# Theory of Dissociation of $H_2^+$ by Fast Electrons*

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Theoretical results for the dissociation of the hydrogen-molecule ion by high-energy electrons are considered with the intention of providing sufficient data for comparison with recent experimental studies of this system. The experimental results and this comparison are given in the preceding paper by Dunn and Van Zyl. The coefficients $A$ and $B$ for the cross-section formula $V_0^2Q=A\ln V_0+B$, where $V_0$ is the relative collision velocity, are given for the discrete transitions $1s\sigma_g-2p\sigma_u$ and $1s\sigma_g-2p\pi_u$ for each of the initial $H_2^+$ vibrational states in the $1s\sigma_g$ potential curve. Similar data, obtained from a closure argument, are given; an estimate of the remaining contributions to the experimental cross section is then possible.

## I. INTRODUCTION

EXPERIMENTAL results on the dissociation of the hydrogen molecule ion ($H_2^+$) by electrons have been published recently[1] and additional data for this system will soon be published.[2] Previous publications[3–6] consider the theory of this system in some detail but present insufficient data to make a meaningful comparison with experiment. In this note we supplement these earlier results and provide, at high impact energies, data for the complete first Born prediction of the experimentally observed cross section.

The experiment detects fragments[1] of $H_2^+$ so it is known that the excitation of $H_2^+$ by electrons to a dissociative state has taken place. In our theoretical model of the experiment, it is assumed that all electronic excitations of $H_2^+$ lead to dissociation and that no other mechanism such as vibrational dissociation contributes to the observed cross section. Several excited electronic states[7] of $H_2^+$ are known to possess minima and perhaps bound vibrational states. However, the important internuclear separations ($R$) are such that transitions to these excited states are expected to go to the repulsive part of the potential curve. Transitions from $H_2^+$ initially in a few higher bound vibrational states of the $1s\sigma_g$ potential curve may prove to be an exception to this argument. However, in the absence of contradictory evidence, the combination of circumstances which may lead to a stable but electronically excited $H_2^+$ will be ignored.

Theoretical results are discussed in Sec. II for the final $2p\sigma_u$ and $2p\pi_u$ orbitals of $H_2^+$. The fact that all final electronic states are assumed to contribute to dissociation makes possible an estimate of the observed cross section by closure. This is discussed in Sec. III. Since we are mainly interested in relatively high collision energies, the cross section $Q$ can be represented as a function of relative collision velocity $V_0$ in the analytical form (cf. 8)

$$V_0^2Q=A\ln V_0+B; \tag{1}$$

hence, just $A$ and $B$ need be tabulated for a given process. This makes possible a rather compact representation of the required data. Equation (1) implies a dipole-allowed transition. Dipole-forbidden transitions will make contributions only to $B$.[8]

The use of the given data to predict the experimental cross section and an analysis of the various approximations are discussed in Sec. IV.

## II. DISCRETE TRANSITIONS

Earlier publications[3–6] adequately document the theoretical approach developed to treat the unusual situation with respect to the rotational and vibrational degrees of freedom of the hydrogen molecule ion. It suffices to say here that this theory is based on the first Born approximation and that the long-range Coulomb interaction between the electron and molecular ion is neglected. These theoretical treatments define the total cross section $Q_\nu(N)$ for the inelastic event

$$e^-+H_2^+(1s\sigma_g)=e^-+H_2^+(N), \tag{2}$$

where $\nu$ indicates the initial vibrational state of $H_2^+(1s\sigma_g)$ and $N$ the final electronic state of $H_2^+$. The total cross section for exciting the final state $N$ is

$$\bar{Q}(N)=\sum_\nu f_\nu Q_\nu(N)/\sum_\nu f_\nu, \tag{3}$$

where the $f_\nu$ are the occupation numbers of the $H_2^+(1s\sigma_g)$ vibrational states before the collision takes place. As has been shown,[4–6] $Q_\nu(N)$, in atomic units, is

$$\begin{aligned}Q_\nu(N)&=(4\pi)^{-1}\int d\mathbf{R}\,|X_\nu(R)|^2(8\pi/V_0^2)\int_{K_1}^{K_2}dK\\&\quad\times K^{-3}|\langle\phi(N)|\exp(i\mathbf{K}\cdot\mathbf{r})|\phi(0)\rangle|^2 \qquad (4)\\&=\int_0^\infty dR\,R^2|X_\nu(R)|^2Q(N;R),\end{aligned}$$

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[1] G. H. Dunn, B. Van Zyl, and R. N. Zare, Phys. Rev. Letters **15**, 610 (1965).

[2] See the preceding paper by G. H. Dunn and B. Van Zyl, Phys. Rev. **154**, 40 (1967); also A. C. H. Smith (to be published).

[3] R. G. Alsmiller, Jr., Oak Ridge National Laboratory Report No. 3232, 1962 (unpublished).

[4] J. M. Peek, Phys. Rev. **134**, A877 (1964).

[5] D. R. Bates and A. R. Holt, Proc. Phys. Soc. (London) **A85**, 691 (1965).

[6] J. M. Peek, Phys. Rev. **140**, A11 (1965).

[7] D. R. Bates, K. Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. London **A246**, 215 (1953).

[8] L. Vriens, Physica **31**, 1081 (1965); **31**, 1333 (1965); A. E. Kingston, Proc. Phys. Soc. (London) **A86**, 467 (1965).

where $R$ is the internuclear separation, $X_\nu$ is the $\nu$th vibrational-state wave function,[9] $K$ is the momentum transfer, $K_1$ and $K_2$ are the minimum and maximum momentum transfer consistent with energy conservation,[6] $V_0$ is the relative collision velocity in atomic units (the velocity of an electron in the first Bohr orbit of a hydrogen atom), and $\phi(0)$ and $\phi(N)$ are the $1s\sigma_g$ and final electronic wave functions, respectively.

The evaluation of Eq. (4) for a given transition and all $\nu$ requires the Born matrix element,

$$|\langle\phi(N)|\exp(i\mathbf{K}\cdot\mathbf{r})|\phi(0)\rangle|^2,$$

over the range $0<R\leq 20.0a_0$ where the need to use accurate wave functions has been clearly established.[10] The existing data[3,4] on this matrix element prove insufficient for our purposes. To supplement these data, the formula

$$Q(N;R)=I(N;R)[\alpha\ln\Delta E(R)+\beta] \quad (5)$$

has proven useful in interpolating and extending existing $Q(N;R)$ as a function of $R$ for a given $V_0$. The form of Eq. (5) is suggested by the dominance of small $K$ in the processes under consideration and the need for two adjustable parameters in interpolating $Q(N;R)$ between two values of $R$. Here

$$I(N;R)=\lim_{K\to 0}(4\pi)^{-1}\int d\Omega(\mathbf{R}) \times|\langle\phi(N)|\exp(i\mathbf{K}\cdot\mathbf{r})|\phi(0)\rangle|^2/K^2 \quad (6)$$
$$\equiv\lim_{K\to 0}\langle|\langle\phi(N)|\exp(i\mathbf{K}\cdot\mathbf{r})|\phi(0)\rangle|^2\rangle_\Omega/K^2,$$

which is related to the dipole moment for the 0-$N$ transition,[4] $\Delta E(R)$ is the energy defect of the 0-$N$ transition, which is a function of $R$, and $\alpha$ and $\beta$ are constants for a given $V_0$. The solid angle element $d\Omega(\mathbf{R})$ consists of the angular integrations associated with $d\mathbf{R}$ of Eq. (4). Investigation of Eq. (5), using linear combinations of atomic orbitals (LCAO) as wave functions to evaluate $Q(2p\sigma_u;R)$ and $I(2p\sigma_u;R)$, indicated that this formula has a considerable range of validity as a function of both $R$ and $V_0$, although it is best suited for use with collision velocities greater than those for which $Q(N,R)$ has its maximum value.

The integration over $R$ required by Eq. (4) was done in the following way.[9] Existing $Q(2p\sigma_u;R)$ for $R=1.4$, 2.0, 3.2 [4] were interpolated using Eq. (5) and available data for $I(2p\sigma_u;R)$.[11] $Q(2p\sigma_u;R)$ for larger $R$ were found by using the LCAO approximation and then scaling by the ratio of $I(2p\sigma_u;R)$ as calculated with the eigenfunctions divided by the LCAO approximation to this matrix element. This scaling was introduced by Bates and Holt.[5]

TABLE I. The coefficients $A$ and $B$ [see Eq. (1)] for the indicated processes tabulated for each of the $H_2^+$ vibrational states in the $1s\sigma_g$ potential curve. If $V_0$ of Eq. (1) is in atomic units, $Q$ will be in units of $\pi a_0^2$.

| $\nu$ | $A_\nu(2p\sigma_u)$ | $B_\nu(2p\sigma_u)$ | $A_\nu(2p\pi_u)$ | $B_\nu(2p\pi_u)$ | $A_\nu(\Sigma'')$ | $B_\nu(\Sigma'')$ |
|---|---|---|---|---|---|---|
| 0 | 3.10 | 1.96 | 2.79 | 0.007 | 3.56 | 1.48 |
| 1 | 3.45 | 2.61 | 2.91 | 0.058 | 3.70 | 1.57 |
| 2 | 3.84 | 3.40 | 3.04 | 0.111 | 3.85 | 1.68 |
| 3 | 4.28 | 4.34 | 3.16 | 0.166 | 3.99 | 1.79 |
| 4 | 4.79 | 5.48 | 3.27 | 0.221 | 4.15 | 1.91 |
| 5 | 5.35 | 6.87 | 3.38 | 0.277 | 4.31 | 2.05 |
| 6 | 6.00 | 8.55 | 3.49 | 0.334 | 4.49 | 2.20 |
| 7 | 6.74 | 10.6 | 3.59 | 0.391 | 4.67 | 2.36 |
| 8 | 7.61 | 13.2 | 3.68 | 0.448 | 4.86 | 2.54 |
| 9 | 8.61 | 16.4 | 3.75 | 0.504 | 5.06 | 2.73 |
| 10 | 9.82 | 20.6 | 3.82 | 0.558 | 5.28 | 2.94 |
| 11 | 11.26 | 25.9 | 3.88 | 0.612 | 5.49 | 3.17 |
| 12 | 13.1 | 33.2 | 3.94 | 0.666 | 5.71 | 3.42 |
| 13 | 15.4 | 43.3 | 4.00 | 0.722 | 5.94 | 3.69 |
| 14 | 18.4 | 58.2 | 4.05 | 0.778 | 6.18 | 3.98 |
| 15 | 22.8 | 82.1 | 4.11 | 0.835 | 6.43 | 4.29 |
| 16 | 30.0 | 126 | 4.17 | 0.892 | 6.72 | 4.59 |
| 17 | 43.9 | 234 | 4.22 | 0.945 | 7.28 | 4.70 |
| 18 | 91.8 | 782 | 4.29 | 0.969 | 10.3 | 2.94 |
| | 4.97[a] | 6.79[a] | 3.20[a] | 0.20[a] | 4.11[a] | 1.90[a] |

[a] Averaged quantities for a Franck-Condon population of $H_2^+(0)$ vibrational states.

The scaled result can be shown to be too small at small or intermediate $R$.[10] Hence, the value of $Q(2p\sigma_u;R)$ used for $R>3.2$ was the larger of the two values predicted by the Bates and Holt scaling method and extrapolation using Eq. (5). It is worth noting that using Eq. (5) exclusively changed $Q_{18}(2p\sigma_u)$ by less than 5%.

The results for the $1s\sigma_g$-$2p\sigma_u$ transition are given in Table I. The coefficients $A$ and $B$ of Eq. (1) are tabulated for each initial vibrational state $\nu$. These numbers were found, in this and the following calculations, by fitting $Q_\nu(2p\sigma_u)$ data for various $V_0$ to the functional form of Eq. (1). The required $Q_\nu(2p\sigma_u)$ were obtained from the numerical integration of Eq. (4). This form of the cross section[12] is accurate to better than 1% for $V_0\geq 3.0$ atomic units (a.u.). $\bar{Q}(2p\sigma_u)$, defined by Eq. (3), is also calculated by using the Franck-Condon[13] factors for the ionization of $H_2$ as the occupation numbers.

Calculations similar to this have been reported earlier.[5,6] The graphical results given in Ref. 5 were based on the LCAO approximation. The cross sections given here are lower by 20–30%, as predicted earlier,[10] and are the preferred data. Calculations of this cross section for proton projectiles by Bates and Holt[5] have been reported for a number of $\nu$. Comparison at high energies, where the two cross sections should become identical, shows good agreement.

[9] The vibrational wave functions used in these calculations are from the work of S. Cohen, J. R. Hiskes, and R. J. Riddell, Jr., Phys. Rev. **119**, 1025 (1960); S. Cohen, J. R. Hiskes, and R. J. Riddell, Jr., University of California Report No. UCRL 8871, 1959 (unpublished). The normalization is such that $RX_\nu(R)$ of Eq. (4) should be identified with their tabulated functions.

[10] J. M. Peek, Phys. Rev. **139**, A1429 (1965).

[11] D. R. Bates, J. Chem. Phys. **19**, 1122 (1951).

[12] Data for lower relative collision velocities, where Eq. (1) cannot be used, are available from the author.

[13] G. H. Dunn, J. Chem. Phys. **44**, 2592 (1966).

The coefficients $A$ and $B$ are also given in Table I for $Q_v(2p\pi_u)$. The comments on the range of validity[11] of Eq. (1) given above also apply to this case.

Equation (4) was evaluated for this case with the aid of Eq. (5). Data necessary to derive $Q(2p\pi_u; 2.0)$ are given in Ref. 4 and similar unpublished data are available for $Q(2p\pi_u; 3.2)$. These two cross sections are sufficient to determine the $\alpha$ and $\beta$ required by Eq. (5). The matrix element $I(2p\pi_u; R)$ is available[14] for $R \leq 5.0a_0$. Values for $5 < R \leq 20a_0$ were obtained by extrapolation; a fairly safe procedure since $I(2p\pi_u; R)$ changes slowly[14] in this range of $R$, and $I(2p\pi_u; \infty)$ is known.

The use of Eq. (5) to extrapolate $Q(2p\pi_u; R)$ to large $R$ was not tested because of the lack of cross-section data. Since the extrapolation variable $\Delta E(R)$ is bounded in this case by $1.5 \geq \Delta E \geq (\frac{3}{8})$ a.u. for $0 \leq R \leq \infty$, the extrapolation is not lengthy. For this reason it is felt that some confidence can be placed in the procedure.

## III. THE CLOSURE ARGUMENT

As was argued in the introduction, contributions from all electronically excited states of $H_2^+$ must be summed to obtain sufficient data for comparison with experiment. Dunn, Van Zyl, and Zare[1] identified the most important states in their comparison for collision energies below 400 eV. They use a classical (Gryzinski) estimate for the ionization events which is probably accurate for low or intermediate energies. However, use of the classical cross section at high energies is questionable because of its $V_0^{-2}$ energy dependence. Certainly an estimate of $A$ appearing in Eq. (1) cannot be found from the classical cross section.

As an alternative, use is made of the identity

$$\sum_n \langle | \langle \phi(0) | \exp(i\mathbf{K}\cdot\mathbf{r}) | \phi(n) \rangle |^2 \rangle_\Omega = 1, \qquad (7)$$

where the sum is over a complete set of functions. The notation $\langle\ \rangle_\Omega$ indicates that the angular integrations over $d\Omega(\mathbf{R})$, see Eq. (6), have been carried out. Since the $Q_v(2p\sigma_u)$ cross section has been treated separately, and contributions from elastic events are not wanted, Eq. (7) may be rearranged to give

$$\begin{aligned}\sum_n{}'' \langle | \langle \phi(0) | \exp(i\mathbf{K}\cdot\mathbf{r}) | \phi(n) \rangle |^2 \rangle_\Omega \\ = 1 - \langle | \langle \phi(0) | \exp(i\mathbf{K}\cdot\mathbf{r}) | \phi(0) \rangle |^2 \rangle_\Omega \\ - \langle | \langle \phi(0) | \exp(i\mathbf{K}\cdot\mathbf{r}) | \phi(2p\sigma_u) \rangle |^2 \rangle_\Omega. \qquad (8)\end{aligned}$$

Forming the desired sum $\sum_n{}'' Q_v(n)$ from Eq. (4), it can be seen that the order of integration over $R$ and $K$ must be interchanged with the sum in order to use Eq. (8). Assuming that the interchanging of summation with these integrations can be shown to converge, another approximation must be made. Namely, it is necessary to replace the true energy loss in computing $K_1$ and $K_2$ for each state $n$ in the sum with an effective $(\Delta E)_{\text{eff}}$. The cross section resulting from this closure argument is designated by $\tilde{Q}_v(\Sigma'')$, where the nature of the sum is indicated in parentheses and the tilde is symbolic of the approximate nature of the cross section. Hence,

$$\sum_n{}'' Q_v(n) \approx \tilde{Q}_v(\Sigma''). \qquad (9)$$

In this calculation $(\Delta E)_{\text{eff}}$ was taken as the energy difference between the $1s\sigma_g$ potential curve and the energy of two protons, at the prevailing internuclear separation,[6] with the ionized electron having zero kinetic energy. Error terms[15] tend to cancel when $(\Delta E)_{\text{eff}}$ is chosen in this way, with contributions from discrete events being too small and ionization contributions being too large. Investigation of individual error terms[15] in the high-energy limit (Bethe's approximation to the first Born cross section) shows that the error tends to vanish like $V_0^{-2}$. This is not an impressive rate when one notes that the Born cross section is proportional to $V_0^{-2} \ln V_0$ in the high-energy limit. However, this does prove the important point that $A$ in Eq. (1) is unaffected by this approximation and is in fact independent of the energy loss of the inelastic process. The use of sum rules, Eq. (7), in situations similar to this is not new[16] but a general error treatment has not as yet been given. Experience gained in testing a rather different scattering system[6] leads one to postulate that $\tilde{Q}_v(\Sigma'')$ as evaluated here, is too large but no bound on the error can be given.

It follows from Eq. (8) that $\tilde{Q}_v(\Sigma'')$ can be evaluated with just knowledge of the $1s\sigma_g$ and $2p\sigma_u$ wavefunctions. The data discussed in Sec. II are sufficient for $\langle | \langle \phi(1s\sigma_g) | \exp(i\mathbf{K}\cdot\mathbf{r}) | \phi(2p\sigma_u) \rangle |^2 \rangle_\Omega$. The situation is not as good with respect to the remaining matrix element required by Eq. (8). The most convenient evaluation of this matrix element would be with the use of the appropriate LCAO approximation to $\phi(1s\sigma_g)$. Since it is known that high-energy inelastic electron scattering is dominated by small $K$, it is advisable to check Eq. (8) in this limit. Thus,

$$\begin{aligned}K^{-2} \sum_n{}'' \langle | \langle \phi(0) | \exp(i\mathbf{K}\cdot\mathbf{r}) | \phi(n) \rangle |^2 \rangle_\Omega \\ = K^{-2} \langle \langle \phi(0) | (\mathbf{K}\cdot\mathbf{r})^2 | \phi(0) \rangle \rangle_\Omega \\ - K^{-2} \langle | \langle \phi(0) | (i\mathbf{K}\cdot\mathbf{r}) | \phi(2p\sigma_u) \rangle |^2 \rangle_\Omega + O(K^{+2}) \qquad (10)\end{aligned}$$

as $K$ becomes arbitrarily small. Data[17] necessary to

[14] D. R. Bates, R. T. S. Darling, S. C. Hawe, and A. L. Stewart, Proc. Phys. Soc. (London) **A66**, 1124 (1953).

[15] Error terms are easily identified in the manner outlined in Sec. IV of Ref. 6. Also see S. T. Butler and L. Parcell, Phys. Letters **14**, 110 (1965). These terms have been investigated in detail for a hydrogenic-type transition with the result that errors are confined to $B$ of Eq. (1) or higher terms of the expansion in $V_0$ of the cross section. This investigation also shows that the inclusion of the entire continuum in Eq. (7), imposed by the completeness requirement, does not give rise to error terms contributing to $A$ of Eq. (1). The author is indebted to T. A .Green for many helpful suggestions on these points.

[16] I. M. Cheshire and H. L. Kyle, Phys. Letters **17**, 115 (1965).

[17] A. Dalgarno and G. Poots, Proc. Phys. Soc. (London) **A67**, 343 (1954).

evaluate the first term of Eq. (10) are available, and the LCAO approximation is found to be about twice the exact value for intermediate $R$. On this basis, a considerable error in the coefficient $A$ of Eq. (1) can be expected if $\phi(1s\sigma_g)$ is approximated by the LCAO wavefunction.

The situation can be improved by replacing Eq. (8) with

$$\sum_n{}''\langle|\langle\phi(0)|\exp(i\mathbf{K}\cdot\mathbf{r})|\phi(n)\rangle|^2\rangle_\Omega = G(K,R)[1-\langle|\langle\phi(0)|\exp(i\mathbf{K}\cdot\mathbf{r})|\phi(0)\rangle|^2\rangle_\Omega] - \langle|\langle\phi(0)|\exp(i\mathbf{K}\cdot\mathbf{r})|\phi(2p\sigma_u)\rangle|^2\rangle_\Omega, \quad (11)$$

where

$$G(K,R)=G(0,R)[1+g(R)K^2], \quad K\leq 2 \quad (12)$$
$$=1, \quad K\geq 2$$

and the LCAO matrix element has been used for $\langle|\langle\phi(0)|\exp(i\mathbf{K}\cdot\mathbf{r})|\phi(0)\rangle|^2\rangle_\Omega$. The scaling function $G(0,R)$ is defined as $\langle\langle\phi(0)|(\mathbf{K}\cdot\mathbf{r})^2|\phi(0)\rangle\rangle_\Omega$ calculated with the $H_2^+$ eigenfunctions divided by the value of the same matrix element found by using the LCAO wave functions. This guarantees that the limiting relationship required by Eq. (10) is satisfied and, consequently, $A$ of Eq. (1) will be correct.

The actual functional form of $G(K,R)$ is dictated by three considerations. First, an argument has been given[10] which indicates that $\langle|\langle\phi(0)|\exp(i\mathbf{K}\cdot\mathbf{r})|\phi(0)\rangle|^2\rangle_\Omega$, as calculated with the LCAO wave functions, becomes reasonably accurate for large $K$. Second, the limit

$$\lim_{K\to\infty}\sum_n{}''\langle|\langle\phi(0)|\exp(i\mathbf{K}\cdot\mathbf{r})|\phi(n)\rangle|^2\rangle_\Omega=1 \quad (13)$$

is required, and third, only even powers of $K$ are known to appear in the small $K$ expansion of Eq. (8).

Data from Ref. 17 provide $G(0,R)$ for $R\leq 3a_0$ and these calculations were extended to $R=5a_0$. At this point it was found that $G(0,5)=0.882$. For $R>5a_0$ it was assumed that $G(0,20)=1.0$ and a smooth curve was used to connect $G(0,5)$ and $G(0,20)$. This procedure could introduce errors of several percent in $G(0,R)$ for $R>5a_0$ but any error would only seriously affect the results for the higher $\nu$. The conditions stated by Eq. (12) are sufficient to determine $g(R)$.

Table I contains $A$ and $B$ for $\bar{Q}_\nu(\Sigma'')$. Some data of a similar nature are provided by Bates and Holt.[5] They calculate the equivalent to $\bar{Q}_\nu(\Sigma'')$ for a few $\nu$, but include in their closure relationship just the dipole-allowed events. The values of $A$ extracted from their data agree well with the present results and their $\bar{Q}_\nu(\Sigma'')$ are about 90 to 95% of the estimate given here. This relationship between the two calculations, the same $A$ but smaller $B$, is consistent with the different closure relationships that were used.

## IV. THE TOTAL DISSOCIATION CROSS SECTION

The total dissociation cross section, for a given initial vibrational state $\nu$, is

$$Q_\nu(D)\equiv Q_\nu(2p\sigma_u)+\sum_n{}'' Q_\nu(n) \approx Q_\nu(2p\sigma_u)+\bar{Q}_\nu(\Sigma'') \quad (14)$$

if the experiment measures the dissociation in some direct manner. The data in Table I are sufficient to determine $Q_\nu(D)$. However, protons from the reaction of Eq. (2) are often detected[1] and this cross section is defined by

$$Q_\nu(P)=Q_\nu(d)+2Q_\nu(c) \quad (15)$$

since each ionization event produces two protons. Here $d$ implies a discrete process and $c$ an ionization event. In terms of the data given in Table I

$$Q_\nu(P)=Q_\nu(D)+Q_\nu(c), \quad (16)$$

where an estimate of $Q_\nu(c)$ must be given. The data of Table I provide an upper bound on $Q_\nu(c)$ which will be defined as

$$Q_\nu(<)\equiv Q_\nu(D)-Q_\nu(2p\sigma_u)-Q_\nu(2p\pi_u)\geq Q_\nu(c). \quad (17)$$

Using the approximations of Eqs. (14) and (17), $Q_\nu(P)$ can be found from Eq. (16).

Considering only the cross sections averaged over the Franck-Condon population of $\nu$ for the sake of brevity, it turns out that $\bar{Q}(<)$ is about 13% of $\bar{Q}(D)$ in the 0.3–1.0-keV energy range. The estimate by Dunn *et al.*[1] gives $\bar{Q}(c)$ as a little less than 10% of $\bar{Q}(D)$ at a collision energy of 340 eV. Since $\bar{Q}(<)$ is an upper bound and the Dunn *et al.* estimate of $\bar{Q}(c)$ may be a little low in this energy range because it came from a classical calculation, the size of $\bar{Q}(c)$ seems fairly well determined. The important point established by the results given here is that $\bar{Q}(c)$ is not a dominant factor in $\bar{Q}(P)$, hence great accuracy is not required for this quantity.

It is worth noting that the most important parameter in the cross section, $A$, can be found by a simple and "independent" calculation. As was argued above, $A$ is not dependent on the conservation of energy for the reaction and can be shown to be (cf. Ref. 18)

$$A_\nu(N)=8\int_0^\infty dR\,R^2|X_\nu(R)|^2 I(N,R), \quad (18)$$

where $I(N,R)$ is defined by Eq. (6) and can be found in the literature[11,14,17] for the states being considered here. This check on the various $A(N)$ gave satisfactory agreement with the data given in Table I. It follows that some confidence can be placed in the predicted slope of plots of $V_0^2Q$ versus $\ln V_0$. The data used for large $R$ for both the $Q_\nu(N)$ and $A_\nu(N)$ calculations may not be the most accurate since LCAO matrix elements were

[18] A. E. Kingston and J. E. Lauer, Proc. Phys. Soc. (London) 87, 399 (1966).

used as a guide. However, these errors should not be large and should be confined to the highest vibrational states.

In conclusion we list the various approximations involved and evaluate them insofar as possible at the present time. The use of the first Born approximation at these collision energies is generally accepted as valid. Because the target is charged, use of the so-called Coulomb-Born approximation is indicated. However, there is evidence[19] that the use of plane waves instead of Coulomb waves for the scattering electron is well justified at the energies being considered here although this point is receiving further theoretical consideration. The treatment of the internal degrees of freedom of $H_2^+$ is essentially untested. Various similar models have been explored[20] and approaches in the spirit of this theory have proven useful. However, this appears to be the first application to such highly excited vibrational states and as a result the cross sections for the higher $\nu$ require further critical study. The comparison given by Dunn *et al.*,[1] at low collision energies, indicates that this theory is at least qualitatively correct. Perhaps it should be pointed out, however, that errors in the Born approximation and in the neglect of Coulomb distortion at low collision energies tend to cancel; the Born approximation is usually too large while the neglect of an attractive Coulomb field will result in a lower cross section.[21] The problems associated with summing contributions from all excited electronic states are discussed in the above paragraphs. A hidden assumption in the use of closure is the Born-Oppenheimer separation of nuclear and electronic variables. This may not be accurate, especially for the ionization events. The choice of the prevailing population of vibrational states in a given experiment is beyond the scope of this work.

[19] D. F. Dance, M. F. A. Harrison, and A. C. H. Smith, Proc. Roy. Soc. (London) **A290**, 74 (1966).

[20] M. R. Flannery and U. Öpik, Proc. Phys. Soc. (London) **A86**, 491 (1965).

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[21] M. J. Seaton, *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), p. 375.

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# Forbidden Photo-Ionization and Electron Spin Polarization

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A new mechanism involving normally forbidden processes, namely spin-dependent electric dipole and spin-dependent magnetic quadrupole transitions, is applied to the photo-ionization of atoms with a single *ns* outer electron. It is shown that, if the incident light is circularly polarized, the spin of the electrons ejected by these forbidden processes gets polarized along the direction of the light propagation as the axis of spin quantization. The cross section of photo-ionization by these transitions is shown to be at its maximum when the propagation vectors of the ejected electrons are parallel to the quantization axis, and is computed for the case of H, Li, and Na. This is in contrast to the spin-independent multipole transitions, where the cross section is zero for electrons ejected in that direction. The photo-ejected electrons are shown to be 100% spin-polarized when they propagate along the quantization axis. However, the spin polarization drops rapidly when the electron propataion vector deviates from that axis. This is illustrated by calculations on H, Li, and Na.

## 1. INTRODUCTION

PHOTO-IONIZATION, the ejection of valence electrons from the material system interacting with light, is a well-known process and has been studied for atomic and molecular systems.[1] Theoretically[2] this process has been treated as an electric dipole interaction between electrons and the incident light. The electron photo-ionized in this way will propagate mostly along the directions which are perpendicular to that of the light, and there will be no electrons propagating along the direction of the light. Since this dipole interaction process is electron-spin-independent, the spin of the ejected electron will remain the same as that of the valence electron in the atom (the effect due to spin-orbit coupling is considered to be very small).

The forbidden photo-ionization considered here is the process due to the electron-spin-dependent part of the

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[1] For a review on this subject, see R. W. Ditchburn and U. Öpik, in *Atomic and Molecular Process*, edited by D. R. Bates (Academic Press Inc., New York, 1964), p. 79.

[2] D. R. Bates, Monthly Notices Roy. Astron. Soc. **106**, 423 and 432 (1946).