Production of near-zero-energy projectile-frame protons in H_2^+-He collisions at 4 keV

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The dominant processes for producing near-zero-energy projectile-frame protons in H_2^+-He collisions at 4-keV ion energy have been experimentally identified. The $1s\sigma_u$ to $2p\pi_u$ and $3d\sigma_g$ transitions that produce these protons occur at internuclear separations of the H_2^+ ion that are 2.5–3 times the equilibrium separation.

INTRODUCTION

The study of inelastic processes in kilo-electron-volt H_2^+-He collisions continues to be of topical interest. Even though this and the He^+-H_2 system have been the subject of numerous investigations over the past 25 years, many aspects of the various inelastic processes in these systems are not well understood. For example, Quintana *et al.*[1,2] recently reported probabilities for He($n=2$) excitation in 1–3-keV H_2^+-He collisions that are larger than expected from the consideration of molecular-orbital (MO) models.[3,4] Russek and Furlan[5] have recently published initial MO calculations, which provide a qualitative picture of how this excitation can occur at c.m.-to-c.m. separations of less than 0.05 nm.

A large number of previous experiments involve the measurement of H^+ laboratory energy spectra that result from the collision-induced dissociation of H_2^+. A continuing problem in these experiments is the identification of the excited states of H_2^+ that contribute to the proton spectra.[6] This is an important problem since the HeH_2^+ system has become a prototype for the study of the dynamics of atom-molecule collisions. If one hopes to understand this system at a fundamental level, the various inelastic processes must be identified. This paper addresses one aspect of this long-standing identification problem.

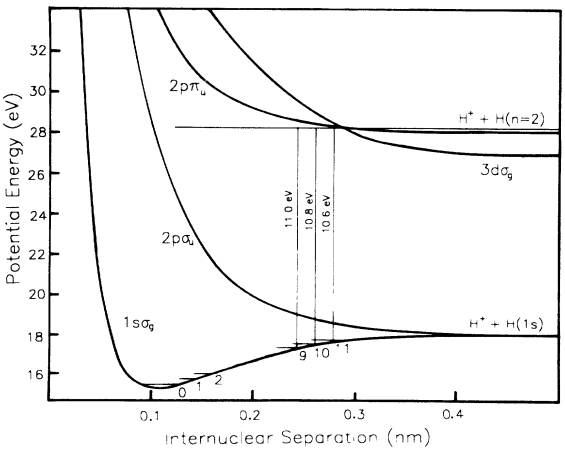

FIG. 1. Relevant electronic states of H_2^+. Location of $v=0,1,2,\ldots,9,10,11$ are also indicated.

The electronic excitation of H_2^+, with the possible exception of the $3d\sigma_g$ and $2p\pi_u$ states at internuclear separations greater than 0.286 nm, leads to direct dissociation into $H^+ + H(nl)$. The bound states of $3d\sigma_g$ can dipole radiate to the antibonding $2p\sigma_u$ state and the $2p\pi_u$ state can radiate to the bound or unbound component of $1s\sigma_g$ state, depending upon the internuclear separation. It has been shown that the $2p\pi_u$ and $3d\sigma_g$ electronic levels support bound vibrational states for internuclear separations greater than about 0.286 nm.[7] At keV collision energies, the rotation and vibration times of H_2^+ are short compared to collision times; therefore, the fixed-nucleus approximation can be used in any description of the collision process. For the case when the final H^+ projectile-frame velocity, upon dissociation, is parallel or antiparallel to the beam direction and assuming no deflection of H_2^+, the H^+ laboratory kinetic energy, due to H_2^+ excitation and dissociation, can readily be written

$$E(H^+)=(E_0-Q)/2+\varepsilon/2\pm\tfrac{1}{2}[(E_0-Q)\varepsilon]^{1/2},$$

where E_0 is the initial kinetic energy of H_2^+, Q is the inelastic energy loss during the collision, and ε is the excitation energy of H_2^+ above the dissociation limit of $H^+ + H(n,l)$. The initial H_2^+ is in a vibrational distribution when produced by ionization of H_2 in an electron impact or H_2-discharge source. Since the electronic eigenenergies are functions of the internuclear separation, a distribution of Q's and associated ε's contributes to a measured H^+ laboratory kinetic energy distribution. Figure 1 shows the bound and excited states that are relevant to our discussion.

EXPERIMENT

A typical H^+ laboratory energy distribution is shown in Fig. 2 for 4-keV H_2^+-He collisions that is similar to that measured by previous investigators.[6] The apparatus used to measure this distribution has been described in our previous work.[8,9] The H_2^+ was formed in a duoplasmatron source; however, for our present measurements, the axial magnetic field of the source was turned

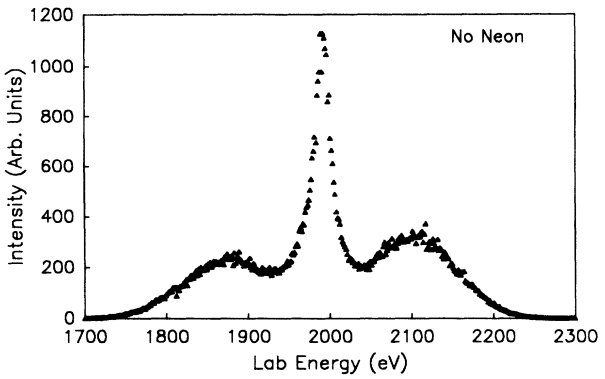

FIG. 2. On-beam-axis laboratory energy spectrum of protons from 4-keV H_2^+-He collisions.

off. After momentum analysis by a magnetic field, the collimated H_2^+ beam was passed through a differentially pumped collison cell maintained at single collision pressures. The kinetic energies of the H^+ produced from H_2^+ excitation and dissociation were measured by a large parallel-plate analyzer placed 0.845 m beyond the collision cell. The acceptance angle of the H^+ detection system at 0° scattering relative to the beam axis was ±0.03°. The distance between the entrance slit of the analyzer and the detector position was 0.5334 m.

The finite-sized detector at 0° is most efficient in collecting protons that have zero or near-zero energy in the c.m. of the moving H_2^+. Thus, the single, central peak in the energy spectra results from protons that dissociate from H_2^+ states with $\varepsilon \cong 0$. Because of this sensitivity the measured laboratory distribution is a maximum at $E(H^+)=(E_0-Q_0)/2$, where Q_0 is the inelastic energy loss associated with transitions to levels of H_2^+ that dissociate with near-zero kinetic energy. The energy loss Q_0 may also have a distribution of values, depending upon the processes that contribute to near-zero-energy protons.

DISCUSSION

Several experimental studies have been directed toward the understanding and identification of the exact processes that produce near-zero-energy protons from the collision-induced dissociation of H_2^+. Fournier *et al.*[6] have most recently discussed some of these and include (a) $1s\sigma_g \rightarrow 2p\sigma_u$ electronic excitation from highly excited vibrational states at very large internuclear separation; (b) vibrational excitation into the continuum, with H_2^+ remaining in the electronic ground state; and (c) predissociation from collisionally produced vibrationally and rotationally excited, quasibound states, by tunneling through the angular momentum barrier.

We have included in Fig. 1 another process, namely, direct electronic excitation of the $2p\pi_u$ and $3d\sigma_g$ states from $1s\sigma_g$ vibrational levels at or near $v=11$. The energies of the $2p\pi_u$ and $3d\sigma_g$ states cross near an internuclear separation of $R=0.286$ nm. This crossing also occurs at an energy that nearly coincides with the $H^+ + H(n=2)$ dissociation limit, so any excitation of these two levels near $R=0.286$ nm, with $\varepsilon \geq 0$, would give rise to protons of near-zero energy in the H_2^+ c.m. frame. Even with $\varepsilon=40$ meV, the dissociation time is on the order of 10^{-13} sec. It also should be noted that the $2p\pi_u$ state has a 40-meV potential barrier at an internuclear separation $R \cong 4$ nm. The indicated electronic excitation at $R=0.286$ nm would give an inelastic energy loss of $Q_0 \cong 10.6$ eV or slightly larger.

The three processes previously mentioned would give inelastic energy losses in the range of 0, 0–3.2, and 0–3.2 eV, respectively. If target excitation were to occur during the excitation, one would need to add another 20 eV to all of these numbers. We mention this possibility because Peek[10] has shown that within the Born approximation there is also the possibility of simultaneous target and H_2^+ excitation. Also the recent experimental and theoretical work of Quintana *et al.*[1] and Russek and Furlan[5] has shown that the target excitation channel in H_2^+-He collisions is readily accessible at small collision distances. At such distances, temporal distortion of the electron cloud, around the three nuclei, during the collision, would change the screening and the interaction force between the two protons. Such a transient change in the effective proton-proton interaction, during the collision, could lead to vibrational excitation to the continuum of the ground electronic state.

From the measured position of the central peak of the H^+ energy distribution, we have determined the value of $(E_0-Q_0)/2$ for 4-keV H_2^+ energies. This energy was chosen to study in detail, because it is in this energy region where the H_2^+ excitation and dissociation into $H(2p)+H^+$ has the largest cross section.[11] We find from 25 separate measurements a value of $Q_0=11.6\pm1.0$ eV, where the quoted error is one standard deviation. Within experimental error, this corresponds to the value of $1s\sigma_g \rightarrow 2p\pi_u$ or $1s\sigma_g \rightarrow 3d\sigma_g$ transitions at or near the internuclear separation of $R \cong 0.286$ nm. The $2p\pi_u$ state leads to $H^+ + H(2p_{\pm 1})$, upon dissociation, with the internuclear axis as the axis of quantization, and the $3d\sigma_g$ state leads to the Stark state, with equal contributions of $H^+ + H(2s)$ and $H^+ + H(2p_0)$.

Thus our initial conclusion from the measurement of Q_0 is that when high vibrational states of H_2^+ are present with sufficient probability ($v \approx 9$ or greater), the dominant process for producing near-zero-energy protons is electronic transitions from the ground $1s\sigma_g$ to the $2p\pi_u$ or $3d\sigma_g$ states, even though these initial vibrational states are not the most highly populated. An H_2^+ vibrational distribution, given by the Franck-Condon overlap of the H_2 ground vibrational state and the vibrational states of the $1s\sigma_g$ state, suggests that about 5% of the H_2^+ ions are in the $v=9$ to $v=11$ vibrational states.[12] We cannot experimentally distinguish between the $2p\pi_u$ and the $3d\sigma_g$ states from analysis of the H^+ states.

To test this conclusion further, we tried to alter the vibrational distribution of the H_2^+ inside the source by using a mixture of Ne and H_2, rather than just H_2. Herman and Pacak[13] have shown that for an electron-impact

source, the reaction at thermal energies within the source,

$$H_2^+(v)+Ne \rightarrow HNe^+ + H ,$$

occurs for H_2^+ vibrational quantum numbers $v \geq 2$ and not for $v=0,1$. When the $p(Ne)p(H_2)$ pressure in their source was run at a 5/1 ratio, the extracted H_2^+ was almost exclusively in the $v=0,1$ states.

We measured nine different H^+ dissociation spectra, all at different $p(Ne)/p(H_2)$ source pressure ratios. The construction of the source did not permit the direct measurement of the source pressure; however, with a quadrupole mass spectrometer, we were able to monitor the ratio in the extractor–einzel-lens region directly outside the source. We varied this ratio from 1.25 to 15. As the $p(Ne)/p(H_2)$ ratio in the source increased, we found that the peak position of the central peaks of the laboratory H^+ spectra decreased in energy, indicating an increasing effective Q. All of the measured values of the inelastic energy loss, as determined from the peak position of the H^+ spectrum, increased upon the insertion of Ne into the source. For example, at a $p(Ne)/p(H_2)$ pressure ratio of 1.25, $Q=14.0\pm1.0$ eV; at $p(Ne)/p(H_2)=5$, $Q=13.0\pm1.5$ eV; and at $p(Ne)/p(H_2)=15$, $Q=21.0\pm1.0$ eV. Here the quoted errors represent the range of three separate measurements at each pressure ratio.

We also found that the central peak of the laboratory energy distribution decreased relative to the "side peaks," indicating a relative decrease in the number of near-zero-energy protons. This effect is shown in the proton spectrum of Fig. 3 taken when the $p(Ne)/p(H_2)$ pressure ratio was 15/1.

Fournier *et al.*[6] found a similar behavior in the central peak by varying the vibrational distribution using a variable-energy–electron-impact source. The relative height of their central peak compared to the side peaks was the lowest when their electron energy was just sufficient to ionize H_2 to the lowest three vibrational states. The peak increased in size as the electron energy increased and as higher vibrational states in the source were populated.

We conclude that the insertion of Ne into the source does indeed depopulate the upper H_2^+ vibrational levels, at least to a degree that processes other than $1s\sigma_g \rightarrow 2p\pi_u, 3d\sigma_g$ electronic transitions become relatively important in producing near-zero c.m.-energy protons. The other possible processes have been mentioned earlier. Fournier *et al.*[6] did not consider this electronic process.

We must also consider the possible effect of significant deflection of the H_2^+ during the collision and the effect of it upon the interpretation of the data. Meierjohann and Vogler have experimentally shown that electronic excitation of H_2^+ in H_2^+-He collisions at 10 keV occurs only for H_2^+ scattering angles of less than 0.10°.[14] This extrapolates to 0.25° for a 4-keV energy if we assume, as in the diatom case, that the product of the laboratory scattering angle and incident ion energy, θE, is a measure of the distance of closest approach. The question arises, whether in the case of 0.25° scattering, there is any alteration of the interpretation of the shift in central peak of the energy spectra. In Fig. 4(a) we schematically show the Newton diagram whereby the H_2^+, with initial momentum $\mathbf{P}_0$, is deflected through some laboratory angle θ_s, with a resulting final laboratory momentum $\mathbf{P}_L$ before dissociation. The recoil momentum of the He target is $\mathbf{P}_R$.

One would still observe a single peak in the H^+ laboratory energy spectrum, on the beam axis, if $\mathbf{v}_{c.m.}$ of the H^+ upon dissociation were 90° to the beam axis, as shown in Fig. 4(b), where $\mathbf{V}_P$ is the H^+ laboratory velocity at the single central peak position. Angles, other than 90°, would result in pairs of front-back peaks relative to the central peak.

From the elementary energy and momentum considerations suggested by Fig. 4 one can show for a given θ_s that the central peak position energy of H^+ can be written

$$E_p(H^+)=E_0/2-(Q_i+\varepsilon+E_R)/2 ,$$

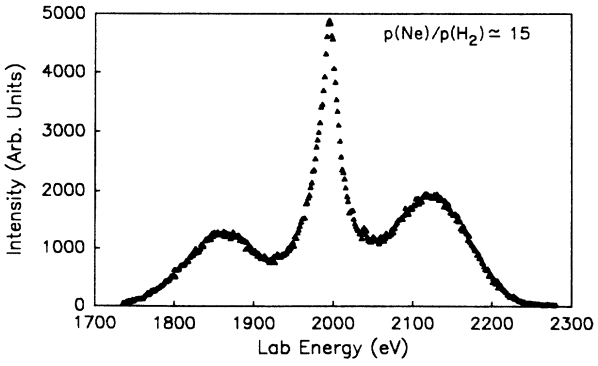

FIG. 3. On-beam-axis laboratory energy spectrum of protons from 4-keV H_2^+-He collisions, with $p(Ne)/p(H_2)$ source ratio 15/1.

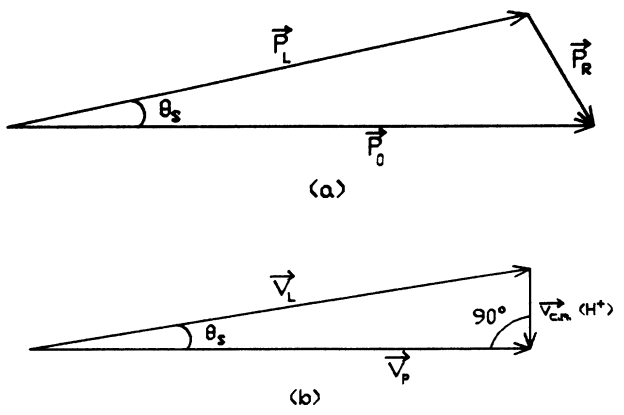

FIG. 4. (a) Momentum scattering diagram when H_2^+ suffers deflection. (b) Velocity diagram necessary to produce a single proton energy peak, if H_2^+ suffers deflection.

where Q_i is the combined inelastic excitation energy of the target and projectile, ε is the excitation energy of H_2^+ above the dissociation limit, and E_R is the recoil energy imparted to the He target.

The shift of this central peak from $E_0/2$ is a measure of the second term above if H_2^+ deflection occurs for a *majority* of the observed protons. Experimentally, we have measured this term to be from 11.6–21 eV, depending upon the $p(\mathrm{Ne})/p(H_2)$ concentration ratio in the source.

As we have pointed out, we expect c.m. deflections of less than 0.25°. The values of Q_i and ε, for any given scattering angle, and any *measured* shift $(Q_i+\varepsilon+E_R)$, must be consistent with the energy-level diagrams of the H_2^+, and He systems. We also require that $Q_i > \varepsilon$.

The recoil energy E_R of the He target is not strongly dependent upon Q_i. For a scattering angle of $\theta_s = 0.50°$, E_R varies from 0.15 to 0.18 eV as Q_i varies from 10 to 30 eV. From Fig. 4, we can determine that $\varepsilon = (E_0 - Q_i - E_R)\sin^2\theta_s$. Using this value of ε in the expression for the shift of the peak position, we find that for $\theta_s = 0.5°$ the Q_i is 0.5 eV less than the Q determined when no H_2^+ scattering was assumed. Thus the original Q of 11.6 eV would have to be decreased by about 0.5 eV if significant deflection occurred. Such a decrease would not change the interpretation of the data regarding the process that produces near-zero-energy protons.

We have also shown that by depleting the higher vibrational states, $v=9$ through 11, the inelastic energy loss for the reaction that produces near-zero-energy protons shifts to 21 eV. Such an inelastic energy loss is consistent with simultaneous excitation of the He target and vibrational excitation of H_2^+ to the continuum and is consistent with the latest work of Quintana *et al.*[1] and Russek and Furlan.[5]

CONCLUSION

We have provided experimental evidence that the dominant process for producing near-zero-energy protons in H_2^+-He collisions, at 4-keV collision energy, is electronic excitation from high vibrational states of the bound $1s\sigma_g$ electronic state to the $2p\pi_u$ and/or $3d\sigma_g$ antibonding states. Such transitions occur for large proton-proton separations of 0.286 nm, which are 2.5–3 times the equilibrium separation. It is interesting that at large internuclear separations these electronic transitions have larger probabilities than transitions to the $2p\sigma_u$ state. The mechanism for such transitions is not yet known. We have also shown that the vibrational distribution of the H_2^+ ion can be altered by insertion of Ne in the H_2 discharge source.

ACKNOWLEDGMENTS

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