Photofragmentation of Thionyl Chloride: Competition between Radical, Molecular, and **Three-Body Dissociations**

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The photodissociation of Cl₂SO (C, symmetry) at 248 and 193 nm has been studied by photofragment translational spectroscopy under various scattering angles. At 248 nm the decay proceeds along the molecular channel to SO + Cl_2 but mainly along the fast $(<10^{-12} \text{ s})$ radical channel yielding Cl + SOCl. The anisotropy parameters show that the molecular and the radical decays arise from initial preparation of two states with A' and A" symmetry, respectively. At 193 nm the molecular and the radical processes are strongly dominated by a three-body dissociation (>80%) producing SO + Cl + Cl. The photofragment anisotropies are consistent with the three competing, subpicosecond dissociation reactions starting on a single potential energy surface accessed via an $A'' \leftarrow A'$ singlet transition. Furthermore, the fragment kinetic energy distribution of the radical channel at 248 and 193 nm indicates that SOCl has an excited electronic state at ~9000 cm⁻¹.

Introduction

The photochemical decay of the well-investigated tetraatomic molecule formaldehyde H₂CO is characterized by a "molecular" and a "radical" mechanism,¹⁻³ according to the scheme

$$X_2AB + h\nu \rightarrow AB + X_2 \tag{I}$$

$$\rightarrow ABX + X$$
 (II)

The same primary decay processes have been proposed for thionyl chloride Cl₂SO^{4,5} and phosgene Cl₂CO.^{3,6} Furthermore, it was suggested that, at an excitation energy exceeding the energy required to break both A-X bonds, also a three-body dissociation

$$X_2AB + h\nu \rightarrow AB + X + X$$
(III)

may take place.^{1,5} If this reaction proceeds on a single potential energy surface (PES) which is repulsive along the two equivalent reaction coordinates AB-X, a simultaneous dissociation is possible,⁷⁻¹⁰ as has recently been shown in the photofragmentation of the structurally similar CF_2I_2 molecule.¹¹ On the other hand, the formation of AB and two X fragments can also occur via a sequential process that involves the primary dissociation II followed by the decay of nascent ABX radicals with sufficient internal energy

$$ABX^* \rightarrow AB + X$$
 (IV)

Compared to the synchronous process, the sequential decay yields fragments with different internal and translational energies and different fragment angular distributions.¹⁰ The present study is concerned with these four elementary reactions in the photodissociation of Cl₂SO after absorption of a photon at 248 and 193 nm. Figure 1 shows the pyramidal geometry (C_s symmetry) of ground-state thionyl chloride, as determined by microwave

spectroscopy.¹² The absorption spectrum of Cl₂SO^{5,13} starts at about 300 nm and shows in the UV region two distinct shoulders at 244 nm ($\sigma = 7.1 \times 10^{-18} \text{ cm}^2$) and at 194 nm ($\sigma = 1.3 \times 10^{-17}$ cm²) well suited for excimer laser excitation at 248 nm and 193 nm. The first absorption band $(S_1 \leftarrow S_0)$ gives rise to the 244-nm shoulder and was assigned to a $\sigma^*_{SCI} \leftarrow n_S$ transition while the second band might be due to a $\sigma^*_{SCl} \leftarrow n_{Cl}$ transition, involving the lone-pair electron on the chlorine atom. The vacuum UV absorption spectrum of Cl₂SO recorded by Okabe¹⁴ between 116 and 135 nm is characterized by diffuse bands superimposed on several continua. On the basis of the fluorescence spectrum of nascent SO and on the lack of any Cl₂ products, photodissociation in the vacuum UV was proposed to proceed according to reaction III, more specifically, $Cl_2SO \rightarrow SO(A^3\Pi_0, B^3\Sigma^-) + 2Cl(^2P_{3/2})$.

In an early study, Donovan et al.⁴ used flash photolysis in the UV region ($\lambda \ge 185$ nm) to explore the photodecomposition of Cl_2SO . They proposed that the primary process is the fission of one sulfur-chlorine bond (process II) and that hot SOCl radicals may undergo unimolecular decomposition to SO + Cl. according to reaction IV. More recently, Kawasaki and co-workers⁵ investigated the photofragmentation of Cl₂SO in a molecular beam by photofragment translational spectroscopy (PTS). Using 193-nm excitation, these authors found the radical channel II to be operative in competition with the three-body dissociation III, creating SO + Cl + Cl. On the basis of a simple model for translational energy release in the simultaneous and the sequential mechanism, they concluded that formation of SO + Cl + Cl occurs mainly via the synchronous channel III. Thus, the sequential process involving reaction IV is considered a minor decay path. At 248 nm photodissociation was found to proceed by the radical and the molecular mechanisms (II,I) with the former dominating the latter.

Using a high-resolution PTS apparatus with a rotatable molecular beam source, we performed time-of-flight (TOF) and anisotropy measurements to reinvestigate the photofragmentation of Cl₂SO, particularly in view of a three-body dissociation process. On the basis of the previous results⁵ and of our recent PTS studies, 11,15-18 thionyl chloride appears to be a very suitable molecule for studying the simultaneous bond breaking III^{7,10,19}

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Figure 1. Structure of thionyl chloride and geometry of its three-body dissociation, showing the recoil directions of the fragments (v_{Cl}, v_{SO}) and the definition of the recoil angle α (see text). The transition dipole moment $\vec{\mu}$ can be either in the plane of symmetry or perpendicular to it.

in competition with a sequential bond breaking and or a molecular elimination process.

Experimental Section

The molecular beam apparatus has been previously described in detail;²⁰ therefore, only a short outline is given here. A pulsed laser beam is directed along the rotation axis of a pulsed molecular beam source which rotates in a plane with the fixed detection axis. The variable angle between the directions of the molecular beam and the detector is denoted as Θ . Following a flight path of 34.5 cm, the neutral fragments created in the intersection region of the laser and the molecular beam are ionized by electron bombardment and selected according to their mass by a quadrupole mass filter (Balzers QMA 160). The time-dependent ion count rate from a secondary electron multiplier was fed into a multichannel scaler with 1000 channels, each of a $1-\mu s$ time width. The time-of-flight (TOF) spectra shown in this work have been corrected for the flight time of the ions through the mass filter.

Most of the TOF spectra were measured using an unpolarized laser beam, which was focused by spherical and cylindrical lenses to a spot size of 3×3 mm. The laser fluence at the focus was ~2.9 J/cm² for 248-nm and ~0.7 J/cm² for 193-nm laser light. For some experiments a dielectric attenuator was introduced to reduce the laser power by a factor of 6. The anisotropy of the photofragment angular distribution was determined with linearly polarized laser light, produced by directing the beam through a pile of 10 quartz plates at Brewster angle and rotating the plane of polarization by a $\lambda/2$ plate. The polarization degree thus achieved was 92% for both wavelengths. The laboratory polarization angle ϵ is defined as the angle between the electric light vector and the detector axis. The velocity distribution in the molecular beam was determined by means of the laser induced depletion method.²¹ The laser (Lambda Physik EMG 101 MSC) was operated at 40 Hz, and $\geq 10^5$ shots were required to accumulate TOF spectra with good S/N ratio.

Thionyl chloride (\geq 99.5% with SO₂Cl₂ + SO₃ \leq 0.1%, S₂Cl₂ + $SCl_2 \leq 0.03\%$; Fluka) was transferred into the inlet system by vacuum distillation from room temperature to -196 °C, which resulted in a colorless liquid of $SOCl_2$. The $SOCl_2$ /He mixture was prepared by leading a stream of He at 500 mbar through a sample of thionyl chloride that was kept at 0 °C.

In a first series of experiments the molecular beam was found to contain a high concentration of SO₂, probably due to a reaction of Cl₂SO on the surface of the copper or brass components of the inlet system. After adoption of an inlet system consisting of only glass, Teflon, and stainless steel, the formation of impurities was effectively suppressed, as was revealed by mass spectroscopic monitoring of the molecular beam. We note, however, that for stable beam conditions passivation of the inlet system for several hours was required.

The constant bath temperature of 0 °C provides a Cl₂SO/He mixture of 1/10. The molecular beam velocity distribution was determined by fitting the laser induced depletion profile with a number density distribution $f(v) \propto v^2 \exp[-[((v-v_0)/\alpha)^2]]$. Under these conditions we obtained $v_0 = 1059$ m/s and $\alpha = 69$ m/s.



Figure 2. TOF distribution of Cl₂ molecules measured at a detection angle of $\theta = 45^{\circ}$. The solid line was calculated from the $P(E_t)$ distribution shown in Figure 3.

In an attempt to reduce the concentration of clusters in the beam, the He pressure was reduced to about 300 mbar and a gas mixture with only 5% of Cl₂SO was applied. Since these precautions provided no significant reduction of cluster formation, the photodissociation experiments were always carried out at 500 mbar and 10% Cl₂SO concentration.

Results and Analysis

General Remarks. After dissociation upon excitation at 248 and 193 nm, the available energy (the energy transferred to the fragments) is given by

$$E_{avl} = E_{t} + E_{v,r} + E_{el} = E_{hv} - D_{0}$$
(1)

where E_t , $E_{v,r}$, and E_{el} are the translational, the vibrational plus rotational, and the electronic energies of the fragments, respectively. $E_{h\nu}$ is the energy of the photon and D_0 the dissociation energy. Fragment electronic states are energetically accessible for SO(X³ Σ^- , a¹ Δ , and b¹ Σ^+), Cl₂(X¹ Σ_g^+ , ³ Π_0^+), and Cl(²P_{1/2} and ${}^{2}P_{3/2}$) and can give rise to high kinetic energy thresholds

$$E_{\rm t}(\rm max) = E_{\rm avl} - E_{\rm el} \tag{2}$$

in the TOF spectra (see e.g. ref 16). The total translational energy distribution $P(E_t)$ of the fragments in the center-of-mass (cm) system was determined from the TOF spectra by a forward convolution method.^{22,23} The procedure takes into account the instrumental effects influencing the resolution, namely, the molecular beam divergence (2.2°) and the viewing angle for the photofragments (0.8°), the effective ionizer length (5 mm), the size of the laser spot, and the velocity spread of the molecular beam (fwhm \sim 5%). For primary dissociation processes, a trial distribution $P(E_t)$ was iteratively fit to the experimental TOF spectrum.

The angular distributions of the fragments emerging from the primary decays were determined by measuring TOF spectra with linearly polarized laser light and then analyzing the recoil anisotropy with the expression $w(\vartheta) \propto 1 + \beta P_2(\cos \vartheta)$.^{24,25} Here P_2 denotes the second Legendre polynomial and ϑ the angle between the electric vector of the laser light and the dissociation direction in the cm frame. The resulting anisotropy parameter β can assume values between $\beta = 2$ and -1, which correspond to the transition dipole moment $\vec{\mu}$ being aligned parallel and perpendicular to the fragment recoil direction, respectively.

The secondary dissociation was treated by taking the recoil distribution of the pertinent primary fragment characterized by β and $P(E_t^{(1)})$ and superimposing a secondary distribution. The

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Figure 3. Center-of-mass total translational energy distribution $P(E_t)$ for the molecular channel. The arrows indicate E_{avl} for the formation of the fragment pair SO + Cl₂ in different electronic states: (1) SO($X^3\Sigma^-$) + Cl₂($^{1}\Sigma_{g}^{+}$); (2) SO($a^{1}\Delta$) + Cl₂($^{1}\Sigma_{g}^{+}$); (3) SO($b^{1}\Sigma^+$) + Cl₂($^{1}\Sigma_{g}^{+}$); (4) SO-($X^3\Sigma^-$) + Cl₂($^{3}\Pi_{0}^{-}$).

TABLE I: Dissociation Energy D_0 (kcal/mol), Available Energy E_{avi} (kcal/mol), and Anisotropy Parameter β for the Three Decay Channels

reaction	D_0	$E_{\rm avl}(\beta)$	
		248 nm	193 nm
$\frac{\text{Cl}_2\text{SO} + h\nu \rightarrow \text{SO} + }{\text{Cl}_2 (I)}$	51.3 ± 0.3^{a}	64.0 ± 0.3 (0.7)	96.9 ± 0.3
\rightarrow SOCI + Cl (II)	57.3 ± 0.3 ^b	$58 \pm 0.3 (0.8)$	$91 \pm 0.3 (0.39)$
\rightarrow SO + Cl + Cl (III)	108.5 ± 0.3^{a}	6.9 ± 0.3	$39.7 \pm 0.3^{\circ}$

^aJANAF Thermochemical Tables. J. Phys. Chem. Ref. Data **1985**, 14 (Suppl. 1). ^bExperimentally determined in this work. ^c For the three-body dissociation the experiment yielded $\beta(SO) = -0.65$ from which we calculate $\beta(Cl) = 0.43$.

latter was described with $P(E_t^{(2)})$ for which a flexible analytical form based on a statistical unimolecular decay²⁶ was used. In the present case we found no evidence for an anisotropic distribution in the observed secondary decays.

Photolysis at 248 nm. Molecular Channel I: $Cl_2SO \rightarrow SO +$ Cl₂. Figure 2 shows the TOF spectrum monitored at m/e = 70, where the signal stems exclusively from the fragment Cl_2 . The solid line represents the fit which was obtained with the $P(E_1)$ distribution displayed in Figure 3; this $P(E_t)$ also fits the spectra measured at $\theta = 39^{\circ}$ and 27°. The arrows mark high-energy thresholds (eq 2) attributed to the onset of the formation of SO and Cl₂ fragments in excited electronic states. Taking $D_0 = 51$ kcal/mol (see Table I) and $E_{h\nu} = 115 \pm 0.2$ kcal/mol (248 ± 0.3 nm), we obtained a value for $E_{avl} = 64$ kcal/mol which is in excellent agreement with the kinetic energy of the fastest fragments observed in the experiment (Figure 3). On the basis of this E_{avb} , the energetically accessible excited electronic fragment states are $SO(a^{1}\Delta)$ with an excitation energy of 18 kcal/mol, $SO(b^{1}\Sigma^{+})$ with 30 kcal/mol, and $Cl_2(X^3\Pi_0^+)$ with 51 kcal/mol, which correspond to thresholds $E_t(\max)$ at 46, 34, and 13 kcal/mol, respectively. While at 34 kcal/mol a threshold in $P(E_t)$ of Figure 3 is discernible, no clear indication is given for the other two. Therefore, we conclude that the molecular channel creates the fragment pairs $SO(b^{1}\Sigma^{+}) + Cl_{2}(X^{1}\Sigma_{g}^{+})$ and $SO(X^{3}\Sigma_{g}^{-}) + Cl_{2}(X^{1}\Sigma_{g}^{+})$ in a ratio of 9/1, where it cannot be excluded that the latter pair is accompanied by SO($a^{1}\Delta$) + Cl₂(X¹ Σ_{g}^{+}). This branching ratio is a rough estimate obtained from a comparison of the respective areas under the $P(E_t)$ distribution. (The counterfragment SO was not selectively monitored for channel I, since its contribution to the TOF signal at m/e = 48 was much smaller than that from the radical channel II, which covers a similar kinetic energy region.)

The anisotropy of channel I, measured at m/e = 70, was found to be $\beta = 0.7 \pm 0.1$, implying that the fragment recoil is predominantly parallel to the electronic transition moment $\vec{\mu}$. Accordingly, if Cl₂SO possesses C_s molecular symmetry also in the excited state (see Figure 1), $\vec{\mu}$ must lie in the plane of symmetry.



Figure 4. TOF distribution of SOCl fragments surviving the electron bombardment, measured with low laser power. The solid line was calculated from $P_2(E_i)$ shown in Figure 6. Using high laser power the same TOF distribution is obtained, except that the shoulder at 250 μ s was slightly reduced. This shoulder, corresponding to the component at 30 kcal/mol in Figure 6, is attributed to an excited electronic state of SOCl.

Finally, we address the possibility of a secondary photodissociation of nascent Cl₂. The two Cl atoms from such a decay would contribute to the signal at m/e = 35. This process can, however, safely be excluded since the absorption coefficient of Cl₂ is $\leq 0.3\%$ of that of Cl₂SO at 248 nm, and, hence, no laser power dependence of the TOF signal at m/e = 35 due to photodissociation of Cl₂ was observed.

Radical Channel II: $Cl_2SO \rightarrow SOCl + Cl.$ Following excitation at 248 nm, the most abundant primary fragments are SOCl and Cl. Figure 4 shows the TOF spectrum recorded at m/e = 83 that represents the distribution of SOCI fragments surviving the electron bombardment in the ionizer. Since most of the SOCl fragments (\sim 80%) do not survive but undergo dissociative ionization to SO⁺ or Cl⁺, the TOF distribution of SOCl is also observed at m/e = 48 and 35, respectively. Figure 5a exhibits the TOF spectrum taken at m/e = 48 by using low laser power. It can be fitted with the translational energy distribution $P_1(E_1)$ displayed in Figure 6, which also fits the TOF spectra recorded at detection angles $\theta = 39^{\circ}$ and 21°. The arrow in Figure 5a marks the maximum of the SO fragment distribution from the molecular channel (see Figure 3) and points to the fact that this contribution is very small and can be neglected. Hence, the TOF spectrum in Figure 5a arises exclusively from SO fragments produced from SOCI in the ionizer. As a consequence, $P_1(E_t)$ represents the translational energy distribution of reaction II.

The TOF spectrum of Cl at m/e = 35 is depicted in Figure 7a-c. According to the SOCl fragmentation in the ionizer, it also contains the TOF distribution of SOCl as revealed by the slow peak with a maximum at $\sim 250 \ \mu s$. The dotted curve 2 was calculated with $P_1(E_1)$. The assignment of this peak to Cl⁺ from dissociative ionization of Cl₂, as suggested previously,⁵ was rejected on the basis of intensity because the molecular channel is merely 3% of the radical channel. Furthermore, since the primary fragments SOCl and Cl are momentum matched, the TOF distribution of the fast primary Cl fragment is readily obtained from $P_1(E_1)$ and included as curve 1 in Figure 7b; it excellently fits the fast part of the spectrum.

The difference in the TOF spectra taken at low and at high laser power (Figure 5a,b) reveals that a part of the primary SOCI fragments undergoes further photolysis at high power according to

$$SOCI + h\nu \rightarrow SO + CI$$
 (3)

The fast peak between 100 and 200 μ s in Figure 5b is in excellent agreement with the TOF distribution of SO from this process (curve 2), as calculated with the expression²⁶

$$P(E_{t}^{(2)}) = A(E_{t}^{(2)})^{a}(E_{av}^{(2)} - E_{t}^{(2)})^{b}$$
(4)



Figure 5. TOF distribution measured at m/e = 48 (SO⁺) using low (a) and high (b) laser power. The main peak is due to SOCl fragments yielding SO⁺ in the ionizer. The solid line in a was calculated with the distribution $P_1(E_t)$ displayed in Figure 6 and a small contribution from the molecular channel (see arrow and curve 1 in b). At high power (b) the photodissociation of SOCl causes an additional signal from secondary SO fragments (curve 2) and a preferential depletion of slow SOCl fragments (at ~250 μ s).



c.m. translational energy (kcal/mol)

Figure 6. Total translational energy distributions for the radical channel. $P_1(E_t)$ provides a fit for the primary Cl fragment (m/e = 35) and SOCI monitored at m/e = 35 and 48. To fit the data at m/e = 83 (SOCl⁺), a slightly different distribution $P_2(E_t)$ was required, indicating preferential cracking of hot SOCl in the ionizer. The observed maximum translational energy provides an upper limit of the dissociation energy: $D_0(S-Cl) \le 57.3 \pm 0.3$ kcal/mol.

Here $E_t^{(2)}$ is the translational energy of the secondary fragments in the cm frame of SOCl, and A is a normalization constant. The energy available for the secondary dissociation products is

$$E_{avl}^{(2)} = E_{h\nu} - D_0(OS - Cl) + E_{int}(SOCl)$$
(5)

with the internal energy of SOCl, $E_{int}(SOCl)$, determined from $P_1(E_1)$ of the primary process. The difference between the D_0



Figure 7. TOF distributions at m/e = 35 measured under three different laboratory angles Θ . Curves 1 and 2 in b are calculated from the translational energy distribution of the radical channel $P_1(E_t)$ which leads to primary Cl atoms (curve 1) and SOCI yielding Cl⁺ in the ionizer (curve 2). Cl atoms from secondary photodissociation of SOCI are represented by curve 3 whereas curve 4 stands for Cl⁺ from dissociative ionization of Cl₂. The solid line in each spectrum is the sum of these four contributions. The remaining signal at low translational energy, particularly apparent at small detection angles, is attributed to the photodissociation of Cl₃SO clusters.

values of channel III and channel II is $D_0(OS-CI) = 51 \pm 0.3$ kcal/mol (see Table I). With the parameter values a = 0.5 and b = 2, we obtained good fits of the TOF distributions at m/e = 48 and 35, as demonstrated by curve 2 in Figure 5b and curve 3 in Figure 7b. The previous assignment of this fast peak to SO from the molecular decay⁵ is, therefore, only correct for the small contribution under low laser power conditions.

Having analyzed the contributions to the TOF spectrum at m/e = 35, the superposition of curves 1-4 (curve 4 is the contribution of the molecular channel) yielded a good fit (solid line) to the

experimental data (Figure 7b) up to a flight time of ~270 μ s. This superposition also fits the TOF spectra of Cl⁺ taken at θ = 21°, 27°, 72°, and 81°. Between 300 and 500 μ s an additional contribution is evidenced which is attributed to photodissociation of Cl₂SO clusters. This contribution, particularly apparent at m/e = 35, was also observed at m/e = 83 and 48 under smaller θ angles, but at correspondingly equal flight times. Moreover, if the molecular beam pulse of about 250- μ s duration is excited not, as usual, into the fast rising part where the cluster portion is very small, but instead into the middle part where the cluster concentration is known to be higher, we observe the expected increase of the TOF signal at longer flight times.

As discussed above, the translational energy distribution of SOCI was obtained from the fit of the TOF spectrum at m/e =48. Adopting this $P_1(E_t)$, we could not, however, satisfactorily reproduce the TOF spectrum at m/e = 83 of Figure 4. The fitting procedure for the latter yielded $P_2(E_1)$ (Figure 6), a distribution which is slightly shifted to higher energy with respect to $P_1(E_t)$. To further verify this effect we measured the TOF spectrum of SOCl⁺ also at $\theta = 21^{\circ}$, 45°, 48°, 54°, and 60° and found that all these spectra could be well fitted with $P_2(E_t)$. (In this context it is noted that the effect of the different chlorine isotopes was always included in the analyzing procedure.) We believe that this difference in the $P(E_t)$ distributions of SOCl is due to an internal energy dependent fragmentation. Since only about 20% of the primary SOCl fragments are ionized without being cracked, it is likely that the surviving SOCI fragments with $P_2(E_t)$ possess less internal energy and thus more translational energy than the ones which are cracked and give rise to $P_1(E_1)$. Such an internal energy dependent fragmentation pattern has previously been found by Continetti et al.²⁷ for the CH₃ radical from the photodissociation of CH₃I and by Covinsky²⁸ in the photodissociation of NO₂Cl.

The translational energy distribution of Figure 6 provides $E_t(\max) = 58 \text{ kcal/mol}$, which corresponds to an upper limit of the dissociation energy of the S-Cl bond in Cl₂SO of D₀(S-Cl) $\leq 57.3 \pm 0.3 \text{ kcal/mol}$. Previous estimates of $D_0(\text{S-Cl})$ from thermochemical and spectroscopic data by Sanderson were 56.6 kcal/mol³⁰ and 65.6 kcal/mol.³¹ From the contributions of the radical channel II and the molecular channel I to the TOF spectrum at m/e = 48 (Figure 5a), it is obvious that channel II dominates channel I. The arrow in Figure 5a marks the peak maximum of the SO fragments from the molecular channel. This very small signal compared to the rest of the TOF spectrum shows that the ratio of radical channel/molecular channel is $\sim 30/1$.

Finally, the anisotropy measurements at m/e = 83 of the radical channel resulted in $\beta = 0.8 \pm 0.1$, indicating $\vec{\mu}$ to be preferentially parallel to the recoil direction. If the C_s symmetry is also retained in the excited state of Cl₂SO, $\vec{\mu}$ is perpendicular to the plane of symmetry and, therefore, the electronically excited state is of A" symmetry as detailed in the discussion. Moreover, this β value is consistent with an excited-state lifetime shorter than a rotational period of the parent molecule.²⁹

Photolysis at 193 nm. Molecular Channel I: $Cl_2SO \rightarrow SO + Cl_2$. In contrast to the previous findings,⁵ excitation at 193 nm also gives rise to the molecular decay. Figure 8 shows the TOF spectrum of Cl_2 at m/e = 70, where the dotted and dashed curves represent two extreme fits to illustrate the possible error range. The corresponding $P(E_1)$ distributions are given in Figure 9, and the best fitting $P(E_1)$ distribution (solid line in Figure 9) was then used to calculate the contribution of the counterfragment SO (curve 3) to the signal at m/e = 48, displayed in Figure 10. Due to the small S/N ratio at m/e = 70 and the superposition of three channels at m/e = 48, measurement of the fragment recoil anisotropy was not possible.

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Figure 8. TOF distribution of Cl_2 molecules from the molecular channel I. The dashed and dotted curves illustrate the possible error range calculated with the corresponding $P(E_1)$ distributions shown in Figure 9.



Figure 9. Center-of-mass total translational energy distributions $P(E_i)$ for the molecular channel after excitation at 193 nm. The best fit is given as a solid line, and the arrows indicate E_{avl} for the formation of the fragment pair SO + Cl₂ in different electronic states: (1) SO($X^3\Sigma^-$) + Cl₂($^{1}\Sigma_{g}^{+}$); (2) SO($a^{1}\Delta$) + Cl₂($^{1}\Sigma_{g}^{+}$); (3) SO($b^{1}\Sigma^+$) + Cl₂($^{1}\Sigma_{g}^{+}$); (4) SO-($X^3\Sigma^-$) + Cl₂($^{3}\Pi_{0}^{-}$).



Figure 10. TOF distribution measured at m/e = 48 with simulated spectrum (solid line) consisting of three contributions. SO from the molecular channel gives rise to the small curve 3 calculated with $P(E_i)$ given in Figure 9. SOCl fragments from the radical channel, characterized by $P(E_i)$ (1) in Figure 12, yields SO⁺ in the ionizer (curve 1). The most important component (curve 2) is due to SO molecules arising from the three-body dissociation (III).

Radical Channel II: $Cl_2SO \rightarrow SOCI + Cl.$ Channel II, selectively detected at m/e = 83, gives rise to the single-peaked TOF

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Figure 11. TOF distribution of SOCI fragments. The solid line was calculated from $P(E_t)$ (1) in Figure 12.



Figure 12. $P(E_t)$ distributions for the two important channels II and III after excitation at 193 nm; (1) total translational energy distribution of the fragment pairs from the radical channel II with E_{avt} indicated by the arrow and (2) total translational energy distribution for the three fragments formed in the three-body dissociation channel III.

spectrum shown in Figure 11. This spectrum has also been measured at $\theta = 27^{\circ}$ and 24°. The analysis of the three spectra yielded the $P(E_t)$ distribution displayed in Figure 12 as curve 1. The maximum translational energy of 65 kcal/mol is noted to be about 26 kcal/mol smaller than E_{avl} (91 kcal/mol) would allow for the formation of SOCl and Cl in their ground states. Therefore, we propose that the "missing" 26 kcal/mol are required to create an electronically excited state of SOCI. The existence of such a species is also consistent with the bimodal shape of $P_1(E_1)$ and $P_2(E_1)$ found at 248 nm and shown in Figure 6. These distributions appear to be a superposition of two Gaussian shaped distributions; the one at lower translational energy would thus correspond to excited SOCl and the one at higher translational energy to SOCl in the ground state. Moreover, the experiment with high laser power at 248 nm, where a second photolysis step (eq 3) occurs, has shown that the species of the low-energy distribution are photolyzed preferentially with respect to those of the high-energy distribution.

From the polarization dependence of the TOF signal at m/e= 83 we determined the anisotropy parameter of the radical channel to be $\beta = 0.4 \pm 0.05$, which implies $\vec{\mu}$ to be parallel to the recoil direction, i.e. perpendicular to the plane of symmetry.

The TOF spectrum at m/e = 35 has been measured at $\theta = 27^{\circ}$ and 45° and is displayed in Figure 13 for $\theta = 45^{\circ}$. The small and narrow peak at short flight times ($\sim 100 \ \mu$ s) is due to the Cl atoms formed in the radical channel II; this feature is also clearly discernible at $\theta = 27^{\circ}$, as well as in Figure 14. The distribution (curve 1) was calculated from $P(E_1)$ optimized to fit the SOCl counterfragments. According to this result, we would expect the large TOF peak with a maximum at $\sim 200 \ \mu$ s to be solely due to the SOCl fragments cracked in the ionizer to Cl⁺. However, the SOCl signal derived from Figures 11 and 12, shown



Figure 13. TOF distribution measured at m/e = 35 with simulated spectrum (solid line) consisting of three contributions. The radical channel, characterized by $P(E_1)$ (1) in Figure 12, yields fast Cl atoms (curve 1) and SOCl fragments (curve 2). The most important component (curve 3) is due to Cl atoms arising from the three-body dissociation (III).



Figure 14. TOF distributions at m/e = 35 measured with linearly polarized laser light. The "perpendicular" distribution (solid line) was recorded with $\epsilon = 43^{\circ}$ where ϵ denotes the angle between the electric vector of the exciting light and the detection direction. The "parallel" distribution (dotted line) was obtained with $\epsilon = -47^{\circ}$.

as curve 2 in Figure 13, cannot account for the shape and the width of this TOF peak, particularly not for the rising part at early flight times ($\leq 180 \ \mu s$). As is shown in the next section, the additional component, which has to be included, stems from Cl atoms produced in channel III. This contribution is indicated as curve 3, which together with curve 2 results in the overall fit.

Channel III: $Cl_2SO \rightarrow SO + Cl + Cl$. The TOF spectrum at m/e = 48 (SO) was measured at $\theta = 24^\circ$, 27°, and 45° and is depicted in Figure 10 for $\theta = 45^\circ$. The SOCI fragments from channel II contribute to this spectrum with the ion SO⁺. Using the $P(E_i)$ from the radical channel (distribution 1 in Figure 12), we obtain curve 1 in Figure 10. Similar to the analysis at m/e = 35, this contribution constitutes only a small part of the TOF signal, indicating that the major part must originate from another channel. This fact is further corroborated by the polarized TOF distribution measurements at m/e = 48 and displayed in Figure 15, where the two apparent components are shown to exhibit an opposed anisotropy behavior. Consistent with the polarization measurements at m/e = 83, the small component at m/e = 48 (curve 1) is enhanced when the electric vector is oriented parallel to the fragment recoil direction.

Among the possible decay processes which can give rise to TOF signals at m/e = 48 and 35 is the sequential decay that involves



Figure 15. TOF distributions at m/e = 48 measured with linearly polarized laser light. The "perpendicular" distribution (solid line) was recorded with $\epsilon = 39^{\circ}$ while the "parallel" distribution (dotted line) was obtained with $\epsilon = -51^{\circ}$. Note the opposite polarization behavior of the two contributions from the radical channel (narrow peak) and from the three-body dissociation (broad peak).

the formation of SOCl (reaction II) followed by a spontaneous decay (reaction IV). This process, however, could be excluded because the calculated TOF spectra were too broad and the calculated signal at m/e = 35 was too fast, independent of the type of secondary $P(E_t)$. Similarly, secondary photodissociation of SOCl was ruled out since the signal from the resulting SO and Cl fragments is calculated to be much faster than was observed, and, moreover, the expected effect due to low and high laser power irradiation is not apparent in the TOF spectra at m/e = 48 and 35. As previously suggested by Kawasaki et al.,⁵ a simultaneous three-body dissociation (reaction III) appears to be a good candidate for the missing channel. While there is no unique way of analyzing such a process without carrying out a coincidence experiment (see e.g. ref 10), one may nevertheless explore the outcome predicted under specific assumptions. As initially suggested by Ondrey and Bersohn³² and further exploited in our investigation of CF₂I₂,¹¹ we consider the implications of linear momentum and energy conservation for the case of symmetric recoil of the two Cl atoms, i.e.

$$m_{\rm SO}v_{\rm SO} = 2m_{\rm Cl}v_{\rm Cl}(\cos\,\alpha) \tag{6}$$

$$2E_{\rm t} = m_{\rm SO} v_{\rm SO}^2 + 2m_{\rm Cl} v_{\rm Cl}^2 \tag{7}$$

Here, v_i denotes the asymptotic recoil velocity of fragment *i* in the cm frame of the parent molecule, and E_t is the total translational energy of the three fragments. The angle α is defined as half of the angle between the recoil directions of the two Cl atoms. The value of α is not known a priori but is expected to be close to half of the Cl-S-Cl bond angle in Cl₂SO, which is between 96° and 97°.¹² On the basis of this model, a fairly good fit of the TOF spectra at m/e = 35 and 48 is achieved (curve 3 in Figure 13 and curve 2 in Figure 10) with the $P(E_t)$ displayed as curve 2 in Figure 12. Even more important is the agreement of the polarization measurements with the geometrical predictions of the three-body process. Our recoil model requires $\vec{\mu}$ oriented parallel to the line connecting the two Cl atoms to give rise to a preferentially parallel recoil direction (positive β value) for the Cl atoms and to a perpendicular recoil for the SO fragments (see Figure 1)

As revealed by Figure 14, the entire TOF peak of the Cl atoms (channel II and channel III) is parallel polarized; i.e. the recoil direction of Cl atoms from channel III is almost parallel to $\vec{\mu}$. Therefore, $\vec{\mu}$ must be perpendicular to the plane of symmetry, and, consequently, the SO fragments recoiling in the plane of symmetry must exhibit a perpendicular polarization. This fact is clearly demonstrated in Figure 15, where the dominant part, due to channel III, shows a perpendicular polarization.

Discussion

Molecular and Radical Decays at 248 nm. Following excitation at 248 nm, we found that Cl_2SO dissociates along the molecular channel I and the radical channel II exclusively; a careful search for other decay pathways yielded nothing. Furthermore, the radical decay strongly dominates the molecular decay, and the molecular channel creates mainly the fragment pair $Cl_2(X^1\Sigma_g^+)$ + $SO(b^1\Sigma^+)$ with a small contribution of $Cl_2(X^1\Sigma_g^+)$ + $SO(X^3\Sigma^-)$.

Information about the nature of the initially prepared excited state at 248 nm is obtained from the anisotropy results of the radical and molecular channels using a simple axial recoil model. Following the suggestions of Yang and Bersohn,²⁹ we factorize the anisotropy parameter into a geometrical and a lifetime part

$$\beta = P_2(\cos \chi) \ y(\tau) \tag{8}$$

where χ denotes the angle between the fragment recoil direction in the cm frame and $\vec{\mu}$. The lifetime factor $y(\tau)$ can assume values in the limits of 2 and 0 for an instantaneous dissociating complex and a long-lived asymmetric parent complex, respectively. In the case of the radical channel II we found $\beta = 0.8 \pm 0.1$ at 248 nm so that, in accordance with $y \leq 2$, the recoil angle $\chi \leq 39 \pm 2^{\circ}$. The S-Cl bonds of the parent molecule in the ground state form an angle of 48° with the symmetry plane σ (see Figure 1) and an angle of 42° with the perpendicular line. Hence, the axial model predicts $\vec{\mu}$ to be perpendicular to σ and the excited state to be of A" symmetry. Furthermore, since the recoil angle χ is indicated to be close to the limiting value of about 40° and consequently $y(\tau) \sim 2$ (instantaneous dissociation limit), we expect a dissociation process that is considerably shorter than a molecular rotational period ($\tau \leq 10^{-12}$ s).

For the molecular channel one has to assume a recoil direction in the symmetry plane, as indicated in Figure 1. Therefore, the positive anisotropy parameter ($\beta = 0.7 \pm 0.1$) measured in this case allows us to conclude that $\vec{\mu}$ lies within the symmetry plane and that the prepared excited state is of A' symmetry. The orientation of $\vec{\mu}$ within the plane is, however, not known, so that merely an upper limit estimate of the lifetime can be given. Using eq 8 with $y(\tau) = \beta = 0.7$, a dissociation lifetime comparable to a parent rotational period or shorter is expected.

Consideration of correlations between the electronic states of the parent and the products provides some further information on channel I. Assuming that C_s symmetry is preserved for Cl_2SO during the product formation, Cl₂, which is formed only in the ground state $(X^1\Sigma_g^+)$, transforms according to A' $(D_{\infty h} \rightarrow C_s)$ while symmetry reduction $(C_{\infty v} \rightarrow C_s)$ turns the SO fragment states $X^{3}\Sigma^{-}$ into A"(triplet), $a^{1}\Delta$ into A' or A", and $b^{1}\Sigma^{+}$ into A'. Therefore the direct product of the fragment symmetry species requires $Cl_2 + SO(b^1 \bar{\Sigma}^+)$ to correlate with an A' parent state and $Cl_2 + SO(a^1\Delta)$ with either A' or A". For the fragment pair Cl_2 + SO(X³ Σ^{-}), an admixture of triplet character is required. The predominating production of $Cl_2 + SO(b^1\Sigma^+)$ in connection with an excitation of an A' state as observed in the experiment is thus fully consistent with symmetry correlation. Moreover, should the excited-state geometry of Cl₂SO be changed from a pyramidal to a planar structure, i.e. from C_s to C_{2v} symmetry, the agreement with the experimental findings would still exist. The radical channel, on the other hand, is not subject to symmetry restriction because the C_s (C_{2v}) symmetry is broken during this process.

The fact that the molecular and the radical decay have different initial states and both can be reached at 248 nm indicates that two electronic transitions, $S_0(A') \rightarrow S_i(A')$ and $S_0(A') \rightarrow S_j(A'')$, respectively, overlap at this excitation wavelength (see UV spectrum¹³). The two dissociation processes are, therefore, expected to proceed on two different potential energy surfaces (PES). The most efficient channel of the molecular decay, which gives rise to the fragment pair SO(b¹\Sigma⁺) and Cl₂(X¹\Sigma_g⁺), can either occur on an excited electronic state PES of A' symmetry or, following internal conversion, on the electronic ground-state PES that also correlates with these fragment states. However, in view of the relatively short dissociation time (equal to or smaller than

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a rotational period of the excited complex), it is not very likely that internal conversion is involved. Fragmentation along the radical channel is a very fast process, and it is thus expected that it proceeds on the excited-state PES (A") as a direct dissociation. On the basis of the fragments with the highest translational energy, the upper limit of the dissociation energy for the S-Cl bondbreaking is determined to be $D_0(OSCI-Cl) \leq 57.3 \pm 0.3$ kcal/mol.

Three-Body Dissociation in Competition with Molecular and Radical Decays at 193 nm. The analysis of the fragment TOF spectra showed three primary dissociation pathways to be operative. Parallel to the excitation at 248 nm, the radical channel II is more efficient than the molecular channel I, but both are strongly dominated by the three-body dissociation which now becomes easily accessible at 193 nm, exceeding the dissociation limit by ~40 kcal/mol (see Table I).

The molecular decay which is least efficient ($\leq 3\%$) can produce (according to energy conservation) various electronic states of the fragments. As indicated by arrows in Figure 9 of the translational energy distribution, Cl₂ can be formed in the X¹ Σ_g^+ or the B³II₀⁴ state, while SO can emerge in the X³ Σ^- , a¹ Δ , or b¹ Σ^+ state. Thus, among the possible fragment pairs only SO(b¹ Σ^-) + Cl₂(X¹ Σ_g^+) and SO(X³ Σ^+) + Cl₂(B³II₀⁴) are in accordance with the spin selection rule and supported by the measured $P(E_t)$, and are therefore expected to be favored.

For the radical channel the increase in available energy of ~ 33 kcal/mol by going from 248 to 193 nm (see Table I) is probably channeled into electronic excitation of the SOCI fragments, as suggested by the maximum translational energy which has been found to be 26 kcal/mol smaller than E_{avl} . Consequently, the radical channel at 248 nm differs from the one at 193 nm in that the latter forms exclusively electronically excited SOCI fragments while the former produces ground- and excited-state species. The recoil anisotropy of the radical channel fragments is found to be positive at 248- and 193-nm excitation; i.e. $\beta = 0.7 \pm 0.1$ and $\beta = 0.4 \pm 0.05$, respectively. In view of the fact that the difference between these β values can already be accounted for by a small structural change in the dissociating parent molecule (e.g. a 5° change in χ), we will not elaborate on this effect.

The efficiency of channel II relative to channel III can be extracted from the TOF spectrum at m/e = 35, given in Figure 13. The small peak with an arrival time $\sim 100 \ \mu s$ stems from channel II, while the intensive one with 200 μs is due to Cl atoms from channel III. A comparison of the peak areas provides, after correction for the velocity-dependent ionization efficiency, an estimate for the efficiency ratio of channel III/channel II $\simeq 5/1$.

The three-body dissociation channel III, gives rise to the strong TOF peaks at m/e = 48 and 35 (see Figures 10 and 13) and their opposite polarization. Before we discuss this reaction a brief review of alternative mechanisms is in order. Donovan et al.⁴ suggested a sequential mechanism that involves the radical decay II followed by the unimolecular decay of the hot SOCl fragments (IV). However, the simulated TOF spectra are significantly broader than the observed ones, and, even more important, the opposite anisotropy at m/e = 48 and 35 was not reproduced.

A contribution from a photoinduced secondary dissociation of SOC1 according to SOC1 + $h\nu \rightarrow$ SO + Cl could also be rejected. Albeit such a process may give rise to an anisotropic recoil of the secondary fragments, the latter would be expected at much earlier arrival times than observed considering the high available energy. Furthermore, the SO fragments and the secondary Cl atoms would show the same anisotropy in the cm frame of SOC1 and thus yield $\beta_{SO} \sim \beta_{Cl}$ in the LAB frame, which is contrary to what is observed.

The TOF simulations for the mechanism which involves a primary molecular decay (I) followed by photodissociation of the nascent Cl₂ fragments are in severe disagreement with the experimental spectra at m/e = 35. In addition the small absorption cross section of Cl₂ at 193 nm³³ would create a laser power dependence of the TOF spectra at m/e = 35 which was not observed.

Finally, we have explored the possible occurrence of a sequential mechanism comprised of the primary molecular decay (I) followed

by spontaneous dissociation of Cl_2 . In contrast with the photoinduced secondary dissociation discussed above, the spontaneous process requires the formation of Cl_2 with an internal energy exceeding the dissociation limit. The overall reaction can be treated as a sequential process provided that the Cl_2 molecules are formed in a metastable state whose dissociation rate is slower than the rate of the primary dissociation of Cl_2SO . Since there are no electronically metastable (i.e. predissociated) states of Cl_2 in the accessible energy range, we are left with the possibility of rotationally metastable Cl_2 . Both the ground state and the $B^3II_0^+$ state of Cl_2^{34} can feature a centrifugal barrier which supports a number of quasibound rovibrational states above the dissociation limit. Although the states near the top of the centrifugal barrier can decay by tunneling, this process is inefficient in Cl_2 due to the large reduced mass.³⁵ Therefore, we can rule out a sequential process involving the secondary decay of Cl_2 .

If Cl_2 is formed in a repulsive state or in the continuum of a bound state, the two Cl atoms will start to separate before the Cl_2 and SO moieties have separated appreciably. Such a situation can no longer be considered as a sequential case and in fact corresponds to a three-body process.¹⁰

The three-body dissociation of Cl₂SO was simulated under the simplification that the Cl atoms recoil at an angle α from the molecular symmetry plane (see Figure 1) in a symmetric fashion. The value of $\alpha = 48^{\circ}$, taken from the ground-state geometry of Cl₂SO, provides a fit for the main peaks in the TOF spectra measured at m/e = 48 and 35 (see Figures 10 and 13). By virtue of eqs 6 and 7, this means that $\alpha = 48^{\circ}$ can "momentum match" the spectra of the two fragment species. The measured β_{SO} = -0.65, together with the geometrical factor $P_2(\cos \chi) = -0.5$ for the SO fragments assumed to recoil at 90° to $\vec{\mu}$, results with eq 8 in the lifetime factor $y(\tau) \simeq 1.3$. Since the Cl atoms have the same lifetime factor as SO and since the recoil angle $\alpha = 48^{\circ}$ corresponds to $\chi = 42^{\circ}$ and $P_2(\cos \chi) = +0.33$, we expect $\beta_{Cl} =$ 0.43. This value is essentially identical to that of the radical channel ($\beta = 0.4 \pm 0.05$, as determined from polarized TOF spectra at m/e = 83). Accordingly, in the TOF spectra at m/e= 35, the signals from the two contributing channels II and III should exhibit the same degree of anisotropy, which is indeed the case (see Figure 14).

The simplified treatment of the three-body dissociation discussed above does not provide a perfect fit of the TOF spectra in that their wings, arising at early and late flight times (see Figure 13), deviate from the simulation. For a refinement, we introduced a distribution of recoil angles instead of a fixed α to account for the presumably large amplitude bending vibration in the excited state of the parent. The improvement, however, was only marginal. A better result, i.e. a slightly broader kinetic energy distribution of the Cl fragments, is expected by an asynchronous but still concerted three-body process,¹⁰ which results in a pairwise formation of a fast and a slow Cl atom. Although our TOF data do not supply enough information for a quantitative analysis of such a process, they appear to favor the asynchronous mechanism of the three-body dissociation.

Conclusion

The collision-free photochemistry of Cl_2SO has been investigated by photofragment translational spectroscopy at 248 and 193 nm. In addition to a previous study by Kawasaki et al.,⁵ we also monitored the heavy photofragments Cl_2 and SOCI at their parent masses and under various scattering angles. Our results provide unequivocal evidence for the occurrence of a molecular and a radical channel in addition to a three-body dissociation at 193 nm.

At 248 nm the radical decay to SOCl + Cl predominates the molecular decay to $Cl_2(X^1\Sigma_g^+)$ + SO, where SO is mainly formed in the $b^1\Sigma^+$ state. From the recoil anisotropy of the fragments

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it is concluded that the fast (direct) radical dissociation and the molecular dissociation originate from two different electronic excited states of A" and A' symmetry, respectively. Therefore, it is expected that the molecular and the radical decay proceed on different potential energy surfaces. Using high laser power, the primary SOCI fragments are further photofragmented to SO and Cl, indicating the existence of a SOCl electronic transition near 40 000 cm⁻¹. Moreover, a low-lying electronic state of SOC1 at \sim 9000 cm⁻¹ (26 kcal/mol) was evidenced from the fragment translational energy distribution at 248 and 193 nm.

After absorption of a photon at 193 nm more than 80% of the Cl_2SO molecules undergo three-body dissociation to SO + Cl +Cl. The rest decays either along the radical or along the minor molecular channel. The anisotropy parameters of all the fragments can be accommodated by an initially excited state of A" symmetry. Therefore, it is not inconceivable, and hence encouraging for a dynamic study based on a quantum chemical PES calculation, 36-39

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that competition between the three dissociation pathways takes place on a single PES. In the recently investigated CF_2I_2 molecule,¹¹ the three-body dissociation to $CF_2 + I + I$ was found to be the only active decay at 248 nm, a selectivity which is favored by the low dissociation energies of the two C-I bonds.

A theoretical study of HgI_2 by Grübele et al.⁹ has shown the branching ratio between the three-body reaction and the singlebond rupture to increase with excitation energy. An extension of the experimental photofragmentation work to include various (most desirable continuously adjustable) excitation wavelengths would certainly be informative and in combination with dynamic calculations on ab initio potential energy surfaces would provide a very detailed picture of the competing dissociation modes in thionyl chloride.

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Photophysical Properties of Fullerenes and Fullerene/N,N-Diethylaniline Charge-Transfer Complexes[⊤]

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Well-resolved fluorescence and phosphorescence spectra of fullerenes in methylcyclohexane and the determination of important photophysical parameters are reported. The fluorescence quantum yield depends on the excitation wavelength, which indicates the occurrence of a very rapid photoprocess directly from upper excited states, in competition with internal conversion to the lowest excited state. For C_{70} the fluorescence quantum yields are 6×10^{-5} at 370 nm, 1.3×10^{-4} at 378 nm, and 2.2 \times 10⁻⁴ at 471 nm. The singlet-triplet energy splitting for C₇₀ is 7.0 kcal/mol. For C₆₀ the fluorescence quantum yields are 1.9×10^{-5} at 405 nm and 3.8×10^{-6} at 370 nm. The singlet-triplet energy splitting for C₆₀ is 5.5 kcal/mol. In the presence of N,N-diethylaniline (DEA), charge-transfer complexes between fullerenes and DEA for formed. In the excited state, luminescence from both the singlet and the triplet exciplex of C₇₀ are observed.

The possible existence of the soccer ball-shaped, 60-carbon molecule has long been speculated.¹⁻⁴ The recent success in generating macroscopic quantities of C_{60} and C_{70} molecules (fullerenes),⁵ following the earlier observation in beam experiments,^{6,7} has confirmed the existence of this interesting class of molecules and opened the doorway for systematic studies of their properties.

Because of their low reduction potentials,^{8,9} one expects to find interesting charge-transfer chemistry in both the ground state and the excited states. In this paper, well-resolved fluorescence and phosphorescence spectra of fullerenes and the determination of important photophysical parameters such as quantum yields and singlet-triplet splittings are first reported. The effects of N.Ndiethylaniline, a good electron donor, on the ground-state and excited-state properties of fullerenes are examined. Recently, the luminescence spectrum of C_{60} solid film,¹⁰ the transient absorption spectrum of C_{60} in solution,¹¹ and the phosphorescence spectrum of C_{70} in polymer film¹² have been reported. To the best of my knowledge, fluorescence from the singlet state has not been reported. Also, all of the reported phosphorescence spectra are either incomplete or not well-resolved.

 $C_{60} \mbox{ and } C_{70}$ are generated in a modified Denton evaporator according to the published procedures. 5,8,13 They are extracted

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