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GENERALIZED OSCILLATOR STRENGTHS

Progress Report

Edwin N. Lassettre

Carnegie-Mellon University
Pittsburgh, Pennsylvania

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DISCLAIMER

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Abstract

Progress is described on research under Contract AT(11-1)-3247 and research still to be completed in the period July 1, 1973 to July 1, 1974. The research objectives defined in the original proposal were closely followed. The principal accomplishments during the period were (a) The introduction of a computer controlled counting system with provision for automatic control and operation of the electron spectrometer currently in use. (b) Electron scattering with excitation of singlet-triplet transitions for helium was studied during the year both to acquire information on collision cross sections and to test a general theory of the abnormally high cross sections for forward scattering found for certain types of transitions. A theoretically predicted minimum in the cross section (at zero scattering angle) was found in a study over the range 100-500 eV of the $1^1S \rightarrow 2^3S$ transition of helium. Abnormally high cross sections for singlet-triplet transitions at high kinetic energy are predicted when the orbital term symbol is unchanged on excitation. As a test of the theory the $X^1\Sigma^+ \rightarrow b^3\Sigma^+$ transition in CO was looked for and found at $\theta = 0°$ at both 200 and 300 eV thus confirming the theory. (c) New electron scattering studies on both CO and CO_2 are described. (d) A new method for the calculation of singlet-triplet energy differences from generalized oscillator strengths is described.

1. INTRODUCTION

Progress in the study of electron scattering and generalized oscillator strengths under contract AT(11-1)-3247 in the period July 1, 1973 to July 1, 1974 is described. The program proposed for this period has been generally followed and steady progress has been made. The experimental phases of several researches have been completed. Others are in progress.

Extensive instrumental changes, begun in the previous contract period, have been completed in the present period. These are described in Section 2.1. An important investigation of singlet-triplet transitions has been carried out during the year and is described in Section 2. Experimental phases of this research were done in the present research program but an important theoretical contribution was made by Winifred M. Huo who is supported on an AFOSR Grant (E. N. Lassettre, Principal Investigator). Some results of her investigation are summarized in Section 2.2 to provide background for the experimental studies and to indicate the significance of the research. Dr. Huo's research was initiated to account for some immense discrepancies between theory and experiment pointed out by Skerbele, Harshbarger and Lassettre in an investigation supported by AEC and her theory has been tested experimentally by Klump and Lassettre as described in Section 2.2. Two other studies on singlet-triplet transitions are also described in Section 2.2. The status of experiments on H_2O, CO_2 and CO is described in Sections 2.3, 2.4 and 2.5, respectively. Deferred studies are mentioned in Section 2.6.

Additional support by the Air Force Office of Scientific Research is mentioned in Section 3. A publication list (including publications sponsored by AFOSR) is given in Section 4. Personnel are listed in Section 5.

2. CURRENT STATUS OF RESEARCH

2.1 Instrumentation

In the last proposal we noted the purchase of an automatic control system consisting of a PDP-8L Digital Computer together with stepping motors, power supplies, scalers, timers, amplifiers, an additional 4K of memory for the computer and all other accessories for the measurement of scattered current and beam current. Solid state electronic devices are employed throughout. Thus, the previous counting system has been replaced completely. This equipment was placed in service just prior to the beginning of the present contract period. During the current contract period computer programs have been developed for controlling the electron spectrometer. Scan of an electron impact spectrum is accomplished with a ten turn potentiometer actuated by a stepping motor. Scattering angle is changed by means of a gear turned by a stepping motor.

For the study of a sharp peak in an electron impact spectrum a program has been developed for stepping through the peak then returning to the peak and collecting a sufficient number of counts for a reliable average. A provision for the rejection of electronic noise bursts has been made. This is essential because, even though the apparatus and its associated electronic devices are electrostatically shielded, certain extreme types of electronic noise penetrate either through the shielding or via the power line. At each point in the spectrum several successive count rates are determined and a running average and standard deviation automatically calculated. Any count rate which departs from the average by more than five standard deviations is rejected (not stored in the memory) and the computer waits for the next count. At very low count rates, between peaks in a spectrum (where accurate quantitative data are less important), this program is bypassed so that inordinate amounts of time will not be spent on the least important portion of the spectrum.

For collision cross section studies there is usually a minimum angle within which data are not collected because low angular resolution introduces such large errors. Computer programs have been worked out by which scattering measurements can be started at a pre-selected large angle and a peak studied in the manner described in the preceding paragraph. The angle is then decreased by a pre-selected amount (usually one degree or a half degree) and the procedure repeated. When the (pre-selected) minimum angle is reached the spectral scan potentiometer automatically adjusts to a point in the spectrum where the count rate is low (to avoid heavy bombardment of the electron multiplier, and possible detrimental decomposition of an adsorbed film on the first dynode, as zero scattering angle is passed). The angle then automatically changes (through zero angle) to the minimum on the opposite side. Measurement is then resumed at progressively larger negative angles to some pre-selected maximum. The angle is then returned to its starting value (after overshooting and reversing to eliminate backlash) and the sequence begins again. Several repetitions are necessary to verify reproducibility. Additional programs to guard against systematic drift, etc., have been introduced and the overall program is constantly being developed and refined. Thus far, automatic operation has been confined to collecting the data on peak scattering with averages and standard deviations for complete angular runs. These are the most tedious operations. Collision cross sections and generalized oscillator strengths are calculated separately after the data have been inspected and its reliability established. Automatic, unattended, operation at night and on weekends is possible and has been successfully done on numerous occasions. Recently, however, we have been plagued by electronic noise which sets in immediately after the end of the working day and continues throughout the night. It stops abruptly at a time almost exactly coincident with the beginning of the new working day. As this is written we have not found the source of this noise. It may be due to some energy conservation measure, recently introduced, but this is only conjectural at present. It certainly is odd that even electronic noise abatement now operates on an eight hour day!

The computer memory is 8K, two 4K units. The first 4K unit contains the Canberra Industries modification of the Digital Equipment Focal Language. The second 4K memory unit is used for data storage and certain frequently used sub-routines entered in Assembly (Machine) Language. Electron impact spectra are usually obtained with a count rate meter and recorder while the spectrum is scanned by continuously rotating a potentiometer with a synchronous motor. This does not use the computer at all. However, for the determination of areas, or the more accurate definition of peak shapes, provision has been made for the automatic (computer controlled) scan of a spectrum (or portion of spectrum) with a stepping motor. Count rates (and standard deviations) are stored in the computer memory and spectra are automatically plotted after a run is completed. This operating mode is employed only when precise quantitative data are needed or when low counting rates make long integration times necessary.

In introducing computer controlled operation, all electronic counting equipment has also been changed. The only unchanged component is the counter tube. Obviously, it has been necessary to fully explore the capabilities of this apparatus by collision cross section studies and to compare with previous results. Apparently, higher scattered currents can be studied without departure from linearity. However, these solid state electronic devices are less rugged than vacuum tube equipment. We have had difficulty with damage due to accidental exposure to high voltages but, hopefully, this has been eliminated (or at least minimized). The new counting system is apparently a substantial improvement, once we have learned to use it properly.

A new magnetic shield, covering the entire spectrometer, has been installed and tested. It has proved to be less satisfactory than our previous method of shielding each analyzer and using Helmholtz coils. Hence we have returned to this latter method, which is simpler and equally accurate.

Instead of controlling emission current we have introduced means for the measurement of beam current actually entering the scattering chamber and have programmed the computer to divide each scattered current by the beam current. In recent experiments, however, the beam current has been constant over such long periods that this step has been omitted in relative measurements such as comparison of inelastic with elastic scattering.

Except for further refinement of computer programs, our instrumental changes have been completed.

2.2 Singlet-Triplet Transitions

Substantial progress has been made in the study of singlet-triplet transitions at high kinetic energy of incident electrons (several hundred electron volts). There is a view, held in some quarters, that (a) singlet-triplet transitions can only be excited with significant probability at low kinetic energies of incident electrons and (b) even at low kinetic energies the collision cross section is small except at large scattering angles. We have discovered that a general class of transitions exists for which both (a) and (b), above, are false. Moreover, these exceptional transitions are more likely to be found in complicated systems of low symmetry which are often encountered in Radiation Chemistry or Biology. The result was discovered during the study of the $1^1S \rightarrow 2^3S$ transition in helium and generalized by means of a theoretical study. The results are summarized in Section 2.21 below. Other aspects of singlet-triplet transitions are mentioned in Sections 2.22 and 2.23.

2.21 Large Cross Sections in Forward Scattering. Influence of Orbital Term Symbols. $1^1S \rightarrow 2^3S$ Transition in Helium

Skerbele, Harshbarger and Lassettre (No. 11 of the Publication List) studied the ratio of the cross section, σ_T, of the transition $1^1S \rightarrow 2^3S$ to that, σ_S, of the transition $1^1S \rightarrow 2^1S$ in helium in forward scattering ($\theta = 0°$) with electrons of initial energy 300, 400, and 500 eV. From the known cross section, σ_S, at 500 eV [Skerbele and Lassettre, J. Chem. Phys. 45, 1077 (1966)] the value of σ_T, 0.0026 atomic units, is obtained. The most elaborate prior computation [R. A. Bonham, J. Chem. Phys. 57, 1604 (1972)] gives a value of σ_T 200 fold smaller than the above observed value. Calculations based only on the first Born approximation with exchange give even worse agreement with the experiment.

A comprehensive theory of singlet-triplet excitation has been developed by Winifred M. Huo, who is supported by AFOSR (see Section 4), including both first and second Born terms with exchange. The second Born term with exchange involves a sum over the spectrum. Using a modification of the Ochkur-Bonham expression for exchange amplitudes at high kinetic energy [V. I. Ochkur, Soviet Phys. JETP 18, 503 (1964)]. She obtained the leading term of an expansion in inverse powers of k_o, where k_o is the wave vector of incident electrons. That leading term can in turn be expressed as the Fourier transform of an effective potential function

$$\int e^{i\underset{\sim}{K}\cdot\underset{\sim}{r}} U_{of}(d_{\underset{\sim}{r}}) + O(1/k_o{}^3) \qquad (1)$$

where $\underset{\sim}{K}$ is the momentum change of the colliding electron and U_{of} is a quantity with the dimensions of energy. Equation (1) is now in a form similar to that obtained by Huo for direct scattering [W. M. Huo, J. Chem. Phys. 56, 3468 (1972)]. Note that the Ochkur-Bonham approximation was used for this precise purpose, i.e. to obtain for the exchange amplitude a relation (valid at high kinetic energy) which is similar in form to the expression for direct scattering. The reasoning previously employed for direct scattering can now be employed for exchange scattering namely, expand the function U_{of} in inverse powers of r; the first non-vanishing term will determine the behavior of the amplitude at small values of K. (This is physically clear because small K means small momentum change which means in turn that the force acting during collision must be small and hence a distant collision is implied. This physically obvious point can be verified in more formal mathematical ways directly from equation (1).)

Huo found (see No. 23 of Publication List) that the first non-vanishing term of U_{of}, in inverse powers of r, varies like α_{of}/r^4 where α_{of} may be accurately described as the *exchange transition polarizability*. Huo showed that the *exchange transition polarizability vanishes unless the orbital term symbols in initial and final states are the same*. Atoms and molecules possess symmetry groups whose elements operate only on the positional spin entirely. The orbital term symbols designate irreducible representations of these groups. For example, for the state 2^3S of helium, S is the orbital term symbol. Skerbele, Harshbarger and Lassettre (No. 11 of Publication List) pointed out the possibility of such a selection rule, as a conjecture based on very little experimental data. Its existence is now demonstrated in the limit of high kinetic energy of incidence for systems of any complexity.

Harshbarger, Skerbele and Lassettre (No. 11 of Publication List) pointed out that the observed ratio σ_T/σ_S exceeds that calculated from the first Born approximation (with exchange) by at least a factor of 500. The selection rule described above is based on the second Born approximation. Obviously, it is only of value if the first and second Born approximations, with exchange, actually account quantitatively for the scattering. Since, however, the first term of the Born series is too small by five hundred fold to account for the collision cross section we certainly cannot assume, without a numerical demonstration, that the first two terms are enough to account quantitatively for the cross section. The simplest substance which exhibits singlet-triplet transitions is helium and hence in this case it is of extreme importance to show by numerical calculation that the first and second Born approximations (with exchange) are capable of accounting for the collision cross section quantitatively. Winifred Huo has done such calculations (No. 23 of Publication List). Her best approximation gives 0.0040 atomic units for the cross section σ_T with incident electrons of kinetic energy 500 eV. The experimental value is 0.0026 ± .0006. The discrepancy is probably attributable to approximations in the theory. A striking feature of the theory is a pronounced minimum in the collision cross section at about 150 eV. The minimum occurs because the collision amplitude in first Born approximation is real, has a different energy dependence than the second Born amplitude, and is opposite in sign to the real part of the second Born amplitude. The minimum occurs at that energy where the two cancel. Since the imaginary part of the second Born amplitude does not vanish the cross section does not vanish.

The minimum in cross section, for forward scattering, is sufficiently interesting to justify an experimental study. Preliminary results were mentioned in our previous proposal. However, doubts (since cleared up) developed about the applicability of the approximate theory used at that time. Hence the experiments were repeated and extended by K. N. Klump on our AEC project. The ratio σ_T/σ_S was systematically studied near $\theta = 0°$. The background is very intense under these conditions, because the unscattered beam (which is very intense) enters the velocity analyzer and is scattered many times from metal parts. Some of these electrons always reach the detector. Since the $1^1S \rightarrow 2^3S$ transition is weak and is superimposed on an intense background (which varies with scattering angle) considerable care must be exercised to avoid gross error. The ratio σ_T/σ_S was determined as a function of angle around $\theta = 0°$ and the beam focus adjusted until the ratio (corrected for background) was symmetrical around $\theta = 0°$. This is a sensitive test for accurate alignment, an important consideration near $\theta = 0°$. Observations were repeated until a reliable average was obtained at each angle. Although simple in principle the experiments were very tedious and time consuming because it is so difficult to obtain accurate beam alignment near $\theta = 0°$. Very slight changes in magnetic field, or even changes in intensity distribution in the incident electron beam lead to an apparent change in beam direction and introduce large changes in intensity. Fortunately, the ratio is less sensitive than the scattered current for either transition, although still variable. The final experimental results for σ_T/σ_S are shown in Fig. 1 together with the calculated triplet cross section curves of Huo. It is known from theoretical calculations by other investigators (checked at some energies by experiment) that σ_S at $\theta = 0°$ is nearly constant over the range 100 to 500 eV. Hence the minimum in the experimental curve (which is certainly real) is due to σ_T. Calculation I, the most accurate, agrees reasonably well with the experiment. Calculation II, using screened hydrogenic functions, is more in error but still possesses a minimum. The existence of a minimum in the calculated curve is not sensitively dependent on the accuracy of the basis set used although the magnitude of the cross section is strongly dependent on this factor. The data of Fig. 1 refer only to $\theta = 0°$. The variation of the ratio with angle was used a criterion of correct beam alignment (the requirement of symmetrical curve around $\theta = 0°$). The remaining data are not reported because an extensive study has been done by Michael A. Dillon (see Section 4) on an AFOSR supported research using a newly developed electron spectrometer of very high aperture. These measurements begin at $\theta = 7.5°$ and provide all the data needed on angular trends. In summary, there can be little doubt that the first and second Born approximations (with exchange) can account quantitatively for the collision cross section

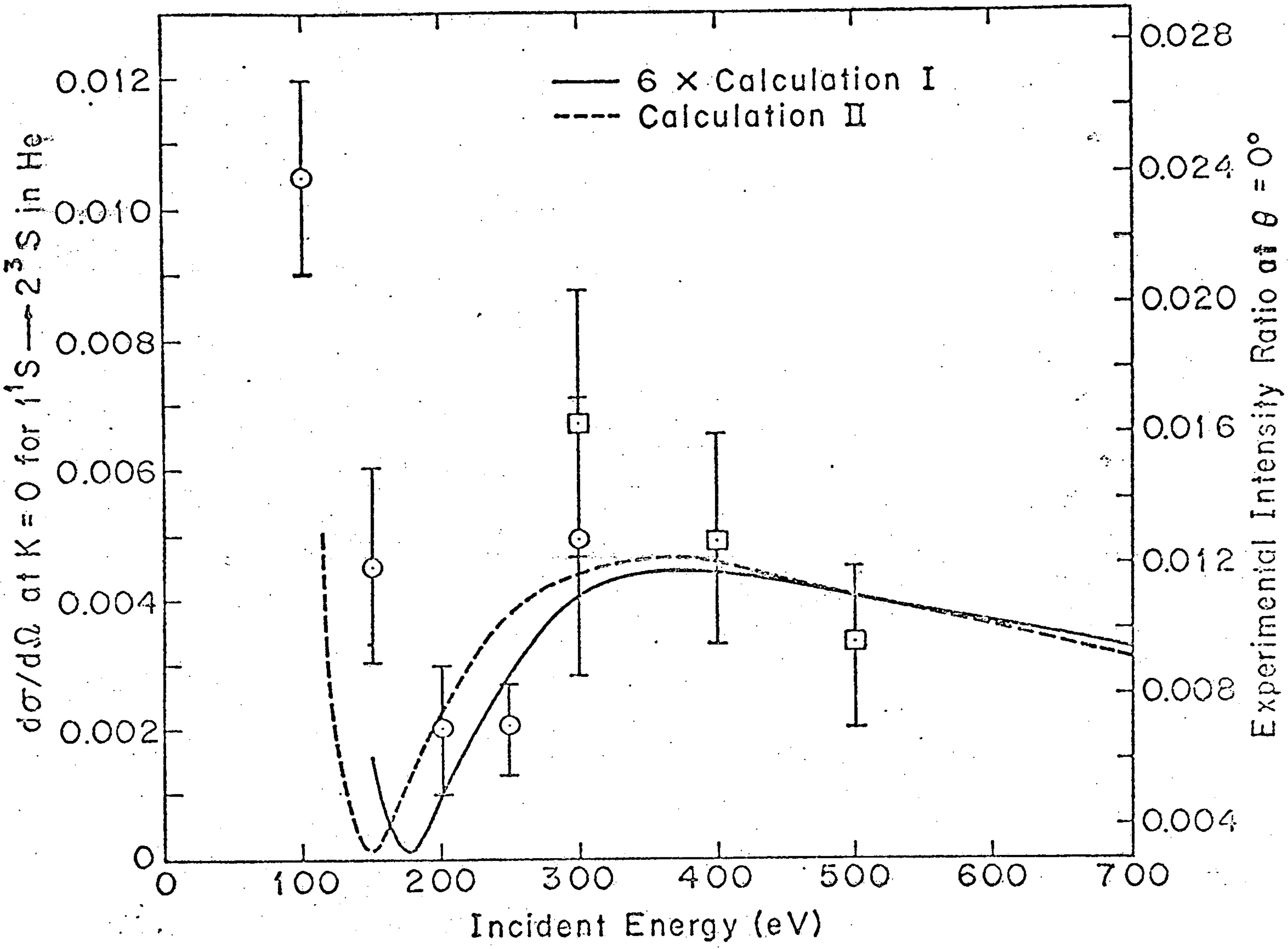
6 × Calculation I
Calculation II
$d\sigma/d\Omega$ at K = 0 for $1^1S \longrightarrow 2^3S$ in He
Experimental Intensity Ratio at $\theta = 0°$
Incident Energy (eV)
0
0.002
0.004
0.006
0.008
0.010
0.012
0.004
0.008
0.012
0.016
0.020
0.024
0.028
0
100
200
300
400
500
600
700

Figure 1

σ_T at $\theta = 0°$. Hence, it is a fair inference that Winifred Huo's demonstration (based on the second Born approximation) of a limiting selection rule at high kinetic energy is applicable to a wide variety of substances. This has far reaching implications which are briefly described below.

For the transition $1^1S \rightarrow 2^3S$ in helium the second Born approximation (with exchange) is far more important, at $\theta = 0°$ and high kinetic energies, than is the first Born approximation (with exchange). However, the selection rule mentioned above implies that the second Born approximation is most important for that class of transitions for which the orbital term symbols in the ground and excited states are the same. In molecules of low symmetry this situation is frequently encountered. Optically active molecules (frequently found in substances of biological interest) have no symmetry except the identity. The identical irreducible representation is the only one for a symmetry group consisting of the identity operator. Hence all electronic states belong to the same irreducible representation, have the same orbital term symbol, and hence the second Born terms cannot be safely neglected for an electronic transition. Conclusions based on the first Born approximation (with exchange) cannot be trusted in applications involving complicated systems.

The selection rule, referred to above, explains an apparent anomaly in the electron impact spectrum of N_2. In 1966, Meyer and Lassettre [J. Chem. Phys. 44, 2535 (1966)] reported a weak transition at 11.86 eV with incident electrons of kinetic energy 400 eV. Although the excitation energy agrees well with the assumption that the E state of nitrogen (a triplet) is the excited state, it seems so unusual to observe a singlet-triplet at such high kinetic energy in forward scattering that we suggested that the excited state was a singlet. The term symbol of the E state is $E^3\Sigma_g^+$ and the ground state of nitrogen is $X^1\Sigma_g^+$. Obviously, the oribtal term symbol is the same in ground and excited state and hence the second Born term (with exchange) will be high. In brief, once the correct mechanism is recognized there is nothing unusual about the excitation of the $E^3\Sigma_g^+$ state at high kinetic energy in forward scattering. The contradiction is completely resolved.

Now that we know what to look for it should be possible to detect other singlet-triplet transitions in forward scattering at high kinetic energy. With this in mind we have re-examined the spectrum of carbon monoxide. A section of the spectrum obtained at $\theta = 0°$ and electrons of kinetic energy 200 eV is shown in Fig. 2. The peak corresponding to excitation of the $b^3\Sigma^+$ state is obvious. The ground state term symbol is $X^1\Sigma^+$ and hence the orbital term symbol, Σ^+, is the same in both ground and excited states. The second order Born terms (with exchange) are no doubt dominant as the selection rule suggests. This excitation is also observed with 300 eV incident electrons. We have not searched with higher kinetic energy electron beams.

It is now confirmed by both theory and experiment that a class of transitions exists whose cross sections in forward scattering are abnormally high at high kinetic energy. It is predicted that transitions of this type will be commonplace for complex molecules of low symmetry.

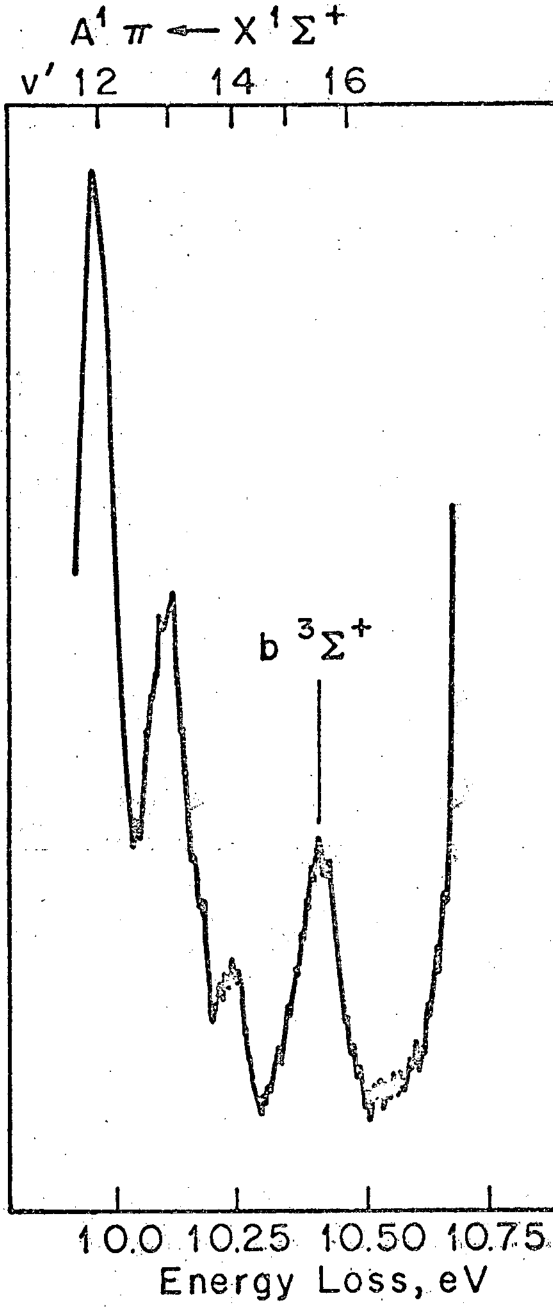
$A^1\pi \leftarrow X^1\Sigma^+$
v' 12
14
16
$b\ ^3\Sigma^+$
10.0
10.25
10.50
10.75
Energy Loss, eV

Figure 2

2.22 Singlet-Triplet Energy Differences

In the last proposal a formula was given for the difference in energy between the singlet, E_S, and the triplet, E_T, arising from the excitation of one electron from a closed shell ground state

$$E_S - E_T = \frac{1}{\Pi g W} \int_0^\infty K^2 f_B dK \qquad (2)$$

where W is the excitation energy of the singlet, g is its degeneracy, and f_B is its generalized oscillator strength as a function of momentum change K. The subscript B indicates that the formula was derived using the formula for f corresponding to the Born approximation. If, therefore, experimental f's are used they must be obtained at high kinetic energy where the Born approximation holds. This research is concluded and a paper describing the research published during the present contract period. (No. 13 of Publication List).

2.23 Water Triplet

As reported in our last proposal, Eq. (2) has been used, together with measured oscillator strengths at small scattering angles, to calculate $E_S - E_T$. An accurate calculation is not possible because oscillator strengths have not been measured at large momentum changes. However, bounds can be placed on $E_S - E_T$ as follows

$$E_S - E_T = 0.58 \pm 0.42 \text{ eV}.$$

This represents a band within which $E_S - E_T$ is presumed to lie. The value

0.58 does not represent our estimate of the most probable value but is merely the center of the range. The true value of $E_S - E_T$ is probably less than 0.58. In any case it is established that the vertical excitation energy of the transition $^1A_1 \rightarrow {}^3B_1$ is 6.82 ± 0.42 eV. The transition $\sim$ 4.5 eV may be a part of the envelope of $^1A_1 \rightarrow {}^3B_1$ but is certainly not the vertical excitation energy of that transition. A paper describing these results has been accepted for publication in the Journal of Chemical Physics (No. 14 of Publication List).

There is a controversy concerning the lowest triplet state of H_2O. Theoretical calculations on the $^3B_1$ state by many investigators have led to the conclusion that the state is not bound relative to either $OH(^2\Pi) + H(^2S)$ or $O(^3P) + H_2(^1\Sigma_g^+)$. Hence these studies predict that no excited triplet state can exist, at any nuclear configuration, which is less than 5.07 eV above the ground state. Experimentally, however, several different investigators have found, by entirely different techniques, excitation at energies down to $\sim$ 4 eV. This discrepancy is of more than academic interest for the following reason. If the lowest energy triplet is not bound then all non-linear excited triplet states are certain to result in dissociation of the molecule for the following reason. There are no forbidden electronic transitions in molecules with symmetry groups C_2V or C_S. Hence, if a stable triplet with either symmetry is excited then it will cascade (by radiation emission) to progressively lower states until it finally reaches the ground state where it will dissociate. Hence, the triplet state radiation chemistry of water will be that of atoms and radicals since these are the dissociation products. If, on the other hand, the lowest triplet possesses bound states, then a long lived triplet must be involved to some degree in the radiation chemistry of water. At present, theoretical quantum chemistry, indicates the former while experiment indicates the latter. The experiments cannot be arbitrarily dismissed as incorrect. They must be accounted for in some other manner than excitation of a triplet. Thus far no such explanation exists.

2.3 Generalized Oscillator Strengths for H_2O

Determination of generalized oscillator strength of 7.4 eV transition in H_2O out to large scattering angles at several kinetic energies is needed in order to apply equation (2) above to water vapor with greater accuracy than was possible in previous research (No. 14 of Publication List). The determinations have been started but were interrupted in order to complete the study of CO_2 described in the next section. The investigation will be resumed as soon as the CO_2 experiments are finished.

2.4 Electron Scattering by CO_2

In the last proposal it was stated that "the experimental phase of these determinations has been completed, but the results have not been fully interpreted". When we finally began to interpret the data, while preparing a paper on CO_2 for inclusion in the R. L. Platzman Memorial Issue of the International Journal of Radiation Chemistry and Physics, we found that additional experiments on the 11.08 eV transition were needed. These experiments, at 500 eV and 300 eV, are in progress. A manuscript will be prepared as soon as these determinations are completed.

Some additional experiments have also been done on the 7-10 eV portion of the CO_2 spectrum. To explain the reason it is necessary to review the background in some detail. Extensive quantum mechanical calculations, involving superposition of up to 1400 configurations, were done by Winter, Bender and Goddard [Chem. Phys. Lett. 20, 489 (1973)]. Only the energies of excited electronic states were calculated. By comparing the calculated excitation energies with peak positions in ultraviolet and electron impact spectra term symbols were assigned to each excited state. Winter, Bender and Goddard referred to these as "definitive" assignments. Two states, $^1\Delta_u$ at 8.38 eV and $^1\Sigma_g^+$ at 9.23 eV, had excitation energies nearly matching the two observed peaks at 8.52 eV and 9.30 eV found in both ultraviolet spectra and electron impact spectra at high kinetic energy and $\theta = 0°$. This is contrary to the assignment of Lassettre and Shiloff [J. Chem. Phys. 43, 560 (1965)]. Despite the good agreement between excitation energies, there are strong arguments against this assignment. These have been described in a recent review (No. 24 of Publication List). The principal objection is that the Franck-Condon Principle was incorrectly applied. In an electron impact spectrum, the intensity distribution for a forbidden electron transition in a polyatomic molecule may change with angle; even the number of peaks may change. This can best be seen by expanding the collision cross section in a power series at high enough energies so that the Born approximation holds. If we are dealing with a transition which is forbidden in the sense that a vertical transition from the equilibrium ground state configuration has a vanishing transition moment then it may still appear weak because an expansion of the transition moment in a power series in the ground state normal (displacement) coordinates will have linear (or higher order) terms which are non-vanishing. In the expansion of the cross section σ in powers of the momentum change, K, the first term is proportional to the square of the electric dipole moment and is proportional to $1/K^2$. At $\theta = 0°$ and high kinetic energy K^2 is small and $1/K^2$ large. Hence the first term dominates the series. The intensity distribution among vibrational levels is determined, for vertically forbidden transitions with non-vanishing linear terms, by integrals like

$$\int q_i \phi_o \phi_n dq \tag{4}$$

where q_i is the i^{th} normal coordinate (ground electronic state) and ϕ_o, ϕ_n are vibrational functions in the ground and excited electronic states, respectively. The integration is over all normal coordinates. The quantity q_i arises from the linear terms in the transition moment expansion mentioned above. For a vertically allowed transition we obtain instead of (4) a normal Franck-Condon integral

$$\int \phi_o \phi_n dq. \tag{5}$$

In a normal Franck-Condon integral like (5) it is well known that ϕ_o is strongly peaked around the equilibrium ground state configuration, $q_i = 0$. The integral (5) has its maximum value for excitation states, n, for which ϕ_n is also peaked around $q_i = 0$. This leads to the familiar construction in which a vertical line is extended upward from the minimum of the ground state potential function to the intersection with the excited state potential function. The nearest energy state is that of greatest intensity.

In (4), however, we must consider the maximum of $q_i\phi_o$ rather than ϕ_o. This will have a maximum at some value $q_i^{(o)}$ different from zero. Hence, to locate the state of maximum intensity we must extend a line upward from $q_i^{(o)}$. In the case of CO_2 q_i may be a bending coordinate. In which case at $q_i^{(o)}$ the molecule is no longer linear. Hence doubly degenerate states like $^1\Delta_u$ and $^1\Pi_g$ split into two components. For the state $^1\Delta_u$ all the linear terms in the expansion of transition moment vanish but for $^1\Pi_g$ the linear terms do not all vanish and one of the non-vanishing components is that which bends CO_2 away from the collinear configuration. It follows that vertical excitation is allowed to <u>both</u> of the split components of $^1\Pi_g$ and we obtain two peaks. The next term in the expansion of σ in powers of K involves K^0, i.e. is independent of K, and Franck-Condon integrals like (5) are involved. At $\theta = 0°$ the first term dominates because K^2 is so small and the intensity distribution contains two peaks. At large angles $1/K^2$ becomes very small and the first term becomes negligible. The second term in the series then dominates. But a normal Franck-Condon factor, like (5), determines the intensity distribution in that case; only <u>one</u> peak is expected. Lassettre and Shiloff showed that the intensity distribution at $\theta = 0°$ does contain two peaks while that at $\theta = 3.9°$ contains only one. Moreover, they also showed that all terms linear in the q_i's vanish for transition to $^1\Delta_u$ and hence they concluded that $^1\Delta_u$ could <u>not</u> be the excited state term symbol for either peak. Winter, Bender and Goddard ignored this argument and made an incorrect assignment. Hall, Trajmar and Chutjian [J. Phys. B <u>6</u>, 1264 (1973)] have studied the electron impact spectrum at very low electron energies, ∿ 12 eV, and excited a state which they identified as $^1\Delta_u$. Even if this is correct, and it is not proven, it is not relevant to either the ultraviolet adsorption spectrum of the high energy electron impact spectrum because at low energies the Born approximation fails and there is no adequate theory of intensities.

Vincent McKoy and his collaborators have been developing the equations of motion method as a means of calculating both excitation energies and intensities. Recently, C. W. McCurdy and V. McKoy have applied this method to CO_2 and have provided us with a preprint. Carrying out their calculations with a linear molecule they obtained results in agreement with Lassettre and Shiloff but since the calculations took no account of deviation from linearity they did not obtain two peaks at $\theta = 0°$. Otherwise, however, the agreement with Lassettre and Shiloff was good. They calculated generalized oscillator strengths for the excitation of both ${}^1\Pi_g$ and ${}^1\Delta_u$. At small K^2, $f_{{}^1\Delta_u}$ is negligible but at $K^2 \simeq 1.1$, an $f_{{}^1\Delta_u}$ and $f_{{}^1\Pi_g}$ are nearly the same. Above $K^2 = 1.1$, $f_{{}^1\Delta_u}$ becomes dominant, at least according to their calculations. An experimental study of the envelope shape of the 7-10 eV region should reveal the development of the transition ${}^1\Sigma_g^+ \rightarrow {}^1\Delta_u$. If this occurs in accord with the calculations of McCurdy and McKoy then the assignment would be definitively established. Hence an experimental study was undertaken with results shown in Fig. 3 which shows the 7-10 eV region of CO_2 at several different scattering angles with incident electrons of 400 eV energy. At $\theta = 0°$ and 5° the envelopes were obtained in the usual way with a count rate meter and recorder. At larger angles it was necessary to test for multiple collisions by varying the pressure over a tenfold range. The count rates were so low that the

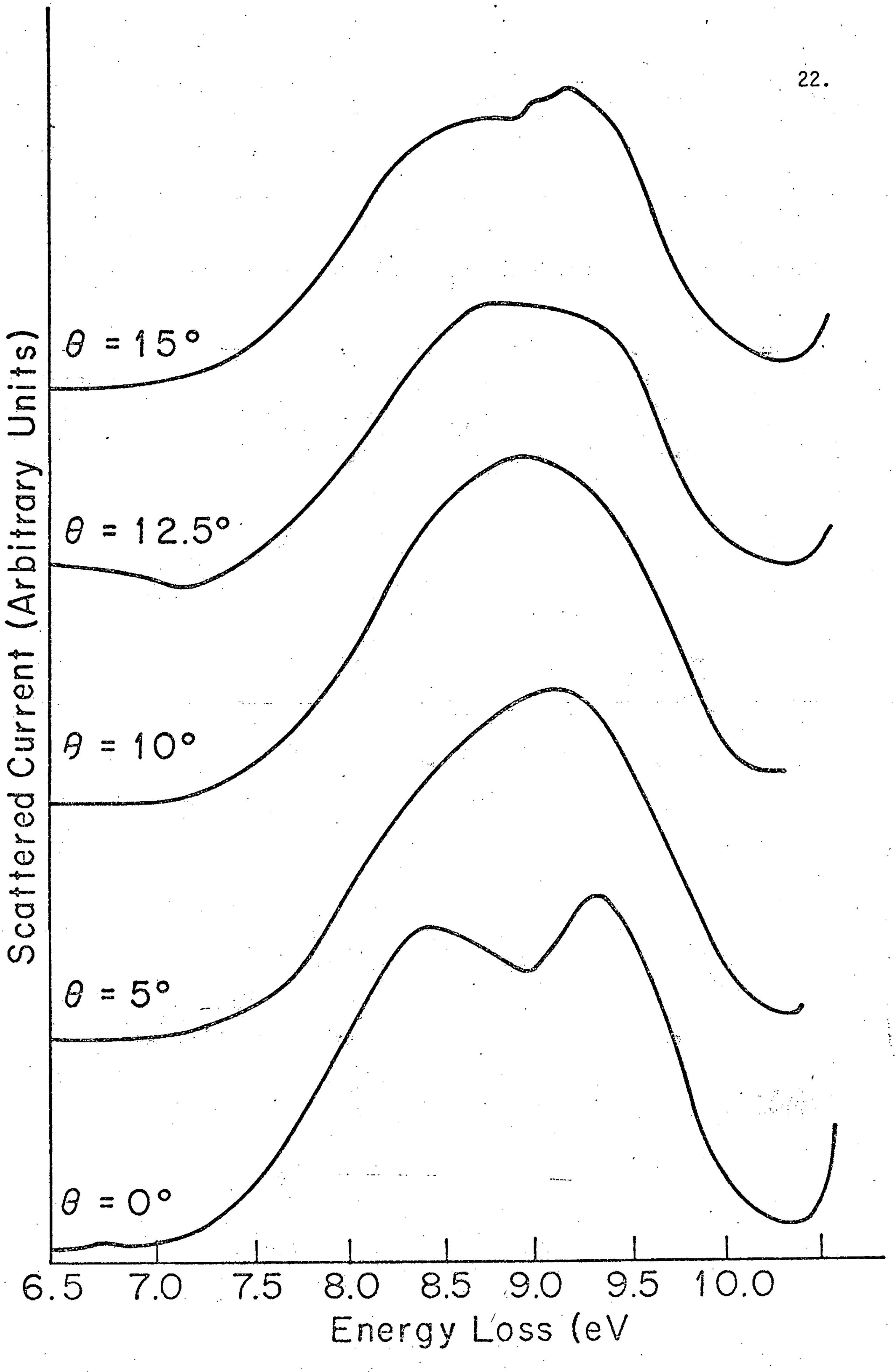
Scattered Current (Arbitrary Units)
θ = 15°
θ = 12.5°
θ = 10°
θ = 5°
θ = 0°
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
Energy Loss (eV

Figure 3

spectra were scanned automatically in the computer controlled mode. Long counting times were employed, to obtain enough counts for statistically significant results. Count rates were stored in the memory and enough repetitions were done to prove reproducibility. At the time this was done, the noise level at night was low and hence automatic operation over long time periods was possible. The data of Fig. 3 are free of error due to multiple collisions and the curve shapes are reliable and reproducible. The two peaks, due to split $^1\Pi_g$, at $\theta = 0°$ are obvious. At 5° only one peak is found. The peak position agrees well with that calculated by Winter, Bender and Goddard for $^1\Pi_g$, as it should. At 10° ($K^2 = 0.887$) the envelope shape has changed in just the way expected if $^1\Delta_u$ were beginning to affect the excitation spectrum. At 12.5° ($K^2 = 1.494$) a further change has occurred which is entirely consistent with the growth of a peak at $\sim$ 8.5 eV, just at the place expected for $^1\Delta_u$ and with approximately the intensity, relative to $^1\Pi_g$, expected from the calculations of McCurdy and McKoy. However, at 15° another peak has developed at $\sim$ 9.0 eV. Apparently a third transition is appearing but we cannot identify it. This new peak also appears in spectra obtained at larger angles but we have not reported these results since the data are less reliable and reproducible. As far as the $^1\Delta_u$ state is concerned we think that we have found it at high energies and large angles and have confirmed the calculations of McCurdy and McKoy. An additional, unidentified state is also indicated. For the present we see no reason for further experiments. Except for the study of the 11.08 eV transition, mentioned above, the CO_2 investigation is finished. The assignment of Lassettre and Shiloff is confirmed.

2.5 The $X^1\Sigma^+ \rightarrow B^1\Sigma^+$ Transition of CO

Generalized oscillator strengths for the transition $X^1\Sigma^+ \rightarrow B^1\Sigma^+$ were determined in 1971 by Skerbele and Lassettre [J. Chem. Phys. 55, 424 (1971)] while testing a new selection rule. The oscillator strength, as a function of K^2, drops steeply to a minimum and then rises to a broad maximum, the Born approximation being obviously violated at the larger values of K^2. ($K^2_{max} \simeq 0.5$ au). McKoy and his collaborators have also calculated, recently, the oscillator strength for this transition. Although their calculations give good agreement with observation for the fourth positive bands the agreement for the transition $X^1\Sigma^+ \rightarrow B^1\Sigma^+$ is poor not only in that the oscillator strength curve has no minimum but the optical oscillator strength ($K^2 = 0$) is in poor agreement with experiment (it is too high). McKoy suggested that breakdown of the Born-Oppenheimer approximation might be responsible for this. This point can be tested experimentally by determining the scattered current ratio for the two vibrational peaks $v' = 0$ and $v' = 1$ of the transition $X^1\Sigma^+ \rightarrow B^1\Sigma^+$. (Predissociation sets in at $v' = 2$.) The ratio as a function of angle at five different incident energies is shown in Fig. 4. At 400 eV, for example, the ratio changes by a factor of ten in going from $\theta = 0°$ to $\theta = 20°$. This is in marked contrast to the case where the Born-Oppenheimer approximation holds. Extensive tests have been done on many such transitions and the relative intensities of vibrational progressions have been found to be constant, or nearly so, in all cases. This point is illustrated in Fig. 5 which shows two carbon monoxide spectra at $\theta = 0°$ and $\theta = 15°$. The relative intensities of the fourth positive bands are the same at the two but the $v' = 0$ and $v' = 1$

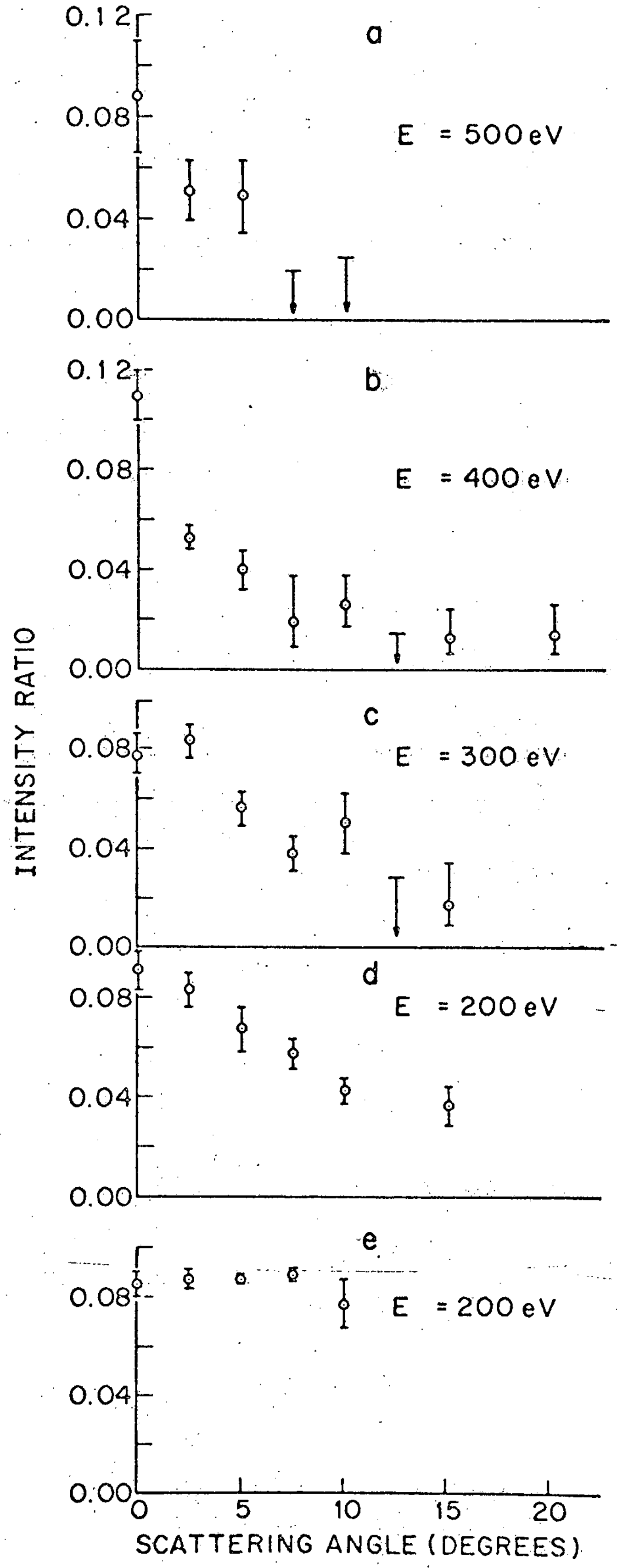
a
E = 500 eV
b
E = 400 eV
c
E = 300 eV
d
E = 200 eV
e
E = 200 eV
INTENSITY RATIO
0.12
0.08
0.04
0.00
SCATTERING ANGLE (DEGREES)
0
5
10
15
20

Figure 4

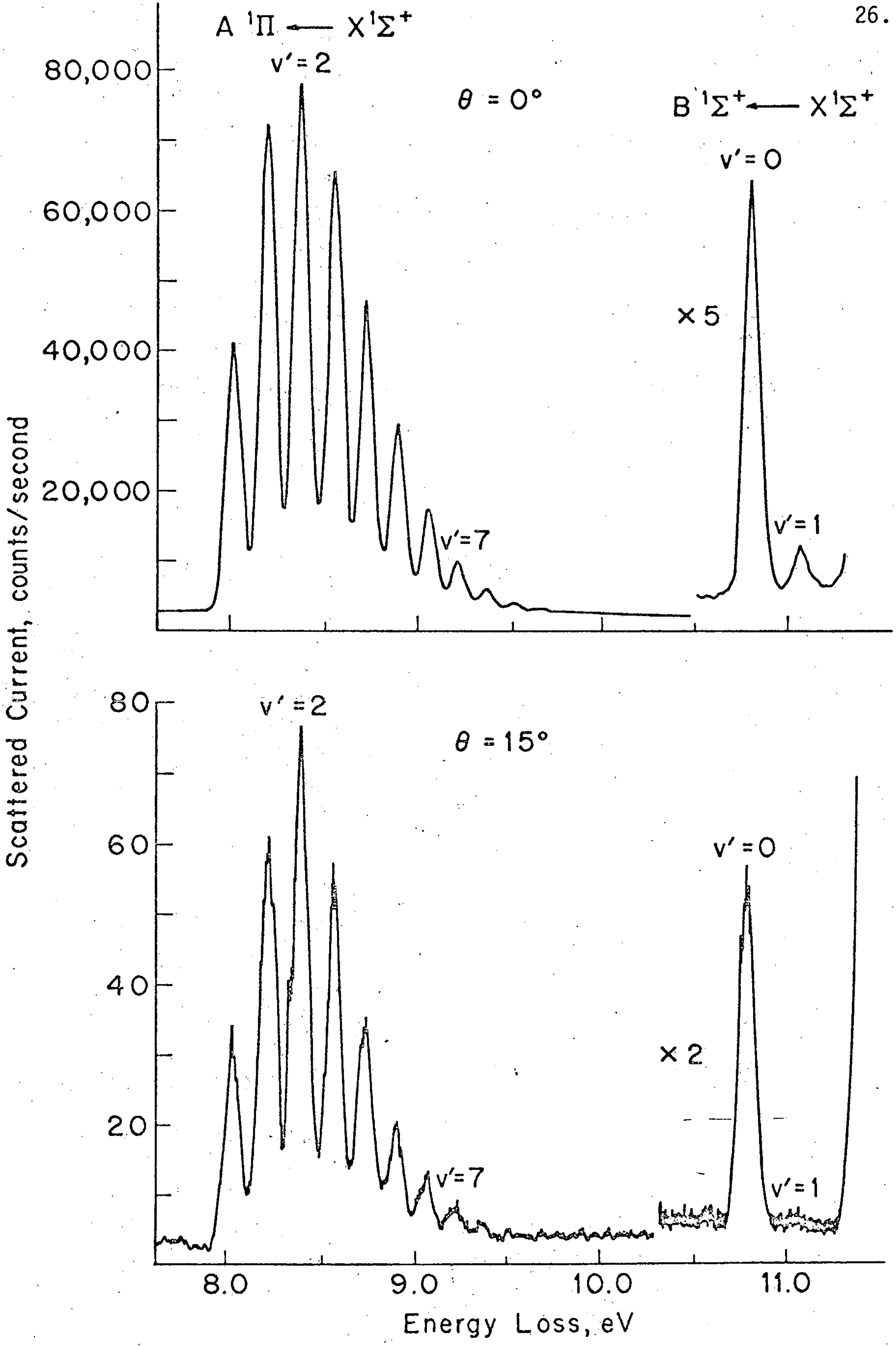
A ¹Π ← X¹Σ⁺
v′=2
θ = 0°
B ¹Σ⁺ ← X¹Σ⁺
v′=0
×5
v′=7
v′=1
80,000
60,000
40,000
20,000
80
60
40
20
v′=2
θ = 15°
v′=0
×2
v′=7
v′=1
8.0
9.0
10.0
11.0
Energy Loss, eV
Scattered Current, counts/second

Figure 5

relative intensities of $X^1\Sigma^+ \rightarrow B^1\Sigma^+$ are greatly different. McKoy's suggestion of a breakdown of the Born-Oppenheimer approximation seems to be confirmed. A manuscript describing these results is in press (No. 16 of the Publication List).

2.6 Other Investigations

In previous proposals an angular study of the $1^1S \rightarrow 2^1P$ and $1^1S \rightarrow 2^1S$ transitions in helium has been mentioned. The investigation of Michael A. Dillon, supported by AFOSR (see Section 4), has been so successful and is so complete that no additional research seems justified. Hence, this project has been abandoned.

An oscillator strength study of benzene has been proposed. This is being postponed, probably until the new contract period.

A study of the $X^1\Sigma_g^+ \rightarrow E^3\Sigma_g^+$ transition in N_2 was proposed for the present contract period. This has been delayed until the studies on H_2O and CO_2 are completed. If necessary the study will be carried over into the new contract period.

Studies at low kinetic energy have been postponed but are very much worthwhile and will be done eventually.

3. STATUS OF AFOSR SUPPORTED RESEARCH

A program of research on inelastic electron scattering by atmospheric gases is supported by the Air Force Office of Scientific Research. Financial support amounting to $49,903 has been provided for 1974. Currently employed are Dr. Winifred M. Huo (full time), Dr. Michael A. Dillon (full time) and Dr. E. N. Lassettre (35% time). A new electron spectrometer is being developed for the study of ionization continua using coincidence counting techniques. The instrument can also be employed for conventional scattering experiments. Dr. Dillon has determined, among others, collision cross sections for the $1^1S \rightarrow 2^3S$, $1^1S \rightarrow 2^1S$, $1^1S \rightarrow 2^1P$ transitions in helium with an accuracy of 5% over the kinetic energy range 200-700 eV. Winifred Huo has completed her theory of singlet-triplet excitations. This research, which is important in the AEC sponsored program, has been summarized in an accompanying progress report and compared with experimental observation.

The electron spectrometer has been successfully used in coincidence. Its development has reached an advanced stage. It is now in use for the study of ionization processes. Plans are in progress for the incorporation of radiative lifetime determinations in such fashion as to eliminate (or minimize) cascading. It is probable that results obtained with this instrument will be of increasing interest in radiation chemistry in the future. The instrument will be available for occasional use in the AEC sponsored program.

4. PUBLICATIONS

All publications sponsored by AEC 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 in the period July 1, 1973 to July 1, 1974 are marked with an asterisk.

4.1 Supported by AEC

4.11 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).

4.12 In Press

*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 (In Press).

15) Lassettre, E. N. and A. Skerbele, "Inelastic Electron Scattering," a chapter in the second edition of Experimental Methods in Molecular Physics (Edited by Dudley E. Williams), Academic Press, 1973 (In Press). A review with 192 references. Proofs have been received.

*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 (In Press).

4.2 Supported by AFOSR

4.21 Published

17) Meyer, V. D. and E. N. Lassettre, "An Experimental Determination of Oscillator Strengths for the CO $A^1\Pi \leftarrow X^1\Sigma^+$ Bands," Journal of Chemical Physics 54, 1608-1610 (1971).

18) Harshbarger, W. R., A. Skerbele and E. N. Lassettre, "Generalized Oscillator Strength of the $\tilde{A} \leftarrow \tilde{X}$ Transition of Ammonia," *Journal of Chemical Physics* *54* (6), 3784 (1971).

19) 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).

20) Huo, W. M., "Effective Long Range Potential for Scattering of Electrons by Atoms and Molecules," *Journal of Chemical Physics* *56* (7), 3468 (1972).

21) Huo, W. M., "Limiting Form of the Effective Potential for Electron Scattering," *Journal of Chemical Physics* *57*, 4800-4813 (1972).

4.22 In Press

*22) 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* (In Press).

*23) 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* (In Press).

*24) Lassettre, E. N., "Absolute Intensities and Classification of Transitions in Electron Impact Spectroscopy," Proceedings of NATO Institute for Advanced Study in Spectroscopy and Photochemistry in the Vacuum Ultraviolet, Valmorin, Quebec, Canada, August 5-17, 1973 (In Press).

5. PERSONNEL

Personnel involved in this project were Dr. Kirby N. Klump (full time) and Dr. Edwin N. Lassettre, Principal Investigator (50% from July 1, 1973 to December 31, 1973; 65% from January 1, 1974 to July 1, 1974). Dr. Lassettre is employed on research for 100% of his time. That portion not devoted to the AEC project is devoted to the AFOSR project mentioned in Section 3.