

Mass spectrum of the butadiynyl radical (C_4H ; $X^2\Sigma^+$)

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Abstract

We utilized the crossed molecular beams method to synthesize the butadiynyl radical, $C_4H(X^2\Sigma^+)$, via the reaction of dicarbon molecules with acetylene, under single collision conditions. Time-of-flight spectra of the radical were recorded at the center-of-mass angle (31°) of the parent ion ($m/z=49$; C_4H^+) and of the fragments at $m/z=48$ (C_4^+), $m/z=37$ (C_3H^+), and $m/z=36$ (C_3^+). This yields relative intensity ratios of $I(m/z=49):I(m/z=48):I(m/z=37):I(m/z=36):I(m/z=25):I(m/z=24)=1.0:0.67\pm 0.07:0.47\pm 0.06:0.2\pm 0.02:0.08\pm 0.02:0.04\pm 0.02$ at 70 eV electron impact energy. Signal at $m/z=13$ (CH^+) and 12 (C^+) contribute less than 0.04 relative to the parent peak; the intensity of the ^{13}C isotopic peak of the butadiynyl radical at $m/z=50$ ($^{13}C^{12}C_3H^+$) depicts an intensity of 0.04 ± 0.01 relative to $m/z=49$. Employing linear scaling methods, the absolute ionization cross section of the butadiynyl radical was computed to be $8.8\pm 1.8\times 10^{-16}$ cm². These data can be employed in future space missions to detect the butadiynyl radical in oxygen-poor combustion flames and in the atmospheres of planets (Jupiter, Saturn, Uranus, Neptune and Pluto) and their moons (Titan, Triton and Oberon) in situ via matrix interval arithmetic assisted mass spectrometry.

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1. Introduction

Free hydrocarbon radicals are important intermediates in combustion flames [1–3], astrochemistry [4], and planetary atmospheres [5,6]. Among the hydrogen-deficient radicals, the butadiynyl molecule, $C_4H(X^2\Sigma^+)$, has received particular attention. Detected in 1978 in the circumstellar envelope of the dying carbon star IRC+10216 [7] and subsequently in the taurus molecular cloud [8] (TMC-1) and photon-dominated regions [9], the butadiynyl radical was observed to be more abundant than many common molecules such as cyclopropenylidene ($c-C_3H_2$) and diacetylene ($HCC-CCH$) [10–12]. Both in the terrestrial settings like combustion flames [13] and extraterrestrial environments such as the interstellar medium [14] and planetary atmospheres [15–17], the butadiynyl radical has also been suggested as a precursor to complex polycyclic aromatic hydrocarbons (PAHs) and possibly fullerenes like C_{60} [18].

Despite the importance of the butadiynyl radical in combustion processes and in the chemical evolution of hydrocarbon rich planetary atmospheres, the mass spectrum of this molecule is still elusive [19]. However, a detailed knowledge of the fragmentation pattern will help to monitor combustion flames in real time and to determine absolute radical concentrations not only via spectroscopic techniques (Fourier transform microwave spectroscopy [20]; laser induced fluorescence [21]) and trapping techniques in cryogenic matrices [22], but also via mass spectrometry coupled to an electron impact ionizer. In terrestrial based laboratories, gas chromatography–mass spectrometry (GC–MS) serves as a powerful tool for off-line analyzes of complex gas mixtures [3]. Adapting GC–MS efficiently to planetary missions, however, suffers from a fundamental limitation. This ex situ technique excludes identification of thermally labile molecules, e.g., cyclobutadiene, C_4H_4 , or reactive radicals such as butadiynyl, which decompose in the GC capillary or react with the coating material. Therefore, these radicals cannot be sampled via GC–MS techniques. Reactive intermediates, however, play an important role in photochemistry of

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outer planets of our solar system [23]. Therefore, an alternative detection scheme of these important intermediates in the atmospheres of planets and their moons is clearly desired. Recently, a combination of quadrupole mass spectrometry (QMS) with matrix interval arithmetic (MIA) has been shown to extract the chemical composition of complex gas mixtures on line and in situ even in the presence of thermally labile molecules [24]. To extend this approach to the detection of radicals, the fragmentation patterns of these molecules such as of the butadiynyl radical are critical. For instance, signal at $m/z = 49$ from C_4H^+ – the parent ion of the butadiynyl radical – can be contaminated from the fragmentation of more complex hydrocarbons such as diacetylene (C_4H_2) and benzene (C_6H_6), which are very common in planetary atmospheres [23]. Therefore, the ion current recorded at, for instance, $m/z = 49$ (I_{49}), presents actually the sum of the ion currents of j molecule contributing to this mass-to-charge ratio each of them holding a partial pressure of p_j (Eq. (1)) (the j f_{49j} values represent the proportionality constants)

$$I_{49} = \sum_j f_{49j} \times p_j \quad (1)$$

Therefore, if the fragmentation patterns and the ionization cross section of the butadiynyl radical are known, the proportionality constants can be computed [24] and, hence, matrix interval arithmetic can be carried out to determine the concentrations of hydrocarbon radicals such as of the butadiynyl molecule in the atmospheres of planets and their moons. Note that in principle, 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 [25]. 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 the butadiynyl radical in the framework of an in situ exploration of hydrocarbon-rich atmospheres of planets and their moons via space crafts. Here, due to the size, weight, and power consumptions and potential misalignments of the optical elements of the laser system induced by the vibrations of the spacecraft during the launch, it would be a challenge to include a VUV laser system. Therefore, mass spectrometry coupled with matrix interval arithmetic presents a viable alternative in the in situ probing of planetary atmospheres.

In this paper, we obtain the mass spectrum of the butadiynyl radical which is synthesized in situ in a crossed molecular beams experiment. The crossed molecular beams technique represents the most versatile approach in the elucidation of the energetics and chemical dynamics of elementary reactions [26]. In contrast to bulk experiments, where reactants are mixed, the main advantage of a crossed beams approach is the capability to form the reactants 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 detector. These features provide an unprecedented approach to observe the consequences of a single collision event and even to *synthesize* unstable radicals, preventing secondary collisions and wall effects.

2. Experimental setup

We generated the butadiynyl radical, $C_4H(X^2\Sigma^+)$, in a crossed molecular beams reaction of the dicarbon molecule, $C_2(X^1\Sigma_g^+/a^3\Pi_u)$, with acetylene, $C_2H_2(X^1\Sigma_g^+)$. Briefly, the main chamber of the crossed beams machine consists of a 2300 l, 304 stainless steel box and is evacuated by three 2000 l s^{-1} magnetically suspended turbo molecular pumps backed by a single scroll pump (10 l s^{-1}) to the low 10^{-8} Torr region. To reduce the background from straight-through molecules into the detector, the vessel is equipped with a cold shield located between the chopper wheel and the interaction region, downstream the skimmer. This oxygen free high conductivity (OFHC) copper shield is interfaced to the first stage (10 K) of a cold head and reduces the vacuum in the main chamber to 4×10^{-9} Torr. This arrangement keeps the pressure in the main chamber during an actual experiment to about 5×10^{-8} Torr. Two source chambers are located inside the main chamber; in its current geometry, both beams cross perpendicularly. Each source chamber is pumped by a 2000 and 430 l s^{-1} maglev pump to the medium 10^{-9} Torr region; operating pulsed sources increases the pressure to about 10^{-5} to 10^{-4} Torr. A dry roots pump (140 l s^{-1}) roughed by two oil-free EcoDry pumps (16 l s^{-1}) backs the turbo pumps of each source chamber.

A pulsed supersonic beam of dicarbon, $C_2(X^1\Sigma_g^+/a^3\Pi_u)$, was generated via laser ablation of graphite at 266 nm [27]. The 30 Hz, 20 mJ output of a Spectra Physics GCR-270-30 Nd:YAG laser is focused onto a rotating carbon rod. Ablated dicarbon molecules are seeded into helium carrier gas released by a Proch-Trickl pulsed valve operating at 60 Hz and $80\ \mu\text{s}$ pulses with 4 atm backing pressure. A four-slot chopper wheel located between the skimmer and the cold shield selects a segment of the seeded dicarbon carbon beam with a peak velocity of $1660 \pm 2\text{ ms}^{-1}$ and a speed ratio S of 5.5 ± 0.1 . The pulsed dicarbon and the pulsed acetylene beam (550 Torr backing pressure; $v_p = 902 \pm 2\text{ ms}^{-1}$; $S = 16.2 \pm 0.1$) pass through skimmers and cross at 90° in the interaction region of the scattering chamber.

The time-of-flight spectra of the fragmentation patterns of the butadiynyl radical 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 of 31° . The Brink-type electron impact ionizer [28] 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) (Fig. 1); the quadrupole mass filter and the Daly-type scintillation particle detector [29] are

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