

Charge-transfer processes in collisions of H^+ ions with H_2 , D_2 , CO , and CO_2 molecules in the energy range 0.2–4.0 keV

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Charge-transfer processes resulting from collisions of H^+ ions with H_2 , D_2 , CO , and CO_2 molecules have been experimentally investigated in the energy range of 0.2–4.0 keV by using the initial growth-rate method. Theoretical analysis based on a molecular-orbital expansion method for H_2 and CO targets was also carried out. The observed cross sections are compared with previous experimental and theoretical data. The present results for H_2 are found to be in excellent accord with the recommended data by Barnett [Oak Ridge National Laboratory Report No. ORNL-6086 (1990)], and hence, confirm the accuracy of the recommended data. But, at 0.2 keV, the present data for D_2 are found to be smaller than those for H_2 . For the CO molecule, the present data qualitatively agree well with most previous measurements, but show the stronger energy dependence, while the present theory shows a pronounced structure at around 0.25 keV and ties well with other low-energy measurements below 0.1 keV. For the CO_2 molecule, the present results are in excellent accord with other measurements above 1 keV, while they show some differences below this energy where our experimental result displays the stronger energy dependence. These data are useful for various applications.

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I. INTRODUCTION

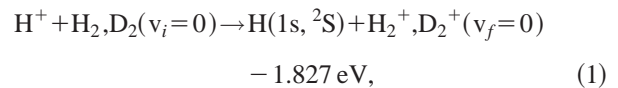
Since a proton (H^+ ion) is one of the most fundamental and important charged particles in the universe, the knowledge of its interaction with various types of matter constitutes the essential part of basic atomic and condensed-matter physics. Among many interactions and dynamical processes, the charge-transfer processes of H^+ ions in collisions with H_2 and various carbon-containing molecules at low collision energies become more and more important in a number of applications such as plasma, material, medical, and astrophysical sciences. In the 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, collisions of H^+ ions with hydrogen and various carbon-containing molecules are critical in understanding features in plasma-based material production. In medical sciences, proton and other heavy-ion beams have been successfully employed for the treatment of deep-seated malignancy [2]. For the astrophysical environment, needless to say, the cosmic ray and solar wind contain a sizable amount of protons, which are involved in various types of

charge-transfer processes, thus initiating a variety of a chain of chemical reactions [3].

Although many investigations have been performed on charge transfer of H^+ ions in collisions with various gas atoms and molecules, cross section data are still fragmentary and are not consistent with each other. This is particularly so for carbon-containing molecules, and more systematic determination of charge-transfer cross sections is needed for further better assessment of available data [4,5].

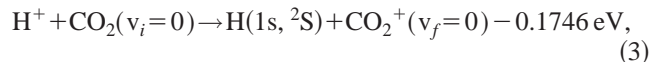
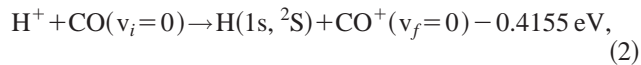
On the other hand, theoretical approaches applicable to slow ion-molecule collisions are also scarce because of the difficulty for treating the intrinsic multicenter nature of molecules accurately. Kimura has calculated the charge-transfer cross sections of H^+ ions colliding with an H_2 molecule earlier based on a molecular-orbital expansion method [6,7] and has applied it to other collision systems [8,9]. In our previous studies for C^+ ions in collisions with various molecules, the theoretical calculations are found to be reasonably in good agreement with the measurement and provide much insight of scattering dynamics [10].

In the present experiment, we determine charge-transfer cross sections of H^+ ions colliding with the H_2 , D_2 , CO , and CO_2 molecules in the energy range of 0.2–4.0 keV by applying an initial growth-rate method to the product atomic hydrogen by charge transfer. The specific processes we are concerned with are, with their asymptotic energy defects:



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where v_i and v_f are the quantum number for the initial and final vibrational states, respectively. These collision processes are endothermic with appreciable energy defect, and hence cross sections are expected to be rather sensitive to the incident energy.

We have also carried out a theoretical analysis for understanding collision dynamics for charge transfer of H^+ ions colliding with H_2 , and CO molecules at low kinetic energies below a few keV by using the molecular-orbital expansion method. Olson has derived a simple formula for evaluating and assessing charge-transfer cross sections by singly charged ions in collisions with an atomic target based on the Demkov-type approximation [11]. This is widely employed successfully to guide experimental studies. In order to assess the applicability of this useful formula to molecular targets, we have also applied this approach. The present cross sections are compared with the previous experimental and theoretical results, and we discuss the origin of discrepancies and propose the best-suggested values of cross sections.

II. EXPERIMENTAL SETUP

A detailed description of the present experimental apparatus and methods has been previously given [10,12,13] and so some essential features will be briefly mentioned here.

A proton beam produced by 30 eV electron impact from H_2 molecules into an electron-impact ion source was mass analyzed with a Wien filter and introduced into a 40-mm long collision cell with 0.5-mm diameter entrance and a 3.5-mm diameter exit apertures. The target gases of high purity (>99.95%) were fed into the cell and the gas pressure was measured with a sensitive Pirani gauge [14] that was calibrated with an 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" cryopump. The ions emerging from the cell after collisions were charge-separated with the electrostatic parallel plates and sent into a position-sensitive detector consisting of a microchannel plate and a resistive anode (MCP-PSD). The output signals from both ends of its anode were converted to the position information in an analog divider [15,16] and recorded on a pulse height analyzer as the charge distribution of ions after collisions. Peak areas corresponding to the singly charged primary ions and product energetic neutral particles were integrated. It may be safe that relative detection efficiencies of the MCP-PSD were 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 electron capture 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 a few percent for most of the present work. Systematic uncertainties due to the determination of the target thickness, the temperature of target gases and so forth are estimated to be from 10.6 to 19.7% for determining the absolute cross sections. 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 these uncertainties involved.

III. THEORETICAL MODEL

Molecular states: Two sets of calculations for molecular electronic states were carried out. However, details of each approach have been described earlier and only a summary of each approach should suffice for the inclusion in this paper [6,8]. (i) For H_2 , the adiabatic potential energies for H_3^+ are obtained by a configuration interaction method modified by an inclusion of a pseudopotential to treat H_2 ($1s^2: X^1\Sigma_g$) as an elongated atom, thus replacing a two-electron system by an explicit one-electron problem [17]. This approach has been proven to be reasonable for an intermediate-to-high energy region [18]. The pseudopotential used is of Gaussian type. Slater-type orbitals are employed as basis functions and linear combinations of Slater determinants are used for constructing molecular wave functions. The present asymptotic energies of the adiabatic potentials are better than 0.2% compared with those of experiment [19]. The nonadiabatic coupling matrix elements are evaluated numerically by using the wave functions obtained above. (ii) For CO , the potential curves of the singlet states are obtained by the multireference single- and double-excitation (MRD-CI) configuration interaction method [20,21], with configuration selection and energy extrapolation using the Table CI algorithm [22]. 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 [23] of 0.32×10^{-6} Hartree has been used in the present treatment. The radial coupling matrix elements are obtained using calculated MRD-CI wave functions by a finite-difference method [24] with an increment of $0.0002a_0$.

Scattering dynamics: A semiclassical MO expansion method with a straight-line trajectory of the incident ion was employed to study the collision dynamics above 30 eV/u [7]. In this approach, the relative motion of heavy particles is treated classically, while the electronic motion is treated quantum mechanically. The total scattering wave function was expanded in terms of products of molecular electronic state 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-dependent Schrödinger equation and retaining the ETF correction up to the first order in the relative velocity between the collision partners, we obtain a set of first-order coupled equations in time t . Nonadiabatic couplings drive

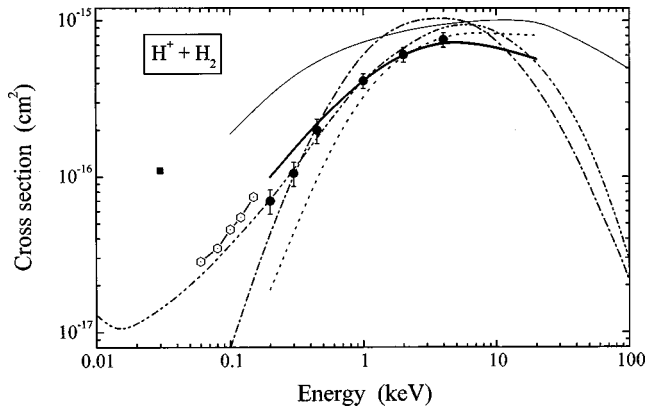


FIG. 1. Charge-transfer cross sections for H^+ ions in collisions with H_2 molecules. Experiment; \bullet , Present data; \circ , the recommended value of Barnett [4]. Theory; hexagon with dot, the present calculation based on the MO method; --- , Kimura [6]; --- , Olson formula [11]; \blacksquare , Baer *et al.* [26]; --- , Kuang [27]; --- , Grozdanov, Janev, and Krstić [28].

transitions between molecular states. By solving the coupled equations numerically, we obtain the scattering amplitudes for transitions: the square of the amplitude gives the transition probability, and integration of the probability over the impact parameter gives the cross section.

States included for the dynamical calculation are: (i) for the H_3^+ , the molecular states included in the dynamical calculations are: $[H^+ + H_2(X^1\Sigma_g^-)]$ for the initial channel, and $[H(1s) + H_2^+(1s\sigma_g)]$ and $[H(1s) + H_2^+(2s\pi_u)]$ for charge-transfer channels, and (ii) for the HCO^+ , the initial channel $[H^+ + CO(X^1\Sigma^+)]$, charge-transfer channel $[H + CO^+(X^2\Sigma^+)]$, and charge-transfer and excitation channel $[H + CO^{+*}(^2\Pi)]$. Vibrational levels for final products are considered for both systems by adjusting the ionization potential for each product.

IV. RESULTS AND DISCUSSIONS

A. Cross sections for H_2 and D_2 targets

The cross sections for H_2 molecules are shown in Fig. 1, together with other measurements and theoretical predictions, and numerical data are given in Table I. As a number of measurements for this target had been reported over a

TABLE I. Charge-transfer cross sections (in units of 10^{-16} $\text{cm}^2/\text{molecule}$) for H^+ ions in collisions with H_2 and D_2 molecules.

Energy (keV)	Target molecules	
	H_2	D_2
0.20	0.699 ± 0.125	0.417 ± 0.083
0.30	1.05 ± 0.19	
0.45	1.99 ± 0.36	1.43 ± 0.29
1.0	4.14 ± 0.44	4.02 ± 0.55
2.0	6.07 ± 0.64	6.57 ± 0.90
4.0	7.56 ± 0.80	8.37 ± 1.15

wide range of the collision energy over the decades, only the data recommended by Barnett [4] are shown (the double-dotted line in Fig. 1). In this collision system with the relatively large endothermicity, the charge-transfer cross sections increase monotonically with the collision energy. The present data are found to be in good agreement with the recommended data of Barnett, except for that at 4 keV, which is slightly smaller. It should be noted that below 0.15 keV, the cross sections could not be accurately evaluated through the present growth-rate method. Indeed, as the target density is increased, not only the peak width of H^+ ions in the charge-distribution spectrum observed with the MCP-PSD became too broad but also the intensities of the primary H^+ ions passing through the collision cell decrease apparently due to their large angle scattering. Then the fraction of product H atoms was found to be not proportional to the target thickness anymore at 0.15 and 0.1 keV. This feature seems to agree with the elastic scattering cross sections in $H^+ + H_2$ collisions that increase as the collision energy decreases [25].

The earlier calculated results of Kimura [6] and the present additional calculation, which extended the previous approach to cover lower energies from 0.15 keV to 60 eV using the MO method, are found to be in excellent agreement with the present data, except for those at the energies below 0.3 keV. As the collision energy decreases below a few hundred eV, the present theoretical model based on the fixed nuclei approximation becomes inappropriate because the vibrational time becomes nearly comparable to the collision time, and hence the model breaks down. Note that the present MO calculation includes vibrationally excited initial and final states in the range of $v_i = 0-3$ and $v_f = 1-10$, although the contribution from $v_f > 5$ in the final state is found to be secondary. The detailed calculation of the cross sections in which vibrationally excited states are resolved was carried out by Baer, Niedner-Schatteburg, and Toennies [26] at only a single energy of 30 eV using the infinite-order sudden approximation. The result thus obtained seems to be too large by nearly an order of magnitude, compared with those recommended values by Barnett. The calculated cross sections based upon the Olson formula [11] are also included in Fig. 1 as a reference. This formula is considered to be useful for some cases in providing the overall general feature of cross sections for molecular targets. For the present $H^+ + H_2$ collisions, however, the results obtained by this formula appear to overestimate the experimental values at least 20% at intermediate energies. Also, both the calculations of Kuang [27] by the modified two-orthogonal state expansion method and the two-state model calculations of Grozdanov, Janev, and Krstić [28] drop rather sharply at lower energy sides, and seemingly fail to reproduce the data in the present energy range. The result of Grozdanov, Janev, and Krstić appears to flatten out at the higher-energy side above 7–8 keV, which is due to a smaller basis size they used. Nevertheless, a simple atomic-orbital expansion method is known to be inappropriate for correctly describing the dynamics for low-energy collisions [7], and hence, their failure is not surprising.

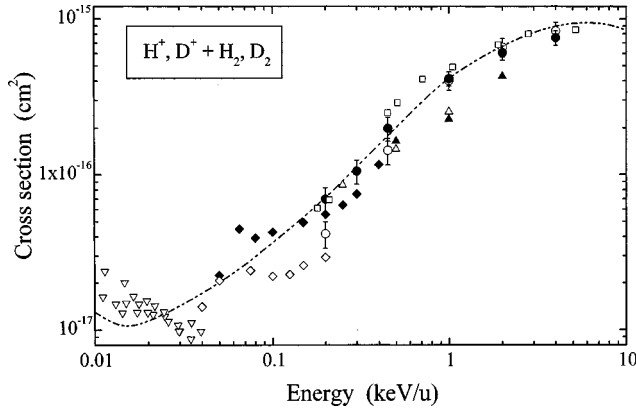


FIG. 2. Comparison of the charge-transfer cross sections for hydrogen ion and molecular isotopes collisions. ●, the present data ($H^+ + H_2$); ○, the present data ($H^+ + D_2$); — · —, the recommended value of Barnett [4]; ◇, Cramer and Marcus ($D^+ + D_2$) [29]; ◆, Cramer ($H^+ + H_2$) [25]; ▲, Abbe and Adloff ($H^+ + H_2$) [30]; △, Abbe and Adloff ($D^+ + H_2$) [30]; □, Berkner *et al.* ($D^+ + H_2$) [31]; ▽, Maier II ($H^+ + D_2$) [32].

In Fig. 2, the present cross sections of the charge transfer of H^+ ions in collisions with hydrogen isotopes H_2 and D_2 molecules are compared with those previously measured for different isotope combinations [25,29–32]. The projectile energy per nucleon in the laboratory frame is used to plot these data for different isotope projectiles. The general trend of the cross-section dependence on the collision energy seems to be similar to that shown in Fig. 1. Since the difference of the binding energy of an electron between H_2 and D_2 is merely 41 meV, there is, within their experimental uncertainties, practically no difference in the present cross sections between $H^+ + H_2$ and $H^+ + D_2$ collisions at energies above 0.45 keV. However, it is very intriguing to point out that the cross sections for $H^+ + D_2$ collisions at 0.2 keV are found to be about 40% smaller than those for $H^+ + H_2$ collisions. This difference due to the isotope effect is outside the uncertainties in the present experiment, and therefore, we regard this difference as real. The similar appearance of the isotope effect even at intermediate energy has been found earlier [33], and this is due to the difference of the vibrational energy between two isotope molecules. The magnitude of the data for $D^+ + D_2$ collisions measured by Cramer and Marcus [29] are about half of those for $H^+ + H_2$ collisions by Cramer [25]. This difference appears to be too large, and is somewhat puzzling since the isotope effect is not expected to be so significant in this collision-energy region, and a careful examination of their experiment is necessary. Except for the present result, other measurements including the differential cross section for charge transfer in $H^+ + H_2$ and D_2 collisions at keV-energy region [34] indicate practically no noticeable difference for charge-transfer cross sections between two isotopes at the present energy. Below a few tens of eV, chemical reactions, such as the particle exchange or rearrangement processes, become dominant and should influence the charge-transfer cross sections [32,35–37]. For these low-eV collisions, Schlier, Nowotny, and Teloy [36] investigated charge-transfer and rearrangement processes based on

TABLE II. Charge-transfer cross sections (in units of $10^{-16} \text{ cm}^2/\text{molecule}$) for H^+ ions in collisions with CO and CO_2 molecules.

Energy (keV)	Target molecules	
	CO	CO_2
0.20	18.9 ± 2.6	21.0 ± 2.9
0.30		18.8 ± 2.6
0.45	15.5 ± 2.1	14.6 ± 2.0
1.0	13.5 ± 1.5	12.8 ± 1.4
2.0	14.3 ± 1.5	12.2 ± 1.3
4.0	13.8 ± 1.5	11.5 ± 1.3

the trajectory surface hopping method as well as based on the experiment for $H^+ + D_2$, $D^+ + H_2$ and $D^+ + D_2$ collisions below 20 eV (the center-of-mass energy). They have found that above a few eV, charge-transfer processes dominate. The charge-transfer results of Abbe and Adloff [30] for $H^+ + H_2$ and $D^+ + H_2$ collisions are nearly the same from 0.25 keV to 2 keV regardless the projectile. Their results for both projectiles, however, begin to diverge from the rest of the data above 1 keV in which their results are smaller by 40% at 2 keV. Maier II [32] measured the charge-transfer cross section for $H^+ + D_2$ collisions below 0.04 keV. As can be seen in Fig. 2, however, his data shows the decreasing trend with the increasing collision energy, and appears not to tie in with any other data at above 0.05 keV. In summary, for some measurements, the cross sections for all $H^+ + H_2$, $H^+ + D_2$, $D^+ + H_2$ and $D^+ + D_2$ collision systems are found to show a sizable difference even at the present intermediate-energy region, which may or may not be real. Therefore, further stricter studies are very important to examine if there is any strong isotope effect in this energy domain, and if any, then how much the isotope effect plays a role in the charge transfer of hydrogen isotope ions at low energies.

B. Cross sections for CO and CO_2 targets

The present cross sections of charge transfer of the H^+ ions in collisions with CO and CO_2 molecules are listed in Table II.

1. CO

The present cross sections of the charge transfer of H^+ ions in collisions with CO molecules are shown in Fig. 3, together with those from earlier publications [31,38–45]. Note that data for D^+ ions by Berkner *et al.* [31] are plotted at the equivalent proton energy. As the collision energy increases, the present charge-transfer cross sections decrease very slowly up to 1 keV and then level off up to 4 keV and finally, are smoothly connected with the data at high energies of Chambers [40], McNeal [42], and Gao *et al.* [45]. There appears to be a shoulder in the cross section around 2 keV, and this shoulder becomes more pronounced for CO_2 as discussed below. The agreement with other experimental data, except for those of Gilbody and Hasted [38], is found to be generally good.

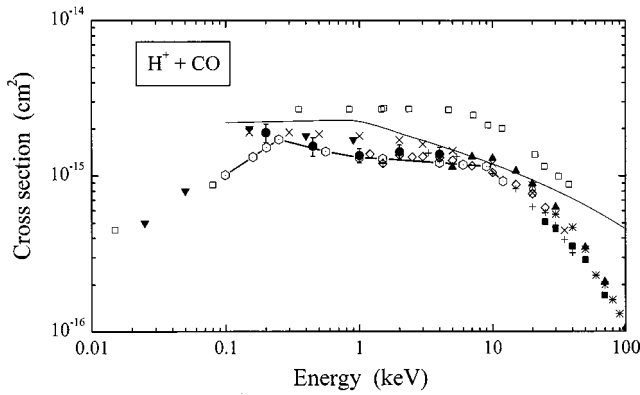


FIG. 3. Charge-transfer cross sections for H^+ ions in collisions with CO molecules. ●, the present data; □, Gilbody and Hasted [38]; ▼, Gustafsson and Lindholm [39]; +, Chambers [40]; ■, Desequelles *et al.* [41]; ×, Berkner *et al.* [31]; ◇, McNeal [42]; ▲, Rudd *et al.* [43]; *, Jones *et al.* [44]; diamond with cross, Gao *et al.* [45]. Theory; hexagon with dot, the present calculations based on the MO method; —, Olson formula [11].

The present calculations for CO molecules based on the MO expansion method, with the vibrational ground-state molecule, show excellent agreement with the present measurement in the entire energy region. If we consider the vibrationally excited molecule of $v_i=1$ in the initial channel, the charge-transfer cross section is found to increase by 20%, thus suggesting the importance of the temperature effect. As the temperature increases above the room temperature, a number of the vibrationally excited molecules is not negligible, and hence their effect should be properly accounted for in the calculation. Below 0.2 keV, the theory indicates the decreasing trend, and they appear to tie up well with those measurements by Gilbody and Hasted [38], and Gustafsson and Lindholm [39] at lower energies. The present theory also suggests a strong molecular orientation (steric) effect for charge transfer. It is important to examine both the steric effect and temperature effect for understanding charge-transfer processes. The calculated values using the Olson formula with the assumption that the target molecules are in the vibrational ground state after collisions ($v_f=0$) are larger in the entire energy region studied, but lie near the present data from 0.2 keV to 10 keV. However, they overestimate the values below 0.3 keV and above 20 keV rather significantly. In addition, this formula does not reproduce the structure seen in the present experiment at around 0.2 keV.

2. CO_2

Figure 4 shows the present cross sections for CO_2 molecules, together with earlier measurements [41–43,45–48]. The present cross sections show some interesting collision-energy dependence: As the collision energy increases, the present cross sections decrease relatively steeply up to 0.45 keV and then the variation becomes much gentler beyond this energy. Finally, the present results are connected smoothly to the data at high energies of McNeal [42], Gao *et al.* [45], and Greenwood, Chutjian, and Smith [48]. On the other hand, the data of Koopman [46] at low energies below

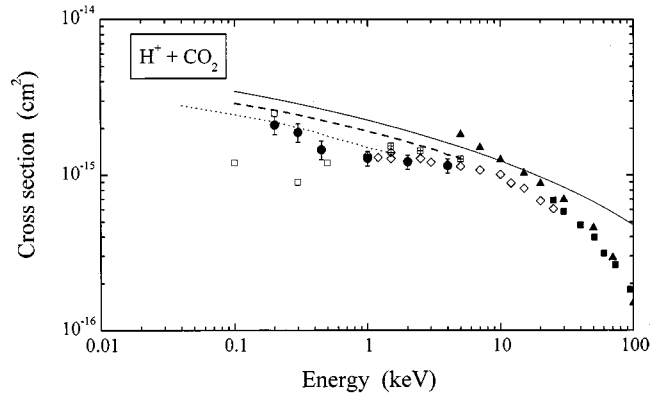


FIG. 4. Charge-transfer cross sections for H^+ ions in collisions with CO_2 molecules. ●, the present data; ■, Desequelles *et al.* [41]; ·····, Koopman [46]; □ Coplan and Ogilvie [47]; ◇, McNeal [42]; ▲, Rudd *et al.* [43]; diamond with cross, Gao *et al.* [45]; ▣, Greenwood *et al.* [48]. Theory; —, Olson formula [11]; ----, Johnson and Parker [49].

2 keV show monotonic dependence on the collision energy. The origin of the shoulder at around 0.3 keV is not clear, but it is highly likely that a few different channels contribute to the charge transfer that show different energy dependence, hence causing some structures when they are summed. Or, another interpretation is that the lowest vibrational excitation for this molecule is the (010) bending mode with the threshold of 0.08 eV. At the room temperature, the (010) vibrationally excited CO_2 molecule constitutes about 16% of the total number that is a non-negligible amount. If the molecule is in a vibrationally excited state, it reduces the energy defect to increase the near-resonant condition, hence making the charge-transfer reaction more favorable. This might cause the increasing trend at lower energies. As seen before, we have found that there is a similar shoulder around 2 keV in the case of the CO molecule. Because of the smallest energy defect among the three molecules studied, this $H^+ + CO_2$ collision system satisfies the near-resonant condition, and hence, the cross section does not show any hint of the decrease even as the collision energy reaches around 0.2 keV. This feature is in strong contrast to other molecular targets in this study. It should, however, eventually do so at much lower energy because of the endothermic reaction. The calculations based upon the Olson formula for the vibrational ground state are larger than the present observed cross sections, but predict a near-resonant feature for this collision system down to 0.1 keV because of the small energy defect as described. Johnson and Parker [49] have dealt with this collision system in more details taking into account the orientation of CO_2 molecules explicitly and their results show a similar amplitude and energy-dependence to those from the Olson formula. Both calculations show simply a monotonic decrease of the cross sections, and fail to reproduce the structure observed in the present experiment.

V. CONCLUDING REMARKS

We have investigated charge-transfer processes from four molecules, H_2 , D_2 , CO, and CO_2 in the energy region from

0.2 keV to 4 keV. We believe that the present measurements are accurate within 10–20% for all systems and in the entire energy region, hence providing benchmark data for use for the normalization of relative data and other applications. We have observed a strong evidence that the temperature (vibrational state) of target molecules significantly affects charge-transfer dynamics and cross sections in $H^+ + CO$, and particularly in $H^+ + C_m H_n$ collisions as we present in a future paper. Therefore, it is extremely interesting and important to study inelastic processes from and to vibrationally excited species to examine the temperature effect more systematically and comprehensively including molecules studied here. In addition, it is interesting to study the steric (molecular-orientation) effect on charge transfer at intermediate collision energy, in which some theoretical studies have suggested that it is in fact very pronounced and hence, can be observable [20]. We plan to initiate these studies in the near future.

Note added in proof. Recently Elizaga *et al.* [50] theoretically predicted the possible significant isotope effect in $H^+ + H_2$ and D_2 , especially at low energies. Their predictions support the present measurement. However, they ignored a

factor of 2 Kimura considered in his original paper [17], and wrongfully compared them.

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