Total cross section for the dissociative excitation of He_2^+ molecular ions in collision with He

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Absolute cross sections have been determined for the dissociative excitation and electron capture followed by ion-pair formation ($He^+ + He^-$) for He_2^+ collisions with He in the energy range of 4–10 keV. The He^+ absolute cross section that is uniquely due to the dissociative excitation was deduced, taking advantage of the measurements of the He^- cross section. The center-of-mass energy for the fragment ions was measured. The available potential-energy curves show that the vibrationally excited ground state may be responsible for the fragment ions. The collisional deactivation of He_2^+ ions using high source pressure showed no effect on the measured cross section. Complete theoretical high-lying repulsive potential-energy curves for He_2^+ ions are currently not available, therefore it is not possible to quantitatively establish the final state of the ions.

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INTRODUCTION

The helium dimer ion has been the subject of theoretical and experimental studies because of its importance in diverse fields ranging from quantum chemistry to plasma physics. More recent investigation has concentrated on the characterization of the ground electronic state of the helium dimer ion using microwave spectroscopy of mass selected molecular ions [1,2]. Due to the interest in helium discharges and helium afterglow, it has been approached many times from both theoretical and experimental points of view [3–8]. In spite of the importance of the helium dimer ion He_2^+, there have been no reported measurements of the cross sections for either the dissociative excitation or the electron capture and ion-pair formation.

The investigation of metastable species in helium plasma has been conducted at room temperature and moderate pressures of helium gas. The ionic precursor to neutral He_2 is the molecular ion He_2^+. Some of the processes that may lead in to He_2^+ are

$$He^+ + 2He \rightarrow He_2^+ + He, \quad (1)$$

$$He^+ + 3He \rightarrow He_2^+ + 2He, \quad (2)$$

$$He^* \ (n \geqslant 3) + He \rightarrow He_2^+ + e. \quad (3)$$

The first process is that of three-body conversion of the atomic ion into a molecular ion. It is postulated that the molecular ion is in a highly vibration excited state. A four-body conversion is presented in the second processes. It has been assumed that it augments the first process [9] and it seems that the four-body process is significant even at modest helium pressures. The third process is called the Hornbeck-Molnar process [10]. It can occur because the potential-energy curve of the ground-state He_2^+ ion is deeply bound with its minimum energy at the same level as the $n=3$ level of atomic helium. Therefore helium atoms excited to $n \geqslant 3$ can, upon collisions with ground-state He, produce the molecular ion and eject an electron. Theoretical work of Mulliken [11] indicated that the resulting molecular ion is in a vibrationally excited state. Recombination processes are mostly responsible for the destruction of the He_2^+ ions. It is an objective of this work to measure the cross sections for the dissociative excitation of He_2^+ leading into He^+ and the electron capture followed by ion pair He^+-He^-, as well as qualitatively establish the vibrational state of the initial He_2^+.

Hornbeck and Molnar [10] produced He_2^+ and He^+ ions by electron impact at gas pressures up to 70 mm Hg. The ratio of the molecular to atomic ion peak heights versus pressure in their work showed a linear variation with pressure over a pressure range of a factor of 10.

The He^+ fragments are the direct result of the dissociative excitation of the He_2^+ parent ions according to the reaction

$$He_2^+(\nu) + He \rightarrow He^+ + He + He.$$

The negative fragments are most probably due to a two-step process, in which the first is that of electron capture,

$$He_2^+ + He \rightarrow He_2 + He^+.$$

That is followed by the dissociation of the He_2 excited molecule through ion-pair formation as $He_2 \rightarrow He^+ + He^-$. At present there is a considerable lack of data on both, the theoretical and experimental levels regarding this molecular ion, that is the second simplest ion next to H_2^+.

EXPERIMENTAL APPARATUS

The experimental apparatus employed in this work was the same as that used in earlier work and is described in detail elsewhere [12,13]. Consequently a relatively brief summary is given here. The molecular ion He_2^+ was produced in a filament-type colutron source and was extracted and accelerated to the desired energy and electrostatically focused into a momentum analyzer. At the entrance of the momentum analyzer, a low conducting canal was installed in

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order that high pressure in the ion source (up to 800 mTorr) can be achieved without affecting the high vacuum in the beam line that was maintained at about 10^{-8} Torr. High-purity research grade He gas was used in the source with 6% of Ar to facilitate the discharge in the ion source. The high source pressure employed during some of the measurements was used in order to achieve the vibrational relaxation of the molecular ions [12,13]. After momentum analyses, the molecular ion beam was sent through a series of collimators into the entrance of a target cell containing He gas and maintained at a constant pressure of less than 0.1 mTorr in order that single collision conditions are maintained. The target cell is located in a differentially pumped region and the dissociation products, after exiting the target exit aperture, enter the detection chamber and are charge separated by an electrostatic field generated by voltage that is applied on a set of plates. The field on the plates directs the charged fragments into the off axes of two open channeltrons situated at 12° and 24° sideways and at a distance of 32 cm from the target cell. On the other side, a parallel-plate electrostatic analyzer was used for the energy analyses of the charged fragments by sweeping the applied voltage on the analyzer with a channeltron detector at the exit slit. The entrance aperture and the exit rectangular slit provided an energy resolution of 0.04. A retractable Faraday cup was used at the exit aperture of the target cell in order to measure the absolute intensity of the ion beam. The setup described provided for all the measurements needed for the total cross section. Different conditions were used in the measurements of the cross sections to ensure total collection of the dissociation fragment, such as changing the entrance and exit apertures sizes of the target cell and the distance of the open channeltrons from the electrostatic deflection plates. The standard method of the growth of fragments with pressure was used in the determination of the cross sections.

RESULTS AND ANALYSES

The He_2^+ ions were produced, accelerated, focused, and allowed to pass through a set of collimators into the target cell that was maintained at a constant pressure. Both parent ions as well as fragments resulting from the dissociative excitation in collision with the target were registered on one of the open channeltrons by setting the required voltage on the electrostatic deflection plates. These measurements were conducted at different distances between the electrostatic deflection plates and the detector. Following that, the distance was chosen to be 14 cm, in which the total collection of both ions was achieved. The result of one scan of the voltage applied on the deflection plates and for a target pressure of 0.1 mTorr is shown in Fig. 1. It can be seen that the voltage required for the fragments is half of that required for the parent molecular ions.

In order to evaluate the behavior of the ion source with respect to the production of both atomic and molecular ions, the output of the ion source for both He_2^+ and He^+ at 7 keV acceleration energy was measured under the same conditions of filament current and anode voltage in a range of source pressures up to 0.800 mm Hg, the results for the He_2^+: He^+ ratio are presented in Fig. 2. Our results for the ratio of molecular to ion peak heights versus pressure show a linear variation with pressure over the pressure range indicated with the intensity of He_2^+ to be proportional to P^2.

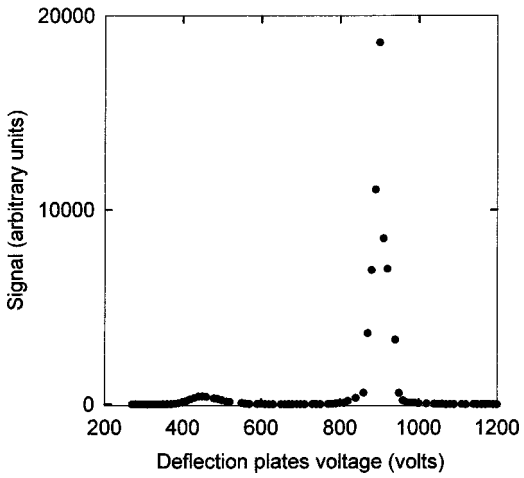

FIG. 1. Spectrum of the parent molecular ion and the fragment He^+ resulting from a scan of both across an open detector.

The total absolute cross sections for the production of He^+ and He^- were measured initially at 100 mTorr source pressure; the source pressure was increased systematically without observing any differences in the measured cross sections beyond the limit of the experimental uncertainties up to ion source pressures of 800 mTorr. The accuracy of our results and the performance of the experimental apparatus were both verified by observing the decline of the H^+ production in the dissociative excitation of H_2^+ in collision with He when the ion source pressure was increased up to 800 mTorr, the results were in accordance with our previous work [12–14]. The absolute total cross sections for the production of He^+ and He^- are shown in Fig. 3 at an intermediate source pressure of 400 mTorr.

One would initially expect that our results would imply that the initial He_2^+ are vibrationally cold even at a source

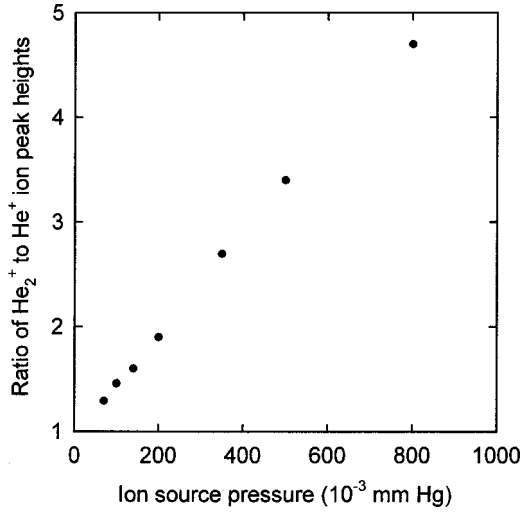

FIG. 2. Ratio of He_2^+ to He^+ ions generated by the ion source as a function of source pressure.

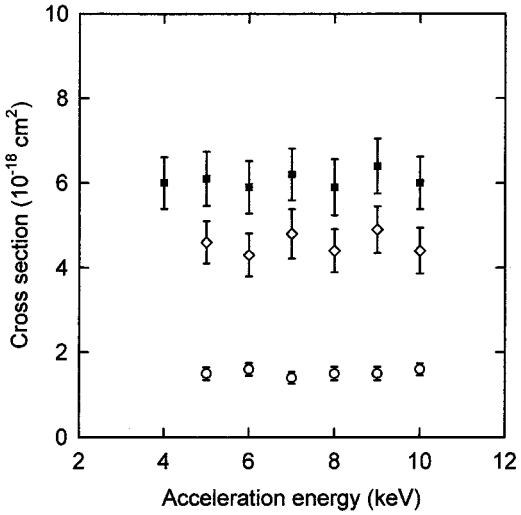

FIG. 3. Cross sections as a function of acceleration energy; solid squares are for the collisional destruction of He_2^+ resulting in He^+ fragments; open circles are those for the H^- fragments resulting from electron capture and ion-pair formation; open diamonds are those for the He^+ fragments resulting uniquely from the dissociative excitation of He_2^+; and the solid squares are those for the total He^+ fragments resulting from the dissociative excitation of He_2^+.

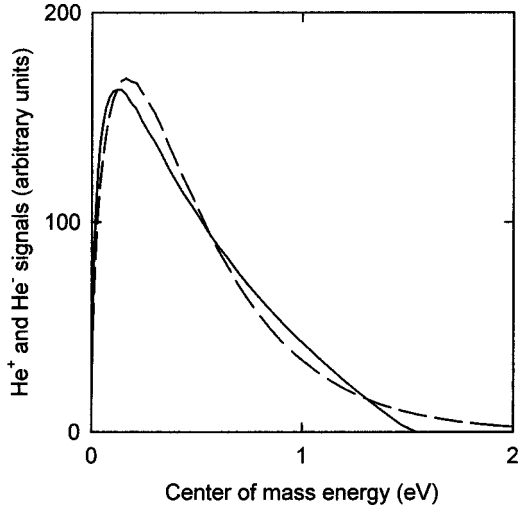

FIG. 4. Center-of-mass energy distribution: solid line for He^- fragments resulting from electron capture that is followed by ion-pair formation and broken line for He^+ fragments resulting from the total dissociative excitation of He_2^+ at 400 mTorr source pressure.

pressure of 100 mTorr, which is the lowest possible working source pressure, since lower pressures lead in to ion-beam intensities that are too low for any meaningful measurements. Hence it is possible to say that the increase in source pressure would not lead into lower internal energy for the He_2^+ ions if they were initially in their ground state and with $\nu=0$. This would explain the behavior of the cross section at low and high source pressure. The vibrational cooling for triatomic molecular ions was found to be effective for triatomic ions in this ion source when the source pressure was increased [12,13]. On the other hand, since the fragments of the process under consideration are of the same mass, the energy liberated by the dissociation processes is shared equally by both fragments, whether positively, negative charged, or neutral, provided they are coming from the same process. The center-of-mass energy distributions for He^+ and He^- fragments are presented in Fig. 4 for source pressure 400 mTorr. It can be seen that both fragments show a center-of-mass energy that peaks around 0.2 eV. If we assume that the initial state is vibrationally excited, the available energy curves [7] shown in Fig. 5 for the $X\ ^2\Sigma_u^+$ ground state of He_2^+ ions indicate that the vibrational levels of $V\geqslant 4$ would lead in to He^+ fragments with a kinetic-energy (KE) release between 0 and about 0.1 eV in the excitation of the $X\ ^2\Sigma_u^+$ state into the repulsive $A\ ^2\Sigma_g^+$ state with the maximum population of the initial state centered around $v=12$, considering that the dissociation energy of He_2^+ ($X\ ^2\Sigma_u^+$) is 2.47 eV and the vibrational energies of the ground state are those from Akermann and Hogreve [16]. The excitation energies were taken using the vibrational energies at the outer turning point of the two internuclear distances R of each of the vibrational levels of $X\ ^2\Sigma_u^+$ [8]. This would lead us to assume that actually the collisional deactivation was not as effective as in the case of triatomic ions and the He_2^+ ions remain with a population of vibrational levels even at source pressures higher than 400 mTorr.

It is also clear that the excitation of $X\ ^2\Sigma_u^+$ ($\nu=0$) in collision with an He target into $A\ ^2\Sigma_g^+$ would lead into He^+ fragments with a K.E. release $\geqslant$3.7 eV in the center of mass,

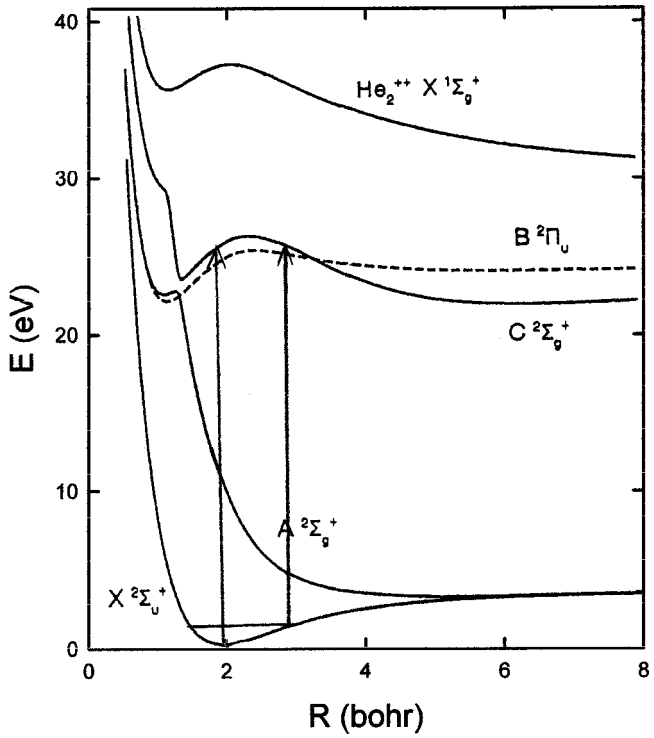

FIG. 5. Potential-energy surfaces for the ground and excited states of He_2^+ taken from Bawagan and Davidson [15] showing ground and excited states of He_2^+. Vertical arrows show the excitation of the vibrational levels $\nu=1$ and 3 of the ground electronic state $X\ ^2\Sigma_u^+$ into the excited $C\ ^2\Sigma_g^+$ state.

yet such fragments are not observed as can be seen in Fig. 4. The absence of fragment ions with such high K.E. release would suggest that the excitation processes in collision of He_2^+ with He target is possibly taking place into higher-lying excited states which is bound at low internuclear separation and repulsive at higher *R*. The dissociative excitation into such state would explain the absence of fragments with a KE release higher than 1.5 eV. In this case the excitation of $X\ ^2\Sigma_u^+$ ($\nu=0-2$) into $C\ ^2\Sigma_g^+$ would not result in fragment He^+ ions, since such excitation is taking place into the bound part of $C\ ^2\Sigma_g^+$ [the outer turning point for $X\ ^2\Sigma_u^+$ ($\nu=2$) is <2.5 bohr], while the excitation of $X\ ^2\Sigma_u^+$ ($\nu \geqslant 3$) into $C\ ^2\Sigma_g^+$ ($R \geqslant 2.5$ bohr) would result in fragment ions with a KE release of less than 1.5 eV, which is in reasonable agreement with the results of this work.

The He^- fragments observed are only possible as a result of the electron capture into an excited He_2 molecule, which is followed by dissociation leading into an ion pair of the fragments of He^+ and He^-. This is possible if the He_2 is in a Rydberg state which may attain a Heitler-London state $He+He^*$, which may end up dissociating into He^+ and He^- fragments [11]. The He^- is stable enough to survive the time of travel between the target and the deflection plates, which is of the order of 1 μs before being detected. Such a process is expected to be rather weak in comparison with the dissociative excitation. This can be clearly seen in Fig. 3. The He^+ resulting from this process contributes to the total measured He^+ signal and cannot be measured directly. Hence under the same conditions, the He^- cross section shown in Fig. 3 should be the same as that of He^+, since they come from the same processes (electron capture and ion-pair formation). Considering that and considering the total cross section for the measured He^+, it is then possible to obtain the cross section for the He^+ fragments resulting uniquely from the dissociative excitation of the He_2^+ in collision with He. The results of that are presented also in Fig. 3.

CONCLUSION

The results presented here show the absolute cross sections for the dissociative excitation of the He_2^+ molecular ion. Also presented here are the absolute cross sections for electron capture and ion-pair formation. Our results show that the initial ions are most likely vibrationally excited and the effect of the vibrational deactivation was negligible. The measured center-of-mass energy of the fragment ions indicates together with the available potential-energy curves that the vibrationally excited ground state may be responsible for the fragment ions. $C\ ^2\Sigma_g^+$ is believed to be the upper final excited state responsible for the resulting fragments. As yet complete theoretical high-lying repulsive potential-energy curves for He_2^+ ions are not fully available, therefore it is not possible to quantitatively establish the final state of the ions.

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