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Direct evidence of a strong isomer effect in electron-impact double ionization of C_3H_4

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The electron-impact double ionization of two isomers of C_3H_4 (allene and propyne) between 25 and 1000 eV has been investigated using time-of-flight mass spectrometry. Unambiguous differences in the partial double-ionization spectra of these isomers are observed over the entire energy range. These isomer effects have been observed in C_3H_4 through the recording of target product channels and, in particular, when hard collisions involving the transfer of a large amount of energy is involved. Measurements of double-ionization events which fragment through Coulomb explosion are also reported. Coincidences between the charged fragment ions and protons were measured and shown to only exhibit isomer effects in the channel involving production of $H^+ + CH_2^+$.

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The Coulomb potential's long-range character makes it very effective at disturbing the stability of many-body systems. Coulomb-driven instabilities in atomic nuclei [1], small molecules [2–5], clusters [6–8], and large biomolecules or droplets [9] usually lead to substantial amounts of energy release which, through evaporation, fission, or explosive fragmentation, decreases the survival possibilities of the parent system. The degradation pattern depends mainly on the amount of energy and charge deposited, and on the size and shape of the system, among other factors. The precise way in which these variables contribute and how the excess energy is internally distributed is not generally known, even in the simplest of cases.

Processes delivering small energy transfers to simple molecules such as photon, electron, or proton ionization usually produce singly charged cations which are either stable or decay through evaporation of one or more atoms and/or ions, as for the example of H^0 loss from CH_4 and H_2O [2,3]. Processes involving large energy transfer, such as collisions with heavy particles, can strongly inhibit the parent ion survival inducing explosive fragmentation [3]. In all these cases, doubly charged cations appear to be a critical charge state concerning both the stability and the dissociation pattern [10]. For example, doubly charged CH_4^{2+} ions have not been observed using time-of-flight spectroscopy, presenting clear evidence for a high degree of fragmentation for both proton and electron impact on CH_4 molecules [2]. For water molecules, the evaporative and explosive fragmentation can be modeled through the knowledge of single and double electron removal mechanisms for essentially any kind of particle impact [3].

It is clear from the above examples that the search for stability limits for doubly charged cations must involve slightly larger molecules. The essentially open question regarding sensitivity to the topology of the charge distribution can be addressed through the study of the fragmentation of doubly charged isomers. C_3H_4 is known to possess three isomers, two of which (allene and propyne) are shown in Fig. 1. Allene is the simplest member of the 1,2-diene class of compounds and is chiefly used in organic synthesis [12]. Much interest has also been given to propyne due to its observation in interstellar gas clouds [13,14] and in the atmosphere of Saturn's moon, Titan [15,16]. Electron-impact processes give rise to the fragmentation and generation of exotic and reactive species which play vital roles in the generation of complex molecules in laboratory plasmas and in interstel-

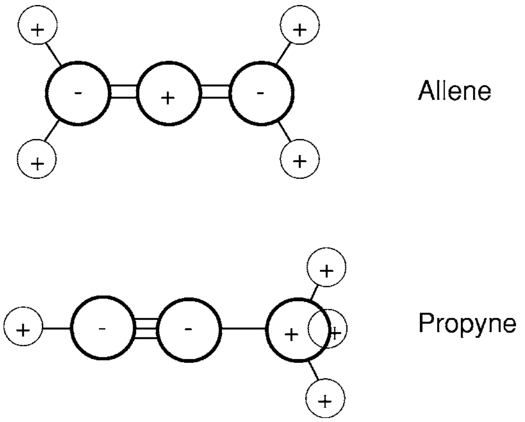

FIG. 1. Molecular structure of allene and propyne. The plus (+) and minus (−) signs indicate where positive and negative charges are more concentrated according to calculations of Kakkar *et al.* [11] for the neutral molecule. The large and small circles represent C and H atoms, respectively.

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lar space. They also have an important impact on chemical processes associated with radiation and environmental chemistry [17]. Isomeric differences are of particular interest in biological chemistry.

It has generally been assumed that isomer effects only occur in collisions that involve long interaction times [18]. Recent electron-scattering experiments have led to the suggestion that isomer effects might only be expected at energies close to threshold where resonances are likely to occur [19,20]. The present work elucidates the details of dissociation pathway differences for allene and propyne after electron-impact-induced ionization. It is shown that the stability of small, doubly charged molecules is strongly dependent on the isomeric configuration. This provides an opportunity to directly quantify the differences between the isomers. The present work also shows that the isomer effect exists at energies well above threshold where resonances are unlikely to occur and interaction times are short.

The crossed-beam experimental arrangement used in the present work was based on the pulsed electron-beam technique developed in this laboratory to carry out electron-impact ionization measurements of atomic hydrogen [21] and multiple ionization measurements of rare gases [22]. For studies involving molecular species target dissociation can occur; therefore the technique was modified and optimized to ensure that all of the fragment ions, including energetic H^+, which carries the majority of the dissociation energy, are collected with almost 100% efficiency. The technique utilizes a beam of electrons composed of narrow pulses (≈ 65 ns duration at a repetition rate of 10^5 pulses/s) which cross a thermal energy beam of the allene or propyne gas at 90°. The gas pressure in the input line was monitored using an MKS Baratron type 170 capacitance manometer. The pressure in the experimental chamber was monitored with an ion gauge. The reader is referred to paper [21] for more technical details.

The interaction region of the two beams is located between two high transparency grids mounted on two conical electrodes. A pulsed electric field ($150\ \mathrm{V\ cm^{-1}}$) was applied to these grids immediately after the electron pulse exited the interaction region. Any positive ions produced after electron impact were therefore accelerated out of the interaction region. The extracted ions were further accelerated through a potential difference of 3.0 kV and detected using a stack of three multichannel plates (MCP).

A time-to-amplitude converter (TAC) operated with start pulses from the extraction pulse generator and stop pulses from the MCP detector provided time-of-flight product ion spectra. These measurements were performed for various electron-beam energies from 25 to 1000 eV. In addition, a second TAC was gated by the output from the single-channel analyzer (SCA) of the first TAC. The window of the SCA was set to give an output when an H^+ ion was detected in the first TAC. The start and stop pulses for the second TAC were the same as for the first but were suitably delayed to eliminate self-coincidences with the H^+ ions. The second TAC therefore provided a product ion spectra that occurred in coincidence with an H^+ ion.

The statistical uncertainties of the time-of-flight integrated spectra are 0.5%–4.5% for the total data and 5%–15% for the coincidence data. The systematic uncertainties due to the determination of pressure and ion-beam current are estimated to be 8%–20%. The total experimental uncertainties are therefore taken as the quadrature sum of these contributing values.

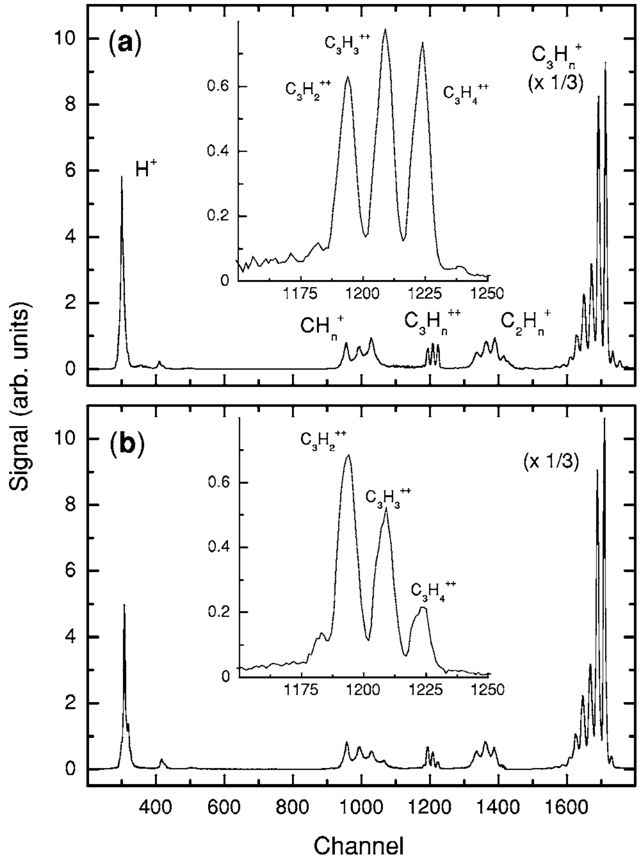

FIG. 2. Time-of-flight mass spectra taken for allene (a) and propyne (b) at 100 eV electron-impact energy. The insets show enlargement of the double-ionization groups, $C_3H_n^{2+}$.

In Fig. 2 we show raw time-of-flight spectra at 100 eV collision energy for (a) allene and (b) propyne with the doubly ionized ion spectra enlarged in the insets. It is evident that the $C_3H_n^+$ channels form the most intense ionization group and that they show only slight differences for the two isomers. This, however, is not the case for double ionization. Although much smaller in magnitude, the doubly ionized $C_3H_n^{2+}$ group *shows significant differences for the two isomers*. Apart from the $C_3H_n^+$ group some isomeric differences were observed in the single-ionization fragmentation channels. Due to the experimental arrangement used, any molecular dications detected must have a minimum lifetime of $\approx 0.7\ \mu s$. It should be noted that the mass spectra obtained for these two molecules differ from the NIST mass spectra. This is probably the result of the improved ion collection efficiency used in the present setup.

The method of recording the various target ion products shows, directly, differences in the covalent channels for the various doubly charged states when neutral hydrogen atoms are extruded from the molecular ion. The fractions for each doubly ionized fragment ($C_3H_n^{2+}$, $n=2-4$) are shown in Fig. 3 as a function of the electron energy. The disparity in these

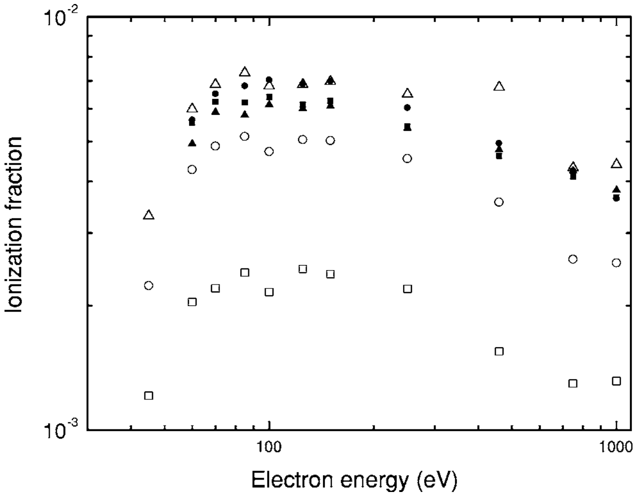

FIG. 3. Electron-impact dissociative double-ionization yields, plotted as fractions of the total target ionization, for production of $C_3H_2^{++}$ (△), $C_3H_3^{2+}$ (○), and $C_3H_4^{2+}$ (□) from allene (solid points) and propyne (hollow points).

spectra for the two isomers is quite evident. The three doubly charged ions produced from allene are approximately equal in magnitude across the entire energy range, within the experimental uncertainties. However, in the propyne case the parent doubly charged ion is considerably smaller than $C_3H_3^{2+}$ and $C_3H_2^{2+}$. The sum of the integrated signals for all of the double-ionization events is the same, within the experimental uncertainties, for both molecules over the energy range studied.

The marked differences in the doubly ionized $C_3H_n^{2+}$ groups shown in Fig. 2 are a clear indication of differences in postcollision stabilities of the parent doubly ionized $C_3H_4^{2+}$ ions. The calculated charge distributions of Kakkar *et al.* [11] represented in Fig. 1 show that a decrease of negative charge density of the acetylenic C–H bond of propyne occurring after double ionization will weaken and induce a selective cleavage of this bond. While the structure of the charged molecule can differ from the ground-state distribution, it has been assumed here that the local characteristic of the acetylenic C-H bond does not change significantly. This cleavage is not unexpected as it also occurs in the photolysis of propyne by 121.6 nm radiation [4]. For allene, the decrease of negative charge is more evenly distributed along the molecule axis, with the new field being able to hold the H atoms and keep the dication stable. The differences in the charge distributions between the two isomers can thus weaken some particular bond and deeply affect the stability of a particular configuration housing an excess of charge. A preliminary calculation for the cross sections of these isomers has been made using the Born treatment for the scattering dynamics and the discrete variable $X\alpha$ (DV-$X\alpha$) method for determining target molecular wave functions [23,24]. This calculation is in reasonable agreement with the above interpretation of the experimental result.

For the cases where Coulomb repulsion is strong enough and the doubly ionized molecule undergoes fragmentation, it is possible to measure two of the ion fragments produced using the coincidence technique mentioned above. This has been performed for all of the ion species produced simultaneously with H^+. Figure 4 shows the relative ion yield as a function of the electron-impact energy for the coincidence measurement of (a) $e^- + C_3H_4 \rightarrow H^+ + C^+$ and (b) the $e^- + C_3H_4 \rightarrow H^+ + CH_2^+$ channels. The $H^+ + CH_2^+$ is the only H^+ coincidence spectra out of all of the possible combinations that show a difference between the two isomeric molecules. It is also the weakest coincidence channel observed.

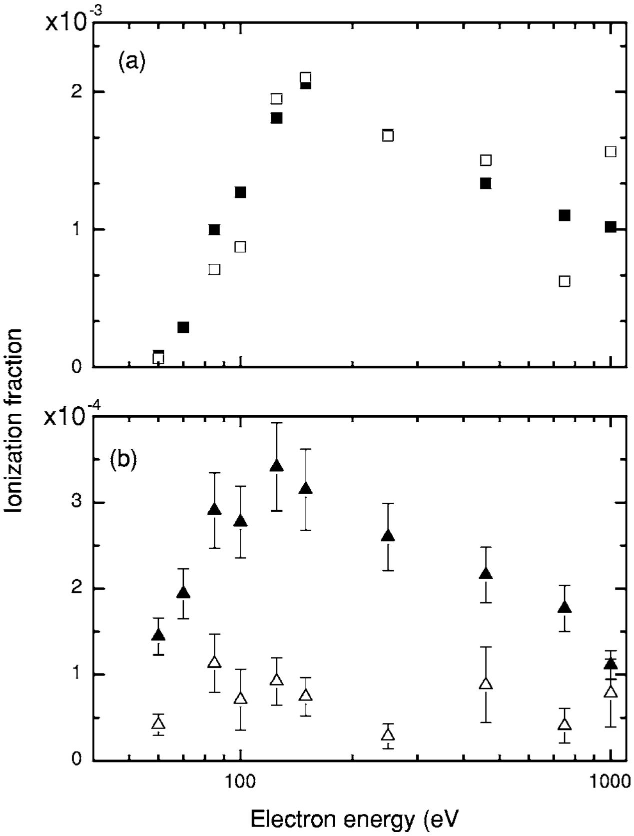

FIG. 4. Coincidence spectra from allene (solid points) and propyne (hollow points). (a) $H^+ + C^+$ coincidences. (b) $H^+ + CH_2^+$ coincidences. These spectra have been plotted as a fraction of the total target ion production at each energy. The $H^+ + C^+$ spectra is a typical example of the coincidence spectra (including groups containing C_2 and C_3 chains) showing no difference between the isomeric molecules.

The reasons for the lack of isomeric differences in the coincidence measurements are not clear. One possibility is that the fission process releases one H^+ to produce, in both cases, the propargyl (H_2CCCH) cation in a manner similar to the photolysis of allene and propyne by broadband UV radiation [4]. Although H^0 is likely to be released through the break of the acetylenic C-H bond of propyne, as mentioned before, apparently there is no substantial H^+ emission through the break of this bond as $H^+ + CH_3^+$ coincidence was not observed for either molecule. This last finding may also be related to the same reason why the $H^+ + CH_2^+$ channel is reduced in propyne as compared to allene—both results can be associated to the strong polarization over the single C bond of propyne, as shown by the charge distribution in Fig. 1, making the cleavage of this bond difficult.

In summary, double-ionization channels surviving for >0.7 μs, and without cleavage of the C-C bonds, have been observed in the electron-impact ionization of isomers of C_3H_4. These channels exhibit highly pronounced differences in products that contain varying numbers of H atoms still remaining attached. Isomer effects have been observed in C_3H_4 through the recording of target channel products and in particular when hard collisions are involved. In the past, isomer effects were inferred from small differences observed in the total scattering cross sections of the projectile product channels [18–20,25–28] and only at low collision energies. In contrast, this work shows that marked differences in the relative magnitude of the doubly ionized species of the two isomers appear over a broad range of electron-impact energies. These differences depend on how the H atoms are bonded to the carbon atoms and on the charge distribution topologies of the molecules.

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