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Angular Distribution of Protons from Collisional Dissociation of H_2^+. I.

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The theory of the angular distribution of H_2^+ dissociation fragments resulting from H_2^+ collisions with neutral or charged targets is developed in the Born approximation. Earlier formulations of the problem are corrected and generalized. Calculations of the angular distributions for collisions which leave the H_2^+ in the $2p\sigma_u$, $2s\sigma_g$, and $2p\pi_u$ electronic states are carried out for He and Ar targets. It is assumed that the target either remains in its ground electronic state or undergoes an allowed transition. It is shown that the angular distributions vary considerably with the final H_2^+ electronic state considered, with the final kinetic energy of the H_2^+ fragments, with the final state of the target, and with the H_2^+ impact energy. Angular distributions for transitions to highly excited and ionized states of H_2^+ are considered in a qualitative way.

I. INTRODUCTION

In the past three years several measurements of the relative angular distribution of the protons resulting from H_2^+ dissociation during collisions with neutral targets have been reported.[1–5] In the more recent experiments the velocity distribution of the protons was also measured. The angular distributions, particularly when transformed to the center of mass (c.m.) frame of H_2^+, are markedly anisotropic and change their angular dependence rather rapidly as the final c.m.

dissociation velocity is varied. The theoretical analysis of the angular distributions is rather treacherous because the observation of a proton of given energy does not fix the final state of the scattering system. A number of final states have to be considered, therefore, if the analysis is to be meaningful. Also, we can expect the initial distribution of H_2^+ vibrational states to contribute both to the complexity of the problem and to the structure of the angular distributions.

This paper is the first of three papers aimed at interpreting the experimental results in a semiquantitative way. In this paper the theory of H_2^+ dissociation-fragment angular distributions is first developed in Born approximation. It is then applied to the dissociation of H_2^+ via its electronic excitation during collisions with He and Ar. The second paper presents an essentially classical evaluation of the dissociation angular distribution for vibrational dissociation of H_2^+. In the third paper the results of the first two are used to interpret the experimental data.

The main numerical results of this paper are c.m. proton angle and velocity distributions for H_2^+ dissociation via electronic excitation of the $2p\sigma_u$, $2p\pi_u$, and $2s\sigma_g$ states of H_2^+. The angle and velocity distributions are sufficiently distinctive that it should be possible in favorable circumstances to identify contributions from these states to the experimental angle and velocity distributions. It is also shown that simultaneous excitation of an allowed transition in the target can profoundly alter the distributions. Most of the comparisons with experiment are deferred until the third paper because the theory of vibrational dissociation (Paper II) is completely different from that presented below and requires considerable discussion itself. The inclusion of everything in a single paper would result in one which is too long and too full of details to be readable.

The theoretical section of this paper corrects an error in previous formulations of the dissociation problem and generalizes earlier treatments in such a way that excited H_2^+ states of all symmetry classes can be treated. The theoretical section also details in a systematic way the the additional approximations, over and above the use of the Born approximation, which were used to obtain the computational formulae for the cross sections.

The use of the Born approximation at the presently available experimental energies (10–20 keV) is open to serious question. However, a more sophisticated calculation – taking account of electron exchange, distortion, and probability conservation, for example, would be prohibitively complicated. At present, the best evidence for the approximate validity of the Born approximation comes from Refs. 3–5, where it is shown that the Born relative angular distributions for dissociation from the $2p\sigma_u$ state of H_2^+ are in qualitative agreement with some of the basic features of the measured angular distributions. Additional and more meaningful comparisons between Born theory and experiment will be made possible by the work presented below.

The theory is developed in Sec. II. The calculations are described in Sec. III, where representative results are shown graphically. Section IV contains relative angular distributions in tabular form for two selected cases. Additional tables, described in Sec. IV, can be obtained from the authors. The Appendix contains a description of how the necessary H_2^+ and target transition matrices were obtained, and a discussion of their accuracy.

II. THEORY

The primary object of this section is to set down the Born-approximation formula for the dissociation cross section and to show what additional approximations are involved in getting from this formula to the one actually used for computation. The formulation is nonrelativistic. The development differs from the conventional presentation as regards the specification of the H_2^+ final state. Therefore this matter is also discussed along the way. The theory is compared with previous theoretical work at the end of the section.

Let the H_2^+ protons be initially treated as distinguishable and given labels A and B. Consider a collision in which H_2^+ dissociates with final c.m. momentum k into the proton B, going in the c.m. direction $\hat{k}$, and the hydrogen atom A, in the nlm quantum state, going in the direction $-\hat{k}$. Let the H_2^+ ion be initially in the $1s\sigma_g$ electronic state and in the vibration-rotation state labeled by $\nu N'M'$. Let the sum over m and average over M' be taken. In first Born approximation the cross section for these collisions is[6]

$$\frac{dQ_\nu(B)}{dk\,d\Omega(\hat{\vec{\mathrm{k}}})} = 4\left(\frac{k}{V_0}\right)^2 \int_{k_0-k_n}^{k_0+k_n} dK\,K^{-3}|\epsilon_T|^2 \times \int_0^{2\pi} d\phi_K \frac{1}{2N'+1} \sum_{mM'} |E_B(-\vec{\mathrm{K}},\vec{\mathrm{k}})|^2 . \tag{1}$$

Here the argument or subscript B indicates that proton B comes off in the direction $\hat{k}$. The vector $\vec{\mathrm{K}}$ is the momentum transferred to the target and ϕ_K is its azimuthal angle in the laboratory frame.[7] Also, $k_0 = \mu V_0$ and $k_n = \mu V_n$, where μ is the H_2^+-target reduced mass, and V_0 and V_n are the relative velocities before and after the collision. The target transition (if any) is described by $|\epsilon_T|^2$; this function of K^2 is discussed in the Appendix but will play no active role in this section. The quantity $E_B(\vec{K},\vec{k})$ describes the H_2^+ transition

$$E_B(\vec{K},\vec{k}) = \int d\vec{R} \int d\vec{r}\, \Psi_B(\vec{k};\vec{r},\vec{R})^* \times [\exp(i\vec{K}\cdot\vec{r}) - 2\cos(\tfrac{1}{2}\vec{K}\cdot\vec{R})] \times \phi_0[\vec{r}\,',R]\, Y_{N'M'}(\theta\psi) R_{\nu N'}(R)/R . \tag{2}$$

Here $\vec{R}$ is a vector going from proton A to proton B and having polar angles $\theta\psi$ in the laboratory frame; $\vec{r}$ locates the H_2^+ electron with respect to the c.m. of the two protons.

The function

$$\phi_0[\vec{r}\,',R]\, Y_{N'M'}(\theta\psi) R_{\nu N'}(R)/R$$

is the initial H_2^+ wave function in the Born-Oppenheimer approximation. Here $\phi_0[\vec{r}\,',R]$ is the $1s\sigma_g$ fixed-nuclei electronic eigenfunction and the other notation is standard.[8] The H_2^+ final-state wave function is $\Psi_B(\vec{k};\vec{r},\vec{R})$. It will now be described.

By definition $\Psi_B(\vec{k};\vec{r},\vec{R})$ is an H_2^+ eigenfunction which for large R tends toward an atomic-hydrogen eigenfunction $\psi(nlm;\vec{r}_A)$, centered on proton A, times a function of $\vec{R}$ which has the outgoing part of a plane wave, plus incoming parts. This boundary condition on $\Psi_B(\vec{k};\vec{r},\vec{R})$ guarantees that the arrival of a proton at a counter in the c.m. direction $\hat{k}$ is correlated with the arrival of an $H(nlm)$ atom in the opposite direction. We wish to construct $\Psi_B(\vec{k};\vec{r},\vec{R})$ as an expansion in terms of Born-Oppenheimer molecular eigenfunctions. To this end, the atomic-hydrogen eigenfunction, $\psi(nlm;\vec{r}_A)$, which is quantized in the laboratory frame, is first transformed to a molecule-fixed frame according to

$$\psi(nlm;\vec{r}_A) = \sum_{\Lambda=-l}^{l} \mathfrak{D}^{(l)}_{\Lambda m}(0\theta\psi)\,\psi(nl\Lambda;\vec{r}_A\,') . \tag{3}$$

The molecule-fixed frame is the one defined by Thorson[9] in terms of a rotation through angle ψ about the z axis followed by a rotation through angle θ about the new y axis. The rotation matrices $\mathfrak{D}^{(l)}{}_{\Lambda m}(0\theta\psi)$ are those given by Edmonds.[10] The vectors $\vec{r}_A$ and $\vec{r}_A\,'$ locate the electron with respect to proton A, and the prime or lack of it indicates that the spherical harmonics in $\psi(nlm;\vec{r}_A)$ are functions of the polar angles of $\vec{r}_A$ in the molecule fixed or laboratory frame, respectively.

Next, the $\psi(nl\Lambda;\vec{r}_A\,')$ are expressed in terms of H_2^+ electronic eigenfunctions for $R\to\infty$. The connection is determined by the long-range interaction (Stark effect) of the hydrogen atom and the distant proton.[11] We write, for $R\to\infty$,

$$\psi(nl\Lambda;\vec{r}_A\,') = \sum_{\alpha=|\Lambda|}^{n-1} S_{\alpha l}\, 2^{-1/2} \{\phi_g[n\Lambda\alpha;\vec{r}\,',R] + \phi_u[n\Lambda\alpha;\vec{r}\,',R]\} , \tag{4}$$

where $S_{\alpha l}$ is a unitary matrix, g and u stand for gerade and ungerade, and $n\Lambda\alpha$ labels the Born-Oppenheimer eigenfunctions, in separated atom notation. If $\psi(nlm;\vec{r}_A)$ of Eq. (3) is now multiplied by the spherical-harmonic expansion of

$$(2\pi)^{-3/2}\exp(i\vec{k}\cdot\vec{R}),$$

the radial parts of the expansion can be modified so as to produce the required expansion of $\Psi_B(\vec{k};\vec{r},\vec{R})$ in terms of Born-Oppenheimer eigenfunctions for H_2^+. The result, obtained through the use of the Clebsch-Gordan series, is

$$\Psi_B(\vec{k};\vec{r},\vec{R}) = \sum_{N=0}^{\infty} \sum_{M} \sum_{\Lambda} \sum_{\alpha} \sum_{J=|N-l|}^{N+l} \left(\frac{2}{\pi}\right)^{\frac{1}{2}} Y_{NM}(\hat{k})^* \times S_{\alpha l}[(2N+1)/4\pi]^{1/2} C(NlJ;Mm)C(NlJ;0\Lambda)2^{-1/2} \times \{\exp(\tfrac{1}{2}i\lambda\pi - i\delta_g)\phi_g[n\Lambda\alpha;\vec{r}\,',R]\,\mathfrak{D}_{\Lambda,M+m}{}^{(J)}(0\theta\psi) \times R_g(k,R)/R + u\text{ term}\} . \tag{5}$$

In Eq. (5) $C(NlJ;M_1M_2)$ is the Clebsch-Gordan coefficient in the notation of Rose.[12] The function $R_g(k,R)$ is the regular solution of the radial equation associated with the gerade molecular state $(n\Lambda\alpha)$. As $R\to\infty$,

$$R_g(k,R) \to k^{-1}\sin(kR - \tfrac{1}{2}\lambda\pi + \delta_g) . \tag{6a}$$

$$\text{Also,}\quad \lambda(\lambda+1) = J(J+1) - \Lambda^2 . \tag{6b}$$

Inside { } in Eq. (5) the notation $+u$ term means the addition of the completely analogous ungerade term. Equations (5), (2), and (1) provide explicit formulae for the cross section. Since Eq. (5) involves the Born-Oppenheimer approximation, $\Psi_B(\vec{k};\vec{r},\vec{R})$ is not an exact H_2^+ eigenfunction. A more complicated expansion would be required to obtain a better approximation.

At this point, before introducing any additional approximations, it is desirable to discuss the final-state function $\Psi_B(\vec{k};\vec{r},\vec{R})$ in relation to the symmetry properties of the dissociation-fragment angular distribution. According to Eq. (5) $\Psi_B(\vec{k};\vec{r},\vec{R})$ is a superposition of g and u H_2^+ eigenfunctions. This choice of final-state differs[13] from the customary one[14–18] which is based on a single g or u electronic state. As shown in Ref. 13 and below, the customary choice of final state implies that the arrival of a proton at a counter in the direction $\hat{k}$ is correlated with the arrival of a proton in the direction $-\hat{k}$ and with the arrival of H atoms in both directions. This is evidently not the right boundary condition for dissociation. Rather, as is the case for $\Psi_B(\vec{k};\vec{r},\vec{R})$, the arrival of a proton at a counter in the direction $\hat{k}$ should be correlated only with the arrival of an H atom at a counter in the direction $-\hat{k}$.

With the customary choice of final state, the c.m. dissociation fragment angular distribution is symmetric about an angle of 90° with respect to the H_2^+ beam.[13] In Ref. 13 it was shown for dissociation into a proton and a ground-state hydrogen atom that when the proper final state is used, the angular distributions need not be symmetric. The analogous proof for the hydrogenic nlm state will now be given. The argument is based on the symmetry properties.

$$\begin{aligned}\phi_g[n\Lambda\alpha;\vec{r},-\vec{R}]&=\phi_g[n-\Lambda\alpha;\vec{r},\vec{R}]\ ,\\ \phi_u[n\Lambda\alpha;\vec{r},-\vec{R}]&=-\phi_u[n-\Lambda\alpha;\vec{r},\vec{R}]\ ,\end{aligned}\tag{7}$$

satisfied by the electronic eigenfunctions when these are expressed in terms of coordinates defined in the laboratory frame. Let the g and u contributions to $\Psi_B(\vec{k};\vec{r},\vec{R})$ and $E_B(\vec{K},\vec{k})$ be isolated, using the definitions,

$$\begin{aligned}\Psi_B(\vec{k};\vec{r},\vec{R})&=2^{-1/2}\,\{\Psi_g(\vec{k};\vec{r},\vec{R})+\Psi_u(\vec{k};\vec{r},\vec{R})\},\\ E_B(\vec{K},\vec{k})&=2^{-1/2}\{E_g(\vec{K},\vec{k})+E_u(\vec{K},\vec{k})\}\ .\end{aligned}\tag{8}$$

From Eqs. (7), (8), (5), and (2), it can be shown that

$$\begin{aligned}\Psi_g(\vec{k};\vec{r},-\vec{R})&=(-1)^{l}\Psi_g(-\vec{k};\vec{r},\vec{R}),\\ \Psi_u(\vec{k};\vec{r},-\vec{R})&=(-1)^{l+1}\Psi_g(-\vec{k};\vec{r},\vec{R}),\\ E_g(\vec{K},-\vec{k})&=(-1)^{l+N'}E_g(\vec{K},\vec{k}),\\ E_u(\vec{K},-\vec{k})&=(-1)^{l+N'+1}E_g(\vec{K},\vec{k}).\end{aligned}\tag{9}$$

Let $\Theta\Phi$ be the polar angles of $\hat{k}$ in the H_2^+ c.m. frame.[7] The transformation $\hat{k}\to-\hat{k}$ then corresponds to the transformation $\Theta\to\pi-\Theta$, $\Phi\to\pi+\Phi$. In addition, from the symmetry properties of the functions which appear in Eq. (2) it can be shown that $\int d\phi_K\cdots$ in Eq. (1) is independent of Φ. Therefore with $E_B(\vec{K},\vec{k})$ expressed in terms of g and u amplitudes through Eq. (8), it follows from Eqs. (9) and (1) that $dQ_\nu(B)/dkd\Omega\,(\hat{k})$ is a sum of two contributions which are symmetric with respect to $\Theta=\frac{1}{2}\pi$ and a contribution which is antisymmetric with respect to $\Theta=\frac{1}{2}\pi$. The symmetric terms come from the first-two terms of

$$|E_B(\vec{K},\vec{k})|^2=\tfrac{1}{2}[|E_g(\vec{K},\vec{k})|^2+|E_u(\vec{K},\vec{k})|^2+2\mathrm{Re}\{E_g(\vec{K},\vec{k})E_u(\vec{K},\vec{k})^*\}],\tag{10}$$

while the antisymmetric term comes from the g-u cross term. Here Re{ } means the real part of { }. If the requirements of the Pauli exclusion principle for the H_2^+ protons are ignored, the cross section for dissociation in which proton A comes off in the direction $\hat{k}$ must be added to $dQ_\nu(B)/dkd\Omega\,(\hat{k})$ in order to get the angular distribution of protons. It is easy to show that this doubles $d\Omega_\nu(B)/dkd\Omega\,(\hat{k})$. If the requirements of the exclusion principle are taken into account, the correct final-state wave functions for dissociation into a proton going in the direction $\hat{k}$ and an atom going in the opposite direction are

$$\Psi_p^{(\pm)}(\vec{k};\vec{r},\vec{R})=2^{-1/2}\{\Psi_B(\vec{k};\vec{r},\vec{R})\pm\Psi_B(\vec{k};\vec{r},-\vec{R})\}\tag{11}$$

for proton singlet or triplet states, respectively. The amplitudes $E_p^{(\pm)}(\vec{K},\vec{k})$ for these functions can be shown to satisfy

$$\begin{aligned}E_p^{(\pm)}(\vec{K},\vec{k})&=2^{\frac{1}{2}}E_B(\vec{K},\vec{k})\\ &=E_g(\vec{K},\vec{k})+E_u(\vec{K},\vec{k}),\end{aligned}\tag{12}$$

through the use of Eqs. (7), (8), (9), and (2), provided it is remembered that N' must be even for proton singlet states and odd for proton triplet states. Thus no matter how the identity of the protons is handled, the cross section for dissociation into a proton going in c.m. direction $\hat{k}$ is obtained by inserting

$$E_g(-\vec{K},\vec{k})+E_u(-\vec{K},\vec{k})=2^{1/2}E_B(-\vec{K},\vec{k})$$

in place of $E_B(-\vec{K},\vec{k})$ in Eq. (1). It is evident from Eq. (10) that had a single g or u electronic state been used to describe the final H_2^+ state, the resulting angular distribution would have been symmetric about $\Theta=\frac{1}{2}\pi$. This point appears to be important since some of the observed angular distributions[3, 13] show marked departures from symmetry about $\Theta=90°$.

The antisymmetric g-u interference term in Eq. (10) does not contribute to the total cross section. Hence, the customary choice of final-state wave functions does lead to correct results for the total dissociation cross sections.[16, 17]

We now return to the task of obtaining the formulae from which the amplitudes $E_g(\vec{K}, \vec{k})$ and $E_u(\vec{K}, \vec{k})$ are actually calculated. The approximations to be discussed do not apply to vibrational dissociation [$E_g(\vec{K}, \vec{k})$ for the $1s\sigma_g$ state]; this case will be treated approximately in the second paper of this series.

The insertion of the g part of Eq. (5) into Eq. (2) shows that $E_g(\vec{K}, \vec{k})$ involves integration over R of expressions containing the quantity

$$\epsilon_g(\vec{K}, \vec{R}) = \int d\vec{r}\, \phi_g[n\Lambda\alpha; \vec{r}\,', R]^* \exp(i\vec{K}\cdot\vec{r})\phi_0[\vec{r}\,', R]. \tag{13}$$

As can be seen from Ref. 6 for example, the $\epsilon_g(\vec{K}, \vec{R})$ and the analogous quantities $\epsilon_u(\vec{K}, \vec{R})$ figure in all Born-approximation calculations of H_2^+ electronic excitation. If they are expanded in terms of spherical harmonics, the angular integrals in $\int d\vec{R}$ can be carried out analytically yielding a spherical-harmonic expansion for $E_g(\vec{K}, \vec{k})$ or $E_u(\vec{K}, \vec{k})$ containing known coefficients, phase shifts, and radial matrix elements. As it would be prohibitively time consuming to evaluate these expressions exactly, an approximation is introduced at this point. We suppose (for electronic excitation only) that the important values of J and N which appear in the expansion of $E_g(\vec{K}, \vec{k})$ are such that $\lambda\frac{1}{2}\pi - \delta_g$, and $R_g(k, R)$ are only weakly dependent on $J(N)$. These quantities are then replaced by their values for $J = J_0$, where J_0 is fixed, independent of N.[19] When this approximation is made $\Psi_g(\vec{k}; \vec{r}, \vec{R})$ simplifies considerably, for the sums over J, N, and M can be carried out. The result is

$$\begin{aligned}\Psi_g(\vec{k}; \vec{r}, \vec{R}) = {}& (2/\pi)^{1/2}\delta(\hat{k} - \hat{R})\textstyle\sum_\Lambda\sum_\alpha S_{\alpha l} \\ & \times \mathfrak{D}^{(l)}{}_{\Lambda m}(0\Theta\Phi)\exp(\tfrac{1}{2}i\lambda\pi - i\delta_g) \\ & \times \phi_g[n\Lambda\alpha; \vec{r}\,', R]R_g(k, R)/R.\end{aligned} \tag{14}$$

In Eq. (14) $\delta(\hat{k} - \hat{R})$ is the Dirac δ function, $\Theta\Phi$ are the polar angles of $\hat{k}$ in the H_2^+ c. m. frame, and it is understood that $(\frac{1}{2}\lambda\pi - \delta_g)$ and $R_g(k, R)$ are evaluated with $J = J_0$. When Eq. (14) is used to evaluate $E_g(\vec{K}, \vec{k})$ the result is

$$\begin{aligned}E_g(\vec{K}, \vec{k}) = {}& (2/\pi)^{1/2}\textstyle\sum_\Lambda\sum_\alpha S_{\alpha l}{}^* \\ & \times \mathfrak{D}_{\Lambda m}{}^{(l)}(0\Theta\Phi)^* Y_{N'M'}(\Theta\Phi) \\ & \times \exp(-\tfrac{1}{2}i\lambda\pi + i\delta_g) \\ & \times \int dR\, R_g(k, R)\epsilon_g(\vec{K}, \hat{k}R)R_{\nu N'}(R).\end{aligned} \tag{15}$$

Equations completely analogous to Eqs. (14) and (15) hold for the ungerade quantities. From Eq. (15) it is evident that $|E_g(\vec{K}, \vec{k}) + E_u(\vec{K}, \vec{k})|^2$ contains interference terms between molecular states having different values of Λ and α. However, when l and m are summed for fixed hydrogenic quantum number n, these interference terms cancel.[20] Averaging over M' in addition, we obtain

$$\begin{aligned}(2N'+1)^{-1} & \sum_{lmM'} |E_g(\vec{K}, \vec{k}) + E_u(\vec{K}, \vec{k})|^2 \\ & = (2/\pi)(4\pi)^{-1}\textstyle\sum_\Lambda\sum_\alpha |\exp(-\tfrac{1}{2}i\lambda\pi + i\delta_g) \\ & \times \int dR\, R_g(k, R)\epsilon_g(\vec{K}, \hat{k}R)R_{\nu N'}(R) + u \text{ term}|^2.\end{aligned} \tag{16}$$

Only the g-u interference terms now remain. If these could be ignored, it could be said that the cross section for all dissociations leading to hydrogen atoms with principal quantum number n is just the sum of the cross sections for transitions to all the molecular states which correlate to these atomic states. This statement is always correct for total dissociation cross sections.

Even with the simplifications inherent in Eq. (16), Eq. (1) is tedious to evaluate because of the necessity of calculating the $R_g(k, R)$ and $R_u(k, R)$. To further simplify the calculation, the reflection method[21] is now introduced in the form

$$R_g(k, R) = \left(\frac{\pi}{2}\right)^{\frac{1}{2}} \frac{1}{k}\left(\frac{-dR_g(k)}{dk}\right)^{\frac{1}{2}} \delta(R - R_g(k)), \tag{17}$$

where $R_g(k)$ is the classical turning point for the radial equation satisfied by $R_g(k, R)$. Thus

$$\begin{aligned}(2N'+1)^{-1} & \sum_{lmM'} |E_g(\vec{K}, \vec{k}) + E_u(\vec{K}, \vec{k})|^2 \\ & = (4\pi k^2)^{-1}\textstyle\sum_\Lambda\sum_\alpha |\exp(-\tfrac{1}{2}i\lambda\pi + i\delta_g) \\ & \times [-dR_g(k)/dk]^{1/2}\epsilon_g(\vec{K}, \hat{k}R_g(k)) \\ & \times R_{\nu N'}(R_g(k)) + u \text{ term }|^2.\end{aligned} \tag{18}$$

In order to express the summand on the right-hand side of Eq. (18) in terms of real quantities, it is helpful to note that $\epsilon_g(\vec{K}, \vec{R})$ and $\epsilon_u(\vec{K}, \vec{R})$ can both be expanded in the form

$$\epsilon(\vec{K}, \vec{R}) = i^{-\Lambda}\textstyle\sum_j a_j(K, R)Y_{j,\,-\Lambda}(\delta, \xi), \tag{19}$$

where (δ, ξ) are the polar angles of $\vec{K}$ in the molecule-fixed frame. In the expansion of $\epsilon_g(\vec{K}, \vec{R})$ j

must be even and $a_j(K,R)$ must be real; in the expansion of $\epsilon_u(\vec{K}, \vec{R})$ j must be odd and $a_j(K,R)$ must be imaginary.[22] According to Eq. (19) we can write

$$\epsilon_g(\vec{K},\vec{R})=\exp[-i\Lambda(\xi+\tfrac{1}{2}\pi)]\bar{\epsilon}_g(K,\delta,R)$$

$$\epsilon_u(\vec{K},\vec{R})=i\exp[-i\Lambda(\xi+\tfrac{1}{2}\pi)]\bar{\epsilon}_u(K,\delta,R), \qquad (20)$$

where $\bar{\epsilon}_g(K,\delta,R)$ and $\bar{\epsilon}_u(K,\delta,R)$ are real. Therefore on the right-hand side of Eq. (18), $|\ldots|^2$ can be written as

$$\begin{aligned}|\ldots|^2={}&[-dR_g(k)/dk][R_{\nu N'}(R_g(k))]^2\\ &\times[\bar{\epsilon}_g(K,\delta,R_g(k))]^2\\ &+[-dR_u(k)/dk]\\ &\times[R_{\nu N'}(R_u(k))]^2[\bar{\epsilon}_u(K,\delta,R_u(k))]^2\\ &+2[-dR_g(k)/dk]^{1/2}[-dR_u(k)/dk]^{1/2}\\ &\times R_{\nu N'}(R_g(k))R_{\nu N'}(R_u(k))\\ &\times\bar{\epsilon}_g(K,\delta,R_g(k))\bar{\epsilon}_u(K,\delta,R_u(k))\\ &\times\sin(\delta_g-\delta_u). \qquad (21)\end{aligned}$$

To find the cross section $dQ_\nu/dkd\Omega(\hat{k})$ for dissociation into a proton going in the direction $\hat{k}$ and a hydrogen atom with principal quantum number n, going in the direction $-\hat{k}$, the right-hand side of Eq. (18) must be inserted as the integrand of $d\phi_K$ in Eq. (1). For $n=1$ the required pair of states is $(1s\sigma_g, 2p\sigma_u)$; for $n=2$ there are 3 pairs of states: $(3d\sigma_g, 4f\sigma_u)$, $(3d\pi_g, 2p\pi_u)$, and $(2s\sigma_g, 3p\sigma_u)$. To date, however, the necessary values of $\bar{\epsilon}(K,\delta,R)$ have been calculated only for the states $2p\sigma_u$, $2s\sigma_g$, and $2p\pi_u$. Thus the antisymmetric contributions of the g-u interference terms in Eq. (21) to the angular distributions cannot be evaluated at present. To simplify the subsequent formulae, therefore, we write

$$\frac{dQ_\nu}{dkd\Omega(\hat{k})}=\sum_\Gamma\frac{dQ_\nu(\Gamma)}{dkd\Omega(\hat{k})}+g\text{-}u\text{ terms}, \qquad (22)$$

where Γ indexes the molecular states (including both g and u states) which correlate to the hydrogen states with principal quantum number n. The form of $dQ_\nu(\Gamma)/dkd\Omega(\hat{k})$ is the same for each molecular state. Dropping the g and u subscripts, we obtain from Eqs. (1), (18), and (21),

$$\begin{aligned}\frac{dQ_\nu(\Gamma)}{dkd\Omega(\hat{k})}={}&(4\pi)^{-1}\left(-\frac{dR(k)}{dk}\right)\\ &\times[R_{\nu N'}(R(k))]^2\sigma(\nu;R(k),\Theta), \qquad (23)\end{aligned}$$

where[23]

$$\begin{aligned}\sigma(\nu;R,\Theta)={}&4V_0^{-2}\int_{k_0-k_n}^{k_0+k_n}dK\,K^{-3}|\epsilon_T|^2\\ &\times\int d\phi_K[\bar{\epsilon}(K,\delta,R)]^2. \qquad (24)\end{aligned}$$

A final simplification now leads to the formulae which were used for the calculations. The only ν dependence in $\sigma(\nu;R,\Theta)$ comes from the presence in k_n of the minimum energy D_ν necessary to dissociate the ν vibrational state. It is a good approximation (based on the Franck-Condon principle) to replace D_ν by $-V(R)$, where $V(R)$ is the potential energy function for the relative proton motion in the $1s\sigma_g$ state.[24] Then $\sigma(\nu;R,\Theta)$ becomes a function $\sigma(R,\Theta)$ which can be calculated once and for all, rather separately for each value of ν.

Comparison with experiment requires that $dQ_\nu(\Gamma)/dkd\Omega(\hat{k})$ be averaged over the population of vibrational levels characteristic of the H_2^+ beam. Let this distribution be described by $f_\nu(\sum_\nu f_\nu=1)$. Then, with $\sigma(\nu;R,\Theta)$ replaced by $\sigma(R,\Theta)$, Eq. (23) shows that

$$\sum_\nu f_\nu\frac{dQ_\nu(\Gamma)}{dkd\Omega(\hat{k})}=\frac{dR(k)}{dk}\,\frac{dP(R(k))}{dR}\,\sigma(R(k),\Theta)/4\pi, \qquad (25)$$

where $dP(R)/dR$ is a normalized radial probability distribution characteristic of the H_2^+ beam. By definition

$$dP(R)/dR=\sum_\nu f_\nu[R_{\nu N'}(R)]^2. \qquad (26)$$

In Eq. (25), as in the previous equations, Θ is the angle between $\hat{k}$ and the H_2^+ beam direction. Equation (17) provides the definition of $R(k)$. Integrating Eq. (25) over Θ and Φ, we obtain the cross section per unit momentum k.

$$\sum_\nu f_\nu\frac{dQ_\nu(\Gamma)}{dk}=-\frac{dR(k)}{dk}\,\frac{dP(R(k))}{dR}\,Q(R(k)), \qquad (27)$$

where

$$Q(R)=(4\pi)^{-1}\int\sin\Theta d\Theta\int d\Phi\,\sigma(R,\Theta). \qquad (28)$$

Finally, integration over k, leads to the total cross section

$$\sum_{\nu} f_{\nu} Q_{\nu}(\Gamma) = \int dR[dP(R)/dR]\, Q(R). \qquad (29)$$

Equations (22)–(29) are the final results. In Sec. III values of $Q(R)$ and the ratio $\sigma(R,\Theta)/Q(R)$ will be presented for several transitions.

The theory outlined above is a natural outgrowth of previous work. The Born-approximation formulation is similar to that of Refs. 14–18, except for the treatment of the H_2^+ final state. The first additional approximation, that of supposing that $\delta_g - \frac{1}{2}\lambda\pi$ and $R_g(k,R)$ are independent of $J(N)$, was worked out independently by R. N. Zare[18] and by the present authors, following a discussion of this and related problems. The second additional approximation, the use of the reflection method, is well known. The theory corrects previous work on dissociation fragment angular distributions through the use of the proper final-state wave function for H_2^+. However, for the reasons given above, the contributions from the antisymmetric terms are not included in the numerical calculations. The theory also extends some of the previous work on angular distributions by establishing a formalism which applies to molecular states of σ, π, δ, etc., symmetry and not just to molecular states of σ symmetry. Finally, unlike the discussions in Refs. 14 and 18, the formalism is not dependent on the use of the linear combination of atomic orbitals LCAO approximation to the H_2^+ electronic eigenfunctions.

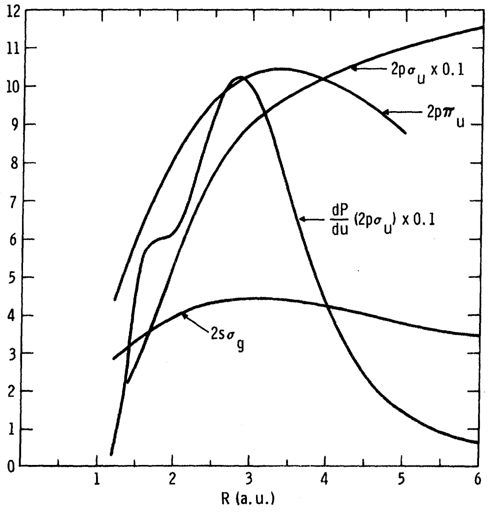

FIG. 1. Cross section $Q(R)$ in units of πa_0^2 for excitation of the $2p\sigma_u$, $2p\pi_u$, and $2s\sigma_g$ states at 10-keV H_2^+ impact energy; dP/du in atomic units for the $2p\sigma_u$ state. Note that $Q(R)$ for the $2p\sigma_u$ state and dP/du have been multiplied by 0.1. In each case $Q(R)$ was calculated for an Ar target which remained in its ground state.

III. ANGLE AND VELOCITY DISTRIBUTIONS FOR DISSOCIATION VIA ELECTRONIC EXCITATION

In this section relative proton angular distributions based on Eq. (24) are presented and discussed along with values of $Q(R)$ based on Eq. (28). Results for transitions to the $2p\sigma_u$, $2p\pi_u$, and $2s\sigma_g$ states of H_2^+ are given; the influence of simultaneous excitation of the target is also considered. The formulae used for $|\bar{\epsilon}(K,\delta,R)|^2$ and $|\epsilon_T|^2$, the computational details, and the precision of the results, are discussed in the Appendix.

Figure 1 exhibits $Q(R)$ for excitation of the $2p\sigma_u$, $2p\pi_u$, and $2s\sigma_g$ states by an Ar target which remains in its ground state. The H_2^+ impact energy is 10 keV. Also shown is

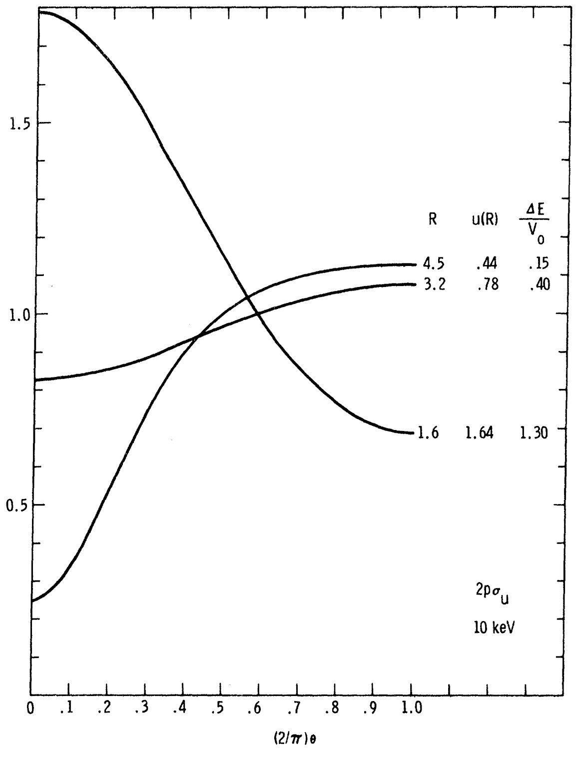

FIG. 2. The ratio $\sigma(R,\Theta)/Q(R)$ for the $2p\sigma_u$ state at 10-keV H_2^+ impact energy. The Ar target remained in its ground state. The abcissa is $(2/\pi)\Theta$ in radians. Values for $0 \leq \Theta \leq \frac{1}{2}\pi$ are shown since the curves are symmetrical about $\Theta = \frac{1}{2}\pi$. The curves are labeled with R. Also given are values of the final c.m. proton velocity $u(R)$ and the ratio $\Delta E/V_0$ in atomic units. Here ΔE is the excitation energy for the collision and V_0 is the H_2^+ impact velocity. The minimum possible momentum transfer $k_0 - k_n$ is closely equal to $\Delta E/V_0$.

$$dP/du \equiv [-dR(u)/du]\, dP(R(u))/dR$$

for $H_2^+(2p\sigma_u)$.[25] According to Eq. (27) $(dP/du)Q(R)$ determines the cross section per unit c. m. proton velocity. Thus Fig. 1 shows that *at a given* R dissociation from $H_2^+(2p\sigma_u)$ should be dominant over dissociation from $H_2^+(2p\pi_u)$ and H_2^+ $(2s\sigma_g)$. However, the quantity of experimental interest is dissociation *at a given* u and this corresponds to a different R for each state, as can be seen from Table I. For example from Fig. 1, Table I, and the information given in footnote 25, it is seen that dP/du has its maximum at $u = 0.93$, 0.69, and 0.92 for the $2p\sigma_u$, $2p\pi_u$, and $2s\sigma_g$ states, respectively.[26] Therefore because of the fairly rapid variation of $(dP/du)\,Q(R)$ with R, the relative contribution of the three H_2^+ states at a given u will generally be different from what would be inferred directly from Fig. 1.

We now turn to the relative angular distributions. These are shown in Figs. 2–4 for the case in which the Ar target remains in its ground state. The selected values of R correspond approximately to $u = 0.5$, 0.8, and 1.7 in each case; the actual values of u are shown in the figures. Each figure also gives the value of the excitation energy ΔE divided by the H_2^+ impact velocity. This is closely equal to the minimum value, K_0, of K which is allowed by energy conservation. The range of important momentum transfers in Eq. (24) is roughly $K_0 \leq K \leq K_0 + 3$. It is evident that the $2p\sigma_u$ angular distributions change rapidly with u. The change in the other angular distributions is less pronounced.

The different dependence of the angular distributions for the three states on u and Θ offers the possibility of distinguishing them on this basis in comparisons between theory and experiment.[27] This is the main computational result of the present paper. It will be taken up again in the third paper of this series.

The effect of simultaneous excitation of an allowed transition in the target on the $2p\sigma_u$ angular distribution for $R = 3.2$ is shown in Fig. 5 for target excitation energies of 0.185, 0.37, and 0.78 a. u. For this case $|\epsilon_T|^2$ was taken to be that for the $(1s)^2 - 1s2p$ transition in He. The change in the relative angular distributions is quite dramatic. However, the values of $Q(R)$ for these cases (0.0223, 0.0003, and 0.0000 πa_0^2, respectively) show that in Born approximation such transitions are predicted to be relatively improbable. The results do suggest nonetheless that if simultaneous target excitation is hypothesized[3,5] in order to explain some feature of the experimental data, it is necessary to make sure that the observed angular distributions are also compatible with this hypothesis.

The trends exhibited in Figs. 1–5 can be under-

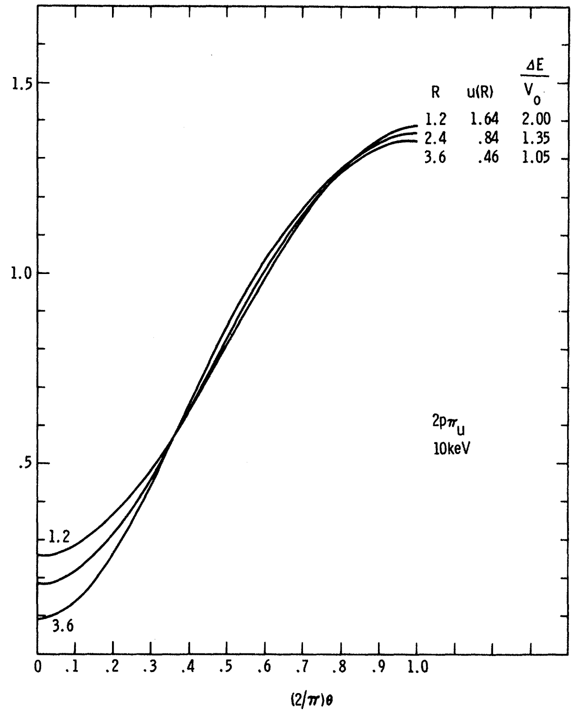

FIG. 3. The ratio $\sigma(R,\Theta)/Q(R)$ for the $2p\pi_u$ state at 10-keV H_2^+ impact energy. The Ar target remained in its ground state. Also see caption to Fig. 2.

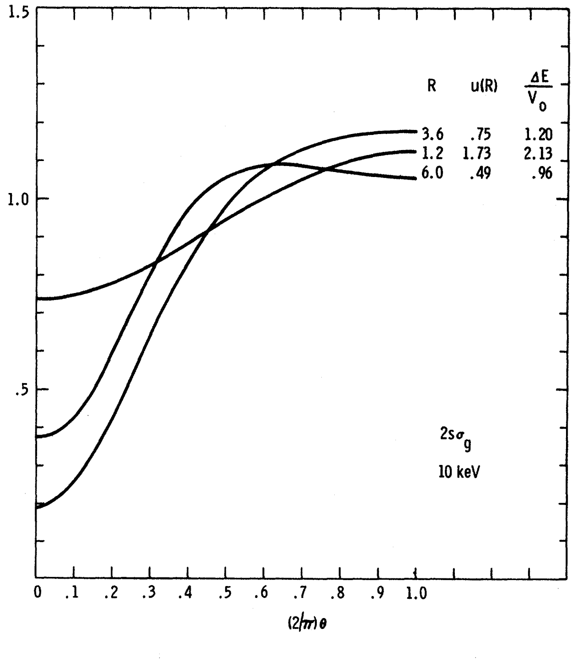

FIG. 4. The ratio $\sigma(R,\Theta)/Q(R)$ for the $2s\sigma_g$ state at 10-keV H_2^+ impact energy. The Ar target remained in its ground state. Also see caption to Fig. 2.

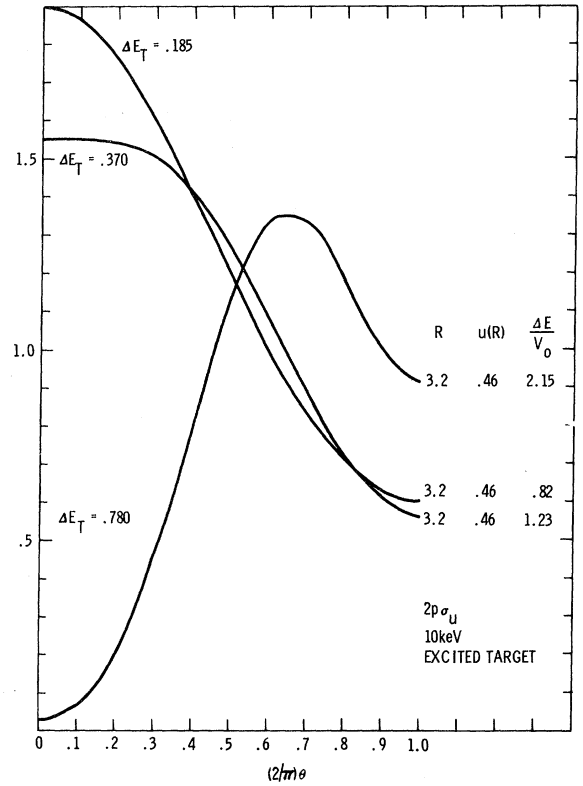

FIG. 5. The ratio $\sigma(R, \Theta)/Q(R)$ for the $2p\sigma_u$ state at 10-keV H_2^+ impact energy. For these curves $|\epsilon_T|^2$ in Eq. (24) was taken to be that for the $1s^2 - 1s2p$ transition in He; ΔE_T is the assumed target excitation energy in atomic units. Also see caption to Fig. 2.

TABLE I. Final c.m. proton velocities as a function of internuclear separation R.

R (a.u.)	$u(2p\sigma_u)$ (10^{-2} a.u.)	$u(2p\pi_u)$ (10^{-2} a.u.)	$u(2s\sigma_g)$ (10^{-2} a.u.)
1.2	2.01	1.64	1.73
1.4	1.81	1.44	1.56
1.6	1.64	1.28	1.41
1.8	1.48	1.15	1.30
2.0	1.35	1.03	1.20
2.2	1.22	0.933	1.12
2.4	1.11	0.843	1.04
2.6	1.02	0.763	0.978
2.8	0.928	0.691	0.922
3.0	0.848	0.626	0.871
3.2	0.775	0.566	0.827
3.4	0.709	0.510	0.786
3.6	0.649	0.458	0.750
3.8	0.594	0.409	0.716
4.0	0.545	0.363	0.686
4.2	0.499	0.318	0.659
4.4	0.457	0.275	0.634
4.6	0.419	0.232	0.610
4.8	0.384	0.188	0.589
5.0	0.352	0.140	0.569
5.5	0.282		0.526
6.0	0.226		0.490

stood qualitatively in terms of the united-atom limits of $|\bar{\epsilon}(K, \delta, R)|^2$ for the three H_2^+ states. These are proportional to $\cos^2\delta$, $\sin^2\delta$, and 1 for $H_2^+(2p\sigma_u)$, $H_2^+(2p\pi_u)$ and $H_2^+(2s\sigma_g)$, respectively. Since δ is the angle between the dissociation direction $\hat{k}$ and the momentum transfer $\vec{K}$, it is necessary to know the predominant angle ξ between $\vec{K}$ and the beam. The sine of ξ is approximately equal to $\{1 - (K_0/K)^2\}^{1/2}$. Now the integrand in Eq. (24) increases from zero at $K=0$ through a maximum in the vicinity of $K=1$ and thereafter decreases rather rapidly. Hence, if K_0 is greater than unity, the important values of K are not too different from K_0, $\sin\xi$ is small, and $\vec{K}$ lies more or less along the beam. If K_0 is small compared to unity, $\vec{K}$ tends to be perpendicular to the beam. For the $2p\sigma_u$ transition we can therefore expect $\sigma(R, \Theta) \sim \cos^2\Theta$ if K_0 is greater than unity and $\sigma(R, \Theta) \sim \sin^2\Theta$ if K_0 is much less than unity. This trend is exhibited in Fig. 2. In the case of transitions to $2p\pi_u$, K_0 is always greater than unity so $\sigma(R, \Theta) \sim \sin^2\Theta$ as indicated in Fig. 3. For the $2s\sigma_g$ state, the united-atom limit gives $\sigma(R, \Theta) \sim 1$. Figure 4 shows that this is roughly the case only for small R. In the cases exhibited in Fig. 5, $\xi \sim 0$, so we would expect that $\sigma(R, \Theta) \sim \cos^2\Theta$.

The rather considerable quantitative deviations from the above estimates arise both from variations in ξ with K and from the terms $\cos(\frac{1}{2}KR \times \cos\delta/\beta)$ and $\sin(\frac{1}{2}KR\cos\delta/\beta)$ in the formulae for $|\bar{\epsilon}(K, \delta, R)|^2$ [Eqs. (A1), (A4), and (A6)]. These terms influence the angular distributions substantially for large values of K_0R.

Lack of space precludes the presentation of results for many other H_2^+ impact energies. Results for the $2p\sigma_u$ transition at 3 and 20.4 keV are given in Sec. IV. Additional results can be obtained from the authors. (See Sec. IV). The essential point is that the angular distributions also change considerably with H_2^+ impact velocity.

One additional conclusion results from our study. The relative angular distributions obtained for a He target which does not undergo simultaneous excitation agree to within about 5% with those obtained for an Ar target which does not undergo simultaneous excitation. This feature of the relative proton angular distributions can also be seen in the experimental data[3,5] provided one subtracts out the contribution from vibrational dissociation. Now if simultaneous target excitation is a probable event, the angular distributions for dissociation via electronic excitation of H_2^+ should be target dependent, owing to the difference in the target excitation energies, as illustrated in Fig. 5. This suggests that, in agreement with the Born prediction, electronic excitation of H_2^+, accompanied by simultaneous excitation of the target is not a probable event at low H_2^+ impact energies.

An additional consequence of the first point made in the previous paragraph is that the relative proton angular distributions – but not $Q(R)$ – are rather insensitive to inaccuracies in $|\epsilon_T|^2$ for a target which remains in its initial state.

An unresolved problem connected with H_2^+ dissociation concerns the contributions from excitation of the higher electronic states of H_2^+ and from the dissociative ionization of H_2^+. The latter process is known to be dominant at H_2^+ impact energies of the order of 100 keV and does not appear to be dominant at energies of the order of 10 keV.[7] At 20 keV, McClure's analysis[1] of the total cross sections suggests that about 30% of the protons arise from dissociative ionization. Other evidence for the importance of dissociative ionization at 20 keV is given in Ref. 5.

What can be said about the relative dissociation-fragment angular distributions for these two classes of states? A clue to the answer may lie in the observation that for moderate values of R the wave function of a highly excited state of H_2^+ is well approximated by the wave function for the united-atom limit ($R = 0$), since the electron is most likely to be far from both protons. We may further argue that when the electron is far from both protons the electronic wave function for the initial state, $H_2^+(1s\sigma_g)$, is also not very different from its united-atom value. On this basis, for the highly excited states, $|E(K, \delta, R)|^2$ can be replaced in zeroth approximation by $|\epsilon(K, \delta, 0)|^2$. This approximation leads to the following conclusion: the proton angular distributions, summed over all the highly excited states of H_2^+, including the ionized states, should be isotropic. The isotropy arises, of course, because we include transitions to all degenerate states which correspond to a given principal quantum number N of He^+, the united-atom limit of H_2^+, and we sum over all directions of motion of the outgoing ionized electron.

The foregoing conclusion can be somewhat sharpened. Suppose that the electronic wave function for $H_2^+(1s\sigma_g)$ is approximated by two terms in the single-center expansion, i.e.,

$$\phi[H_2^+(1s\sigma_g)] = a(R)R_{10}(r)Y_{00}(\hat{r}\cdot\hat{R}) + b(R)\chi(r)Y_{20}(\hat{r}\cdot\hat{R}), \qquad (30)$$

where $a(R)$, $b(R)$, $R_{10}(r)$, and $\chi(r)$ are positive functions.[28] The notation $R_{10}(r)$ indicates that $R_{10}(r)$ should be similar to the radial wave function for the ground state of He^+. It can then be shown for transitions to He^+(NLM) that, neglecting the terms in $b(R)^2$,

$$\sum_M |\epsilon_{NLM}(K, \delta, R)|^2 = (2L+1)a(R)^2(I_{NL})^2 + (20)^{1/2}(2L+1)a(R)b(R)P_2(\cos\delta) \times \sum_J i^{(L-J)} C^2(L2J;00) I_{NL} J_{NLJ}, \qquad (31)$$

where

$$I_{NL} = \int r^2 dr\, R_{NL}(r) R_{10}(r)\, j_L(Kr),$$
$$J_{NLJ} = \int r^2 dr\, R_{NL}(r)\chi(r) j_J(Kr)\ . \qquad (32)$$

Here $j_J(Kr)$ is the spherical Bessel function. The essence of Eq. (31) is that

$$\sum_M |\epsilon_{NLM}(K, \delta, R)|^2 = A(K, R) + B(K, R)P_2(\cos\delta), \qquad (33)$$

where $A(K, R) > 0$. It is plausible to assume that Eq. (32) also holds, in the same approximation, for dissociative ionization.

The qualitative character of the proton angular distributions for the highly excited and ionized states of H_2^+ depends on the sign of $B(K, R)$. In particular, if $B(K, R) > 0$, the angular distributions will resemble those for excitation of $H_2^+(2p\sigma_u)$, for which

$$|\bar{\epsilon}(K, \delta, R)|^2 \sim \cos^2\delta = \tfrac{1}{3}[1 + 2P_2(\cos\delta)] .$$

Experimental evidence supporting $B(K, R) > 0$ can be found in Ref. 5 in connection with the angular distribution of protons from dissociation events which the authors of this reference attribute to dissociative ionization.

Quantitative evaluation of Eqs. (31) and (32) would be possible, using values of $R_{10}(r)$ and $\chi(r)$ from Ref. 28. We will limit the present discussion to a few additional remarks which indicate the likelihood that $B(K, R) > 0$. Suppose first, as seems reasonable, that in Eqs. (31) and (32) the important values of Kr and L are, respectively, large enough and small enough that the asymptotic formulae

$$j_L(Kr) = (Kr)^{-1}\sin(Kr - \tfrac{1}{2}L\pi)$$

is valid. Then

$$\sum_M |\epsilon_{NLM}(K, \delta, R)|^2 = (2L+1)a(R)^2(I'_{NL})^2 + (20)^{1/2}(2L+1)a(R)b(R)\, I'_{NL} J'_{NLL} P_2(\cos\delta)\ , \qquad (34)$$

where the prime means the use of the asymptotic formula for $j_L(Kr)$ in Eqs. (32). Then $B(K,R) > 0$ in Eq. (33) is equivalent to $I'_{NL}\, J'_{NLL} > 0$ in Eq. (34). This latter inequality should indeed be valid provided that the positive functions $R_{10}(r)$ and $\chi(r)$ are not qualitatively too different from each other over the range of important r values in Eqs. (32).

A somewhat analogous and more rigorous conclusion can be drawn about dissociation via electronic excitation for very large values of R (very low c.m. dissociation velocities). Consider all electronic transitions leading to dissociation into a proton and a hydrogen atom in the nth quantum level for $n > 1$. At sufficiently large R the energies of all the related H_2^+ electronic states are about equal, and the LCAO value of $\bar{\epsilon}(K,\delta,R)$ for each of these states is reasonably accurate. It can then be shown that in the sum over molecular states implied by Eq. (22) the angular variations of the various $\underset{\sim}{\sigma}(R,\Theta)$ are mutually compensating and $dQ_v/dkd\Omega(\hat{k})$ is isotropic. This observation may account partially for the isotropy evidenced in the results shown near zero lab angle in Fig. 9 of Ref. 1. However, for a complete analysis, one needs to take vibrational dissociation into account.

IV. TABLES OF dP/du, $Q(R)$ AND $\sigma(R,\Theta)/Q(R)$

Tables II and III contain values of dP/du, $Q(R)$, and $\sigma(R,\Theta)/Q(R)$ for the excitation of $H_2^+(2p\sigma_u)$ by an Ar target which remains in its ground state.

TABLE II. dP/du, $Q(R)$, and $\sigma(R,\Theta)/Q(R)$ for excitation of $H_2^+(2p\sigma_u)$ at 3-keV H_2^+ impact energy. The Ar target remains in its ground state. See the text, Sec. IV, and Eqs. (23)–(28) for an explanation of the symbols and units used.

$R=$	1.4	1.6	2.0	2.4	2.8	3.2	3.6	4.5	5.0	6.0
$dP/du=$	29.08	56.72	61.66	85.36	102.34	90.21	64.66	24.16	14.43	6.13
$Q(R)=$	5.64	12.10	44.05	108.09	186.62	253.68	299.40	350.54	365.47	384.34
$(2/\pi)\Theta$					$\sigma(R,\Theta)/Q(R)$					
0.0	1.60	1.62	1.72	1.80	1.78	1.62	1.37	0.72	0.44	0.14
0.1	1.60	1.61	1.70	1.76	1.72	1.57	1.33	0.74	0.52	0.30
0.2	1.57	1.57	1.62	1.63	1.57	1.42	1.22	0.81	0.68	0.61
0.3	1.51	1.50	1.50	1.46	1.38	1.25	1.11	0.88	0.83	0.85
0.4	1.40	1.38	1.34	1.28	1.20	1.11	1.03	0.94	0.94	0.98
0.5	1.25	1.23	1.17	1.11	1.05	1.11	0.98	0.99	1.01	1.03
0.6	1.07	1.05	1.01	0.96	0.94	0.94	0.96	1.02	1.05	1.06
0.7	0.88	0.88	0.86	0.85	0.87	0.91	0.95	1.04	1.07	1.07
0.8	0.72	0.73	0.75	0.78	0.83	0.89	0.95	1.05	1.08	1.08
0.9	0.61	0.63	0.68	0.73	0.80	0.88	0.96	1.06	1.08	1.08
1.0	0.57	0.60	0.65	0.72	0.80	0.88	0.96	1.06	1.08	1.08

TABLE III. dP/du, $Q(R)$, and $\sigma(R,\Theta)/Q(R)$ for excitation of $H_2^+(2p\sigma_u)$ at 20.4-keV H_2^+ impact energy. The Ar target remains in its ground state. See the text, Sec. IV, and Eqs. (23)–(28) for an explanation of the symbols and units used.

$R=$	1.4	1.6	2.0	2.4	2.8	3.2	3.6	4.5	5.0	6.0
$dP/du=$	29.08	56.72	61.66	85.36	102.34	90.21	64.66	24.16	14.43	6.13
$Q(R)=$	20.09	24.87	33.59	40.21	44.48	47.08	48.85	52.21	53.92	56.53
$(2/\pi)\Theta$					$\sigma(R,\Theta)/Q(R)$					
0.0	1.54	1.42	1.15	0.89	0.65	0.47	0.32	0.13	0.07	0.02
0.1	1.52	1.40	1.14	0.89	0.67	0.51	0.38	0.23	0.20	0.21
0.2	1.44	1.33	1.11	0.90	0.73	0.61	0.53	0.47	0.49	0.57
0.3	1.34	1.24	1.07	0.91	0.80	0.73	0.70	0.71	0.75	0.84
0.4	1.21	1.15	1.03	0.94	0.88	0.86	0.85	0.89	0.92	0.98
0.5	1.09	1.06	1.00	0.97	0.95	0.96	0.97	1.00	1.02	1.04
0.6	0.98	0.98	0.98	1.00	1.02	1.03	1.05	1.07	1.07	1.07
0.7	0.90	0.92	0.97	1.02	1.06	1.09	1.10	1.11	1.10	1.08
0.8	0.84	0.88	0.97	1.05	1.10	1.12	1.14	1.13	1.11	1.08
0.9	0.80	0.86	0.97	1.06	1.11	1.14	1.16	1.14	1.12	1.09
1.0	0.79	0.85	0.97	1.06	1.12	1.15	1.16	1.14	1.12	1.09

The H_2^+ impact energies are 3 and 20.4 keV, respectively. The first column gives values of $(2/\pi)\Theta$ in radians. The remaining columns refer to the values of R given in atomic units in the first row. $Q(R)$ is given in units of πa_0^2;dP/du is given in atomic units. The ratio $\sigma(R,\Theta)/Q(R)$ is dimensionless. The precision of the results is discussed in the Appendix.

Similar tables for the $2p\sigma_u$, $2p\pi_u$, and $2s\sigma_g$ transitions induced by collisions with He and Ar at H_2^+ impact energies of 3, 10, 20.4, 50, and 100 keV are available from the authors. Also available are tables based on an allowed transition in the target as well as some tables for the excitation of the $4f\sigma_u$ state of H_2^+. This state may be of some interest because the relation between u and R for this state is virtually the same as that for dissociative ionization. Hence, on the basis of velocity analysis alone, protons from this state can be confused with those due to dissociative ionization.[5]

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APPENDIX. COMPUTATIONAL DETAILS AND DISCUSSION OF THE FORMULAE USED FOR $|\bar{\epsilon}(K,\delta,R)|^2$ IN EQ. (24)

According to Eq. (24), to obtain $\sigma(R,\Theta)$ we first integrate $|\bar{\epsilon}(K,\delta,R)|^2$ over ϕ_K; this result is then multiplied by $K^{-3}|\epsilon_T|^2$ and integrated over K. Accurate values of $|\bar{\epsilon}(K,\delta,R)|^2$ for the states mentioned above have been obtained by Peek[29] for several values of R over the ranges $0 \leqslant \delta \leqslant \frac{1}{2}\pi$ and $0 \leqslant K \leqslant 2$. For the present calculation this information had to be supplemented by values of $|\bar{\epsilon}(K,\delta,R)|^2$ for larger values of K and R. In addition, it seemed desirable to do the ϕ_K integration analytically. Therefore approximate formulae for $\bar{\epsilon}(K,\delta,R)$ were used in the computations.

For the $2p\sigma_u$ state the LCAO expression for $\bar{\epsilon}(K,\delta,R)$ was modified to make it agree as closely as possible with the values tabulated by Peek at $R=1.4$, 2, and 3.2 a.u. The formula used is

$$|\bar{\epsilon}(K,\delta,R)|^2=\frac{F\sin^2(\frac{1}{2}KR\cos\delta/\beta)}{(1-S^2)(1+\frac{1}{4}K^2/Z^2)^4}\ , \qquad \text{(A1)}$$

with
$$S=(1+ZR+\tfrac{1}{3}Z^2R^2)\,e^{-ZR}\ . \qquad \text{(A2)}$$

The values chosen for the adjustable parameters F, β, and Z are given by the formulae

$$\begin{aligned}
&F=1-0.901\,e^{-1.175R}, && \\
&\beta=1.058, && R\leqslant 3.2 \\
&\beta=1+0.058\,e^{-(R-3.2)^2/9}, && R>3.2 \quad (2p\sigma_u) \qquad \text{(A3)} \\
&Z=1.10, && R\leqslant 2 \\
&Z=1+0.10\,e^{-0.481(R-2)^2}, && R>2\,.
\end{aligned}$$

The parameter β was determined at $R=1.4$, 2, and 3.2 from the relative angular dependence of the tabulated values of $\bar{\epsilon}(K,\delta,R)$ for $0\leqslant K\leqslant 2$. The parameters Z and F were determined for these values of R by matching the K dependence of the tabulated values[29] of

$$\int_0^1 d\cos\delta\,|\bar{\epsilon}(K,\delta,R)|^2$$

as closely as possible in the interval $0.5\leqslant K\leqslant 2$.[30] The extrapolations of F, β, and Z beyond $R=3.2$ are designed to make $|\bar{\epsilon}(K,\delta,R)|^2$ change smoothly into the LCAO value, reaching it in the vicinity of $R=5$. Equation (A1) as well as the equations given below for the other H_2^+ states, should be regarded only as an approximate interpolation formula. Its relation to the actual H_2^+ eigenfunctions cannot be established rigorously.

The formula used for the $2p\pi_u$ state is

$$\begin{aligned}
|\bar{\epsilon}(K,\delta,R)|^2 = {} & 72Z^{10}F(1+2^{-15/2}3^5I_2)^2 \\
& \times\cos^2(\tfrac{1}{2}KR\cos\delta/\beta)K^2\sin^2\delta \\
& \times[(1+S)(1+T)(K^2+9Z^2/4)^6]^{-1}\,. \qquad \text{(A4)}
\end{aligned}$$

Here S is given in Eq. (A2) while the R-dependent quantities I_2 and T are defined by Bates *et al.*[31] The K and δ dependence of Eq. (A4) results from taking the two-center integrals in the LCAO expression for $\bar{\epsilon}(K,\delta,R)$ to be equal to $2^{-15/2}3^5I_2$ times the one-center integrals. This *ad hoc* procedure is justified only by the fact that Eq. (A4) fits the accurate value of $|\bar{\epsilon}(K,\delta,R)|^2$ quite well and is correct both as $R\rightarrow 0$ and $R\rightarrow\infty$. In addition, the parameters F, Z, and β are introduced as indicated. Their formulae are

$$\begin{aligned}
&F=1+0.419R\,e^{-0.181(R/2)^2}, \\
&Z=1+e^{-0.981(R/2)^{1.404}}, \quad (2p\pi_u) \qquad \text{(A5)} \\
&\beta=1+0.637\,e^{-0.01482R^2}\ .
\end{aligned}$$

These were determined at $R=2$ and $R=3.2$ in the manner described for the $2p\sigma_u$ state.[32] The somewhat arbitrary extrapolations are chosen to make $|\bar{\epsilon}(K,\delta,R)|^2$ agree with the LCAO value beyond $R=15$ and with the exact united-atom value at $R=0$.

The formula for the $2s\sigma_g$ state is

$$|\bar{\epsilon}(K,\delta,R)|^2 = 32Z^8K^4(1+G)^2\{\cos(\tfrac{1}{2}kR\cos\delta/\beta) + (g/K)\sin(\tfrac{1}{2}KR\cos\delta/\beta)\cos\delta\}^2 \times [2(1+S)(K^2+9Z^2/4)^6]^{-1} \; . \quad \text{(A6)}$$

Again the two-center integrals in the LCAO formula for $\bar{\epsilon}(K,\delta,R)$ were taken to be proportional (proportionality factor G) to the one-center integrals. The quantity S is given by Eq. (A2) and the adjustable parameters are given by

$$\left.\begin{aligned} G &= e^{-0.128(R/2)^{2.25}}, \\ Z &= 1+e^{-0.602R}, \\ \beta &= 1+0.824\,e^{-0.25R}, \\ g &= 1.5(1-e^{-0.2944(R/2)^{1.25}}). \end{aligned}\right\} \quad (2s\sigma_g) \qquad \text{(A7)}$$

The additional parameter g is related to the amount of H($2p$) wave function which is mixed with the H($2s$) wave function in the LCAO approximation to the wave function of $H_2^+(2s\sigma_g)$. For this state, tabulated values are available only for $R=2$.[33] The somewhat arbitrary extrapolations guarantee that $|\bar{\epsilon}(K,\delta,R)|^2$ smoothly reaches the LCAO value at about $R=15$ and the exact united-atom value at $R=0$. The values of $|\bar{\epsilon}(K,\delta,R)|^2$ are somewhat uncertain for $3 \leqslant R \leqslant 10$. However, as can be seen from Fig. 1 of Sec. III, dissociation from the $2s\sigma_g$ state should be of minor importance.

The values of $|\epsilon_T|^2$ for a target of nuclear charge Z_T will now be discussed. For the case in which the target was left in its initial state, the coherent x ray scattering factor $F_T(K)$ of Lea was used in the formula $\epsilon_T = Z_T - F_T(K)$.[34]

An optically allowed excitation of the target was simulated by using the value of $|\epsilon_T|^2$ for the $(1s)^2 \rightarrow 1s2p$ transition in He and several illustrative target excitation energies. The case of simultaneous excitation was not studied in detail because in Born approximation at H_2^+ impact energies near 10 keV, H_2^+ excitation accompanied by target excitation is predicted to be very improbable compared to H_2^+ excitation during which the target remains in its ground electronic state.

The formulae adopted for $|\bar{\epsilon}(K,\delta,R)|^2$ allow the result of the ϕ_K integration in Eq. (24) to be expressed in terms of Bessel functions and elementary functions. The K integrations were done using Simpson's rule. A severe check on the formulae and numerical procedures was obtained by numerically integrating $\sigma(R,\Theta)$ over Θ and making sure that the resulting values of $Q(R)$ agreed with the results of an independent calculation in which the integrations over Θ and Φ were done analytically before those over K and ϕ_K.

We conclude the discussion with some remarks about the influence on $\sigma(R,\Theta)/Q(R)$ and $Q(R)$ of inaccuracies in the approximate formulae (A1)–(A7) for $|\epsilon(K,\delta,R)|^2$. The ratio $\sigma(R,\Theta/Q(R)$ is independent of those functions of R which merely multiply $|\epsilon(K,\delta,R)|^2$ in Eqs. (A1), (A4), and (A6); it is also fairly insensitive to the choice of Z. However, the ratio is quite sensitive to the choice of β whenever the ratio turns out to be small compared to unity. This occurs only for $\Theta \leqslant 0.3 \times (\pi/2)$.

The $2p\sigma_u$ ratios should be accurate to within several percent for all R and Θ. The $2p\pi_u$ ratios should be accurate to within 10% for $1.6 \leqslant R \leqslant 3.6$, except when the ratios are small compared to unity. Outside this range of R the errors could be larger for small values of Θ. The $2s\sigma_g$ ratios are quite accurate at $R=2$ and for $R<2$, should range in accuracy from 5 to 20%, the largest uncertainties being associated with the smallest values of R and Θ. For $R>2$ the ratios should be accurate to about 10% for $\Theta > 0.3(\pi/2)$; for smaller values of Θ, the results may be quite inaccurate at the larger values of R.

The values of $Q(R)$ are influenced directly by the over-all normalization of $|\epsilon(K,\delta,R)|^2$ and are most uncertain in the region of R between the largest value of R for which Peek's accurate values were obtained and the R beyond which the LCAO value is correct.

The unknown accuracy of $|\epsilon_T|^2$ for Ar also influences $Q(R)$ directly. Assuming this to be about 5% for $0.5 \leqslant K \leqslant 3$, the $2p\sigma_u$ cross section should be accurate to about 10%. The same estimate applies to the $2p\pi_u$ cross section for $2 \leqslant R \leqslant 3.2$ and to the $2s\sigma_g$ cross section close to $R=2$. At other values of R the values of these cross sections are less certain. They should not be grossly in error, however.

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[1] G. W. McClure, Phys. Rev. 140, A769 (1965).

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[6] Compare J. M. Peek, T. A. Green, and W. H. Weihofen, Phys. Rev. 160, 117 (1967). The Appendix indicates, for H_2^+-H_2 collisions, how Eq. (1) can be derived.

[7] Atomic units (a.u.) are used throughout. The z axes of the laboratory frame and the H_2^+ c.m. frame are taken along the H_2^+ beam direction.

[8] The prime on $\vec{r}$ in $\phi_0[\vec{r}\,', R]$ is used to indicate that $\phi_0[\vec{r}\,', R]$ is expressed in terms of the coordinates of $\vec{r}$ in a molecule-fixed frame. There are two possible choices for the function $R_{\nu N'}(R)$ according to whether the diagonal part of the perturbation term which couples the electronic and nuclear motions is omitted from or included in the potential energy function for $R_{\nu N'}(R)$. The formalism developed below applies to either choice.

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[11] We depart here from the discussion given in Ref. 9. See W. R. Thorson, J. Chem. Phys. 50, (1969).

[12] M. E. Rose, Multipole Fields (John Wiley & Sons, Inc., New York, 1955) Chap. II, Sec. 7.

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[19] This approximation appears reasonable for dissociation via electronic excitation provided k is not too small. During electronic excitation, the H_2^+ rotational angular momentum should not change much. Therefore, the range of the important values of N in Eq. (5) should be fairly small. Moreover, the influence of the variable $J(N)$ on $R_g(k, R)$ will be small provided that the electronic interaction dominates the J-dependent centrifugal term. For a narrow range of $J(N)$, this will usually be the case for all R's of importance in Eq. (2), except possibly for large values of R, where the electronic potential becomes very small. By the Franck-Condon principle large values of R correspond to small dissociation energies. Hence, unless k is too small the approximation should be good.

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[21] E. U. Condon, Phys. Rev. 32, 858 (1928). J. A. Winans and E. C. G. Stueckelberg, Proc. Natl. Acad. Sci. 14, 876 (1928). A. S. Coolidge, H. M. James, and R. D. Present, J. Chem. Phys. 4, 193 (1936). In the form given in Eq. (17) the approximation is compatible with Parseval's theorem for expansions of an arbitrary function of R in terms of the $R_g(k, R)$ provided the potential curve from which $R_g(k, R)$ is calculated does not support bound states.

[22] These properties can be deduced from Eq. (13).

[23] The relations $\epsilon_g(-\vec{K}, \vec{R}) = \epsilon_g(\vec{K}, \vec{R})$ and $\epsilon_u(-\vec{K}, \vec{R}) = -\epsilon_u(\vec{K}, \vec{R})$ were used in obtaining Eq. (24).

[24] J. M. Peek and T. A. Green, to be published.

[25] See Eqs. (25)–(29). At this point we introduce the c.m. proton velocity u (= k divided by the proton mass) in place of k since u is the variable used in the experimental papers. The plots of $[-dR(u)/du][dP(R(u))/dR]$ for the $2p\pi_u$ and $2s\sigma_g$ states are qualitatively quite similar in shape to that shown in Fig. 1 for the $2p\sigma_u$ state and also have their maxima at $R = 2.8$.

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[32] The angular dependence of $\bar{\epsilon}(K, \delta, R)$ agrees with the tabulated values to within 4%. For $K = 0.5$ the integral $\int_0^1 d\cos\delta\, |\bar{\epsilon}(K, \delta, R)|^2$ is, respectively, 7 and 15% high at $R = 2$ and 3.2; it agrees with the tabulated values of Ref. 29 to better than 3% for $1 \leq K \leq 2$.

[33] At $R = 2$, β and g were chosen to fit the angular dependence of $\bar{\epsilon}(K, \delta, R)$ to within 10% for $0 \leq K \leq 2$. The parameters G and Z were chosen to make $\int_0^1 d\cos\delta \times |\bar{\epsilon}(K, \delta, R)|^2$ agree with the tabulated values to 10% at $K = 0.5$ and to within 2% for $1 \leq K \leq 2$.

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