber UPS Machine-II which was built specially, as described elsewhere,[17] to detect transient species. A continuous flowing CH_3N diradical beam is produced in situ by pyrolysis of CH_3N_3 at 145(±0.5) °C in a quartz tube by using a double heater inlet system, the heater was capable of producing 1200 °C. Thus, the new species was produced within 1–2 cm of the photoionization region of the spectrometer, it then passed through the photoionization point and was quickly pumped out. The double heaters were installed inside of the sample chamber. The PE spectrum of the CH_3N diradical was measured at a resolution of about 30 meV as indicated by the $Ar^+(^3P_{3/2})$ photoelectron band. Experimental vertical ionization energies (E_v in eV) were calibrated by simultaneous addition of a small amount of NO to the sample, the first PES band with NO fine vibrational structure can be used for calibration the of the fine vibrational structure of the new species, NO can also stabilize the new species.[22]

Gaussian 2 and improved DFT calculations: to assign the PES bands of the CH_3N diradical, both G2 and DFT calculations were performed on the $^3A_2$ ground state of the CH_3N diradical in the C_{3v} symmetry and the ground and several ionic states of the CH_3N radical cation. The G2 theoretical procedure has been described in detail by Curtiss et al.[15] The improved density functional theory (DFT) calculations are described in refs. [17–22]. The computed ionization energies (E_v in eV) were obtained from the difference between the total energy of the resulting radical cation $^3A_2$ ground state in the C_{3v} symmetry to the total energy of the CH_3N diradical.

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