

# Isotope effect in charge-transfer collisions of slow $H^+$ and $D^+$ ions with $H_2$ , HD, and $D_2$ molecules

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Marked characteristics in charge-transfer cross sections between collisions of  $H^+$  and  $D^+$  ions with  $H_2$ , HD, and  $D_2$  molecules, the so-called *isotope effect*, are observed in the energy range from 0.18 to 1.0 keV/u. The observed cross-section ratios  $\sigma(D^+ + D_2)/\sigma(H^+ + H_2)$  of charge transfer in  $D^+ + D_2$  and in  $H^+ + H_2$  collisions are found to be 0.665 at 0.18 keV/u and gradually increases, finally approaching unity at higher energies. Similar behavior and magnitude within the error bars of the cross-section ratios  $\sigma(H^+ + HD)/\sigma(H^+ + H_2)$  and  $\sigma(D^+ + HD)/\sigma(H^+ + H_2)$  have been observed, although the present calculation predicts a sizable difference for heteronuclear molecules. The cross section differences due to the *target isotope effect* are pronounced even in the high-eV to low-keV region. On the other hand, charge-transfer cross-section ratios for the same target but different projectile isotopes, e.g.,  $\sigma(H^+ + HD)/\sigma(D^+ + HD)$  and  $\sigma(D^+ + D_2)/\sigma(H^+ + D_2)$ , are constant near unity, which indicates a minor role of collision-induced vibrations as compared to the target vibrational spacing. It is understood that the isotope effect in the charge transfer of ion-molecule collisions originates from the combination of a small offset in binding and vibrational energies and the different spaces occupied by the wave functions of the target  $H_2$ , HD, and  $D_2$  molecules.

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## I. INTRODUCTION

Among many interactions and dynamical processes, the charge-transfer process of slow  $H^+$  ions in collisions with  $H_2$  molecules is the most fundamental “ion-molecule” collision. Therefore a number of measurements for the  $H^+ + H_2$  collision have been reported over a wide range of the collision energy in recent decades, and recommended cross-section values have been proposed by Barnett [1] and Phelps [2]. At energies between 0.063 and 2.0 keV, the values recommended by Phelps [2] have been determined, based especially on the experimental data by Gealy and Van Zyl [3]. It has long been believed that there is no, or very little, difference in the charge-transfer cross sections between  $H^+ + H_2$  and  $H^+ + D_2$  collisions at collision energies above a few tens of eV, because the difference of the binding (ionization) energy, one of the most critical parameters in charge transfer, of an electron between  $H_2$  and  $D_2$  is merely 41 meV [4] (cf. Table I for the molecular constants), and these collisions with energy above a few tens of eV should show no effect of such a small difference of the binding energy. Only one data set of earlier experimental attempts suggested a possible differ-

ence. In particular, the magnitude of the charge-transfer cross sections for  $D^+ + D_2$  collisions by Cramer and Marcus [5] was found to be about one-half of those for  $H^+ + H_2$  collisions by the same author [6] in the energy range between 0.05 to 0.4 keV/u. But this observation of the difference in different isotope targets has been left unnoticed and not much attention had been paid since then. We have recently reconsidered this problem and indeed clearly observed a significant difference in charge-transfer cross sections for  $H^+$  ions between  $H_2$  and  $D_2$  at energies below 2.0 keV [7,8].

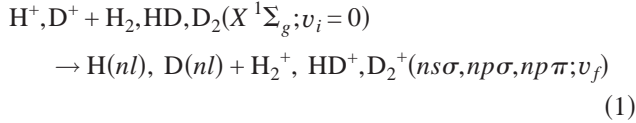
The above charge-transfer processes at low collision energies are known to be important in a number of applications. In particular, in research into the controlled thermonuclear fusion, these collisions play a key role in low-temperature edge plasmas of the current fusion devices [9,10].

In order to obtain a more comprehensive understanding about the isotope effect on charge transfer in ion-molecule collisions of the hydrogen family, therefore, we conduct, in the present study, a joint experimental and theoretical study on charge-transfer cross sections of  $H^+$  ions colliding with HD molecules in the energy range of 0.18 to 1.5 keV and  $D^+$  ions colliding with HD and  $D_2$  molecules in the energy

TABLE I. Molecular constants of H<sub>2</sub>, HD, and D<sub>2</sub> molecules.

Molecule	H <sub>2</sub>	HD	D <sub>2</sub>
Reduced mass (u)	0.504	0.672	1.007
Equilibrium internuclear distance (Å)	0.7414	0.7414	0.7415
Ionization potential (eV)	15.4259	15.445	15.467
Polarizability (10 <sup>-24</sup> cm <sup>3</sup> )	0.8023	0.7976	0.7921
Vibrational frequency (cm <sup>-1</sup> )	4401.21	3813.1	3115.5
Vibrational energy (eV)	0.54568	0.47277	0.38628
Dissociation energy (eV)	4.478	4.514	4.556

range of 0.3 to 2 keV. An elaborate theoretical analysis used is based on the molecular-orbital expansion method [11], which is believed to be the most suited for intermediate- to low-energy collisions and has successfully been applied extensively in recent years [12–14]. The specific processes we are concerned with are charge transfer from the ground electronic and vibrational states of target molecules, viz.,



where  $v_i$  and  $v_f$  are the quantum numbers for the initial and final vibrational states, respectively, and  $n$  and  $l$  represent the final principal and angular quantum numbers of the hydrogen atom, respectively.

## II. EXPERIMENTAL AND THEORETICAL APPROACHES

### A. Experiment

A detailed description of the present experimental apparatus and methods has been given previously [7,8,15–17]. Only the essential features and different points are mentioned here.

First, proton or deuteron beams were generated in the ion source by 50-eV electron impact on H<sub>2</sub> or D<sub>2</sub> molecules, respectively. Then the ion beam mass separated with a Wien filter was introduced into a 4-cm-long collision cell, filled with target gases of high purity (H<sub>2</sub>, 99.999%; D<sub>2</sub>, 99.9%; HD, 97.0%). The ions and energetic neutral particles emerging from the cell after the collisions were charge separated by using electrostatic parallel plates and detected with a position-sensitive microchannel plate detector (MCP-PSD) [16]. The charge-transfer cross sections were derived based on the so-called growth rate method. The target gas pressure was directly measured in the present study with an MKS-Baratron capacitance manometer, and ranged from 10<sup>-2</sup> to 1 Pa.

Although the deuteron beam may contain impurity H<sub>2</sub><sup>+</sup> ions produced from the residual water molecules, which are estimated to be less than 6% under the present experimental conditions, we could not measure the charge-transfer cross sections of D<sup>+</sup> ions in collisions with H<sub>2</sub>, because the amount of impurity H<sub>2</sub><sup>+</sup> ions steeply increases on increasing the pressure of the H<sub>2</sub> target gas due to back-streaming into the ion source from the target chamber.

The statistical uncertainties of the cross sections derived from the growth curves are less than 4.7% for the present work. Systematic uncertainties in the determination of (i) the target gas pressure during the measurements, (ii) the effective collision length, and (iii) the temperature of the target gases are estimated to be 5%, 5%, and 3%, respectively. It has also been found that, in general, the peak width in the charge spectrum measured with the MCP-PSD becomes broader as the incident ion energy decreases. Therefore the systematic uncertainty due to the determination of the region of each peak in the charge spectrum is estimated to be large at low collision energies (6% for 0.18, 0.25, and 0.35 keV; 4% for 0.5 and 0.7 keV; 2% for 1 and 1.5 keV).

The total systematic uncertainties are then estimated to be from 8.5% at high energies to 12% at low energies including the systematic uncertainties due to the influence of impurity of the target gas and ion beam (for D<sup>+</sup> ions). The total experimental uncertainties of the absolute cross sections are determined as the quadratic sum of the above uncertainties. Note that the present gas temperature used was in the range of 291–295 K. Therefore, we estimate that target hydrogen molecules in the present experiments are predominantly in the vibrational ground state,  $v_i=0$ . Accordingly, we carried out a theoretical dynamical study of targets that are vibrationally in the ground state.

### B. Theory

A detailed description of the present theoretical approaches has been given previously [7,8,11–14]. Only the essential features and different points are mentioned here.

The collision dynamics process and charge-transfer cross sections were calculated by using the molecular-orbital close-coupling (MOCC) method within the semiclassical framework [11]. The potential curves of the singlet states for MOCC calculations were obtained by the multireference single- and double-excitation configuration-interaction (MRD-CI) method [18], with configuration selection and energy extrapolation using the TABLE CI algorithm [19]. In the CI calculations, the two lowest molecular orbitals are always kept doubly occupied, whereas the two highest ones are discarded. A small selection threshold [19] of  $0.32 \times 10^{-6}$  hartree has been used in the present treatment. The radial coupling matrix elements are obtained using the calculated MRD-CI wave functions by a finite-difference method [18] with an increment of  $0.0002a_0$  ( $a_0$  is the Bohr

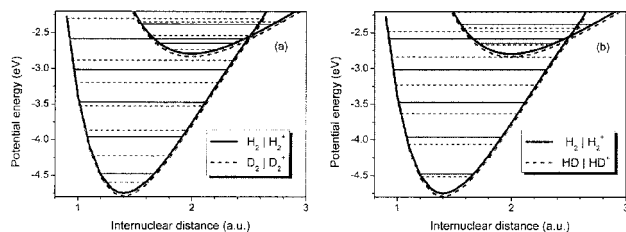


FIG. 1. Asymptotic potential surface in  $H^+ + H_2$  collision as compared to the  $D_2$  (a) and  $HD$  (b) molecular targets.

radius). In the MOCC method, the relative motion of heavy particles is treated classically, while 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), which ensures 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 the 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 yields the cross section [11–14].

States included for the dynamical calculation are [ $H^+ + H_2, D_2, HD (X^1\Sigma_g^+; v_i=0)$ ] for the initial channel, and [ $H (1s, 2s, 2p) + H_2^+, D_2^+, HD^+ (1s\sigma_g, 2p\sigma_u, 2p\pi_u; v_f)$ ] for charge-transfer channels, in addition to excitation channels [ $H^+ + H_2, D_2, HD (A^1\Pi_g; v_f)$ ]. Vibrational levels for the final products are explicitly considered up to  $v_f=5$  for excitation and  $v_f=10$  for charge transfer, respectively.

All of the collision process investigated are endothermic, if the initial vibrational level  $v_i < 4$  for  $H_2$ ,  $v_i < 6$  for  $D_2$ , and  $v_i < 5$  for  $HD$ , and this apparent difference, viz., the isotope effect, should certainly cause a difference in dynamics as we have found previously for  $H_2$  and  $D_2$ . The question arising is, however, in which energy range and how the effect begins to become significant or die down. If the initial vibrational level

of the target is in one of these excited states, then it makes the collision more near resonant and hence more favorable. An example of asymptotic potential surfaces of the target molecule when the distance between the incident ion and the target is set at  $10a_0$  is shown in Fig. 1, which highlights the small difference in the binding energy and the vibrational spacing. The  $(H_2, H_2^+)$  vibrational state distributions are compared with those of  $(D_2, D_2^+)$  in Fig. 1(a), and those of  $(HD, HD^+)$  in Fig. 1(b).

### III. RESULTS AND DISCUSSION

The present experimental cross sections of the charge transfer by  $H^+$  ions with  $HD$ , and  $D^+$  ions with  $HD$  and  $D_2$  are listed in Table II together with the previous results for charge transfer in collisions of  $H^+$  ions with  $H_2$  and  $D_2$ . The charge-transfer cross sections calculated with the MOCC method and their ratios are compared to experimental data in Figs. 2–6. The theoretical results are found to agree quite well with the present experimental values within the error bars except for one case where analysis is made below. In the following, we discuss each collision process separately.

#### A. $H^+, D^+ + H_2$ collisions

In order to make a detailed discussion as well as to show the quality of our measurements [7,8], other cross sections measured by Gealy and Van Zyl [3], Cramer [6] for  $H^+$  ions, and Berkner *et al.* [20] for  $D^+$  ions with  $H_2$  are also included in Fig. 2 together with the theoretical calculations by Kusakabe *et al.* [8], Elizaga *et al.* [21], Errea *et al.* [22], Ichihara, Iwamoto, and Janev [23], and the recommended values tabulated by Phelps [2]. As discussed in previous work [7,8], our experimental results are in excellent accord with those by Gealy and Van Zyl [2]. Both the present theory and the theoretical results by Elizaga *et al.* [21] based on a secondary sudden approximation (SEIKON) are found to be also in reasonable agreement with the experimental results in the energy region above 0.25 keV/u, but those by Elizaga *et al.* [21] are found to gradually decrease and become smaller than our results as the collision energy decreases. Recently, Errea *et al.* carried out a vibronic close-coupling treatment

TABLE II. Charge-transfer cross sections of  $H^+$  and  $D^+$  ions in collisions with  $H_2$ ,  $HD$ , and  $D_2$  molecules.

Energy (keV/u)	Cross section ( $10^{-17} \text{ cm}^2$ )				
	$H^+ + H_2$	$H^+ + HD$	$H^+ + D_2$	$D^+ + HD$	$D^+ + D_2$
0.15					$2.91 \pm 0.34$
0.18	$6.42 \pm 0.59$	$6.70 \pm 0.76$	$3.80 \pm 0.35$	$6.22 \pm 0.68$	$4.27 \pm 0.48$
0.25	$7.76 \pm 0.70$	$7.96 \pm 0.83$	$5.59 \pm 0.52$	$7.32 \pm 0.80$	$5.79 \pm 0.63$
0.35	$12.1 \pm 1.1$	$12.7 \pm 1.4$	$9.67 \pm 0.89$	$13.0 \pm 1.5$	$11.1 \pm 1.2$
0.50	$17.6 \pm 1.4$	$18.4 \pm 1.7$	$16.4 \pm 1.3$	$16.7 \pm 1.7$	$16.4 \pm 1.7$
0.70	$28.2 \pm 2.2$	$29.1 \pm 2.7$	$26.3 \pm 2.1$	$26.1 \pm 2.6$	$28.5 \pm 2.8$
1.0	$40.6 \pm 2.9$	$40.5 \pm 3.5$	$36.9 \pm 2.6$	$39.9 \pm 3.9$	$39.8 \pm 3.9$
1.5	$55.9 \pm 3.9$	$56.1 \pm 4.8$	$55.3 \pm 3.9$		

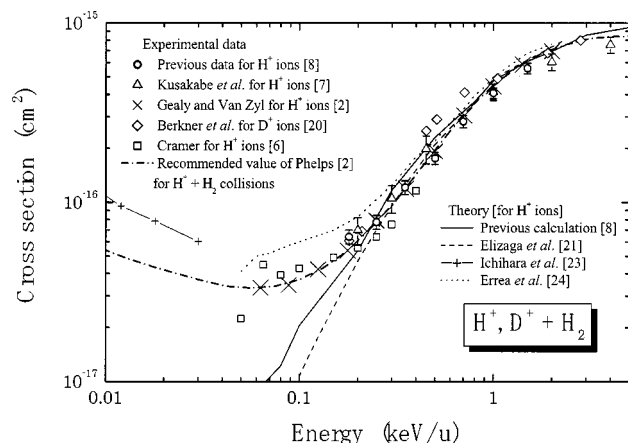


FIG. 2. Charge-transfer cross sections for  $H^+$  and  $D^+$  ions in collisions with  $H_2$  molecules as a function of the collision energy per nucleon. Experiment:  $\triangle$ ,  $\circ$ , previous data for  $H^+$  ions [7,8];  $\times$ , Gealy and Van Zyl for  $H^+$  ions [2];  $\diamond$ , Berkner *et al.* for  $D^+$  ions [20];  $\square$ , Cramer for  $H^+$  ions [6]. ---, recommended values of Phelps [2] for  $H^+ + H_2$  collisions. Theory: —, previous calculation [8]; -----, Elizaga *et al.* [21]; —+—, Ichihara *et al.* [23]; ..... Errea *et al.* [24].

[22] based on the “two-step” collision mechanism, in which at first the ground state  $H_2$  target molecule is vibrationally excited by  $H^+$  impact on the incoming trajectory, and in the next step the charge transfer follows at small distance [24]. Although their results appear to give a similar energy dependence to the experimental results in the energy range between 0.05 and 0.2 keV/u, their total cross section is enhanced as compared with that of the “single-step” process, and their values are found to be larger by 30% than the experimental data. The idea of the “two-step” mechanism may be valid only for such collisions in which the region for vibrational excitation and that of charge transfer can be clearly separated spatially. In the present low-keV energy range, both processes are expected to take place rather simul-

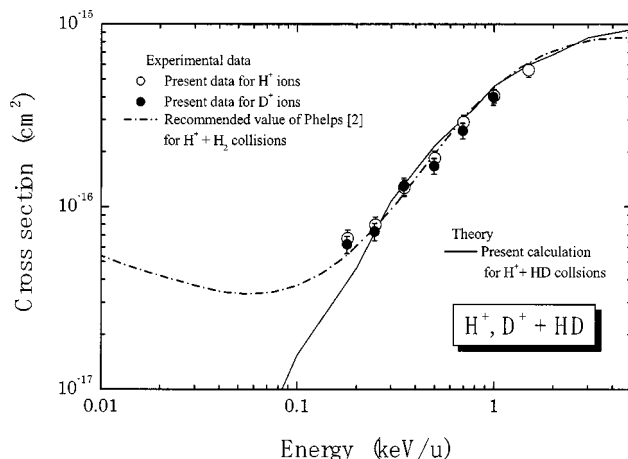


FIG. 3. Charge-transfer cross sections for  $H^+$  and  $D^+$  ions in collisions with  $HD$  molecules as a function of the collision energy per nucleon. Experiment:  $\circ$ , present data for  $H^+$  ions;  $\bullet$ , present data for  $D^+$  ions. ---, recommended values of Phelps [2] for  $H^+ + H_2$  collisions. Theory: —, present calculation.

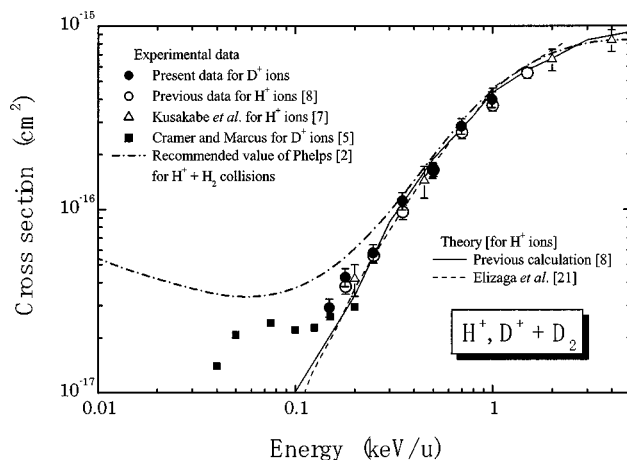


FIG. 4. Charge-transfer cross sections for  $H^+$  and  $D^+$  ions in collisions with  $D_2$  molecules as a function of the collision energy per nucleon. Experiment:  $\triangle$ ,  $\circ$ , previous data [7,8] for  $H^+$  ions;  $\bullet$ , present data for  $D^+$  ions;  $\square$ , Cramer and Marcus for  $D^+$  ions [5]. ---, recommended values of Phelps [2] for  $H^+ + H_2$  collisions. Theory: —, previous calculation [8]; -----, Elizaga *et al.* [21].

taneously within an inseparable spatial region (this corresponds to the high-velocity case in Ref. [22]).

Another approach including the charge-transfer process with proton exchange was employed by Ichihara, Iwamoto, and Janev [23] below 30 eV/u. In the initial growth method for the primary ions, charge transfer with proton exchange cannot be distinguished from pure charge transfer, and all processes are mixed in our results. However, it is essential for the proton transfer to occur when the incoming proton approaches very close to one of the target nuclei, and interacts with it during a sufficient time before the nuclear replacement, which should require the proton to stay there for at least a few vibrational periods of time except for a knock-on process. Hence, we believe that the contribution of this process should be very small in the collision energy range above 0.1 keV/u.

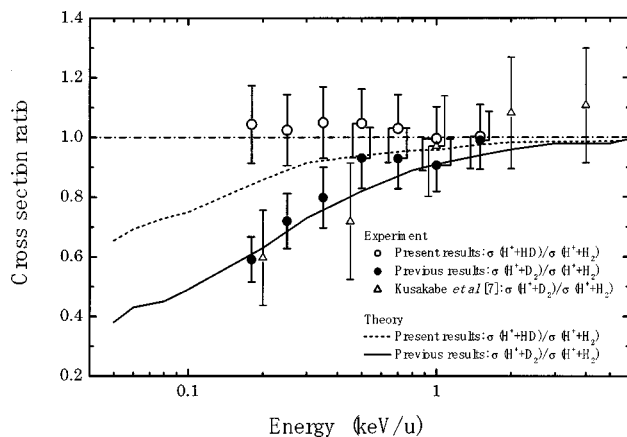


FIG. 5. Cross-section ratios of charge transfer for  $H^+ + HD$  and  $D_2$  to  $H^+ + H_2$  collisions as a function of the collision energy per nucleon. The dot-dashed line shows the position of unity. Experiment:  $\triangle$ ,  $\bullet$ , the previous data for  $D_2$  molecules [7,8];  $\circ$ , present data for  $HD$  molecules. Theory: —, previous calculation [8] for  $D_2$  molecules; -----, present calculation for  $HD$  molecules.



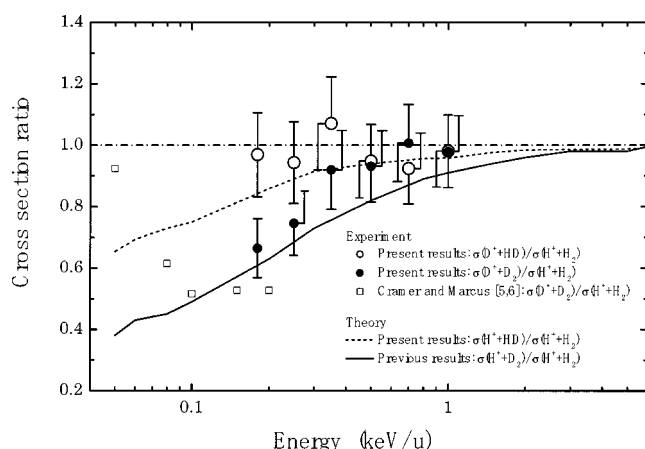


FIG. 6. Cross-section ratios of charge transfer for  $D^+ + HD$  and  $D_2$  to  $H^+ + H_2$  collisions as a function of the collision energy per nucleon. The dot-dashed line shows the position of unity. Experiment:  $\bullet$ , the present data for  $D_2$  molecules;  $\circ$ , present data for  $HD$  molecules;  $\square$ , Cramer and Marcus [5] and Cramer [6]. Theory: —, previous calculation [8] for  $H^+ + D_2$  molecules; -----, the present calculation for  $H^+ + HD$  molecules.

The differences seen in calculated cross sections below 100 eV/u or so in Fig. 2 reflect the lower accuracy in the results of the semiclassical approximation and the increasing importance of a more explicit treatment of the vibrational degrees of freedom in this collision energy region. As an indication, a newer semiclassical calculation of Errea *et al.* [24] somewhat overestimates the experimental data by Gealy and Van Zyl, while a previous one by Elizaga *et al.* [21] grossly underestimates the same data by an order of magnitude. This has been attributed in part to the importance of the orientation-averaging procedure [24] and the limits of the vibrational sudden approximation [22]. The calculation by Ichihara, Iwamoto, and Janev [23] using the trajectory-surface-hopping method explicitly accounted for target vibrations. Their values, which are somewhat higher as compared to the measurement, may consistently correspond to neglect of quantum transition phases at the surface crossing point, although the experimental trend in Fig. 2 is reproduced nicely. The lower magnitude of the quantal calculation including the previous result [8] as compared to semiclassical values below 100 eV/u is indicative that the semiclassical approximation begins to break down and a more explicit treatment of vibrational motion on the complete three-dimensional potential surface is desirable.

### B. $H^+, D^+ + HD$ collisions

In Fig. 3, the present experimental cross sections of the charge transfer by  $H^+$  and  $D^+$  ions reacting with  $HD$  are shown together with the present theoretical calculations and the recommended values by Phelps [2] for  $H^+ + H_2$  collisions. Both the present measurements for  $H^+$  and  $D^+$  ions are found to be nearly identical with each other within experimental uncertainties and are very close to the values of Phelps [2] for  $H^+ + H_2$  collisions. The present theory is in reasonable accord with the present measurements above 0.2 keV/u, but

is found to become smaller in magnitude below 0.2 keV/u. The difference between the present measurement and theory widens as the energy lowers, manifesting itself in the cross-section ratio as discussed later for further comparison.

### C. $H^+, D^+ + D_2$ collisions

In Fig. 4, the present cross sections of the charge transfer by  $D^+$  ions reacting with  $D_2$  are shown together with the earlier measurements of Cramer and Marcus [5], the previous data for  $H^+$  ions on  $D_2$  [7,8], the theoretical calculations [8,21], and the evaluated values by Phelps [2] for  $H^+ + H_2$  collisions. Both our measurements for  $H^+$  and  $D^+$  ions agree perfectly well with each other within experimental uncertainties and can smoothly tie in with those of Cramer and Marcus at 0.2 keV/u [5]. Both our previous calculation employed the MOCC and the theoretical work by Elizaga *et al.* [21] based on the SEIKON treatment are found to be also in reasonable agreement with the experimental results.

Note that Okuno studied the  $H_2$  and  $D_2$  systems experimentally using an octopole ion beam guide (OPIG) technique in the energy region below 1 keV/u [25]. His cross sections for  $H^+ + H_2$  and  $H^+ + D_2$  collisions based upon the attenuation of the primary ions are found to be larger than our data in the whole energy region studied. His cross sections for  $D^+ + H_2$  collision at energies above 0.3 keV/u are in good agreement with the recommended curve of Phelps for  $H^+ + H_2$ , but those below 0.3 keV/u steeply increase with decreasing collision energy. This feature may be caused by the effect of elastic scattering of primary ions in spite of the use of the OPIG technique.

### D. Cross-section ratio

In Fig. 5, the present results for the cross-section ratio of the charge transfer by  $H^+$  ions on  $HD$  and  $H_2$ , i.e.,  $\sigma(H^+ + HD)/\sigma(H^+ + H_2)$ , are shown together with the previous results of the cross-section ratio of the charge transfer by  $H^+$  ions with  $D_2$  and  $H_2$ , i.e.,  $\sigma(H^+ + D_2)/\sigma(H^+ + H_2)$ . As apparent, the ratio of  $\sigma(H^+ + D_2)/\sigma(H^+ + H_2)$  decreases to a smaller value than unity below 1 keV/u, and reaches a value of 0.57 at the collision energy of 0.18 keV/u. Our theoretical results are in excellent accord with the experimental results in the entire energy region.

Contrary to the case of  $H^+ + H_2$  and  $D_2$ , the experimental  $\sigma(H^+ + HD)/\sigma(H^+ + H_2)$  ratios are found to be almost unity in the entire energy region from 0.18 to 1.5 keV/u investigated. The present theoretical calculations, however, begin to show a decreasing trend below 1 keV/u, and reach a ratio of 0.75 at the collision energy of 0.1 keV/u and 0.65 at 0.05 keV/u, respectively. Above 0.18 keV/u, the lowest energy in experiment, the theoretical ratios show the decreasing feature as discussed above, but they still lie within the error bars. However, at 0.18 keV/u, the theoretical values are outside the error bars and below this energy, they decrease very steeply. It would be highly desirable to carry out the experimental investigation at lower energies in order to observe the trend we have seen in theory as an apparent fingerprint of the weak case of the isotope effect, in which only one of the H atoms

in a hydrogen molecule is replaced with its isotope.

In Fig. 6, the present results of the cross section ratio of the charge transfer by  $D^+$  ions on HD and  $H^+$  ions with  $H_2$ , i.e.,  $\sigma(D^+ + HD)/\sigma(H^+ + H_2)$ , and  $D^+$  ions with  $D_2$  and  $H^+$  ions with  $H_2$ , i.e.,  $\sigma(D^+ + HD)/\sigma(H^+ + H_2)$ , are shown together with the previous and present theoretical results. As apparent, the present experimental ratio of  $\sigma(D^+ + D_2)/\sigma(H^+ + H_2)$  becomes smaller than unity below 1 keV/u, and reaches a value of 0.665 at the collision energy of 0.18 keV/u. Our previous theoretical results for  $\sigma(H^+ + D_2)/\sigma(H^+ + H_2)$  are again in excellent accord with the present experimental results in the entire energy region. The present experimental  $\sigma(D^+ + HD)/\sigma(H^+ + H_2)$  ratios are again almost unity.

As we have investigated and discussed carefully earlier [8], such an isotope effect can be explained as follows. It should be pointed out (as seen in Fig. 1) that there are two small differences in the energy involved in the charge transfer for  $H_2$ , HD, and  $D_2$  molecules. First, the electron binding energy for HD and  $D_2$  is larger by 19 and 41 meV, respectively, than that of  $H_2$  molecules. Second, the potential energy curves for the initial and final channels show a larger energy defect by the amount of the vibrational energy for the  $[H^+ + HD]$  and  $[H^+ + D_2]$  collisions than that of  $[H^+ + H_2]$ . The energy defect between the  $v_i=0$  level in the initial  $X^1\Sigma_g^+$  state and  $v_f=0$  in the  $1s\sigma_g$  state (see Fig. 1) is roughly 16 and 37 meV more endothermic for the HD and  $D_2$  molecules than that for the  $H_2$  molecules. In addition, the vibrational spacing is denser for the HD and  $D_2$  molecules than that for the  $H_2$  molecule, and hence the nuclear wave functions are more contracted within a smaller spatial region, thus giving rise to a smaller Franck-Condon factor than that for the  $H_2$  case for the transitions between the two potential curves. As for indirect processes and/or when the target is first vibrationally excited, subsequent transitions are favored to the nearest vibrational levels of the molecular ion. Since the target nuclear wave functions in case of HD and  $D_2$  molecules are more oscillatory within a narrower space in the same energy region as compared to  $H_2$ , the overlap integrals for this mechanism were also found to be smaller. These differences seen in binding energy and vibrational spacing and their consequence are small but non-negligible. These combined effects become decisive to the collision dynamics below a few keV/u and tend to make the charge transfer less favorable for HD and  $D_2$  molecules, particularly below keV energies. Therefore, the ratio is expected to be less than unity

before other processes such as reactive scattering become dominant, hence influencing the ratio below low eV energies.

#### IV. SUMMARY

In summary, we have measured the cross sections of charge transfer of  $H^+$  ions in collisions with HD and  $D^+$  ions in collisions with HD and  $D_2$  molecular targets in the collision energy region from 0.15 to 1.5 keV/u. A significant difference of the cross sections between  $D^+ + D_2$  and  $H^+ + H_2$  collisions has been observed at low energies below 1 keV. This difference is similar to the previous results for  $H^+ + D_2$  and  $H^+ + H_2$  collisions [8]. For HD target molecules, almost no difference from the cross sections in  $H^+ + H_2$  collisions is experimentally observed. However, the present theoretical calculation predicts appreciable differences between charge transfer from HD and  $H_2$  molecules below 1 keV collision energy, and the difference widens as the energy lowers below 0.2 keV/u. The calculated cross-section ratio for  $[H^+ + HD]$  and  $[H^+ + H_2]$  is closer to unity than that of the  $[H^+ + D_2]$  and  $[H^+ + H_2]$  case, but the difference is still observable. From the present theoretical analysis, it is found that this difference arises from the combination of small offset in the binding energies and in the vibrational energies of  $H_2$ , HD, and  $D_2$  molecules in their dynamic collision processes. Finally, the measured cross sections for charge transfer in  $[H^+ + HD]$  and  $[D^+ + HD]$  collisions and in  $[H^+ + D_2]$  and  $[D^+ + D_2]$  collisions are practically identical, if the speed of both projectiles is set equal. In the present energy domain, no strong projectile isotope effect is detected, although there should be some indication for slower collisions arising from the differences in the three-body binding energy.

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- [1] C. F. Barnett, Oak Ridge National Laboratory Report No. ORNL-6086, 1990 (unpublished).
  - [2] A. V. Phelps, J. Phys. Chem. Ref. Data **19**, 653 (1990).
  - [3] M. W. Gealy and B. Van Zyl, Phys. Rev. A **36**, 3091 (1987).
  - [4] A. A. Radzig and B. M. Smirnov, in *Reference Data on Atoms, Molecules, and Ions*, Springer Series in Chemical Physics Vol. 31, edited by J. P. Toennies (Springer, Berlin, 1985), pp. 340 and 376.
  - [5] W. H. Cramer and A. B. Marcus, J. Chem. Phys. **32**, 186 (1960).
  - [6] W. H. Cramer, J. Chem. Phys. **35**, 836 (1961).
  - [7] T. Kusakabe, K. Asahina, J. P. Gu, G. Hirsch, R. J. Buenker, M. Kimura, H. Tawara, and Y. Nakai, Phys. Rev. A **62**, 062714 (2000).
  - [8] T. Kusakabe, M. Kimura, L. Pichl, R. J. Buenker, and H. Tawara, Phys. Rev. A **68**, 050701(R) (2003).

- [9] R. K. Janev, in *Atomic and Molecular Processes in Fusion Edge Plasmas*, edited by R. K. Janev (Plenum, New York, 1995), pp. 1–13.
- [10] F. Linder, R. K. Janev, and J. Botero, in *Atomic and Molecular Processes in Fusion Edge Plasmas* (Ref. [9]), pp. 397–431.
- [11] M. Kimura and N. F. Lane, *Adv. At. Mol. Phys.* **26**, 76 (1989).
- [12] L. Pichl, Y. Li, H.-P. Liebermann, R. J. Buenker, and M. Kimura, *J. Chem. Phys.* **118**, 4872 (2003).
- [13] T. W. Imai, M. Kimura, J. P. Gu, G. Hirsch, R. J. Buenker, J. G. Wang, P. C. Stancil, and L. Pichl, *Phys. Rev. A* **68**, 012716 (2003).
- [14] L. Pichl, R. J. Buenker, and M. Kimura, *Adv. Quantum Chem.* **46**, 165 (2004).
- [15] T. Kusakabe, K. Hosomi, H. Nakanishi, H. Tawara, M. Sasao, Y. Nakai, and M. Kimura, *Phys. Rev. A* **60**, 344 (1999).
- [16] T. Kusakabe, M. Ohmiya, and K. Wada, *Jpn. J. Appl. Phys., Part 1* **31**, 4093 (1993).
- [17] T. Kusakabe, T. Horiuchi, Y. Nakai, and H. Tawara, *Jpn. J. Appl. Phys., Part 1* **37**, 369 (1998).
- [18] R. J. Buenker and S. D. Peyerimhoff, *Theor. Chim. Acta* **35**, 33 (1974); **39**, 217 (1975); R. J. Buenker, *Int. J. Quantum Chem.* **29**, 435 (1986); S. Krebs and R. J. Buenker, *J. Chem. Phys.* **103**, 5613 (1995).
- [19] R. J. Buenker, in *Proceedings of the Workshop on Quantum Chemistry and Molecular Physics, Wollongong, Australia*, edited by P. G. Burton (University Press, Wollongong, 1980); in *Studies in Physical and Theoretical Chemistry, Current Aspects of Quantum Chemistry Vol. 21*, edited by R. Carbo (Elsevier, Amsterdam, 1981), p. 17; R. J. Buenker and R. A. Phillips, *J. Mol. Struct.: THEOCHEM* **123**, 291 (1985).
- [20] K. H. Berkner, R. V. Pyle, and J. W. Stearns, *Nucl. Fusion* **10**, 145 (1970).
- [21] D. Elizaga, L. F. Errea, J. D. Gorfinkiel, L. Mendez, A. Macias, A. Riera, and A. Rojas, *J. Phys. B* **33**, 2037 (2000).
- [22] L. F. Errea, A. Macias, L. Mendez, I. Rabadan, and A. Riera, *Phys. Rev. A* **65**, 010701(R) (2001).
- [23] A. Ichihara, O. Iwamoto, and R. K. Janev, *J. Phys. B* **33**, 4747 (2000).
- [24] L. F. Errea, A. Macias, L. Mendez, I. Rabadan, and A. Riera, *Int. J. Mol. Sci.* **3**, 142 (2002).
- [25] K. Okuno, *At. Plasma-Mater. Interact. Data Fus.*, **10**, 163 (2002).