GENERALIZED OSCILLATOR STRENGTHS

Progress Report

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ABSTRACT

Generalized oscillator strengths are given for the $\tilde{X}^1A_1 \rightarrow \tilde{A}^1B_1$ transition in H_2O at electron kinetic energies of incidence of 300, 400, 500 and 600 eV. The data have been used to calculate the excitation energy of the 3B_1 state (lowest) of H_2O . The result is 7.0 ± 1 eV where the uncertainty is an estimate not an upper bound. This confirms our previous conclusion that the 4.5 eV excitation, observed by several investigators, cannot be due to vertical excitation to the lowest 3B_1 state. The 4.5 eV excitation is not yet identified. Generalized oscillator strength determinations on CO_2 are also reported together with preliminary results on a survey of N_2 spectra, at several kinetic energies and angles, in the vicinity of 11.87 eV, the excitation energy for the transition $X^1\Sigma_g^+ \rightarrow E^3\Sigma_g^+$. Cross section determinations on $1^1S \rightarrow 2^3S$ transition in helium at high kinetic energy (supported by AFOSR) are also briefly described since the results are of considerable interest in the present research.

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1. INTRODUCTION

The following progress report is prepared for the period July 1, 1974 to July 1, 1975. Since the report was written in March, there still remains three months before the end of the contract period. In the report, those researches which are still in progress are mentioned.

In order that progress can be compared with the proposal which preceded it, the same main section numbers and section headings are employed except for Section 2.3. Subsections correspond, however, to the research actually undertaken and may be more specific and detailed than the proposal.

The research promised in the proposal has either been carried out or is in progress except for the collision cross section study of benzene. This has been deferred for good reasons which are discussed in the report.

2. CURRENT STATUS OF RESEARCH

Two categories of research are contained in the proposal for the current year's research. The first of these consists of inelastic electron scattering experiments at high kinetic energy. Among these are generalized oscillator strength determinations at initial kinetic energies of several hundred electron volts, which were begun (or promised) in the previous contract period but not completed. Three substances, H_2O , CO_2 , and C_6H_6 , are in this category. Moreover, a survey of electron impact spectra has been carried out in the vicinity of the nitrogen transition $X \ ^1\Sigma_g^+ \rightarrow E \ ^3\Sigma_g^+$ at 11.87 eV excitation energy. The status of each of these investigations is discussed in Section 2.1 below.

The second research category involves a projected extension of our research to low kinetic energy and especially a study of singlet-triplet transitions in which the term symbol is the same in ground and excited states. These transitions have (in theory at least) abnormally high collision cross sections at small scattering angles and high kinetic energies and, hence these are the conditions of special interest. However, since singlet-triplet transitions of all types become relatively more intense at low kinetic energies, it was proposed that the investigation be extended to low kinetic energies and a search for new singlet-triplet transitions, of the special type mentioned above, be made. The status of these investigations is described in Section 2.2 below. In preparation for studies at low

kinetic energy, the question of interference by negative ions has been studied theoretically. It was concluded that such interference was possible for at least one substance, H_2O . The results are briefly mentioned in Section 2.2.

2.1 Continuing Studies Not Completed In Previous Contract Period (July 1, 1973 to July 1, 1974).

2.11 Generalized Oscillator Strengths for H_2O

Determinations of generalized oscillator strengths for the 7.4 eV excitation, in water vapor were undertaken during the last contract period but were interrupted in favor of similar determinations on CO_2 in a vain attempt to complete these in time for the Platzmann memorial issue of the International Journal of Radiation Chemistry. The study of H_2O was resumed after the CO_2 research was finished and has been completed during the present contract period.

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 formula [E. N. Lassettre and M. A. Dillon, J. Chem. Phys. **59**, 4778 (1973)] (in atomic units)

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

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 (1), 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 (1) 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 Lassetre and Skerbele [J. Chem. Phys. 60, 2464 (1974)] before the discovery of equation (1) and the determinations did not extend to large enough values of ΔP . The determinations have been extended during the present contract period.

We have used the following formula (in atomic units) to define the generalized oscillator strength, f ,

$$f = \frac{W}{2} \frac{P_o}{P_n} (\Delta P)^2 \sigma \quad (2)$$

where W is the excitation energy, P_o , P_n are the momenta of the incident electron before and after scattering, $(\Delta P)^2 = P_o^2 + P_n^2 - 2P_o P_n \cos \theta$ with θ being the scattering angle, and σ is the differential collision cross section. A determination of f involves the measurement of each quantity on the right of equation (2). To apply equation (1), we need f_B , the generalized oscillator strength in Born approximation. To obtain f_B , it is essential to perform experiments at high kinetic energy since f of equation (2) only approaches f_B in the limit of high kinetic energies at fixed ΔP .

The results of determinations at kinetic energies of 300, 400, 500, and 600 eV are given in Fig. 1. 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.

In order to extract f_B from the experimental data, we proceed as follows. The Born approximation appears to be satisfied for $(\Delta P)^2 < 0.8$ since our data and the data of Lassetre and Skerbele are independent of E_o to within the experimental error of this region (see

FIGURE 1
Generalized oscillator strength vs. $(\Delta P)^2$ for 7.4 eV excitation in H_2O .

Fig. 1). Although this behavior is a necessary consequence of the Born approximation, the reverse has not been proven, especially when only a restricted energy range is involved. Nevertheless, it is a plausible assumption that the Born approximation holds when f depends only on $(\Delta P)^2$, and we have assumed this in the following discussion.

In light of the above discussion, we make three assumptions concerning the Born approximation to the generalized oscillator strength, f_B : (1) f_B equals the experimental f for $(\Delta P)^2 < 0.8$; (2) it equals zero at $(\Delta P)^2 = 1.35$; and (3) it is less than experiment for $(\Delta P)^2 > 0.8$ and $E_0 = 600$ eV.

In order to extrapolate the Born approximation beyond $(\Delta P)^2 = 0.8$, we have fit the data of Lassetre and Skerbele and our data (Fig. 1) for $(\Delta P)^2 < 0.8$ to the series expansion of Lassetre [J. Chem. Phys. **43**, 4479 (1965)] and Vriens [Phys. Rev. **160**, 100 (1967)] and Vriens and Carriere [Physica **49** 517 (1970)], which is valid for the Born approximation,

$$f(\Delta P)^2 = (1 + x^2)^{-6} \sum_{n=0}^N f_n [x^2/(1 + x^2)]^n \quad (3)$$

with the constraint that $f(1.35) = 0$. Here $X = \Delta P/\alpha$, $\alpha = \sqrt{2I} + \sqrt{2(I - W)}$ with I the ionization potential and W the excitation energy (atomic units). Polynomials [equation (3)] of degrees $N = 4, 6, 8$ were employed. The polynomial of degree 4 gave an f at $(\Delta P)^2 = 3.5$ a.u. which is much too small, while that of degree 8 gave an f at 3.5 a.u. which is much greater than the observed value at 600 eV, and hence is

unsatisfactory. It follows that only the value $N = 4$ is satisfactory. The solid curve of Fig. 1 is the result obtained with this polynomial. The integral in equation (1) can now be evaluated, and 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 I, with the experimental values of Knoop and Trajmar. Table I also contains the calculated value obtained in a very elaborate calculation by Buenker and Peyerimhoff. Lassetre and Dillon showed that equation (1) 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.

In a technical sense, the generalized oscillator strengths for H_2O were very difficult (and time consuming) to measure. This arose partly because such low pressures were needed to eliminate the possibility of multiple collisions at large scattering angles. Since we were determining the ratio of peak envelope areas of inelastic to elastic peaks, it was not necessary to have precise pressure measurements and

TABLE I
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).

this is fortunate since with the pressure gauge in use, the pressures could not be accurately measured. Moreover, the count rates at large angles were very low. Because of these factors, the experiments were extremely tedious (like those on CO_2 described in the next section), and we think that apparatus modifications are essential before any further experiments of this type are undertaken at large scattering angles and high kinetic energies. The proposal for next year (July 1, 1975 to July 1, 1976) suggests apparatus modifications aimed at speeding up such experiments.

2.12 Collision Cross Section Study of CO_2

Generalized oscillator strengths for the 11.04 eV and 11.38 eV excitations in CO_2 have been determined as a function of momentum change. The results are shown in Fig. 2. The determinations at 300 eV and 500 eV incident kinetic energy are more accurate than those at 400 eV because the area under each peak was determined as a function of scattering angle. Because of the area determination, these measurements were even more tedious and time consuming than those for H_2O reported in the preceding section. This further supports the need for instrument modification contained in the proposal accompanying this progress report.

Oscillator strengths have been previously determined, at low resolution where the 11.04 and 11.38 eV transitions were not resolved, by Lassetre and Shiloff [J. Chem. Phys. **43**, 560 (1965)]. Foo, Brion and Hasted [Proc. Roy. Soc. (London) A **322**, 535 (1971)] have also determined scattered current as a function of angle for CO_2 and reported that the results (at incident kinetic energy of 300 eV) were in serious

FIGURE 2
Generalized oscillator strength vs. $(\Delta P)^2$ for 11.04 eV (upper) and 11.38 eV (lower) transitions in CO₂.

disagreement with the results of Lassetre and Shiloff. It is principally for this reason that new determinations have been done. At 300 eV, the determinations shown in Fig. 2 disagree with the results of Foo, et al. In view of the care used in our determinations at 300 eV and 500 eV, we are confident of their accuracy. Moreover, the resolution was sufficient to separate the 11.04 and 11.38 eV transitions at all angles. We can offer no explanation for the disagreement with Foo, et al.

Since the experiments of Lassetre and Shiloff were done at much lower resolution than those of Fig. 2, a direct comparison is difficult. We have still to calculate areas from the spectra given by them before a meaningful comparison is possible. This will be done before the end of the contract period and a paper prepared for publication.

2.13 Study of $X\ ^1\Sigma_g^+ \rightarrow E\ ^3\Sigma_g^+$ Transition in N_2

In our previous proposal one item concerned the study of this transition with high kinetic energy electrons. We have decided to extend the measurements to low kinetic energy as well, and the results at both high and low energies are described in Section 2.22 below.

2.14 $1^1S \rightarrow 2^3S$ Transition in Helium

In the last progress report, we reported the determination of the ratio of the electron collision cross section (σ_T) for the helium transition $1^1S \rightarrow 2^3S$ to that (σ_S) for the transition $1^1S \rightarrow 2^1S$. These determinations were done in forward scattering ($\theta = 0^\circ$) in order to test a theory of singlet-triplet transitions developed by Winifred M. Huo.

In the interim, a paper describing these results (by Kirby N. Klump and Edwin N. Lassettre) has been written and published (No. 17 of the Publication List). An account of Dr. Huo's theory (developed on a project supported by AFOSR) has also been published (No. 26 of the Publication List). This completes the research at zero scattering angle. At larger scattering angles, absolute collision cross sections for the transition $1^1S \rightarrow 2^3S$ have been determined by Michael A. Dillon on our AFOSR program. Support of this program by the Air Force Office of Scientific Research was terminated after the collision cross section study was completed but before the data were fully interpreted and a manuscript prepared for publication. Since the singlet-triplet transition involved belongs to the class with the same orbital term symbols in ground and excited states and since these absolute differential collision cross sections are the only ones ever determined at high kinetic energies for such a transition, the results are of great interest in the present research program which is currently emphasizing the investigation of this class of transitions. Hence, Dr. Dillon has been transferred to the present research project for three months to prepare a paper for publication and also to use a newly developed electron spectrometer in a brief study of the ionization continuum of H_2O . The investigation of the H_2O continuum has been delayed by a vacuum problem (see Section 2.3), but the cross section data on helium have been interpreted as far as is now feasible and a manuscript prepared for publication (it is now in the hands of the typist). A few conclusions are mentioned in Section 3.

2.15 Cross Section Study of Benzene

This investigation is deferred until instrument modifications mentioned in Sections 2.11 and 2.12 (and outlined in next year's proposal) are completed. Using the present (unmodified) spectrometer, benzene would be even more difficult to study than either H_2O or CO_2 .

2.2 Research at Low Kinetic Energies. Singlet-Triplet Transitions.

A principal objective of the present program is the study of singlet-triplet transitions in which the orbital term symbol is unchanged on transition. Such transitions have, in theory at least, high cross sections at small scattering angles and high kinetic energies of incidence. It is the behavior at high kinetic energy which is of prime interest in our present program. Why then do we wish to conduct experiments at low kinetic energy? The answer is that such transitions are difficult to detect because they tend to be obscured by neighboring and much more intense, singlet-singlet transitions. (The reason for this was discussed in last year's proposal and will not be repeated.) As the kinetic energy is reduced, however, these transitions (like other singlet-triplet transitions) become more intense relative to singlets, and hence (hopefully) easier to detect. Moreover, we wish to extend our cross section capability to lower kinetic energy. Hence, after the cross section measurements at high kinetic energy (see Section 2.1) were completed, a survey of electron impact spectra was undertaken at both high and low kinetic energy. Only after this is completed will cross section measurements be undertaken. As a preliminary to research at low kinetic energy, we have considered the possibility of negative ion interference (see

Section 2.21). Then, a study of the $X\ ^1\Sigma_g^+ \rightarrow E\ ^3\Sigma_g^+$ transition in N_2 was begun (Section 2.22).

2.21 Negative Ion Contamination of Electron Impact Spectra

Since electron optical systems based on electrostatic fields transmit equally all particles of the same charge and kinetic energy regardless of their masses, there is a possibility that peaks in a supposed electron impact spectrum might be due to ions like H^- if the cross sections were high enough. In the case of H_2O , the maximum cross section for H^- production occurs for electrons of 6.4 eV kinetic energy and the cross sections are high enough so that spectral contamination is highly probable. In fact, after our research was published, Trajmar and Hall [*J. Phys. B* **7**, L1458(1974)] observed several peaks in the H_2O spectrum due to H^- . Their initial electron kinetic energy was near 6.4 eV. At higher kinetic energies, the cross sections are too low for contamination to be a serious factor. As far as our own investigations are concerned at kinetic energies down to 25 eV, we need not be concerned about negative ion interference.

2.22 Electron Impact Spectra of N_2 . Relative Intensities of the $X\ ^1\Sigma_g^+ \rightarrow E\ ^3\Sigma_g^+$ and $X\ ^1\Sigma_g^+ \rightarrow a''\ ^1\Sigma_g^+$ Transitions

The states $E\ ^3\Sigma_g^+$ and $a''\ ^1\Sigma_g^+$ constitute a singlet-triplet pair arising from the same molecular orbital configuration. The transition from the ground state to each of these is fully resolved in the electron impact spectrum and for each transition the orbital term symbol, Σ_g^+ , is the same in both initial and final state. Obviously, this is a pair

of transitions of just the type we wish to study. Since we are extending our investigation to low kinetic energies using an electron optical and mechanical system different from any which we have used before at low energies, this pair of transitions is ideally suited to an exploratory study in which we are not only collecting useful data, but we are, at the same time, developing our spectrometer for use at low kinetic energies. This also prepares the way for the study of other substances and for the later determination of collision cross sections. Before discussing the results, some comments on the collision cell and electron lenses is needed.

The collision cell in our electron spectrometer has been electrically insulated so that its potential, relative to ground, can be changed. By changing the cell potential, the kinetic energy of the entering electrons can be changed without disturbing the velocity analyzers. In particular, electrons can be retarded to low kinetic energy before entering the cell. Since the entrance and exit slits for electrons into and out of the cell are the widest (0.04 inch) along the entire electron path, this is obviously the most advantageous place for low electron energies, since the transmission coefficient of electrons through slits is largest when the slits are widest. However, although a change in cell potential leaves the velocity analyzers unchanged, the same is not true of the electrostatic lenses between cell and velocity analyzers. A major change lies in the fact that electrons are now retarded between the monochromator and the collision cell. This shifts the principal planes of the composite electrostatic lens to the opposite

side of the lens center. The change amounts to more than a half inch, and hence its effect is not negligible. A similar change occurs in the lens on the downstream side of the collision cell. The lens performance (although less than optimal) may still be adequate for our purposes. It is well known that at low kinetic energies space charge and spurious surface fields can have an important effect on the performance of an electron optical system. We have already, several years ago, determined electron impact spectra at kinetic energies down to about 35 eV [J. Chem. Phys. 48, 5066 (1968)]. In these experiments, however, the electrons were accelerated (not retarded) between monochromator and collision cell, and hence the empirical phase of our instrument development (related to space charge, surface potentials, etc.) cannot be carried over to the changed configuration now in use. We need to systematically study some substance both to gain information about singlet-triplet transitions with unchanged term symbol and also to develop our electron spectrometer for use at low kinetic energies. The two transitions in nitrogen, discussed in the first paragraph of this section, are extremely well suited to both these purposes and an investigation is now in progress. Conceivably, some changes in lens design may result from these studies, but specific needs have not yet emerged and our proposal for next year contains no specific recommendations. If needed, however, changes will be made.

In the study of N_2 , we have begun at high kinetic energy and worked downward. For cross section measurements (at some stage in the future) good stability and reproducibility are essential, as well as

good symmetry in scattered current with change in angle around $\theta = 0^\circ$. These are being tested as electron impact spectra are determined. Electron impact spectra for N_2 at various kinetic energies and small scattering angles are shown in Fig. 3. Resolution is not high but is adequate for the two transitions, at 11.87 and 12.25 eV, for the determination of relative intensities. Electron impact spectra at different scattering angles, and kinetic energy, 200 eV are shown in Fig. 4. The lowest kinetic energy in Fig. 3 is 50 eV. Intensities and reproducibility are adequate at this kinetic energy. We have verified that adequate scattered current is obtained also at 25 eV, although more complete studies are necessary. We plan to investigate electron impact spectra at least to 15 eV kinetic energy, and perhaps lower. In general, the relative intensities of the transitions to $E\ 3\Sigma_g^+$ and $a''\ 1\Sigma_g^+$ behave in a manner quite similar to the transitions to 2^3S and 2^1S in helium. Until the investigation has progressed further, we cannot be more specific.

2.23 Other Substances

Studies of CH_3F and propylene similar to that on nitrogen in the preceding section are planned as soon as the nitrogen experiments are completed. Hopefully, this will be soon.

2.3 Ionization Continuum of H_2O

A new electron spectrometer, with fast coincidence capability, was developed on a program supported by AFOSR and is available, temporarily, along with Dr. M. A. Dillon for research on the current project. Two researches are planned on H_2O : (i) A brief study of the angle dependence

FIGURE 3
Nitrogen spectra at small
(or zero) angles at several
kinetic energies of inci-
dence from 400 eV to 50 eV.
Note peaks due to
 $X \ ^1\Sigma_g^+ \rightarrow E \ ^3\Sigma_g^+$ and
 $X \ ^1\Sigma_g^+ \rightarrow a'' \ ^1\Sigma_g^+$ at 11.87 eV
and 12.25 eV.

FIGURE 4
Nitrogen spectra at
incident kinetic
energy 200 eV and
several scattering
angles. Note
relative intensities
of the two transi-
tions $X \ ^1\Sigma_g^+ \rightarrow E \ ^3\Sigma_g^+$

and $X \ ^1\Sigma_g^+ \rightarrow a'' \ ^1\Sigma_g^+$
at 11.87 eV and
12.25 eV.

of the electrons ejected in ionizing collisions, and (ii) a study of the dependence of relative excitation probabilities of positive ion states on scattering angle and energy loss on collision. Dr. Robert Blaunstein has been informed about these plans.

This research has been held up by a vacuum problem. A vacuum pump had to be returned to the factory for repairs. It should be available soon.

3. STATUS OF AFOSR SUPPORTED RESEARCH. SPONSORSHIP BY NSF.

A new electron spectrometer, for the study of ionization continua using fast coincidence techniques, has been under development for several years on a program supported by AFOSR. When their grant terminated on December 31, 1974, it was not renewed. A proposal for support of the experimental part of the program was submitted to the National Science Foundation in early September, 1974, and we were notified in March, 1975, that NSF would support the program, at the requested level for two years, beginning May 1, 1975. This involves 35% of the salary of E. N. Lassettre and 100% that of Michael A. Dillon, the same percentages prevailing under the AFOSR Grant. The cost of the program for the first year is \$61,946 of which \$40,946 will be supplied by NSF the remainder by Carnegie-Mellon University. A proposal to the Petroleum Research Fund for support of a theoretical program (Winifred M. Huo) is pending.

As noted in Section 2.13, one research completed (as far as experimental work is concerned) with AFOSR support is of direct interest to the ERDA program covered in the present progress report. This concerns the collision cross section study of the transition $1^1S \rightarrow 2^3S$ in helium. Note that the orbital term symbol is unchanged in transition. Collision cross sections for this transition with incident electrons of kinetic energy 200, 300, 400, and 500 eV are shown in Fig. 5. 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

FIGURE 5
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.

can be assessed. The comparison is made in Fig. 6 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. 7, 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. 6 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. 5 over angle. That cross section is shown in the lower curve of Fig. 8. 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 Jough and 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. 5 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

FIGURE 6
Differential collision cross section vs. θ for $1^1S \rightarrow 2^3S$ transition in helium. Experimental cross section at 200 eV kinetic energy at top. Theoretical cross section (225 eV) at bottom.

FIGURE 7

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

FIGURE 8

Log Ω^{-1} vs. Log E for $1^1S \rightarrow 2^3S$ (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 $1^1S \rightarrow 4^3S$ transition; taken from Van Rann, DeJongh, Van Eck and Heideman, *Physica* 53, 45 (1971).

exchange scattering, although experiments show a simple dependence on energy.

A manuscript describing these results has been prepared and will be submitted for publication soon. ERDA will be given joint credit for support along with AFOSR for reasons stated in Section 2.13.

4. PUBLICATIONS

All publications sponsored by ERDA since the beginning of the project are listed. Those sponsored by AFOSR over the same period are also listed. Those papers either submitted or published since the last proposal are marked with an asterisk.

4.1 Supported by ERDA

4.1.1 Published

- 1) Skerbele, A. and E. N. Lassette, "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. Lassette, "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) Lassette, E. N., "Further Selection Rules in Excitation by Electron Impact at Small Momentum Changes," Journal of Chemical Physics **53** (10), 3801 (1970).
- 4) Lassette, 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. Lassette, "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. Lassette, "Absolute Generalized Oscillator Strengths for Three Transitions in the Mercury Spectrum," Journal of Chemical Physics **56**, 845-850 (1972).
- 7) Lassette, 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. Lassette, "Electron Impact Spectra of CH_4 and CF_4 ," Journal of Chemical Physics **58**, 1505 (1973).

- 9) Lassetre, 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. Lassetre, "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. Lassetre, "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. Lassetre, "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) Lassetre, E. N. and M. A. Dillon, "Singlet-Triplet Energy Differences Calculated from Generalized Oscillator Strengths," Journal of Chemical Physics 59, 4778 (1973).
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- *15) Lassetre, 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. Lassetre, "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. Lassetre, "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).
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4.12 In Press

- *19) Klump, K. N. and E. N. Lassetre, "Excitation Energy of 3B_1 State of H_2O Calculated from Generalized Oscillator Strengths," Canadian Journal of Physics (In Press).

4.2 Supported by AFOSR

4.21 Published

- 20) Meyer, V. D. and E. N. Lassette, "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).
- 21) Harshbarger, W. R., A. Skerbele and E. N. Lassette, "Generalized Oscillator Strength of the $A \leftarrow X$ Transition of Ammonia," Journal of Chemical Physics 54 (6), 3784 (1971).
- 22) Lassette, 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).
- 23) Huo, W. M., "Effective Long Range Potential for Scattering of Electrons by Atoms and Molecules," Journal of Chemical Physics 56 (7), 3468 (1972).
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- *25) Lassette, 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).
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- *27) Lassette, 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 (1974) pages 43-70.

4.22 In Press

- *28) Dillon, M. A. and E. N. Lassette, "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 (In Press).
- *29) Dillon, M. A. and E. N. Lassette, "Test of Born Approximation on the 60 eV Autoionized Transition in Helium," Journal of Chemical Physics (In Press).
- *30) 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 (In Press).

5. PERSONNEL

Dr. E. N. Lassetre (65% for 12 months), Dr. Kirby N. Klump
(100% for 12 months), Dr. Michael A. Dillon (100% for three months).