

# Charge-transfer processes in collisions of slow $H^+$ ions with hydrocarbon molecules: $CH_4$ , $C_2H_2$ , $C_2H_6$ , and $C_3H_8$

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Charge-transfer processes in collisions of  $H^+$  ions with  $CH_4$ ,  $C_2H_2$ ,  $C_2H_6$ , and  $C_3H_8$  molecules have been studied based on joint experimental and theoretical approaches in the collision energy from 0.2 to 4.0 keV. In the present experiment, the initial growth rate method was employed for determination of cross sections, while in the present theory, the molecular orbital expansion method was utilized for  $CH_4$  and  $C_2H_2$  molecules. Both experimental and theoretical results indicate that if one assumes vibrationally excited molecular ions ( $CH_4^+$ ,  $C_2H_2^+$ ,  $C_2H_6^+$ , and  $C_3H_8^+$ ) in the exit channel, then charge-transfer processes are sometimes found to become more favorable due to an accidental resonant condition. This is the clear indication of the role of vibrational excited states for charge transfer, and is found to be particularly so as the molecular size increases.

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## I. INTRODUCTION

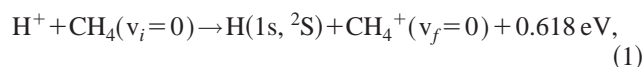
Charge-transfer processes of  $H^+$  ions in collisions with various hydrocarbon molecules at low collision energies become increasingly important in a number of applications such as plasma, material, medical, and astrophysical sciences. In research of the controlled thermonuclear fusion, these collisions 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], because hydrocarbons are now known to be present as impurities and play a crucial role for the energy loss and distribution in the fusion reactor. Also, they are critical in understanding various important features in high-tech applications such as plasma-based material production through ion-beam etching or thin-film techniques. Needless to say, the charge-transfer process also constitutes an important part of carbon chemistry in interstellar chemistry, since the process is thought to be responsible for the formation of carbon-bearing molecules [2].

Although many investigations have been performed on charge transfer of  $H^+$  ions in collisions with various atoms and molecules, reliable cross-section data for molecular targets, particularly for hydrocarbons, are still limited, or nearly nonexistent. Previous cross-section data for a  $CH_4$  target may be found in comparatively many experimental papers

(Chambers [3], Collins and Kebarle [4], Koopman [5], Toburen, Nakai, and Langley [6], Berkner, Pyle, and Stearns [7], McNeal [8], Eliot [9], Varghese [10], Rudd *et al.* [11], Jones *et al.* [12], and Gao *et al.* [13]), but those for  $C_2H_2$ ,  $C_2H_6$ , and  $C_3H_8$  are still scarce and data are merely fragmentary (Toburen, Nakai, and Langley [6], Eliot [9], Varghese [10], and Jones *et al.* [12]).

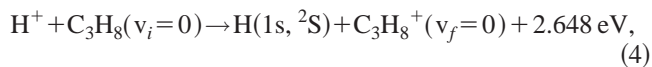
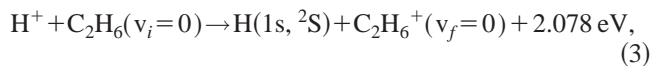
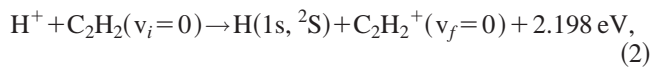
On the other hand, theoretical approaches applicable to slow ion-molecule collisions are also scarce. Kimura and co-workers have developed and applied extensively a molecular-orbital expansion method [14,15]. Recently, they studied charge-transfer processes of  $H^+$  ions in collisions with  $CH_4$  and  $C_2H_2$  together with details of molecular orientation between collision partners [16,17]. In our previous studies for  $H^+$  and  $C^+$  ions in collisions with  $H_2$ ,  $D_2$ ,  $CO$ , and  $CO_2$  molecules, their theoretical calculations for  $H_2$  and  $CO$  targets are found to give good agreement with the measurements [18,19] and hence, the theoretical approach used is considered to be sound for providing a rationale to the experimental analysis.

As a continuation of our joint effort, in our present work we have carried out studies for understanding the collision dynamics for charge transfer of  $H^+$  ions colliding with  $CH_4$ ,  $C_2H_2$ ,  $C_2H_6$ , and  $C_3H_8$  molecules at low kinetic energies. In the present experiment, we determine these charge-transfer cross sections in the energy range of 0.2 to 4.0 keV by applying an initial growth-rate method to the product atomic hydrogen by charge transfer. The specific processes considered, combined with their asymptotic energy differences, are:



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where  $v_i$  and  $v_f$  are the quantum number for the initial and final vibrational states of target molecules, respectively. All of these collision processes are exothermic with appreciable energy difference, although it is relatively weak for the case of  $\text{CH}_4$ . In the present theory, the molecular-orbital expansion method is applied to the  $\text{H}^+ + \text{CH}_4$  and  $\text{C}_2\text{H}_2$  collisions combined with the target molecular orientation. The lowest vibrational excited level for  $\text{CH}_4$ - $\text{C}_3\text{H}_8$  molecules is in the neighborhood of 0.07 eV due to the CH bending mode, and at the room temperature, this vibrational excited species amounts to about 20% of total molecules. Vibrational excited molecules in the initial channel increase the exothermicity, making a large energy difference, i.e., off-resonance condition, and hence, are expected to reduce the charge-transfer cross section. On the other hand, vibrational excited states in the product channel reduce the exothermicity, which may lead to the larger cross section. Hence, charge transfer from/to the vibrational excited state needs to be examined. Calculations using a simple formula presented by Olson [20] are also compared with the experimental data.

## II. METHODS

### A. Experiment

A detailed description of the present experimental apparatus and methods has been previously given [18,19,21] and hence, only essential features are briefly summarized here.

A  $\text{H}^+$  ion beam produced by 30 eV electrons impact on  $\text{H}_2$  gas in an electron-impact ion source was mass analyzed with a Wien filter and sent into a 40-mm long collision cell filled with the target gases of high purity (>99.9%). The target gas pressure was measured with a highly sensitive Pirani gauge [22], which was calibrated with an MKS Baratron capacitance manometer for each gas target. After collisions, both the incident protons and neutral hydrogen atoms formed through the charge transfer were charge-separated with an electrostatic deflector and detected with a microchannel plate position-sensitive detector (MCP-PSD) [23]. The charge-transfer cross sections were derived based upon the growth-rate method. The target gas pressure was adjusted to the region of 0.01–0.2 Pa for  $\text{C}_2\text{H}_2$  and of 0.003 to 0.07 Pa for  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{C}_3\text{H}_8$ , respectively, so that the fraction  $F_0$  of neutral hydrogen atoms may change to 0.2 from 0.01. Although the observed fractions  $F_0$  were almost proportional to the target gas pressure, the effect by the square term of the pressure gradually appears, when the fraction exceeds 0.1. Then, the cross sections were derived by fitting the observed fractions of neutral hydrogen atoms to a quadratic function of the target gas thickness (length of the collision cell  $\times$  density of target gas molecules).

The statistical uncertainties of the cross sections that were determined from the least-squares fitting described above are a few percent for most of the present work. As a factor of systematic uncertainties, the following were considered: the determination of sensitivity coefficient of the Pirani gauge (5–10%); the fluctuation of target gas pressure during the cross-section measurements (5–10%); the determination and fluctuation of the temperature of target gases (3%); the effective length of the collision cell (5%), the target gas impurity (1%), and peak separation on the position (charge) spectrum measured with the MCP-PSD (5–10%). Total systematic uncertainties given as the quadratic sum of these uncertainties involved are estimated to be from 10.6% to 16.2% for determining the absolute cross sections. Since the Pirani gauge [22] used for the present study was unstable for  $\text{C}_2\text{H}_2$  molecules below about 0.03 Pa, the systematic uncertainty due to the measurement of target gas pressure gives larger values for  $\text{C}_2\text{H}_2$  molecules than other target molecules. In general, the peak width on the charge spectrum measured with the MCP-PSD becomes broader as the incident ion energy decreases, so that the systematic uncertainty due to the determination of region of each peak onto the charge spectrum is estimated to be large at low collision energies. Total experimental uncertainties of the absolute cross sections are given as the quadratic sum of statistical and systematic uncertainties.

### B. Theory

For  $\text{CH}_4$  and  $\text{C}_2\text{H}_2$ , the potential curves of the singlet and triplet states are obtained by the multireference single- and double-excitation configuration-interaction (MRD-CI) method [24,25], with configuration selection and energy extrapolation using the Table CI algorithm [26]. In the CI calculations, the two lowest molecular orbitals (MOs) are always kept doubly occupied, whereas the two highest ones are discarded. A small selection threshold [27] of  $0.32 \times 10^{-6}$  Hartree has been used for determining eigenvalues in the present treatment. The radial coupling matrix elements are obtained using the calculated MRD-CI wave functions by a finite-difference method [28] with an increment of  $0.0002a_0$ , a sufficiently small step to adequately search a peak value in the coupling. In the present calculation, we have adjusted the value of asymptotic potential energies to take vibrationally excited states both for initial and final states into account. These values are typically in the range of 0.3 eV–0.8 eV.

A fully quantum-mechanical MO expansion method was employed to study the collision dynamics above 30 eV [15]. In this approach, both the relative motion of heavy particles and electronic motions were treated quantum mechanically. The total scattering wave function was expanded in terms of products of a molecular electronic state, nuclear wave function and atomic-type electron translation factors (ETFs), in which the inclusion of the ETF satisfies the correct scattering boundary condition. Substituting the total wave function into the time-independent Schrödinger equation and retaining the

TABLE I. The observed charge-transfer cross sections (in units of  $10^{-16}$  cm<sup>2</sup>/molecule) for H<sup>+</sup> ions in collisions with CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub> molecules.

Energy (keV)	Target molecules			
	CH <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>8</sub>
0.20	30.3±4.3	9.7±1.6	39.1±6.4	48.6±6.7
0.30	25.0±3.5			
0.45	23.4±3.3	11.0±1.7	35.2±5.8	37.2±5.1
1.00	21.9±2.3	14.7±2.1	28.6±4.0	36.7±3.9
2.00	20.0±2.1	15.1±2.1	25.8±3.6	33.7±3.6
4.00	15.8±1.7	15.2±2.1	23.6±3.3	28.9±3.1

ETF correction up to the first order in the relative velocity between the collision partners, we obtain a set of second-order coupled equations. Nonadiabatic couplings drive transitions between molecular states. By solving the coupled equations numerically, we obtain scattering  $S$ -matrix elements for transitions, and the standard procedure gives the transition probability, and the cross section.

States included for the dynamical calculations are the initial, charge-transfer, and target electronic-excitation channels for these two molecular targets. Vibrational excitation levels in the final product are considered by adjusting the ionization potential of molecular ions.

### III. RESULTS AND DISCUSSION

The present data for the cross sections of charge transfer of H<sup>+</sup> ions from CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>6</sub> molecules are given in Table I, and are illustrated graphically in Figs. 1–4. Below, we discuss each molecule separately, and provide general features for all molecules later.

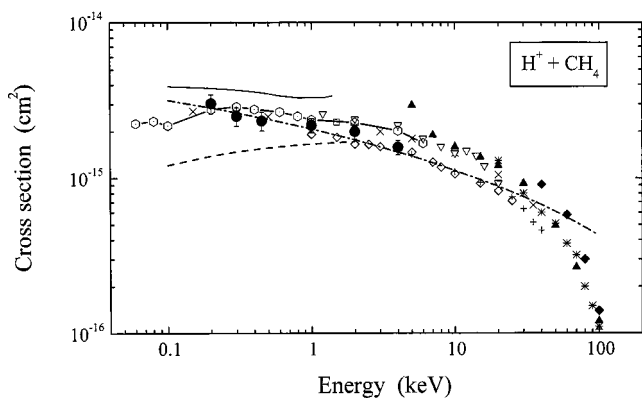


FIG. 1. Charge-transfer cross sections for H<sup>+</sup> ions in collisions with CH<sub>4</sub> molecules. ●, Present data; +, Chambers [3]; —, Koopman [5]; ◆, Collins and Kebarle [4]; ×, Berkner, Pyle, and Stearns [7]; ◇, McNeal [8]; ▽, Eliot [9]; ▲, Rudd *et al.* [11]; \*, Jones *et al.* [12]; □, Gao *et al.* [13]. The hexagonal symbols with solid lines are the present calculations based upon the molecular expansion method. The dotted chain and dashed curves correspond to the calculations by the Olson formula [20] for with and without the vibrational excitation of the product molecular ion, respectively.

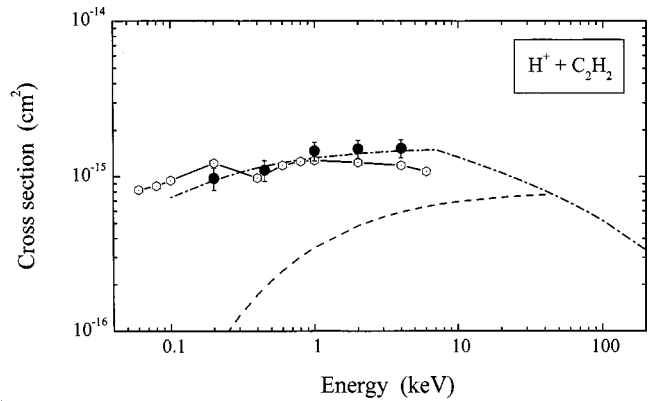


FIG. 2. Charge-transfer cross sections for H<sup>+</sup> ions in collisions with C<sub>2</sub>H<sub>2</sub> molecules. ●, Present data. The hexagonal symbols with solid lines are the present calculations based upon the molecular expansion method. The dotted chain and dashed curve correspond to the calculations by the Olson formula [20] for with and without the vibrational excitation of the product molecular ion, respectively.

#### A. CH<sub>4</sub>

The cross sections for CH<sub>4</sub> molecules are as shown in Fig. 1 together with those previously published [3–5,7–9,11–13]. Though there are small deviations among measured data, the general feature of these experimental data seems to be in reasonable accord. As the collision energy increases, the charge-transfer cross sections decrease monotonically in which the present data are in harmony with others. It is noted that Berkner, Pyle, and Stearns [7] used deuterons instead of protons, and their data are plotted at the equivalent proton energy. A set of the data by Berkner, Pyle, and Stearns [7], Eliot [9], and Gao *et al.* [13] gives slightly larger cross sections, while that of McNeal [8] and Chambers [3] gives somewhat smaller values, and in fact the present results lie in between these two sets of the data. The data of Koopman [5] are found to be too large in comparison to the present data and others. The energy difference of H<sup>+</sup>+CH<sub>4</sub> collisions is 0.618 eV, which is the smallest among all systems studied. The present theoretical results were obtained by carrying out

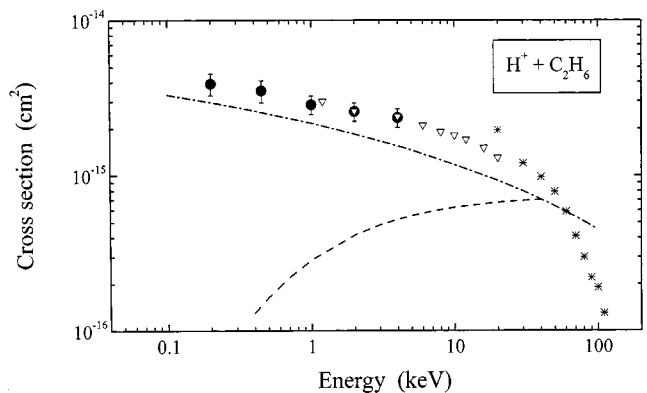


FIG. 3. Charge-transfer cross sections for H<sup>+</sup> ions in collisions with C<sub>2</sub>H<sub>6</sub> molecules. ●, Present data; ▽, Eliot [9]; \*, Jones *et al.* [12]. The dotted chain and dashed curve correspond to the calculations by the Olson formula [20] for with and without the vibrational excitation of the product molecular ion, respectively.

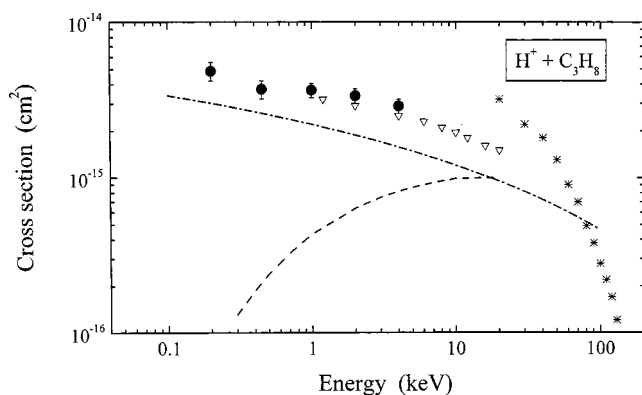


FIG. 4. Charge-transfer cross sections for  $H^+$  ions in collisions with  $C_3H_8$  molecules. ●, Present data; ▽, Eliot [9]; \*, Jones *et al.* [12]. The dotted chain and dashed curve correspond to the calculations by the Olson formula [20] for with and without the vibrational excitation of the product molecular ion, respectively.

the new calculation with inclusion of vibrational excited states in the product molecular ions into the previous approach [16] (i.e., charge transfer+vibrational excited final molecular ions). In the present treatment, the energy difference was adjusted in order to simulate vibrational excited states of the target molecular ion up to 0.3 eV (half of the original exothermicity) in the exit channel. The present results show good agreement with most of the experimental data except for the low-energy region. The results have a broad peak around at 0.3 keV, and on both sides of this energy they gradually decrease. Note that the present result, which includes the vibrational excitation in the product molecular ion, is found to be larger by 30% than the previous one, and shows a slightly different energy dependence. The results based on the Olson formula, under the assumption that the target molecule results in the vibrationally ground state after charge transfer, are consistently smaller than all measurements and increase gradually as the collision energy increases up to about 2 keV. If vibrational excited states in the product molecular ions are taken into account, then this extra internal energy makes the energy defect smaller, and helps enforce an accidental resonant condition. Hence, a smaller energy defect may help bring the magnitude of the cross section closer to the experimental value. It should be noted that although this Olson formula, based on the Demkov theory for atomic targets, is sometimes helpful in providing the general trend of cross sections for various collision systems without large-scale calculations, it may not always offer accurate results for molecular targets.

### B. $C_2H_2$

Figure 2 shows the present cross sections for charge transfer of  $H^+$  ions from  $C_2H_2$  molecules. To the best of our knowledge, the cross sections for this molecule have not been reported so far except for one attempt by Varghese [10] in a much higher energy region (0.8–3 MeV). The present cross sections increase slowly as the incident energy increases and levels off at around 3–4 keV.

### C. $C_2H_6$ and $C_3H_8$

In the previous theoretical study, Kimura *et al.* [17] had calculated the charge-transfer processes in  $H^+ + C_2H_2$  collisions for two molecular configurations, i.e.,  $C_{2v}$  and  $C_{\infty v}$  symmetries, assuming that the vibrationally ground state of the product molecular ion is formed, and had found that the cross sections show rapid increase as the collision energy increases. We have carried out the new additional calculation by taking the energy difference for the vibrationally excited final states ( $v_i = 1-8$ ) of the product molecular ion into account. This change of vibrational states of the product makes the exothermicity smaller to between 2.13 and 1.2 eV. The effect of vibrationally excited states in the product is found to be more significant for the  $[H^+ + C_2H_2]$  process than the  $[H^+ + CH_4]$  system. The new theoretical results, summed over all vibrationally excited final products, are now closer to the present measurement. The vibrational excited state of the target molecular ions of this system is more favorable energetically for the resonant conditions, hence extremely increasing the cross sections.

So far, we have been concerned with the vibrationally excited state in the product. Although it will give a reducing effect for charge transfer when the vibrationally excited molecule is used in the initial channel, it is interesting to examine the degree of the effect. As a test, we have performed the calculation for charge transfer from the molecular target in a vibrationally excited state ( $v_i = 1-3$ ). As described above, it apparently increases the exothermicity of the energy defect, and hence, the calculation thus obtained proves it to reduce the effectiveness of charge transfer in the entire energy. The effect is found to be particularly conspicuous below 1 keV and as the  $v_i$  value increases from 1 to 3, the cross section becomes smaller by a factor of two and decreases at a much faster rate with the decreasing energy.

As another check on the present experimental results, the Olson formula was employed to calculate the cross sections for the vibrational ground state as well as the excited states of the product molecular ions. Similar to the MO results discussed above, the cross sections for the vibrational ground-state product significantly underestimate the magnitude. Contrary, if the vibrationally excited states are taken into account up to  $v_i = 5$  for the product molecular ion, then the results are found to show good agreement with the present experimental result.

Under the normal experimental condition, a room temperature is used, in which some molecules and their ions are known to be in a low vibrational excited state while their rotational states are highly excited. As seen, a vibrational excited state either in the initial molecule, or the product molecular ion, or in both, is extremely important for correctly assessing dynamics for the charge-transfer process in molecular targets, and hence it is essential for examining this effect more closely and carefully. A systematic study of this effect, the temperature effect, for a variety of molecules would be desirable for the better understanding of charge transfer.

Figures 3 and 4 show the present cross sections for charge transfer in  $H^+ + C_2H_6$  and  $H^+ + C_3H_8$  collisions, respectively,

together with those previously published by Eliot [9] and Jones *et al.* [12]. The present cross sections for both target molecules decrease almost monotonically as the collision energy increases, a feature similar to the CH<sub>4</sub> target. The observed collision energy dependence of the cross sections suggest that the accidental quasisonant charge transfer reaction channels involving the vibrational excitation of the product target molecular ions play a dominant role. Indeed the cross sections calculated by using the Olson formula for the vibrational ground-to-ground state charge transfer process are found to be too small, compared with the experimental results, while by including the vibrationally excited state of the product molecular ions, the situation has been drastically improved as similarly seen in the C<sub>2</sub>H<sub>2</sub>. Although the asymptotic energy differences for C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> are close to that of C<sub>2</sub>H<sub>2</sub>, the energy dependence of the charge transfer cross section for C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> is different from that for C<sub>2</sub>H<sub>2</sub> as seen in Figs. 2–4. This characteristic seems to arise from the difference between the vibrational energy involved.

#### IV. CONCLUDING REMARKS

The observed cross sections of the charge-transfer processes show the gradual increase as the collision energy decreases for all the present collision systems of H<sup>+</sup>+CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> investigated, except for C<sub>2</sub>H<sub>2</sub>, in the collision-energy range between 0.2 and 20 keV. This feature can be understood as arisen from charge transfer plus vibrationally excited product molecular ions, and in fact is confirmed by theoretical calculations based on the MO method by taking a number of the vibrationally excited states of

product molecular ions into account. In this way, vibrationally excited product states enforce the “accidental” resonance condition in the charge-transfer processes. Even in C<sub>2</sub>H<sub>2</sub> targets where the cross sections increase only slightly as the collision energy increases, it is expected that vibrational excited states of product C<sub>2</sub>H<sub>2</sub><sup>+</sup> ions also play a crucial role in charge transfer. It should also be noted that the observed cross sections at the present collision energy tend to become large as the ionization energy of target molecules become small, and there seems to be an apparent systematic relationship with the number of electrons or atoms in the target molecules. We will discuss details of this point elsewhere [29]. It has been also well known that dissociative electron attachment (DEA) is very sensitive to the initial molecular vibrational state [30]. For example, for e+HCl collisions, the DEA cross section increases three orders of magnitude when the vibrational state increases from v<sub>i</sub>=0 to 3 of the HCl molecule. Therefore it is extremely important and necessary to understand the temperature effect of target molecules and product molecular ions for charge transfer more carefully and systematically for a variety of molecules.

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