Electron-impact excitation of low-lying electronic states in CS$_2$, OCS, and SO$_2$[a]

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Variable angle, electron-impact energy-loss spectra of CS$_2$, OCS, and SO$_2$ have been obtained at incident electron energies of 25, 40, and 70 eV for CS$_2$, and 30 and 55 eV for OCS and SO$_2$. Singlet→triplet excitations are observed with peaks at transition energies of 3.36 eV in CS$_2$, 4.94 eV in OCS, and 3.40 eV in SO$_2$. A feature which peaks at 3.65 eV in CS$_2$ is observed to have singlet→triplet character. The CS$_2$ and OCS spectra do not confirm the existence of several spin-forbidden transitions reported in solid phase ultraviolet absorption studies of these molecules. In SO$_2$, no evidence is found of transitions to the $1\,^3A_2$ and $1\,^3B_2$ states, believed to lie near the well-known $\tilde{a}\,^3B_1$ state.

I. INTRODUCTION

The excited electronic states of the three sulfur-containing triatomic molecules carbon disulfide (CS$_2$), carbonyl sulfide (OCS), and sulfur dioxide (SO$_2$) have been the subjects of extensive experimental investigations.[1-22] However, due to the complexity of the observed band systems, and the lack of accurate *ab initio* calculations of the electronic state energies, few state assignments are certain. Considerable information about singlet → triplet transitions in these molecules is available,[3, 5-7, 10, 12-15, 21, 22] but a comparison of recent studies[13, 21, 22] indicates that knowledge of such forbidden transitions is quite incomplete. Furthermore, CS$_2$, OCS, and SO$_2$ have been used extensively in photochemical electronic energy transfer experiments,[23-29] and interpretation of these investigations would be facilitated by more detailed information about the number, location, and identity of low-lying transitions in these molecules. In order to obtain such information, we have used the technique of low energy, variable angle electron-impact spectroscopy[30-33] to study the electronic transitions of CS$_2$, OCS, and SO$_2$.

The spectrometer employed in these experiments has been described in detail previously.[30-32] Basically, it consists of five sections—a multistage electron gun, a hemispherical electrostatic energy monochromator, a flexible collision chamber, an energy-loss analyzer identical to the monochromator, and an electron multiplier with associated pulse counting equipment. Pulses are counted and stored by a 1024 channel scaler. A given spectrum is obtained by sweeping the spectrometer repeatedly through the chosen energy-loss range, at a preselected incident electron energy and scattering angle of detection. Typically, each molecule is studied

at eight–ten different scattering angles (θ) in the range 0°–80°, and at two or more impact energies (E_0). It is usually possible to identify transitions as spin-allowed or spin-forbidden by measuring the dependence of the inelastic scattering intensities on impact energy and scattering angle.[30-33]

In the present work, spectra of CS$_2$ were obtained at incident electron energies of 25, 40, and 70 eV, while OCS and SO$_2$ were studied primarily at impact energies of 30 and 55 eV. The energy-loss range which was investigated extended to 20 eV,[32(b)] but we report in this paper only the low-lying transitions. In addition, relative differential cross sections (DCS) in the scattering angle range 10°–80° were obtained for a number of low-lying transitions. The incident electron beam current was chosen to lie in the range 10–100 nA, while the sample pressure in the collision chamber was estimated to be approximately 5 mTorr, on the basis of the measured background pressure (5×10^{-7} Torr) in the vacuum chamber. Previous experience with many other polyatomic gases, where the scattering chamber pressure gauge was used, indicates that the scattering chamber pressure is typically four orders of magnitude larger than the background pressure. The usual sample pressure measuring Schulz–Phelps gauge was not used in this study because it was found that sulfur-containing compounds quickly destroyed the gauge filament. Most of the spectra were obtained with a selected energy resolution of 0.10–0.15 eV, as measured from the full width at half maximum (FWHM) of the elastically scattered peak. However, a number of spectra were obtained using a better resolution of 0.06–0.08 eV FWHM. The transition energies presented below, corresponding to the peaks of the observed excitations, have an estimated uncertainty of 0.03 eV.

The CS$_2$ used in these experiments was obtained from Allied Chemical Company, and had a stated boiling point range of 46.1–46.6 °C. The OCS and SO$_2$ were both obtained from Matheson Gas Products, and had stated minimum purities of 97.5% and 99.98%, respectively. All samples were vacuum-degassed prior to use.

II. CARBON DISULFIDE

Table I summarizes the transition energies of the low-lying energy-loss features observed in this investi-

TABLE I. Low-lying excited electronic states of CS_2, OCS, and SO_2.

Molecule	Excited state	Molecular orbital transition[a]	Transition energy (eV)[b]			
					Electron impact	
			Optical	Threshold	$E_0 = 100$ eV[c]	Present work
Carbon disulfide	$^3A_2(1\,^3\Delta_u)^d$	$\pi_g \to \pi_u^*$	3.26–3.66[d]	3.3,[e] 3.4[f]	⋯	3.36
	Triplet[g]	$\pi_g \to \pi_u^*$	⋯	⋯	⋯	3.65
	$^1A_2(1\,^1\Delta_u)^d$	$\pi_g \to \pi_u^*$	3.65[d]	⋯	⋯	⋯
	$^1B_2(1\,^1\Delta_u)^d$	$\pi_g \to \pi_u^*$	3.89[h]	3.8,[f] 3.9[e]	3.9_5	3.91
	$^3\Pi_g$[g]	⋯	4.53,[i] 4.1_5–4.5_5[j]	6.1[e,f]	⋯	⋯
	$^1\Pi_g$[g]	⋯	5.13[i]	5.0,[k] 5.5[e]	⋯	⋯
	$^1B_2(1\,^1\Sigma_u^+)^{h,l}$	$\pi_g \to \pi_u^{*\,\prime}$	5.81,[i] 6.29[h]	⋯	6.3	6.27
	$^1\Pi_g$[g]	$\pi_g \to ns\sigma_g$	6.81,[h] 6.82[m]	6.6,[e] 6.85[f]	6.8	6.79
Carbonyl sulfide	$^3\Sigma^{+}$[n]	$\pi \to \pi^*$	4.3[n,o]	⋯	⋯	⋯
	$^3\Delta$[g,n]	$\pi \to \pi^*$	4.7[n,o]	⋯	⋯	⋯
	$^3\Sigma^{+}$[k]	$\pi \to \pi^*$	⋯	4.85,[k] 4.9[f]	⋯	4.94
	$^1\Delta$[h]	$\pi \to \pi^*$	5.54,[h] 5.73[n]	5.35,[k] 5.6[f]	5.5_3	5.53
	⋯[p]	⋯	5.85–5.96[q]	⋯	5.8_7	⋯
	⋯[p]	⋯	6.05–6.67[q]	⋯	6.3	⋯
	$^3\Pi$[n]	$\sigma \to \pi^*$[g]	6.9[h]	6.8,[k] 6.9[f]	⋯	⋯
	$^1\Pi$[h]	$\sigma \to \pi^*$[g]	7.44,[h] 7.57[n]	7.35,[k] 7.5[f]	7.4	7.36
	$^1\Sigma^{+}$[h]	$\pi \to \pi^*$	(8.01, 8.12)[h]	8.05,[k] 8.2[f]	(8.0, 8.1)	(8.02, 8.11)
Sulfur dioxide	$^3B_1$[r]	$8a_1 \to 3b_1$	3.31[s]	⋯	⋯	$3.40[3.0_5$–$3.7_5]^t$
	$^1B_1$,[u] $^1A_2$[v]	$8a_1 \to 3b_1, 5b_2 \to 3b_1$	4.28[w]	⋯	4.2_5	$4.31[3.7_5$–$5.3]^t$
	$^1B_2$	$1a_2 \to 3b_1$	6.19[x]	⋯	6.1	$6.20[5.3$–$7.3]^t$

[a]All assignments for CS_2 and OCS are from Ref. 10. Those for SO_2 are from Ref. 40.

[b]Most of the transition energies listed correspond to the maximum intensity of the given band system. If this value was not determined, the Franck–Condon limits of the transition are given. Values enclosed in parentheses are vibronic bands of the electronic transition.

[c]All values listed are from Ref. 11. With the exception of the 6.3 eV transition in CS_2, they were obtained by interpolation from the spectra which appear in that paper.

[d]Reference 15.

[e]Reference 13(b).

[f]Reference 22.

[g]The orbital symmetry or valence/Rydberg character of the excited state is uncertain. See text for further discussion.

[h]Reference 10.

[i]Reference 21(b), solid state transitions.

[j]These transition energies were determined from a graph in Ref. 14 of uv absorption of CS_2 in an isopentane–cyclohexane glass at 77 K.

[k]Reference 13(a).

[l]Reference 7(b).

[m]Reference 1(a).

[n]Reference 21(a), solid state transitions.

[o]The existence of this feature has not yet been confirmed.

[p]These features may represent impurity absorptions.

[q]Reference 1(b).

[r]Reference 12.

[s]Reference 2.

[t]Values in brackets are estimated Franck–Condon limits of the band system.

[u]Reference 17(b).

[v]Reference 20.

[w]Reference 5.

[x]References 17(a) and 17(c).

gation. It also includes some of the results of numerous ultraviolet absorption studies of CS_2, OCS, and SO_2, as well as those of other electron-impact investiga-tions[11,13,22] of these molecules. As a basis for the discussion of the low-lying excited states of CS_2, we note that the valence shell orbital occupancy of ground state CS_2,
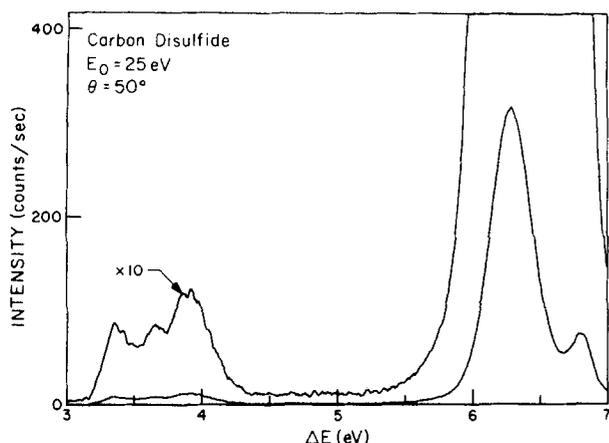
FIG. 1. Electron energy-loss spectrum of carbon disulfide at an impact energy (E_0) of 25 eV and a scattering angle (θ) of 50°; 22 namp incident electron current; 0.13 eV energy resolution (FWHM).

in the molecular orbital (MO) notation,[10] is $(\sigma_g)^2(\sigma_u)^2(\sigma_g)^2(\sigma_u)^2(\pi_u)^4(\pi_g)^4(\pi_u^*)^0$. Electron promotions of the type $\pi_g \rightarrow \pi_u^*$ lead to $^{1,3}\Sigma_u^-$, $^{1,3}\Delta_u$, and $^{1,3}\Sigma_u^+$ excited electronic states, and it is these states which we expect to form the basis for interpreting the low energy-loss region of the electron-impact spectrum.

Figure 1 shows that the lowest energy electronic transition which we observe in CS_2 peaks at 3.36 eV. The relative DCS for this feature (Fig. 2), at an impact energy of 40 eV, is relatively isotropic in the 10°–80° scattering angle range. Similar behavior was observed at $E_0 = 70$ eV. A DCS of this type is highly characteristic of spin-forbidden excitations,[30–33] and we therefore assign the 3.36 eV feature to a singlet $\rightarrow$ triplet transition in CS_2. Consistent with this assignment is the fact that it is more than two orders of magnitude weaker than the optically allowed $\tilde{X}^1\Sigma_g^+ \rightarrow 1^1\Sigma_u^+$ transition at 6.27 eV. Analysis of ultraviolet observations[15] of the weak spin-forbidden band system indicates that it represents excitation of a $^3A_2$ state which is the lower Renner–Teller component of the linear $1^3\Delta_u$ state. The location of the upper component ($^3B_2$) of the $1^3\Delta_u$ state is not yet known, nor is the location of the $^3B_2(1^3\Sigma_u^+)$ state, which is predicted to be the lowest energy triplet state.[15, 34]

A second peak, with maximum intensity at 3.65 eV, can be seen in Fig. 1. Because this feature could not be resolved adequately from the adjacent peaks in a number of the spectra, no DCS curve for this transition is shown in Fig. 2. However, the data which were obtained[32(b)] concerning the angular dependence of the scattering intensity of this feature indicate that one or more singlet $\rightarrow$ triplet transitions occur in this region. At $E_0 = 40$ eV, for example, the intensity of the 3.65 eV feature relative to that of the optically allowed 6.27 eV transition increases by a factor of 25 as θ increases from 30° to 80°. However, this behavior of the DCS ratio is much less pronounced at both $E_0 = 25$ eV and $E_0 = 70$ eV, so that the singlet $\rightarrow$ triplet assignment must be considered tentative. It seems probable that several excited triplet states which have not yet been detected, such

as the $^3B_2(1^3\Delta_u)$, $^3B_2(1^3\Sigma_u^+)$, and $^3A_2(1^3\Sigma_u^-)$ states, have excitation energies in the vicinity of the 3.65 eV peak.[15] In uv absorption, a spin-allowed transition with maximum intensity at about 3.65 eV has been identified as an excitation to the $^1A_2(1^1\Delta_u)$ state.[15] This state, which is the singlet analogue of the $^3A_2$ one at 3.36 eV, is the lower Renner–Teller component of the linear $1^1\Delta_u$ state. Although the $^1A_2$ state may be excited weakly in our electron-impact spectra, we do not believe that it contributes appreciable intensity to the 3.65 eV feature shown in Fig. 1 because of the relatively large scattering angle used to obtain that spectrum. However, at low scattering angles, it is possible that the transition to the $^1A_2$ state has significant electron-scattering intensity.

A transition observed at 3.91 eV (Fig. 1) has a DCS (Fig. 2) with a quantitative behavior different from that of either of the two lower energy features. At all impact energies investigated, the DCS for the 3.91 eV transition is peaked in the forward scattering region. However, as can be seen in Fig. 2, it is considerably less forward peaked than the optically allowed 6.27 eV transition. In addition, the ratio of the intensities of the 3.91 and 6.27 eV transitions shows slight oscilla-
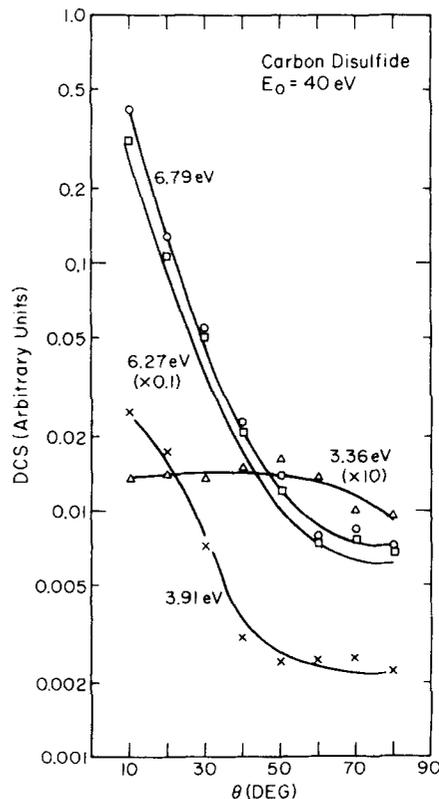

FIG. 2. Relative differential cross sections (DCS) as a function of scattering angle (θ) for several inelastic transitions in carbon disulfide at an impact energy (E_0) of 40 eV. The maximum intensity transition energy is shown next to each DCS curve. The arbitrary units used were the same for all transitions in this molecule and were determined by setting the DCS value for elastic scattering at 40° to 1.0. The curve for the 3.36 eV transition has been multiplied by a factor of 10, while that for the 6.27 eV transition has been multiplied by a factor of 0.1.
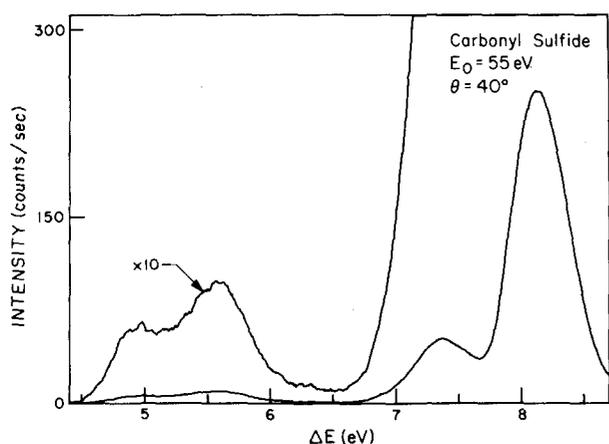
FIG. 3. Electron energy-loss spectrum of carbonyl sulfide at an impact energy (E_0) of 55 eV and a scattering angle (θ) of 40°; 65 namp incident electron current; 0.15 eV energy resolution (FWHM).

tions with scattering angle.[32(b)] Such behavior is frequently observed in excitation of spin-allowed, electric dipole-forbidden transitions.[30–32] These results are therefore consistent with the uv absorption assignment[15] for this transition, $\tilde{X}^1\Sigma_g^+ \to {}^1B_2(1\,{}^1\Delta_u)$. In this band system, the $^1B_2$ state is the upper Renner-Teller component of the $1\,{}^1\Delta_u$ state.

We observe no transitions in the 4.3–5.5 eV energy-loss region of CS$_2$, in spite of a careful search. This is in agreement with gas phase uv absorption data,[10,14] moderate energy electron-impact spectra,[11] and one threshold electron-impact study.[22] However, studies of solid phase absorption spectra[14,21(b)] indicate the presence of at least one or possibly two[21(b)] electronic transitions in this region of the spectrum. In addition, Hubin-Franskin and Collin[13(a)] reported a weak feature beginning near 4.5 eV and peaking near 5 eV in their deconvoluted threshold electron-impact spectrum of CS$_2$ in the gas phase. More recently, these authors[13(b)] reported additional CS$_2$ spectra in which there is no transition below 5 eV, but they do observe a shoulder near 5.5 eV. Bajema, Gouterman, and Meyer[14] observed a number of very weak bands between 4.1_5 and 4.5_5 eV in an investigation of uv absorption by CS$_2$ in an isopentane-cyclohexane glass at 77 K. These bands were not observed in similar studies of pure solid CS$_2$, nor in matrix-isolated CS$_2$.[14] More recently, Monahan, Russell, and Walker[21(b)] reported the observation of transitions at 4.53 and 5.13 eV in the uv absorption spectra of solid CS$_2$ films. They assigned the excited states of these features as $^3\Pi_g$ and $^1\Pi_g$, respectively. It is not clear whether these assignments refer to valence $(\sigma_u \to \pi_u^*)\Pi_g$ states or to Rydberg $(\pi_g \to ns\sigma_g)\Pi_g$ states, although the valence assignment would appear to be preferable, based upon the appearance of these features in the solid phase spectra and their low transition energies. However, Monahan et al. correlate these states with $^{3,1}\Pi_g$ Rydberg $(\pi_g \to 3s\sigma_g)$ states analogous to those described in a theoretical investigation[35] of the CO$_2$ electronic spectrum. The validity of the solid state assignments is challenged by threshold electron-impact data,[13,22] which show a

transition at 6.1 eV, presumably involving excitation of a $^3\Pi_g$ state, again of unspecified nature.

A very intense transition in CS$_2$ is observed with a maximum intensity at 6.27 eV energy loss (Fig. 1). On the basis of a partial rotational analysis of the uv band system,[7(b)] this excitation has been assigned to the fully allowed $\tilde{X}^1\Sigma_g^+ \to 1\,{}^1\Sigma_u^+$ transition. In agreement with this assignment, the DCS of the 6.27 eV transition (Fig. 2) is strongly forward peaked. At 6.79 eV, a transition is observed which has been previously identified as the first member of a symmetry forbidden $\pi_g \to ns\sigma_g$ Rydberg series.[10] However, this transition has a relatively large optical oscillator strength ($f = 0.06$), and the shape of its DCS (Fig. 2) is virtually identical to that of the optically allowed $\tilde{X}^1\Sigma_g^+ \to 1\,{}^1\Sigma_u^+$ transition at 6.27 eV. This is strongly suggestive of the possibility that this 6.79 eV feature is due to an optically allowed transition.

III. CARBONYL SULFIDE

The uv absorption spectrum of OCS has also been studied by a number of investigators[1(b),4,8–10,21(a)] and three electron-impact studies have been reported.[11,13(a),22] In Fig. 3, we display the 4.4–8.7 eV energy-loss region of the OCS spectrum. The lowest observed feature has a maximum intensity at 4.94 eV, and its relative DCS (Fig. 4) is that of a spin-forbidden transition. In addi-
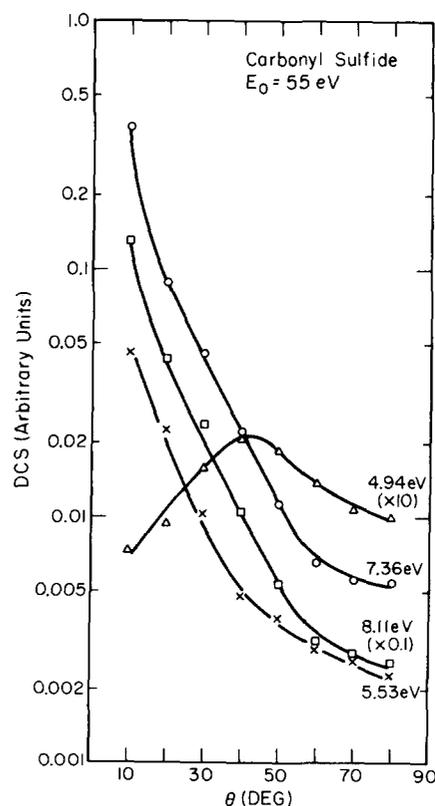

FIG. 4. Relative differential cross sections (DCS) as a function of scattering angle (θ) for carbonyl sulfide at an impact energy (E_0) of 55 eV. The DCS curve for the 4.94 eV transition has been multiplied by a factor of 10, while that for the 8.11 eV transition has been multiplied by a factor of 0.1. For additional remarks, see Fig. 2 caption.
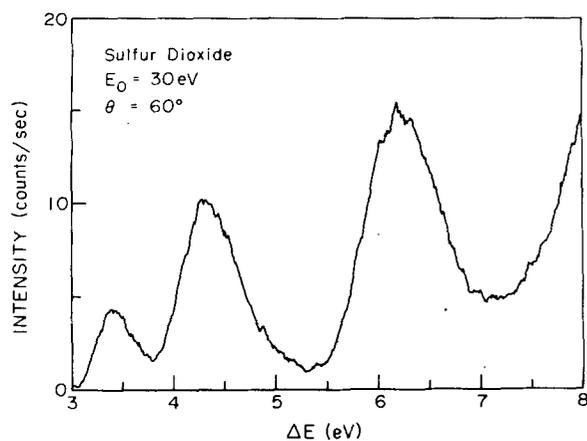
FIG. 5. Electron energy-loss spectrum of sulfur dioxide at an impact energy (E_0) of 30 eV and a scattering angle (θ) of 60°; 55 namp incident electron current; 0.18 eV energy resolution (FWHM).

tion, the relative intensity of this feature is greater at a lower impact energy ($E_0 = 30$ eV) than at a higher one ($E_0 = 55$ eV), for all scattering angles observed. This dependence on incident electron energy confirms the singlet → triplet assignment.[30-33] The transition was first reported in threshold excitation experiments[13(a),22] and it has been suggested[13(a)] that the excited state (presumably $^3\Sigma^+$) might be populated in Hg $^3P_1$ photosensitization of OCS.[23] There is some indication from threshold electron-impact data[22] that the 4.9 eV feature may actually be a composite of several transitions, since the peak shifts from 4.9 to 5.1 eV with increasing trapping potential.

The next higher energy transition which can be observed in Fig. 3 peaks at 5.53 eV. The DCS of this feature (Fig. 4) is qualitatively similar to that of the 3.91 eV transition in CS_2, in that both are forward peaked, but less so than the DCS curves of fully allowed transitions in the respective molecules. Both the weakness and the angular dependence of the scattering intensity suggest that the 5.53 eV transition is spin allowed, but electric dipole forbidden. Although both $^1\Sigma^-$ and $^1\Delta$ states have been invoked as assignments for the excited state,[9,10,18] the forward-peaked nature of the DCS at low angles ($\theta < 20°$) permits us to exclude the $^1\Sigma^-$ assignment. The basis of this exclusion is a rigorous electron-impact selection rule[36,37] which states that $^1\Sigma^+ \to {}^1\Sigma^-$ transitions should have vanishing intensity in both forward and backward scattering directions. In such cases, the DCS in general decreases with decreasing θ when θ is less than 20°. Our assignment of the state at 5.53 eV as the $^1\Delta$ state agrees with the assignment of Rabalais et al.[10]

Intense transitions in OCS are observed with peaks at 7.36 and 8.11 eV, and their relative DCS curves (Fig. 4) confirm their fully allowed nature. Rabalais et al.,[10] who studied these features by uv absorption, have assigned them to $\bar{X}^1\Sigma^+ \to {}^1\Pi$ and $\bar{X}^1\Sigma^+ \to 1\,{}^1\Sigma^+$ transitions, respectively. Accurate theoretical calculations on OCS would be helpful in determining whether the $^1\Pi$ state at 7.36 eV is valence (σ, π^*) or Rydberg (π, ns).

As in the case of CS_2, a number of new transitions in OCS have been reported recently in uv absorption studies of solid films.[21(a)] In spite of a careful search for these features, we did not find them. Among the transitions observed in the solid phase spectra were peaks at 4.3, 4.7, 6.9, and 7.57 eV, and these were assigned as excitations to the $^3\Sigma^+$, $^3\Delta$, $^3\Pi$, and $^1\Pi$ states, respectively.[21(a)] Recent threshold electron-impact spectra of OCS[22] support the assignments of the 6.9 and 7.57 eV solid phase uv features. However, the assignment of the 4.7 eV feature was a tentative one, and it is currently being reexamined in view of the present experimental results.[38] An alternative interpretation of the solid phase transitions in OCS can be based on the assumption that the excited states corresponding to the 4.7, 6.9, and 7.57 eV features may have considerable exciton character. If this were the case, transitions to these states in the solid phase might be slightly red shifted (rather than blue shifted) with respect to their gas phase analogs. We could then identify the 4.7, 6.9, and 7.57 eV solid phase features with the 4.94, 7.36, and 8.11 eV electron-impact transitions to the $^3\Sigma^+$, $^1\Pi$, and $^1\Sigma^+$ states, respectively. With these assignments, the only unresolved discrepancy is the presence of a transition at 4.3 eV in the solid phase spectra which has no analog in the electron-impact studies.

In some of the OCS spectra obtained at low scattering angles ($\theta < 10°$), we detect a very weak shoulder with a maximum intensity at 6.2-6.3 eV energy loss. Electronic transitions in the range 5.85-5.96 eV and 6.05-6.67 eV were observed in gas phase uv absorption by Price and Simpson,[1(b)] and weak features in these same regions were observed in the electron-impact investigation of OCS gas by Foo et al.[11] No such features were reported in the threshold electron-impact spectra,[13(a),22] nor in solid phase uv absorption.[21(a)] Although we cannot preclude the possibility that the feature which we observe is a strongly forward-peaked transition in OCS, it is also possible that it is an impurity transition, since three of the most likely impurities—CS_2, SO_2, and H_2S—have strong transitions with maxima in the range 6.2-6.3 eV.[32(b)]

IV. SULFUR DIOXIDE

In recent years, the uv absorption spectrum of SO_2 has received considerable attention.[3,5,12,17,20] Much of this research was stimulated by the desire to understand mechanisms for the removal of SO_2 from the atmosphere. Dissociation of SO_2 into SO and atomic oxygen is endothermic by 5.69 eV, and detailed studies have made it apparent that the photochemistry of SO_2 in the absorption region below this energy is due to reactions, other than unimolecular decomposition, of the electronically excited states of SO_2.[39] Unlike CS_2 and OCS, SO_2 has a bent configuration in its ground electronic state, due to the presence of two extra valence electrons. As a result, low-lying states involve $a_1 \to b_1(n \to \pi^*)$, $b_2 \to b_1(\pi \to \pi^*)$, and $a_2 \to b_1(\pi \to \pi^*)$ electron promotions.[40]

The lowest energy feature observed in the energy-loss spectrum of SO_2 (Fig. 5) peaks at 3.40 eV. This transi-
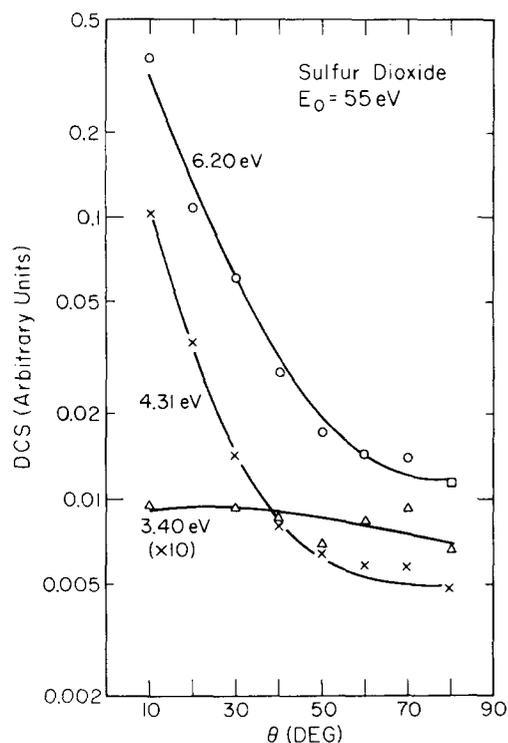
FIG. 6. Relative differential cross sections (DCS) as a function of scattering angle (θ) for sulfur dioxide at an impact energy (E_0) of 55 eV. The DCS curve for the 3.40 eV transition has been multiplied by a factor of 10. For additional remarks, see Fig. 2 caption.

tion has a DCS (Fig. 6) and an impact energy dependence which confirm that it is spin-forbidden. Rotational analysis[12(a)] of the 0–0 band of the weak ($f \approx 10^{-6}$) uv band system in this excitation energy region has shown that the excited state is $\tilde{a}\,^3B_1$. However, higher vibronic bands of the $\tilde{X} - \tilde{a}$ transition are heavily perturbed,[12(b)] and vibronic interactions with a nearby $^3A_2$ state, as well as rotational-electronic interactions with a neighboring $^3B_2$ state have been postulated to explain these observations.[12(b)] Three close-lying triplet states have also been postulated to explain the results of some photochemical self-quenching and energy-transfer experiments.[24–27] Kelley, Meagher, and Heicklen[28] suggested that photolysis of gas mixtures containing SO$_2$ and acetylene involves the reactions of two triplet states and one excited singlet state. However, their conclusion has recently been questioned by Su and Calvert.[24(b)] Our spectra indicate the presence of only one low-lying singlet → triplet transition, and we feel that it is not likely that there are any transitions below 3.2 eV which have an intensity comparable to that of the $\tilde{X} \rightarrow \tilde{a}$ excitation. However, we cannot preclude additional singlet → triplet contributions to the high energy side of the 3.40 eV feature.

We also detect separate electronic transitions in SO$_2$ with maxima at 4.31 and 6.20 eV (Fig. 5). Both features have the intensity and angular dependence of fully allowed transitions. On the basis of uv absorption data,[17(b),20] it seems that both $\tilde{X}\,^1A_1 - {}^1A_2(\pi - \pi^*)$ and $\tilde{X}\,^1A_1 - {}^1B_1(n - \pi^*)$ transitions contribute to the intensity of the

4.31 eV feature. Several bands in the low energy tail (< 5.77 eV) of the 6.20 eV transition have been assigned to the $\tilde{X}\,^1A_1 - {}^1B_2(\pi - \pi^*)$ excitation.[17(a)] This transition is believed to extend to beyond 7.5 eV excitation energy.[17(c)]

V. CONCLUSION

In summary, we have used the technique of variable angle electron-impact spectroscopy to confirm the existence of singlet → triplet transitions with maxima at 3.36 eV in CS$_2$, 4.94 eV in OCS, and 3.40 eV in SO$_2$. We suggest that a feature we observe at 3.65 eV in CS$_2$ has singlet → triplet character. We were unable to detect in CS$_2$ and OCS several low-energy features which were previously reported in solid phase uv absorption spectra.

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