For many electron-diatomic molecules it is clear that a single-center Slater determinant provides the practical counterpart of the zeroth-order wave function. This also allows polarization to be handled in analogy with electron-atom scattering.[9,23] This approximation will also automatically yield at least part of the quadrupole potential.

With regard to the further applicability of single-center wave functions to collision problems, Khare[24] has found that single-center wave functions yield surprisingly good results for excitation of H_2 by electron impact when used within the confines of the Born-Ochkur approximation. More recently[25] he has extended his calculations to the photoionization of H_2 using final-state wave functions of the present method suitably modified to the equilibrium separation $R_{AB}=1.4$ of H_2. His results thus far are very encouraging.

ACKNOWLEDGMENTS

We should like to extend a very special note of thanks to Allan Silver for his extremely capable programming and associated analytical work. One of us (A. T.) expresses his gratitude to Professor A. Dalgarno for a very incisive remark concerning the utility of the single-center wave function in molecular scattering calculations.

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[23] D. G. Thompson, Proc. Roy. Soc. (London) **A294**, 160 (1966).

[24] S. P. Khare, Phys. Rev. **149**, 33 (1966); **152**, 74 (1966); **157**, 107 (1967).

[25] S. P. Khare (private communication).

PHYSICAL REVIEW VOLUME 160, NUMBER 1 5 AUGUST 1967

Theory of High-Energy Inelastic Collisions between Molecular Systems. Dissociation of H_2^+ on Collision with H_2†

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(Received 28 November 1966; revised manuscript received 6 March 1967)

Inelastic collisions between the hydrogen molecule ion (H_2^+) and the hydrogen molecule are investigated theoretically within the framework of the first Born approximation. The possibility that H_2^+ may be in an excited vibrational state before the collision takes place is given special consideration. Appropriate sums of the theoretical cross sections are identified with the experimental measurements of the cross section σ_1, for the dissociation of H_2^+ into a proton and hydrogen atom, and of $\sigma_1+\sigma_2$, where σ_2 is the ionization cross section of H_2^+. Agreement is good between theory and σ_1 for collision energies greater than 50 keV and between theory and $\sigma_1+\sigma_2$ for collision energies greater than 1 MeV. Any discrepancies between experiment and theory can be identified as either the expected failure of the Born approximation at low energies or the omission of certain inelastic processes in the theoretical results.

I. INTRODUCTION

A SERIES of recent papers[1–4] has treated the electronic excitation of the hydrogen molecule ion (H_2^+) when scattered by a structureless charged particle. One of these publications[3] also included a treatment of H_2^+ collisions with hydrogen atoms and a recommendation that the approach developed in this paper could be used for complicated neutral targets. A study of this nature for the $H_2^+-H_2$ scattering system is the object of the present paper.

The collision of interest is

$$H_2^+(0)+H_2(0)=H_2^+(n)+H_2(N). \qquad (1)$$

The electronic states are indicated in parentheses; the zeros stand for the ground electronic states and it is stipulated that $n\neq 0$ but N may be equal to 0. If it is assumed that (1) all n lead to the dissociation of H_2^+ and (2) no other mechanism, such as direct vibrational dissociation, contributes in an important way to dissociation, the experimental results on H_2^+ dissociation can be identified with the theoretical data provided here. Experimental studies detect fast protons and/or hydrogen atoms from the dissociation of H_2^+ and the final state of the target is usually not specified. The cross section for proton–plus–hydrogen-atom production is designated σ_1 and the total proton production is called $\sigma_1+2\sigma_2$, where σ_2 is the cross section for

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† This work was supported by the U.S. Atomic Energy Commission.

* 1965 Summer employee of Sandia Laboratory.

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

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

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

[4] J. M. Peek, Phys. Rev. **154**, 52 (1967).

H_2^+ ionization. Then on the basis of assumptions (1) and (2), σ_1 will be equal to a sum of cross sections for reaction (1) which includes all N and those n for which the final electronic state of H_2^+ is discrete. Likewise, σ_2 will be equal to the sum of cross sections for reaction (1) over all N and over the continuum electronic states of H_2^+.

The first assumption mentioned above has received some experimental justification[5] from H_2^+ dissociation by charged particles. The second assumption seems reasonable if the model is restricted to the relatively high collision energies where the first Born approximation can be assumed to be valid.

The choice of the $H_2^+-H_2$ scattering system for this study is dictated by two considerations. First, and most important, H_2^+ is a molecular species and H_2 is a target whose individual molecular properties are relatively well understood from a theoretical viewpoint. Unless the structure of the individual collision partners is well understood, it would seem pointless to attempt the prediction of their inelastic scattering in any detail. Second, the $H_2^+-H_2$ system has had a rather thorough experimental investigation (cf. Refs. 6–8) over a wide range of collision energies and only minor discrepancies exist between the results quoted by a number of different laboratories. In addition, a number of interesting speculations concerning the behavior of the experimental results for this system can be tested from a theoretical viewpoint. For instance, it will be shown that several diverse observations of the effect of the population of H_2^+ vibrational states before collision can be qualitatively rationalized. Also, an explanation of the double peak in the $\sigma_1+2\sigma_2$ cross section will be shown to be partially correct.

A brief review of the adaptation of the first Born approximation to molecular scattering on neutral targets is given in Sec. II, and additional details are provided in the Appendix. Section III contains a comparison of the theoretical results for σ_1 and $\sigma_1+\sigma_2$ with experiment. This comparison supports the conclusion that quantitative predictions of total cross sections for inelastic events involving complex scattering systems are possible and practical to effect. To the author's knowledge, this is the first direct test of Born-theoretic results for scattering systems of this nature,[3] so perhaps some caution is advisable.

II. FORMALISM

Using the techniques and approximations of Ref. 1, it is a simple matter to generalize the results given in Sec. IV of Ref. 3 to the collision indicated by Eq. (1). With appropriate changes in the notation of Ref. 3,

$$Q_{\nu\mu}(n, N)$$

$$\int_0^\infty \int_0^\infty R^2 dR\, P^2 dP\, |\mathrm{X}_\nu(R)|^2 |\Xi_\mu(P)|^2 Q(R, P; n, N) \tag{2}$$

gives the first Born total cross section for a collision between H_2^+ and H_2. The subscripts on the cross section Q indicate the initial vibrational states of H_2^+ and H_2, respectively, and the final electronic states, appropriate to the collision defined by Eq. (1), are given in parentheses. The H_2^+ internuclear separation is R, its initial vibrational wave function is X_ν, and the analogous quantities for H_2 are P and Ξ_μ. Here

$$Q(R, P; n, N)$$
$$=8\pi V_0^{-2}\int_{K_0}^{K_1} dK\, K^{-3}\, |\epsilon_n(K, R)|^2 |E_N(K, P)|^2, \tag{3}$$

where V_0 is the relative collision velocity in atomic units, K is the momentum transfer, K_0 is the minimum momentum transfer, and K_1 is the maximum momentum transfer. In Eq. (3)

$$|\epsilon_n(K, R)|^2=(4\pi)^{-1}\int d\Omega(\mathbf{R}) \left| \int d\mathbf{r}\, \phi_0\phi_n^* \exp(-i\mathbf{K}\cdot\mathbf{r}) \right|^2, \tag{4}$$

$$|E_N(K, P)|^2=(4\pi)^{-1}\int d\Omega(\mathbf{P}) \left| \int d\mathbf{r}_1 d\mathbf{r}_2\, \psi_0\psi_N^* [\exp(i\mathbf{K}\cdot\mathbf{r}_1)+\exp(i\mathbf{K}\cdot\mathbf{r}_2)] \right|^2 \tag{5}$$

for the case in which H_2 is in an excited electronic state after the collision, and

$$|E_0(K, P)|^2=(4\pi)^{-1}\int d\Omega(\mathbf{P}) \left| \int d\mathbf{r}_1 d\mathbf{r}_2\, \psi_0\psi_0^* [\exp(i\mathbf{K}\cdot\mathbf{r}_1)+\exp(i\mathbf{K}\cdot\mathbf{r}_2)-2\cos(\tfrac{1}{2}\mathbf{K}\cdot\mathbf{P})] \right|^2 \tag{6}$$

for the case in which H_2 is left in its ground state after the collision. The electronic eigenfunctions of H_2^+ and H_2 are ϕ_n and ψ_N, respectively, and $d\Omega$ is the element of solid angle for the indicated vector. If the populations of the vibrational states, before collision, of H_2^+ and H_2 are f_ν and g_μ, respectively,

$$Q(n, N)=\sum_\nu\sum_\mu f_\nu g_\mu Q_{\nu\mu}(n, N)/\sum_\nu\sum_\mu f_\nu g_\mu \tag{7}$$

defines the cross section for reaction (1). All quantities are in atomic units.

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[5] G. H. Dunn and B. Van Zyl, Phys. Rev. **154**, 40 (1967).

[6] G. W. McClure, Phys. Rev. **130**, 1852 (1963).

[7] J. F. Williams and D. N. F. Dunbar, Phys. Rev. **149**, 62 (1966).

[8] K. H. Berkner, S. N. Kaplan, R. V. Pyle, and J. W. Stearns, Phys. Rev. **146**, 9 (1966).

A detailed derivation of Eqs. (2)–(6) is given in the Appendix. To make the significance of the cross section defined by Eq. (2) apparent without getting into the details provided in the Appendix, an interpretation of the derivation is now given. The basic framework of this approach is the first Born approximation. In addition, it has been assumed that the molecular wave functions can be written as a product of electronic, rotational, and vibrational functions. The rotation of the molecules in their electronic ground state is assumed to be that of a linear system or a spherical top. To arrive at Eq. (2), a sum over all rotational and vibrational states of the final electronic states of the molecules has been performed. In addition, the contributions from the degenerate levels of the initial rotational levels have been averaged. Hence the cross section defined by Eq. (2) will not show any structure due to the final rotational or vibrational states but has an explicit dependence on the initial vibrational states of the molecular systems. In performing the required sums, either energy conservation is lost or a restrictive assumption concerning the excited-state vibrational functions must be made. The first method is discussed in Ref. 1 and the second in Ref. 3; it has been established that the two models lead to essentially the same results.[3]

It is possible to proceed numerically from this point in a straightforward manner, but available knowledge of the system allows further simplification with little loss of accuracy. The usual experimental conditions are such that H_2 will be in its ground vibrational state. It should then be a good approximation to replace $Q(R, P; n, N)$ by $Q(R, P^*; n, N)$, where P^* is the internuclear separation of H_2 at which $|\Xi_0(P)|^2$ has its maximum. The integration in Eq. (2) over P can be carried out immediately with the result for this case that

$$Q_{\nu 0}(n, N) = \int_0^\infty R^2 dR\, |\mathrm{X}_\nu(R)|^2 Q(R, P^*; n, N). \quad (8)$$

Under these conditions, Eq. (7), of course, reduces to a single sum over ν. This result is equivalent to a slightly different model of the hydrogen-molecule target. Equation (8) will be the direct result of assuming that H_2, prior to collision only, is a rigid rotator with no vibrational degrees of freedom. This model, provided the initial rotation of the target is that of a rigid rotator or rigid spherical top, is useful for treating a more general class of targets.

As discussed above a sum over all final electronic states of the target is necessary since the final state of the target is unspecified for existing experimental data. Hence

$$\sum_N Q_{\nu 0}(n, N) = Q_{\nu 0}(n, 0) + \sum_N{}' Q_{\nu 0}(n, N) \quad (9)$$

is required, where the sum over N includes all electronic states of H_2. A single prime alludes to the fact that the appropriate ground-state term is omitted from the sum, a double prime indicates that the next lowest term is also omitted, etc. For convenience and because of the lack of excited-state wave functions for H_2, the techniques discussed in Ref. 3 utilizing the closure relationship were used to obtain the primed sum with the result

$$\sum_N Q_{\nu 0}(n, N) \cong Q_{\nu 0}(n, 0) + \tilde{Q}_{\nu 0}(n, \Sigma') + \Delta Q_{\nu 0}(n, \kappa) \equiv \tilde{Q}_{\nu 0}(n, \Sigma). \quad (10)$$

Sums over cross sections that are evaluated by a closure argument are indicated by the tilde and the nature of the sum is signified by the symbols in parentheses. The term ΔQ is a correction term to the closure result. The nature of the closure argument used here is analogous to that discussed in Sec. IV of Ref. 3 and the correction terms are also derived in the same section. The symbol κ refers to an electronic continuum state; hence the correction term in Eq. (10) refers to the H_2 continuum correction term. An integration over the entire continuum is understood.

The matrix elements necessary to evaluate the first term of Eq. (10) are given by Eqs. (4) and (6). The H_2 molecule matrix element for the second term is

$$|E_{\Sigma'}(K, P^*)|^2 = (4\pi)^{-1} \int d\Omega(\mathbf{P}^*) \Big[\int d\mathbf{r}_1 d\mathbf{r}_2\, \psi_0 \psi_0^* \{2 + \exp[i\mathbf{K}\cdot(\mathbf{r}_1 - \mathbf{r}_2)] + \exp[i\mathbf{K}\cdot(\mathbf{r}_2 - \mathbf{r}_1)]\} - \Big| \int d\mathbf{r}_1 d\mathbf{r}_2\, \psi_0 \psi_0^* [\exp(i\mathbf{K}\cdot\mathbf{r}_1) + \exp(i\mathbf{K}\cdot\mathbf{r}_2)] \Big|^2 \Big], \quad (11)$$

and for the third term of Eq. (10) is

$$|E_\kappa(K, P^*)|^2 = (4\pi)^{-1} \int d\boldsymbol{\kappa} \int d\Omega(\mathbf{P}^*) \Big| \int d\mathbf{r}_1 d\mathbf{r}_2\, \psi_0 \psi_\kappa^* [\exp(i\mathbf{K}\cdot\mathbf{r}_1) + \exp(i\mathbf{K}\cdot\mathbf{r}_2)] \Big|^2. \quad (12)$$

Here ψ_κ is an H_2 electronic continuum eigenfunction.

The sum of the cross sections σ_1 and σ_2, discussed in Sec. I, requires a sum over all excited electronic states of H_2^+. For a given initial vibrational state of H_2^+, the sum

$$\sum_n{}' \sum_N Q_{\nu 0}(n, N) = \sum_n{}' Q_{\nu 0}(n, 0) + \sum_n{}' \sum_N{}' Q_{\nu 0}(n, N) \quad (13)$$

is needed. Using closure arguments again, and ignoring all correction terms,

$$\sum_n{}'\sum_N Q_{\nu 0}(n,N)\cong Q_{\nu 0}(2p\sigma_u,0)+\tilde{Q}_{\nu 0}(\Sigma'',0)$$
$$+\tilde{Q}_{\nu 0}(2p\sigma_u,\Sigma')+\tilde{Q}_{\nu 0}(\Sigma'',\Sigma')\equiv\tilde{Q}_{\nu 0}(\Sigma',\Sigma). \quad (14)$$

A sum of $\tilde{Q}_{\nu 0}(\Sigma',\Sigma)$ over the initial vibrational population of H_2^+ [see Eq. (7)] will then be our approximation to the experimentally determined $\sigma_1+\sigma_2$. The matrix elements required in addition to Eqs. (11) and (12) are defined by Eq. (4) and

$$|\epsilon_{\Sigma''}(K,R)|^2=1-|\epsilon_0(K,R)|^2-|\epsilon_{2p\sigma_u}(K,R)|^2. \quad (15)$$

See Eqs. (A8) and (A11) for the definition of ϵ_0. Since we have neglected all correction terms to this "double closure" result, predictions of $\sigma_1+\sigma_2$ are limited to relatively large collision energies. "Relatively large" in this context means energies at which $\sigma_1+\sigma_2$ starts to show the V_0^{-2} asymptotic behavior.

In order to evaluate the cross sections of interest, the wave functions ϕ_0 and $\phi_{2p\sigma_u}$ are needed[4] over the range of internuclear separations $0\leq R\leq 20a_0$. These are approximated by the appropriate linear combination of atomic orbitals (LCAO) functions. The $H_2^+(1s\sigma_g)$ vibrational functions required by Eq. (8) have been tabulated numerically[9] and in the present notation are normalized such that

$$\int_0^\infty R^2dR\,|X_\nu(R)|^2=1. \quad (16)$$

The H_2 ground-state wave function is approximated by the Wang function[10] with the scaling parameter equal to 1.166 and $P^*=1.40a_0$. The continuum correction term in Eq. (10) was approximated by multiplying the hydrogenic continuum correction term,[3] evaluated with an energy defect appropriate to H_2, multiplied by 1.73. This procedure gives results for the ionization of H_2 which are rather similar to the prediction of H_2 ionization obtained from the classical scaling of H ionization.[11]

These wave functions give sufficient information for the calculation of $\tilde{Q}_{\nu 0}(2p\sigma_u,\Sigma)$ and $\tilde{Q}_{\nu 0}(\Sigma',\Sigma)$. In the following discussion, need will arise for $\tilde{Q}_{\nu 0}(n,\Sigma)$, where n is some higher discrete state of H_2^+. Of these cases we will, out of necessity, treat only the $1s\sigma_g-2p\pi_u$ transition and use the approximation

$$\tilde{Q}_{\nu 0}(2p\pi_u,\Sigma)\cong\tilde{Q}(R^\ddagger,P^*;2p\pi_u,\Sigma). \quad (17)$$

The use of Eq. (17) in place of Eq. (2) is equivalent to ignoring the vibrational degrees of freedom of both H_2 and H_2^+.

The approximation of Eq. (17) has been tested by comparing $\tilde{Q}(2.0,P^*;2p\pi_u,\Sigma)$ and $\tilde{Q}(3.2,P^*;2p\pi_u,\Sigma)$. Unpublished data for $|\epsilon_{2p\pi_u}(K,3.2)|^2$, based on the H_2^+ eigenfunctions and similar to those data available[1] for $|\epsilon_{2p\pi_u}(K,2.0)|^2$, were used for this test. The two cross sections are found to differ by less than 5% except near their maxima, where the difference increases to as much as 25%. Hence, in contrast to the results found for the $1s\sigma_g-2p\sigma_u$ transition,[3,5] it may be a reasonably accurate approximation to ignore the effects of excited vibrational states of H_2^+ on transitions to higher electronic states with the possible exception of the energy range near the maximum of the cross section. A discussion of the experimental results in the following section provides further justification for this approximation.

The use of the LCAO (linear combination of atomic orbitals) functions for H_2^+ has been discussed elsewhere in detail.[12] It was concluded in Ref. 12 that these approximate functions will give rather accurate results for cross sections, such as these, where intermediate and large momentum transfers play a dominant role. The arguments of Ref. 12 also imply that variational wave functions optimized with respect to the electronic energy tend to give more accurate values for the Born matrix element at high momentum transfers than at low momentum transfers. Hence, use of the Wang function for H_2 is a better function for $H_2^+-H_2$ scattering than it would be for e^--H_2 scattering calculations.

III. RESULTS AND COMPARISON WITH EXPERIMENT

Because of space considerations and the fact that no experimental data resolving initial vibrational states

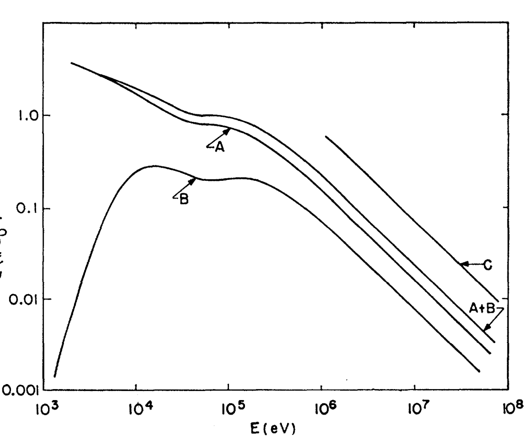

FIG. 1. The theoretical cross sections A, B, and C, which are defined in the first paragraph of Sec. III, shown as a function of the collision energy.

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[9] 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).

[10] W. Kauzmann, *Quantum Chemistry* (Academic Press Inc., New York, 1957), p. 450.

[11] B. L. Schram, F. J. de Heer, M. J. van der Wiel, and J. Kistemaker, Physica **31**, 94 (1964); W. C. Lineberger, J. W. Hooper, and E. W. McDaniel, Phys. Rev. **141**, 165 (1966).

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

of H_2^+ have been published, only cross sections of the type $Q(n', N)$ will be given. It has been assumed[13] that the initial vibrational distribution of H_2^+ is given by the Franck-Condon factors[14] for ionization of H_2. The data available for comparison with experiment are shown in Fig. 1. In terms of the notation of Sec. II, the curves A, B, and C are defined as

$$A=Q(2p\sigma_u,0)+\tilde{Q}(2p\sigma_u,\Sigma')+\Delta Q(2p\sigma_u,\kappa),$$

$$B=Q(3.2,1.4;2p\pi_u,0)+\tilde{Q}(3.2,1.4;2p\pi_u,\Sigma')+\Delta Q(3.2,1.4;2p\pi_u,\kappa),$$

and

$$C=Q(2p\sigma_u,0)+\tilde{Q}(\Sigma'',0)+\tilde{Q}(2p\sigma_u,\Sigma')+\tilde{Q}(\Sigma'',\Sigma')=\tilde{Q}(\Sigma',\Sigma).$$

It can be seen that these cross sections have, at first sight, some unusual characteristics. Apparently the maximum in A occurs at collision energies less than 1 keV. This is due to the relative importance of high vibrational states in the $Q(2p\sigma_u, 0)$ cross section for which the energy loss ΔE of the inelastic process becomes quite small. This behavior is analogous to the electron dissociation cross section[5] for H_2^+ which has a maximum, if one exists, for collision energies below 13 eV. The importance of high vibrational states is of course strongly dependent on the initial population of these states and any conclusion in this energy range will be strongly influenced by the assumed population.[13] Inspection of the published curves[3] for H_2^+ collisions with H indicates that the assumed population will play only a minor role for collisions above 20 keV. The low-energy behavior of B, for which ΔE never becomes very small, is more typical of inelastic cross sections. Rather than the usual single maximum, both A and B show structure at high energies. From previous work[3,15] this is known to be the result of excitation of the target molecule. In this case, simultaneous excitation events are roughly 80% or more of A or B at high energies. Simultaneous excitations also explain why the asymptotic V_0^{-2} behavior occurs at such high energies. It is interesting to note that C starts to deviate from the asymptotic behavior at 1-2 MeV.

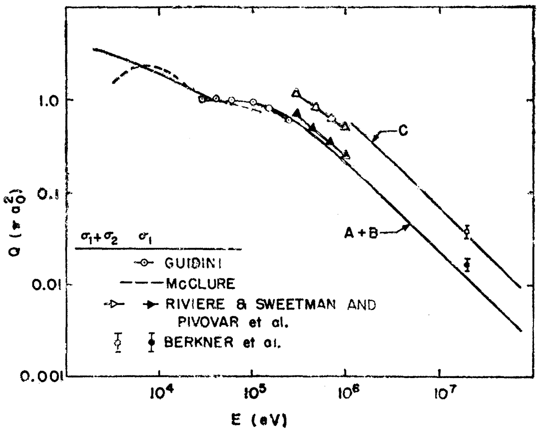

FIG. 2. This graph shows the comparison of the theoretical results for $A+B$ and C with σ_1 and $\sigma_1+\sigma_2$, respectively, as determined by the indicated experimentalists. J. Guidini (see Ref. 18); G. W. McClure (see Ref. 19; this curve was derived from measurements of other collision processes); A. C. Riviere and D. R. Sweetman (see Ref. 23); L. I. Pivovar *et al.* (see Ref. 20); K. H. Berkner *et al.* (see Ref. 8).

TABLE I. The high-energy coefficient α, of $E\sigma=\alpha$, from various theoretical estimates and experiment for σ_1 and $\sigma_1+\sigma_2$. α (πa_0^2 MeV/molecule).

	σ_1	$\sigma_1+\sigma_2$
S[a]	···	0.28–0.51
P[b]	(>) 0.237	0.707
B(S)[c]	0.521	0.805
B(G)[d]	1.52	2.11
B(expt)[e]	0.328	0.732

[a] Reference 16.
[b] Present results.
[c] Salpeter's theory; see Ref. 8.
[d] Gryziński's theory; see Ref. 8.
[e] Experiment from Ref. 8.

No theoretical results are available for comparison with the present results other than the calculations reported by Salpeter[16] and by Berkner *et al.*,[8] which are applicable only in the asymptotic region. In this energy range the total cross section can be written $E\sigma=\alpha$, where E is the collision energy and α is a constant. Berkner *et al.*[8] perform two calculations; one is an improvement of the Salpeter calculation which includes the influence of the H_2^+ vibrational motion on the energy defect of the reaction, and the other is a Gryziński[17] calculation for the same model of the collision system. These various results are compared in Table I. It is interesting that the improved Salpeter calculation, the present results, and experiment agree rather well, while the Gryziński theory is significantly in error.

For the comparison given in the preceding paragraph and in the following discussion, the identifications

$$A+B\leq\sigma_1$$

and

$$C=\sigma_1+\sigma_2$$

have been made. The inequality for σ_1 results from the fact that all discrete states of H_2^+ are included in the experimental measurement. The inequality tends toward an equality for decreasing collision energies and the inequality is emphasized for large collision energies.

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[13] There is some experimental justification for this assumption. See Ref. 5 and D. W. Turner and D. P. May [J. Chem. Phys. **45**, 471 (1966)] for studies of two different ionization mechanisms which give supporting evidence. However, as discussed in the last paragraph of this section, ion source conditions have a real effect on the vibrational population, so this assumption will not be appropriate for all experimental situations.

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

[15] D. R. Bates and G. Griffing, Proc. Phys. Soc. (London) **A66**, 961 (1953); **A67**, 663 (1954); **A68**, 90 (1955).

[16] E. E. Salpeter, Proc. Phys. Soc. (London) **A63**, 1295 (1950).

[17] M. Gryziński, Phys. Rev. **138**, A336 (1965).

Comparison of the present theoretical results with experiment[8,18–20] over an extended energy range is shown in Fig. 2. For a more complete review of the experimental situation see Refs. 7 and 8. Experiment and theory are in essential agreement between 10^4 and 10^6 eV for σ_1. Below 10^4 eV the data derived from experiment show a maximum where the Born theory does not. Use of the first Born approximation in this energy range is questionable although, as pointed out above, the necessity of assuming a vibrational population makes critical comparison with experiment especially difficult in this energy range. Also, dissociation by direct vibrational excitation may become an important mechanism in this energy range. As the collision energy increases, above 5×10^5 eV, it appears that $A+B$ tends to become increasingly smaller than the experimental value for σ_1. This is consistent with the inequality discussed in the preceding paragraph of this section. The high-energy estimate of $\sigma_1+\sigma_2$ appears to agree well with experiment for collision energies greater than 10^6 eV. Extending this type of calculation to lower energies results in greater disagreement with experiment. This shortcoming is easily identified with the omission of correction terms in the $\sigma_1+\sigma_2$ calculation similar to those used in the σ_1 calculation.

The appearance of a double maximum in the $\sigma_1+2\sigma_2$ cross section[7] (not shown here) has been explained[21] by attributing the first maximum to the dissociation of H_2^+ into a proton and hydrogen atom and the second maximum to direct ionization of H_2^+. However, in the dissociation of H_2^+ on other targets the high-energy maximum is either not found or is much less distinct. This dependence on the target is easily explicable in the present model. The cross section near the second maximum is a superposition of several processes with a major contribution coming from events in which the target is also excited.

Studies of the effect of varying the conditions under which the H_2^+ ion is produced on various experimentally measured cross sections have been made and from these studies it has been concluded that any changes in the observed cross section are due to changes in the initial vibrational-state population of H_2^+ (cf. Ref. 6). In the following discussion it will be shown that the experimental observations and the proposed explanation are qualitatively in agreement with theory. The qualitative nature of this discussion is necessary since no information on the actual populations is available. Theory predicts that $\tilde{Q}(2p\sigma_u,\,\Sigma)$ is a dominant part of both σ_1 and $\sigma_1+2\sigma_2$ at low energies. From the curves in Ref. 3 and from the unpublished $\tilde{Q}_{v0}(2p\sigma_u,\,\Sigma)$ cross sections of the present study it can be seen that vibrational effects should be quite important for collision energies near 1 keV and steadily decrease in importance as the energy increases. It was argued in Sec. II that vibrational effects are of secondary importance for excitation of H_2^+ to electronic states higher than the $2p\sigma_u$ state. Measurements[22] in the 1–2-keV range have disclosed changes in $\sigma_1+2\sigma_2$ of a factor of 3 or more by varying the ionizing electron energy used to produce H_2^+ from H_2. Varying source conditions have brought about changes in $\sigma_1+2\sigma_2$ of 30% at 6 keV,[7] 20% at 10 keV,[6] and less than 10% in the 50–670-keV range.[7,23] This energy dependence of vibrational effects is consistent with the preceding theoretical discussion. Measurements[23] of the variations of σ_2 with changes in the H_2^+ source in the 280–670-keV energy range disclosed effects which were almost statistically insignificant. This is supporting evidence for the conclusion that vibrational effects in transitions other than $\tilde{Q}(2p\sigma_u,\,\Sigma)$ are not of primary importance.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to Mrs. Marcella Madsen for assistance with the numerical analysis and use of the digital computer, and to Gordon W. McClure and Robert V. Pyle for many stimulating discussions during the course of this work.

APPENDIX

The derivation of Eqs. (2)–(6) is now given. The first Born approximation to the total cross section Q for a collision which excites the initial state of the scattering system i to the final state f, neglecting all rearrangement reactions, is[24]

$$Q=(2\pi)^{-1}V_0^{-2}\int_{K_0}^{K_1} KdK\,|\langle\Gamma_f\,|\,V\,|\,\Gamma_i\rangle|^2. \qquad \text{(A1)}$$

The units are as defined in Sec. II. The interaction potential V between H_2^+ and H_2 is

$$\begin{aligned}V=&\,|\mathbf{r}-(\mathbf{r}_1-\mathbf{r}_0)|^{-1}+|\mathbf{r}-(\mathbf{r}_2-\mathbf{r}_0)|^{-1}-|\mathbf{r}-(\tfrac{1}{2}\mathbf{P}-\mathbf{r}_0)|^{-1}\\&-|\mathbf{r}-(-\tfrac{1}{2}\mathbf{P}-\mathbf{r}_0)|^{-1}-|\mathbf{r}-(\mathbf{r}_1-\tfrac{1}{2}\mathbf{R})|^{-1}\\&-|\mathbf{r}-(\mathbf{r}_2-\tfrac{1}{2}\mathbf{R})|^{-1}-|\mathbf{r}-(\mathbf{r}_1+\tfrac{1}{2}\mathbf{R})|^{-1}\\&-|\mathbf{r}-(\mathbf{r}_2+\tfrac{1}{2}\mathbf{R})|^{-1}+|\mathbf{r}-\tfrac{1}{2}(\mathbf{P}+\mathbf{R})|^{-1}\\&+|\mathbf{r}-\tfrac{1}{2}(\mathbf{P}-\mathbf{R})|^{-1}+|\mathbf{r}-\tfrac{1}{2}(-\mathbf{P}+\mathbf{R})|^{-1}\\&+|\mathbf{r}-\tfrac{1}{2}(-\mathbf{P}-\mathbf{R})|^{-1}. \qquad \text{(A2)}\end{aligned}$$

The vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ are from the center of the H_2 internuclear line to the two electrons bound to H_2, $\mathbf{r}_0$

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[18] J. Guidini, Compt. Rend. **253,** 829 (1961).

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

[20] L. I. Pivovar, V. M. Tubaev, and M. T. Novikov, Zh. Eksperim. i Teor. Fiz. **40,** 34 (1961) [English transl.: Soviet Phys.—JETP **13,** 817 (1961)].

[21] R. N. Il'in, B. I. Kikiani, V. A. Oparin, E. S. Solov'ev, and N. V. Fedorenko, Zh. Eksperim. i Teor. Fiz. **46,** 1208 (1964) [English transl.: Soviet Phys.—JETP **19,** 817 (1964)].

[22] J. Wm. McGowan and L. Kerwin, Can. J. Phys. **42,** 972 (1964); N. N. Tunitskii, P. M. Smirnova, and M. V. Tikhomirov, Dokl. Akad. Nauk SSSR **101,** 1083 (1955).

[23] A. C. Riviere and D. R. Sweetman, Proc. Phys. Soc. (London) **78,** 1215 (1961).

[24] D. R. Bates, *Atomic and Molecular Processes,* edited by D. R. Bates (Academic Press Inc., New York, 1962), p. 549.

is from the center of the H_2^+ internuclear line to the electron bound to H_2^+, $\mathbf{r}$ is from the center of the H_2 internuclear line to the center of the H_2^+ internuclear line, and $\mathbf{R}$ and $\mathbf{P}$ are the vectors between the nuclei of H_2^+ and H_2, respectively. The first Born wave functions are

$$\Gamma_i=\Phi_i(\mathbf{r}_0,\mathbf{R})\Psi_i(\mathbf{r}_1,\mathbf{r}_2,\mathbf{P})\exp(i\mathbf{k}_i\cdot\mathbf{r}), \quad \text{(A3)}$$

$$\Gamma_f=\Phi_f(\mathbf{r}_0,\mathbf{R})\Psi_f(\mathbf{r}_1,\mathbf{r}_2,\mathbf{P})\exp(i\mathbf{k}_f\cdot\mathbf{r}), \quad \text{(A4)}$$

where Φ is an eigenfunction for isolated H_2^+, which includes the rotational and vibrational degrees of freedom of this system and Ψ is a similar eigenfunction for H_2. The vectors $\mathbf{k}_i$ and $\mathbf{k}_f$ represent the relative momenta of the two molecular systems before and after collision; hence, the momentum transfer is $\mathbf{K}=\mathbf{k}_i-\mathbf{k}_f$. Writing out the matrix element required for Eq. (A1) from Eqs. (A2), (A3), and (A4) and using Bethe's integral[24] to integrate over the volume element $d\mathbf{r}$,

$$\int d\mathbf{r}\exp(i\mathbf{K}\cdot\mathbf{r})(|\mathbf{r}-\mathbf{r}_\alpha|)^{-1}=4\pi K^{-2}\exp(i\mathbf{K}\ \mathbf{r}_\alpha),$$

the relationship

$$\begin{aligned}\langle\Gamma_f|V|\Gamma_i\rangle=4\pi K^{-2}\int d\mathbf{r}_0d\mathbf{r}_1d\mathbf{r}_2d\mathbf{R}d\mathbf{P}\,\Psi_f^*\Psi_i\Phi_f^*\Phi_i\{&\exp[i\mathbf{K}\cdot(\mathbf{r}_1-\mathbf{r}_0)]+\exp[i\mathbf{K}\cdot(\mathbf{r}_2-\mathbf{r}_0)]-\exp[i\mathbf{K}\cdot(\tfrac{1}{2}\mathbf{P}-\mathbf{r}_0)]\\ &-\exp[i\mathbf{K}\cdot(-\tfrac{1}{2}\mathbf{P}-\mathbf{r}_0)]-\exp[i\mathbf{K}\cdot(\mathbf{r}_1-\tfrac{1}{2}\mathbf{R})]-\exp[i\mathbf{K}\cdot(\mathbf{r}_2-\tfrac{1}{2}\mathbf{R})]-\exp[i\mathbf{K}\cdot(\mathbf{r}_1+\tfrac{1}{2}\mathbf{R})]-\exp[i\mathbf{K}\cdot(\mathbf{r}_2+\tfrac{1}{2}\mathbf{R})]\\ &+\exp[\tfrac{1}{2}i\mathbf{K}\cdot(\mathbf{P}+\mathbf{R})]+\exp[\tfrac{1}{2}i\mathbf{K}\cdot(\mathbf{P}-\mathbf{R})]+\exp[\tfrac{1}{2}i\mathbf{K}\cdot(-\mathbf{P}+\mathbf{R})]+\exp[\tfrac{1}{2}i\mathbf{K}\cdot(-\mathbf{P}-\mathbf{R})]\}\end{aligned} \quad \text{(A5)}$$

is established. A little manipulation of the term in brackets in Eq. (A5) shows that this equation can be rewritten as

$$\begin{aligned}\langle\Gamma_f|V|\Gamma_i\rangle=4\pi K^{-2}\int d\mathbf{r}_0d\mathbf{R}\,\Phi_f^*\Phi_i[\exp(-i\mathbf{K}\cdot\mathbf{r}_0)-2\cos(\tfrac{1}{2}\mathbf{K}\cdot\mathbf{R})]&\\ \times\int d\mathbf{r}_1d\mathbf{r}_2d\mathbf{P}\,\Psi_f^*\Psi_i[\exp(i\mathbf{K}\cdot\mathbf{r}_1)+\exp(i\mathbf{K}\cdot\mathbf{r}_2)-2\cos(\tfrac{1}{2}\mathbf{K}\cdot\mathbf{P})]&.\end{aligned} \quad \text{(A6)}$$

Equation (A6) represents a very important and general property of the first Born approximation: The interaction matrix element for the scattering of two complex systems separates into a product of matrix elements, one of which is identical to an interaction matrix element representing electron scattering by one of the complex systems while the other represents electron scattering by the remaining complex system. This property and its use have been previously reported.[3,15,25,26] The total cross section can now be rewritten as

$$\begin{aligned}Q=8\pi V_0^{-2}\int_{K_0}^{K_1}dK\,K^{-3}\left|\int d\mathbf{r}_0d\mathbf{R}\,\Phi_f^*\Phi_i[\exp(-i\mathbf{K}\cdot\mathbf{r}_0)-2\cos(\tfrac{1}{2}\mathbf{K}\cdot\mathbf{R})]\right|^2&\\ \times\left|\int d\mathbf{r}_1d\mathbf{r}_2d\mathbf{P}\,\Psi_f^*\Psi_i[\exp(i\mathbf{K}\cdot\mathbf{r}_1)+\exp(i\mathbf{K}\cdot\mathbf{r}_2)-2\cos(\tfrac{1}{2}\mathbf{K}\cdot\mathbf{P})]\right|^2&.\end{aligned} \quad \text{(A7)}$$

If we assume the Born-Oppenheimer separation of electronic and nuclear variables for both H_2^+ and H_2 and, in addition, take advantage of the symmetry of the ground electronic states of these systems, the functions required by Eq. (A7) become

$$\Phi_i=\phi_0(\mathbf{r}_0,R)Y_{LM}(\delta,\xi)\mathrm{X}_{\nu L}(R),$$

$$\Psi_i=\psi_0(\mathbf{r}_1,\mathbf{r}_2,P)Y_{L'M'}(\zeta,\omega)\Xi_{\mu L'}(P),$$

$$\Phi_f=\phi_n(\mathbf{r}_0,R)F_{l(n)}(\mathbf{R}),$$

and

$$\Psi_f=\psi_N(\mathbf{r}_1,\mathbf{r}_2,R)G_{l'(N)}(\mathbf{P}).$$

The functions ψ and ϕ represent electronic states, Y is a spherical harmonic, $\mathbf{X}$ and Ξ are initial vibrational states, and F and G represent the motion of the nuclei in the final electronic states. The quantum numbers 0, n, and N describe the electronic states of the molecules, LM and $L'M'$ the initial rotational states, νL and $\mu L'$ the initial vibrational states, and $l(n)$ and $l'(N)$ the final eigenstates of the nuclei. The angles δ and ξ orient $\mathbf{R}$ with respect to the quantization axis and ζ and ω serve the same purpose for $\mathbf{P}$. Using these functions and the definitions,

$$\epsilon_n(\mathbf{K},\mathbf{R})=\int d\mathbf{r}_0\,\phi_n^*\phi_0[\exp(-i\mathbf{K}\cdot\mathbf{r}_0)-2\cos(\tfrac{1}{2}\mathbf{K}\cdot\mathbf{R})], \quad \text{(A8)}$$

$$\begin{aligned}E_N(\mathbf{K},\mathbf{R})=\int d\mathbf{r}_1d\mathbf{r}_2\,\psi_N^*\psi_0[&\exp(i\mathbf{K}\cdot\mathbf{r}_1)+\exp(i\mathbf{K}\cdot\mathbf{r}_2)\\ &-2\cos(\tfrac{1}{2}\mathbf{K}\cdot\mathbf{P})],\end{aligned} \quad \text{(A9)}$$

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[25] D. B. Bouthilette, J. A. Healey, and S. N. Milford, *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 1081.

[26] T. A. Green, Phys. Rev. **157**, 103 (1967).

the cross section can be rewritten as

$$Q=8\pi V_0^{-2}\int_{K_0}^{K_1} dK\,K^{-3}\left|\int d\mathbf{R}\;Y_{LM}\mathrm{X}_{\nu L}F_{l(n)}{}^{*}\epsilon_n\right|^2 \times\left|\int d\mathbf{P}\;Y_{L'M'}\Xi_{\mu L'}G_{l'(N)}{}^{*}E_N\right|^2. \quad \text{(A10)}$$

Equation (A10) is the first Born approximation for the scattering of H_2^+ by H_2.

High-energy molecular scattering experiments[6–8] do not resolve effects due to the final rotational and vibrational states, and the initial rotational states are believed to be unimportant factors. However, as discussed in Secs. I and II, the electronic states and the initial vibrational states of the molecules very likely contribute in an important way to the structure of the total cross section as a function of collision energy. Hence, there appears little motivation to study the detail represented by Eq. (A10) at the present time. Instead, we proceed by summing over the final rotational and vibrational states and by averaging the degenerate levels of the initial rotational levels of the molecules. In addition, the dependence of the initial vibrational state on the total angular momentum of the initial rotational state is ignored.

The appearance of a product of matrix elements, each identical to the appropriate electron-molecule Born matrix element, makes it possible to treat each molecule separately and in the same manner that has been established for electron-molecule scattering. The procedures for treating electron-molecule collisions have been discussed in detail elsewhere[1–3] and will not be repeated here. We conclude by observing that Eqs. (2)–(6) result from the application of these procedures to Eq. (A10). Note that Eqs. (A8) and (A9) are related to Eqs. (4), (5), and (6) in the following manner[27]:

$$|\epsilon_n(K,R)|^2=(4\pi)^{-1}\int d\Omega(\mathbf{R})\;|\epsilon_n(\mathbf{K},\mathbf{R})|^2, \quad \text{(A11)}$$

$$|E_N(K,P)|^2=(4\pi)^{-1}\int d\Omega(\mathbf{P})\;|E_N(\mathbf{K},\mathbf{P})|^2. \quad \text{(A12)}$$

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[27] If n and N designate states other than the ground electronic states, the cosine terms in ϵ_n and E_n will disappear because of the orthogonality of these electronic functions.

PHYSICAL REVIEW VOLUME 160, NUMBER 1 5 AUGUST 1967

Equivalence of the Sudden Approximation to the High-Energy Limit of the First Born Approximation*

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(Received 16 March 1967)

The ratio of total cross sections for two different inelastic events in a given target as predicted by the sudden approximation is shown to be equal to the high-energy limit of the corresponding first Born approximation to the ratio. This relationship between the two theories is established for the special cases of the ratio of single to double ionization of helium atoms by electrons and by hydrogen atoms. The electron–helium-atom ratio is found to be the same as the hydrogen-atom–helium-atom ratio. The proof supposes that the same approximate wave functions were used in both theories and that the dominant term in the high-energy expansion of the first Born total cross section is independent of energy-conservation requirements. This latter point is established for a general ionization event.

A THEORETICAL model for the prediction of the ratio of total cross sections for different inelastic events in a given target has been proposed which is extremely attractive because of its simplicity. The model is an adaptation of the sudden approximation (SA) which has proven useful in the study of certain x-ray phenomena.[1] In the application to atomic collision processes, it has been used[2,3] to study the production of various states in He^+, including doubly ionized helium, in electron–helium-atom collisions. The SA model predicts the ratio of two cross sections to be independent of the collision energy E. The range of collision energies for which the SA is valid has not been established, although the nature of this theory suggests the SA ratio is most likely valid for high-energy collisions.[2,3] It will be shown that the SA ratio is, in fact, the high-energy limit. This will be done by establishing the identity of the SA ratio to the high-energy limit of the ratio of total cross sections as calculated in the first Born approximation, BI. This equivalence presumes that the same approximate wave functions are used in both the SA and BI calculations of the ratios.

To display the character of the SA and establish the result which is to be shown to be identical to the high-

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* This work was supported by the U.S. Atomic Energy Commission.

[1] F. Bloch, Phys. Rev. **48**, 187 (1935).

[2] W. E. Lamb, Jr., and M. Skinner, Phys. Rev. **78**, 539 (1950).

[3] M. H. Mittleman, Phys. Rev. Letters **16**, 498 (1966); **16**, 779 (1966).