GENERALIZED OSCILLATOR STRENGTHS

Final Technical Report

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MASTER

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ABSTRACT

Progress in the study of generalized oscillator strengths since January 1, 1970 is reviewed. The status of methods for the experimental determination of electron collision cross sections and generalized oscillator strengths is discussed including (i) the comparison of inelastic and elastic scattering when elastic cross sections are available, (ii) the use of a comparison gas with a transition of known cross section, and (iii) the determination of optical oscillator strengths from forward scattering spectra. Outstanding discrepancies between limiting generalized oscillator strengths (at zero momentum change) and optical oscillator strengths are resolved for the most part. There are no longer any outstanding discrepancies involving refractive indices.

Two new selection rules, one relating to singlet-singlet transitions, the other to singlet-triplet transitions are described. Other deviations from the Born approximation at large momentum changes are discussed.

Generalized oscillator strengths are applied to the calculation of cross sections (in Born approximation) for resonant energy transfer in collision between two molecules one of which is excited.

1. INTRODUCTION

On September 3, 1969, a proposal was made to the Radiological Physics and Instrumentation branch of the Division of Biology and Medicine of the Atomic Energy Commission (now E.R.D.A.), for a study (three years) of inelastic electron scattering at comparatively high kinetic energies (300 - 500 eV). In 1973 this was extended for an additional three years. A terminal extension of one year was granted in 1976. This coincides with the retirement of E. N. Lassettre on June 30, 1977. A six-year technical progress report was prepared in 1976. The present report (which summarizes the accomplishments from Jan. 1, 1970 to June 30, 1977) incorporates the previous six-year progress report with some minor changes plus an account of the research during the terminal year.

Although E.R.D.A. (AEC) has supported this electron scattering research only since January 1970, a program of investigation of inelastic scattering has been in progress, under the direction of E. N. Lassettre, since 1946; first at Ohio State University then (since 1962) at Mellon Institute and finally (since 1967) at Carnegie-Mellon University after the merger of Mellon Institute with the Carnegie Institute of Technology. The results of this research have been summarized, and related to the research of other investigators, in four review articles.

1. E. N. Lassettre, "Collision Cross Section Studies on Molecular Gases and the Dissociation of Oxygen and Water," *Radiation Research*, Suppl. 1, 530-540 (1959).
2. E. N. Lassettre, *Can. J. Chem.* 47, 1733 (1969).
3. E. N. Lassettre and A. Skerbele, "Inelastic Electron Scattering," Methods of Experimental Physics; Vol. 3 Molecular Physics, Edited by D. Williams; Academic Press, New York (1974), pp. 868-951.
4. E. N. Lassettre, "Absolute Intensities and Classification of Transitions in Electron Impact Spectroscopy," Chemical Spectroscopy and Photochemistry in the Vacuum Ultraviolet, Edited by C. Sandorfy, P. J. Ausloos,

and M. B. Robin, D. Reidel Publishing Co., Dordrecht/Boston (1974), pp. 43-70.

The first two reviews cover the period up to 1970 while reviews 3 and 4 cover the period since that time. All four are largely, but not entirely, devoted to the research of E. N. Lassette and his collaborators.

The primary purpose of the research supported by E.R.D.A. (AEC) has been the determination and interpretation of the generalized oscillator strength which is related to the differential electron collision cross section, σ , by the defining formula

$$f = \frac{W}{2} \frac{P_1}{P_2} (\Delta P)^2 \sigma \quad (1)$$

Here, W is the excitation energy for the transition studied, P_1 , P_2 are the momenta of the colliding electron before and after collision and ΔP is the absolute magnitude of the vector difference between the electron momenta before and after collision. Atomic units are employed. If the excited state belongs to a continuum, the appropriate quantity may be $f' = \frac{df}{dW}$ and we have generally used a mixed unit, electrons per volt, for this quantity.

In order to determine generalized oscillator strengths it is essential that the collision cross section σ be measured precisely. The method adopted involved the construction of two electron spectrometers, one for the determination of absolute elastic collision cross sections and the second a high-resolution spectrometer with electrostatic lenses corrected so that the ratio of peak areas in an electron impact spectrum is equal to the ratio of collision cross sections. With this spectrometer

the ratio of an inelastic to the elastic peak areas can be determined and hence from the cross section for elastic scattering the cross section for inelastic scattering can be calculated. The apparatus for the determination of absolute elastic collision cross sections was developed by Phillip Bromberg [J. Chem. Phys. 50, 3906 (1969)] and the high-resolution spectrometer by Lassettre and collaborators [E. N. Lassettre, A. Skerbele, M. A. Dillon and K. J. Ross, J. Chem. Phys. 48, 5066 (1968)]. By January 1, 1970, when the E.R D.A (AEC) research program began, this technique had already been developed and the study of generalized oscillator strengths could begin immediately.

An important application of collision cross section measurements is the determination of optical oscillator strengths. Previous to 1969 the basic theory depended on the Born approximation. However, it is now known that the limiting relation between generalized oscillator strengths and optical oscillator strength does not depend on the Born approximation. This is briefly discussed in Section 2 of the following report.

The technique of collision cross section determination is briefly described, with reference to our own research publications, in Section 3.

Section 4 of the following report contains a summary of generalized oscillator strength studies on various transitions in selected substances. Each of these transitions was selected, from an immense field, in order to illustrate a general principle related to selection rules, deviation from the Born approximation, a conflict between quantities deduced from different types of experiment, or some other factor connected with the mechanism of collision or the structure of the target system. As our investigation continued we have obtained results which were entirely unexpected, which raised new questions, and which influenced the choice of

of transitions for subsequent study. This is reflected in the organization of Section 4.

The first Born approximation (without exchange) is approached when the kinetic energy is increased, at fixed momentum change for the colliding electron, for transitions in which there is no change in multiplicity (e.g. singlet-singlet transitions). A study of singlet-triplet transitions at high kinetic energy (several hundred electron volts) reveals no noticeable approach to the first Born approximation with exchange (the Born-Oppenheimer exchange amplitude). In certain cases the discrepancy at $\theta=0^\circ$ may be several orders of magnitude and agreement is poor at all kinetic energies and scattering angles thus far studied. The results thus far obtained and the reasons for the discrepancies (which are now known) are discussed in Section 5. A new selection rule is apparently involved.

Several theoretical studies which involve the interpretation, or application, of collision amplitudes are described in Section 6.

It has gradually become evident that collision amplitudes at intermediate or high kinetic energy of incidence are exceptionally useful for theoretical purposes. Several instances of this are discussed in Section 7. These include (a) an expression for the exchange integral (arising in Quantum Chemistry) in terms of generalized oscillator strength, (b) an expression for singlet-triplet energy difference in terms of generalized oscillator strength, and (c) a formula for resonant energy transfer cross sections (in Born approximation) in terms of generalized oscillator strengths. There are strong indications that a complete knowledge of collision amplitudes at high kinetic energy would also enable us to calculate higher order approximations which involve deviations from the Born approximation. This possibility is discussed in Section 9 as an example of a field which deserves further study.

2. OPTICAL OSCILLATOR STRENGTHS. LIMIT THEOREM.

When the Born approximation holds equation (1) becomes

$$f = 2W\epsilon\epsilon^*/(\Delta P)^2 \quad (2)$$

where

$$\epsilon = \langle \psi_2 | \sum_j Z_j e^{i\Delta P \cdot \tilde{r}_j} - \sum_s e^{i\Delta P \cdot \tilde{r}_s} | \psi_1 \rangle \quad (3)$$

In equation (3) $\tilde{r}_j$ is a position vector to the j th nucleus of atomic number Z_j and $\tilde{r}_s$ is a position vector to the s th target electron. ψ_1, ψ_2 are eigenfunctions of the target (atom or molecule) in the initial and final states respectively and the integration in the matrix element extends over the target coordinates (including spin) in center-of-mass coordinates. As $\Delta P \rightarrow 0$, f approaches f_0 where

$$f_0 = 2W\epsilon_1\epsilon_1^* \quad (4)$$

$$\epsilon_1 = i\langle \psi_2 | \sum_j Z_j \tilde{n} \cdot \tilde{r}_j - \sum_s \tilde{n} \cdot \tilde{r}_s | \psi_1 \rangle \quad (5)$$

and $\tilde{n}$ is a unit vector parallel to ΔP . The quantity $\epsilon_1\epsilon_1^*$, is the square of the matrix element of the component of the electric dipole parallel to the momentum change vector, and f_0 is the optical oscillator strength. It was shown by Lassettre, Skerbele and Dillon [J. Chem. Phys. 50, 1829 (1969)] that when f is defined by equation 1 then

$$\lim_{\Delta P \rightarrow 0} f = f_0 = 2W\epsilon_1\epsilon_1^* \quad (6)$$

regardless of whether the Born approximation holds. Hence, optical oscillator strengths can be obtained by extrapolating, to $\Delta P=0$, generalized oscillator strengths determined at moderate kinetic energies. The minimum momentum change attainable by experiment is greater at low kinetic energy of incidence than at high energy. As a practical matter the kinetic energy must be high enough so that the extrapolation to $\Delta P=0$ is not too long. Examples are given later. (See Section 4). Previous to 1969, comparison of optical oscillator strengths obtained by optical methods (e.g. radiation absorption) with the limiting value of the generalized oscillator strength at $\Delta P=0$ was considered a test of the Born approximation. Once the limit theorem was discovered, however, it became evident that the Born approximation had no relevance in such comparisons. Discrepancies between limiting oscillator strengths and optical oscillator strengths must then be due to experimental error or to error in the deduction of optical oscillator strengths from other data (e.g. life times). Hence, almost exactly coinciding with the beginning of the current program in 1970 a drastic change took place in the interpretation of discrepancies between optical and limiting oscillator strengths. Two major discrepancies were outstanding at the time. The first was a 25% disagreement between the values of $n-1$ (n the refractive index) observed for N_2 , O_2 and H_2O and the values of $n-1$ calculated from the dispersion formula using limiting oscillator strengths obtained from generalized oscillator strengths determined at Ohio State University prior to 1960. The second discrepancy existed between oscillator strengths obtained for the fourth positive bands of CO by electron impact and the oscillator strength calculated from lifetime

measurements. The two differed by a factor of two. It was important to resolve these discrepancies for the following reason. The fact that the limit of the generalized oscillator strength (at $\Delta P=0$) is equal to the optical oscillator strength means that the limiting electron impact spectrum is identical with the radiation absorption spectrum transition by transition for every substance. Thus a natural law of great generality is implied and hence every apparent discrepancy must be studied in detail and resolved. This has been done (see Section 4) and the discrepancies have been resolved. In the process some new general principles have been discovered.

It is of interest to note that the limit theorem described above has been confirmed in a different way by the theoretical studies of Winifred Huo for both direct [J. Chem. Phys. 57, 4800 (1972)] and exchange [J. Chem. Phys. 60, 3544 (1974)] scattering.

3. TECHNIQUE OF COLLISION CROSS SECTION MEASUREMENT.

As noted in the introduction our method for collision cross section determination involves two instruments, one for the determination of absolute elastic collision cross sections (developed by J. P. Bromberg) and the second a high-resolution device producing spectra in which the ratio of peak areas is the ratio of collision cross sections. The high-resolution spectrometer is described in a paper by Lassettre et. al [J. Chem. Phys. 48, 5066 (1968)]. It has been used to obtain electron impact spectra at kinetic energies of incidence from 35 to 500 eV and has been used for collision cross section measurements most often in the kinetic energy range 300-500 eV although recently some determinations have been done at kinetic energies as low as 50 eV. That version of this instrument which is currently in use has been described in review No. 3 listed in the introduction (Section 1). A cross section drawing is shown on page 875 of that review. After scattering, the spectrum is scanned by keeping the velocity analyzer fixed (i.e. fixed voltages applied to the electrodes) and electrons are re-accelerated with an electrostatic lens system. The lens employed is shown on page 879 of review No. 3. During the present research project two important changes in the spectrometer were introduced. First, an additional bellows (shown in the figures on pages 875 and 879 of the above review) has been introduced which permits accurate measurement of beam current (i.e. the total electron current entering the collision chamber) at each scattering angle. Second, data acquisition has been expedited and automated by introduction of a minicomputer which automatically scans a portion of a spectrum and also changes scattering angle. It must be emphasized, however, that collision cross section measurement is not a

routine matter. Every transition is different and must be re-studied in detail if accurate measurements are to be made. We have made numerous efforts to speed up collision cross section determinations but all such efforts have merely resulted in the collection of inferior data which create problems instead of resolving them. Three types of determinations have been investigated and are briefly described below.

3.1 Cross Sections as a Function of Angle.

We illustrate the technique by means of a determination on the transition $a''^1\Sigma_g^+ \leftarrow X^1\Sigma_g^+$ in nitrogen. The excitation energy is 12.25 eV and the kinetic energy of incidence is 400 eV. Elastic cross sections have been determined by Bromberg [J. Chem. Phys. 50, 3906 (1969)] and are shown, at 400 eV, in column two of Table 1 under the heading σ_e . These values are accurate to 3%. As the first step in an inelastic cross section determination the high-resolution spectrometer is focussed on the elastic peak and the peak current I_e is determined as a function of scattering angle θ . Over the angle range of Table 1 the collision geometry is such that $I_e \sin\theta$ should be proportional to the elastic cross section, σ_e , of Bromberg. If this is not true, a situation quite often encountered in the first trial on a new transition, the reason must be found and corrected. If accurate proportionality is obtained then the proportionality factor needed to best fit Bromberg's data is determined and the elastic cross section, σ_e' , is obtained. The ratio of this cross section to Bromberg's value, σ_e , must be unity to within experimental error (3%). The comparison is made in column three of Table 1. By fixing on the inelastic peak to be studied the peak scattered current I_i can be determined and,

in the same run, the current I_e for elastic scattering. The relevant quantity is the ratio I_i/I_e which is shown in column 4 of Table 1. Scattered currents are determined at both positive and negative angles and the scattering curves must be accurately symmetrical and the symmetry lines must be the same for elastic and inelastic scattering and must coincide with the mechanically defined direction of incidence. If this is not the case, then the reason must be found and corrected. We have now found the ratio of peak currents but we need the ratio of peak areas. It is found experimentally that the ratio b of peak area to peak height is independent of scattering angle for a wide variety of transitions. Hence we can concentrate on the peak currents at first and determine the b 's later. The inelastic peaks are found to be broader than the elastic, due to unresolved rotational levels. The ratio of the area to height, b_i , for an inelastic peak to that b_e for the elastic peak is 1.07 in the example of Table 1. The inelastic cross section σ_i can now be calculated and is shown in column 5. Using equation 1 the generalized oscillator strength can be calculated and is shown in column 6. The square of the momentum change, $(\Delta P)^2$ is shown in column 7. Note that small scattering angles are employed (see Table 1). This is done because we wish to test the limit theorem. Hence we must determine f_i at the smallest possible values of $(\Delta P)^2$ so that the extrapolation to $(\Delta P)^2=0$ is short. The extrapolation is discussed in Section 4.1. The conclusions from these measurements are also discussed there.

3.2 Forward Scattering.

For the determination of optical oscillator strengths it is frequently

Table I. Measurement of Absolute Inelastic Cross Sections and Generalized Oscillator Strengths^a with a $^1\Sigma_g^+ \leftarrow X^1\Sigma_g^+$ in N_2

θ	σ_e	σ_e'/σ_e	I_1/I_0	σ_1	f_1	$(\Delta P)^2$
2.0	72.00	0.971	0.00659	0.507	0.0049	0.042
2.5	65.61	0.999	0.00634	0.444	0.0063	0.062
3.0	61.34	0.986	0.00588	0.385	0.0076	0.086
3.5	55.17	1.004	0.00542	0.319	0.0084	0.115
4.0	51.40	0.998	0.00511	0.280	0.0095	0.148
5.0	43.60	1.000	0.00404	0.188	0.0098	0.227
6.0	36.71	0.998	0.00309	0.121	0.0090	0.324
7.0	30.87	1.008	—	—	—	—
8.0	26.06	1.005	—	—	—	—
9.0	21.78	0.997	—	—	—	—
10.0	18.05	1.032	—	—	—	—

^aCross sections and momentum changes ΔP are in atomic units and $E = 400$ eV.

possible to use electron impact spectra obtained in forward scattering, $\theta=0^\circ$. For electric dipole allowed transitions the Born approximation is accurate at small momentum changes and this provides the following relation (valid at small angles) for the angle dependence of the cross section

$$\sigma = \frac{4\bar{E}f_o/W^3}{1+(\theta/\alpha)^2} \quad (7)$$

where f_o is the optical oscillator strength, $\bar{E}$ is the mean kinetic energy of the colliding electron before and after scattering, W is the excitation energy and

$$\alpha = W/2\bar{E}. \quad (8)$$

In a typical case where $W = 10$ eV and $\bar{E} = 500$ eV we find from (8) that $\alpha = 0.01$ radian. In forward scattering with typical spectrometers (including that used in the present research) the uncertainty in scattering angle is ~ 0.02 radians. Since the scattered current is proportional to the mean cross section $\bar{\sigma}$, averaged over the range of angles allowed by the instrument when the nominal angle is $\theta=0^\circ$, it follows that a correction factor must be employed to convert the observed scattered current back to cross section at $\theta=0^\circ$. The mean cross section is

$$\bar{\sigma} = 4\bar{E}f_o\beta/W^3 \quad (9)$$

where

$$\beta = \langle 1/[1+(\theta/\alpha)^2] \rangle_{av}. \quad (10)$$

Fig. 1: Helium (top) and mercury (bottom) spectra. The figure illustrates how helium and mercury can be used as comparison spectra in the study of a third substance (illustrated here by carbon monoxide - the middle spectrum). Note that most of the carbon monoxide spectrum occurs at energy losses less than 19 eV and hence there is no interference from helium.

For a spectrometer (like that employed in the present research) which contains slits whose lengths are much greater than the width the following formula is obtained for β when electrons are scattered from the collision chamber center and the incident beam is perfectly collimated

$$\beta = (\alpha/\eta) \tan^{-1}(\eta/\alpha) \quad (11)$$

where η is the uncertainty in scattering angle (determined by slit length and electrostatic lens magnification). For an apparatus employing pinholes like that used by Huebner et. al. [J. Chem. Phys. 59 5434 (1973)] β is given by the formula

$$\beta = (\alpha/\theta_0)^2 \ln[1+(\theta_0/\alpha)^2] \quad (12)$$

where θ_0 is the apex angle of the cone into which scattering takes place.

It seemed advisable to determine η of eq. 11 experimentally and this was done, for the spectrometer employed in the present research, by studying mixtures of He-CO and Hg-CO. The electron impact spectra of He, CO, and Hg are shown in Figure 1. Optical oscillator strengths for the following three transitions

have been determined by extrapolating generalized oscillator strengths to $\Delta P=0$ for the last two and there is a reliable calculated value (confirmed

by experiment) for the first. The respective values are $f_o = 0.276, 0.0429, 0.0285$ obtained by Schiff and Pekeris [Phys. Rev. 134, A 638, (1964)], Lassettre and Skerbele [J. Chem. Phys. 54, 1597 (1971)] and Skerbele and Lassettre [J. Chem. Phys. 56, 845 (1972)]. To determine η Harshbarger and Lassettre [J. Chem. Phys. 58, 1505 (1973)] prepared mixtures of Helium and CO of known composition (determined with a capacitance manometer by adding first one gas then a second to the collision cell) and measured the relative intensities of the two transitions shown in (13). This determines $\bar{\sigma}_{\text{He}}/\bar{\sigma}_{\text{CO}}$. Then using (8) and (11) the value of η can be calculated since $\bar{E}$, f_o , and W are known for each transition. Using six He-CO mixtures and 18 He-Hg mixtures the average value of η was found to be $1.15^\circ \pm 0.15\%$ or $\eta = 0.020 \pm 0.002$ radian.

3.3 Comparison Gases.

Fig. 1 also illustrates how helium gas can be used as a comparison gas in the determination of collision cross sections. Since the first excited state of helium exceeds 19 eV and since the discrete spectra of many molecules occur at excitation energies well below 19 eV (see CO spectrum of Fig. 1 as an example), then the helium spectrum does not interfere with that of the second gas. It follows that by mixing helium with another gas at known partial pressure and determining the composite spectrum we can determine the ratio of cross sections for the second gas to that for some prominent transition in helium, e.g. $2^1P \leftarrow 1^1S$. If the cross section for the helium transition is known then cross sections for transitions in the second gas can be calculated. Although this could be applied at any angle it is especially simple at zero angle. The reason

is that, according to the limit theorem, the generalized oscillator strength f approaches the optical oscillator strength f_0 as $\Delta p \rightarrow 0$. At moderate kinetic energies the momentum change is so small at $\theta=0^\circ$ that f differs negligibly from f_0 and hence f_0 can be used for comparison purposes for an allowed transition like that to 2^1P . Since f_0 for that transition is known to be 0.276, with high accuracy, helium is an ideal comparison gas. Harshbarger and Lassette applied this to CH_4 and CF_4 [J. Chem. Phys. 58, 1505 (1973)]. The oscillator strength, integrated over the excitation energy range 8.55 to 10.95 eV, was found to be 0.277 ± 0.035 . Electrons of 500 eV kinetic energy were employed. Huebner, Fergurson, Celotta, and Mielczarck determined this same oscillator strength, using the spectrometer developed at the National Bureau of Standards, and obtained 0.290 for the oscillator strength. (Preprint obtained from Dr. Huebner.) Their kinetic energy of incidence was 100 eV and they normalized their spectrum to an optical value (determined by radiation absorption) at one point in the continuum. The agreement is, of course, highly satisfactory. Oscillator strengths for CF_4 were also obtained by Harshburger and Lassette.

Obviously, the forward scattering spectrum can be successfully used to obtain optical oscillator strengths by comparison with helium. Accurate partial pressure determinations are essential. These can be done with a good pressure gauge (e.g. a capacitance manometer) if some means can be found for insuring that the partial pressure of the first gas remains constant as the second gas is added. If e.g. we are preparing a mixture of CO and He the electron spectrometer could be fixed on a CO peak of low excitation energy where there is no helium scattering (see Fig. 1). As helium is added there will be no change in count rate if the

CO partial pressure is constant. Meyer and Lassettre [J. Chem. Phys. 54, 1608 (1971)] showed that no change in CO count rate took place under these conditions. The procedure can be applied to any gas.

Helium can also be used as a comparison gas at any angle since cross sections are now known as a function of angle for initial electron kinetic energies from 200 eV to 700 eV [M. A. Dillon and E. N. Lassettre, J. Chem. Phys. 62, 2373 (1975)]. At scattering angles greater than 2° electron impact spectra are produced, for a single substance, in which the ratio of peak areas is equal to the ratio of collision cross sections. No correction factors like β of equations (10) or (11) are needed. When gas mixtures are used, like CO and helium, it is possible to separate the contributions of CO and helium because a helium peak like that of 21.22 eV excitation energy is superimposed on a CO continuum (see Fig. 1) which can be easily subtracted to give only the helium contribution. A CO peak, like $v' = 2$ of fourth positive, occurs in a region free of helium scattering, and hence the CO contribution is obtained directly. If the helium and CO peak areas are divided by the respective partial pressures then the area ratio is the ratio of collision cross sections. This method has not been applied to CO, because the existence of accurate elastic cross section measurements makes it unnecessary. However, in Section 8 a cross section determination on benzene is described where a comparison gas is essential since no elastic cross sections are available. In some cases Hg is also useful for comparison purposes (see Section 8).

4. GENERALIZED OSCILLATOR STRENGTHS. SINGLET-SINGLET TRANSITIONS.

The techniques described in Section 3 have been used in the investigation of generalized oscillator strengths for several transitions which are important for understanding of the mechanism of collision. Several of these are discussed in the remainder of this section.

4.1 Deviations from the Born Approximation at Small Momentum Changes. Selection Rules.

We once thought that the Born approximation would hold at kinetic energies of a few hundred volts but we soon discovered, when accurate cross section determinations (at fairly high resolution) became possible, that deviations were often encountered. At small momentum changes these deviations follow well defined rules. This was first encountered in the investigation of two transitions in nitrogen $a''^1\Sigma_g^+ \rightarrow X^1\Sigma_g^+$ and $a''^1\Pi_g \rightarrow X^1\Sigma_g^+$. The generalized oscillator strengths are shown in Fig. 2. [A. Skerbele and E. N. Lassettre, J. Chem. Phys. 53, 2806 (1970)]. Both transitions are forbidden in the sense that the matrix element of electric dipole moment vanishes. (We refer to such transitions as electric-dipole-forbidden). If the Born approximation holds it is known that f 's determined as a function of $(\Delta P)^2$ at different kinetic energies of incidence all lie on a common curve. The fact that all points lie on a common curve implies that the Born approximation is holding but this has not been rigorously established. Inspection of Fig. 2 shows that for one transition the Born approximation certainly does not hold but for the second it may hold. The Born approximation definitely fails for that transition for which the term symbol in the ground state is the same as that in the excited state. Since the term

Fig. 2. Generalized oscillator strengths f versus $(\Delta P)^2$ for two electric dipole forbidden transitions in N_2 , $a^1\Pi_g \leftarrow X^1\Sigma_g^+$, and $a^1\Sigma_g^+ \leftarrow X^1\Sigma_g^+$. The experimental points for the $a^1\Sigma_g^+ \leftarrow X^1\Sigma_g^+$ transition separate with E as K^2 increases, indicating breakdown of the Born approximation. Note, $\lim f = 0$ as $(\Delta P)^2 \rightarrow 0$. Values are 300 eV ($\circ$), 400 eV (Δ), and 500 eV ($\square$).

symbols designate irreducible representations of the symmetry group of the scatterer this strongly suggests that the terms in the collision amplitude which represent deviations from the Born approximation are proportional, at small momentum changes, to the matrix element of an operator which is invariant under all operations of the symmetry group. A theoretical study of this point was undertaken by Lassettre [J. Chem. Phys. 53, 3801 (1970)] who obtained an invariant operator as the first term of an operator expansion and gave plausible arguments to show that higher terms in the series were small. Winifred Huo [J. Chem. Phys. 56, 3468 (1972)] in a later research, supported by AFOSR, also showed (by an entirely different argument) that large deviations from the Born approximation are expected when term symbols in ground and excited states are the same.

As a further test of this hypothesis two transitions in CO were studied. The first, $A^1\Pi \leftarrow X^1\Sigma^+$, is one for which the term symbol changes on excitation and the Born approximation seems to hold (see Fig. 3). [E. N. Lassettre and A. Skerbele, J. Chem. Phys. 54, 1597 (1971)]. The second, $B^1\Sigma^+ \leftarrow X^1\Sigma^+$, is one in which the term symbol is the same in ground and excited states and the Born approximations clearly does not hold (see Fig. 4). [A. Skerbele and E. N. Lassettre, J. Chem. Phys. 55, 424 (1971)]. These results confirm the existence of a selection rule.

Note in Fig. 4 the abrupt upward turn in f at small values of $(\Delta P)^2$. (See Section 8 for another example.) This begins at such small scattering angles that the f 's are not quantitatively reliable but it is believed that the general trend is correct. This behavior indicates something quite exceptional about the transition. That conclusion is re-inforced by the observation [K. N. Klump and E. N. Lassettre, J. Chem. Phys. 60, 4830 (1974)] that the vibrational peaks $V'=0$ and $V'=1$ associated with the transition $B^1\Sigma^+ \leftarrow X^1\Sigma^+$ change radically in relative intensity with

Fig. 3. Generalized oscillator strength f as a function of $(\Delta P)^2$ for the $A^1\Pi \leftarrow X^1\Sigma^+$ transition in CO with $v' = 2$ at 300 eV ($\circ$), 400 eV (Δ), and 500 eV ($\square$).

Fig. 4. Generalized oscillator strength f versus the square of momentum change $(\Delta P)^2$ for the $B^1\Sigma^+ \leftarrow X^1\Sigma^+$ transition in carbon monoxide with $v' = 0$. Incident electron energy: $\square$, 300 eV; Δ , 400 eV; $\circ$, 500 eV. The inset shows extension of the generalized oscillator strength curves to zero scattering angle. Optical oscillator strengths measured by J. M. F. Aarts and F. J. de Heer [J. Chem. Phys. 52, 5354 (1970)] and by J. E. Hesser [J. Chem. Phys. 48, 2518 (1968)] are also shown at $K^2 = 0$. Measurements at angles less than 2° shown by filled in symbols. Open symbols designate measurements at 2° and greater.

change in scattering angle. This is illustrated by Fig. 5 which shows electron impact spectra at $\theta=0^\circ$ and $\theta=15^\circ$. The drastic change in relative intensity of the two vibrational peaks is obvious. This has never been observed with any other of the scores of transitions studied previously. The normal behavior is that shown by the fourth positive bands $A^1\Pi-X^1\Sigma^+$, in Fig. 5, i.e. no change in relative intensity with change in angle. In the paper referred to above, a breakdown of the Born Oppenheimer approximation (separability of electronic and nuclear motion) is suggested as the reason.

Another example of a transition in which the term symbol changes on excitation is the $6^1P_1 \leftarrow 6^1S_0$ transition in mercury. The generalized oscillator strengths were determined by Skerbele and Lassettre [J. Chem. Phys. 52, 2708 (1970)] at three different kinetic energies. All three sets of data lie on a common curve as expected. (See Fig. 6.) However, at larger momentum changes this ceases to hold. (See next section.)

If transitions which involve no change in term symbol do not satisfy the Born approximation then all elastic scattering must be included. For elastic scattering f of eq. 1 cannot be used since $W=0$. Hence we omit $2W$ and plot the quantity η defined by the equation

$$\eta = \frac{WP_1}{4P_2} (\Delta P)^2 \sigma. \quad (14)$$

We have not studied elastic scattering on our ERDA supported project but J. P. Bromberg has determined such cross sections on a program supported by AFOSR (Principal Investigator: E. N. Lassettre). Determinations of η at three different kinetic energies are shown in Fig. 7. Obviously, the Born approximation does not hold (as expected) since three different

FIG. 5. Electron impact spectra of carbon monoxide. Incident electron energy is 300 eV.

FIG. 6. Generalized oscillator strength vs $(\Delta P)^2$ for the $6^1S_0 \rightarrow 6^1P_1$ transition in mercury. Initial kinetic energies are: $\bigcirc$, 300 eV; $\triangle$, 400 eV; $\square$, 500 eV. The solid curve is a least-squares line (see text) and the experimental points do not depart from the line by more than experimental error. (See text and also Table II for experimental uncertainties.)

Fig. 7. Plot of η versus $(\Delta P)^2$ for elastic scattering by carbon monoxide calculated from the elastic cross section data of J. P. Bromberg [J. Chem. Phys. 51, 4117 (1969)] at values of 300 eV ($\circ$), 400 eV (Δ), and 500 eV ($\square$):

curves are obtained.

In general, at small momentum changes the Born approximation tends to hold best when the term symbol for the target system changes, on collision. When the term symbol is the same in ground and excited states large deviations from the Born approximation are observed even at small momentum changes.

4.2 Deviation from the Born Approximation at Large Momentum Changes.

In the preceding section it was pointed out that graphs of f vs $(\Delta P)^2$ determined at three different kinetic energies coincide to form a single curve thus confirming the hypothesis that deviations from the Born approximation are minimal for transitions in which the term symbols change on excitation. Shortly after this research was completed Hanne and Kessler [Phys. Rev. A 5, 2457 (1972)] extended these measurements to much larger scattering angles and found that f 's obtained at different kinetic energies of incidence lay on distinctly different curves and hence the Born approximation could not hold at large momentum changes. They normalized their results to our data at small momentum changes and disagreed with one of our determinations at large momentum change. Hence we repeated our experiments, extended them to larger angles, and studied several additional transitions in mercury [Skerbele and Lassetre, J. Chem. Phys. 56, 845 (1972)]. Results for the $6^1P_1 \rightarrow 6^1S_0$ transition are shown in Fig. 8. The data are in essential agreement with the results of Hanne and Kessler and show that the Born approximation is not holding at large momentum changes. The situation observed for mercury is very similar to that predicted theoretically for Neon and Argon by Sawada, Purcell and

Figure 8

Green [Phys. Rev. A4, 193 (1972)]. They employed distorted wave calculations (based on model potentials) to obtain more accurate generalized oscillator strengths at low electron impact energies, and found that the Born approximation remains valid for small values of momentum change, but fails in the vicinity of zeros even at relatively high kinetic energies. Therefore, it is of great importance to collect quantitative data on those transitions where minima in generalized oscillator strengths are likely to occur.

Winifred Huo, in a research supported by AFOSR, considered the behavior of the collision amplitude for direct scattering in very general terms. She concluded that large deviations from the Born approximation will be encountered for any substance at high kinetic energy if the momentum change becomes large enough. [W. M. Huo, J. Chem. Phys. 57, 4800 (1972)]. She also showed that the first Born approximation is not approached if the kinetic energy is increased at fixed scattering angle but it is approached if the kinetic energy is increased at fixed momentum change. The separation of curves at different energies as the momentum change increases (as in Fig. 8 for mercury) is the normal behavior although it is probably more exaggerated for an atom of high atomic number like mercury than for an atom of low atomic number. However, Dillon and Lassettre [J. Chem. Phys. 62, 2373 (1975)], in a research supported by AFOSR, showed that large separation of f curves obtained at different kinetic energies also occurred for helium thus extending the prior research of Opal and Beaty [J. Phys. B 5, 627 (1972)] which had already shown that large deviations from the Born approximation occurred at large scattering angles. This behavior is apparently general.

4.3 Oscillator Strengths from Lifetimes, Fourth Positive Bands of CO.

The generalized oscillator strength in CO for the transition $A^1\Pi(v'=2) \leftarrow X^1\Sigma^+(v''=0)$ is shown in Fig. 3. By using measured relative intensities within the fourth positive bands the values of f for excitation to the various vibrational levels of the excited state can be obtained. When summed over all vibrational levels in the upper state the value 0.195 is obtained for f_0 . From lifetime measurements Hesser [J. Chem. Phys. 48, 2518 (1968)] obtained 0.094 for the same oscillator strength. In order to calculate an (absorption) oscillator strength from a lifetime the dependence of electronic transition moment must be known. This dependence was neglected by Hesser. Mumma, Stone, and Zipf [J. Chem. Phys. 54, 2627 (1971)] showed that the major part of the discrepancy was eliminated when the correct dependence of transition moment on internuclear distance is taken into account. For further discussion and reference see Review No. 3 of the Introduction, pages 915-920, and Review No. 4, pages 46-47. In the case of atoms the calculation of oscillator strengths from lifetimes is straight forward but not in the case of molecules.

4.4 Differential Versus Total Cross-Sections.

It has frequently been stated that the Born approximation holds for electron-atom (or molecule) collisions at kinetic energies of incidence above 100 eV. This holds true only for total (not differential) collision cross sections. This result was obtained in a theoretical study by Sawada, Purcell and Green [Phys. Rev. A4, 193 (1972)] of the rare gases Neon, Argon and Krypton. Similar results were obtained for helium by Hidalgo

and Geltman [J. Phys. B5, 617 (1972)]. This point has not been experimentally tested in the present research program supported by AEC/ERDA. However in a companion program, directed by E. N. Lassettre and supported (until December 31, 1974) by AFSOR, such tests have been done on two transitions in helium [E. N. Lassettre and M. A. Dillon J. Chem. Phys. 62, 2373 (1975)]. The integrated cross sections from 200 - 700 eV differed from the Born approximation (with a small correction for exchange) by less than five percent for both the $2^1P \leftarrow 1^1S$ and $2^1S \leftarrow 1^1S$ transitions despite the fact that the differential cross sections at large momentum change differed from the Born approximation by more than an order of magnitude in several cases.

4.5 Refractive Index Calculations.

Previous to the beginning of the present (ERDA supported) research, generalized oscillator strengths for O_2 and N_2 [S. M. Silverman and E. N. Lassettre J. Chem. Phys. 40, 2922 (1964); J. Chem. Phys. 42, 3420 (1965)] were determined at low resolution (~ 0.4 eV) throughout the spectra to 70 eV excitation energy. Extrapolated oscillator strengths at zero momentum change ($\Delta P=0$) were also obtained by extrapolation. Although resolution was not high, the extrapolated oscillator strengths could be used in the dispersion formula to calculate $n-1$ (n the refractive index) and compare it with experiment. The experimental value is 25% lower than the calculated. Low resolution is not a handicap where summation over an entire spectrum is involved and hence cannot account for the error. When the experiments were first done this error was attributed to a failure of the Born approximation. When, however, the

limit theorem was discovered in 1969 (see Section 2) it became apparent that an experimental error was involved. When the new experimental techniques, described in Section 3, were fully developed, new determinations on N_2 and CO were undertaken by Lassettre and Skerbele (see Section 4.1) and compared with these earlier determinations. The ratio of the new values to the old was 0.754 ± 0.027 . When this factor is applied to the earlier cross section determinations on N_2 and O_2 the refractive indices are brought into accurate agreement with experiment. There was also an unpublished investigation of H_2O (by Lassettre and White) available at the time. The same correction factor, 0.754, also brought $n-1$ into agreement for H_2O . Now for all three substances the maximum difference between calculated and experimental values of $n-1$ is 3%. See page 914 of Review No. 3 listed in the introduction. The oscillator strengths for H_2O (properly corrected) have now been published [E. N. Lassettre and E. R. White, J. Chem. Phys. 60, 2460 (1974)]. The discrepancy is probably due to a streaming error in the McLeod gauge used to calibrate the Knudsen gauge actually employed. The existence of a streaming error was first pointed out by Ishii and Nakayama [Trans. 8th Nat'l. Vacuum Symp. 1, 319 (1962)].

Electron impact spectra for all the fluorine substituted methanes have been determined [Harshbarger, Robin and Lassettre, J. Electron Spectrosc., 1, 319 (1973)]. Molecular orbital assignments have been made for all transitions using methods developed by Robin.

4.6 Oscillator Strengths for CO_2

Lassettre and Shiloff [J. Chem. Phys. 42, 569 (1965)] determined collision cross sections through the spectrum of CO_2 somewhat similar to those on N_2 , O_2 and H_2O mentioned in the first paragraph of subsection 4.5.

Fig. 9

It was not certain that the same correction factor (0.75) as for N_2 , O_2 and H_2O applies to these data. Hence two transitions in CO_2 have been reinvestigated using the more advanced techniques described in Section 3. The generalized oscillator strengths are shown as a function of $(\Delta P)^2$ in Figure 9. Initial kinetic energies are shown in the Figure. The solid lines in Figure 9 have been calculated theoretically by McCurdy and McKoy [J. Chem. Phys. 61, 2820 (1974)] using the Equations of Motion method. Excitation energies were also calculated and the allowed transition of lowest excitation energy is $1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$. The allowed transition of lowest excitation energy in the observed electron impact spectrum is that at 11.04 eV. Therefore the calculated f curve of McCurdy and McKoy presumably corresponds to this transition. Theory and experiment are compared in the upper curve of Figure 9. The next higher excitation energy for an allowed transition is that for $1\Pi_u \leftarrow X^1\Sigma_g^+$. Hence the calculated f curve for this transition is shown in the lower part of Figure 9. Theory and experiment are in poor agreement in both cases. The experimental data have been thoroughly checked and are believed to be reliable. Even for a substance as simple as helium calculated cross sections are not in good agreement with experiment and hence precise agreement cannot be expected for a substance as complicated as CO_2 . In one respect, mentioned below, the discrepancy is especially serious.

The limiting value of the generalized oscillator strength at $(\Delta P)^2 = 0$ is the optical oscillator strength. The data of Figure 9 have been extrapolated using the following formula to fit the data.

$$f = \frac{1}{(1+x^2)^6} \sum_{n=0}^N f_n u^n \quad (15)$$

where $x = \Delta P/\alpha$, $\alpha = \sqrt{2I} + \sqrt{2(I-W)}$, and

$$u = \frac{x^2}{1+x^2} \quad (16)$$

In these equations I is the ionization potential for removing the electron excited and W is the excitation energy. In extrapolating the data it is best to use only a few terms of (15) and employ only the f values when $(\Delta P)^2$ is small.

Using $N = 1$ and the data points below some maximum value of $(\Delta P)^2$ the results of Table 2 are obtained. The theoretical values of f_0 (McCurdy and McKoy) are in the wrong order in comparison with experiments. That the theory is grossly in error is obvious from Figure 10 which shows two electron impact spectra for CO_2 for electrons with initial kinetic energy 500 eV. From the spectrum at $\theta = 0^\circ$ it is obvious that the transition at 11.04 eV is much more intense than that at 11.38 eV. For transitions as close in excitation energy as the two under discussion the ratio of peak areas is the ratio of collision cross sections. Moreover, the generalized oscillator strength is nearly equal to the optical at $\theta = 0^\circ$ for 500 volt electrons. Hence from the area ratio for several spectra at $\theta = 0^\circ$ (2.48) we can deduce the ratio of limiting f 's. We find 2.4 as the ratio. The ratio of observed f_0 's in Table 2 is 2.7, in fair agreement with that from zero angle spectra. The ratio of theoretical f_0 's, however, is 0.69 in gross disagreement with experiment.

Limiting f_0 's were determined by Meyer and Lassettre [J. Chem. Phys. 42, 3436 (1965)]. The value $f_0 = 0.167$ was found for the 11.04 eV transition. The pressure gauge was subject to a streaming error like that for N_2 , O_2 , H_2O mentioned in Section 4.5 above. The ratio of f_0 's $.12/.167 \approx 0.72$

Figure 10

Electron Impact Spectra of CO_2

Table 2. Limiting values of f for two transitions in CO_2 .

Transition	Data ^a Points	W		$\frac{f_0}{\text{Theory}}$
		This research	This research ^b	
$1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$	11	11.04 eV	$0.12 \pm .01$	.116
$1\pi_u \leftarrow X^1\Sigma_g^+$	11	11.38 eV	$0.004 \pm .008$	.168

a) All values of f with $(\Delta P)^2 < 0.5$ are used.

b) Uncertainties are twice the standard deviations obtained from the formulas of regression analysis. They measure the reliability of an extrapolation performed using the same number of data points taken at the values of $(\Delta P)^2$ and the same initial electron energies and fitted with the same formula. The uncertainties are not reliable measures of absolute error since systematic departures from the extrapolation function are possible at values of $(\Delta P)^2$ below the the last measured point. The extrapolation is a long one and the error uncertainties must be viewed skeptically in the present case.

is almost the same as that found for N_2 , O_2 and H_2O . In view of the substantial possible error in the above ratio it seems reasonable to apply the same factor, 0.75, to the data of Lassetre and Shiloff, mentioned at the beginning of this subsection, as that used in correcting the data on N_2 , O_2 and H_2O .

Note in Figure 10 the broad region between 8 and 10 eV which changes shape with angle. The interpretation of this spectral region is discussed in detail in Review No. 4 listed in Section 1. Further detail is given in item 24 of the publication list.

5. EXCITATION OF SINGLET-TRIPLET CROSS SECTIONS AT HIGH KINETIC ENERGY

5.1 Singlet-Triplet Transitions in Helium. A Selection Rule.

The transition $1^1S \rightarrow 2^3S$ in helium has been studied in the present (ERDA supported) program at 500 eV over a range of scattering angles [A. Skerbele, W. R. Harshbarger, and E. N. Lassettre, J. Chem. Phys. 58, 4285 (1973)]. At $\theta = 0^\circ$ the ratio of the cross section to that for the $1^1S \rightarrow 2^1S$ transition is 0.01 (see Table 2). Using Ochkur's approximation [V. I. Ochkur, Soviet Phys. JETP, 18, 503 (1964)], and some additional reasonable approximations, the ratio of the cross section, σ_T , for the first of the above transitions to that, σ_S , for the second is

$$\sigma_T/\sigma_S \approx 3(\Delta P/P_0)^4 \quad (17)$$

where ΔP is the momentum change and P_0 is the initial momentum, expressed in atomic units. At $\theta = 0^\circ$ and $E = 500$ eV, this relation gives $\sigma_T/\sigma_S = 5 \times 10^{-7}$ (see Table 3) which is grossly different from the observed value. An indication that σ_T was peaking in forward scattering is contained in the results of Vriens, Simpson and Mielczarek [Phys. Rev. 165, 7 (1968)] who studied the cross section to 225 eV kinetic energy but not at zero angle. Steelhammer and Lipsky [J. Chem. Phys. 53, 1445 (1970)] pointed out that the Ochkur approximation needed modification at low kinetic energies and they extended the expansion in inverse powers of k_0 to one additional term and obtained much better agreement with the data of Vriens, et. al. At 500 eV, however, their formulas give $\sigma_T/\sigma_S = 2 \times 10^{-5}$ which is still too small by a factor of 500 (see Table 2). Comparable results have been obtained (see Table 2) by Bonham [J. Chem. Phys. 57, 1604 (1972)].

TABLE 3

Cross Section Ratio at $\theta = 0^\circ$. $E = 500$ eV.

$\frac{\sigma_T}{\sigma_S}$	<u>Method</u>
0.01	Experiment
5×10^{-7}	Ochkur (Theory)
2×10^{-5}	Steelhammer-Lipsky (Theory)
5×10^{-5}	Bonham (Theory)

As the scattering angle increases, the ratio σ_T/σ_S decreases rapidly. (See Table 4.) Beyond $\theta = 3^\circ$ the triplet excitation is obscured by the background but it reappears again at larger angles. According to equation(14) the ratio should increase as θ increases and becomes equal to 0.01 (calculated) at $\theta = 14^\circ$. This should be detectable experimentally and the transition is found, under favorable conditions, at $\theta = 14^\circ$ with an intensity of 0.02 (experiment Table 3). Over the range 10° to 20° the ratio conforms to equation(17) with an error of about a factor of three. Observational errors are also large (see Table 3) but the transition is definitely observed and equation(17) gives the correct order of magnitude for the ratio.

At 300 eV, the situation is similar for the excitation of 2^3S but now excitation of the 2^3P state is also observed at 16° but not at 0° or 3° . This suggests a selection rule, similar to that discussed for singlet-singlet transitions in Section 4.1. In the case of singlet-triplet transitions, however, large deviations from the Born approximation (with exchange) are being observed at small angles for those transitions in which the orbital (spatial) term symbol is unchanged in excitation.

The above results were obtained (by Harshbarger, Skerbele, and Lassettre) using the high-resolution electron spectrometer referred to in Section 3. With this instrument the excitation of the 2^3S state was barely perceptible at a scattering angle of 15° and hence quantitative cross section measurements could not be done. However, a new electron spectrometer had been developed, on a project sponsored by AFOSR, for the study of ionization continue using coincidence counting techniques. Angular apertures in this instrument are high and energy resolution (although not maximal) is adequate for the study of the transition $2^3S \leftarrow 1^1S$ in helium.

TABLE 4
Cross Section Ratio. $E = 500$ eV.

θ	σ_T/σ_S	$3(\Delta P/P_0)^4$
0	$0.0096 \pm 25\%$	5×10^{-7}
0.5	0.0076	6.6×10^{-7}
1.0	0.0051	14×10^{-7}
1.5	0.0032	35×10^{-7}
2.0	0.0027	76×10^{-7}
.		
.		
.		
14°	$0.02 \pm .01$	0.010
16°	$0.03 \pm .01$	0.017

FIGURE 11
Differential collision cross section (in atomic units) as a function of $(\Delta P)^2$ for the transition $1^1S \rightarrow 2^3S$ in helium at various kinetic energies of incidence. Inset shows cross section at small momentum changes. X's represent points determined by Klump and Lassettre No. 17 of publication list.

Hence a cross section study is feasible and was undertaken by Dr. Michael A. Dillon. This investigation was still incomplete when the AFOSR Grant was terminated at the end of 1974. Hence Dr. Dillon was transferred to the present (ERDA supported) research project and the investigation was completed and published [M. A. Dillon, J. Chem. Phys. 63 2035 (1975)]. Collision cross sections, with incident electrons of kinetic energy 200, 300, 400, and 500 eV, are shown in Fig. 11. Note the high collision cross sections at small momentum changes. By comparing the observed cross section with that calculated from the first Born approximation with exchange, the applicability of first order theory can be assessed. The comparison is made in Fig. 12 for electrons of kinetic energy 200 eV. The upper curve is experimental and the lower, theoretical. Obviously, the first order theory is not even qualitatively correct when $\theta < 15^\circ$. At the larger angles, the trend of cross section with angle parallels the theoretical curve, approximately at least. However, a more detailed examination shows that even at large scattering angles the theory is inaccurate in detail. This is illustrated in Fig. 13, which shows cross section (on a log scale) vs. incident electron energy at a fixed momentum change squared of seven atomic units. The data are fitted by a straight line of slope $3/2$. First order theory, in the high energy (Ochkur-Bonham) limit, gives a slope of 2 which is clearly incorrect. Hence, the parallelism between first order theory and experiment indicated in Fig. 12 is shown to be only a rough approximation when closely examined. Further evidence is obtained from the total cross section computed by integrating the cross sections of Fig. 11 over angle. That cross section is shown in the lower curve of Fig. 14. First order theory would give a line of slope 3, but experiment fits a line of slope 2. The upper line is taken from the data of de Jongh and

Figure 12.

Differential collision cross section vs. θ for $1^1S + 2^3S$ transition in helium. Experimental cross section at 200 eV kinetic energy at top. Theoretical cross section (225 eV) at bottom.

FIGURE 13

$\text{Log}(|A|^{-2})$ vs. $\text{Log } E$ where A is collision amplitude and E the initial kinetic energy for $1^1\text{S} \rightarrow 2^3\text{S}$ transition in helium at $(\Delta P)^2 = 7$. Theoretical slope (Ochkur-Bonham) $n = 2$, observed $n = 3/2$.

FIGURE 14
 $\log \Omega^{-1}$ vs. $\log E$ for $1^1S + 2^3S$ (lower curve) in helium where Ω is the total collision and E is the initial kinetic energy. Lower curve from present research. Upper curve refers to $1^1S + 4^3S$ transition; taken from Van Rann, DeJongh, Van Eck and Heideman, *Physica* 53, 45 (1971).

Van Eck (obtained by an entirely different method) for the transition $1^1S \rightarrow 4^3S$. The same energy dependence is indicated for this transition again in disagreement with first order theory.

The measurements shown in Fig. 11 are the first to be done on a singlet-triplet transition at high kinetic energy. The new electron spectrometer has made such measurements possible for the first time. Obviously, there is no limiting high energy theory of any value for exchange scattering, although experiments show a simple dependence on energy.

It was mentioned above that the $2^3S \leftarrow 1^1S$ transition has a cross section which is highest at $\theta = 0^\circ$ while the $2^3P \leftarrow 1^1S$ transition is undetectable at $\theta = 0^\circ$ but is observed at larger angles. It was suggested by Skerbele, Harshbarger and Lassettre [J. Chem. Phys. 58, 4285 (1973)] that a selection rule was operating, namely that those transitions for which the orbital term symbol (like S in $2^3S \leftarrow 1^1S$) is the same in ground and excited states have abnormally high cross sections in forward scattering. In an investigation supported by AFOSR, Winifred M. Huo [J. Chem. Phys. 60, 3544 (1974)] has shown that at high kinetic energy a transition potential for exchange scattering exists whose Fourier transform gives the collision amplitude. Moreover, this transition potential behaves at large distances like $-\beta/2r^4$ where β is a quantity which vanishes unless the orbital term symbol is the same in ground and excited states. From an impact parameter viewpoint the cross section at small scattering angles is determined primarily by the behavior of the transition potential at large distances. It follows that the cross section is expected to have abnormally high values at $\theta = 0^\circ$ in agreement with experiment on the $2^3S \leftarrow 1^1S$ transition in helium. The inverse fourth power term in the transition potential arises from the second Born approximation with exchange.

Since the first Born approximation (with exchange) is negligible compared with the second Born approximation (with exchange) serious doubts about convergence will arise unless the second approximation can be shown to give the correct cross section. Huo calculated the cross section at 500 eV and obtained 0.0040 atomic units. In view of approximations in the theory this is considered adequate agreement with the experimental value 0.0026 ± 0.0006 . Huo's theory shows that the cross section for a singlet-triplet transition in any substance tends to be abnormally high at $\theta = 0^\circ$ if the term symbols in ground and excited states are the same.

Huo also showed that the collision cross section in forward scattering, as a function of kinetic energy of incidence, has a minimum at ~ 180 eV. An experimental study (on the present ERDA supported program) by Klump and Lassettre [J. Chem. Phys. 62, 1838 (1975)] has confirmed the existence of a minimum but at 225 eV. In the same research an additional singlet-triplet transition in CO with the same orbital term symbols in ground and excited states has been found. A third transition in N_2 has been known for some time. The selection rule described above is confirmed in all cases thus far studied and is on firm theoretical ground. Cross section determinations on the $E^3\Sigma_g^+ \leftarrow X^1\Sigma_g^+$ transition in N_2 , an example of an abnormal singlet-triplet transition, are discussed in the next section.

5.2 A Cross Section Study on the $E^3\Sigma_g^+ \leftarrow X^1\Sigma_g^+$ Transition in N_2

The singlet-triplet transition under consideration occurs at an energy loss of 11.87 eV. The transition $a''^1\Sigma_g^+ \leftarrow X^1\Sigma_g^+$ is the corresponding singlet-singlet transition and occurs at an energy loss of 12.26 eV. The behavior of these two transitions with change in scattering angle at two different kinetic energies of incidence, 100 eV and 200 eV are shown in Figures 15 and 16, respectively. The two transitions of interest are apparent at the extreme right of each figure. The transition at 11.87 eV is superimposed on other, less intense, transitions which appear as a "background" which must be subtracted off in cross section determinations. Designate the cross section for the singlet-triplet transition by σ_T , that for the singlet-singlet transition by σ_S , and the cross section for elastic scattering by σ_e . Then it is the usual procedure to first determine the ratio σ_T/σ_S . Then the ratio σ_S/σ_e is determined in cases where the elastic cross section is known. Then from the ratio σ_S/σ_e and the value of σ_e the value of σ_S can be obtained. σ_T is found from the ratio σ_T/σ_S .

A singlet-triplet transition for which the orbital term symbol is the same in ground and excited state has abnormally high cross section at small scattering angles and high kinetic energy. This, at least, is the hypothesis which is being experimentally tested. Obviously, high kinetic energy and small scattering angle must be employed in testing the hypothesis. The apparatus employed is that referred to in Section 3 above. [See J. Chem. Phys. 48, 5066 (1968)]. It is not the same spectrometer as that employed by Dillon in obtaining the cross section data of Figure 11. Because of large background corrections, referred to above, and the need for high angular apertures (large slits) precision is lower than normal in the study of other transitions.

FIG. 15 Electron energy loss spectra of N_2 . Energy of incident electrons is 100 eV. Scattering angle is (a) 10° , (b) 5° , (c) 0° .

FIG. 16 Electron energy loss spectra of N_2 . Energy of incident electrons is 200 eV.

Collision cross sections for the singlet-triplet transition are shown in Table 5. The large scatter at 300 eV is due to the weakness of the singlet-triplet transition relative to background. Despite the scatter in the data it is evident that at each kinetic energy, the cross section decreases steadily with increase in scattering angle. This is qualitatively similar to the behavior found by Dillon (see Figure 11) for the transition $2^3S \leftarrow 1^1S$ in helium over the same range of scattering angle. Hence, the abnormal behavior of the singlet-triplet transition in nitrogen is confirmed.

5.3 Singlet-Triplet Transitions. Conclusion.

There is a special class of singlet-triplet transitions for which the collision cross sections at high kinetic energy are highest at $\theta = 0^\circ$ and which, at this angle, greatly exceed the values expected (see equation 17) from the first Born approximation with exchange (the so-called Born-Oppenheimer approximation). These occur when the orbital term symbols in ground and excited states are the same. The experiments on the nitrogen singlet-triplet transition described above are in complete agreement with this hypothesis and the quantum theory of scattering provides a secure basis for the application of this principle to other systems which have not been experimentally studied. As noted above, these transitions constitute a special class. Only very recently, as the result of our research, has it been possible to formulate the above general principle which tells us when to expect such transitions.

The importance of this result can be appreciated by considering two important classes of biologically important substances, proteins and carbohydrates. Solutions of these substances rotate the plane of polarized light,

TABLE 5

N_2 : Cross-sections for $E^3 \Sigma_g^+ \leftarrow X^1 \Sigma_g^+$ Scattering Summary

θ (deg.) \ E_o (eV)	$\sigma_T \times 10^4$ (Atomic Units)		
	100	200	300
2	--		40.4 $\pm$ 16.5
3	--		20.7 $\pm$ 7.2
4	--	8.44 $\pm$ 1.37	7.08 $\pm$ 1.48
5	24.8 $\pm$ 3.2	6.375 $\pm$.977	5.59 $\pm$ 1.95
6	27.2 $\pm$ 6.7	4.736 $\pm$.589	2.69 $\pm$ 1.97
7	17.60 $\pm$ 3.50	3.819 $\pm$.504	2.61 $\pm$ 1.90
8	14.96 $\pm$ 1.37	2.442 $\pm$.407	--
9	12.78 $\pm$ 1.49	1.743 $\pm$.411	--
10	11.50 $\pm$ 1.46	1.181 $\pm$.287	--
12	7.59 $\pm$ 1.45	0.533 $\pm$.307	--
14	3.96 $\pm$.72	--	--

i.e., these substances are optically active. Such substances have no symmetry or, more precisely, their symmetry groups contain only one operator, the identity. Hence there is only one irreducible representation, the identical representation, to which all quantum states belong. Hence the term symbol for every state is the same and the orbital term symbol is the same in initial and final states for every transition. Thus the differential cross sections should be "abnormally" high in the forward direction in comparison to expectations based on the first Born approximation with exchange. In brief, the "abnormal" for simple systems, like atoms or diatomic molecules, becomes "normal" for complicated systems with no symmetry.

The existence of a comprehensive, simply stated, general principle (like that contained in the first paragraph of this section) has other uses as well. For example, the transition $E^3\Sigma_g^+ \leftarrow X^1\Sigma_g^+$ in nitrogen, which is discussed in Section 5.2, has been previously encountered. Meyer and Lassettre [J. Chem. Phys. 44, 2535 (1966)] observed the transition in forward scattering with electrons of initial kinetic energy 402.12 eV. It seemed so unexpected (on the basis of the Born-Oppenheimer theory of exchange scattering) to observe a singlet-triplet transition in forward scattering that we suggested that the excited state must be a singlet rather than a triplet. Of course, we now recognize that the transition is one for which the orbital term symbol is the same in ground and excited states. Hence it is expected that the singlet-triplet transition will be abnormally strong in forward scattering.

This principle has not been previously recognized because triplet states of the required type are usually surrounded and overlaid, by singlets so that the singlet-triplet transition is buried under more intense singlet-singlet transitions.

6. THEORETICAL STUDIES

Three theoretical studies are of interest. The first (Section 6.1) involved the development of a new series expansion for electrostatic potentials. [E. N. Lassettre, J. Chem. Phys. 57, 4357 (1972).] This contribution is essentially mathematical but is strongly collision related. The second research (Section 6.2) [E. N. Lassettre, J. Chem. Phys. 58, 1991 (1973)] shows that the Hartree-Fock equations in momentum space reduce to integral equations whose kernels are the collision amplitudes for the scattering of an additional electron by the atom or molecule to which the Hartree-Fock equations apply. Three, a study of momentum eigenfunctions is mentioned in Section 6.3.

6.1 Power Series Expansion of Collision Amplitudes. Electrostatic Potentials.

By means of a conformal transformation $t = K/\sqrt{K^2 + \alpha^2}$ (where, in physical applications, K is the momentum change of a colliding electron) the complex K plane is mapped onto the complex t plane. With cuts from $i\alpha$ to $i\infty$ and from $-i\alpha$ to $-i\infty$, the mapping is one to one. Let I be the ionization potential from a one-electron orbital ϕ_i and W the excitation potential from ϕ_i to ϕ_j . Then if $\alpha = \sqrt{2I} + \sqrt{2(I - W)}$ a region of the K plane, which contains (a) no singular point of the form factor $\epsilon = \int e^{iK \cdot r} \phi_i \phi_j^* (dr)$ and (b) the entire real axis of K , is mapped into the unit circle in the t plane. That portion of the K plane which is mapped into the unit circle in the t -plane is the shaded area of Fig. 17. The singular points of ϵ are at $K = \pm i\alpha$ and neither of these is in the shaded area.

if
Hence ϵ is expanded into a power series in t the series converges when $t < 1$

K Plane

Figure 17

and the region of convergence includes all real values of K . Moreover, the coefficients of the power series in t can be simply obtained from the coefficients of a series for ϵ in powers of K . This extends to the collision amplitude a result which had previously been obtained for the generalized oscillator strength [E. N. Lassettre, J. Chem. Phys. 43, 4479 (1965)]. The extension is non-trivial since the power series in K for ϵ contains both even and odd powers while that for oscillator strength contains only even powers of K .

A particular series expansion for ϵ , which takes account of the behavior of ϵ at both large and small K , is exploited to obtain a series expansion for an electrostatic potential function. This is possible because of the following equation, made familiar by the Born approximation,

$$\frac{1}{(2\pi)^{3/2}} \int e^{i\mathbf{K} \cdot \mathbf{r}} v_{ji}(\mathbf{r}) d\mathbf{r} = \sqrt{\frac{2}{\pi}} \frac{\epsilon}{K^2}$$

where

$$v_{ji} = \int \frac{\phi_i^* \phi_j}{|\mathbf{r} - \mathbf{r}_1|} d\mathbf{r}_1$$

Inverting the Fourier transform gives

$$v_{ji} = \frac{1}{2\pi^2} \int e^{-i\mathbf{K} \cdot \mathbf{r}} (\epsilon/K^2) d\mathbf{K}$$

and this provides the desired potential function when an appropriate series for ϵ is inserted into the integral on the right. A particular expansion,

which expresses the potential function in terms of a set of generalized moments, is obtained, discussed in detail, and illustrated with some simple examples. The details are described in Ref. No. 7 of the Publication List and will not be repeated here.

The potential function should be useful in treating the excitation of rotational and vibrational quantum states by electron impact, when supplemented with polarization potentials. Winifred Huo is also using expansions of the collision amplitude in the calculation of resonant energy transfer cross sections. Many other applications are apparent but have not been carried through.

6.2 Collision Amplitudes and Molecular Electron Distributions

It has been demonstrated that the Hartree-Fock integral equations in momentum space can be put into a form where the kernel function is the collision amplitude in Born approximation (with exchange) for the collision of an additional incident electron with the system under consideration. The possibility of an experimental determination of the kernel function is discussed. Approximations to the exchange amplitude are obtained similar to those employed in collision theory. One approximation to the collision amplitude leads, when transformed back to positional coordinates, to an approximate exchange potential. [E. N. Lassettre, J. Chem. Phys. 58, 1991 (1973)]. The potential has not yet been numerically tested, but preparations for a numerical test have been completed in connection with a study of momentum eigenfunctions described in the next section.

6.3 Momentum Eigenfunctions.

An investigation of momentum eigenfunctions has been undertaken for two reasons. First, the mathematical methods used in the study of form factors (Section 6.1) can be applied with little or no modification to momentum eigenfunctions for atoms and molecules. Second, we need (for molecules) approximate eigenfunctions similar to Hartree-Fock functions for atoms in order to carry out approximate collision amplitude calculations to use in directing our experiment, especially on singlet-triplet transitions. Although quantum chemists have made impressive progress on energy calculations using Gaussian basis sets the eigenfunctions are never published and are almost completely inaccessible to us. Therefore the problem of expressing the potential energy V of an electron in a molecule as a sum of atom centered potentials, using the potential function mentioned in Section 6.2, has been considered. Next, we have considered the potential function U_n from which we can obtain atomic orbitals ϕ_n which participate in linear combinations to form molecular orbitals Ψ

$$\Psi = \sum_n C_n \phi_n$$

The function ϕ_n satisfies a one-electron Schrodinger type equation

$$-1/2\nabla^2 \phi_n + U_n \phi_n = W_n \phi_n.$$

If successful in obtaining U_n , this equation could be integrated by conventional methods, somewhat similar to the self consistent field procedure. It is possible to formulate this problem in a manner suitable for numerical

calculation. This has been done, a manuscript has been prepared and accepted for publication. (Item 21 of the publication list). Questions have arisen about the potential function mentioned in Section 6.2 which would require an investigation of many months duration, too long to be of value in the present project. Fortunately a grant from the Petroleum Research Fund has been obtained for the support of Winifred M. Huo. The potential function is being studied under these auspices. Nothing further has been done in the present research program.

7. THEORETICAL APPLICATIONS OF GENERALIZED OSCILLATOR STRENGTHS.

Two applications of generalized oscillator strengths are of special interest. The first, described in Section 7.1 below, involves the approximate calculation of the difference in energy between the 1B_1 and 3B_1 states of H_2O . The second involves the calculation of resonant energy transfer cross sections in Born approximation (without exchange) by using generalized oscillator strengths. This is discussed in Section 7.2.

7.1 Singlet-Triplet Energy Difference for H_2O .

The generalized oscillator strengths for H_2O were needed in order to calculate the energy difference between the singlet, E_S , and triplet, E_T , excited states 1B_1 and 3B_1 of H_2O according to the approximate formula [E. N. Lassettre and M. A. Dillon, J. Chem. Phys. 59, 4778 (1973)] (in atomic units)

$$E_S - E_T = (\pi W g)^{-1} \int_0^\infty K^2 f_B dK. \quad (18)$$

Here, W is the excitation energy of the singlet, f_B is the generalized oscillator strength (in Born approximation) for excitation of the singlet, K designates the momentum change (ΔP) of the colliding electron, and g is the degeneracy of the excited state singlet. An indirect means, such as equation (18), must be used to locate the triplet for the following reason. There is a low lying excitation in H_2O at ~ 4.5 eV which has been observed by several investigators using entirely different experimental techniques. The term symbol for the excited state is not definitely known

but 3B_1 has been frequently suggested. When, however, excitation energies are calculated theoretically by other investigators, using vastly improved techniques recently developed, the energy of the 3B_1 state is found to be above the ground state by an amount much greater than 4.5 eV. Moreover, quantum mechanical calculations by other investigators indicate that the 3B_1 state is not bound (at any nuclear configuration thus far examined) relative to the dissociation products $H(^2S) + OH(^2\Pi)$ or $O(^3P) + H_2(^1\Sigma_g^+)$. Hence, several theoretical chemists have suggested that the scattering observed at ~ 4.5 eV is an experimental error. This situation is reviewed, with references, in publications Nos. 14, 18, and 19 of the Publication List. In view of this situation, it is worthwhile to apply a relation like equation (18) to determine whether the vertical excitation energy for 3B_1 is 4.5 eV or something much higher.

Previous determinations of generalized oscillator strengths for the excitation of the 1B_1 state of H_2O at 7.4 eV have been done by Lassette and Skerbele [J. Chem. Phys. 60, 2464 (1974)] before the discovery of equation (18) and the determinations did not extend to large enough values of ΔP . The determinations have been extended by Klump and Lassette [Can. J. Phys. 53, 1825 (1975)].

The results of determinations at kinetic energies of 300, 400, 500, and 600 eV are given in Fig. 18. The minimum in f at $(\Delta P)^2 = 1.35 \pm 0.08$ is apparent. Since the value of f at the minimum decreases steadily with increase in energy, we have assumed that the value approached is zero. The calculations of Miller, Krauss and Mielczarek [J. Chem. Phys. 51, 26 (1969)] also indicate a zero at $(\Delta P)^2 = 1.4$ atomic units.

The solid curve of Fig. 18 is the value of f_B obtained by Klump and Lassette. The integral in equation (18) can now be evaluated, and

FIGURE 18
Generalized oscillator strength vs. $(\Delta P)^2$ for 7.4 eV excitation in H_2O .

TABLE 6
Experimental and Theoretical Positions of the
 $\tilde{A} \ ^3B_1$ State of Water (in Electron Volts)

E_T	$E_S - E_T$	Reference
7.2	0.2	Knoop (1972) ^a
7.1 ± 0.1	0.3	Trajmar (1974) ^b
6.89	0.33	Yeager <u>et al.</u> (1974) ^c
6.90	0.40	Buenker and Peyerimhoff (1974) ^d
6.82 ± 0.42	0.58 ± 0.42	Lassettre and Skerbele (1974) ^e
7.02	0.38	This research

^a F. W. Knoop, H. H. Brongersma, and L. J. Osterhoff, Chem. Phys. Lett. **13**, 20 (1972).

^b S. Trajmar and R. I. Hall, J. Phys. B **7**, L 458 (1974).

^c D. Yaeger, V. McKoy, and G. A. Segal, J. Chem. Phys. **61**, 755 (1974).

^d R. J. Buenker and S. D. Peyerimhoff, Chem. Phys. Lett. **29**, 253 (1974).

^e E. N. Lassettre and A. Skerbele, J. Chem. Phys. **60**, 2464 (1974).

we obtain for $E_S - E_T$ the value 0.38 eV. Using 7.4 eV for E_S (referred to ground state), we obtain for E_T the value 7.02 eV. This is compared, in Table 4, with the experimental values of Knoop and Trajmar. Table 6 also contains the calculated value obtained in a very elaborate calculation by Buenker and Peyerimhoff. Lassettre and Dillon showed that equation (15) provides values for He and CO which differ from experiment by an average of 15%. If this percentage is transferable to H_2O , then an uncertainty 0.06 eV is indicated. Rounding this to 0.1 eV and using 7.4 eV for the singlet, we find for E_T (referred to ground state) 7.0 ± 0.1 eV.

The above results confirm our earlier conclusion that the excitation ~ 4.5 eV cannot be due to vertical excitation from the ground state to the 3B_1 state of H_2O . We have suggested that the 4.5 eV peak may be a part of the envelope of the transition to 3B_1 , but this is not definitely proven. Further discussion is contained in No. 19 of the Publication List.

7.2 Resonant Energy Transfer Cross Sections.

A typical energy transfer reaction takes place when an excited molecule D' collides with A and excites it to A' while D' undergoes transition to a lower energy state D with energy evolution ΔE , i.e.

After some manipulation, which will be omitted, the Born approximation for the differential collision cross section can be put into the form

$$\frac{d\sigma}{d\Omega} = \frac{k_f}{k_o} \frac{M_\mu^2}{W_A W_D} f_D f_A \quad (19)$$

where M_μ is the reduced mass and

$$f_A = \frac{2W_A}{K^2} \left| \langle \Psi_A | \sum_j e^{i\mathbf{K} \cdot \mathbf{r}_{jA}} | \Psi_A \rangle \right|^2$$

$$f_D = \frac{2W_D}{K^2} \left| \langle \Psi_D | \sum_j e^{i\mathbf{K} \cdot \mathbf{r}_{jD}} | \Psi_D \rangle \right|^2$$

In these formulas $\mathbf{r}_{jA}$ represents the position vector to the j^{th} electron in molecule A and the summation extends over all electrons of molecule A. The eigenfunctions in the ground and excited states are $\Psi_A, \Psi_{A'}$. The corresponding quantities for molecule D are obvious. Also k_o and k_e are the initial and final (relative) momenta and W_A, W_D are the excitation energies. The vector $\mathbf{K}$ is the relative momentum change of the center of mass of A in collision. That for D is $-\mathbf{K}$. The quantities f_A and f_D have precisely the same form as the generalized oscillator strengths in electron molecule collisions but $\mathbf{K}$ is now the momentum change of the colliding electron and k_o, k_f are the initial and final momenta. Because M_μ is so much bigger than the mass of an electron the momentum change K accompanying the collision of molecules A and D' (to produce $A' + D$) covers about the same range for molecules in the thermal energy range as K does for molecule collisions with electrons having kinetic energies of hundreds of volts, just the region which we are studying experimentally. The fact that a collision cross section (in Born approximation) for molecule-molecule scattering is obtainable from generalized oscillator strengths obtained by electron-molecule scattering seems to us to be highly significant because

it makes possible the precise determination of the cross section in Born approximation.

The importance of the formula for the Born cross section can be illustrated by considering the following reaction

This has been done by Huo [J. Chem. Phys., 66, 3572 (1977)]. A test of equation (19) on the system acetone-benzene is described in Section 8 below.

The results described above were obtained while Winifred Huo was supported in part (20%) on our ERDA supported program from July 1, 1975 to December 31, 1975. She is now supported by a Petroleum Research Fund (American Chemical Society) Grant (since January 1, 1976). The investigation has continued under those auspices.

8. RESEARCH IN TERMINAL YEAR

8.1 Energy Transfer Cross Sections in Relation to Generalized Oscillator Strengths for the Donor-Acceptor Pair Benzene-Acetone*

Generalized oscillator strengths have been determined for the $\tilde{A}^1B_{2u} \leftarrow \tilde{X}^1A_{1g}$ transition in benzene and the $\tilde{A}^1A_2 \leftarrow \tilde{X}^1A_1$ transition in acetone (see Fig. 19). From the data, and the spectroscopic data and analysis of other investigators, the generalized oscillator strengths for the reverse transition in benzene have been calculated approximately. Huo's theory of energy transfer cross sections [J. Chem. Phys. 66, 3572 (1977)], the generalized oscillator strengths and eq. 19 have been used to calculate the integrated (over angle) cross section for the energy transfer process

The energy transfer cross section calculated in this way is found to be $39 \text{ \AA}^2$ with an estimated uncertainty of $\pm 8 \text{ \AA}^2$. The experimental value is $33 \pm 2 \text{ \AA}^2$ [K. Janda and F. S. Wettack, J. Am. Chem. Soc. 94, 305 (1972)].

Huo's theory is based on the Born approximation, neglecting electron exchange. The agreement between calculated and observed cross sections shows that the Born approximation (without exchange) is holding even though the molecules are colliding with relative velocities in the thermal range.

It is of incidental interest that the generalized oscillator strengths were determined using a gas mixture in which helium is the

is the comparison gas. The mixture method is usable for benzene because a more sensitive pressure gauge (a capacitance manometer) is now available and because accurate collision cross sections are available for helium [Lassetre and Dillon, J. Chem. Phys. 62, 2373 (1975)]. Full details are given in item 22 of the publication list.

Fig. 19 Generalized oscillator strength versus momentum change squared.

Incident electron energy is 500 eV. Top: Acetone $\tilde{A}^1A_2 + \tilde{X}^1A_1$.

Bottom: Benzene $\tilde{A}^1B_{2u} + \tilde{X}^1A_{1g}$. Open circles with error bars are experimental points; solid curves are least squares fit.

8.2 Limiting Oscillator Strength for the $\tilde{A}^1B_{2u} \leftarrow \tilde{X}^1A_{1g}$ Transition of Benzene

The generalized oscillator strength for benzene seems to be approaching a limit (see Figure 19) which is only half the value obtained by other investigators ($\sim 1.3 \times 10^{-3}$) from radiation absorption spectra. We know, however, that limiting oscillator strength at $\Delta P = 0$ should equal the optical value. A discrepancy as large as a factor of two is obviously a matter of concern and hence a further investigation has been carried through. The principal concern here is an apparent violation of the limit principle. (Section 2) As far as energy transfer is concerned equation (19) can be used to show the transfer cross section is insensitive to a change in f_0 for benzene by a factor of 2.

As a first step the generalized oscillator strength has been determined at 400 eV initial electron kinetic energy. The results, together with the previous determinations at 500 eV, are shown in Figure 20. The data at both 400 eV and 500 eV fall on a common curve as expected if the Born approximation is holding. The minimum angle studied is 2.5° at both kinetic energies. (The minimum angle at which adequate angular resolution is obtained is 2° .) When a function such as that of equation (15) is fitted to the data of Figure 20 by least squares with various values of N from 1-5 very erratic values of f_0 are obtained. Hence it was concluded that the data at scattering angles above 2° were not sufficient to determine f_0 .

In order to remedy this deficiency a study of forward scattering [where $(\Delta P)^2$ is so low that f and f_0 can be considered equal] was undertaken. In order to avoid the determination of the quantity η of equation (11) mercury has been chosen as the comparison gas because it contains an excitation with excitation energy 4.9 eV, almost identical with the symmetry line of the

Fig. 20. Generalized oscillator strength of benzene $\tilde{A}^1B_{2u} \leftarrow \tilde{X}^1A_{1g}$ transition versus momentum change squared (atomic units). $\circ$ - incident electron energy equals 500 eV; $\square$ - 400 eV; X - optical determination of reference 10; $\bullet$ - electron impact of this research; solid curve - see text.

benzene excitation. Under these conditions the ratio of peak areas per unit partial pressure is equal to the ratio of collision cross sections. In this way we find for f_0 $(1.51 \pm 0.20) \times 10^{-3}$ in essential agreement with a typical optical value $f_0 = 1.3 \times 10^{-3}$ [A. Trombetti and C. Zauli, Boll. Sci. Fac. Chem. Ind. Bologna 21, 206 (1963)]. The solid curve of Figure 20 was obtained by setting f_0 of equation (15) equal to 1.51×10^{-3} and adjusting the remaining coefficients, up to f_5 , by least squares. The fit is fair (about 6% in the mean). Note, however, the steep drop in f as $(\Delta P)^2$ increases from 0 to 0.07. This is similar in appearance to the oscillator strength curve for the transition $B^1\Sigma^+ \leftarrow X^1\Sigma^+$ in CO (see Figure 3). Otherwise, however, the two cases have little in common. For the benzene transition the Born approximation holds but not for CO. The reason for the abrupt change in CO is not known. In benzene, however, the observed f is the superposition of oscillator strengths to two different series of vibrational levels in the excited state. The excitation to one set of vibrational levels is electric dipole allowed. The second set is electric octupole allowed. As $(\Delta P)^2$ increases the dipole transitions become weaker and the octupole become stronger. This gives rise to the minimum followed by a maximum. The correctness of this model can be tested in another way described below.

Detailed studies of ultraviolet absorption spectra by other investigators have shown that the molecule possesses symmetry D_{6h} in both ground and excited states. It can be shown that the multidimensional integrals (Franck-Condon factors) which determine intensity distributions among vibrational levels actually factor into products of integrals of lower dimensions, there being one such factor for each irreducible representation containing one or more normal coordinates. The longest progressions are

those for which the normal mode causes the greatest change in dimension or frequency. For the benzene transition under consideration a normal mode, A_{1g} , belonging to the identical representation is changed most on excitation. The Franck-Condon factor containing that mode is a factor of both the dipole and octupole oscillator strengths. Hence the spacing $h\nu_1$ should appear in both. The electric dipole progression arises because a vibrational coordinate (usually designated by Q_6) distorts the molecule in such a way that the transition becomes allowed. Because of this the two (dipole and octupole) vibrational progressions differ by $h\nu_6 \approx 0.065$ eV. Hence, as the scattering angle [and $(\Delta P)^2$] increases the progression with spacing $h\nu_1$ should shift by $h\nu_6$ to a new progression with the same spacing $h\nu_1$. Moreover, since the Franck-Condon factor containing Q_1 is a factor of both progressions the relative intensity should be the same for both dipole and octupole transitions. Two spectra, taken at initial kinetic energy 300 eV where the most intense vibrations are resolved, are shown in Figure 21. The relative intensities of the band envelopes are obviously the same at 2° and 6.5° but the whole envelope is shifted to lower excitation energies by $h\nu_6 = 0.065$ eV. This shift is indicated by the two arrows in the figure. The observations are in complete accord with assumption of transfer from dipole to octupole excitation with increasing ΔP .

These observations on the excitation process establish the mechanism. Similar reasoning was used to obtain the Franck-Condon factor for the octupole transition in the reverse transition mentioned in Section 8.1.

Full details on the material of this section are given in item 23 of the publication list.

Fig. 21. Energy loss spectra of benzene. Incident electron energy is 300 eV. Upper curve - scattering angle, $\theta = 6.5^\circ$. Lower curve - $\theta = 2.0^\circ$. The arrows at 4.72 eV and 4.79 eV indicate the position of the calculated vibrationless origin and the vibronic origin (observed in optical spectra), respectively. The distance between them is $h\nu_6$.

8.3 Generalized Oscillator Strength for p-difluoro-benzene.

The generalized oscillator strength for the first allowed excited state of p-difluoro-benzene has been determined. The results are shown in Fig. 22. The limiting oscillator strength at $(\Delta P)^2 = 0$ has been determined and found to be $(1.55 \pm .15) \times 10^{-2}$. There are no problems with extrapolation like those encountered in benzene. The only observed optical oscillator strength has been calculated from a lifetime the value being 6.5×10^{-2} . Since oscillator strengths calculated from lifetimes for molecules are notably unreliable (see Section 4.3 for an example) the discrepancy is not unexpected. It is believed that the electron impact value is correct.

The original intent was to calculate the energy transfer cross section for the reaction of excited p-difluoro-benzene with acetone. However, the spectroscopic data are less complete than for benzene and we have not been able to complete the analysis in time for this report.

FIGURE 22. Generalized oscillator strength for p-difluoro-benzene. Initial kinetic energy 500 eV.

9. CURRENT STATUS. FUTURE PROSPECTS.

9.1 Current Status

As noted in the introduction to this report, the principal objective of the program is the determination and interpretation of generalized oscillator strengths. As far as the determination of these quantities is concerned the methods developed (Section 3) have been thoroughly tested on a considerable number of substances. All outstanding inconsistencies and discrepancies have been resolved. We must note, however, that the determination of generalized oscillator strengths at comparatively high resolution and high kinetic energy is a difficult undertaking because each transition and each substance has a personality of its own and a sustained investigation is almost always necessary to avoid error and to fully reveal the trend of oscillator strength curves. This fact, which complicates the determination of generalized oscillator strengths, indicates the need for interpretation (or classification) of transitions so that we can anticipate in advance what behavior to expect in special cases. The selection rule discussed in Section 4.1 serves this purpose. An analogous selection rule, applicable to singlet-triplet transitions, is another example (Section 5). Despite these aids in the recognition of unusual transitions we can still encounter surprises. The benzene transition described in Section 8.2 is an excellent example which was encountered in the very last year of this program. In that case two transitions of very different behavior were superimposed and the behavior of the composite was unexpected. Despite the complication it is well worthwhile to study generalized

oscillator strengths both for their own sake and because of the growing awareness that they (and the associated collision amplitudes) are the basic raw material for the understanding a whole array of phenomena which, at first sight, do not seem related to electron collision processes.

Examples are given in the next section.

9.2 Future Prospects. Applications of First Order Collision Amplitudes.

One of the most promising areas for future investigation is the application of collision amplitudes for electron scattering to the calculation of collision amplitudes for other processes. An example is given in Section 7.2 where the differential cross section for the resonant energy transfer cross section, in Born approximation, for collision between molecules is expressed in terms of generalized oscillator strengths for collisions between electrons and molecules. This makes it possible to determine for the first time, using experimentally determined generalized oscillator strengths, whether the Born approximation holds when two molecules come in an excited state, collide with the transfer of energy from one molecule to the other.

Since the spectra of polyatomic molecules are very dense, almost continuous, it is almost always possible in collisions between an excited molecule and a molecule in the ground state for energy transfer to occur with nearly zero resonant energy gap. The same should also be true for the collision of an excited atom with a molecule. Hence we encounter one of the rare instances in which we expect the Born approximation to hold better for the collision of complicated systems than for the collision

of atoms because in the latter case small resonant energy gaps are rare since atomic spectra are so sparse especially in the lower excited states. Moreover, if the resonant energy gap is zero then energy transfer can take place between systems which are stationary relative to each other. Hence relative velocity influences the collision cross section in very different fashion from that encountered in analogous processes such as the collision of electrons with molecules. Much of our theoretical knowledge of cross sections for resonant energy transfer is derived from the study of energy transfer in the collision of atoms. The results obtained in Section 7.2 of the above report together with the acetone-benzene example of Section 8.1, strongly suggest that this concentration on atoms, for purposes of computational simplicity, has obscured the true simplicity of the energy transfer cross section in the collision of atoms with molecules and molecules with molecules. For this reason, and also because it expands the area of use for generalized oscillator strengths, it would be of considerable value to experimentally test this relationship. One example is given in Section 8.1. Further study would be rewarding.

The potential application of first order collision amplitudes is much wider than the above example indicates. It can be shown that the second Born approximation to the energy transfer cross section is expressible as a functional of first order collision amplitudes. The formulas are complicated, however, and substantial theoretical research would be necessary in order to apply the results in actual cases. We know in advance that productive research is possible and we believe that this is the most promising area for future research. This, however, must be left to other investigators.

10. PUBLICATIONS

All publications sponsored by ERDA since the beginning of the project (Jan. 1, 1970) are listed. Those sponsored by AFOSR, NSF or PRF (Petroleum Research Fund) over the same period are also listed (see Section 11 for comments on other support) since they deal with inelastic electron scattering.

10.1 Supported by ERDA

10.11 Published

- 1) Skerbele, A. and E. N. Lassettre, "Generalized Oscillator Strengths for the $6^1S_0 \rightarrow 6^1P_1$ Transition in Mercury," Journal of Chemical Physics **52** (5), 2708-2711 (1970).
- 2) Skerbele, A. and E. N. Lassettre, "Absolute Electron Collision Cross Sections for Two Forbidden Transitions in Nitrogen at Kinetic Energies of 300-500 eV," Journal of Chemical Physics **53** (10), 3806 (1970).
- 3) Lassettre, E. N., "Further Selection Rules in Excitation by Electron Impact at Small Momentum Changes," Journal of Chemical Physics **53** (10), 3801 (1970).
- 4) Lassettre, E. N. and A. Skerbele, "Absolute Generalized Oscillator Strengths for Four Electronic Transitions in Carbon Monoxide," Journal of Chemical Physics **54**, 1597-1607 (1971).
- 5) Skerbele, A. and E. N. Lassettre, "New Selection Rule, Illustrated by Collision Cross Section Studies on the $B^1\Sigma^+ \leftarrow X^1\Sigma^+$ and the $C^1\Sigma \leftarrow X^1\Sigma^+$ Transitions in Carbon Monoxide at Kinetic Energies of 300, 400, and 500 eV," Journal of Chemical Physics **55** (1), 424-434 (1971).
- 6) Skerbele, A. and E. N. Lassettre, "Absolute Generalized Oscillator Strengths for Three Transitions in the Mercury Spectrum," Journal of Chemical Physics **56**, 845-850 (1972).
- 7) Lassettre, E. N., "Power Series Expansion of Collision Amplitudes. Electrostatic Potentials," Journal of Chemical Physics **57**, 4357-4369 (1972).
- 8) Harshbarger, W. R. and E. N. Lassettre, "Electron Impact Spectra of CH_4 and CF_4 ," Journal of Chemical Physics **58**, 1505 (1973).

- 9) Lassettre, E. N., "Collision Amplitudes and Molecular Electron Distributions," Journal of Chemical Physics 58, 1991-1998 (1973).
- 10) Harshbarger, W. R., M. B. Robin and E. N. Lassettre, "The Electron Impact Spectra of the Fluoromethanes," The Journal of Electron Impact Spectroscopy and Related Phenomena 1 (4), 319-332 (1973).
- 11) Skerbele, A., W. R. Harshbarger and E. N. Lassettre, "Excitation of Forbidden Transitions in Helium by Electron Impact at Kinetic Energies of 300-500 eV. Singlet-Triplet Transitions at High Kinetic Energies," Journal of Chemical Physics 58, 4285 (1973).
- 12) Skerbele, A. and E. N. Lassettre, "Generalized Oscillator Strengths for the Excitation of Heavy Atoms: $6^1S_0 \rightarrow 6^1P_1$, $6^1S_0 \rightarrow 7^1S_0$ and $6^1S_0 \rightarrow 7^1P_1$ Transitions in Mercury," Journal of Chemical Physics 58, 2887 (1973).
- 13) Lassettre, E. N. and M. A. Dillon, "Singlet-Triplet Energy Differences Calculated from Generalized Oscillator Strengths," Journal of Chemical Physics 59, 4778 (1973).
- 14) Lassettre, E. N. and A. Skerbele, "Generalized Oscillator Strengths for 7.4 eV Excitation of H_2O at 300, 400 and 500 eV Kinetic Energy. Singlet-Triplet Energy Differences," Journal of Chemical Physics 60, 2464 (1974).
- 15) Lassettre, E. N. and A. Skerbele, "Inelastic Electron Scattering," Methods of Experimental Physics; Vol. 3 Molecular Physics, Edited by D. E. Williams; Academic Press, New York (1974) pages 868-951. A Review with 192 references.
- 16) Klump, K. N. and E. N. Lassettre, "Relative Vibrational Intensities for the $B^1\Sigma^+ \leftarrow X^1\Sigma^+$ Transition in Carbon Monoxide," Journal of Chemical Physics 60, 4830 (1974).
- 17) Klump, K. N. and E. N. Lassettre, "Electrostatic Polarization in the Exchange Scattering of Electrons of High Kinetic Energy. $1^1S \rightarrow 2^3S$ Transition in Helium. Singlet-Triplet Excitation in CO," Journal of Chemical Physics 62, 1838 (1975).
- 18) Lassettre, E. N. and Winifred M. Huo, "Negative Ion Contamination of Electron Impact Spectra," Journal of Chemical Physics 61, 1703 (1974).
- 19) Klump, K. N. and E. N. Lassettre, "Excitation of Energy of 3B_1 State of H_2O Calculated from Generalized Oscillator Strengths," Canadian Journal of Physics 53, 1825 (1975).
- 20) Dillon, M. A., "Electron Impact Excitation of the $1^1S \rightarrow 2^3S$ Transition in Helium; Differential Cross-Section Determinations at High Kinetic Energies," Journal of Chemical Physics 63, 1035 (1975).

- 21) Lassettre, E. N., "Momentum Eigenfunctions in the Complex Momentum Plane. Local Potential Functions," Journal of Chemical Physics 64, 4375 (1976).

10.12 Submitted

- 22) Klump, K. N. and E. N. Lassettre "Energy Transfer Cross Sections in Relation to Generalized Oscillator Strengths for the Donor-Acceptor Pair Benzene-Acetone" Journal of Chemical Physics (submitted).
- 23) Klump, K. N. and E. N. Lassettre "Generalized Oscillator Strength for the Transition $\tilde{A}^1B_{2u} \leftarrow \tilde{X}^1A_{1g}$ in Benzene at Initial Kinetic Energies of 400 eV and 500 eV" Chemical Physics Letters (submitted).

10.13 In Preparation

- 24) Klump, K. N. and E. N. Lassettre "Generalized Oscillator Strengths for Two Transitions in Carbon Dioxide" Journal of Electron Spectroscopy.

10.2 Supported by AFOSR/NSF/PRF Since Jan. 1, 1970

10.21 Published

- 25) Meyer, V. D. and E. N. Lassettre, "An Experimental Determination of Oscillator Strengths for the $\text{CO } A^1\Pi \leftarrow X^1\Sigma^+$ Bands," Journal of Chemical Physics **54**, 1608-1610 (1971).
- 26) Harshbarger, W. R., A. Skerbele and E. N. Lassettre, "Generalized Oscillator Strength of the $A \leftarrow X$ Transition of Ammonia," Journal of Chemical Physics **54** (6), 3784 (1971).
- 27) Lassettre, E. N., A. Skerbele and M. A. Dillon, "Absolute Generalized Oscillator Strength of $1^1S \rightarrow 2^1P$ Transition in Helium," Journal of Chemical Physics **52** (5), 2797-2799 (1970).
- 28) Huo, W. M., "Effective Long Range Potential for Scattering of Electrons by Atoms and Molecules," Journal of Chemical Physics **56** (7), 3468 (1972).
- 29) Huo, W. M., "Limiting Form of the Effective Potential for Electron Scattering," Journal of Chemical Physics **57**, 4800-4813 (1972).
- 30) Lassettre, E. N. and E. R. White, "Generalized Oscillator Strengths Through the Water Vapor Spectrum to 75 eV Excitation Energy; Electron Kinetic Energy 500 eV," Journal of Chemical Physics **60**, 2460 (1974).
- 31) Huo, W. M., "A High Energy Approximation for Exchange Scattering and Application to $1^1S \rightarrow 2^3S$ Excitation of He by Electron Impact," Journal of Chemical Physics **60**, 3544 (1974).
- 32) Lassettre, E. N., "Absolute Intensities and Classification of Transitions in Electron Impact Spectroscopy," Chemical Spectroscopy and Photochemistry in the Vacuum Ultraviolet, Edited by C. Sandorfy, P. J. Ausloos and M. B. Robin, D. Reidel Publishing Company, Dordrecht/Boston 43-70 (1974).
- 33) Dillon, M. A. and E. N. Lassettre, "Absolute Differential Electron Collision Cross Sections for the $1^1S \rightarrow 2^1P$ and $1^1S \rightarrow 2^1P$ Transitions in Helium at Kinetic Energies of 200 eV, 300 eV, 400 eV, 500 eV and 700 eV," Journal of Chemical Physics **62**, 2373 (1975).
- 34) Dillon, M. A. and E. N. Lassettre, "Test of Born Approximation on the 60 eV Autoionized Transition in Helium," Journal of Chemical Physics **62**, 4240 (1975).

- 35) Huo, Winifred M., "A Time Dependent Variation-Perturbation Method for the Calculation of Transition Properties and its Relation to the Random Phase Approximation." The Journal of Chemical Physics 62, 2072 (1975).
- 36) Huo, Winifred M., "Singularities of the Born-Oppenheimer Exchange Amplitude," Journal of Chemical Physics 63, 4013 (1975).
- 37) Huo, Winifred M., "Resonant Energy Transfer Cross Section Formulated in Terms of Form Factors: An Appraisal of the First Born Approximation" Journal of Chemical Physics 66, 3572 (1977).
- 38) Huo, Winifred M. and M. A. Dillon, "Effect of the Reverse Reaction on the Experimental Determination of Energy Transfer Rate Constants" Journal of Chemical Physics 66, 3588 (1977).

10.22 In Press

- 39) Dillon, M. A. and E. N. Lassettre, "An (e,2e) Investigation of the $(2s\ 2p)^1P$ Autoionized Transition in Helium: Comparison with an Accurate Born Approximation" Journal of Chemical Physics (In Press).

11. PERSONNEL RELATED RESEARCH SUPPORT

11.1 Personnel

Personnel involved in research under contract E(11-1)-3247
(and its predecessors) since January 1, 1970 are as follows:

1. Dr. Edwin N. Lassettre
2. Dr. Ausma Skerbebe
3. Dr. William R. Harshbarger
4. Dr. Kirby N. Klump
5. Dr. Winifred M. Huo
6. Dr. Michael A. Dillon

Drs. Huo and Dillon were only employed for short periods
(20% time for the last six months of 1975 and for three months, full time,
beginning February 1, 1975, respectively). Currently, only E. N. Lassettre
and K. N. Klump are employed. No graduate students have been employed.

11.2 Status of Research Supported by AFOSR, NSF and PRF

A electron spectrometer with fast coincidence capability has been developed on a program supported with a grant from the Air Force Office of Scientific Research. This grant terminated on December 31, 1974 and was not extended. We did not have enough notice to obtain a replacement grant by January 1, 1975. However, a grant from the National Science Foundation was received for two years effective May 1, 1975. This enables the experimental part of the program to go forward with two persons, E. N. Lassettre, Principal Investigator (35%) and Michael A. Dillon, Co-Principal Investigator (100%). This research involves the study of ionization continua using a newly developed spectrometer and fast coincidence techniques. There is no overlap or conflict with the research supported by ERDA, but the results are of considerable interest in several areas of Radiological Physics. This program also terminates on June 30, 1977 coincident with the retirement of E. N. Lassettre.

The above grant from the National Science Foundation provides for Dr. Michael A. Dillon, who was supported by the AFOSR project before its termination. Dr. Winifred M. Huo was also supported by the AFOSR Grant before its termination on December 31, 1974. During all of 1975, Dr. Huo was supported mostly by Carnegie-Mellon University endowment funds except for 10% of her time on the present contract (she obtained equation 19 of Section 7.2 and tested it numerically during this time) and 10% on another project. To obtain further support for her, a proposal was submitted to the Petroleum Research Fund of the American Chemical Society (ACS). This grant was approved effective September 1, 1976, but we received

permission to make an early beginning, January 1, 1976. The grant (E. N. Lassettre - Principal Investigator) paid 2/3 of Dr. Huo's salary. Carnegie-Mellon University paid the remainder. Dr. Huo has obtained a position at the Radiation Laboratory at Notre Dame University. She terminates at Carnegie-Mellon University on June 30, 1977, coincident with the retirement of E. N. Lassettre.

All of the research mentioned above is concerned with the theoretical or experimental study of inelastic electron scattering and it complemented, to some degree, the research supported by ERDA. Hence a list of publications is included in Section 10.