

Mass spectra of the 2,4-pentadiynylidyne (C_5H ; $X^2\Pi$) and 2,4-pentadiynyl-1 ($n-C_5H_3$; X^2B_1) radicals

Xibin Gu, Ying Guo, Ralf I. Kaiser*

Department of Chemistry, University of Hawai'i at Manoa, Honolulu, HI 96822, USA

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Abstract

We employed the crossed molecular beams method to synthesize the 2,4-pentadiynylidyne, C_5H ($X^2\Pi$), and the 2,4-pentadiynyl-1, $n-C_5H_3$ (X^2B_1), radicals *in situ* under single collision conditions via the reactions of tricarbon molecules with acetylene and ethylene, respectively. Time-of-flight spectra of the radicals were recorded at the center-of-mass angles at various mass-to-charge ratios from $m/z=63$ ($C_5H_3^+$) to $m/z=36$ (C_3^+). Integrating these time-of-flight spectra and normalizing them to the most intense peak, intensity ratios of $I(m/z=61):I(m/z=60):I(m/z=49):I(m/z=48):I(m/z=37):I(m/z=36)=0.49\pm 0.04:0.27\pm 0.03:1:0.15\pm 0.02:0.32\pm 0.03:0.11\pm 0.04$ can be extracted for the 2,4-pentadiynylidyne radical. In case of the 2,4-pentadiynyl-1 molecule, we find intensity ratios of $I(m/z=63):I(m/z=62):I(m/z=61):I(m/z=60):I(m/z=51):I(m/z=50):I(m/z=49):I(m/z=48):I(m/z=39):I(m/z=38):I(m/z=37):I(m/z=36)=0.39\pm 0.04:0.50\pm 0.05:0.32\pm 0.03:0.10\pm 0.03:0.03\pm 0.01:1.0:0.24\pm 0.02:0.02\pm 0.01:0.24\pm 0.03:0.65\pm 0.05:0.57\pm 0.05:0.36\pm 0.03$ at an electron impact energy of 70 eV. The absolute ionization cross sections of the 2,4-pentadiynylidyne and 2,4-pentadiynyl radicals were estimated to be $8.6\pm 1.7\times 10^{-16}\text{ cm}^2$ and $9.7\pm 1.9\times 10^{-16}\text{ cm}^2$, respectively. Our data can be employed in future space missions to detect the C_5H and C_5H_3 radicals – crucial reaction intermediates in the formation of polycyclic aromatic hydrocarbon molecules – in the atmospheres of hydrocarbon rich planets (Jupiter, Saturn, Uranus, Neptune, Pluto) and their moons (Titan) and also in combustion flames via mass spectrometry coupled with matrix interval arithmetic. © 2006 Elsevier B.V. All rights reserved.

Keywords: Electron impact ionization; Fragmentation pattern; Mass spectrum; Free radical

1. Introduction

During the last years, the 2,4-pentadiynylidyne (C_5H ($X^2\Pi$)) and of the 2,4-pentadiynyl-1 (C_5H_3 (X^2B_1)) radicals have received considerable attention in the astrochemistry [1–7] and in the combustion chemistry communities [8–10] due to their prospective roles as precursors to polycyclic aromatic hydrocarbons (PAHs) [11] and fullerenes [12–14]. The 2,4-pentadiynyl-1 radical (C_5H_3 ; X^2B_1), for instance, could either react with a methyl radical (CH_3 , X^2A_2' ; (reaction (1))) [15] or with the C_5H_5 isomers 1-methylbutatrienyl [$H_2CCCCCH_3$; X^2A''] [16], 4-methylbutatrienyl [$HCCCCH(CH_3)$; X^2A''] [16], 1-vinylpropargyl [$HCCCH(C_2H_3)$; X^2A''] [17,18], or 3-vinylpropargyl [$H_2CCC(C_2H_3)$; X^2A''] [17,18], (reaction (2)) to access the C_6H_6 and $C_{10}H_8$ potential energy surfaces (PES) potentially leading to benzene and naphthalene/azulene in com-

busion flames and in planetary atmospheres via successive isomerization steps. These molecules are thought to build up even more complex polycyclic aromatic hydrocarbons (PAHs) yielding ultimately soot particles [19–23]:



Due to their importance in combustion processes, detailed information on the mass spectra and on the fragmentation patterns of both radicals will help to follow the concentration of the 2,4-pentadiynylidyne and of the 2,4-pentadiynyl-1 radicals in combustion flames in real time and to determine absolute radical concentrations not only via spectroscopy such as Fourier transform microwave spectroscopy [24], but also via mass spectrometry coupled to an electron impact ionizer on line and *in situ*. Very recently, a combination of quadrupole mass spectrometry (QMS) with matrix interval arithmetic (MIA) has been shown to be capable of extracting the chemical composition of complex

* Corresponding author. Tel.: +1 808 9565730; fax: +1 808 9565908.
E-mail address: kaiser@gold.chem.hawaii.edu (R.I. Kaiser).

gas mixtures even in the presence of highly reactive radicals and closed shell molecules [25]. To expand this approach to radicals, the fragmentation patterns of these molecules such as of the linear C_5H and C_5H_3 species are imperative. For instance, ion counts at $m/z=63$ from $C_5H_3^+$ – the parent ion of the C_5H_3 radical – can also originate from dissociative ionization and fragmentation of more complex hydrocarbons such as benzene (C_6H_6). Therefore, the actual ion current recorded at $m/z=63$ depicts the sum of the ion currents of all molecules contributing to this mass-to-charge ratio. Note that selective photoionization utilizing a tunable ultraviolet photon source – a soft ionization technique which effectively eliminates the fragmentation of the radical cation to smaller fragments – coupled to a mass spectrometric device is feasible to reveal the time dependent concentrations of radicals in combustion flames [26]. However, since this technique requires a tunable vacuum ultraviolet light source – either a synchrotron or four wave mixing schemes – this method can hardly be utilized to identify radicals in the framework of, for instance, an *in situ* exploration of hydrocarbon-rich atmospheres of planets and their moons via space crafts. In this paper, we derive the first mass spectra of the 2,4-pentadiynylidyne ($C_5H(X^2\Pi)$) and 2,4-pentadiynyl-1 radicals ($n-C_5H_3(X^2B_1)$) which are generated *in situ* under single collision conditions in crossed molecular beams experiment via the reaction of tricarbon molecules with acetylene and ethylene, respectively [27,28]. In contrast to bulk experiments, where reactants are mixed, the key benefit of a crossed beams method is the capability to form both reactants, here tricarbon (C_3) molecules and the hydrocarbon beam, in separate supersonic beams. The reactants of each beam are made to collide only with the molecules of the other beam, and the products formed fly undisturbed towards the mass spectrometric detector. These features provide an unmatched method to *synthesize* unstable radicals like $C_5H(X^2\Pi)$ and $C_5H_3(X^2B_1)$.

2. Experimental setup

We synthesized the 2,4-pentadiynylidyne ($C_5H(X^2\Pi)$) and 2,4-pentadiynyl-1 radicals ($n-C_5H_3(X^2B_1)$) in crossed molecular beams reactions of the tricarbon molecule, $C_3(X^1\Sigma_g^+)$, with acetylene, $C_2H_2(X^1\Sigma_g^+)$, and ethylene, $C_2H_4(X^1A_g)$, *in situ*. Briefly, the main chamber of the crossed beams machine is evacuated to the low 10^{-8} Torr region [29]. Two source chambers are located inside the vessel. A pulsed supersonic beam of tricarbon molecules, $C_3(X^1\Sigma_g^+)$, was generated via laser ablation of graphite at 266 nm [30]. Here, the 30 Hz, 25 mJ output of a Spectra Physics GCR-270-30 Nd:YAG laser is focused onto a rotating carbon rod and the ablated species were seeded into helium carrier gas released by a Proch-Trickl pulsed valve operating at 60 Hz and 80 μ s pulses with 4 atm backing pressure. A four slot chopper wheel located between the skimmer and a cold shield selects segments of the seeded beam with peak velocities of 3880 ± 100 ms^{-1} (acetylene experiment) and 3197 ± 100 ms^{-1} (ethylene experiment) and speed ratios S of 1.5 ± 0.1 and 1.9 ± 0.1 , respectively. The operation conditions were optimized so that the ablation beam contains mainly tricarbon 80% and only to a less extent dicarbon

(5%) and atomic carbon (15%). The pulsed tricarbon and the pulsed hydrocarbon beams (550 Torr backing pressure; acetylene: $v_p = 902 \pm 5$ ms^{-1} ; $S = 15.7 \pm 0.1$; ethylene: $v_p = 890 \pm 5$ ms^{-1} ; $S = 15.7 \pm 0.1$) pass through skimmers and cross at 90° in the interaction region of the scattering chamber. The time-of-flight spectra of the parent and of the fragmentation patterns of the newly formed C_5H and C_5H_3 radicals were recorded in the plane of both beams using a rotatable quadrupole mass spectrometer with an electron impact ionizer at the center-of-mass angle of the reaction. The Brink-type electron impact ionizer [31] is surrounded by a liquid nitrogen shield and is located in the third region of a triply differentially pumped ultra high vacuum chamber (10^{-11} Torr); the quadrupole mass filter and the Daly-type scintillation particle detector [32] are connected to the second region. Recall that the fragmentation patterns of a molecule strongly depend on the kinetic energy of the electron. Here, we recorded these patterns at 70 eV electron energy, i.e., the *standardized* electron energy utilized to setup the NIST mass spectral database.

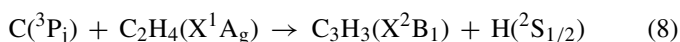
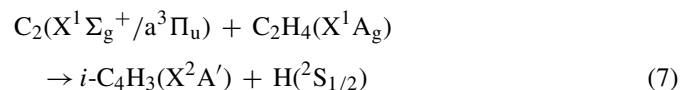
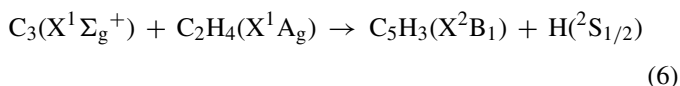
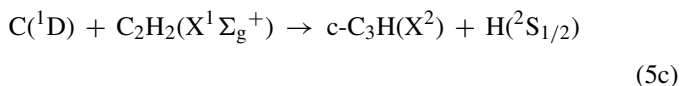
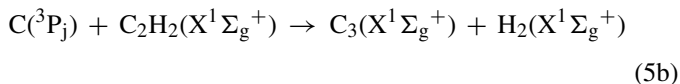
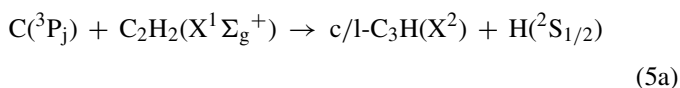
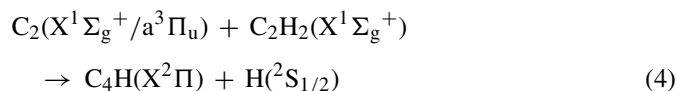
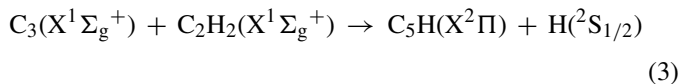
3. Results

The data analysis procedure is similar to the one utilized previously in our laboratory to extract the mass spectrum of the linear butadiynyl radical, $C_4H(X^2\Sigma^+)$ [33], and of the 1-butene-3-yne-2-yl radical, $i-C_4H_3(X^2A')$ [34]. Most importantly, we have to consider that the ablation beam does not contain solely the desired tricarbon molecule, but also carbon atoms and dicarbon molecules, $C_2(X^1\Sigma_g^+/a^3\Pi_u)$ [30]. Tricarbon molecules were found to react with acetylene and ethylene to the 2,4-pentadiynylidyne radical ($C_5H(X^2\Pi)$) and to the 2,4-pentadiynyl-1 radical ($n-C_5H_3(X^2B_1)$) through tricarbon versus atomic hydrogen exchange pathways (reactions (3) and (6), respectively) [35]. Considering the acetylene system, bimolecular collisions of dicarbon, $C_2(X^1\Sigma_g^+/a^3\Pi_u)$, with acetylene yielded the butadiynyl radical, $C_4H(X^2\Sigma^+)$, plus atomic hydrogen (reaction (4)) [33]. The situation of the carbon atoms is more complicated. At the present velocity of the ablation beam, the latter contains carbon atoms both in their electronic ground (3P) and first electronically excited states (1D) [36]. The reaction of $C(^3P)$ with acetylene was found to yield the cyclic and linear C_3H isomers (reaction (5a)) as well as tricarbon plus molecular hydrogen (reaction (5b)) [37]. On the other hand, $C(^1D)$ was suggested to react only to the cyclic C_3H isomer plus atomic hydrogen (reaction (5c)) [36]. In a similar way, the carbon, dicarbon, and tricarbon species can react with ethylene via multiple pathways as summarized in reactions (6)–(8). These considerations suggest that we have to find a technique to distinguish if the reactive scattering signal actually comes from the reaction of tricarbon molecules or from dicarbon molecules/carbon atoms with acetylene and ethylene.

Considering the acetylene reaction, the mass of the C_5H radical of 61 amu dictates that signal of the parent ion at $m/z=61$ and of the fragmentation pattern at 60 (C_5^+) originates solely from the C_5H molecule. However, ions at lower mass-to-charge ratios such as of 49 (C_4H^+), 48 (C_4^+), and 37 (C_3H^+) could originate from dissociative ionization of the C_5H parent ($m/z=49$,

48, 37), from the ionized C_4H parent molecule formed in reaction (4) ($m/z = 49$), from dissociative ionization of the C_4H parent ($m/z = 48, 37$), and from the ionized C_3H parent molecule formed in reactions (5a) and (5c). Signal at $m/z = 36$ (C_3^+) has contributions from reactions (3)–(5) (fragmentation and reactive scattering signal) as well as from elastically scattered tricarbon molecules from the acetylene beam.

In case of the ethylene system, the mass of the C_5H_3 radical of 63 amu dictates that signal of the parent ion at $m/z = 63$ and of the fragmentation patterns at 62 ($C_5H_2^+$), 61 (C_5H^+), and 60 (C_5^+) originate only from the C_5H_3 molecule. However, the ions at lower mass-to-charge ratios of 51 ($C_4H_3^+$), 50 ($C_4H_2^+$), 49 (C_4H^+), and 48 (C_4^+) originate from dissociative ionization of the C_5H_3 parent molecule (reaction (6)) and also from ionization of the i - C_4H_3 parent (reaction (7)) as well as from the fragments formed via dissociative ionization of i - C_4H_3 . Finally, signal at even smaller mass-to-charge ratios of 39 ($C_3H_3^+$), 38 ($C_3H_2^+$), 37 (C_3H^+), and 36 (C_3^+), can come from dissociative ionization of the $C_5H_3(X^2B_1)$ and i - $C_4H_3(X^2A')$ parents molecules ($m/z = 39$ – 36), from ionization of the propargyl radical (reaction (8)) ($m/z = 39$), dissociative ionization of the propargyl radical ($m/z = 38$ – 36), and elastic scattering of the tricarbon molecule with ethylene ($m/z = 36$):



To extract the desired fragmentation patterns of the 2,4-pentadiynylidyne and of the 2,4-pentadiynyl-1 radicals, it is crucial to distinguish these pathways. To carry out this endeavor, we perform a transformation of the coordinate system from the laboratory system to the center-of-mass reference frame [33,34]. The latter is convenient to get information on the dynamics of reactions (3)–(8). Recall that the experimentalist ‘sits’ on the center-of-mass and watches how the ablated species collide with the hydrocarbon molecule and in which direction the reaction products fly apart. Fig. 1 compiles the relationship between

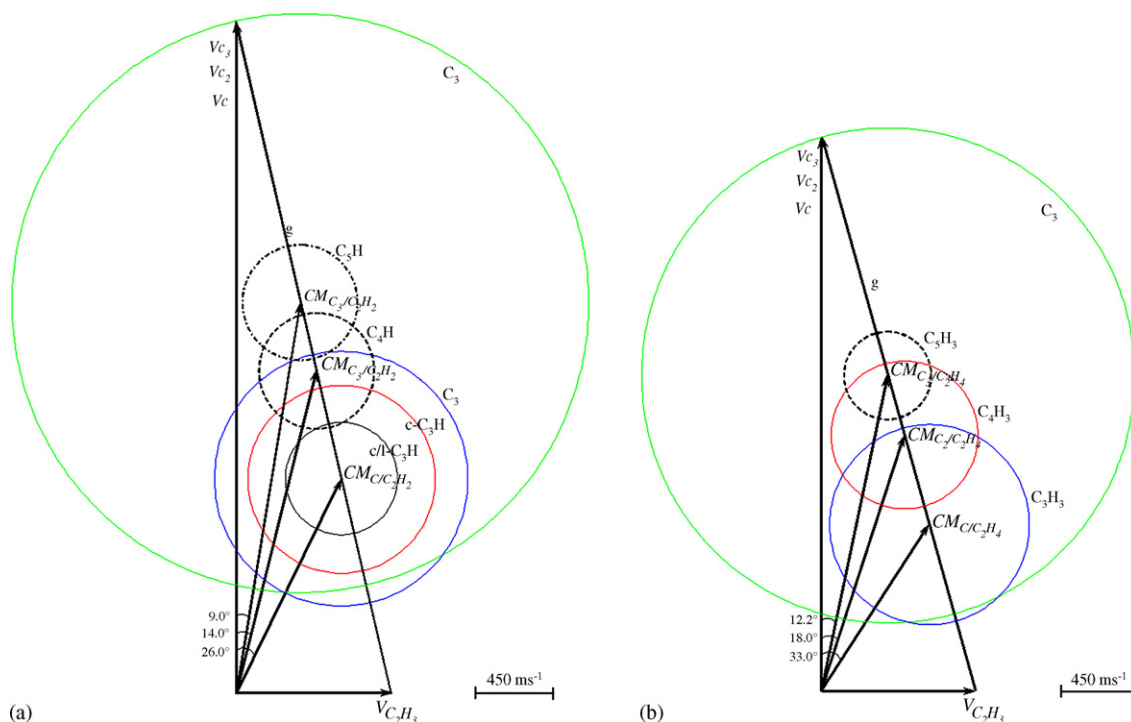


Fig. 1. (a) Newton diagram of the reactions of carbon atoms, dicarbon molecules, and tricarbon molecules with acetylene via Eqs. (3)–(5). The maximum recoil velocities of the products of the reactions are shown in black-dashed dotted (3), black-dashed (4), black-solid (5a), red (5c), blue (5b), and green (elastically scattered tricarbon molecules). (b) Newton diagram of the reactions of carbon atoms, dicarbon molecules, and tricarbon molecules with ethylene via Eqs. (6)–(8). The maximum recoil velocities of the products of the reactions are shown in black-dashed (6), red (7), blue (8), and green (scattered tricarbon molecules). See text for a detailed definition of the symbols. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

both coordinate systems and incorporates the dynamics of the reactions (3)–(5) (acetylene reactions) and (6)–(8) (ethylene reactions). We would like to elucidate briefly on the acetylene system as a typical example so that the reader can follow the procedure. In the present experiment, a beam of the tricarbon, dicarbon, and atomic carbon reactants with lab velocities V_{C_3} , V_{C_2} , and V_C , respectively, crosses a supersonic beam of acetylene with a lab velocity $V_{C_2H_2}$ at 90° (Fig. 1a). These velocities are represented as vectors. The vector connecting the tips of the tricarbon and acetylene vectors defines the relative velocity vector \mathbf{g} . Note that in the laboratory system, the center of mass frame moves with the velocity \mathbf{V}_{CM} . With respect to the primary beam, this vector holds fixed center-of-mass angles, Θ_{CM} , of 9° , 14° , and 26° for the reactions of acetylene with tricarbon, dicarbon, and carbon atoms, respectively. For each reaction, the center-of-mass velocity vector originates at the crossing point of the reactant beams and terminates at the center-of-mass of the system which is actually located on the relative velocity vector \mathbf{g} . Since we have three reactions – those of acetylene with tricarbon, dicarbon, and atomic carbon – this dictates the definition of three center-of masses as CM_{C_3/C_2H_2} , CM_{C_2/C_2H_2} , and CM_{C/C_2H_2} which are all positioned on the relative veloc-

ity vector \mathbf{g} . These center-of-masses play a key role to extract if the signal at lower mass-to-charge ratios between 49 and 36 originates from reactions (3), (4) and (5) alone or a combination of these pathways together with inelastic scattering of the tricarbon–acetylene system.

A detailed inspection of the recoil circles of the heavy reaction products, the so called *Newton circles*, presents essential guidance for the crossed beams experiment and for the extraction of the mass spectra of the 2,4-pentadiynylidyne and 2,4-pentadiynyl-1 radicals. Let us consider the acetylene system as a typical example and follow the line starting at the crossing point of the supersonic tricarbon and the acetylene beams along the center of mass of the velocity vector of the tricarbon–acetylene at 9° relative to the tricarbon vector – to the center-of-mass of the reaction, CM_{C_3/C_2H_2} . This vector crosses first the Newton circle of the inelastically scattered tricarbon molecule (green), followed by the Newton circles of the tricarbon product formed via reaction (5b) (blue), of C_3H generated via reaction (5c) (red), of C_4H synthesized via reaction (4) (black; dashed), and of the C_5H radical (reaction (3); black-dashed dotted). These considerations suggests that TOF spectra recorded at m/z values of 61 and 60 only contain one component of C_5H^+ and C_5^+ (dissociative

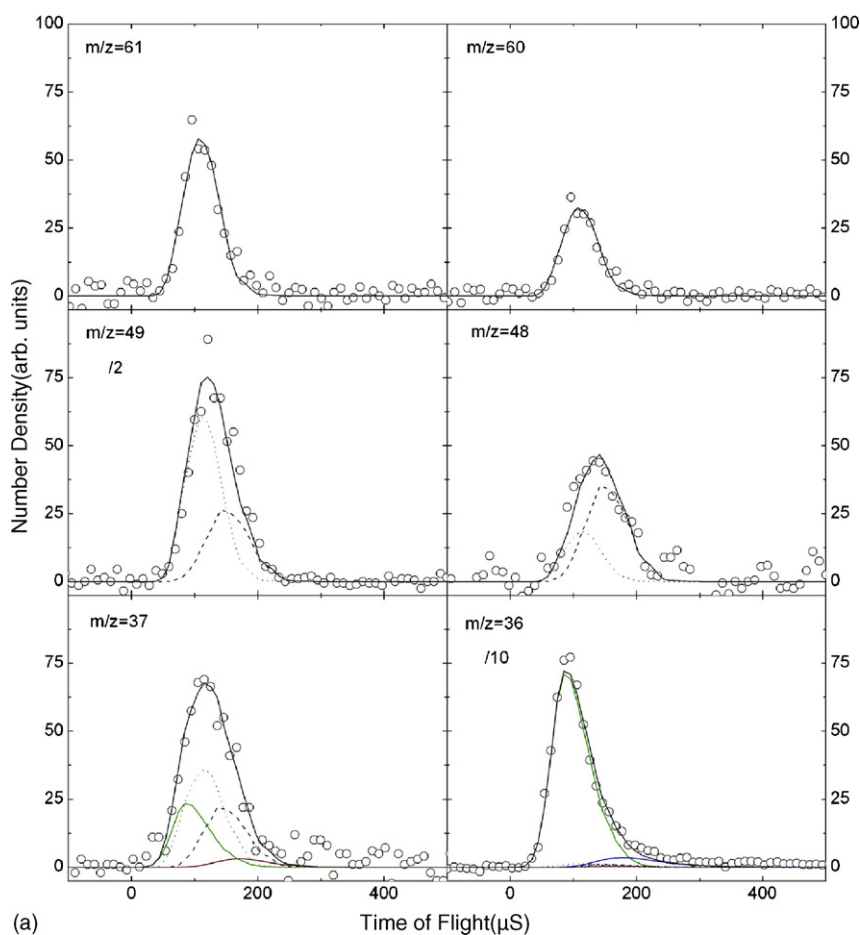


Fig. 2. (a) Time-of-flight spectra of the 2,4-pentadiynylidyne radical and its fragmentation pattern at various mass-to-charge ratios. The circles represent the experimental data, the lines show the fits. The color code of the scattering systems is compiled in Fig. 1a. (b) Time-of-flight spectra of the 2,4-pentadiynyl-1 radical and its fragmentation pattern at various mass-to-charge ratios. The circles represent the experimental data, the lines the fits. The color code of the scattering systems is compiled in Fig. 1b.

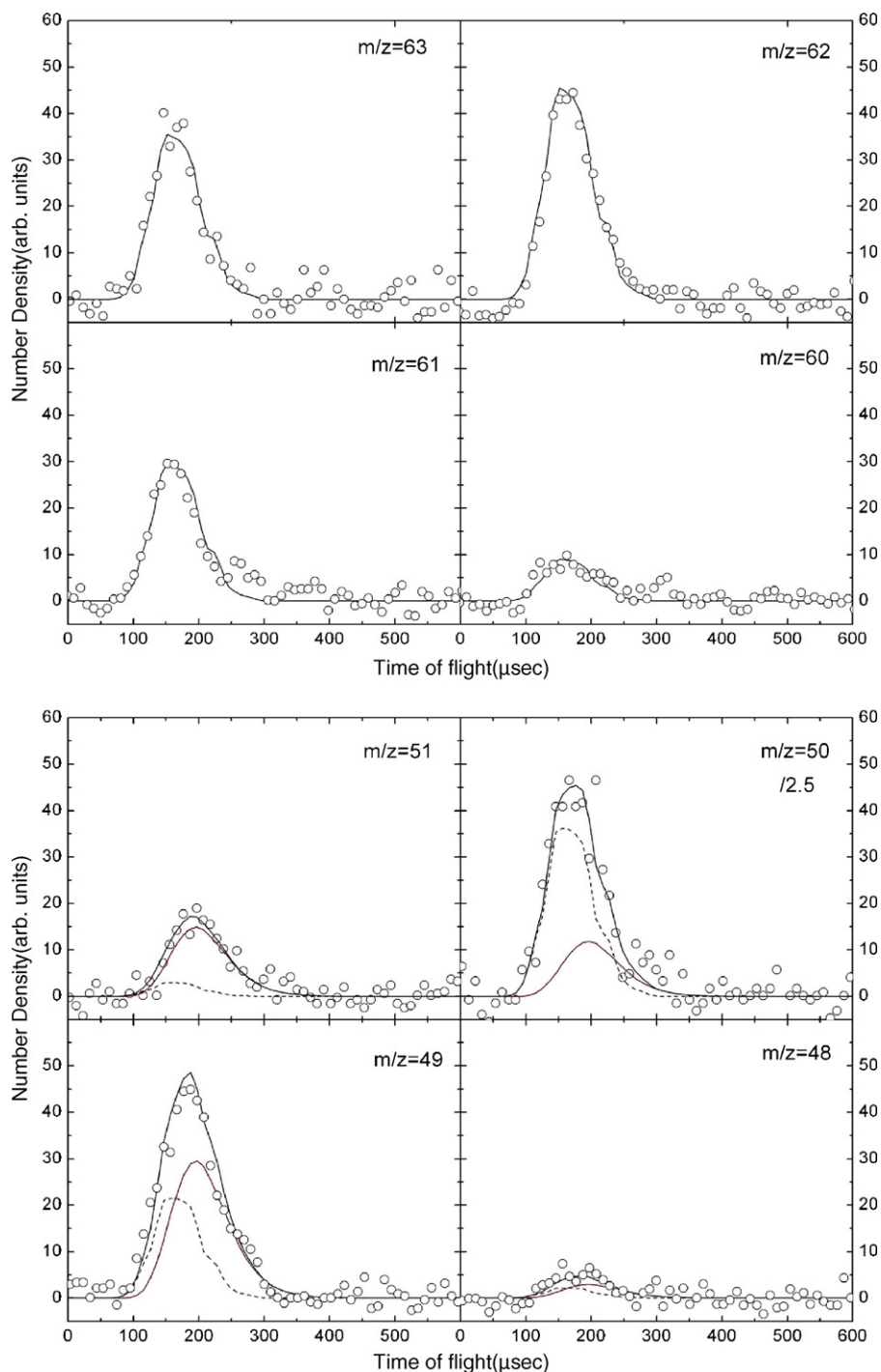


Fig. 2. (Continued)

ionization of C_5H), respectively (Fig. 2). On the other hand, the TOF spectra recorded at $m/z=49$ and 48 had to be fit with two components each: the ionized C_4H product of reaction (4) ($m/z=49$) and the C_4H^+ fragment of the C_5H product (reaction (3)) ($m/z=49$) as well as the C_4^+ fragments ($m/z=48$) from the C_5H and C_4H radicals formed in reactions (3) and (4), respectively. It is evident that the TOF of $m/z=37$ has to be fit with four contributions. These are the C_3H^+ ions formed in the dissociative ionization of the C_5H (reaction (3)) and C_4H radicals (reaction

(4)) and the primary products of reactions (5a) and (5c). Finally, the TOF spectrum at $m/z=36$ is the most complex one. Here, it is necessary to include six components: dissociative ionization of the products formed in reactions (3), (4), (5a), and (5c), the ionization of the primary tricarbon product (reaction (5b)), and inelastically scattered tricarbon molecules. Therefore, this procedure allows extracting the contribution of ion counts originating from the 2,4-pentadiynylidyne radical from each TOF spectrum.

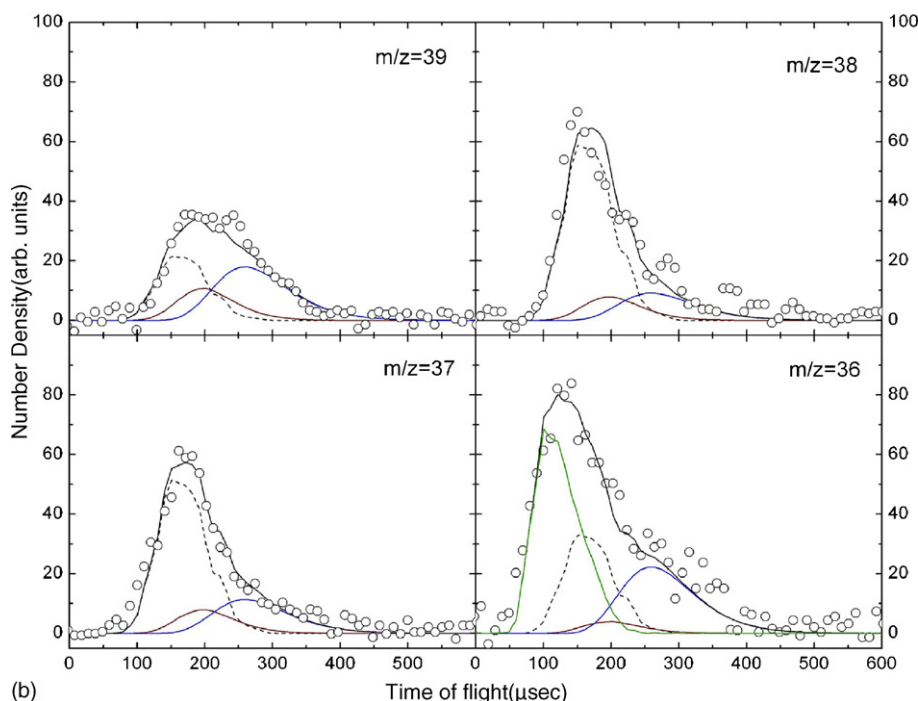


Fig. 2. (Continued).

A similar approach can visualize that in case of the ethylene reaction time-of-flight (TOF) spectra recorded in the range of $m/z = 63$ – 60 only contain a single component each from the C_5H_3 radical and its fragmentation patterns. On the other hand, the TOF spectra recorded at $m/z = 51$ – 48 had to be fit with two components: the ionized C_4H_3 product of reaction (7) ($m/z = 51$) together with the $C_4H_3^+$ fragment of the C_5H_3 product ($m/z = 51$) as well as the lower mass fragments of both the C_4H_3 and C_5H_3 radicals ($m/z = 50$ – 48). It is evident that the TOF spectra at $m/z = 39$, 38 , and 37 have to be fit with three contributions. These are the $C_3H_2^+$ ($m/z = 38$) and C_3H^+ ($m/z = 37$) ions formed in the dissociative ionization of the C_5H_3 (reaction (6)), C_4H_3 (reaction (7)), and C_3H_3 radicals (reaction (8)). Note that the TOF spectrum at $m/z = 36$ is the most complex one; it required four components: three channels of the dissociative ionization of the products formed in reactions (6)–(8) and also scattered tricarbon molecules from the ethylene beam.

All The TOF spectra were fit using a forward-convolution routine which is described in detail in Refs. [38–40]. This procedure initially assumes an angular distribution $T(\theta)$ and a translational energy distribution $P(E_T)$ in the center-of-mass reference frame (CM). TOF spectra and the corresponding laboratory angular distribution were then calculated from these $T(\theta)$ and $P(E_T)$ taking into account the beam spreads and the apparatus functions. Best fits of the TOF and laboratory angular distributions were achieved by refining the $T(\theta)$ parameters and the points of the $P(E_T)$. Also, since the reactions of carbon atoms and dicarbon molecules are barrier-less, but the reactions of tricarbon involve entrance barriers, we accounted for the collision energy (E_c)-dependent cross sections, $\sigma(E_c)$, of the reactions via the relationships $\sigma(E_c) \sim E_c^{-1/3}$ for carbon and dicarbon as well

as $\sigma(E_c) \sim [1 - E_0/E_c]$ for the tricarbon reactions with E_0 being the entrance barrier of the reaction [41].

By integrating these time-of-flight spectra and normalizing them to the most intense peak, this yields relative intensity ratios for the 2,4-pentadiynylidyne radical of $I(m/z = 61):I(m/z = 60):I(m/z = 49):I(m/z = 48):I(m/z = 37):I(m/z = 36) = 0.49 \pm 0.04:0.27 \pm 0.03:1:0.15 \pm 0.02:0.32 \pm 0.03:0.11 \pm 0.04$ at an electron impact energy of 70 eV. Upper limits at mass-to-charge ratios of 25, 24, 13, and 12 were derived to be 0.02 ± 0.01 . Note that the intensity of the ^{13}C isotopic peak of the 2,4-pentadiynylidyne radical at $m/z = 62$ ($^{13}C^{12}C_4H^+$) is about 0.05 ± 0.02 relative to $m/z = 61$. Considering the 2,4-pentadiynyl-1 radical, intensity ratios of $I(m/z = 63):I(m/z = 62):I(m/z = 61):I(m/z = 60):I(m/z = 51):I(m/z = 50):I(m/z = 49):I(m/z = 48):I(m/z = 39):I(m/z = 38):I(m/z = 37):I(m/z = 36) = 0.39 \pm 0.04:0.50 \pm 0.05:0.32 \pm 0.03:0.10 \pm 0.03:0.03 \pm 0.01:1.0:0.24 \pm 0.02:0.02 \pm 0.01:0.24 \pm 0.03:0.65 \pm 0.05:0.57 \pm 0.05:0.36 \pm 0.03$ were obtained. Upper limits at mass-to-charge ratios of 28–24, and 14–12 were determined to be 0.02 ± 0.01 ; the intensity of the ^{13}C isotopic peak of the 2,4-pentadiynyl-1 radical at $m/z = 64$ ($^{13}C^{12}C_4H_3^+$) is about 0.05 ± 0.02 relative to $m/z = 63$. Note that the derived fragmentation patterns of the i - C_4H_3 radicals are in excellent agreement with those determined earlier in the dicarbon–ethylene system [34]. The synthesized mass spectra of the 2,4-pentadiynylidyne and of the 2,4-pentadiynyl-1 radicals are depicted in Fig. 3.

To measure the concentrations of the radicals in planetary atmospheres and in hydrocarbon flames, it is important to determine their absolute, total ionization cross sections at 70 eV electron energy. Note that in the range of 70–80 eV, the total electron impact ionization cross section, σ_{ion} , is – within

$\pm 20\%$ – proportional to the averaged molecular polarizability, α [42]. Summers approximated the molecular polarizability via the sum of the atomic polarizabilities. Taking the atomic polarizabilities of carbon and hydrogen as $1.76 \times 10^{-24} \text{ cm}^3$ and $0.6668 \times 10^{-24} \text{ cm}^2$ [43], we can calculate the ratio of the cross sections of acetylene to the C_5H radical to 0.51 ± 0.11 and of acetylene to the C_5H_3 radicals to 0.45 ± 0.10 . Acetylene has been used as a reference molecule because the structure of the acetylene molecule (carbon–carbon triple bond) and the radicals are similar; since the absolute electron impact ionization cross section of acetylene is $4.37 \times 10^{-16} \text{ cm}^2$ at 70 eV [44], we can approximate the total, absolute ionization cross sections of the C_5H and C_5H_3 radicals to be $8.6 \pm 1.7 \times 10^{-16} \text{ cm}^2$ and $9.7 \pm 1.9 \times 10^{-16} \text{ cm}^2$, respectively.

4. Conclusions

We utilized the crossed molecular beams method to synthesize the 2,4-pentadiynylidyne radical, $\text{C}_5\text{H}(\text{X}^2\Pi)$, and the 2,4-pentadiynyl-1 radical ($\text{C}_5\text{H}_3(\text{X}^2\text{B}_1)$) *in situ* under single collision conditions via the reaction of tricarbon molecules with acetylene and ethylene, respectively. Time-of-flight spectra of the radical and of the fragments were recorded at the corresponding center-of-mass angles at various mass-to-charge ratios between $m/z = 63$ and $m/z = 36$. Integrating these time-of-flight spectra and normalizing them to the most intense peak, intensity ratios of $I(m/z = 61):I(m/z = 60):I(m/z = 49):I(m/z = 48):I(m/z = 37):I(m/z = 36) = 0.49 \pm 0.04:0.27 \pm 0.03:1:0.15 \pm 0.02:0.32 \pm 0.03:0.11 \pm 0.04$ can be extracted for the 2,4-pentadiynylidyne radical. In case of the 2,4-pentadiynyl-1 molecule, we find intensity ratios of $I(m/z = 63):I(m/z = 62):I(m/z = 61):I(m/z = 60):I(m/z = 51):I(m/z = 50):I(m/z = 49):I(m/z = 48):I(m/z = 39):I(m/z = 38):I(m/z = 37):I(m/z = 36) = 0.39 \pm 0.04:0.50 \pm 0.05:0.32 \pm 0.03:0.10 \pm 0.03:0.03 \pm 0.01:1:0:0.24 \pm 0.02:0.02 \pm 0.01:0.24 \pm 0.03:0.65 \pm 0.05:0.57 \pm 0.05:0.36 \pm 0.03$ at an electron impact energy of 70 eV. It should be emphasized that the fragmentation pattern may be also influenced by the internal energy of the radical to be ionized. We conducted our experiments over a broad range of collision energies from 78 to 128 kJ mol^{-1} ; the energy-dependent fluctuation of the fragmentation pattern lies within the error limits of our measurements. The absolute ionization cross sections of the 2,4-pentadiynylidyne and 2,4-pentadiynyl radicals were estimated to be $8.6 \pm 1.7 \times 10^{-16} \text{ cm}^2$ and $9.7 \pm 1.9 \times 10^{-16} \text{ cm}^2$, respectively. Our data can be employed in future space missions to detect the C_5H and C_5H_3 radicals – crucial reaction intermediates in the formation of polycyclic aromatic hydrocarbon molecules – in the atmospheres of hydrocarbon rich planets (Jupiter, Saturn, Uranus, Neptune, Pluto) and their moons (Titan) and also in combustion flames via mass spectrometry coupled with matrix interval arithmetic.

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References

- [1] J. Cernicharo, M. Guélin, C. Kahane, *Astron. Astrophys. Suppl.* 142 (2000) 181.
- [2] J.M. Brown, T.J. Millar, *Mon. Not. R. Astron. Soc.* 339 (2003) 1041.
- [3] Y.C. Minh, E.F. van Dishoeck, *Astrochemistry: From Molecular Clouds to Planetary Systems*, Astronomical Society of the Pacific, San Francisco, 2000.
- [4] T.J. Millar, P.R.A. Farquhar, K. Willacy, *Astron. Astrophys. Suppl. Ser.* 121 (1997) 139.
- [5] S.D. Doty, C.M. Leung, *ApJ* 502 (1998) 898.
- [6] *Faraday Discussions, Chemistry and Physics of Molecules and Grains in Space*, 109 (1998) 1.
- [7] M.B. Bell, P.A. Feldman, J.K.G. Watson, M.C. McCarthy, M.J. Travers, C.A. Gottlieb, P. Thaddeus, *ApJ* 518 (1999) 740.

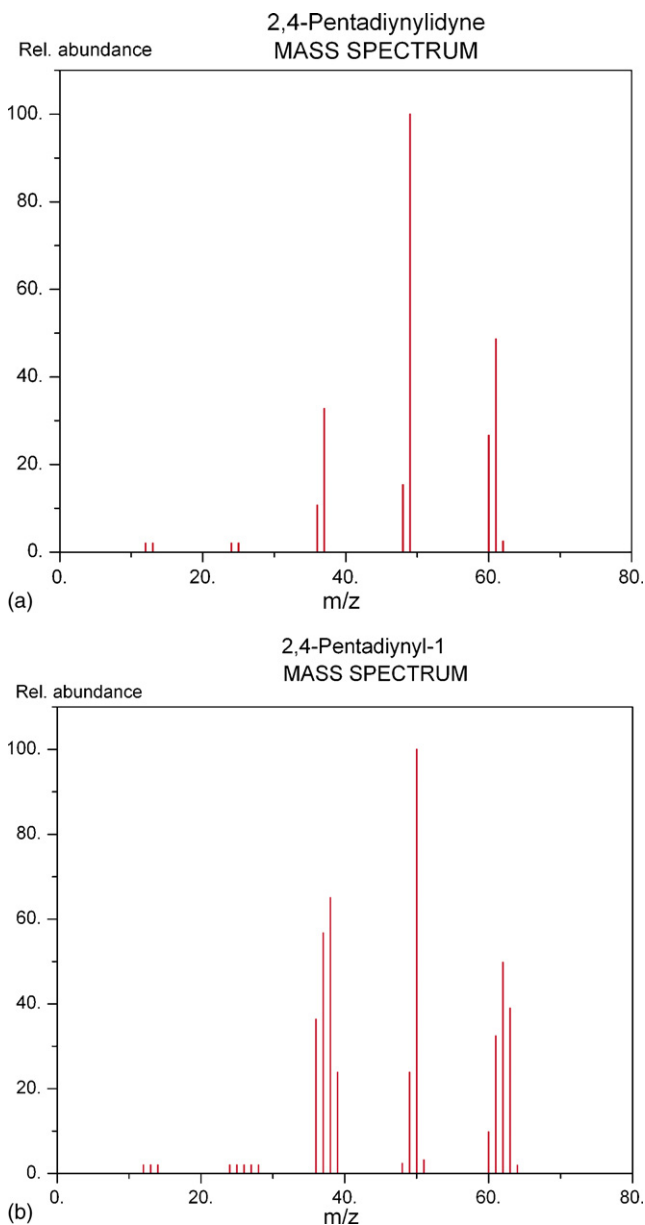


Fig. 3. (a) Mass spectrum of the 2,4-pentadiynylidyne radical synthesized from the recorded parent peak and fragmentation pattern. (b) Mass spectrum of the 2,4-pentadiynyl-1 radical synthesized from the recorded parent peak and fragmentation pattern. Both spectra are presented in a NIST standardized format.

- [8] J.H. Kiefer, S.S. Sidhu, R.D. Kern, K. Xie, H. Chen, L.B. Harding, *Combust. Sci. Technol.* 82 (1992) 101.
- [9] M. Hausmann, K.H. Homann, *Proceedings of the International Annual Conference of ICT 22nd (Combustion React. Kinetics)*, 1991, p. 1.
- [10] H.Y. Zhang, J.T. McKinnon, *Combust. Sci. Technol.* 107 (1995) 261.
- [11] A. Mayer, J. Czerwinski, M. Wyser, P. Mattrel, A. Heitzer, *Society of Automotive Engineers [Special Publication] SP (2005) SP-1978 (CI Engine Performance for Use with Alternative Fuels, and New Diesel Engines and Components)*, 2005, p. 137;
K. Kohse-Hoeinghaus, A. Schocker, T. Kasper, M. Kamphus, A. Brockhinke, *Z. Phys. Chem.* 219 (2005) 583;
A. Kitajima, T. Hatanaka, M. Takeuchi, H. Torikai, T. Miyadera, *Combust. Flame* 142 (2005) 72;
W.M. Baird, L.A. Hooven, B. Mahadevan, *Environ. Mol. Mutagen.* 45 (2005) 106.
- [12] F. Cataldo, *Fullerenes Nanotubes Carbon Nanostruct.* 13 (2005) 21.
- [13] J.R. Heath, in: G.S. Hammond, V.J. Kuck (Eds.), *Fullerenes*, American Chemical Society, Washington, 1992.
- [14] R.P.A. Bettens, E. Herbst, *ApJ* 478 (1997) 585.
- [15] A.M. Mebel, S.H. Lin, X.M. Yang, Y.T. Lee, *J. Phys. Chem. A* 101 (1997) 6781.
- [16] N. Balucani, H.Y. Lee, A. Mebel, Y.T. Lee, R.I. Kaiser, *J. Chem. Phys.* 115 (2001) 5107.
- [17] L.C.L. Huang, H.Y. Lee, A.M. Mebel, S.H. Lin, Y.T. Lee, R.I. Kaiser, *J. Chem. Phys.* 113 (2000) 9637.
- [18] I. Hahndorf, H.Y. Lee, A.M. Mebel, S.H. Lin, Y.T. Lee, R.I. Kaiser, *J. Chem. Phys.* 113 (2000) 9622.
- [19] C.J. Pope, J.A. Miller, *Proc. Combust. Inst.* 28 (2000) 1579.
- [20] H. Richter, J.B. Howard, *Prog. Energy Combust. Sci.* 26 (2000) 565.
- [21] S.E. Wheeler, W.D. Allen, H.F. Schaefer III, *J. Chem. Phys.* 121 (2004) 8800.
- [22] S.J. Klippenstein, J.A. Miller, *J. Phys. Chem. A* 109 (2005) 4285.
- [23] X. Krokidis, N.W. Moriarty, W.A. Lester Jr., M. Frenklach, *Int. J. Chem. Kinet.* 33 (2001) 808.
- [24] M. Nakajima, Y. Sumiyoshi, Y. Endo, *Rev. Sci. Instrum.* 73 (2002) 165.
- [25] R.I. Kaiser, P. Jansen, K. Petersen, K. Roessler, *Rev. Sci. Instrum.* 66 (1995) 5226.
- [26] N. Hansen, S.J. Klippenstein, J.A. Miller, J. Wang, T.A. Cool, M.E. Law, P.R. Westmoreland, T. Kasper, K. Kohse-Hoeinghaus, *J. Phys. Chem. A* 110 (2006) 4376;
N. Hansen, S.J. Klippenstein, C.A. Taatjes, J.A. Miller, J. Wang, T.A. Cool, B. Yang, R. Yang, L. Wei, C. Huang, J. Wang, F. Qi, M.E. Law, P.R. Westmoreland, *J. Phys. Chem. A* 110 (10) (2006) 3670–3678.
- [27] R.I. Kaiser, *Chem. Rev.* 102 (2002) 1309;
A.F. Furlan, G.E. Hall, *J. Chem. Phys.* 109 (1998) 10390;
A. Furlan, *J. Phys. Chem. B* 103 (1999) 1550;
X. Yang, K. Liu, *Modern Trends in Chemical Dynamics*, World Scientific, Singapore, 2003;
R.A. Dressler, *Chemical Dynamics in Extreme Environments*, World Scientific, Singapore, 2001.
- [28] R.I. Kaiser, *Chem. Rev.* 102 (2002) 1309;
A.F. Furlan, G.E. Hall, *J. Chem. Phys.* 109 (1998) 10390;
A. Furlan, *J. Phys. Chem. B* 103 (1999) 1550;
X. Yang, K. Liu, *Modern Trends in Chemical Dynamics*, World Scientific, Singapore, 2003;
R.A. Dressler, *Chemical Dynamics in Extreme Environments*, World Scientific, Singapore, 2001.
- [29] Y. Guo, X. Gu, E. Kawamura, R.I. Kaiser, *Rev. Sci. Instrum.* 77 (2006) 034701;
X. Gu, Y. Guo, H. Chan, E. Kawamura, R.I. Kaiser, *Rev. Sci. Instrum.* 76 (2005) 116103;
X. Gu, Y. Guo, E. Kawamura, R.I. Kaiser, *Rev. Sci. Instrum.* 76 (2005) 083115.
- [30] R.I. Kaiser, A.G. Suits, *Rev. Sci. Instrum.* 66 (1995) 5405.
- [31] G.O. Brink, *Rev. Sci. Instrum.* 37 (1966) 857.
- [32] N.R. Daly, *Rev. Sci. Instrum.* 31 (1960) 264.
- [33] X. Gu, Y. Guo, R.I. Kaiser, *Int. J. Mass Spectrom.* 246 (2005) 29.
- [34] Y. Guo, X. Gu, R.I. Kaiser, *Int. J. Mass Spectrom.* 249/250 (2006) 420.
- [35] R.I. Kaiser, T.N. Le, T.L. Nguyen, A.M. Mebel, N. Balucani, Y.T. Lee, F. Stahl, P.v.P. Schleyer, H.F. Schaefer III, *Faraday Discuss.* 119 (2001) 51.
- [36] R.I. Kaiser, A.M. Mebel, Y.T. Lee, *J. Chem. Phys.* 114 (2001) 231.
- [37] R.I. Kaiser, C. Ochsenfeld, M. Head-Gordon, Y.T. Lee, A.G. Suits, *Science* 274 (1996) 1508.
- [38] M.S. Weis, Ph.D. Thesis, University of California, Berkeley, 1986.
- [39] M. Vernon, M. Thesis, University of California, Berkeley, 1981.
- [40] I. Kaiser, C. Ochsenfeld, D. Stranges, M. Head-Gordon, Y.T. Lee, *Faraday Discuss.* 109 (1998) 183;
R.I. Kaiser, A.M. Mebel, N. Balucani, Y.T. Lee, F. Stahl, P.v.R. Schleyer, H.F. Schaefer, *Faraday Discuss.* 119 (2001) 51.
- [41] R.D. Levine, *Molecular Reaction Dynamics*, Cambridge, 2005.
- [42] R.L. Summers, *Empirical observations of the sensitivity of hot cathode ionization type vacuum gauges*, NASA Technical Note TN D-5285, 1969;
R. Holanda, *Sensitivity of hot cathode ionization vacuum gauges in several gases*, NASA Technical Note TN D-6815, 1972.
- [43] *CRC Handbook of Chemistry and Physics*, National Institute of Standards, Boca Raton, 2004.
- [44] C. Tian, C.R. Vidal, *Chem. Phys. Lett.* 288 (1998) 499;
C. Tian, C.R. Vidal, *J. Phys. B* 31 (1998) 895.