Production of He^+ in He_2^+-He Collisions near Threshold

T. R. Grossheim and J. J. Leventhal
Department of Physics, University of Missouri-St. Louis, 8001 Natural Bridge Road, St. Louis, Missouri 63121

H. H. Harris
Department of Chemistry, University of Missouri-St. Louis, 8001 Natural Bridge Road, St. Louis, Missouri 63121

(Received 24 October 1972)

The relative cross section for production of He^+ in He_2^+-He collisions has been measured near threshold. Convolution integrals taking account of the thermal motion of the target He atoms are numerically calculated for several forms of the threshold cross section and compared to the data. For the threshold laws considered, threshold is in the range 2.0–2.4 eV, in agreement with theoretical values of the dissociation energy of $X\,^2\Sigma_u^+$ He_2^+. By using Liu's recent rigorous lower bound for this dissociation energy, a possible form of threshold law is obtained. The experiments also indicate that significant amounts of He_2^+ resulting from He*-He interactions are formed in excited vibrational-rotational states of the $X\,^2\Sigma_u^+$.

INTRODUCTION

Recent theoretical studies[1] and experiments in gaseous electronics,[2] spectroscopy,[3] atomic collisions,[4] and low-temperature physics[5] have involved the He_2 and He_2^+ molecular species. For much of this work it would be desirable to know the dissociation energy of these species. The experiments reported here were designed to obtain information on the dissociation energy of the He_2^+ ion through study of the reaction

$$He_2^+ + He \rightarrow He^+ + He + He \ . \qquad (1)$$

Since it has been shown that, neglecting zero-point energy differences, the dissociation energy of the $A\,^1\Sigma_u^+$ state of He_2 and the dissociation energy of the $X\,^2\Sigma_u^+$ state of He_2^+ differ by $\sim 6\times10^{-4}$ eV,[6] the experiments provide information about the He_2 molecule also. Recent work by Chantry[7] on the interpretation of threshold data for processes such as reaction (1) as well as theoretical predictions for the threshold behavior of cross sections[8,9] for these processes was further stimulation for the experiment. To employ the method of Chantry to the interpretation of data, a specific form for the energy dependence of the cross section near threshold must be assumed. It was found in these experiments that several forms of cross section produced adequate agreement with the data, and that the threshold energy was between 2.0 and 2.4 eV for all cases considered. This is consistent with previous theoretical work; using Liu's[1] rigorous lower bound for the dissociation energy, a possible form of the cross section is obtained.

The effect of internal excitation of the He_2^+ ions on the threshold behavior was found to be substantial. It is deduced from these experiments that He_2^+ ions produced by the well-known processes[10]

$$e + He \rightarrow He^* + e \ , \quad He^* + He \rightarrow He_2^+ + e \qquad (2)$$

are formed in excited vibrational-rotational states of the $X\,^2\Sigma_u^+$ electronic state. The population of these excited states was reduced by increasing the He-gas pressure in the electron-impact ion source. Evidence will be presented to support the conclusion that above about 0.1 torr the He_2^+ ions are almost totally deexcited when the He_2^+-He collisions occur.

EXPERIMENTAL

A mass- and velocity-selected electron-impact-produced beam of He_2^+ ions was directed into a collision cell containing target He gas at room temperature. Ions emerging from the collision region were mass analyzed with a high-transmission quadrupole mass filter, and detected with the aid of a Channeltron particle multiplier and conventional single-particle counting equipment.

It was found that the electron-accelerating voltage in the source which yielded usable He_2^+ beams was in the range 25–30 V, depending on the He-gas pressure. This pressure was monitored with a conventional ionization gauge located immediately outside the source and calibrated (for He) against an oil manometer mounted directly on the source. The source was never exposed to the manometer while an experiment was in progress. The 127° cylindrical electrostatic velocity selector immediately preceding the collision cell was fixed to transmit ions of 10.0 ± 0.2-eV laboratory or 3.33 ± 0.067-eV center-of-mass kinetic energy. Ions emerging from the velocity selector were accelerated or decelerated to the desired collision energy prior to the He_2^+-He interaction. Since the energy dependence of the cross section for reaction (1) is desired, collection efficiency effects dependent on ion energy through the mass filter were minimized by adjustment of the dc potential of the filter. When He_2^+ ions were transmitted, the potential between

the ion source and the filter was maintained at 32 V for all collision energies. When He^+ ions were transmitted, the dc potential between the collision chamber and the filter was fixed at 17.5 V for all collision energies; this assures that the He^+ energy through the mass filter is constant to within the small excess kinetic energy acquired in the dissociation process. Since the shape of the threshold cross section is desired over a small range of relative energies (about 2 eV), neither this excess kinetic energy nor the increasing maximum scattering angle with increasing kinetic energy is expected to significantly distort the shape of the cross-section–vs–kinetic-energy curve.

TREATMENT OF THE DATA

Chantry[7] has shown that threshold determinations for endothermic processes such as reaction (1) can be severely affected by the spread in relative collision energy introduced by the thermal motion of target molecules even if the incident ion beam is monoenergetic. However, since the distribution function is known, an assumed form of the cross section may be convoluted for comparsion with the data. If E is the true relative He_2^+-He kinetic energy and E_0 is the nominal relative energy ($E = E_0$ at 0 °K), the apparent cross section $\sigma(E_0)$ is given by

$$\sigma(E_0) \propto \int_0^\infty (E/E_0)^{1/2} \sigma(E) f(E_0, E)\, dE , \tag{3}$$

where $\sigma(E)$ is the cross section and $f(E_0, E)$ is the distribution function. $\sigma(E)$ contains the dependence on E_T, the threshold kinetic energy. The nominal kinetic energy is the center-of-mass energy of the incident He_2^+ beam assuming no target-molecule motion. The energy spread of this beam is determined by the geometry of the velocity selector[11] and the beam energy through the selector. The full width at half-maximum (FWHM) of the beam is 0.13 eV in the center-of-mass system, which may be compared to $W_{1/2}$, the FWHM of the center-of-mass energy distribution resulting from thermal motion (300 °K) of the target molecules

$$W_{1/2}(\text{eV}) = 0.44\,[E_0(\text{eV})]^{1/2} . \tag{4}$$

Since the threshold energy is near $E_0 = 2$ eV, $W_{1/2}$ is of the order of 0.6 eV, so that the effects of thermal motion are, indeed, larger than that of the ion-beam energy spread. Evaluation of the convolution integral, Eq. (3) is most easily accomplished under the assumption of a monoenergetic ion beam. Chantry has shown that the effect of ion-beam energy spread may be approximately accounted for by retaining the monoenergetic beam assumption and replacing the temperature with an increased "effective temperature," the calculation of which is based on the beam-energy spread. For these experiments the effective temperature is 330 °K.

Two different functional dependencies of threshold cross section were considered. The first σ_1 is due to a method based on optical-model considerations[8]:

$$\begin{aligned} &\sigma_1(E) = 0, && E < E_T \\ &\sigma_1(E) \propto (E - E_T)^{2.5}/E, && E \geq E_T . \end{aligned} \tag{5}$$

The second form of the cross section considered, σ_2, is that determined by the density of final states for reaction (1). This has been given by Maier[9]:

$$\begin{aligned} &\sigma_2(E) = 0, && E < E_T ; \\ &\sigma_2(E) \propto (E - E_T)\beta/(E)^{1/2}, && E \geq E_T , \ 1 \leq \beta \leq 2 ; \end{aligned} \tag{6}$$

where $\beta = 2$ corresponds to a pure density-of-final-states calculation, and $\beta = 1$ obtains if the interaction mechanism tends to favor certain fixed relative angles of separation of the final three particles.[9]

In comparing the data to the convoluted cross sections, the range over which the threshold law is taken to be valid must be wide enough to include enough points to allow a fit to be made with confidence. On the other hand, the narrower this range, the less the determination is influenced by variations in experimental conditions such as collection efficiency or angular scattering. As noted earlier, efforts have been made to minimize collection-efficiency effects. A criterion set forth in Ref. (7) is that the maximum value of E_0, E_{max}, be at least one half-width of the center-of-mass energy distribution higher than the determined threshold, E_T. The number of half-widths, n, above this threshold is a measure of the confidence which can be placed on the fit. Application of this technique has proven to be successful with values of n as low as 1.0, although a somewhat higher value is desirable.[7] For these experiments

$$n = 4.35\,(E_{max} - E_T)/(E_{max})^{1/2} . \tag{7}$$

RESULTS

Both the observed threshold and the magnitude of the cross section near threshold for reaction (1) were found to be dependent on the He-gas pressure in the ion source. As this pressure was increased, the apparent threshold for reaction (1) was observed to increase and the magnitude of the cross section decreased. Figure 1 illustrates this feature. The open circles represent data taken with He_2^+ ions produced at 0.3-torr ion-source pressure, and the solid circles at 0.013 torr. These results are consistent with the interpretation that He_2^+ ions as initially formed in the source are produced in excited vibrational-rotational states of the $X^2\Sigma_u^+$ ground electronic state. Increasing the pressure increases the number of He_2^+-He collisions that occur before He_2^+ ions emerge from the source so that collisional deexcitation may occur.

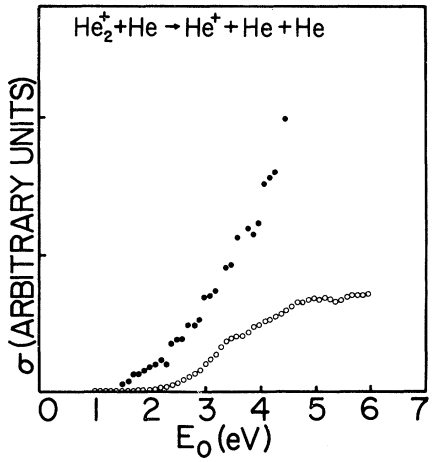

FIG. 1. Relative cross section σ vs nominal kinetic energy (center of mass) E_0. Open circles are data taken at ion-source pressure 0.3 torr, closed circles are at 0.013 torr.

At the lowest ion-source pressure He_2^+ are likely formed by reaction (2). As the pressure is increased other more complex mechanisms of formation can occur, for example, [12]

$$He^+ + 2He \rightarrow He_2^+ + He \ . \qquad (8)$$

Curran[13] has measured the appearance potential for He_2^+ ions formed at low pressure and obtained a value of 23.1 ± 0.05 eV, indicating that the excited states of He which participate in reaction (2) must have energy at least that much above the ground state. The internal-energy change for the second process of reaction (2) is given by

$$\Delta E_0^0 = I(\mathrm{He}) - E(\mathrm{He}) - D_0(\mathrm{He}_2^+) \ , \qquad (9)$$

where $E(\mathrm{He})$ is the internal energy of the He* atom, $D_0(\mathrm{He}_2^+)$ is the dissociation energy of He_2^+ and $I(\mathrm{He})$ is the ionization potential of He (24.58 eV). If the He-He* reaction is to proceed in the source withou initial translational kinetic energy, then $Q \gtrsim 0$. Taking $E(\mathrm{He}) = 23.1$ eV, it may be inferred that $D_0(\mathrm{He}_2^+)$ must be at least 1.5 eV. Most theoretical values of $D_0(\mathrm{He}_2^+)$ for ground-state He_2^+ are in the range 2.0–2.5 eV, indicating that 0.5–1eV can go into the kinetic energy of He_2^+ and the electron and/or vibrational-rotational excitation of the $X\,^2\Sigma_u^+$ state of He_2^+. The ion-source pressure dependence just discussed shows that a significant fraction of this energy does indeed go into internal energy of the He_2^+ molecular ion.

It is desired to perform the dissociation experiment, reaction (1), with ground-state He_2^+ ions. Attempts to produce a beam with all the ions in the ground state were made by raising the He-gas pressure in the source (as well as keeping the electron-accelerating voltage as low as possible). The

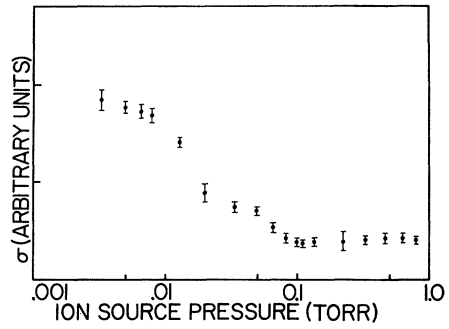

FIG. 2. Relative cross section σ as a function of ion-source pressure for $E_0 = 3.0$ eV.

variation of the cross section as a function of source pressure was investigated at a fixed collision energy in an effort to obtain information on the population of excited states in the beam. Figure 2 shows the results for $E_0 = 3.0$ eV. The constancy of the cross section above ~0.1 torr may be taken as evidence that the beam has reached some constant population of excited states. Clearly it cannot be firmly concluded that this constant population

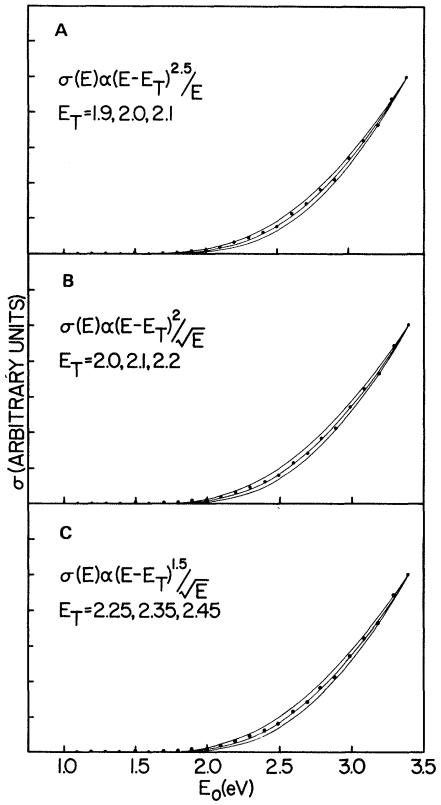

FIG. 3. Relative cross section σ as a function of E_0. The solid circles are the data; the curves are the normalized convoluted cross sections with the indicated values of E_T from left to right, respectively. (a) σ_1, (b) σ_2 ($\beta = 2$), (c) σ_2 ($\beta = 1.5$).

consists only of ground-state ions; however, this seems to be a reasonable assumption. The apparent threshold did not shift when the experiment was performed at ion-source pressures in the range 0.1–0.8 torr.

The data at 0.3-torr ion-source pressure were compared to the threshold behavior obtained from the convolutions of σ_1 and σ_2. Results are shown in Figs. 3(a) and 3(b). E_{max} in these figures is 3.4 eV, corresponding to $n = 3.1$ and 3.3, respectively. The threshold as determined by this procedure was essentially independent of E_{max}. Figure 3(a) the comparison with σ_1, indicates a value of E_T of 2.0 eV. Figure 3(b), the comparison with σ_2(for $\beta = 2$), indicates a value of E_T of 2.1 eV. Both of these values are slightly lower than recent theoretical predictions of the He_2^+ ground-state binding energy. Liu,[1] using configuration-interaction techniques, obtained a rigorous lower bound of 2.454 eV and a best value of 2.469 eV for the binding energy D_e. (D_e does not include subtraction of the zero-point energy, which is of the order of 0.1 eV.[14]) The convolution integral was calculated with $E_T = 2.25$, 2.35, and 2.45 eV and several values of β for σ_2. Figure 3(c) shows the comparison of this calculation with the data for $\beta = 1.5$, the value giving the desired range of E_T; for this threshold $n = 2.5$. For values of $\beta < 1.5$, the data systematically deviate from the convolution integral, regardless of the E_T value chosen.

The inconsistency of the lower bound for D_0 and the value of E_T obtained with σ_2 and $\beta = 2$ may indicate that the three-body phase space is not uniformly populated by the separating atoms. As detailed by Maier[9] the derivation of this threshold law (σ_2) though intuitively appealing is crude, so that agreement with the data and the lower bound produced by a different value of β is not unreasonable. In addition, completely different analytic forms having similar shapes near threshold could give adequate agreement with the data for a particular E_T.

The value of E_{max} in Fig. 3 is 3.4 eV, which involves the assumption that the threshold laws are valid up to at least 1 eV above E_T. This assumption may be unwarranted; however, examination of Fig. 3 shows that E_T is substantially unchanged if lower values of E_{max} are used. For some processes it is known that threshold laws are valid for intervals much smaller than 1 eV[15]; for others (such as single ionization by electron impact)[16] the range may extend several electron volts. It is difficult to estimate the range of validity for the present case: however, the agreement for values of E_{max} lower than 3.4 eV indicates that as long as this range is not less than about 0.5 eV the results obtained here should be valid.

The most serious experimental uncertainties associated with the experiment are the possibility of excited states in the He_2^+ beam and the possibility of loss of He^+ ions due to angular scattering. The latter effect would be most serious at the highest energies above threshold and would tend to lower the determined E_T. The presence of excited states in the He_2^+ beam would permit He^+ to be produced at energies lower than the threshold for dissociation of ground vibronic state He_2^+. An additional complication would be the necessity to modify the threshold law to include the properly weighted linear combination of cross sections for each state present.

ACKNOWLEDGMENTS

The authors wish to thank their colleagues, Dr. P. B. James and Dr. G. R. North, for many discussions of this work. We wish to acknowledge support by Research Corporation in the form of Frederick Gardner Cottrell grants to H. H. H. and J. J. L. One of us (H. H. H.) wishes to acknowledge support by a University of Missouri–St. Louis Summer Faculty Research Fellowship.

[1] B. Liu, Phys. Rev. Lett. **27**, 1251 (1971), and references contained therein.

[2] R. A. Gerber and M. A. Gusinow, Phys. Rev. A **4**, 2027 (1971); P. L. Patterson, Phys. Rev. A **4**, 1154 (1970); D. K. Bohme, N. G. Adams, M. Mosesman, D. B. Dunkin, and E. E. Ferguson, J. Chem. Phys. **52**, 5904 (1970).

[3] M. L. Ginter and C. M. Brown, J. Chem. Phys. **56**, 672 (1972).

[4] R. E. Olson and C. R. Mueller, J. Chem. Phys. **46**, 3810 (1967).

[5] J. W. Keto, M. Stockton, and W. A. Fitzsimmons, Phys. Rev. Lett. **28**, 792 (1972); C. M. Surko and F. Reif, Phys. Rev. **175**, 229 (1968).

[6] M. L. Ginter and R. Battino, J. Chem. Phys. **52**, 4469 (1970).

[7] P. J. Chantry, J. Chem. Phys. **55**, 2746 (1971).

[8] R. D. Levine and R. B. Bernstein, Chem. Phys. Lett. **11**, 552 (1971).

[9] W. B. Maier, II, J. Chem. Phys. **41**, 2174 (1964).

[10] J. A. Hornbeck and J. P. Molnar, Phys. Rev. **84**, 621 (1951).

[11] J. J. Leventhal and G. R. North, Rev. Sci. Instrum. **41**, 120 (1971).

[12] E. C. Beaty and P. L. Patterson, Phys. Rev. 137, A346 (1965); A. V. Phelps and S. C. Brown, Phys. Rev. **86**, 102 (1952).

[13] R. K. Curran, J. Chem. Phys. **38**, 2974 (1963).

[14] G. Herzberg, *Spectra of Diatomic Molecules, Molecular Spectra and Structure*, 2nd ed. (Van Nostrand, Princeton, N.J., 1950), Vol. I; P. N. Reagan, J. C. Browne, and F. A. Matsen, Phys. Rev. 132, 304 (1963).

[15] D. G. Truhlar, J. Chem. Phys. **51**, 4617 (1969).

[16] J. D. Morrison, J. Chem. Phys. **40**, 2488 (1964).