Use of Inelastic Electron Scattering Data to Obtain Accurate Born Cross Sections for Atom-Atom and Other Heavy-Particle Collisions. I. Proton Excitation of the Schumann-Runge Continuum in O_2†

THOMAS A. GREEN
Sandia Laboratory, Albuquerque, New Mexico
(Received 8 December 1966)

It is pointed out that the accurate generalized oscillator strengths obtained by Lassettre and his co-workers from inelastic electron scattering experiments make it possible to evaluate the first-Born-approximation cross sections for certain ion-atom, atom-molecule, etc. collisions with greater accuracy than can usually be obtained if the generalized oscillator strengths are calculated from the electronic wave functions of the colliding particles. The idea is illustrated by a comparison of the experimental generalized oscillator strength for the excitation of the Schumann-Runge transition in O_2 with a theoretical generalized oscillator strength based on Kotani's wave functions for O_2, and by the calculation of the Born total cross section for proton excitation of this transition. The cross section is compared with that obtained by Breene via an impact-parameter calculation.

I. INTRODUCTION AND PRESENTATION OF THE MAIN IDEA

In an interesting series of papers,[1–12] Lassettre and his co-workers have described measurements of differential cross sections for inelastic scattering of nearly monoenergetic electrons by a number of atoms and molecules. Their use of energy analysis following single scattering often makes it possible to measure absolute differential cross sections for collisions which cause transitions from the ground electronic state of the target to just one of its excited electronic states. The experiments are conducted with electrons having initial energies of the order of 500 eV and hence, as Lassettre has demonstrated experimentally,[3,5,12] the first Born approximation can be used to analyze the cross sections theoretically. This makes it possible, in case a particular target transition has been isolated via the electron energy loss, to determine the generalized oscillator strength[3] for the transition as a function of the momentum transferred to the target. At energy losses above a target ionization or dissociation limit, continuum oscillator strengths[3,9] can be obtained as functions of energy loss and momentum transfer. In case the energy losses for two or more discrete transitions cannot be resolved, the sum of the generalized oscillator strengths for these transitions can be obtained.[3] The accuracy of the measured generalized oscillator strengths appears to be of the order of 10%. Once the generalized oscillator strength for a transition has been obtained, it can be used to calculate the total electron scattering cross section for the transition at all energies for which the Born approximation is valid.[11] The accuracy of the total cross section is essentially the same as that of the oscillator strength from which it is derived.

The purpose of this paper is to point out and illustrate the fact that generalized oscillator strengths determined experimentally from inelastic electron scattering can also be used to obtain accurate Born-approximation cross sections for inelastic ion-atom, atom-molecule, etc., collisions. This possibility follows from the structure of the first Born approximation. It can be shown that with a proportionality constant which depends only on a power of the momentum transfer and trivial kinematical factors, the differential cross section for a heavy-particle collision in which the target undergoes one transition while the projectile undergoes another is proportional to the product of the generalized oscillator strengths for the two transitions.[13] If no transition occurs in one collision partner, its oscillator strength is replaced by the appropriate elastic electron scattering factor.[14] In case the projectile is a structureless charged particle, such as an electron or a bare nucleus, the dif-

† Work supported by the U. S. Atomic Energy Commission.
[1] E. N. Lassettre and S. A. Francis, J. Chem. Phys. **40**, 1208 (1964).
[2] E. N. Lassettre and E. A. Jones, J. Chem. Phys. **40**, 1218 (1964).
[3] E. N. Lassettre and E. A. Jones, J. Chem. Phys. **40**, 1222 (1964).
[4] E. N. Lassettre, A. S. Berman, S. M. Silverman, and M. E. Krasnow, J. Chem. Phys. **40**, 1232 (1964).
[5] E. N. Lassettre, M. E. Krasnow, and S. Silverman, J. Chem. Phys. **40**, 1242 (1964).
[6] E. N. Lassettre and M. E. Krasnow, J. Chem. Phys. **40**, 1248 (1964).
[7] E. N. Lassettre and S. M. Silverman, J. Chem. Phys. **40**, 1256 (1964).
[8] E. N. Lassettre, S. M. Silverman, and M. E. Krasnow, J. Chem. Phys. **40**, 1261 (1964).
[9] S. M. Silverman and E. N. Lassettre, J. Chem. Phys. **40**, 1265 (1964).
[10] A. M. Skerbele and E. N. Lassettre, J. Chem. Phys. **40**, 1271 (1964).
[11] S. M. Silverman and E. N. Lassettre, J. Chem. Phys. **40**, 2922 (1964).
[12] S. M. Silverman and E. N. Lassettre, J. Chem. Phys. **44**, 2219 (1966).
[13] D. B. Bouthilette, J. A. Healey, and S. N. Milford, in *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 1081. The quantity $|J_{nn'}{}^{a}|^2$ of this work is equal to the generalized oscillator strength for the transition $n \rightarrow n'$ times the square of the momentum transfer divided by twice the energy difference between the states labeled by n and n'. It is the same as the quantity $|\epsilon|^2$ in Ref. 2.
[14] J. D. Lea, PhD. dissertation, University of Texas, 1963 (unpublished) (University Microfilms, Inc., Ann Arbor, Michigan).

ferential cross section is proportional to the generalized oscillator strength for the transition in the target.[1,15] The oscillator strengths required for a knowledge of these differential cross sections can, of course, be obtained by any means, either theoretical or experimental, at one's disposal.

The important point, now, is that in many cases a generalized oscillator strength determined by Lassettre's technique will be considerably more reliable than that which can be calculated from first principles in terms of the Fourier transform of the product of the initial and final electronic wave functions for the transition. Except in the case of a one-electron atom, the calculation of this transform to an accuracy of 10% or better is a major accomplishment. At present, errors of from 25 to 50% can be expected to occur frequently in theoretical calculations of generalized oscillator strengths for even relatively simple systems[16] and errors of the order of 100% or more will not be uncommon in the case of complicated ones. Eventually, the work now in progress on atomic and molecular wave functions will make the calculation of accurate generalized oscillator strengths possible for a large variety of systems. However, for some time to come, the experimentally determined generalized oscillator strengths, when available, will often be a good deal more reliable than most of those calculated from first principles.

In this paper the point just discussed is illustrated through the evaluation of the total cross section for proton excitation of the transition $^3\Sigma_g^- \rightarrow {}^3\Sigma_u^-$ in O_2. This transition, which is associated with the Schumann-Runge dissociation continuum, has been chosen because of its intrinsic interest, because a previous theoretical calculation[17] exists for comparison, and because an approximate theoretical calculation of the generalized oscillator strength can be carried out. In a subsequent paper,[18] Lassettre's generalized oscillator strengths for He will be used to evaluate the total cross section for the dissociation of H_2^+ upon collision with He.

Lassettre's group has undertaken the most extensive exploration of the possibility of measuring generalized oscillator strengths via high-energy inelastic electron scattering. However, it is important to note that similar and equally impressive experiments have been carried out on H_2 by Geiger,[19] Boersch, and their co-workers. Geiger's experimental results for the excitation of the B and C states of H_2 have been recently compared with a theoretical calculation by Khare.[20]

Atomic units are used except where other units are specifically indicated.

II. PROTON EXCITATION OF THE TRANSITION $^3\Sigma_g^- \rightarrow {}^3\Sigma_u^-$ IN OXYGEN

In this section an appropriate Born-approximation formula for the cross section is first developed for use with the generalized oscillator strength obtained by Silverman and Lassettre.[11] The experimentally determined oscillator strength is then compared with that which can be deduced using the O_2 electronic wave functions of Kotani *et al.*[21] Finally, the result for the cross section is presented, discussed, and compared with that obtained in Ref. 17.

It is known from both the optical-absorption spectrum[22] and the electron energy-loss spectra[8] that only a very small percentage of the transitions from the $^3\Sigma_g^-$ ground electronic state of O_2 are to the bound vibrational levels of the $^3\Sigma_u^-$ excited electronic state. Most of the transitions are to the dissociation continuum of the excited state. In Refs. 8 and 11 the energy-loss spectra show a well-isolated peak centered at an energy loss of 8.44 eV. This energy loss corresponds closely to a Franck-Condon transition at internuclear separation $R=2.29$ atomic units (a.u.) from the lowest vibrational level of O_2 to the potential curve for $^3\Sigma_u^-$. Lassettre integrates the scattered intensity with respect to energy loss over the 8.44-eV peak from 6.56 to 9.46 eV. This corresponds to including in the integrated scattered intensity, along with the main contribution from the dissociation continuum, the relatively small contributions from the upper-bound vibrational levels of $^3\Sigma_u^-$. Thus the integrated scattered intensities closely approximate sums over all vibration-rotation states of the excited electronic state. On this basis the final vibrational and rotational degrees of freedom can be treated by closure,[23] using 8.44 eV as the most probable energy loss. Alternatively, a δ-function approximation can be used for the $^3\Sigma_u^-$ radial vibrational wave functions.[24] In the case of O_2, for which the initial vibrational wave function is peaked in a small interval near the internuclear separation $R=2.29$ a.u., both methods lead to the result that, to a very good approximation, the total cross section Q for excitation of the transition $^3\Sigma_g^- \rightarrow {}^3\Sigma_u^-$ is given by Eqs. (3) and (4) of Ref. 24. In terms of the momentum transfer K,

$$Q=(4\pi/v_n^2)\int d(K^2)\,|\,\epsilon(K,R)\,|^2K^{-4}, \qquad (1)$$

where the limits of integration on K^2 follow from those

[15] D. R. Bates, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), p. 550. The quantity $|\mathcal{J}(\text{p.q.})|^2$ in this work is the same as $|J_{nn'}{}^a|^2$ in Ref. 13 and $|\epsilon|^2$ in Ref. 2.

[16] See J. M. Peek [Phys. Rev. **139**, A1429 (1965)] for a study of the effect of the use of approximate wave functions on the generalized oscillator strength for a transition in H_2^+.

[17] R. G. Breene, Jr., Phys. Rev. **131**, 2560 (1963).

[18] T. A. Green and J. M. Peek, Phys. Rev. (to be published).

[19] J. Geiger, Z. Physik **181**, 413 (1964).

[20] S. P. Khare, Phys. Rev. **149**, 33 (1966).

[21] M. Kotani, Y. Mizuno, and K. Kayama, J. Phys. Soc. Japan **12**, 707 (1957).

[22] K. Watanabe, E. Inn, and M. Zelikoff, J. Chem. Phys. **21**, 1026 (1952).

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

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

in Eq. (3) of Ref. 24, v_n is the initial relative speed, and

$$|\epsilon(K,R)|^2=(4\pi)^{-1}\int d\Omega \times\left|\int d\tau\,\Psi_{n'}{}^*\Psi_n\sum_i \exp(i\mathbf{K}\cdot\mathbf{r}_i)\right|^2. \quad (2)$$

In Eq. (2), R is the equilibrium internuclear separation of O_2 and $\int d\Omega$ means integration over all orientations of the internuclear line, as shown in Eq. (4) of Ref. 24. The $\mathbf{r}_i$ are the coordinates of the 16 oxygen electrons relative to the midpoint of the internuclear line and $d\tau$ indicates integration over all the $\mathbf{r}_i$. The initial and final electronic wave functions are Ψ_n and $\Psi_{n'}$, respectively.

The quantity $|\epsilon(K,R)|^2$ is closely related to the sum of the generalized oscillator strengths over the final discrete and continuum vibration-rotation states for the ${}^3\Sigma_g^-\rightarrow{}^3\Sigma_u^-$ transition. It follows from the discussion in Ref. 8 that

$$|\epsilon(K,R)|^2/K^2=\int dU\, f'(U)/(2U) =bf_{\max}'/(2U_{\max}), \quad (3)$$

where $f'(U)$ is the experimental differential oscillator strength corresponding to the energy loss U, $f_{\max}'$ is its peak value, and $U_{\max}$ is the value of U at which the peak occurs. The quantity b is determined experimentally to have the value 1.388 eV. The limits on the integral above are 6.56 and 9.46 eV, as was mentioned in the preceding paragraph. It is also possible to express $|\epsilon(K,R)|^2$ in terms of the integrated generalized oscillator strength,

$$f=\int dU f'(U)=b'f_{\max}'. \quad (4)$$

Here the experimental constant b' has the value 1.35 eV.[8] From Eqs. (3) and (4),

$$|\epsilon(K,R)|^2/K^2=(b/b')[f/(2U_{\max})]. \quad (5)$$

Using Eq. (3), with the values of f' tabulated in Ref. 8, or Eq. (5), with the values of f tabulated in Ref. 11, Eq. (1) can be used to calculate Q in first Born approximation for any structureless charged particle.

The calculation of the cross section for proton excitation of O_2 can now be presented. Figure 1 shows values of $|\epsilon(K,R)|^2/K^2$ obtained from Eq. (5). Also shown is the value of $|\epsilon(K,R)|^2/K^2$ obtained from Eq. (2), using the wave functions of the CI(π) approximation in Ref. 21. Let us consider the theoretical result first. Although it agrees quite well with experiment near $K^2=0$, the disagreement is marked for larger values of K^2. Experience[16] with the dependence of $|\epsilon(K,R)|^2$ on the electronic wave functions for a rather

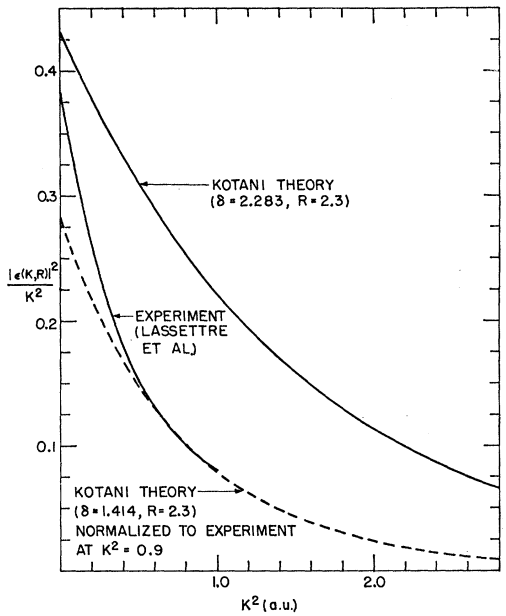

FIG. 1. Comparison of experimental and theoretical values of $|\epsilon(K,R)|^2/K^2$. The quantity K is the momentum transferred during the collision, δ is the p-orbital screening parameter, and R is the internuclear separation for which the wave functions were calculated. The dashed curve was used to extrapolate the experimental data to values of $K^2>1$ in the manner described in the text.

similar transition in H_2^+ makes it appear likely that the unavoidable use by Kotani *et al.* of unoptimized screening parameters in the wave function is a major source of error in the value of $|\epsilon(K,R)|^2$ for large K^2. Since the values of $|\epsilon(K,R)|^2$ obtained from Eq. (5) should be accurate to about 10%, it is clear that the experimental value of $|\epsilon(K,R)|^2$ is more reliable than the theoretical one.[25]

Figure 1 illustrates a problem which is characteristic of the use of the experimental data. Because of intensity problems, the data only extend to values of K^2 close to unity. In the case of charged-particle excitation of allowed transitions, this causes only a minor error in the total cross section, which is dominated at all but the lowest energies by values of K^2 which are small compared to unity. In order to include some reasonable contribution to Q from values of $K^2>1$, the extrapolation shown as the dashed curve in Fig. 1 was used. It was obtained from the theoretical expression for $|\epsilon(K,R)|^2$ with a choice of screening parameter which gave a good fit to the slope and value of $|\epsilon(K,R)|^2/K^2$ near $K^2=1$. The theoretical extrapolation guarantees that as $K^2\rightarrow\infty$, $|\epsilon(K,R)|^2$ tends toward zero as a high power of K^2, a behavior which is also suggested by known results for transitions in atoms and in H_2^+.

[25] The CI(π) approximation is not the most accurate one considered by Kotani *et al.* Since the screening parameters in the more accurate wave functions are also not optimized, the expenditure of the considerable effort which would be required to calculate the generalized oscillator strength from them does not appear to be warranted.

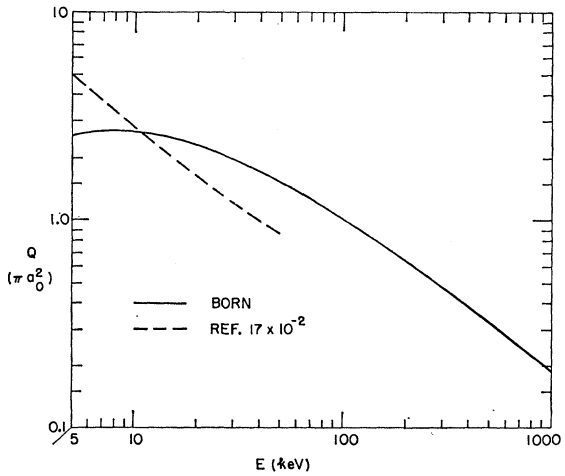

FIG. 2. Total cross section Q for proton excitation of the transition $^3\Sigma_g^- \rightarrow {}^3\Sigma_u^-$ in O_2 plotted versus incident proton energy E.

The result for Q is shown in Fig. 2. It was obtained by numerical integration of Eq. (1), a cubic spline function being used to obtain a smooth curve from the tabulated experimental oscillator strength. Numerical procedures were used which guarantee an over-all numerical precision of 0.1%. At energies above 1000 keV, the formula

$$EQ=38.09 \ln E-76.13 \quad (6)$$

describes the result of the calculation to 0.1%; for 100 keV $<E<1000$ keV, the same formula describes the result of the calculation to better than 2%. In Eq. (6), Q is expressed in units of πa_0^2, where a_0 is the Bohr radius, and E is expressed in keV. It was found that the contribution to Q from values of $K^2>1$ in Eq. (1) ranged from 25% for $E\sim6$ keV, through 8% for $E\sim30$ keV, to 2% for $E\sim1000$ keV. This shows that only a very small error is introduced in Q by any reasonable extrapolation of the experimental oscillator strength to values of $K^2>1$. For energies above about 150 keV, Q has essentially the same value as the cross section for electrons of the same velocity and is in substantial agreement with the result obtained for electrons by Silverman and Lassettre.[11,26]

The dashed curve in Fig. 2 shows the cross section obtained in Ref. 17 via the impact-parameter method. A study of Ref. 17 indicates that the most questionable approximation which was made in this inherently more difficult calculation was the setting of $\cos[(k-k')x]$ equal to unity in going from Eq. (8) to Eq. (17) of that reference. Here k and k' are equal to 2π times the initial and final wave numbers of the proton, and x is the proton-position variable along the straight-line collision path. Since $k-k'$ is closely equal to the energy defect for the transition divided by the initial relative velocity, the above approximation amounts to doing the calculation as if the energy defect for the reaction were zero. The omission of $\cos[(k-k')x]$ from the integrand in Eq. (17) of Ref. 17 led to the introduction of a cutoff whose value is responsible for the large cross section shown in Fig. 2.[27]

III. DISCUSSION

The results obtained for oxygen in Sec. II should be representative of the advantages to be gained by using experimentally determined generalized oscillator strengths in connection with excitation of atoms and molecules by structureless heavy charged particles. A study of Refs. 1–11 will suggest a number of similar applications. When both colliding particles are capable of internal excitation, even more interesting applications are possible. However, in this case, some special problems arise which will be discussed in Ref. 18.

In conclusion, one additional aspect of the use of inelastic electron scattering in connection with fast heavy-particle collisions is worthy of note. In Lassettre's experiments the electron energy loss can sometimes be used to identify the final state of the target without the uncertainties which usually attend the identification (if any) of the individual excited states of the target and projectile in a heavy-particle collision. Thus electron-scattering measurements of generalized oscillator strengths will allow the calculation of accurate Born-approximation cross sections for some atom-atom and atom-molecule reactions whose cross sections would be very difficult to measure directly.

ACKNOWLEDGMENTS

The author is deeply indebted to J. M. Peek for making him aware of Lassettre's experiments and for extensive discussions of many aspects of the work presented above. He also wishes to thank Mrs. Marcella Madsen for programming the calculations.

[26] In Ref. 11, Q for electrons is calculated from a formula which is equivalent to setting (b/b') equal to unity in Eq. (5). In addition, the upper limit in Eq. (1) is taken to be unity since the experimental oscillator strength data do not extend to larger values of K^2.

[27] Breene has recently corrected the error in Ref. 17 which was mentioned above. His new results are reported in J. Chem. Phys. 45, 3876 (1966).