Use of Electron Scattering Data to Obtain Accurate Born Cross Sections for Atom-Atom and Other Heavy-Particle Collisions. II. Breakup of Fast H_2^+ upon Collision with He†

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In an earlier paper it was suggested that, in Born calculations of total cross sections for heavy-particle collisions, it might be more practical, if accuracies of the order of 10% are acceptable, to obtain the necessary matrix elements by measuring differential electron-atom and electron-molecule cross sections than it would be to calculate the matrix elements from the wave functions of the initial and final atomic or molecular states. In this paper the foregoing idea is explored for H_2^+-He collisions. Experimental electron cross sections are used only for He, theoretical ones being used for H_2^+. Since Lassettre's electron-He measurements do not extend to large enough momentum transfers to allow calculation of the H_2^+-He total cross sections for all transitions of interest, theory is introduced to provide quantitative extrapolations of the experimental data to larger momentum transfers. By this means the extent to which the H_2^+-He total cross sections are determined by the unextrapolated electron-He measurements is examined. At the same time, ranges of momentum transfer are determined, over which the electron-He cross sections need to be measured if they are to be adequate for H_2^+-He total cross-section calculations, without the use of quantitative extrapolation. By a generalization of the H_2^+-He results, analogous ranges are determined for the electron scattering measurements relevant to most heavy-particle collisions of practical interest. The general results show that the most extensive of Lassettre's electron excitation measurements are adequate for heavy-particle collisions in which both collision partners undergo transitions to discrete excited states. Measurements of electron cross sections out to larger momentum transfers than this are required, however, for other combinations of the possible final states of the colliding particles. A table of the upper limits of the required ranges of momentum transfers is given in the hope that it may stimulate additional experimental work. Of particular importance is the measurement of differential electron ionization cross sections out to large values of momentum transfer and energy loss. From the H_2^+-He cross sections, theoretical cross sections are obtained for the breakup of H_2^+ via electronic excitation during collisions with He. These are compared with experiment.

I. INTRODUCTION

HIGH-ENERGY collisions between atomic or molecular systems should be describable in terms of the first Born approximation. However, despite this approximation's simplicity, useful theoretical predictions are difficult to make. The main sources of the difficulties are the following:

(1) The experimental data usually involve sums over many final internal states of both projectile and target so that many cross sections must be computed before comparison between theory and experiment is meaningful.

(2) Accurate electronic wave functions for the target and projectile are necessary to evaluate the Born matrix elements. These wave functions are unavailable for most of the excited states of most atoms and molecules. Moreover, the available accurate wave functions are difficult to use in matrix-element calculations.

(3) In the case of molecules, the vibrational and rotational degrees of freedom must be taken into account, and this leads to nontrivial complications and further approximations. Because of these difficulties, as well as those inherent in the measurement of collision cross sections, comparisons between first Born theory and high-energy experiments have been made to date only for H-H,[1,2] H_2^+-H_2,[3] H-He,[4] and H_2^+-He [5,6] collisions.[7–9]

This paper concerns the Born-approximation calculation of cross sections for breakup of H_2^+ ions upon collision with He. It contains the detailed discussion of the methods used to obtain the results reported briefly in Ref. 5. The calculations are compared with the experimental cross section σ_1 for all processes which lead to a proton and a hydrogen atom and to the cross section $\sigma_1+\sigma_2$, where σ_2 is the cross section for all processes which lead to H_2^+ breakup into two protons and an electron. The cross section σ_1 is compared to the sum, $Q(1\text{–}3;0\text{–}4)$, of the cross sections for H_2^+ transitions to the states $H_2^+(2p\sigma_u)$, $H_2^+(2p\pi_u)$, and $H_2^+(2s\sigma_g)$, each of these cross sections being summed over transi-

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[1] A. B. Wittkower, G. Levy, and H. B. Gilbody, Proc. Phys. Soc. (London) **91**, 306 (1967).

[2] G. W. McClure, Phys. Rev. **166**, 22 (1968).

[3] J. M. Peek, T. A. Green, and W. H. Weihofen, Phys. Rev. **160**, 117 (1967).

[4] D. R. Bates and D. S. F. Crothers, Proc. Phys. Soc. (London) **90**, 73 (1967). This work goes beyond the Born approximation through the introduction of the Ochkur-Rudge treatment of exchange.

[5] T. A. Green and J. M. Peek, in *Proceedings of the Fifth International Conference on the Physics of Electronic and Atomic Collisions* (Publishing House Nauka, Leningrad, 1967).

[6] J. E. G. Farina, Proc. Phys. Soc. (London) **90**, 323 (1967).

[7] In addition to the above results obtained by Born's approximation, semiclassical H_2^+ breakup cross sections for several target gases have been given by E. Salpeter [Proc. Phys. Soc. (London) **A63**, 1295 (1950)] and by K. Berkner *et al.* [Phys. Rev. **146**, 9 (1966)].

[8] First Born cross sections for the excitation of H upon collision with Li have been given by I. Cheshire and H. L. Kyle, Phys. Letters **17**, 115 (1965). These cross sections have not yet been compared with experiment.

[9] The foregoing summary does not include many reactions in which one of the particles is a structureless charged particle such as an electron or a proton.

tions to the 1^1S, 2^1S, 2^1P, 3^1P, and continuum states of the He target. The experimental results for $\sigma_1+\sigma_2$ are compared, at asymptotically high energies only, with a theoretical result, $\tilde{Q}(\Sigma',\Sigma)$, obtained, using closure on the excited electronic states of both collision partners.

A principal part of this work, beyond the calculation of the cross sections just mentioned, has been a study of the extent to which the existing experimental differential cross sections for electron scattering by He can be used to evaluate the He transition matrix elements which appear as factors in the H_2^+-He cross sections. The general idea involved here was outlined in an earlier paper.[10] In that paper it was pointed out that in Born approximation the differential cross section for an atom-atom collision is proportional to the product of two electron-atom differential cross sections, one for each atom, provided that all the cross sections are evaluated at the same momentum transfer. It was then argued that, given the present state of the art of atomic- and molecular-structure calculations, particularly for excited electronic states, it might be more practical, if accuracies of the order of 10% are desired, to measure the above-mentioned electron-atom cross sections than to calculate them.

At present there are serious obstacles to the general use of this idea. As can be seen from the articles cited in Ref. 10, most of which are due to Lassettre and his collaborators, differential electron cross sections have been measured only for a few transitions in a restricted number of atoms and molecules. In addition, as will be shown in detail below, most of these measurements do not extend to sufficiently large values of momentum transfer to cover the entire range of momentum transfers which are important in atom-atom total cross sections. The general use of experimental electron-atom scattering data to evaluate atom-atom total cross sections will therefore be possible only if differential electron scattering cross sections are measured, for a wide variety of atoms and molecules, out to larger values of momentum transfer than has been the practice to date.

One object of our work, therefore, has been to establish the ranges of important momentum transfers in the total cross sections for atom-atom collisions, for this information will allow the experimentalist to decide whether the necessary electron scattering measurements are feasible. Our study of momentum transfer ranges begins with an analysis of H_2^+ electronic excitation during H_2^+-He collisions. The results thus obtained are then generalized to cover most heavy-particle collisions of practical interest. Helium was chosen as the basic target because the existing electron-He cross-section measurements are more extensive than those for any other system and because the theory of high-energy electron-He scattering is relatively well developed. H_2^+ was chosen as the projectile because accurate theoretical electron-H_2^+ cross sections are available and because measured H_2^+-He total cross sections allow the final results to be compared with experiment. The results of the study, which are given in Table II, can be summarized as follows[11]:

If both of the collision partners in an atom-atom collision undergo transitions to discrete excited states, the upper limit of the range of important momentum transfers in the total cross section is about 1.6 atomic units (a.u.). If one and only one of the collision partners undergoes such a transition, the upper limit is about 2 a.u. If neither collision partner undergoes such a transition—i.e., if each partner either remains in its ground electronic state or is ionized—the upper limit increases as the atomic numbers of the collision partners increase, and lies in the range 4–14 a.u. for most systems of practical importance.

From this summary it is seen that atom-atom collisions can be divided into two classes according to whether discrete electronic excitation occurs in at least one collision partner or not. If the necessary differential electron-atom and electron-molecule cross sections can be measured out to momentum transfers of 2 a.u., the total cross sections for all heavy-particle collisions of the first class can be calculated from the electron scattering data. Electron scattering measurements out to much larger values of momentum transfer are required for heavy-particle collisions of the second class.

The status of experiment at present is that the most extensive electron excitation cross-section measurements extend to momentum transfers of about 1.6 a.u., the most extensive ionization measurements extend to about 1.1 a.u., and the most extensive elastic scattering measurements extend to about 7 a.u. In the case of electron ionization measurements particularly, the momentum transfer gap which needs to be filled for the purpose of heavy-particle total cross-section calculations is large indeed. However, the authors hope that the utility of such measurements, as well as the great value they would have for the testing of future ionization theories, will stimulate someone to undertake them.

Until electron scattering cross sections are measured out to larger momentum transfers than at present, theory will be needed for the extrapolation of the measured inelastic cross sections to larger values of momentum transfer. Lassettre has given a theoretical expansion for electron excitation cross sections which appears quite promising as a basis for extrapolation when no detailed quantitative theory is available. This expansion was used in our work and is discussed in Sec. III. A qualitative method for the extrapolation of

[10] T. A. Green, Phys. Rev. **157**, 103 (1957). This paper contains a fairly complete list of references to the relevant experimental work as of that date. For brevity, we shall usually refer to atom-atom scattering in the discussion which follows. However, the discussion also applies to molecules and ions.

[11] Note: The summary should not be used as a substitute for Table II and the discussion which accompanies it in Sec. IV.

electron ionization data, using tabulated inelastic electron scattering factors as a guide, is described in the Appendix. Provided that differential electron ionization cross sections can be measured out to momentum transfers of from 1.4 to 1.7 a.u., and to electron energy losses of about 3 a.u., the method should provide reasonably good extrapolations of the data to larger values of momentum transfer, and can be used in situations where no quantitative ionization theory is available.

The organization of the rest of the paper will now be outlined. The scattering formalism and the treatment of the H_2^+ projectile are discussed in Sec. II. In Sec. III, the way in which theory is used to extrapolate the experimental electron-He cross sections to larger values of momentum transfer is described. In addition, the adequacy of the experimental electron-He data for use in H_2^+-He total cross sections and the ranges of important momentum transfers for these cross sections are determined. Section IV is concerned with the ranges of important momentum transfers for general atom-atom collisions, its principal content being summarized in Table II. In Sec. V, the calculated H_2^+-He total cross sections are compared with experiment and with other calculations. The conclusions which may be drawn from the comparisons are discussed.

II. SUMMARY OF THE THEORETICAL FORMULAS AND DISCUSSION OF THE H_2^+ TRANSITION MATRIX ELEMENTS

Consider a collision in which initially the H_2^+ projectile is in the νth vibrational level of its ground electronic state and the He target is in its ground state. Let the final electronic states of H_2^+ and He be designated by n and N, respectively. For each n and N, let the cross section be summed over all final H_2^+ vibration-rotation degrees of freedom and averaged over initial rotation projection quantum numbers, using approximations discussed previously.[3,12–14] The Born cross section for the collision then takes the form[15]

$$Q_\nu(n,N)=\int_0^\infty R^2dR|\chi_\nu(R)|^2Q(R;n,N), \qquad (1)$$

where χ_ν is the normalized initial H_2^+ vibrational wave function, R is the H_2^+ internuclear separation, and

$$Q(R;n,N)$$
$$=4\pi V_0^{-2}\int_{K_0^2}^{K_1^2}d(K^2)K^{-4}|\epsilon_n(K,R)|^2|E_N(K)|^2. \qquad (2)$$

In Eq. (2), V_0 is the initial relative velocity, K is the momentum transferred during the collision, and $K_{1,0}$ are, respectively, the maximum and minimum values of K allowed by energy conservation.[16] The quantity $|\epsilon_n(K,R)|^2$ is defined in Eqs. (4), (A8), and (A11) of Ref. 3 and it also appears in the theory of H_2^+-electron scattering.[12,13] The quantity $|E_N(K)|^2$ is defined by

$$|E_N(K)|^2=\sum_{m_{Jf}}\left|\int d\mathbf{r}_1d\mathbf{r}_2 \times\{\phi_0\phi_N^*\sum_{j=1}^{2}\exp(i\mathbf{K}\cdot\mathbf{r}_j)\}-2\delta_{N,0}\right|^2, \qquad (3)$$

where $\phi_{0,N}$ are helium singlet-state wave functions, $\mathbf{r}_j$ is a helium electron coordinate vector, and $\delta_{N,0}$ is the Kroneker symbol. The notation $\sum_{m_{Jf}}$ in Eq. (3) means summation over total orbital angular-momentum projection quantum numbers of the final state. Equation (3) applies to the discrete excited states of He. In the case of transitions to the continuum, ϕ_N is replaced by the continuum wave function for single ionization and $\sum_{m_{Jf}}$ is replaced by an integral over the wave vector which labels the continuum states. The magnitude of the continuum wave vector is limited by energy conservation, so for ionization E_N depends on the initial velocity V_0 as well as on K.

The derivation of Eqs. (1)–(3) is completely analogous to the derivation of the corresponding equations for H_2^+-H_2 collisions, except for simplifications resulting from the fact that He is an atom while H_2 is a molecule. Equations (1) and (2) above correspond, respectively, to Eqs. (8) and (3) of Ref. 3. Equation (3) above is the analog of Eqs. (5) and (6) of Ref. 3. Since the derivation of the above equations of Ref. 3 was discussed in some detail in that paper, the analogous discussion of the derivation of Eqs. (1)–(3) above will not be repeated here.

The experimental H_2^+ beam consists of a mixture of ions in different vibrational states ν of the ground electronic state. Thus the effective cross section $Q(n,N)$ for transitions to the final states described by n and N is given by

$$Q(n,N)=\sum_\nu f_\nu Q_\nu(n,N)/\sum_\nu f_\nu, \qquad (4)$$

where f_ν is proportional to the number of ions in the νth vibrational state. The f_ν, which are not very well known at present and which may vary from one experimental ion source to another, were taken to be equal to the Franck-Condon factors for ionization of H_2 by electrons.[17]

As in Ref. 3, the calculation of individual cross sections for each initial vibrational state of H_2^+ is essential for the treatment of transitions to the $H_2^+(2p\sigma_u)$

[12] J. M. Peek, Phys. Rev. **140**, A11 (1965).
[13] J. M. Peek, Phys. Rev. **154**, 52 (1967).
[14] J. M. Peek, Phys. Rev. **134**, A877 (1964).
[15] Atomic units are used except where other units are explicitly indicated.
[16] The H_2^+ excitation energy for transitions to the state n was taken to be the energy difference between this state and the ground state at the internuclear separation R for which $Q(R;n,N)$ was being calculated.
[17] See Ref. 3 for discussion and references.

state.[18] However, in the case of transitions to the $H_2^+(2p\pi_u)$ and $H_2^+(2s\sigma_g)$ states, $Q(R;n,N)$ in Eq. (1) varies slowly enough with R that it can be set equal to $Q(R^\ddagger;n,N)$ for some suitable $R^\ddagger$ and then taken outside the integral. In these cases Eq. (4) simplifies to $Q(n,N)=Q(R^\ddagger;n,N)$. To check the accuracy of this approximation, the calculations for transitions to $H_2^+(2p\pi_u)$ were carried out with $R^\ddagger=3.2$ and $R^\ddagger=2.0$. The cross section calculated with $R^\ddagger=2.0$, when summed over the five He states included in the calculation of σ_1, exceeds that for $R^\ddagger=3.2$ by 20% at H_2^+ energies of about 50 keV, where the discrepancy is the largest. The sum $\sum_{n=1}^{3}\sum_{N=0}^{4}Q(n,N)$,[19] calculated with $R^\ddagger=2.0$ for the $2p\pi_u$ state, differs from that calculated with $R^\ddagger=3.2$ by less than 4% at worst, and by less than 2% at energies above 200 keV. The value $R^\ddagger=3.2$ was used in the final results. For transitions to $H_2^+(2s\sigma_g)$, $R^\ddagger=2.0$ was used, in order to take advantage of existing values[14] of $|\epsilon_3(K,R)|^2$.

The quantities which are compared with experiment and with each other are now defined in terms of a notation designed to indicate which final states are being summed. In connection with σ_1 we define

$$Q(1\text{–}3;0)=\sum_{n=1}^{3}Q(n,0),$$

$$Q(1\text{–}3;1\text{–}4)=\sum_{n=1}^{3}\sum_{N=1}^{4}Q(n,N),$$

and

$$Q(1\text{–}3;0\text{–}4)=Q(1\text{–}3;0)+Q(1\text{–}3;1\text{–}4). \qquad (5)$$

It is $Q(1\text{–}3;0\text{–}4)$ which is compared to the experimental cross section σ_1.[20]

At high energies it is advantageous to sum over all He final states, using closure. As in Ref. 3, cross sections $\tilde{Q}(R;n,\Sigma')$ are defined by summing over all $N\geq 1$ in Eq. (2) and using the He first ionization potential for all the He excitation energies.[21] This leads to a formula for $\tilde{Q}(R;n,\Sigma')$ in which in Eq. (2) $|E_N(K)|^2$ is replaced by the inelastic electron scattering factor. Cross sections $\tilde{Q}(n;\Sigma')$ are then defined via Eqs. (1) and (4). For comparison with the cross sections of Eq. (5), cross sections

$$\tilde{Q}(1\text{–}3;\Sigma')=\sum_{n=1}^{3}\tilde{Q}(n,\Sigma') \qquad (6a)$$

and

$$\tilde{Q}(1\text{–}3;\Sigma)=Q(1\text{–}3;0)+\tilde{Q}(1\text{–}3;\Sigma') \qquad (6b)$$

are defined.

A theoretical prediction of the experimental cross section $\sigma_1+\sigma_2$ is obtained by using closure on both target and projectile. We define the appropriate cross section $\tilde{Q}(\Sigma',\Sigma)$ by the relation

$$\tilde{Q}(\Sigma',\Sigma)=Q(1,0)+\tilde{Q}(1,\Sigma')+\tilde{Q}(\Sigma'',0)+\tilde{Q}(\Sigma'',\Sigma'). \qquad (7)$$

Here, $\tilde{Q}(\Sigma'',0)$ is defined by summing Eq. (2) over all H_2^+ excited states except $H_2^+(2p\sigma_u)$, using an effective H_2^+ excitation energy equal to that for ionization, and making use of closure as in Eq. (15) of Ref. 3. The cross section $\tilde{Q}(\Sigma'',\Sigma')$ is analogously defined. The calculations of $\tilde{Q}(\Sigma'',0)$ and $\tilde{Q}(\Sigma'',\Sigma')$ were carried out only for $R^\ddagger=3.2$. Unpublished calculations for an H_2 target indicate that the error caused by the evaluation of $\tilde{Q}(\Sigma',\Sigma)$ at a single internuclear separation is of the order of a few percent.

The integration in Eq. (2), as well as the integration over the energy of the ionized electron during the calculation of $|E_4(K)|^2$ in Eq. (3), was done with a Gaussian quadrature routine which allowed the integration accuracy to be controlled by a convergence test. The quadratures in Eq. (1) and the averaging in Eq. (4) were done, for the $2p\sigma_u$ state only, with the same program used in Ref. 3. The over-all precision of the numerical results is better than 1%.

This section will be concluded with a brief statement of how the $|\epsilon_n(K,R)|^2$ were obtained. In the case of $H_2^+(2p\sigma_u)$, values from Table I of Ref. 14 were used for $R=1.4$, 2.0, and 3.2.[22] For several larger values of $R\leq 20$, linear combinations of atomic orbitals (LCAO) wave functions were used to compute $|\epsilon_n(K,R)|^2$. Cross sections were calculated for these values of R from Eq. (2) and used to generate a cubic spline function $Q(R;n,N)$ for use in Eq. (1) with the same functions $\chi_\nu(R)$ as in Ref. 3. Data from Table I of Ref. 14 were also used for the $H_2^+(2p\pi_u)$ and $H_2^+(2s\sigma_g)$ states, extrapolation formulas like that of Ref. 22 being employed for large values of K. As previously explained, only one value of R was used for these cases. The H_2^+ closure calculations of $\tilde{Q}(\Sigma'',0)$ and $\tilde{Q}(\Sigma'',\Sigma')$ were done using Eqs. (11) and (12) of Ref. 13. The $|\epsilon_n(K,R)|^2$ are generally more accurate than those used in Ref. 3, where LCAO values were used throughout.

III. $|E_N(K)|^2$ FOR He; ADEQUACY OF THE EXPERIMENTAL ELECTRON-He CROSS SECTIONS FOR H_2^+-He CALCULATIONS

In this section the $|E_N(K)|^2$ are described, along with the methods used to extrapolate the experimental data to large momentum transfers. Results concerning the

[18] This point is well illustrated for H_2^+-H collisions in Ref. 12.

[19] Values of N are assigned to the He states as follows: 1^1S, $N=0$; 2^1S, $N=1$; 2^1P, $N=2$; 3^1P, $N=3$; continuum, $N=4$. Values of n are assigned to the states of H_2^+ as follows: $1s\sigma_g$, $n=0$; $2p\sigma_u$, $n=1$; $2p\pi_u$, $n=2$; $2s\sigma_g$, $n=3$.

[20] The cross section $Q(1\text{–}3;0)$ relates to collisions in which He is in its ground electronic state after the collision as well as before. We shall refer to such transitions as 0-0 transitions, or transitions to the ground electronic state, rather than use the term "elastic scattering." In the case of molecules, 0-0 transitions include rotational and vibrational transitions as well as elastic scattering.

[21] The symbol $\sim$ over a cross-section symbol Q indicates that at least one closure approximation was involved in its calculation.

[22] The values from Table I of Ref. 21 were extrapolated to large values of K by means of formulas of the form const$\times(4+K^2)^{-4}$, the constant being chosen to make $|\epsilon_n(K,R)|^2$ continuous at the joining point.

adequacy of the measured electron-He scattering cross sections for use in H_2^+-He total cross-section calculations are then presented. We begin with a few prelinimary remarks.

Because of the relative simplicity of the He atom, there is an abundance of theory concerning its wave functions and its differential electron scattering cross sections. Indeed, a completely theoretical treatment of H_2^+-He collisions would be possible, using available electron cross sections, and would lead to results about 5% lower than those obtained here, using experimental data. Also, owing to the lack of ionization data, our treatment of He ionization relies heavily on theory. The available theoretical results for electron-He differential cross sections are adequately discussed elsewhere,[23–27] so only those used in our calculations will be discussed in any detail. Except for momentum transfers approaching zero, where comparison can be made with results obtained with very accurate wave functions for a few ^1P states, the accuracy of the theoretical calculations is not known.

Our results were obtained using experimental electron-He data due to Lassettre and his collaborators. Recently, measurements of the cross sections for 2^1P and 2^1S excitation have been reported by Vriens, Simpson, and Mielczarek.[28] The results of the two groups are not in complete agreement. However, a recalculation of the H_2^+-He cross sections, using the data of Ref. 28, showed that $Q(1\text{–}3;0\text{–}4)$ of Eq. (5) is thereby decreased by at most a few percent.

A. $|E_N(K)|^2$ for Transitions to Discrete States

The scattering factor $|E_0(K)|^2$ for 0-0 transitions, i.e., for elastic electron-He scattering, can be obtained either from the experimental data of Hughes, McMillen, and Webb[29] or from the very accurate theoretical calculations of Bartell and Gavin.[30] Although the two results are in quite good agreement,[25] the scatter in the experimental data is such that it was more convenient for the numerical calculations, as well as more accurate, to obtain $|E_0(K)|^2/K^2$ by fitting a cubic spline function in K^2 to values of $|E_0(K)|^2/K^2$ obtained from Ref. 30.

Values of $|E_1(K)|^2/K^2$ were obtained from a simple formula due to Lassetter[31] which fits the experimental data[32–34] well and provides a reasonable extrapolation of it for values of K^2 greater than 2.5 a.u., where the data end.

Lassettre and his collaborators have shown that their experimental values[32,33,35] of $|E_2(K)|^2/K^2$ agree very well in shape with the best available theoretical calculation.[23] For convenience in our numerical work, the theoretical formula was used both to represent the experimental data smoothly and to extrapolate it to values of K^2 greater than 2.5 a.u., where the data end. To within a few percent the same H_2^+-He cross sections are obtained if a cubic spline is fitted to the experimental data for $0\leq K^2\leq 2.5$ and a formula of the type $A(\alpha^2+K^2)^{-6}$ from Ref. 31 is used to extrapolate the data beyond $K^2=2.5$. Here A is an adjustable constant and α^2 is determined by the arguments given in Ref. 31.

The measurements[32,35] of $|E_3(K)|^2/K^2$ extend only to $K^2=0.9$ a.u., and exhibit a fair amount of scatter. A smooth curve was drawn through the data and then used to define a cubic spline function for the region $0\leq K^2\leq 0.9$. For extrapolation to values of $K^2>0.9$, the coefficients in a four-term formula of the type proposed in Ref. 31 were determined from the data for $K^2\leq 0.9$.

As can be seen from the preceding discussion, we feel that the expansion developed for generalized oscillator strengths in Ref. 31 provides a useful way of extrapolating measured generalized oscillator strengths to larger values of momentum transfer. However, the theoretical basis of the expansion does not guarantee that if the expansion represents the true generalized oscillator strength accurately for momentum transfers less than some given value, it will continue to represent the true generalized oscillator strength accurately at much larger values. Measurement and further theoretical study of generalized oscillator strengths for large momentum transfers is therefore very desirable.

B. He Ionization; $|E_4(K)|^2/K^2$

The problem of having limited experimental data is most acute for ionization. The continuum generalized oscillator strength measurements[32,33] extend to mo-

[23] See E. N. Lassettre and E. A. Jones [J. Chem. Phys. **40**, 1218 (1964)] for a comparison of three calculations concerning the 2^1P state.

[24] See M. A. Fox [Proc. Phys. Soc. (London) **86**, 789 (1965)] for a comparison of three calculations concerning the 2^1S state.

[25] See N. F. Mott and H. S. W. Massey [*The Theory of Atomic Collisions* (Oxford University Press, London, 1965), 3rd ed., Chap. XVI, Secs. 2, 3, 7, and 8] for several comparisons, including one for elastic scattering.

[26] See J. Van den Bos [doctoral dissertation, University of Amsterdam, 1967, Chap. VIII (unpublished)], for a valuable survey of theoretical generalized oscillator strengths for He, including results for the 3^1P state.

[27] The generalized oscillator strength $f_N(K^2)$ which appears in Refs. 23, 25, and 26 is equal to $2W_N|E_N(K)|^2/K^2$, where W_N is the excitation energy for the state N. The differential cross section for electron scattering is given by $4(V_N/V_0)|E_N(K)|^2/K^4$, where V_N is the final electron velocity.

[28] L. Vriens, J. A. Simpson, and S. R. Mielczarek (to be published). The authors wish to express their gratitude for the opportunity to see a preprint of this paper in advance of publication.

[29] A. L. Hughes, J. A. McMillen, and G. M. Webb, Phys. Rev. **41**, 154 (1932).

[30] L. S. Bartell and R. M. Gavin, Jr., J. Chem. Phys. **43**, 856 (1965).

[31] E. N. Lassettre, J. Chem. Phys. **43**, 4479 (1965). See Eqs. (36) and (37).

[32] E. N. Lassettre, M. E. Krasnow, and S. M. Silverman, J. Chem. Phys. **40**, 1242 (1964).

[33] S. M. Silverman and E. N. Lassettre, J. Chem. Phys. **40**, 1265 (1964).

[34] A. M. Skerbele and E. N. Lassettre, J. Chem. Phys. **45**, 1077 (1966).

[35] A. M. Skerbele and E. N. Lassettre, J. Chem. Phys. **40**, 1271 (1965).

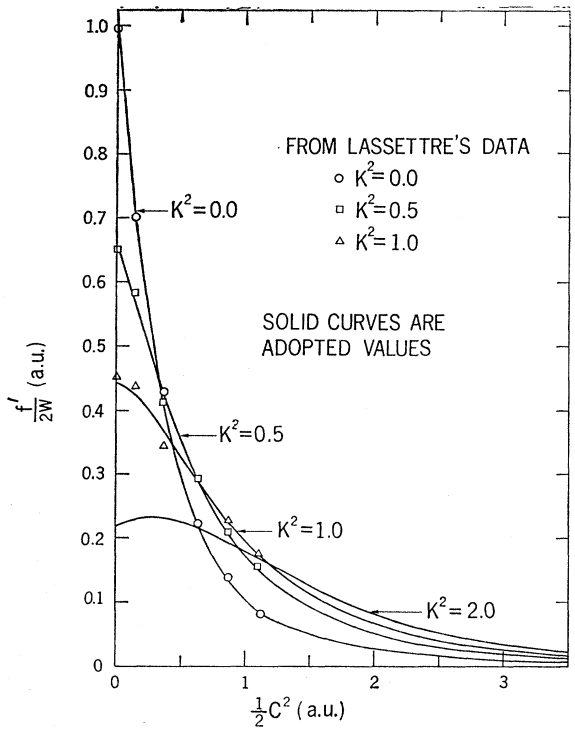

FIG. 1. Continuum transition matrix elements for He. The quantity f' is the continuum generalized oscillator strength for momentum transfer K and ionized electron kinetic energy $\frac{1}{2}C^2$. The excitation energy W is equal to $0.904+\frac{1}{2}C^2$. The solid lines are the values used in the H_2^+-He calculations; the individual points represent the experimental data.

mentum transfers of about unity and to scattered electron energy losses of about 2 a.u. Lassettre's representation[31] for generalized oscillator strengths does not apply to the continuum, so for our calculations we used the theoretical expression III of Mapleton[36] to extrapolate the experimental data. This theory yields a total cross section for H^+-He ionization in good agreement with experiment.[37] It can be shown that for $K^2=0$ Lassettre's experimental continuum oscillator strength agrees well with quite accurate calculations and with the results of photo-ionization experiments.[38] Mapleton's formula is rather inaccurate in this limit, however, and so the data of Refs. 32 and 33 were used to modify the theoretical result so as to make it agree with the data wherever data existed. This was done by first smoothing out the fluctuations in the ratio $\bar{H}(K^2,C^2)$ of the experimental and theoretical generalized oscillator strengths. Here $\frac{1}{2}C^2$ is the energy of the ionized electron. A table of the smoothed values of $\bar{H}$ covering the region $0\leq K^2\leq 1.1$, $0\leq C^2\leq 2.2$ was then used to define a two-dimensional cubic spline function $H(K^2,C^2)$ which, when multiplied by the theoretical generalized oscillator strength, gave the value used in our calculations. For each K, $H(K^2,C^2)$ was extended to values of $C^2>2.2$ by making it take on for all such C^2 the value it had at $C^2=2.2$. For $C^2\leq 2.2$ and $K^2\geq 1.1$, the formula

$$H=(1+0.02066[2.2-C^2]^2)(2.3+K^2)/(2+K^2)$$

was used. Its K^2 dependence was selected so that the closure relation was satisfied to within a few percent. The continuum generalized oscillator strength thus obtained leads to a cross section for ionization of He by protons which is about 5% larger than that obtained by Mapleton at energies near 100 keV and agrees with that obtained by Mapleton at high energies.

The results obtained this way are illustrated in Fig. 1, which shows the adopted continuum generalized oscillator strength f', divided by twice the scattered electron energy loss W, plotted versus $\frac{1}{2}C^2$ for several values of K^2. The experimental data are also shown, to illustrate the liberties which were taken in the smoothing process. The largest changes ($\sim$7%) were made for $C^2=0.73$; all other changes were less than 4%. Mapleton's treatment does not account for the experimentally observed auto-ionization perturbations of the generalized oscillator strength at energy losses of 2.21 and 2.33 a.u.[33] Since their effect on the total cross sections is negligible, they have not been taken into account in our calculations.

C. Adequacy of the Electron-He Measurements for Use in H_2^+-He Collisions

According to Eq. (2), the range of important momentum transfers in $Q(R;n,N)$ depends on the K^2 dependence of $|\epsilon_n(K,R)|^2|E_N(K)|^2/K^4$. In order to judge the adequacy of the measured electron-He cross sections for H_2^+-He calculations, the integral in Eq. (2) was divided at the momentum transfer K_{exp}, beyond which no experimental data were available. This allowed the fractional contribution to $Q(R;n,N)$ for $K^2\geq K_{\text{exp}}^2$ to be computed. For $N=0$, where no experimental data were used, K_{exp}^2 was set equal to 4 in order to obtain illustrative results for this type of collision. Some of the fractions thus obtained are given in Table I. The decrease in the fractions with increasing impact velocity V_0 reflects the fact that K_0 in Eq. (2) decreases as V_0 increases. For a given V_0, the fractions for $Q(2;3,N)$ are larger than the corresponding ones for $Q(3.2;1,N)$ because the K_0 are larger for $Q(2;3,N)$ and because at large K^2, $|\epsilon_3(K,2)|^2$ decreases less rapidly than $|\epsilon_1(K,3.2)|^2$.

Table I shows that the measurements for 2^1S and 2^1P excitation are adequate[39] for H_2^+-He calculations, except for $Q(2;3,N)$ at $V_0=1$. The measurements for

[36] R. A. Mapleton, Phys. Rev. **109**, 1166 (1958).
[37] E. W. McDaniel, *Collision Phenomena in Ionized Gases* (John Wiley & Sons, Inc., New York, 1964), p. 282.
[38] See A. L. Stewart and G. T. Webb, Proc. Phys. Soc. (London) **82**, 532 (1963).

[39] By definition, and somewhat arbitrarily, we consider the measurements to be adequate if the fraction in Table I is $\leq$0.2. Under these circumstances, qualitative french-curve extrapolation of the measured electron cross sections to momentum transfers beyond K_{exp} is usually sufficient to obtain the atom-atom total cross sections to within several percent.

TABLE I. Fractional contribution to Q from collisions with momentum transfers greater than K_{exp}.[a]

V_0 (a.u.)	$Q(3.2;1,N)$[b] 1^1S[b]	2^1S	2^1P	3^1P	Cont.	$Q(2;3,N)$ 1^1S	2^1S	2^1P	3^1P	Cont.
1.0	0.06	0.08	0.04	1	1	0.16	0.73	0.75	1	1
1.4	0.06	0.04	0.01	0.48	0.75	0.15	0.19	0.11	1	1
2.0	0.06	0.03	0.01	0.28	0.51	0.15	0.11	0.04	0.70	0.89
3.0	0.06	0.03	0.01	0.21	0.38	0.15	0.09	0.03	0.48	0.70
20	0.06	0.03	0.00	0.16	0.27	0.15	0.09	0.02	0.42	0.57
ΔE[c] (a.u.)	0.18	0.94	0.96	1.03	1.09	0.75	1.50	1.52	1.59	1.65
K_{exp}^2 (a.u.)	4[d]	2.5	2.5	0.9	1.1	4	2.5	2.5	0.9	1.1

[a] K_{exp} is the largest momentum transfer for which experimental data are available.
[b] See Eq. (2) and Ref. 19 for the notation.
[c] The quantity ΔE is the sum of the target and projectile excitation (ionization) energies.
[d] The choice $K_{exp}^2=4$ for the 1^1S final state is made for illustrative purposes. No data are involved.

3^1P excitation and ionization are generally inadequate. By plotting $|\epsilon_n(K,R)|^2|E_N(K)|^2/K^4$ for these cases, it was determined that $K_{exp}^2=2.5$ would be adequate for 3^1P excitation and $K_{exp}^2=4$ would be adequate for ionization. The 1^1S columns of Table I show that $K_{exp}^2=4$ would be adequate for these collisions if measured values of $|\epsilon_n(K,R)|^2$ and $|E_0(K)|^2$ were being used. Additional calculations for the 1^1S cases, with $K_{exp}^2=2.5$, led to the ratios 0.2 and 0.4, showing that this smaller value of K_{exp}^2 would not generally be adequate for collisions of this type.

The results just described determine, for H_2^+-He collisions, the ranges of important momentum transfers in the total cross sections for collisions in which one collision partner (H_2^+) undergoes electronic excitation while the other undergoes a 0-0 transition, electronic excitation, or ionization. In Sec. IV, these results will be generalized so as to apply to most heavy-particle collisions of practical interest.

IV. RANGES OF IMPORTANT MOMENTUM TRANSFERS IN TOTAL ATOM-ATOM CROSS SECTIONS

In this section upper limits $\bar{K}$ of the ranges of important momentum transfers in the total cross sections for general atom-atom collisions are deduced.[40] The results are given in Table II, in which the collisions are classified into types according to the transitions which occur in the target and projectile. The results in the table will be obtained by similar methods to those used in Sec. III C for H_2^+-He collisions. This requires values of the transition matrix elements for 0-0 transitions, excitation, and ionization, which are representative of many-electron atoms and molecules. For 0-0 transitions Lea's tabulation[41] of elastic electron scattering factors is used. For excitation it is assumed that the matrix elements for H_2^+ and He used in our calculations are sufficiently representative of excitation matrix elements in general. Thus for collisions of type 1 in Table II, $\bar{K}^2$ is taken to have the same value 2.5 which was obtained for H_2^+-He collisions of this type in Sec. III C. For ionization, we rely on the similarity between $|E_4(K)|^2/K^2$ and K^{-2} times the inelastic electron scattering factor, and we use the tabulated scattering factors of Pohler and Hanson[42] for estimates of $\bar{K}$ involving ionization. The similarity mentioned above is illustrated in Fig. 2 for He. For more complex systems the curves would be qualitatively quite similar. The values of $\bar{K}$ for ionization which are obtained this way should be quite accurate at the higher impact velocities. They will be conservative at the lower impact velocities since, for large K^2, $|E_4(K)|^2/K^2$ decreases more rapidly then K^{-2} times the inelastic electron scattering factor. The use of the inelastic scattering factor is also advantageous because it takes account of inner shell ionization, multiple ionization, etc.

It was found instructive to study the values of $\bar{K}$ for complex atoms by comparing them with He. This was done by calculating the ratios of the elastic and inelastic scattering factors for the atoms I, Cl, and C to the corresponding ones for He. The ratios are shown in Fig. 3, where they are labeled by the appropriate chemi-

TABLE II. Approximate upper limit $\bar{K}$ of important momentum transfers for heavy-particle collisions.[a]

Transition in first collision partner[b]	Transition in second collision partner	Type[c]	$\bar{K}$ (a.u.)
Electronic excitation	Electronic excitation	1	1.6
Ionization	Electronic excitation	2	2
0-0 transition	Electronic excitation	3	2
Ionization	Ionization	4	4–7
0-0 transition	Ionization	5	6–10
0-0 transition	0-0 transition	6	7–14

[a] See text for the complete definition of $\bar{K}$.
[b] The notation, 0-0 transition, means that the atom or molecule referred to remains in its ground electronic state.
[c] The type designations are introduced only for convenience in the text.

[40] In order to define more precisely what is meant by the "range of important momentum transfers" in an atom-atom total cross section, we adopt the same criterion used in Sec. III C, Ref. 39, for the definition of "adequate." Thus, collisions with momentum transfers in the "range of important momentum transfers" comprise at least 80% of the total cross section.

[41] J. D. Lea, Ph.D. thesis, University of Texas, 1963 (unpublished). Available from University Microfilms, Inc., Ann Arbor, Mich.

[42] R. F. Pohler and H. P. Hanson, J. Chem. Phys. 42, 2347 (1965).

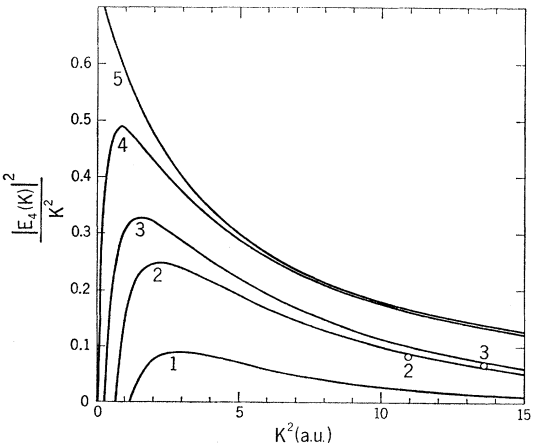

FIG. 2. Integrated continuum transition matrix elements for He. Curves 1–4 represent $|E_4(K)|^2/K^2$ for the following values of the number pair $(V_0,\Delta E)$, where ΔE has the same meaning as in Table I: curve 1, (1,1.08); curve 2, (2,1.65); curve 3, (2,1.08); curve 4, (4,1.08). Curve 5 represents K^{-2} times the inelastic electron scattering factor for He. The circled points are discussed in the Appendix.

cal symbols and a prime is used to distinguish ratios of inelastic scattering factors from ratios of elastic ones.

Values of $\bar{K}$ for collisions of types 2 and 3 in Table II are now readily obtained. For H_2^+ excitation by He these were studied in Sec. III C, where results equivalent to $\bar{K}=2$ were obtained for both types of collision. Suppose now that He is replaced by C, Cl, or I. The new integrand in Eq. (2) is just that for H_2^+ excitation by He times the appropriate ratio from Fig. 3. If the ratio were independent of K^2, the new value of $\bar{K}$ would be the same as that for He. Actually, the ratios all decrease with increasing K^2 (or remain essentially constant) over the interval $0\leq K^2\leq 9$, from which all

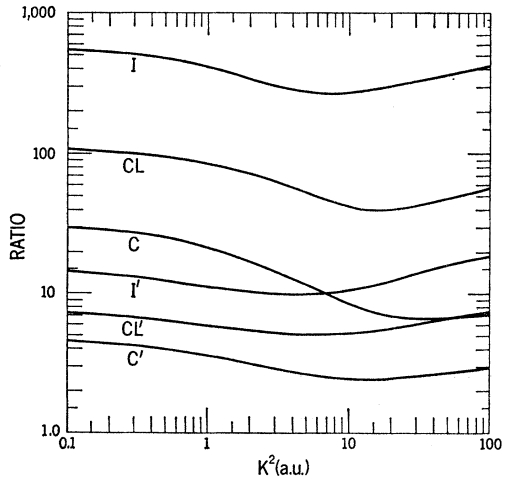

FIG. 3. Elastic and inelastic electron scattering factors for iodine, chlorine, and carbon, divided by the corresponding factors for He. The primes are used to distinguish ratios of inelastic scattering factors from ratios of elastic ones.

but a fraction of a percent of the cross section comes. Consequently, the value of $\bar{K}$ for He also provides a conservative estimate of $\bar{K}$ for C, Cl, and I. The results from Sec. III C were therefore used in Table II for collisions of types 2 and 3.

Collisions of types 4–6 are not involved in our H_2^+-He calculations and so supplementary calculations were carried out using the elastic and inelastic scattering factors. For each type of collision, the lowest value of $\bar{K}$ in Table II corresponds to He-He collisions; the largest value corresponds to I-I collisions.

Although the values of $\bar{K}$ in Table II were derived from atomic scattering factors, they should also apply to collisions involving molecules. The primary limitation of Table II is that the values of $\bar{K}$ will be too small at very low impact velocities for collisions involving large excitation energies. This effect is illustrated in Table I for $Q(2;3,1)$ and $Q(2;3,2)$. The excitation energies for these transitions are about 40 eV.

V. H_2^+-He CROSS SECTIONS

The results relative to σ_1 will be discussed first. Figure 4 shows how $Q(1\text{–}3;0)$, $Q(1\text{–}3;4)$, $Q(1\text{–}3;1\text{–}4)$, and $\tilde{Q}(1\text{–}3,\Sigma')$ compare.[43,44] The relative values of these cross sections follow the pattern first demonstrated by Bates and Griffing[45] for H-H collisions and their interest for us lies primarily in connection with the generalization to targets having large atomic numbers. The point we wish to make, and which can be understood from the cross-section formulas in Sec. II and the ratios given in Fig. 3, is that as the atomic number Z of the target increases, the value of $Q(1\text{–}3;0)$ increases more rapidly than the value of $\tilde{Q}(1\text{–}3,\Sigma')$. As a result, for targets having even moderate values of Z, $Q(1\text{–}3;0)$ exceeds $\tilde{Q}(1\text{–}3;\Sigma')$ at all impact energies, and for very large Z, $Q(1\text{–}3;0)$ dominates all the other cross sections. The importance at all energies of 0-0 transitions in targets having moderate to large values of Z contrasts with the situation for H and He, where, as is shown in Fig. 4, for example, these transitions are dominant only at low energies.

Experiment[46–49] and theory are compared in Fig. 5. In the region between 3×10^5 and 3×10^6 eV, $Q(1\text{–}3;0\text{–}4)$ lies from 75 to 40% below the experimental curves. This result is fairly compatible with the need to include contributions from additional excited states of H_2^+

[43] See Eqs. (5)–(7) and Ref. 19 for the notation.

[44] Values of the individual $Q(n,N)$, and $Q_\nu(1,N)$ of Eq. (1), can be obtained from the authors.

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

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

[47] L. I. Pivovar, V. M. Tubaev, and M. T. Novikov, Zh. Eksperim. i Teor. Fiz. **40**, 34 (1961) [English transl.: Soviet Phys.—JETP **13**, 23 (1961)].

[48] D. R. Sweetman (private communication to G. W. McClure).

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

in the calculation.[50] However, it appears possible that the theoretical prediction is somewhat low. At energies from 2×10^4 to 3×10^5 eV, the theory appears to be definitely low. In this region the use of the first Born approximation is, of course, open to question. It is surprising, however, that at 21 MeV, $Q(1\text{–}3;0\text{–}4)$ is only 50% of the experimental result obtained in Ref. 49.

The theoretical result $\tilde{Q}(\Sigma',\Sigma)$ of Eq. (7) provides a good high-energy extrapolation of the lower-energy values of $\sigma_1+\sigma_2$. Again, however, the theoretical curve lies somewhat farther below the 21-MeV data than one might have hoped.

The experimental values of σ_1 and $\sigma_1+\sigma_2$ include contributions from direct vibrational dissociation, i.e., dissociation in which the H_2^+ electronic state does not change. This contribution is estimated in Ref. 49 to be $0.9\times10^{-3}\ \pi a_0^2$ at 20MeV.[51] Assuming an E^{-1} energy dependence for this cross section, it can be seen that while its contribution to σ_1 is small at high energies, it would appear to be important at energies below 100 keV. It should be noted, however, that no E^{-1} dependence is evident in the experimental curve at these energies.

At 21MeV our results can be compared with those of the partly classical calculation presented in the columns labeled B in Table III of Ref. 49. This theoretical value includes contributions from all H_2^+ excited states. It is twice as large as $Q(1\text{–}3;0\text{–}4)$ and agrees almost exactly with the experimental value obtained in Ref. 49. The theoretical value of $\sigma_1+\sigma_2$ from Ref. 49 is about 20% higher than our value. The differences in the two sets of results arise primarily from the way in which the classical binary-collision model used in Ref. 49 treats the electronic excitation and ionization of H_2^+. We believe that at 21 MeV the Born calculation rests on a firmer theoretical foundation than the binary collision model.

Comparison of our results with those of Ref. 6 is also possible. In that work the sum of $Q(1,0)$ and the cross section for direct vibrational dissociation was calculated. As regards $Q(1,0)$ the two calculations are in essential agreement, allowing for minor differences in approximations. However, the treatment of direct vibrational dissociation given in Ref. 6 appears to be incorrect, owing to the neglect of the terms representing vibrational and rotational excitation in going from Eq. (28) to Eq. (30). We believe that this approximation is responsible for the abnormally large value obtained in Ref. 6 for the sum of the two cross sections in question.

Some comment on the over-all accuracy of $Q(1\text{–}3;0\text{–}4)$ is appropriate at this point. We estimate

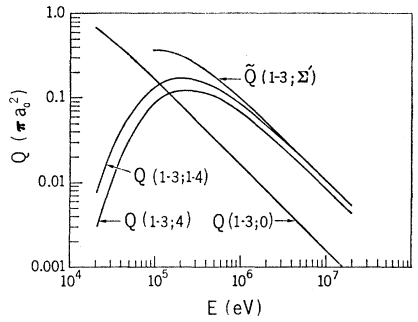

FIG. 4. Theoretical H_2^+-He cross sections. These cross sections are sums of cross sections for transitions to various final states of H_2^+ and He. The summation conventions are defined in Eqs. (5) and (6). Numbering of the states is defined in Ref. 19.

that approximations made in the treatment of the H_2^+ vibration-rotation degrees of freedom and in the H_2^+ electronic wave functions lead to errors of less than $\pm10\%$. We estimate that discrete excited states of He not included in $Q(1\text{–}3;0\text{–}4)$ will increase it by about 5%. Lassettre has not given error limits for his generalized oscillator strengths. However, as $K^2\to0$, they are known to be accurate to about $\pm5\%$. For our estimate we rather arbitrarily assign error limits of $\pm15\%$ to the He generalized oscillator strengths. We also suppose that the elastic and inelastic electron scattering factors for He are exact for our purposes. These considerations lead to error limits of about $\pm25\%$ for $Q(1\text{–}3;0\text{–}4)$ at energies below 10^6 eV. At higher energies the closure approximation is accurate and utilizes only the He elastic and inelastic scattering factors. At these energies we therefore estimate the error limits on $Q(1\text{–}3;0\text{–}4)$ to be $\pm10\%$.

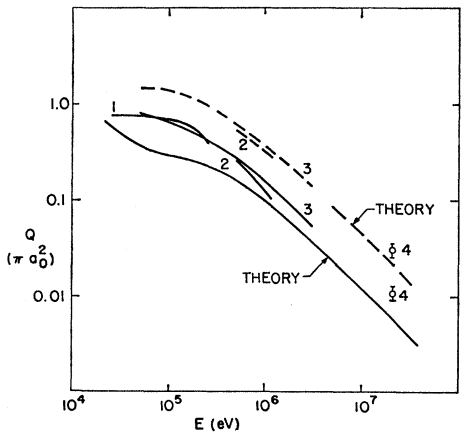

FIG. 5. Cross sections for breakup of H_2^+ upon collision with He. The dashed curves refer to $\sigma_1+\sigma_2$; the solid curves refer to σ_1. The curves labeled "theory" represent $Q(1\text{–}3;0\text{–}4)$ in the case of σ_1 and $\tilde{Q}(\Sigma',\Sigma)$ in the case of $\sigma_1+\sigma_2$. These cross sections are defined in Eqs. (5) and (7), respectively. Contributions from H_2^+ states not included in $Q(1\text{–}3;0\text{–}4)$ should raise the theoretical curve by of the order of 30%. $\tilde{Q}(\Sigma',\Sigma)$ is an upper bound for the Born approximation. The remaining curves represent experimental data from the following references: 1, Ref. 46; 2, Ref. 47; 3, Ref. 48; 4, Ref. 49.

[50] It is difficult to give a reliable estimate of contributions to σ_1 from transitions to the discrete excited states of H_2^+ which are not included in $Q(1\text{–}3;0\text{–}4)$ of Eq. (5). On the basis of crude quantum number scaling arguments, it is not hard to believe that transitions to the additional states will increase $Q(1\text{–}3;0\text{–}4)$ by as much as 30 or 40%. However, it is hard to see how these transitions could double it.

[51] The accuracy of this classical calculation is unknown.

It is interesting to consider a possible origin of the discrepancy between $Q(1\text{–}3;0\text{–}4)$ and σ_1 at energies below 300 keV. Here, a 30% addition[50] to $Q(1\text{–}3;0\text{–}4)$ from the excitation of higher discrete states of H_2^+ is insufficient to produce agreement between theory and experiment. At these energies an obvious source of error in the Born approximation is the neglect of exchange. Indeed, there is considerable experimental evidence that exchange scattering is quite important at energies ($\sim$50 keV) such that the impact velocity is about one atomic unit.[26,52,53] In H_2^+-He collisions, the exchange of an electron in a collision which leaves the ion in a discrete excited state produces dissociation and leaves the target in an excited triplet state. This produces a contribution to σ_1 which is omitted in the Born calculation. The inclusion of exchange also modifies the amplitudes for transitions to He singlet states; this modification can either increase or decrease the corresponding contribution to σ_1. Calculations including exchange, perhaps similar to those of Bates and Crothers[4] for H-He collisions, would be of interest.

In conclusion, it is worth noting that much of the experimental data for H_2^+-He and other heavy-particle collisions relate to impact energies at which the closure approximations are invalid. Thus if the data are to be compared with calculations based on Born approximation, with or without exchange, individual transition matrix elements must be obtained either theoretically or experimentally for both target and projectile. In this connection, measured high-energy differential electron scattering cross sections can be of great value, if the measurements are carried out to the largest possible values of momentum transfer and energy loss.

ACKNOWLEDGMENTS

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APPENDIX: QUALITATIVE EXTRAPOLATION OF ELECTRON IONIZATION DATA FOR COMPLEX SYSTEMS

Quantitative theoretical ionization cross section formulas such as those available for H and He are not available for most other atoms and molecules. Therefore, guidelines for the qualitative extrapolation of experimental ionization cross sections to larger values of C^2 and K^2 are of considerable interest, particularly in view of the values of $\bar{K}$ in Table II for collisions in which ionization occurs. Presented below are some comments concerning qualitative extrapolation, which may be helpful until the theory is more fully developed. The basic assumption underlying the discussion is that the main qualitative features of the electron ionization cross sections for He and H are also possessed by the electron ionization cross sections for more complicated systems.

Extrapolation with respect to C^2 can be discussed with the help of Fig. 1. The data end at $C^2=2.2$. However, as can be seen from Eq. (A1) below, values of $f'/(2W)$ for larger values of C^2 are usually required. For a given value of K, the maximum value of C^2 allowed by energy conservation is

$$C_{\max}^2=2V_0K-2\Delta E-K^2/\mu. \qquad \text{(A1)}$$

Here V_0 is the H_2^+ impact velocity and μ is the H_2^+-He reduced mass. The quantity ΔE is the sum of the He ionization energy and the excitation energy of the H_2^+ transition under study. The last term in Eq. (A1) can usually be neglected for the purpose of estimating $C_{\max}^2$, as it is very small. With $K^2=1$ and $\Delta E=1$, for example, it can be seen from Eq. (A1) and Fig. 1 that for $V_0=2$ no extrapolation of the experimental data with respect to C^2 is required, while for $V_0=4$, the area under the extrapolated portion of the curve is about 30% of the total allowed by energy conservation. Since the matrix element $|E_4(K)|^2/K^2$ which figures in Eq. (2) is just the allowed area under the curves of Fig. 1, it can be seen that for $K^2\leq 1$ fairly accurate values of $|E_4(K)|^2/K^2$ can be obtained, even if qualitative "french-curve" extrapolation of $f'/(2W)$ with respect to C^2 is used in place of the quantitative theory. However, it is also evident that it would be desirable to extend the measurements to larger values of C^2. This is essential for the larger values of K^2 because for $K^2\geq 4$, $f'/(2W)$ has a broad maximum in the vicinity of $C^2=K^2$.

In the case of an atom or molecule for which no quantitative theory is available, the above discussion suggests that qualitative extrapolation with respect to C^2 will not produce gross errors in the values of $|E_4(K)|^2/K^2$ provided the measurements extend far enough that $f'/(2W)$ has passed its maximum, if any, and is beginning to decrease. This type of extrapolation has already been used by Silverman and Lassettre in connection with the electron ionization data for O_2.[54]

The problems connected with the extrapolation of $|E_4(K)|^2/K^2$ are exhibited in Fig. 2. The striking thing exhibited here is the way in which each of the ionization curves, 1–4, runs roughly parallel to the inelastic scattering curve, 5, once the ionization curve has passed its maximum. Since inelastic scattering factors are available for most atoms, and can also be calculated from ground-state electronic wave functions, this suggests that the inelastic scattering factor can be used as a

[52] F. J. de Heer, L. Wolterbeek Muller, and R. Geballe, in *Proceedings of the Fourth International Conference on the Physics of Electronic and Atomic Collisions, Quebec, 1965*, edited by L. Kerwin and W. Fite (Science Bookcrafters, Hastings-on-Hudson, N. Y., 1965) p. 309.

[53] M. E. Rudd and D. V. Lang, Ref. 52, p. 153.

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guide for qualitative extrapolation of $|E_4(K)|^2/K^2$ when no quantitative theory of ionization is available. For this purpose measurements of $f'/(2W)$ out to values of $K^2=2$ or $K^2=3$ are needed, so that values of $|E_4(K)|^2/K^2$ can be determined out to or beyond its maximum. The accuracy of such an extrapolation can be increased in the following way. Assume, as seems reasonable, that as a function of C^2 for large fixed K^2, $f'/(2W)$ has a maximum of fairly symmetrical shape near $C^2=K^2$. It then follows that for large K^2 the ratio of $|E_4(K)|^2$ to the inelastic scattering factor is close to unity or small compared to unity when $C_{\max}^2$ is, respectively, much greater than or much less than K^2 and that this ratio is close to $\frac{1}{2}$ when $C_{\max}^2$ is close to K^2. Numerical calculations for He and H show that when $C_{\max}^2=K^2-1$, or solving for K, when $K=V_0+(V_0^2+1-2\Delta E)^{1/2}$, the ratio of $|E_4(K)|^2$ to the inelastic scattering factor is equal to $\frac{1}{2}$ to within 10%. Given V_0, ΔE, and measurements of $f'/(2W)$ out to $K^2=2$ or $K^2=3$, the experimental data would determine $|E_4(K)|^2$ out to or past its maximum. Extrapolation would then be carried out by using the value of $C_{\max}^2$ to determine approximately where the curve should be placed relative to the inelastic scattering curve. Except at low velocities, the relation $C_{\max}^2=K^2-1$ determines a particular point through which the extrapolated curve should pass. Curves 1–4 of Fig. 2 illustrate the foregoing ideas for low, intermediate, and high impact velocities. The circled points labeled 2 and 3 were determined by setting $|E_4(K)|^2$ equal to one-half the inelastic scattering factor at the value of K for which $C_{\max}^2=K^2-1$.

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Optical Third-Harmonic Coefficients for the Inert Gases

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Optical third-harmonic coefficients are calculated for the inert gases and are compared with recent experimental values. We find them to range from 0.9×10^{-39} esu/atom for He to 222×10^{-39} esu/atom for Xe. Our calculated values, expressed as ratios to the optical third-harmonic coefficient of He, compare favorably with one of two sets of recently reported experimental values.

RECENTLY New and Ward[1] measured the optical third-harmonic coefficient for the inert gases relative to glass. Since they did not measure the absolute values of the coefficient for any gas, they presented their values scaled to $\alpha_{zzzz}(3\nu)=4.5\times10^{-39}$ esu/atom for He. Also their data reduction scheme led to two sets of experimental values.

In this paper, we calculate the optical third-harmonic coefficients for the inert gases by a very simple procedure. We find that $\alpha_{zzzz}(3\nu)=0.9\times10^{-39}$ esu/atom for He. We also find that the calculated values for the other inert gases, relative to He, fall within the experimental error of one set of experimental values of New and Ward.

We base our calculations of $\alpha_{zzzz}(3\nu)$ on a procedure commonly used to compute the linear polarizability. The linear polarizability is given by

$$\alpha_{zz}^{L}(\nu)=\frac{2e^2}{h}\sum_{\text{electrons}}\sum_{i}\nu_{ig}Z_{gi}Z_{ig}\frac{1}{\nu_{ig}^2-\nu^2}, \qquad (1)$$

ν_{ig} being the frequency difference between some excited state i and the ground state g, with Z_{ig} the corresponding dipole matrix element, summed over all excited states and over all electrons. Replacing the sum over all electrons by a constant N_0 (which may be thought of as some effective number of electrons), replacing ν_{ig} in $(\nu_{ig}^2-\nu^2)$ by some average energy ν_0, and using the Thomas-Reiche-Kuhn sum rule, we obtain

$$\alpha_{zz}^{L}(\nu)\simeq\frac{N_0e^2}{4\pi^2m}\left[\frac{1}{\nu_0^2-\nu^2}\right]. \qquad (2)$$

Using Eq. (2), Culbertson[2] obtained a good fit to the experimental index of refraction for the inert gases by regarding N_0 and ν_0 as parameters for each gas. Culbertson's values for N_0 and ν_0 are reproduced in Table I.

Using the expression for the nonresonant optical third-harmonic coefficient derived by Armstrong *et al.*[3],

$$\alpha_{zzzz}(3\nu)=\frac{e^4}{h^3}\sum_{\text{electrons}}\sum_{i,j,k}\nu_{ig}Z_{gi}Z_{ij}Z_{jk}Z_{kg}A_{ijk}, \qquad (3)$$

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