

The diradical $(\text{CH}_3)_2\text{CHN}$ and its isomeric molecule $(\text{CH}_3)_2\text{CHN}$: Generation and characterization

Sun Zheng, Wang Dong, Ding Rui, Ge Maofa, Wang Dianxun et al.

Citation: *J. Chem. Phys.* **119**, 293 (2003); doi: 10.1063/1.1577316

View online: <http://dx.doi.org/10.1063/1.1577316>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v119/i1>

Published by the [American Institute of Physics](#).

Additional information on *J. Chem. Phys.*

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT

**AIP**Advances

Submit Now

**Explore AIP's new
open-access journal**

- **Article-level metrics
now available**
- **Join the conversation!
Rate & comment on articles**

The diradical $(\text{CH}_3)_2\text{CHN}$ and its isomeric molecule $(\text{CH}_3)_2\text{C}=\text{NH}$: Generation and characterization

Sun Zheng,^{a)} Wang Dong, Ding Rui, Ge Maofa, and Wang Dianxun^{b)}

The Center for Molecular Sciences, Institute of Chemistry, The Chinese Academy of Science, Beijing 100080, People's Republic of China

Chau Foo-Tim^{c)} and D. K. W. Mok

Department of Applied Biology and Chemical Technology, The Polytechnic University of Hong Kong, Hung Hom, Kowlong, Hong Kong

(Received 7 January 2003; accepted 3 April 2003)

A continuously flowing $(\text{CH}_3)_2\text{CHN}$ beam is generated by pyrolysis of $(\text{CH}_3)_2\text{CHN}_3$ at $113(\pm 0.5)^\circ\text{C}$ using normal inlet system with an 8 mm bore of the exit of the quartz tube under the presence of molecular sieve (30 Å) and stabilizing NO gas, and its HeI photoelectron (PE) spectrum is also recorded *in situ*. A spectrum recorded further away from the pyrolysis catalyst or by using a 0.4 mm bore of the quartz tube is the PE spectrum of $(\text{CH}_3)_2\text{C}=\text{NH}$, which comes from the isomerization of $(\text{CH}_3)_2\text{CHN}$. The ionization energies of $(\text{CH}_3)_2\text{CHN}$ and $(\text{CH}_3)_2\text{C}=\text{NH}$ are determined for the first time by the photoelectron spectroscopy experiment, and Gaussian 2 and improved density functional theory calculations. Experimental and theoretical results agree reasonably well, and show that $(\text{CH}_3)_2\text{CHN}$ is a diradical with C_s symmetry and has a $^3A''$ ground state, and $(\text{CH}_3)_2\text{C}=\text{NH}$ is a closed shell molecule with C_s symmetry. © 2003 American Institute of Physics. [DOI: 10.1063/1.1577316]

I. INTRODUCTION

The nitrenes, molecules of the form R–N, have received increasing attention in experimental and theoretical studies in recent years not only because the nitrenes contain electron-deficient nitrogen atoms and are short-lived intermediates in many organic and inorganic reactions, but also because of the small energy separation between their lowest single and triplet states.^{1–5} The most thoroughly studied nitrenes are amidogen NH^6 and phenylnitrene $\text{C}_6\text{H}_5\text{N}^7$. In contrast to aromatic nitrenes, much less is known about alkylnitrenes such as $\text{CH}_3\text{-N}$, $\text{CH}_3\text{CH}_2\text{-N}$, $(\text{CH}_3)_2\text{CH-N}$, and $(\text{CH}_3)_3\text{C-N}$. Even basic physical and chemical data, such as ionization energies, are not available for nitrenes yet.

When combined with *ab initio* calculations, ionization energies are the most important information provided by HeI photoelectron spectroscopy (PES). Pople⁸ and Ng⁹ pointed out that *ab initio* Gaussian 2 (G2) calculations can correctly predict the first ionization energy of the species studied.

Thermal decomposition of covalent azides usually results in the unimolecular loss of N_2 .¹⁰ However, pyrolysis studies on alkyl azides, which were done by Bock,^{11–13} did not observe signals due to nitrenes. Instead, they found signals of a mixture of alkymines and different by-products such as HCN, NH_3 , CH_4 , H_2 , etc. From a careful analysis of Bock's experimental process, it is obvious that: the pyrolysis temperature (higher than 620 K) was much too high to record the PES signals of the short-lived and unstable

transient species, such as nitrenes in their PES experiment the distance from the pyrolysis point to the photoionization point was too long (maybe more than half meter).²

Through pyrolysis of well-selected parent compounds, we reported a lot of the PES studies on reactive open-shell species, such as NO_3 ,¹⁴ CH_3O ,¹⁵ CH_3S ,¹⁵ CH_3SS ,¹⁶ $\text{CH}_3\text{CH}_2\text{S}$,¹⁷ and $(\text{CH}_3)_3\text{CO}$.¹⁸ Recently, both CH_3N^{19} radical and $\text{CH}_3\text{CH}_2\text{N}^{20}$ diradicals were obtained by respective pyrolysis of CH_3N_3 at $145(\pm 0.5)^\circ$ and $\text{CH}_3\text{CH}_2\text{N}_3$ at $135(\pm 0.5)^\circ\text{C}$, their PE spectra were also recorded *in situ*. But the pyrolysis details have not been discussed in detail. In this paper, we describe not only the new experimental conditions that allowed us to generate the short-lived species, but also the PE spectra of the diradical $(\text{CH}_3)_2\text{CHN}$ (**1**) and the close-shell molecule $(\text{CH}_3)_2\text{C}=\text{NH}$ (**2**) which results from isomerization of **1**. In order to assign the PE bands of **1**, G2 and improved density functional theory (DFT) calculations are performed. The assignment of the PE spectrum of **2** is based on the Koopmans approximation²¹ to an *ab initio* self-consistent field calculation applying a 6-31G** basis set. The molecular geometry of **2** is optimized at the same level.

II. EXPERIMENT

A. Synthesis of $(\text{CH}_3)_2\text{CHN}_3$ (**3**) compound

The precursor compound **3** was synthesized according to a previously reported method.²² The purity of **3** was checked by MS and nuclear magnetic resonance. The PES profile of **3** is very similar to those of CH_3N_3 and $\text{CH}_3\text{CH}_2\text{N}_3$ which were reported previously,^{11–13} and did not vary in different experiments.

^{a)}Present address: Physik Chemie II, Technische Universitat Munchen, 85748 Garching, Germany.

^{b)}Electronic mail: wangdx@infoc3.icas.ac.cn

^{c)}Electronic mail: bcfchau@polyu.edu.hk

B. Pyrolysis of $(\text{CH}_3)_2\text{CHN}_3$ (**3**) using the normal inlet system

Pyrolysis experiments are performed using a double-chamber UPS machine-II, which was specifically built to detect transient species as described elsewhere.¹⁴ A continuously flowing radical beam is produced *in situ* by pyrolysis of a parent compound in a quartz tube using a double-heater inlet system which is capable of creating temperature up to 1200 °C. The diameter of the exit of the quartz tube is usually 8 mm. With this equipment, the new species is generated within 1–2 cm of the photoionization region in the sample chamber. Then it passes the photoionization point and is quickly pumped out. The advantage of this normal inlet system is that further pyrolysis of the new species can be effectively avoided, because the residence time of the new species in the heating region is very short. The quartz tube was filled with a molecular sieve powder supported on the quartz wool.^{23,24} In fact, a lot of radicals can only be obtained by us under the presence of the molecular sieve as catalyst, because the molecular sieve can effectively reduce pyrolysis temperature, as the short-lived species is unstable at high temperature.^{23,24} Our experiences also show that a molecular sieve with a large hole size must be used, e.g., for pyrolysis of large parent components, an 8 Å molecular sieve for the pyrolysis of CH_3N_3 and a 20 Å molecular sieve for the pyrolysis of $\text{CH}_3\text{CH}_2\text{N}_3$.

C. Pyrolysis of $(\text{CH}_3)_2\text{CHN}_3$ using the new inlet system to provide longer reaction times

To prolong the residence time of the parent compounds in the heating region, a reasonable design for the pyrolysis inlet equipment is reducing diameter of the exit of the quartz tube, because the velocity of the PES pumping system is constant. Different residence times of parent compounds in the heating region could also be realized through reducing the bore of the quartz tube in proper order.²³ A 0.4 mm bore of the quartz tube was found to be appropriate in this study.

The PE spectra of pyrolysis products of **3** are measured *in situ* at a resolution of about 25 meV as indicated by the $\text{Ar}^+(^2P_{3/2})$ PE peak. Experimental vertical ionization energies (I_v in eV) are calibrated by adding NO to the sample, because the first PE band of NO at 9.54 eV with a vibrational frequency of $2260 \pm 60 \text{ cm}^{-1}$ is accurate enough for the calibration of other bands. In addition, NO is a good stabilizing reagent of some radicals.^{18,23,24}

III. G2 AND IMPROVED DFT CALCULATIONS (REF. 14)

The G2 theoretical procedure has been described in detail by Curtiss *et al.*⁸ To assign the PE bands of **1**, G2 calculation is performed for the $^3A''$ ground state of **1** in C_s symmetry and for the $^2A''$ ground and several ionic states of the $(\text{CH}_3)_2\text{CHN}^+$ cation. The calculated ionization energies (E_v in eV) are obtained as total energy differences between the neutral ground state $^3A''$ and the state of the ion.

The improved DFT calculation has also been used to obtain vertical ionization energies (E_v in eV) for different ionic states of **1**, as described in Refs. 14–18, 23, 24. The

geometry used in the calculation of the neutral radical is taken from optimization results at the UMP2/6-311G* level of theory.

IV. RESULTS AND DISCUSSION

The G2 and DFT calculations for **1** predict a C_s symmetry with electron configuration of the valence shell:

$$\sim (6a')^2(7a')^2(3a'')^2(8a')^2(4a'')^2(9a')^2 \\ \times (5a'')^2(10a')^2(11a')^1(6a'')^1.$$

This shows that **1** is a diradical, because the two unpaired electrons occupy two orbitals with different energy. In contrast of CH_3N , the highest occupied molecular orbital (HOMO) $6a''$ and the second highest occupied molecular orbital (SHOMO) $11a'$ of **1** are singly occupied. Owing to spin conservation, the cleavage of the singlet **3** should lead to N_2 in its singlet ground state and to **1** in a singlet state. But according to Hund's rule, the state with two spin-parallel unpaired electrons is expected to have the lowest energy. In fact, the energy of the $^3A''$ state is found to be 1.750 eV (G2) and 1.717 eV (DFT) lower than that of the $^1A''$ state. This implies that the ground state of **1** is $^3A''$. That is, the primarily formed $^1A''$ state is relaxed quickly to the triplet ground state.

Removal of an electron from the $6a''$ and $11a'$ orbitals leads to $^2A'$ and $^2A''$ ionic states, respectively. The G2 and DFT calculations show that the $6a''$ is essentially a lone-pair orbital with N_{2P_z} character. The removal of an electron from this orbital should give a sharp peak in the PE spectrum.²⁵ The $11a'$ is a strongly bonding orbital, and its corresponding PE band should be broader and may have fine structure.

Ab initio self-consistent field (SCF) 6-31G** calculations for **2** show that the energy of the lowest triplet state is 4.266 eV higher than the singlet ground state. This shows that **2** is a closed shell molecule with c_s symmetry and an electron configuration of the valence shell:

$$\sim (6a')^2(7a')^2(3a'')^2(8a')^2(9a')^2(4a'')^2 \\ \times (5a'')^2(10a')^2(6a'')^2.$$

$6a''$ and $10a'$ are bonding orbitals with different contributions on N and C atoms. Removal of the electron from these two orbitals should give the broad PE bands.²⁵

A. The $(\text{CH}_3)_2\text{CHN}$ biradical (**1**) obtained by pyrolysis of $(\text{CH}_3)_2\text{CHN}_3$ (**3**)

Figure 1(d) is the PE spectrum of pyrolysis products of **3** at $113(\pm 0.5)^\circ\text{C}$ using our normal inlet system that consists of an 8 mm bore of the quartz tube filled with molecular sieve (30 Å). NO is added as a stabilizing reagent and as calibration gas. The PE spectrum of NO is given in Fig. 1(a). Figure 1(b) is the PE spectrum of **3**, which is the same as the spectrum measured by Bock and co-workers.¹³ Figure 1(c) results from a mixture of NO and **3**. An expanded view of the low energy part of Fig. 1(d) is given in Fig. 2(a).

It is clearly seen from Figs. 1(d) and 2(a) that the band starting at 9.26 eV with a vibrational spacing $2260 \pm 60 \text{ cm}^{-1}$ is the first PES band of NO. Sharp peaks at 16.56 eV with

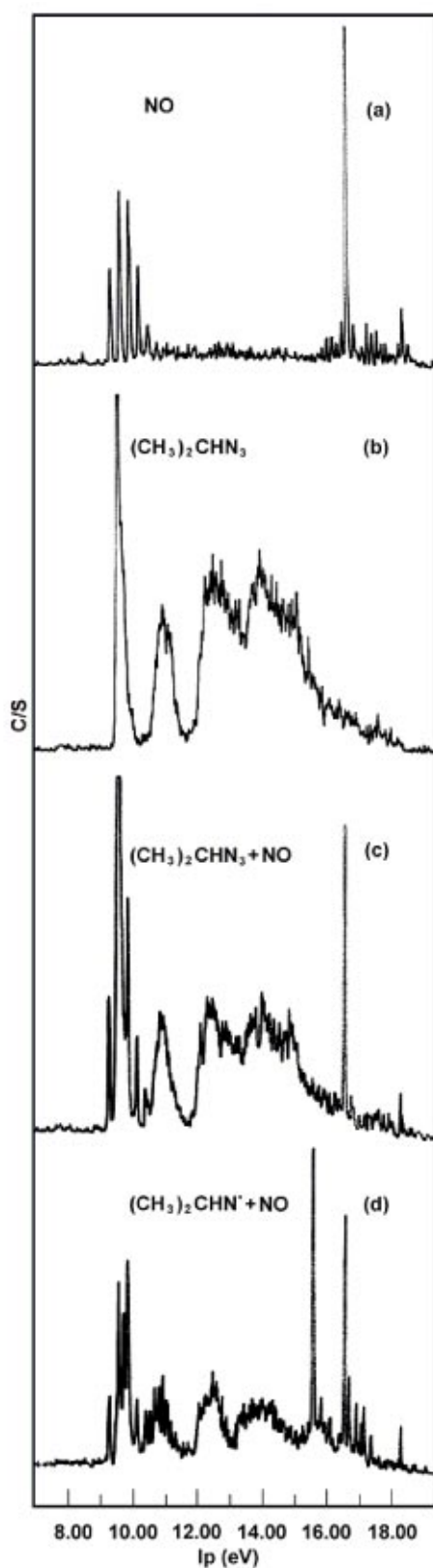


FIG. 1. (a) PE spectrum of NO. (b) PE spectrum of $(\text{CH}_3)_2\text{CHN}_3$. (c) Mixed PE spectra of NO and $(\text{CH}_3)_2\text{CHN}_3$. (d) PE spectrum of $(\text{CH}_3)_2\text{CHN}$ generated by pyrolysis of $(\text{CH}_3)_2\text{CHN}_3$ at $113(\pm 0.5)^\circ\text{C}$ using the normal inlet system with an 8 mm bore of the quartz tube filled with 30 \AA molecular sieve powder supported on the quartz wool.

high intensity and at 18.32 eV also arise from NO [Fig. 1(a)].²⁵ The peak at 15.60 eV with the highest intensity [Fig.

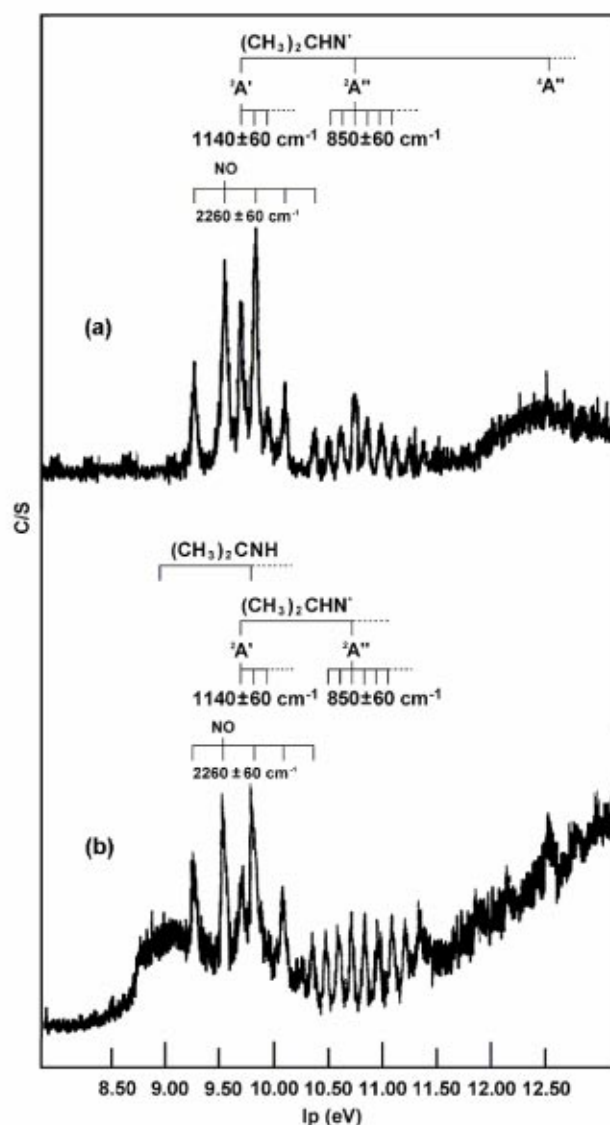


FIG. 2. (a) The expanded PE spectrum of the low energy part ($<12.50 \text{ eV}$) of Fig. 1(d) for $(\text{CH}_3)_2\text{CHN}$. (b) The expanded PE spectra of the low energy part ($<12.50 \text{ eV}$) of Fig. 3 for $(\text{CH}_3)_2\text{CHN}$ and $(\text{CH}_3)_2\text{C}=\text{NH}$.

1(d)] and the band at 16.98 eV with a vibrational spacing $1810 \pm 60 \text{ cm}^{-1}$ belong to the PES bands of N_2 .²⁵ This implies that pyrolysis of **3** at $113(\pm 0.5)^\circ\text{C}$ leads to the loss of N_2 . The sharp peak at 9.70 eV with a short vibrational progression, the sharp peak at 10.72 eV with a long vibrational progression, and the two broad bands centered near 12.56 and 14.05 eV , respectively, must result from the second pyrolysis product. First, no bands of N_2 and NO are present between 10.10 and 15.00 eV . Second, the bands of **3** have disappeared below the detection limit. The latter also indicates that the pyrolysis of **3** at $113(\pm 0.5)^\circ\text{C}$ is quite complete. Similar to the generations of CH_3N and $\text{CH}_3\text{CH}_2\text{N}$ by respective pyrolysis of CH_3N_3 at $145(\pm 0.5)^\circ\text{C}$ and $(\text{CH}_3)_2\text{CH}_2\text{N}_3$ at $135(\pm 0.5)^\circ\text{C}$, the pyrolysis of $(\text{CH}_3)_2\text{CHN}_3$ at $113(\pm 0.5)^\circ\text{C}$ yields $(\text{CH}_3)_2\text{CHN}$ via unimolecular loss of N_2 , i.e.,

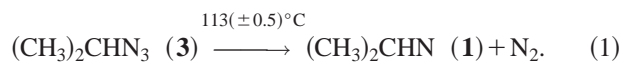


TABLE I. Experimental vertical ionization energies (I_v in eV), calculated ionization energies (E_v in eV) according to C_s symmetry by both G2 and DFT methods, and relative intensities according to the statistical ratio (stat. ratio) of the observed PE signals from different ionic states of $(\text{CH}_3)_2\text{CHN}$ diradical.

Experimental I_v (eV) ^a	G2 E_v (eV)	DFT E_v (eV)	Cationic state	Associated orbital	Relative intensity	
					This work ^b	Stat. ratio
9.70	10.311	10.232	$^2A'$	$6a''$		
10.72	10.314	10.236	$^2A''$	$11a'$		
12.56	12.442	12.331	$^4A''$	$10a'$	2.0	2
14.05	13.963	13.851	$^2A''$	$10a'$	0.8	1

^a ± 0.02 eV.

^bCorrected for analyzer sensitivity ± 0.02 eV.

Thus, the band starts with a sharp peak at 9.70 eV and with a vibrational spacing $1140 \pm 60 \text{ cm}^{-1}$, the band around 10.72 eV with a vibrational spacing $850 \pm 60 \text{ cm}^{-1}$, and two broad bands centered near 12.56 and 14.05 eV are assigned to **1** [see Figs. 1(d) and 2(a)]. The vibrational peak at 9.82 eV must result from an overlap of the third vibrational component of the first band of NO with the second peak of the first band of **1**. It is because the second vibrational component of the first band of NO at 9.54 eV has the highest intensity. The rapid decrease in the intensities of the peaks at 9.70, 9.82, and 9.94 eV and a short vibration progression with the highest intensity component corresponding to the O–O transition strongly indicate that this band comes from the ionization of the electron of a nonbonding or lone-pair orbital. This is consistent with that the HOMO $6a''$ of **1** is the N_{2p_z} lone-pair orbital, as mentioned earlier. The calculated value 10.311 eV (G2) and 10.232 eV (DFT) for the ionic state $^2A'$ matches the experimental values fairly well. This fact also shows that the ground state of **1** is the $^3A''$ state, because if the ground state is $^1A''$ state, a peak at ionization energy 8.56 eV ($10.311 - 1.750 = 8.561$) should appear on the PE spectrum. Table I lists the vertical ionization energies (I_v in eV) of **1** obtained from this experiment as well as those deduced from G2 and DFT calculations.

The second PE band of **1** (Fig. 2) consists of a long vibrational progression with a O–O transition at 10.51 eV, a vertical one at 10.72 eV, and a well-resolved vibrational spacing $850 \pm 60 \text{ cm}^{-1}$. Thus, it should correspond to ionization of the electron of a bonding or antibonding orbital. According to the electronic configuration and bonding properties of **1**, this band results from the removal of an electron from the SHOMO ($11a'$) which has dominant N_{2p_y} character with some contribution from the C_{2p_y} . The position of this band matches well with the calculated ionization energies 10.314 eV (G2) and 10.236 eV (DFT).

From Table I it is obvious that the difference between the experimental ionization energies of the ionic states $^2A'$ and $^2A''$ ($10.72 - 9.70 = 1.02$ eV) is much larger than the calculated value. This may indicate that the interaction between the two CH_3 groups and the N_{2p_z} lone-pair orbital (i.e., forming *pseudo* Π_{CH_3} bond) lowers the ionization energy of $6a''$, because the symmetry of the CH_3 group and the N_{2p_z} lone-pair orbital is the same.

Removal of an electron from $10a'$ leads to $^4A''$ and $^2A''$ ionic states. The broad band centered near 12.56 eV is assigned to $^4A''$, because their energies predicted by G2

(12.442 eV) and DFT (12.331 eV) are close to the experimental value and its intensity is about two times than that of the broad band centered near 14.05 eV. The relative statistical weight requires that the intensity of the band of the $^4A''$ ionic state is two times that of the $^2A''$ ionic state (see Table I). The band corresponding to the $^2A''$ state is expected to be part of the fourth band centered near 14.05 eV, because this band is very broad, and it is most likely that the band results from more than one electron ionization. That is, the PES assignment of the spectrum of **1** is reasonably supported by G2 and DFT calculations (see Table I).

Due to the donor action of CH_3 group, the increased alkyl substitution leads to a reduction of the first ionization energy of the RN series, e.g., 11.04 eV for CH_3N ,¹⁹ 10.19 eV for $\text{CH}_3\text{CH}_2\text{N}$,²⁰ and 9.70 eV for $(\text{CH}_3)_2\text{CHN}$. As the same, a reduction of the vibrational spacing in the RN series is also understood if we assume that the active mode is the stretching mode of the C–N bond. Increased substitution with CH_3 group increases the mass of R group, and thereby lowers the R–N vibrational frequency, i.e., PES values $1040 \pm 60 \text{ cm}^{-1}$,¹⁹ $910 \pm 60 \text{ cm}^{-1}$,²⁰ and $850 \pm 60 \text{ cm}^{-1}$ matched, respectively, to B3LYP/6-311++G** calculation values 1063 cm^{-1} for CH_3N , 1013 cm^{-1} for $\text{CH}_3\text{CH}_2\text{N}$, 949 cm^{-1} for $(\text{CH}_3)_2\text{CHN}$. That is, the systematic analysis of the PES data for the RN series also supports that the PE spectrum of the new species obtained from pyrolysis of **3** at $113(\pm 0.5^\circ\text{C})$ is assigned to **1**.

B. Conversion of the pyrolysis product of $(\text{CH}_3)_2\text{CHN}_3$

In order to study the conversion of pyrolysis products at later times, a new experiment was designed in which the heater was installed outside of the sample chamber of the PE spectrometer. In this way, the PE spectra of both CH_2NH and CH_3CHNH (which were already measured by Bock and co-workers) could be obtained from the pyrolysis of CH_3N_3 at $225(\pm 0.5)^\circ\text{C}$ with molecular sieve (8 Å) and $\text{CH}_3\text{CH}_2\text{N}_3$ at $213(\pm 0.5)^\circ\text{C}$ with molecular sieve (20 Å).^{19,20}

By reducing the diameter of the exit of the quartz tube in proper order, the residence time of the parent compounds in the heating region is effectively prolonged.²³ Figure 3 is the PE spectrum of the pyrolysis products of $(\text{CH}_3)_2\text{CHN}_3$ at $113(\pm 0.5)^\circ\text{C}$ using the new inlet system with a 0.4 mm bore of the quartz tube. An expanded view of the low energy part of Fig. 3 (< 12.50 eV) is given in Fig. 2(b).

By comparing Fig. 3 with Fig. 2(b) with Fig. 1(d) and

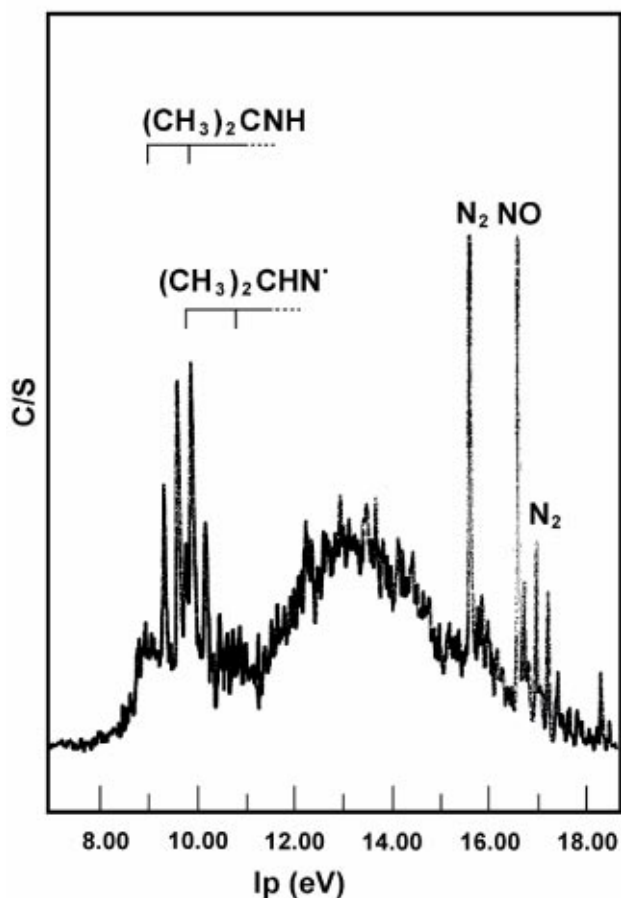
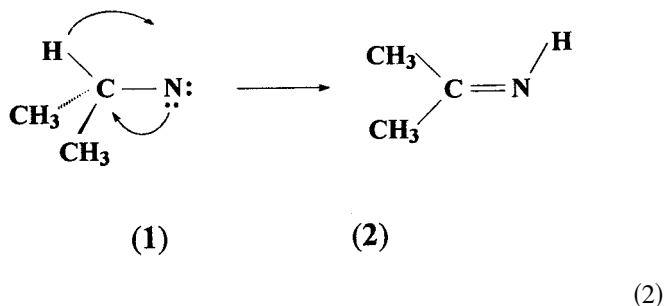


FIG. 3. PE spectra of $(\text{CH}_3)_2\text{CHN}$ and $(\text{CH}_3)_2\text{C}=\text{NH}$ generated by pyrolysis of $(\text{CH}_3)_2\text{CHN}_3$ at $113(\pm 0.5)^\circ\text{C}$ using the new inlet equipment with a 0.4 mm bore of the quartz tube filled with molecular sieve (30 Å) powder supported on the quartz wool.

Fig. 2(a), new additional bands are found. The first band of NO at 9.54 eV and the first band of **1** at 9.70 eV overlap on the bands of a new species. A broad band starting at 8.95 eV and a band centered near 9.80 eV are the bands of this new species. The broad and unresolved band in the high energy region (from 12.00 to 15.50 eV) must result from an overlap of the new species and **1**, because there are no bands of NO and N_2 in this region. A reasonable assignment of the bands centered near 8.95 and 9.80 eV involves $(\text{CH}_3)_2\text{C}=\text{NH}$ (**2**). Due to product conversion, a part of **1** generated by pyrolysis of $(\text{CH}_3)_2\text{CHN}_3$ at $113(\pm 0.5)^\circ\text{C}$ can isomerize into **2**:



It is well known that CH_2NH and CH_3CHNH show two broad separate bands in the low energy region (<12.00

TABLE II. Experimental vertical ionization energies (I_v in eV) as calculated eigenvalues ($-\epsilon_i$ in eV) using *ab initio* SCF 6-31G** basis set level for $(\text{CH}_3)_2\text{C}=\text{NH}$ molecule.

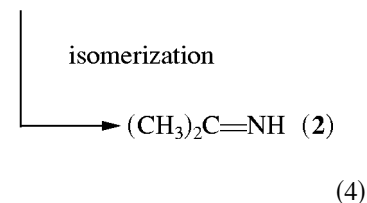
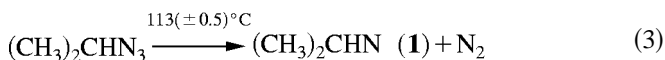
I_v (eV) ^a	$-\epsilon_i$ (eV)	MO	Character
8.95	9.250	$6a''$	$\pi_{\text{N}=\text{C}}$
9.80	9.410	$10a'$	σ_{NCH}
12.52	12.851	$5a''$	$\pi_{\text{N}-\text{CH}_3}$
13.63	13.459	$4a''$	$\pi_{\text{N}-\text{CH}_3}$
14.38	14.085	$9a'$	σ_{CH_3}

^a ± 0.02 eV.

eV).^{11-13,23,24} The ionization energies corresponding to these two bands are 10.54 and 12.42 eV for CH_2NH . Replacing one of the H atoms by a methyl group lowers the ionization energies to 9.20 and 11.20 eV in the case of CH_3CHNH . This is attributed to the electron donating power of the substituted CH_3 group. Assuming that the trend remains, we assign the broad bands centered near 8.95 and 9.80 eV as bands of **2**, because the further reduction in the lowest and second lowest ionization energies is due to an additional methyl group. This assignment is also supported by *ab initio* SCF 6-31G** calculations. The calculated ionization energies ($-\epsilon_i$) based on the Koopmans approximation²¹ are listed in Table II for **2**. The molecular orbital (MO) associated with each ionization is designated according to its atomic and bonding character. The experimental ionization energy is given in Table II in the form of overlapping band maxima because the observed bands are associated with a varying number of orbital ionizations.

From Table II it is seen that the calculated energies of 9.250 and 9.410 eV for the HOMO $6a''$ and SHOMO $10a'$ of **2** match well the experimental values 8.95 and 9.80 eV. The $6a''$ and $10a'$ of **2** are bonding orbitals with different contributions from N and the C atom connected directly to the nitrogen atom. Ionizations of electrons from $6a''$ and $10a'$ should lead to broad bands. Due to the overlap of the bands of **2** and **1**, there is an unresolved band in the high energy region (from 12.00 to 15.50 eV). Considering the two bands centered near 12.56 and 14.05 eV of **1** in this region, the bands of **2** can also be designated according to the *ab initio* calculation, i.e., the bands embody mainly contribution of two CH_3 groups (see Table II). This assignment is also consistent with the high intensity broad band in the high energy region if there are CH_3 groups in the molecule.²⁵

By using new inlet system with a 0.4 mm bore of the quartz tube filled by molecular sieve (30 Å), **1** and **2** are generated, and their PE spectrum is also recorded *in situ*. That is due to the fact that the residence time of **3** in the heating region at $113(\pm 0.5)^\circ\text{C}$ is prolonged, a part of the generated **1** isomerized into **2**, i.e.,



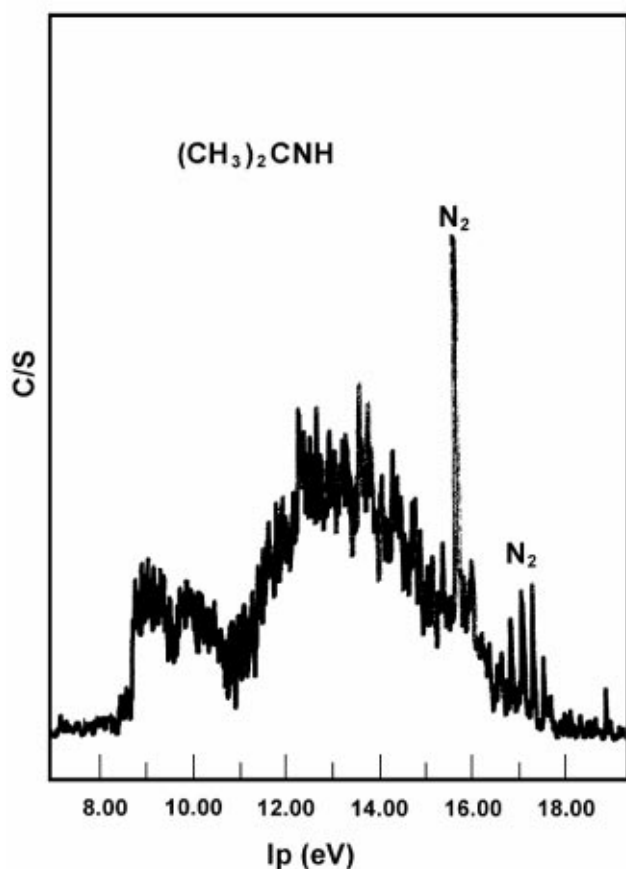


FIG. 4. PE spectrum of $(\text{CH}_3)_2\text{C}=\text{NH}$ generated by pyrolysis of $(\text{CH}_3)_2\text{CHN}_3$ at $345(\pm 0.5)^\circ\text{C}$ using normal 8 mm bore of the quartz tube without molecular sieve filled.

Conversely speaking, normal inlet equipment with an 8 mm bore of the quartz tube provides a good opportunity for us to generate the short-lived radicals by pyrolysis of the parent compound, because further decomposition or isomerization of the generated diradicals is effectively avoided.

Pure PE spectrum of **2** (Fig. 4) is also obtained from pyrolysis of **3** at $345(\pm 0.5)^\circ\text{C}$ by using an 8 mm bore of the quartz tube without the molecular sieve (30 Å). The experiment using a 0.4 mm bore of the quartz tube shows that at the $345(\pm 0.5)^\circ\text{C}$ the PES bands of HCN and NH_3 also appeared on the PE spectrum, because the residence time of **3** in the heating region is prolonged.²³ This further shows that the molecular sieve (30 Å) is not only necessary to generate **1**, but also greatly reduces the pyrolysis temperature. And it also shows that the organic species is burned to the least fragments, i.e., the short-lived organic species cannot exist in high temperature (maybe $>300^\circ\text{C}$).

C. Speculation on the actions of the molecular sieve and NO

NO was found to be a stabilizing reagent of $(\text{CH}_3)_3\text{CO}$ radical in pyrolysis of $(\text{CH}_3)_3\text{CONO}$ ¹⁸ and used to generations of the nitrenes.^{19,20,23} As a stabilizing reagent for some radicals, a possible explanation of the NO action is that once the diradicals RN (or RO) are generated on the surface of the molecular sieve, a complex species RN–NO between NO

and RN may be formed, and then this species is quickly decomposed on photoionization point. So the generating and detecting of the short-lived species should be *in situ*, because along a longer path the RN·NO species is not only decomposed, but also isomerized.²³

Since ten years ago our laboratory has been pursuing to generate and trap the short-lived radicals, such as RO, RS, and RN [$\text{R}=\text{CH}_3$, CH_3CH_2 , $(\text{CH}_3)_2\text{CH}$, and $(\text{CH}_3)_3\text{C}$] by pyrolysis of well-selected compounds. These radicals were only obtained under condition of the molecular sieve as a catalyst, and pure PE spectra were recorded *in situ*. The experience also shows that pyrolysis of a big parent compound must use a molecular sieve with a large hole size. This implies that the pyrolysis of the parent compounds is achieved in the inner-surface of the hole of the molecular sieve through accelerating decomposition of the parent compounds. In other words, the molecular sieve provides just the right framework for pyrolysis of the parent compounds and seems to be a “delivery room” to generate the radicals.

V. CONCLUSIONS

- (1) A continuously flowing beam of **1** is generated by pyrolysis of **3** at $113(\pm 0.5)^\circ\text{C}$ using normal inlet system with an 8 mm bore of the quartz tube filled the molecular sieve (30 Å) powder supported on the quartz wool. From this inlet equipment the PE spectrum of **1** is recorded *in situ* for the first time.
- (2) To prolong the residence time of the generated radical in the heating region, a smaller diameter of the exit of the quartz tube has been used. Both **1** and **2** could have been generated by pyrolysis of **3** at $113(\pm 0.5)^\circ\text{C}$ using a 0.4 mm bore of the quartz tube filled with the molecular sieve powder (30 Å) supported on the quartz wool, and their PE spectra are also recorded *in situ*. This shows that under these experimental conditions a part of **1** is isomerized to **2**.
- (3) A pure PE spectrum of **2** is recorded by pyrolysis of **3** at $345(\pm 0.5)^\circ\text{C}$ using normal 8 mm bore of the quartz tube without molecular sieve. Using a 0.4 mm bore of the quartz tube without the molecular sieve, the bands of HCN and NH_3 are appeared on the PE spectrum of the products that result from a pyrolysis of **3** at $345(\pm 0.5)^\circ\text{C}$. This shows not only that the molecular sieve is the precondition of the generation of the radicals, but also the short-lived species cannot exist in high temperature.
- (4) To assign the PES bands of **1**, G2 and DFT calculations are performed. The experimental and theoretical results agree reasonably well, and show that **1** is a diradical with C_s symmetry and has a $^3A''$ ground state.
- (5) *Ab initio* SCF 6-31G** calculations show that **2** is a closed-shell molecule with C_s symmetry. On the basis of Koopmans theorem,²¹ the PE spectrum of **2** is also designated.

ACKNOWLEDGMENTS

This project was supported by the National Natural Science Foundation of China (Contracts No. 29973051 and No. 20073052) and the Basic Bureau of Chinese Academy of Sciences (Contract No. KJCXZ-H2-01). S.Z. would like to thank the Chinese Academy of Sciences for receipt of a scholarship during the period of this work. D.K.M. and F.T.C. would like to thank the University Grants Council (UGC) of Hong Kong Special Administration Region (HKSAR) (Grant No. CA 02) and the Research Committee of the Hong Kong Polytechnic University (Grant No. G-YY31).

- ¹C. Wentrup, *Relative Molecules: The Neutral Reactive Intermediates in Organic Chemistry* (Wiley, New York, 1984), Chap. 4.
- ²R. S. Berry, in *Nitrenes*, edited by W. Lwowski (Wiley-Interscience, New York, 1970), p. 13.
- ³M. S. Platz, *Acc. Chem. Res.* **28**, 487 (1995).
- ⁴M. J. Travers, D. C. Cowles, E. P. Clifford, and G. B. Ellison, *J. Chem. Phys.* **111**, 5349 (1999).
- ⁵J. F. Arenas, J. I. Marcos, I. L. Tocon, J. C. Otero, and J. Soto, *J. Chem. Phys.* **113**, 2282 (2000).
- ⁶(a) A. Gilles, J. Masanet, and C. Vermeil, *Chem. Phys. Lett.* **25**, 345 (1974); (b) F. Rohrer and F. Stuhl, *J. Chem. Phys.* **88**, 4788 (1988).
- ⁷(a) S. J. Kim, T. P. Hamilton, and H. F. Schaefer III, *J. Am. Chem. Soc.* **114**, 5349 (1992); (b) D. A. Hrovat, E. E. Waali, and W. T. Borden, *ibid.* **114**, 8701 (1992).
- ⁸L. A. Curtiss, L. D. Kock, and J. A. Pople, *J. Chem. Phys.* **95**, 4040 (1991).
- ⁹Z. X. Ma, C. L. Liao, C. Y. Ng, Y. S. Cheung, W. K. Li, and T. Baer, *J. Chem. Phys.* **100**, 4870 (1994).

- ¹⁰E. F. V. Scriven and K. Turnbull, *Chem. Rev.* **88**, 298 (1988).
- ¹¹H. Bock, R. Dammel, and L. Horner, *Chem. Ber.* **114**, 220 (1981).
- ¹²H. Bock and R. Dammel, *Angew. Chem., Int. Ed. Engl.* **26**, 504 (1987).
- ¹³H. Bock and R. Dammel, *J. Am. Chem. Soc.* **110**, 5261 (1988).
- ¹⁴D. X. Wang, P. Jiang, X. M. Qian, and G. Y. Hong, *J. Chem. Phys.* **106**, 3003 (1997).
- ¹⁵X. J. Zhu, M. F. Ge, J. Wang, Z. Sun, and D. X. Wang, *Angew. Chem., Int. Ed. Engl.* **39**, 1940 (2000).
- ¹⁶M. F. Ge, J. Wang, Z. Sun, X. J. Zhu, and D. X. Wang, *J. Chem. Phys.* **114**, 3051 (2001).
- ¹⁷M. F. Ge, J. Wang, X. J. Zhu, Z. Sun, and D. X. Wang, *J. Chem. Phys.* **113**, 1866 (2000).
- ¹⁸Z. Sun, S. J. Zheng, J. Wang, M. F. Ge, and D. X. Wang, *Chem.-Eur. J.* **7**, 2995 (2001).
- ¹⁹J. Wang, Z. Sun, J. Wang, M. F. Ge, and D. X. Wang, *Angew. Chem., Int. Ed. Engl.* **40**, 3055 (2001).
- ²⁰X. J. Yang, Z. Sun, M. F. Ge, S. J. Zheng, L. P. Meng, and D. X. Wang, *Chem. Phys. Chem.* **11**, 963 (2002).
- ²¹T. Koopmans, *Physica (Amsterdam)* **1**, 104 (1934).
- ²²G. O. Olah and D. J. Donovan, *J. Org. Chem.* **43**, 864 (1978).
- ²³Z. Sun, Ph.D. thesis, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China, 2002.
- ²⁴X. M. Qian, Master's thesis, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China, 1997; C. H. Li, Master's thesis, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China, 1998; X. J. Zhu, Master's thesis, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China, 2000; J. Wang, Master's thesis, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China, 2001.
- ²⁵K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules* (Japan Scientific Societies, Tokyo, 1980), pp. 214, 47.