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Observation of the Isomer Effect on Charge Transfer from C_3H_4 Molecules (Allene and Propyne) at keV Energies

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The apparent isomer effect on charge transfer processes in collisions of the ground-state C^+ ions with allene and propyne, which have the same C_3H_4 molecular chemical notation, has been observed experimentally in the collision energy from 0.2 to 4.5 keV. The difference in total charge transfer cross sections between the two isomers was found to be 32% at 0.2 keV, although it decreases to 10% at 4.5 keV. This difference is out of experimental uncertainty of 14.6% at least below the collision energy of 0.5 keV and should be regarded as a real isomer effect. Theoretical analysis based on a molecular orbital expansion method has also confirmed the experimental finding and provided the rationale.

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Our understanding of charge transfer processes in collisions of ions and hydrocarbons above intermediate collision energies has been extremely limited due to the complexity of the target. However, it becomes more and more important in a number of applications such as plasma, material, medical, and astrophysical sciences. In research of the controlled thermonuclear fusion, these collisions play a key role in low temperature edge plasmas of the current fusion devices with carbon-coated or graphite-lined walls as plasma facing materials [1]. Also they are critical in understanding various important features in high-tech applications such as plasma-based material production [2]. The process obviously constitutes an important part of astrochemistry [3].

For hydrocarbon molecules, as the number of carbon atoms increases, in general, the number of isomers increases. The C_3H_4 molecule is known to possess two stable isometric-molecular structures, i.e., allene (propadiene; $H_2C{=}C{=}CH_2$) and propyne (methylacetylene; $HC{\equiv}C{-}CH_3$). It has been well known that isomers always show conspicuous differences in various physical and chemical properties in stationary or dynamical aspects in the interaction energy equivalent to the thermal energy domain. And indeed, recently strong isomer effects have been observed in total and differential elastic cross sections for C_3H_4 isomers [4] and other systems earlier [5] by electron impact. However, as a natural consensus, it has been thought that the isomer effect would quickly disappear as the collision energy increases above a few tens of eV regime because of a shorter interaction time, and hence, has entirely been ignored in experimental studies in the past.

We have observed, for the first time, rather prominent isomer effects in charge-transfer processes in collisions of C^+ ions with allene and propyne even at the collision energy as high as a few hundred eV. The present charge transfer cross sections for allene are found to be systematically larger than those for propyne in the entire energy range studied up to 4.5 keV. In order to understand the details, we have carried out the theoretical analysis based on the DV-Xα method [6] for molecular structures and a semiclassical molecular-orbital close coupling approach [7] for scattering dynamics. It would be important to investigate for understanding the degree of the effect on charge transfer depending upon the molecular structure as well as electronic structure of the isomers, which, in turn, provides the general guideline of a systematic understanding of the dependence of scattering dynamics to the molecular structure.

We summarize some molecular properties of these isomers in Table I [8].

The specific processes we have studied are collisions of the ground state $C^+(^2P)$ ion with the allene and propyne (C_3H_4) molecules:

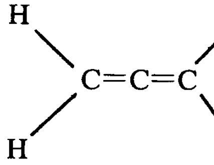
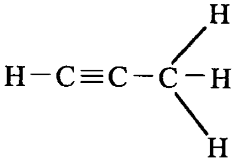
$$C^+(^2P) + C_3H_4(v_i = 0) \rightarrow C(^3P) + C_3H_4{}^+(v_f) + 0.90 \text{ eV for propyne,} \quad (1)$$

$$C^+(^2P) + C_3H_4(v_i = 0) \rightarrow C(^3P) + C_3H_4{}^+(v_f) + 1.57 \text{ eV for allene,} \quad (2)$$

where v_i and v_f describe the initial and final vibrational quantum numbers, respectively, of a target molecule.

In the present experiments, a carbon ion beam produced from CO molecules was extracted from a conventional electron impact ion source where the electron accelerating voltage could be varied up to 50 V. The incident C^+ ion beam was mass analyzed with a Wien filter and introduced

TABLE I. Molecular properties of C_3H_4 (allene and propyne) molecules [8].

Allene		**Propyne**	
Molecular structure			
 D_{2d} symmetry		 C_{3v} symmetry	
Bond length (Å) and angle			
C-H	1.071	C^3-H	1.112
		C^1-H	1.060
C-C	1.335	C^3-C^2	1.458
		C^2-C^1	1.207
∠HCH	113° ± 1	∠HC^3H	108.4°
Dipole moment (Debye)			
0.2D		0.77D	
Ionization potential (eV)			
9.69 ± 0.01		10.36 ± 0.01	

into a 40-mm-long collision cell with a 0.5-mm diameter entrance and a 3.5-mm diameter exit aperture. The target gases of high purity (allene 97%; propyne: 98%) were introduced into the cell and the gas pressure was measured with a sensitive Pirani gauge [9] which was calibrated with a MKS-Baratron capacitance manometer. The front and main chambers were evacuated down to the base pressure less than about 6×10^{-6} Pa by a 500 l/s turbomolecular pump and a 6 in. cryo pump. The ions emerging from the cell after collisions were charge separated with a pair of the electrostatic parallel plates and sent into a position-sensitive detector consisting of a microchannel plate and a resistance anode (MCP-PSD). The output signals from both ends of its anode were converted to the position information in an analog divider [10] and recorded on a pulse height analyzer as the charge distribution of ions after collisions. Relative detection efficiencies of MCP-PSD were assumed to be the same for both the singly charged ions and neutral particles as the front end of the MCP was grounded. After subtracting dark current noises of the MCP-PSD, the fractions of singly charged ions and of neutrals, F_1 and F_0, were determined as a function of the target gas thickness. The charge transfer cross sections were derived based upon the growth rate method by fitting the observed fractions F_0 to a quadratic function of the target gas thickness.

The statistical uncertainties of the cross sections are 0.2%–3.2% for the present work. Systematic uncertainties due to those of the target thickness, the temperature of target gases, and so forth is estimated to be from 11.3% at high energies to 14.2% at low energies. Total experimental uncertainties of the absolute cross sections are given as the quadratic sum of these uncertainties involved.

The purely ground-state $C^+(^2P)$ ions were carefully prepared from CO molecules by electron impact. The threshold electron energies for producing the ground-state $C^+(^2P)$ ions and the metastable-state $C^{+*}(^4P)$ ions from the ground-state CO molecules are known to be 22.4 and 27.7 eV, respectively. Based on the previous study [11] that carefully avoided the appearance of metastable ions, the effective energy of the ionizing electrons in the ion source was set to be 25.3 eV during measurements, and the present cross sections should be regarded totally due to the ground-state $C^+(^2P)$ ions.

Molecular-state calculations are performed using the DV-Xα method [6] within a fixed-nuclei approximation of the target molecule, in which intranuclear coordinates of the target molecule are frozen at the equilibrium distance during the collision with values as shown in Table I. The orientation of the incident ion with respect to the C_3H_4 molecular axis considered is three different molecular configurations. Three molecular states are included in dynamical calculations. This DV-Xα approach is simple and efficient and is known to be very useful to apply for larger molecular and cluster systems, but it is less accurate compared to more rigorous *ab initio* approaches.

Adiabatic potential for the initial channel of $[C^+ + C_3H_4]$ lies energetically higher by 0.90 eV for propyne and 1.57 eV for allene than those for charge transfer channel of the ground $[C(^3P) + C_3H_4{}^+]$ state, and therefore, these reactions are exothermic. In between these two channels, there should be several target-excited ionic states for propyne and both projectile-excited and target-excited ionic states for allene. Adiabatic potential curves for the initial and first charge transfer channels in the present two systems are found to be rather smooth without strong avoided crossings because a polarization potential dominates. There are, however, some strong avoided crossings among the excited states at small internuclear distances below 3–4 a.u. Because of the weak coupling feature among low-lying states, the dynamical coupling scheme is due to a typical Demkov-type mechanism. In Fig. 1, a schematic asymptotic energy diagram is shown. Dashed lines represent vibrational levels of the initial molecules while short solid lines represent those of the final molecular ions.

The present experimental charge transfer cross sections are displayed in Fig. 2 for allene and propyne from 0.2 to 4.5 keV along with the present theoretical results. Charge transfer cross sections for allene are consistently larger than those of propyne in the entire energy studied. The difference between these two sets of the cross sections becomes more pronounced in the collision energy below 0.5 keV, and it is 32.5% and 21.7% at 0.2 keV and 0.3 keV, respectively. These numbers are much larger than the present total absolute experimental uncertainty of 14.6%. Therefore, the difference in two sets of the cross section in the isomers is considered to be real, at least at two lowest energy points. The present theoretical cross sections for both of the two isomers are found to be much larger than those of the corresponding experiment over the entire

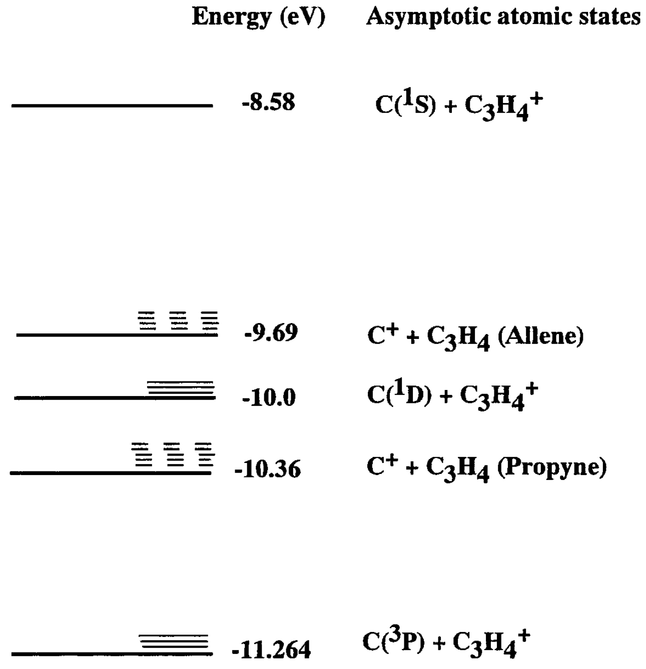


FIG. 1. Schematic asymptotic energy diagram of $C^+ + C_3H_4$ (allene and propyne) collisions. Short solid lines represent vibrational levels for the final molecular ions, while short dashed lines are those for the initial molecules.

energy range studied. The magnitude of the theoretical results is not quite as good as the energy dependence because the present molecular states used are less accurate.

Figure 3 illustrates the ratio of the charge transfer cross section for allene and propyne. Note that in this figure, the relative uncertainty for the ratio of the two experimental results is less than 12.8%. Agreement between the present experiment and theory is found to be excellent in the entire energy range studied, although the present theoretical ratio shows a slower increase than the experimental one as the collision energy decreases. It is quite apparent that the present theoretical model may become poorer as the energy decreases since the calculation becomes more sensitive to details of potentials and couplings.

The asymptotic energy defect between the initial and charge transfer channels of the ground state [see Eqs. (1) and (2)] suggests that charge transfer from propyne is favorable over allene. Furthermore, the length of the molecules is roughly 3.85 Å for allene and 4.84 Å for propyne, respectively, although their widths are comparable in size (1.79 Å vs 1.80 Å). Therefore, from the consideration of the molecular size, it is naturally conceivable to consider that charge transfer propyne is likely to be larger than that from allene.

The experimental results as well as theoretical ones, however, show the contrary. Close inspection of the entire adiabatic potential curves obtained reveals (as shown in Fig. 1) that the projectile-excited $[C(^1D) + C_3H_4^+]$ state for allene lies merely 0.31 eV below the initial state causing this process to be weakly exothermic, while that state is above the initial state for propyne by 0.36 eV making this reaction weakly endothermic. Another projectile-excited $[C(^1S) + C_3H_4^+]$ state lies above both initial channels by 1.11 eV for allene and 1.78 eV for propyne, respectively, and the stronger endothermicity is expected to make this channel less favorable for both isomers. The present calculation also suggests that the $[C(^1D) + C_3H_4^+]$ channel is dominant for charge transfer below a few keV for both collisions. As the collision energy increases, then the ground $[C(^3P) + C_3H_4^+]$ state begins to play an important role for both collision systems. Another important factor for the dynamics is the formation of vibrationally excited $C_3H_4^+$ molecular ions for allene. This situation further reduces the endothermicity for allene making the reaction near resonant, while, contrarily, this effect increases the exothermicity of the reaction for propyne making the process far less favorable. Indeed, our test calculation mimicking the temperature effect of the molecules by changing the

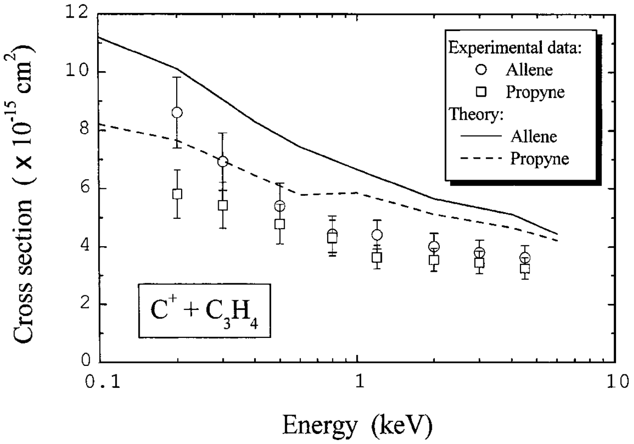


FIG. 2. Charge transfer cross sections for $C^+ + C_3H_4$ (allene and propyne) collisions. ○, the present data for allene; □, the present data for propyne. The experimental error bars denote the absolute total uncertainty. Theoretical results for allene and propyne are included in solid and dotted lines, respectively.

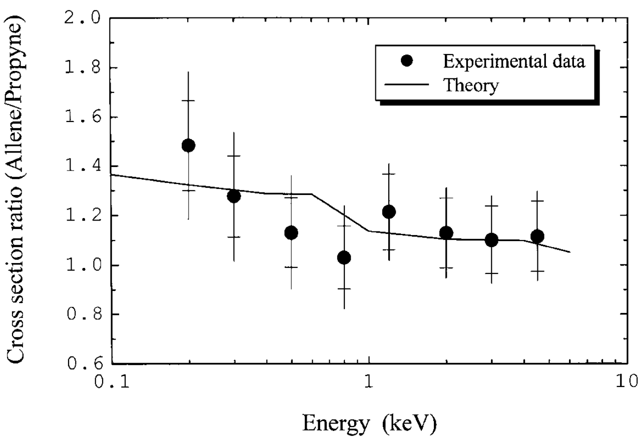


FIG. 3. The present experimental and theoretical ratios of charge transfer cross sections for allene and propyne are shown as a function of the collision energy. Horizontal lines in each experimental error bar indicate the relative total uncertainties, while vertical lines indicate absolute total uncertainties.

potential defect from 0.1 to 0.5 eV artificially has shown the drastic increase of the cross section for allene, while it has caused the significant decrease for propyne. The theoretical result including the vibrationally excited state up to $v_f = 5$ for the product molecular ion shows much better agreement with the measurement in the energy dependence. This trend has been pointed out for the first time by the present authors earlier [12,13]. Charge transfer to the ground $[\mathrm{C}(^3\mathrm{P}) + \mathrm{C_3H_4}^+]$ channel constitutes approximately 15% for allene and 25% for propyne of the total charge transfer at 1 keV. Its contribution, however, rapidly increases for propyne as the collision energy decreases, becoming about 60% at 0.1 keV, while its contribution for allene stays nearly a constant within the energy range studied. Hence, these isomers may be used for selective product formations. From the different point of view, if the initial molecules are in vibrationally excited states, then the energy defect between the initial channel and final $[\mathrm{C}(^1\mathrm{D}) + \mathrm{C_3H_4}^+]$ channel for allene increases, while that for propyne decreases. This feature may help weaken the isomer effect, or for a certain case, the isomer effect may entirely disappear.

In summary, we have observed the conspicuous isomer effect for charge transfer in collisions of the ground-state C^+ ions with allene and propyne (chemical notation: $\mathrm{C_3H_4}$) even at intermediate collision energy. The isomer effect for charge transfer stems from the small exothermicity for allene between the initial $[\mathrm{C}^+(^2\mathrm{P}) + \mathrm{C_3H_4}]$ channel and the dominant charge-transfer $[\mathrm{C}(^1\mathrm{D}) + \mathrm{C_3H_4}^+]$ channel, and small endothermicity for propyne between the same two channels. Although there is an obvious difference in the molecular size between two isomers, in addition to the smaller energy defect between the initial and the ground charge-transfer channels for propyne making the scattering dynamics more favorable, these factors are found to be secondary in the present processes and do not appear to control the dynamics at the intermediate energy. We have pointed out the importance of final vibrational states of molecular ions after charge transfer. For allene, if the molecular ion is in the vibrationally excited state, then charge transfer is more favorable, while for propyne, this situation reverses due to the increasing exothermicity. We have found the difference in final fragmented products between two isomers that may be used for selective productions of specific atomic and molecular species. In addition, we have speculated that if the initial molecules are in vibrationally excited states (heated molecules are used), then the isomer effect may weaken, or totally disappear because this will make the larger energy defect for allene and the smaller one for propyne. Therefore, it is extremely interesting to carry out a more detailed experimental study on the temperature effect in charge transfer and ionization from a molecular target with different initial and final vibrational states and also to examine exactly in which energy the isomer effect disappears or shows up in general, which should provide much insight for the relationship between the molecular structure and its dynamical consequences.

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