Ion-formation total cross sections from dissociative collisions of vibrationally relaxed H_3^+, D_3^+, and HD_2^+ molecular ions with He

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Total cross sections for the positive and negative fragments resulting from dissociative collisions with He of vibrationally relaxed H_3^+, D_3^+, and HD_2^+ molecular ions have been measured in the energy range 3–9.8 keV. The measured absolute total-cross-section values are more than one order of magnitude smaller than those previously reported with the molecular ions without vibrational relaxation. When the cross sections are plotted as a function of the projectile speed and normalized to compensate for the relative fragment yield, the values for the production of deuterium fragments are higher than those for hydrogen ions in the energy range of the present study. These results are consistent with the theoretical predictions for the behavior of triatomic molecular ions with high rovibrational excitation.

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I. INTRODUCTION

H_3^+, as the simplest polyatomic molecular ion, plays an important role in molecular physics and in astrophysics. It has received considerable attention, since it is the most abundant molecule in interstellar clouds. Besides its important role in interstellar chemistry, in hydrogen discharges H_3^+ is the most abundant molecular ion. A review of the properties and importance of H_3^+ can be found, for example, in Refs. [1–4]. The formation of the H_3^+ as noted in Ref. [5] has been studied extensively, but in contrast, the information about its destruction is very scarce. Additionally, there is inconsistency in the measurements concerning the total cross sections for the fragment ion production from hydrogenic molecular ions. This is mainly due to the pronounced difficulties associated with the preparation of a beam with a well-known internal energy. Data about the formation and destruction of hydrogen molecular ions are particularly important in plasma modeling and in fusion research. The purpose of this paper is to present the total, absolute cross-section measurements for the production of the positive and negative fragments resulting from the collision-induced dissociation of vibrationally cooled H_3^+, D_3^+, and HD_2^+ beams in collision with He.

II. EXPERIMENTAL APPARATUS

The apparatus used in this experiment is shown in Fig. 1. The method and the test employed to obtain vibrational relaxation in the H_3^+ beam has been described in detail elsewhere [6,7].

Briefly, the triatomic molecular ions were produced in an electron bombardment ion source. The ions were extracted and electrostatically focused into a mass spectrometer to be momentum analyzed. A low conducting channel was installed prior to the deflecting magnet allowing the pressure in the source to be increased to about 120 Pa without affecting the high vacuum in the beam line, which was of the order of 10^{-6} Pa. The high gas pressure in the source was achieved with a mixture of 6% Ar and 94% of research purity H_2 or D_2 gases. This high pressure allowed the collisional relaxation of the molecular ions (H_3^+, D_3^+, or HD_2^+). To obtain the HD_2^+ beam, a mixture of H_2 and D_2 was injected into the ion source. The momentum analyzed and vibrationally cooled beam was sent through a series of collimators into the entrance of the interaction cell containing He gas at a constant pressure of less than 0.01 Pa, thereby guaranteeing single-collision conditions. The target cell was located in a differentially pumped vacuum chamber. The dissociation products entered the detection chamber and were charge separated by an electric field produced by the appropriate voltage applied to a pair of plates. This field diverted the charged fragments 12 deg from the path of the undeflected beam direction. On one side, a parallel-plate electrostatic analyzer was located 20 cm away from the edge of the plates and oriented at 45 deg between the charged fragment direction and the field. A channel electron multiplier (CEM) was positioned at the exit of the analyzer. A rectangular slit of 0.3 mm width and 10 mm long was placed in front of the CEM, and a collimator of 2.8 mm diameter at the entrance of the energy analyzer provided the energy analysis of the charged fragments by sweeping the applied voltage between the

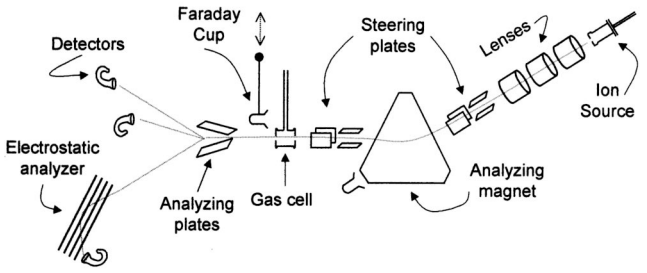

FIG. 1. Schematic of the experimental apparatus.

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plates of the analyzer. These conditions result in an energy resolution ($\Delta E/E$) of 0.04. In this work, the parallel-plate analyzer was used to register the energy distribution of the H^+, H^-, and $H_2{}^+$ fragments. On the opposite side from the undeflected beam direction, a CEM (with a 0.9-cm-diameter active area) was located to register the total fragment count rate.

A retractable Faraday cup was placed at the exit of the target cell to measure the total current of the triatomic beam. The detectors and the analyzer were shielded to prevent unwanted events. This setup allows the measurement of the laboratory energy distribution of the charged fragments, the current intensity of the initial ion beam, and the total intensity of the fragments, all necessary for the measurement of the absolute total cross sections. Due to the energy liberated in the dissociation process, and to ensure the detection of all particles, the cross sections were measured under different conditions. The diameter of the entrance aperture of the collision cell was reduced from 1 to 0.45 mm, and the distance from the exit aperture to the detectors was decreased by 10 cm; no significant change in the measurements for the total cross sections was found.

III. RESULTS AND DISCUSSION

The main dissociation paths leading to the production of ionic fragments are

$$H_3{}^+ + He \rightarrow \begin{cases} H^+ + H_2 + He, & (1) \\ H_2{}^+ + H + He, & (2) \\ H^+ + H^- + H^+ + He. & (3) \end{cases}$$

The same paths are present for the reaction $D_3{}^+ + He$. The $HD_2{}^+$ has more dissociation paths:

$$HD_2{}^+ + He \rightarrow \begin{cases} H^+ + D_2 + He, & (4) \\ D^+ + HD + He, & (5) \\ H + D_2{}^+ + He, & (6) \\ D + HD^+ + He, & (7) \\ D^+ + H^- + D^+ + He, & (8) \\ H^+ + D^- + D^+ + He. & (9) \end{cases}$$

A wide variety of channels can produce positive fragments as is known from the available potential-energy curves [8]. On the other hand, the negative fragments are produced from the polar dissociation channel (3, 8, 9) and as a result of the following two-step process [9]:

$$H_3{}^+ + He \rightarrow H_2^{**} + H^+ + He \hookrightarrow H^+ + H^- + H^+ + He. \quad (10)$$

If such a process does contribute significantly to the measured H^+ signal, then the protons resulting from this process would show higher and broader center-of-mass (c.m.) energy distributions depending on the internal energy distribution within the H_2^{**} molecule. Such distribution was not observed in the H^+ and H^- signals measured in coincidence [7]. Previous work on the polar dissociation channel [7] showed a good agreement with theoretical work related to the repulsive channels leading into polar three-body fragmentation [10], indicating that the two-step process (10) may not contribute significantly to the signal measured in this particular experiment.

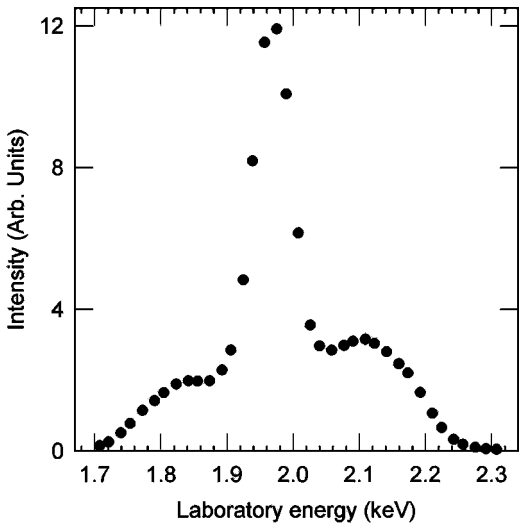

FIG. 2. Energy distribution of the H^+ fragment from the $H_3{}^+$ primary beam at 6 keV in collision with a He target.

The charge transfer is unlikely with He as a target in the energy range of the present experiment (He ionization potential is 24 eV [5]). To obtain information about the initial and final states involved, the energy distributions of H^+ and $H_2{}^+$ fragments were registered and are shown in Figs. 2 and 3.

They display lateral bumps around a central peak, located at about 1/3 of the primary beam energy for H^+ and at 2/3 for the $H_2{}^+$ fragment. In both cases, the lateral bumps are originated from the excitation of the ground state into repulsive states. The energy released in such processes is shared by the fragments resulting in the above-mentioned distributions, they correspond to vertical transitions in the Frank-Condon region. It has been established [11,12] that the cen-

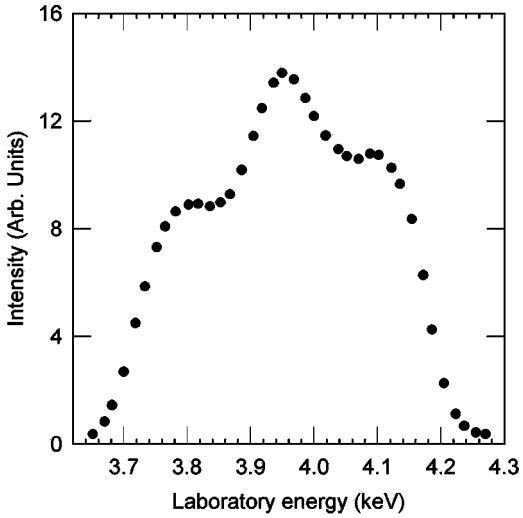

FIG. 3. Energy distribution of the $H_2{}^+$ fragment from the $H_3{}^+$ primary beam at 6 keV in collision with a He target.

tral peak, formed of near-zero-energy released protons, results from long-lived initial ions that are in rotationally excited quasibound states lying above or below the dissociation limit. The excitation of these states in collision with He, to final predissociating states with short enough lifetimes (those that dissociate within the time required to travel the distance from the collision cell to the electrostatic deflection plates of 31 cm) will be accounted for.

It is also established [12] that tunneling through the rotational barrier would result in fragment protons with such near-zero c.m. energy. More recently [13], irradiating vibrationally relaxed H_3^+ with 1.165-eV light [from a 1064-nm Nd:YAG laser (yttrium aluminum garnet) was found to cause an increase in the intensity of the H^+ fragment, while no such an increase was found for the H_2^+ signal under the same conditions. It was concluded that such an effect is due to the promotion of loosely bound molecular ions of the ground state into predissociative final states lying above the dissociation limit followed by dissociation of these final states leading to H^+.

The near-zero-energy peak in the H_2^+ distribution is the product of a different process. In a photodissociation experiment of H_3^+ using a YAG-pumped dye laser [14], an increase in the H_2^+ was observed with no change in the H^+ fragment signal. The photon energy was varied from 2 to 4.5 eV. The interpretation of the signal behavior was that the H_2^+ fragments originate from the excitation of the higher vibrational levels within the electronic ground state to the overlapping dissociation channel $H_2^+(\nu=0)+H(1s)$, leading the H_2^+ fragment with very low energy in the c.m. frame. The cross sections reported in the present paper may arise from two main processes: one, from the initial molecular ions with $\nu=0$, and the other, from the weakly bound rotational excited ground-state molecular ions. The quantitative contribution of both processes to the total cross sections was not possible in the present experimental work.

The cross sections for the production of the positive fragments from H_3^+ incident on He have been reported in Ref. [17]. The energy range of their investigation was 2–50 keV and the operating conditions of the ion source were chosen to obtain the maximum cross section, indicating that the initial state of the ions was vibrationally excited. Nevertheless, they observed a variation of a factor of 3 with different ion source conditions.

The cross sections for the negative ion formation from H_3^+, D_3^+, and HD_2^+ ions on He have been previously reported [15], the energy range of the primary beam was from 1 to 4.8 keV. The total absolute cross section was obtained by numerical integration over the absolute differential cross sections measured in a different experimental setup. No attempt to test the vibrational population of the beams was reported.

To the best of our knowledge and for the present energy range, no other absolute total cross section for the production of charged fragments has been reported from vibrationally relaxed H_3^+, D_3^+, and HD_2^+ molecular ions. The cross sections were determined by the standard method based on the measurement of the growth of the intensity of the fragments as a function of the He pressure in the target cell. We applied the first- and second-order approximations for the solution of the coupled differential equations that describe the growth of the intensity of each fragment as a function of the pressure. The difference between both values being less than 3%. Then the cross sections were determined from the linear regression of the growth of the intensity of each fragment as a function of pressure. The results are shown in Figs. 4, 5, and 6 together with the measurements from Refs. [5,15,17]. By modifying the ion source parameters it was possible, within the experimental error, to verify the values given in Ref. [17], see Fig. 4.

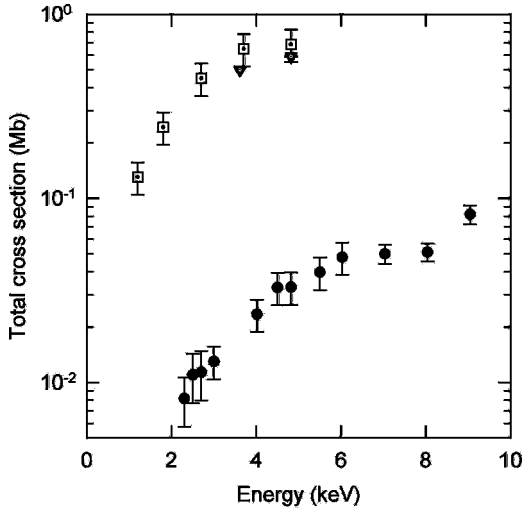

FIG. 4. Absolute cross sections for the production of the H^- fragment. Solid dots represent the present values with the H_3^+ beam being vibrationally cooled. Down triangles represent those with the beam being vibrationally excited. Squares represent cross sections from Ref. [15].

The cross sections for the H^- production $\sigma(H^-)$, are plotted as a function of collision energy in Fig. 4. The present measurements on vibrationally cooled H_3^+ are smaller by one order of magnitude than those of Ref. [15].

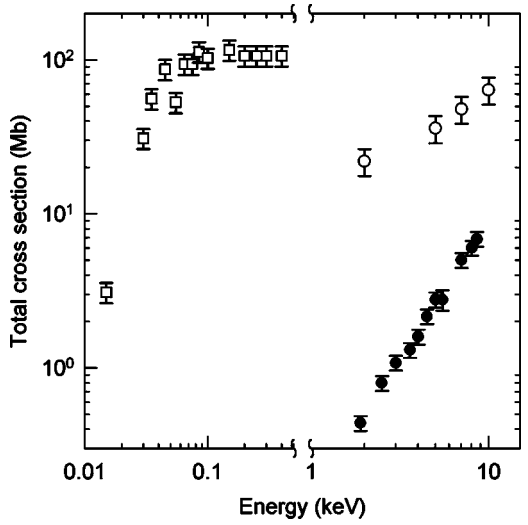

FIG. 5. Absolute cross sections for the production of the H^+ fragment. Solid dots represent the present values with the H_3^+ beam being vibrationally cooled. Open squares represent the data from Ref. [16] and open dots represent the data from Ref. [17].

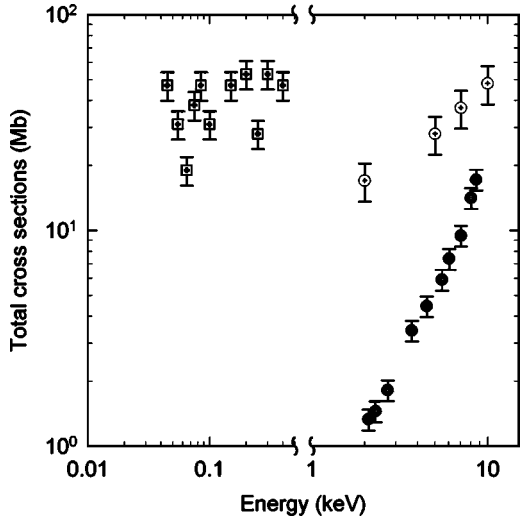

FIG. 6. Absolute cross sections for the production of the H_2^+ fragment. Solid dots with + represent present results with the vibrationally cooled H_3^+ beam. Open dots with + represent the values from Ref. [17]. Squares with + represent data from Ref. [16].

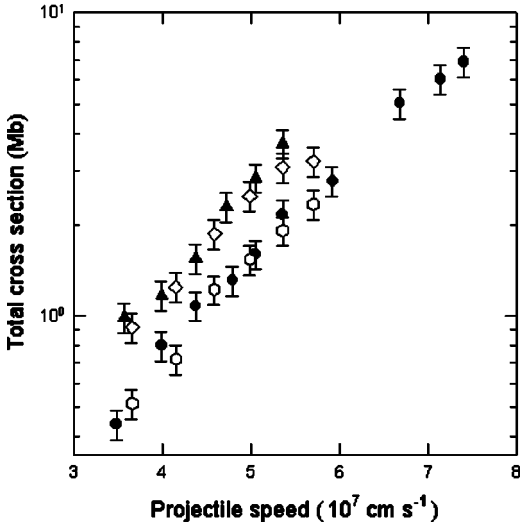

FIG. 7. Total cross sections for the present H^+ and D^+ fragments from vibrationally cooled H_3^+, D_3^+, and HD_2^+. Solid dots represent those of H^+ from H_3^+. Up triangles represent those of D^+ from D_3^+. Open diamonds are for D^+ from HD_2^+. Open hexagons are for H^+ from HD_2^+. The cross sections from HD_2^+ are normalized to compensate for the relative fragment yield in order to compare the mass effect over the dissociation processes, i.e., $3\sigma(H^+)$ has been plotted.

The present $\sigma(H^+)$ cross-section measurements are shown in Fig. 5, together with data from Refs. [5,17]. The difference between the cross-section values is about one order of magnitude. This is due to the vibrational cooling in the present H_3^+ parent beam. The values reported in Ref. [5] at lower energies, where the chemical processes are important, follow a very different trend. No explanation regarding this difference is available at this moment. Figure 6 displays the $\sigma(H_2^+)$ cross sections together with the data from Refs. [5,17]. The previous comments on $\sigma(H^+)$, are valid for the $\sigma(H_2^+)$ cross sections. As it can be observed from Figs. 4, 5, and 6, differences in the cross-section values for vibrationally cooled and vibrationally excited H_3^+ is about one order of magnitude for the three fragments.

In Fig. 7 the cross sections for positive monatomic $\sigma(H^+,D^+)$ are plotted. Figure 8 shows the values for positive diatomic fragments $\sigma(H_2^+, D_2^+, HD^+)$ and, in Fig. 9 the values for negative $\sigma(H^-,D^-)$ fragments coming from the dissociation of either H_3^+, D_3^+, or HD_2^+ is shown. In order to investigate the mass effect in the dissociation processes, the data are plotted as a function of the projectile speed. The cross sections from HD_2^+ beam are multiplied by a factor to compensate for the different relative fragment yield compared to that of H_3^+ or D_3^+, see captions.

The error bars associated with the data correspond to one standard deviation 1. A common feature over the dissociation process is that the cross sections for the production of deuterium ions, positive or negative, are in general higher than the cross sections involving hydrogen ions. The preponderance of the $\sigma(D^+)$ and $\sigma(D_2^+)$ values over those of $\sigma(H^+)$ and $\sigma(H_2^+)$ values can be explained in terms of the effect of the high gas pressure in the ion source over the dissociation dynamics.

Increase of the gas pressure in the ion source produces vibrational relaxation. Levels as low as $\nu=0$ will be populated with higher probability. At the same time, rovibrational excitation occurs in such vibrationally cold ions. As a result, some of them will be promoted to a high angular momentum creating a centrifugal barrier that plays an important role in the dissociation behavior. This effect has been recently studied [18] in the photodissociation of HD_2^+ molecular beam using a Nd:YAG laser (1064 nm). A variation of the ion

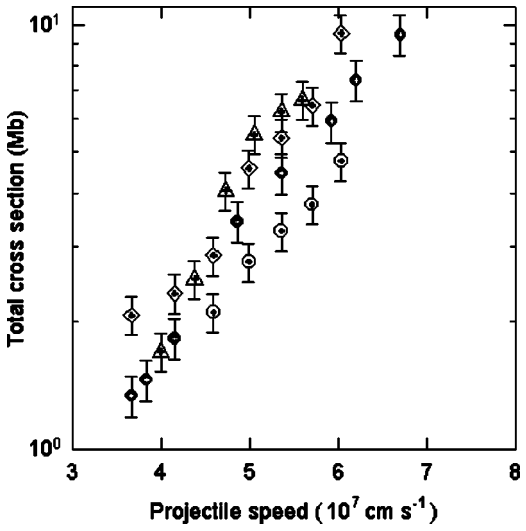

FIG. 8. Total cross sections for the present H_2^+, D_2^+, and HD^+ fragments from vibrationally cooled H_3^+, D_3^+, and HD_2^+. Solid dots with + represent those of H_2^+ from H_3^+. Open up triangles with + represent D_2^+ from D_3^+. Open diamonds with + represent D_2^+ from HD_2^+. Open dots with + represent HD^+ from HD_2^+. The cross sections from HD_2^+ are normalized to compensate for the relative fragment yield in order to compare the mass effect over the dissociation processes, i.e., $1.5\sigma(D^+)$ has been plotted.

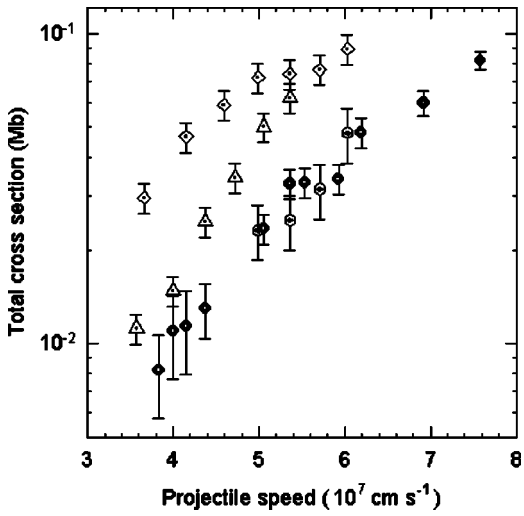

FIG. 9. Cross sections of the negative fragments from vibrationally cooled H_3^+, D_3^+, and HD_2^+. Solid dots with · represent H^- from H_3^+. Open up triangles with · represent D^- from D_3^+. Open diamonds with · represent D^- from HD_2^+. Open hexagons with + represent H^- from HD_2^+. The cross sections from HD_2^+ are normalized to compensate for the relative fragment yield in order to compare the mass effect over the dissociation processes.

source gas pressure induces a change of the D^+:H^+ branching ratio that runs from 1.3 to 5. Using an ion source having two orders of magnitude lower pressure, the production of H^+ and D^+ fragments induced by the photodissociation of the HD_2^+ has been measured [19]. They reported on a H^+ fragment production three times higher than that for D^+ fragments. The mass effect over the dissociation of the triatomic hydrogenic ions has been discussed theoretically in Refs. [11,19–21]. The present results are consistent with their theoretical treatments.

IV. CONCLUSIONS

In this paper we present absolute, total cross sections for the ion fragments production from H_3^+, D_3^+, and HD_2^+ beams in collision with He in the energy range 3–9.8 keV. The beams have been vibrationally cooled. The effective vibrational relaxation has been experimentally confirmed by studying the polar dissociation channel [7]. The ionic fragment cross sections arising from the vibrationally relaxed H_3^+ are about one order of magnitude lower. The ion fragment cross sections from H_3^+, D_3^+, and HD_2^+ have been plotted as a function of the projectile velocity and normalized in order to observe the mass effect, using vibrationally cooled molecular ions. As it can be observed, for the present conditions, the formation of D^+, D_2^+, and D^- is preferred to the formation for H^+, H_2^+, and H^-. This is consistent with the theoretical predictions for these molecular ions at high rovibrational excitation. State selective measurements regarding the dynamics of three-atom molecules are needed in order to understand their structure in more detail.

ACKNOWLEDGMENTS

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