Primary Photophysical Processes in the Photochemistry of Sulfur Dioxide at 2875 Å[1]
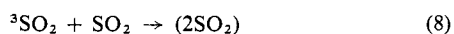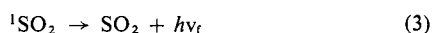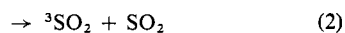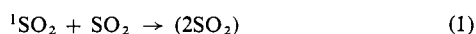
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Abstract: The quantum yields of fluorescence and phosphorescence of sulfur dioxide excited by 2875-Å radiation and the quantum yields of SO_2-sensitized biacetyl phosphorescence have been measured in pure sulfur dioxide and in its mixtures with small amounts of biacetyl. From the variation of functions of these quantum yields with varied experimental parameters and the previously published lifetime data for singlet ($^1SO_2$) and triplet ($^3SO_2$) sulfur dioxide molecules, values of the rate constants (in l.–mole–sec units) for all of the individual primary photophysical processes in sulfur dioxide photolysis have been determined: $^1SO_2 + SO_2 \rightarrow (2SO_2)$ (1), $k_1 = (2.0 \pm 1.0) \times 10^{10}$; $^1SO_2 + SO_2 \rightarrow {}^3SO_2 + SO_2$ (2), $k_2 = (0.18 \pm 0.08) \times 10^{10}$; $^1SO_2 \rightarrow SO_2 + h\nu_f$ (3), $k_3 = (5.1 \pm 4.0) \times 10^3$; $^1SO_2 \rightarrow SO_2$ (4), $k_4 = (1.7 \pm 0.4) \times 10^4$; $^1SO_2 \rightarrow {}^3SO_2$ (5), $k_5 = (1.5 \pm 0.8) \times 10^3$; $^3SO_2 \rightarrow SO_2 + h\nu_p$ (6), $k_6 = (0.10 \pm 0.06) \times 10^2$; $^3SO_2 \rightarrow SO_2$ (7), $k_7 = (1.3 \pm 0.2) \times 10^2$; $^3SO_2 + SO_2 \rightarrow (2SO_2)$ (8), $k_8 \cong (2.5 \pm 0.5) \times 10^7$; $^3SO_2 + Ac_2 \rightarrow SO_2 + {}^3Ac$ (9), $k_9 = (9.3 \pm 5.2) \times 10^9$.

There are many features of both the spectroscopy and the photochemistry of sulfur dioxide which attract the interest of the scientist. The structural simplicity of the sulfur dioxide molecule and the demonstrated participation of both singlet and triplet excited states in its photochemistry offer promise of an evaluation of the reactivity differences between the two spin states and an understanding of the factors that control spin inversion. Also of great practical value would be the evaluation of the significance of sulfur dioxide photochemistry in the SO_2-removal mechanisms operative in the polluted atmosphere.

Light absorption by sulfur dioxide in the first allowed optical transition extends from 3300 to 2300 Å. Although this band has not been analyzed successfully, it is probably the $^1B_1 \leftarrow {}^1A_1$ transition.[2] A second, forbidden transition may also occur within this region.[3] The primary processes in the photochemistry of sulfur dioxide can be described through the following reaction mechanism.

$$SO_2 + h\nu \rightarrow {}^1SO_2 \tag{I}$$

$$^1SO_2 + SO_2 \rightarrow (2SO_2) \tag{1}$$

$$\rightarrow {}^3SO_2 + SO_2 \tag{2}$$

$$^1SO_2 \rightarrow SO_2 + h\nu_f \tag{3}$$

$$\rightarrow SO_2 \tag{4}$$

$$\rightarrow {}^3SO_2 \tag{5}$$

$$^3SO_2 \rightarrow SO_2 + h\nu_p \tag{6}$$

$$\rightarrow SO_2 \tag{7}$$

$$^3SO_2 + SO_2 \rightarrow (2SO_2) \tag{8}$$

The superscripts 1 and 3 designate excited singlet and triplet states, respectively.

The $^1B_1$ state of sulfur dioxide has an anomalously long lifetime, $(4.2 \pm 0.2) \times 10^{-5}$ sec, about 10^2 times that

expected from the integrated absorption data.[4,5] When sulfur dioxide is excited to the $^1B_1$ state, emission is seen from both this state and the $^3B_1$ state. Caton and Duncan[6] have estimated the lifetime of the $^3B_1$ state from which it can be estimated that $k_6 + k_7 = (1.43 \pm 0.16) \times 10^2$ sec^{-1}. Recently Strickler and Howell[7] and Mettee[8a] have carried out studies of the emission of sulfur dioxide excited at a variety of wavelengths. The reactivity of the singlet species was shown to be a function of the exciting light. However, the limiting value of the quantum yield of fluorescence at low sulfur dioxide concentrations approached unity,[8a] and the ratio of the quantum yield of phosphorescence to that of fluorescence approached zero.[7,8a] These data confirm theoretical expectations that reactions 4 and 5 are unimportant. It was reported that the singlet and triplet excited species show greatly different quenching rates in reactions with ground-state sulfur dioxide molecules;[6,7] presumably the $^1B_1$ state is quenched upon every kinetic collision with ground-state SO_2 molecules,[4,7,8] while the $^3B_1$ state suffers destruction in only one collision in about 10^4.[7,9] Several results suggest that there is little or no vibrational relaxation of the $^1B_1$ state during its lifetime: (1) the fluorescence emission spectrum is strongly wavelength dependent with its onset at the wavelength of the exciting light;[8a] (2) collisional processes remove the $^1B_1$ electronic state so efficiently that the competing reaction of vibrational relaxation of the $^1B_1$ state cannot be important; (3) results from experiments with added gases show that neither the value of $k_1 + k_2$ nor the wavelength distribution of the fluorescence emission is significantly dependent on the presence of the added gas.[8b] In contrast the $^3B_1$ state of sulfur dioxide is largely vibrationally equilibrated during its lifetime since phosphorescence emission from this state

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(2) G. Herzberg, "Molecular Spectra and Molecular Structure." III. "Electronic Spectra and Electronic Structure of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1966, p 605.

(3) A. D. Walsh, *J. Chem. Soc.*, 2266 (1953).

(4) (a) K. F. Greenough and A. B. F. Duncan, *J. Am. Chem. Soc.*, **83**, 555 (1961); (b) K. F. Greenough, Ph.D. Thesis, University of Rochester, 1961.

(5) A. E. Douglas, *J. Chem. Phys.*, **45**, 1007 (1966).

(6) R. B. Caton and A. B. F. Duncan, *J. Am. Chem. Soc.*, **90**, 1945 (1968).

(7) S. J. Strickler and D. B. Howell, *J. Chem. Phys.*, **49**, 1947 (1968).

(8) (a) H. D. Mettee, *ibid.*, **49**, 1784 (1968); (b) H. D. Mettee, private communication, submitted for publication.

(9) R. B. Caton, private communication to one of the authors (S. S. C.).

originates largely from the zeroth vibrational level.[4] Of course, it is possible that some vibrationally excited $^3B_1$ molecules are collisionally deactivated directly to the ground electronic state. In all the considerations made in this work vibrational relaxation of the $^1B_1$ state is assumed to be unimportant while relaxation of the $^3B_1$ state is assumed to be complete.

Previous kinetic and spectroscopic studies have not allowed a separation of the competitive reactions of the singlet and triplet states. Thus only the sums of two or more rate constants could be determined: $k_1 + k_2$, $k_3 + k_4 + k_5$, and $k_6 + k_7$. In this work we have coupled the previous published data on sulfur dioxide with the presently reported quantum yield measurements of the fluorescence and phosphorescence excited in sulfur dioxide, and the SO_2-sensitized phosphorescence excited in biacetyl (Ac_2), and have succeeded in deriving estimates for all of the individual primary photophysical processes in the reaction sequence 1–8. We have made use of the reactions 9, 10, and 11 to accomplish this result.

$$^3SO_2 + Ac_2 \rightarrow SO_2 + {}^3Ac_2 \qquad (9)$$

$$^3Ac_2 \rightarrow Ac_2 + h\nu_p' \qquad (10)$$

$$\rightarrow Ac_2 \qquad (11)$$
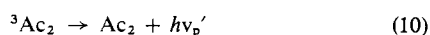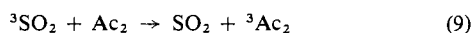
Experimental Section

All emission data were determined on the Turner absolute spectrofluorimeter, Model 210.[10] Samples of pure sulfur dioxide and its mixtures with biacetyl were prepared in a mercury-free vacuum line, and the 1-cm² fluorescence cell containing the sample was then transferred to the spectrofluorimeter cell compartment. The excitation monochromator of the Turner was set at 2875 Å with a 150-Å band width and with the emission monochromator set at 100-Å band width. Absolute quantum yields of sulfur dioxide emission were determined in one set of experiments using pure sulfur dioxide. The reference quantum yield of fluorescence chosen was that of a quinine bisulfate solution ($3.57 \times 10^{-7} M$) in $0.1 N$ sulfuric acid; the excitation of the quinine bisulfate was effected at 3480 Å, and its quantum yield of fluorescence for these conditions was taken as 0.57.[11] The measured molar extinction coefficient of quinine bisulfate was $6.55 \times 10^3 \text{ l./(mole cm)}$ at 3480 Å. Light absorption by sulfur dioxide followed the Beer–Lambert law well at 2875 Å over the concentration range employed here, and the apparent extinction coefficient at 2875 Å was 220 l./(mole cm) as determined on the Turner instrument using the same excitation band widths employed in the fluorescence work. The method of calculation of emission yields which was employed was essentially that described by Turner.[10,11] The equation which applies is $\phi_1 = \phi_Q A_1 \lambda_Q \varepsilon_Q c_Q / A_Q \lambda_1 \varepsilon_1 c_1$, where ϕ represents the quantum yield of emission, A is the area under the appropriate corrected emission spectrum (directly recorded by the Turner instrument), λ is the wavelength of light used for excitation of the emission, ε is the molar extinction coefficient, and c is the concentration; the subscripts Q and 1 on the symbols refer to quinine bisulfate and sulfur dioxide, respectively. The relatively low quantum yield of emission of sulfur dioxide required that we use rather large monochromator slit openings, and as a result there was a rather large contribution of the scatter peak to the intensity of light measured near the 2875-Å excitation band; see Figure 1. Thus only that portion of the sulfur dioxide fluorescence at wavelengths greater than 3250 Å, together with all of the phosphorescence, were measured. The area between the base line and the emission curve (determined by electronic integration) for the wavelength region 3250–4700 Å was used in the relation for quantum

(10) G. K. Turner, *Science*, 146, 183 (1964).

(11) (a) G. K. Turner, "Notes on the Determination of a Quantum Efficiency with the Model 210 Spectrofluorimeter," G. K. Turner Associates Inc., Palo Alto, Calif.; based on comparative measurements with the more concentrated H_2SO_4 solutions used by Melhuish and the value of 0.55 reported by him: (b) W. H. Melhuish, *New Zealand J. Sci. Technol.*, B37, 142 (1955); (c) *J. Phys. Chem.*, 64, 762 (1960); (d) *ibid.*, 65, 229 (1961).
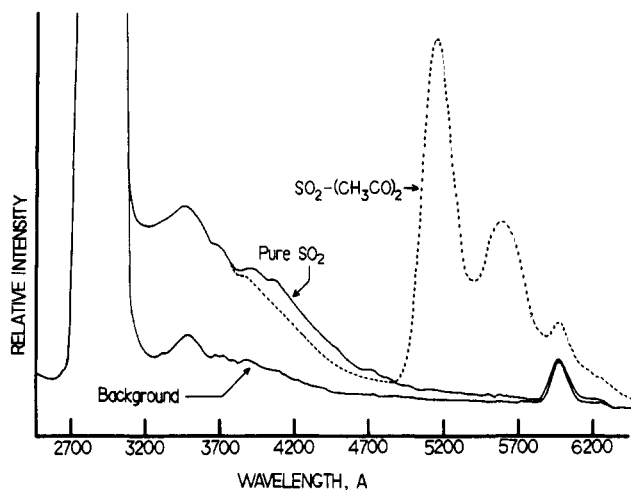

Figure 1. Typical low-resolution spectrofluorimeter trace of the fluorescence and phosphorescence emission from pure SO_2 (solid curve) excited by a band centered at 2875 Å ($[SO_2] = 8.62 \times 10^{-5} M$) and from a mixture (dashed curve) of SO_2 ($8.62 \times 10^{-5} M$) and biacetyl ($0.0218 \times 10^{-5} M$); note that in the mixture the fluorescence emission from SO_2 is unchanged, but the phosphorescence of SO_2 is quenched considerably (68%) and the sensitized phosphorescence emission of biacetyl appears.

Table I. Quantum Yields of Fluorescence from Pure SO_2 Excited at 2875 Å and 25°

$[SO_2]$, $M \times 10^5$	$\phi_f \times 10^3$	$[SO_2]$, $M \times 10^5$	$\phi_f \times 10^3$
11.6	1.30	1.29	9.66
9.91	1.65	0.996	11.7
8.19	1.53	0.784	15.1
6.47	2.12	0.612	17.2
5.17	2.78	0.377	25.4
3.45	3.91	0.283	33.9
2.59	4.79	0.195	48.7
1.72	7.74	0.138	55.7

yield of emission, and an apparent emission yield was calculated, ϕ_e(uncor). This apparent emission quantum yield is related to the true fluorescence (ϕ_f) and phosphorescence (ϕ_p) quantum yields by ϕ_e(uncor) $= (\phi_f/a) + \phi_p$, or the true fluorescence quantum yield is given by $\phi_f = \phi_e$(uncor)$/[(1/a) + (\phi_p/\phi_f)]$. From the shapes of emission curves of sulfur dioxide at narrow slit widths.[8a] the shape of the emission curve in the 3250–2875-Å region was defined for our conditions and the factor $a = 1.38$ evaluated. The needed ratio ϕ_p/ϕ_f was estimated for the high concentration region by the following procedure. The pure fluorescence spectrum of sulfur dioxide was determined in mixtures of sulfur dioxide with added biacetyl. Relatively small concentrations of biacetyl ($0.2 \times 10^{-5} M$) completely quenched the observed phosphorescence (3800–4700 Å) of sulfur dioxide at concentrations of (3.45–12) $\times 10^{-5} M$ and did not lower detectably the fluorescence of sulfur dioxide. Note in Figure 1 the spectrum for a sample in which the phosphorescence is partially quenched; for this experiment $[SO_2] = 8.62 \times 10^{-5} M$ and $[Ac_2] = 2.18 \times 10^{-7} M$. From the areas of the total emission spectra for the totally quenched and the unquenched experiments and their difference, it was determined that $\phi_p/\phi_f = 0.14 \pm 0.02$ for sulfur dioxide excited at 2875 Å. This is in excellent agreement with the value determined recently by Mettee[8a] in experiments at 2850 Å ($\phi_p/\phi_f = 0.14$). Mettee has found that the ratio ϕ_p/ϕ_f is independent of the sulfur dioxide concentration for $[SO_2] \geq 1.3 \times 10^{-5} M$ but that it falls off below this concentration. From his data at 2850 Å estimates of ϕ_p/ϕ_f were made. The quantum yields of fluorescence calculated from these data are summarized in Table I.

In other series of experiments the quantum yields of SO_2-triplet sensitized phosphorescence of biacetyl were determined. The areas

Table II. Quantum Yields of SO_2-Sensitized Biacetyl Phosphorescence (Φ_{sens}) and SO_2 Phosphorescence (ϕ_p) in Sulfur Dioxide–Biacetyl Mixtures Excited at 2875 Å and 25°

Concentration, $M \times 10^5$			
SO_2	Ac_2	$\Phi_{sens} \times 10^3$	$\phi_p \times 10^4$
3.45	0.000	...	5.9
3.45	0.026	6.9	...
3.45	0.033	7.1	1.6
3.45	0.041	7.9	...
5.17	0.000	...	4.1
5.17	0.020	5.5	2.0
5.17	0.026	7.1	1.8
5.17	0.033	7.5	...
5.17	0.046	7.5	1.6
5.17	0.056	8.3	1.4
5.17	0.211	12.1	...
5.17	0.263	11.1	...
8.62	0.000	...	2.5
8.62	0.016	4.0	1.2
8.62	0.020	5.3	...
8.62	0.022	5.3	...
8.62	0.033	4.9	0.99
8.62	0.046	6.3	0.99
8.62	0.057	10.8	...
8.62	0.066	10.6	...
8.62	0.131	14.7	...
8.62	0.200	12.0	...
8.62	0.305	8.9	...
12.93	0.000	...	1.7
12.93	0.016	3.5	1.1
12.93	0.059	7.8	0.78
12.93	0.079	7.5	0.62

of the biacetyl emission (4850–6700 Å), related to Φ_{sens} through the area of the fluorescence standard and the other parameters shown previously, were determined by use of a planimeter in this case. The quantum yields of sulfur dioxide phosphorescence in the biacetyl–SO_2 mixtures were determined in one of two ways. In the first method the area difference was determined between the SO_2 emission curve for a given experiment with added biacetyl and the curve for an equal sulfur dioxide concentration but with the biacetyl added in sufficient quantity to completely quench the triplet (fluorescence unchanged); this area is related directly to the phosphorescence yield through the other parameters involved. A second method which was employed involved the use of the measured intensities of emission ($I_{t\lambda}$) for the SO_2 mixtures as read directly from the Turner recorder chart at the wavelengths 3350 Å (pure fluorescence in every case), and 3950, 4100, 4200, 4350, and 4450 Å (fluorescence plus phosphorescence). The relative intensity of pure fluorescence at each of these wavelengths was determined in a series of experiments in which biacetyl addition quenched the sulfur dioxide phosphorescence completely: 3350 Å, 1.00; 3950 Å, 0.498; 4100 Å, 0.380; 4200 Å, 0.285; 4350 Å, 0.215; 4450 Å, 0.178. The contribution of fluorescence ($I_{f\lambda}$) to the measured intensity at each of the wavelengths was calculated from these ratios and the intensity at 3350 Å. Then the intensity of the phosphorescence ($I_{p\lambda}$) at each of the five wavelengths was found from the difference: $I_{t\lambda} - I_{f\lambda}$. At each wavelength an independent estimate of ϕ_p for each run was calculated from $I_{p\lambda}$ for the mixture, $I_{p\lambda}{}^0$ for pure sulfur dioxide at the same concentration as in the mixture, and the phosphorescence yield $\phi_p{}^0$ as calculated from the known ϕ_p/ϕ_f ratio and the least-squares equation for ϕ_f for pure sulfur dioxide at this concentration: $\phi_p = (I_{p\lambda}/I_{p\lambda}{}^0)\phi_p{}^0$. An average of the five independent estimates was used to derive the ϕ_p reported for the given experiment. The two methods gave results which were consistent, but the second method seemed to be less subject to instrumental variations, and it was used in most of the runs; see Table II.

Discussion of the Results

The Nature of the Excited Singlet Quenching Reactions. An Estimation of k_1 and k_2.

It has been reported previously, and it is confirmed here, that the sum of the

rates of reactions 1 and 2, the quenching of excited singlet sulfur dioxide molecules by ground-state molecules, is very efficient. A steady-state treatment using the proposed

$$^1SO_2 + SO_2 \rightarrow (2SO_2) \qquad (1)$$
$$\rightarrow {}^3SO_2 + SO_2 \qquad (2)$$
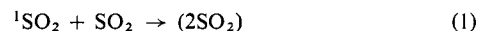
mechanism as outlined in the introduction yields the usual Stern–Volmer quenching relation 12. In Figure 2 a plot

$$\frac{1}{\phi_f} = \frac{[SO_2](k_1 + k_2) + k_3 + k_4 + k_5}{k_3} \qquad (12)$$

of $1/\phi_f$ vs. $[SO_2]$ is given from the data of Table I. A reasonably good straight line is observed. Using all of the data, $1/\phi_f = 19.3 \pm 16.6 + (6.55 \pm 0.32) \times 10^6$ (l./mole)$[SO_2]$;[12] using only the low concentration data ($[SO_2] \leq 1 \times 10^{-5}$ M) for which the intercept determination is more accurate, $1/\phi_f = 7.13 \pm 3.2 + (7.93 \pm 0.57) \times 10^6[SO_2]$. From the ratio of the slope (all data) to the intercept (low $[SO_2]$ data) and the value of $k_3 + k_4 + k_5$ of Greenough and Duncan,[4] an estimate of $k_1 + k_2$ can be made.

$$k_1 + k_2 = (2.2 \pm 1.0) \times 10^{10} \text{ l./(mole sec)}$$

It is interesting to compare this estimate of $k_1 + k_2$ with that found by previous workers. Greenough and Duncan[4] studied the lifetime of the $^1SO_2$ state as a function of sulfur dioxide pressure in experiments in which excitation was effected using a band of wavelengths near the maximum absorption of sulfur dioxide (2700–3100 Å). The slope of the plot of reciprocal of the lifetime vs. P_{SO_2} gave the estimate, $k_1 + k_2 = (4.3 \pm 0.3) \times 10^{10}$ l./(mole sec).[4b,13] Strickler and Howell[7] made relative fluorescence measurements from sulfur dioxide excited at several wavelengths. From their experiments at 2894 Å, the estimate of $k_1 + k_2 = (6.4 \pm 1.1) \times 10^{10}$ l./(mole sec),[14] can be derived from the plot of the function $(I_f{}^\infty/I_f) - 1$ vs. $1/P_{SO_2}$ for which the slope $= (k_3 + k_4 + k_5)/(k_1 + k_2)$. $I_f{}^\infty$ is the limiting value of the fluorescence intensity at high sulfur dioxide pressures. Mettee has made quantum yield measurements for sulfur dioxide fluorescence as a function of P_{SO_2} at several wavelengths of excitation. From his experiments at 2850 Å, the $1/\phi_f$ vs. P_{SO_2} plot, treated as in this work, gives $k_1 + k_2 = (14 \pm 8) \times 10^{10}$ l./(mole sec). There is actually much better agreement between our data and that of Mettee than the estimates of $k_1 + k_2$ would indicate. The slopes of the two plots of $1/\phi_f$ vs. $[SO_2]$ are in good agreement; using all the data we find the slope $= (6.55 \pm 0.32) \times 10^6$, while Mettee finds the slope $= (5.62 \pm 0.56) \times 10^6$ moles/l. $k_1 + k_2$ was derived from the ratio of the slope to the intercept of the plot. Thus the apparent disagreement between the two estimates of $k_1 + k_2$ enters through the difference in the intercepts. From the experiments at low pressures, Mettee finds the intercept $= 0.96 \pm 0.56$, and we estimate the intercept to be 7.13 ± 3.2. Later in this paper an independent estimate of ratio $(k_3 + k_4 + k_5)/k_3$, the intercept, is made; it will be seen that it supports the

(12) In every case in this work, the error limits shown represent the 95% confidence limits (twice the standard deviation) as determined by the method of least squares.
(13) The error limits were estimated by the authors by a least-squares treatment of the original Greenough data.[4b]
(14) The error limits shown were estimated by the authors by a least-squares treatment of the Strickler and Howell data for experiments at 2894 Å.

$$\frac{1}{\Phi_{sens}} = \frac{1}{[Ac_2]}\left[\left(\frac{k_{10} + k_{11}}{k_9 k_{10}}\right)\left(\frac{[SO_2](k_1 + k_2) + k_3 + k_4 + k_5}{[SO_2]k_2 + k_5}\right)([SO_2]k_8 + k_6 + k_7)\right] +$$

$$\left[\frac{\{[SO_2](k_1 + k_2) + k_3 + k_4 + k_5\}(k_{10} + k_{11})}{([SO_2]k_2 + k_5)k_{10}}\right] \quad (13)$$

reliability of our intercept estimate. In view of all the data we believe that the Mettee intercept estimate is in error. Thus the present estimate of $k_1 + k_2$ is seen to be in reasonable agreement with the previous estimates of this quantity within the experimental error.

All of the data suggest that the rate with which $^1SO_2$ is deactivated upon collision with SO_2 is within an order of magnitude of the rate with which collisions occur between these species; the collision number is 1.4×10^{11} l./(mole sec) at 25°, assuming a collision diameter of 4.04 Å for both $^1SO_2$ and SO_2. Both Douglas[5] and Strickler and Howell[7] have been able to rationalize this high rate by consideration of the excited singlet state as a composite of excited singlet, triplet, and ground vibronic states. As far as collisions are concerned, the $^1SO_2$ molecule is similar to a highly vibrationally excited ground-state molecule, and collisional relaxation is fast. However, since only the $^1SO_2$ component of the hybrid state can combine radiatively with the low-lying vibrational levels of the ground state, radiative decay is slow. It is interesting to speculate on what fraction of the deactivating collisions results in spin inversion, reaction 2, and what fraction leads to vibrationally relaxed ground-state molecules, reaction 1. It was noted by the authors that in principle an independent measurement of k_2 could be had utilizing energy-transfer experiments.

The photochemistry of biacetyl has been most thoroughly studied, largely through the effort of Noyes and co-workers,[15] and it appeared to be a reasonable choice for the triplet energy acceptor. Indeed, when small amounts of biacetyl are added to 2875-Å irradiated sulfur dioxide, a decrease in the phosphorescence of sulfur dioxide occurs, and the sensitized phosphorescence of biacetyl is observed; see the spectra of Figure 1. There is no detectable quenching of the shorter lived singlet state even when sufficient biacetyl is added to quench the $^3SO_2$ state nearly completely. Thus in a series of experiments the sensitized quantum yield of biacetyl emission (Φ_{sens}) was determined at various sulfur dioxide and biacetyl concentrations. Since quenching of the $^1SO_2$ state is not observed at the low biacetyl concentrations employed here, the reaction sequence 1–11 should describe the system completely. In theory Φ_{sens} should be related to the biacetyl and sulfur dioxide concentrations by relation 13. The data from a series of runs at fixed $[SO_2]$ should show a linear relation between $1/\Phi_{sens}$ and $1/[Ac_2]$. Data were determined at four sulfur dioxide concentrations (Table 11), and a test of the fit to relation 13 is given in Figure 3. Within the experimental error the data follow the expected form. The least-squares treatment of the results shows a near-common intercept for all the series: 96 ± 40 at $[SO_2]$ = $3.45 \times 10^{-5} M$; 81 ± 13 at $[SO_2] = 5.17 \times 10^{-5} M$;

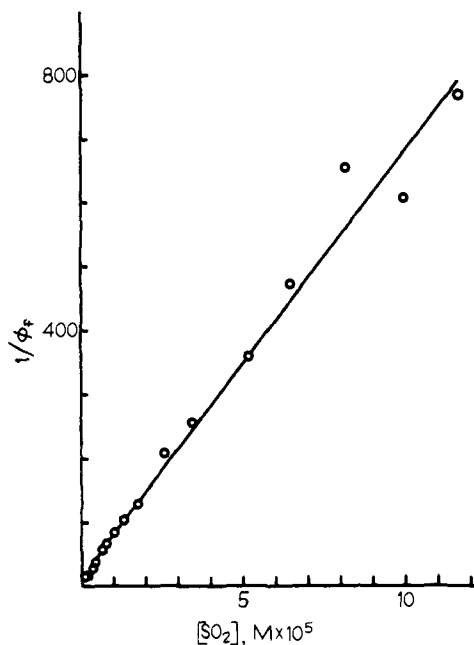Figure 2. Stern–Volmer plot of the quantum yields of fluorescence from SO_2 excited at 2875 Å; the line drawn is the least-squares fit of all of the data.

74 ± 30 at $[SO_2]$ = $8.62 \times 10^{-5} M$; 83 ± 26 at $[SO_2]$ = $12.9 \times 10^{-5} M$. If both the conditions, $[SO_2](k_1 + k_2) \gg k_3 + k_4 + k_5$ and $[SO_2]k_2 \gg k_5$, are met, then a common intercept is expected for this family of curves. From the known rate-constant data one can calculate that at the lowest $[SO_2]$ employed where the contribution of $k_3 + k_4 + k_5$ to the term $[SO_2](k_1 + k_2) + k_3 + k_4 + k_5$ is the largest, it amounts to only 3%. Then if $k_5 \ll [SO_2]k_2$ the observed common intercept would be expected in theory. As we shall see from the k_5 and k_2 estimates derived later, this inequality holds well. Thus from an average of the intercepts of the lines of Figure 3 we find

$$\frac{(k_{10} + k_{11})(k_1 + k_2)}{k_{10}k_2} = 83 \pm 14$$

Recently Collier, Slater, and Calvert[16] redetermined the quantum yield of biacetyl phosphorescence excited at 4358 Å; they found $k_{10}/(k_{10} + k_{11}) = 0.149 \pm 0.009$.[17] This estimate checks well with the original data of Almy and Gillette.[18] They found 0.145 ± 0.03 in experiments made years ago using less sophisticated equipment. Taking our estimate of $k_{10}/(k_{10} + k_{11})$, we find

$$k_2/(k_1 + k_2) = 0.080 \pm 0.014$$

(15) (a) W. A. Noyes, Jr., G. B. Porter, and J. E. Jolley, Chem. Rev., 56, 49 (1956); (b) H. Okabe and W. A. Noyes, Jr., J. Am. Chem. Soc., 79, 801 (1957); (c) J. Heicklen and W. A. Noyes, Jr., ibid., 81, 3858 (1959); (d) H. Ishikawa and W. A. Noyes, Jr., 84, 1502 (1962); J. Chem. Phys., 37, 583 (1962).

(16) S. S. Collier, D. H. Slater, and J. G. Calvert, J. Photochem. Photobiol., 7, 737 (1968).

(17) Three independent determinations of $k_{10}/(k_{10} + k_{11})$ gave the values 0.144, 0.149, and 0.153.

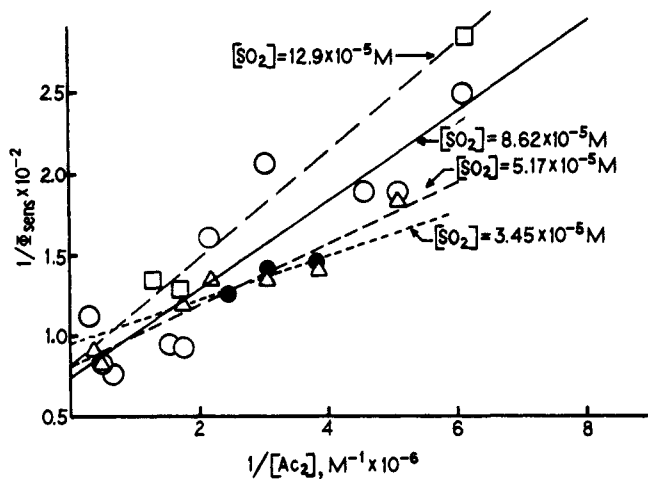(18) G. M. Almy and P. R. Gillette, J. Chem. Phys., 11, 188 (1943).

Figure 3. Plots of the reciprocal of the quantum yield of the $^3SO_2$-sensitized phosphorescence from biacetyl vs. the reciprocal of the [Ac$_2$]; the symbols designate the given [SO$_2$] used in the different series: □, $12.9 \times 10^{-5} M$; ○, $8.62 \times 10^{-5} M$; △, $5.17 \times 10^{-5} M$; ●, $3.45 \times 10^{-5} M$: In theory the intercepts are equal to $(k_{10} + k_{11})(k_1 + k_2)/k_{10}k_2$.
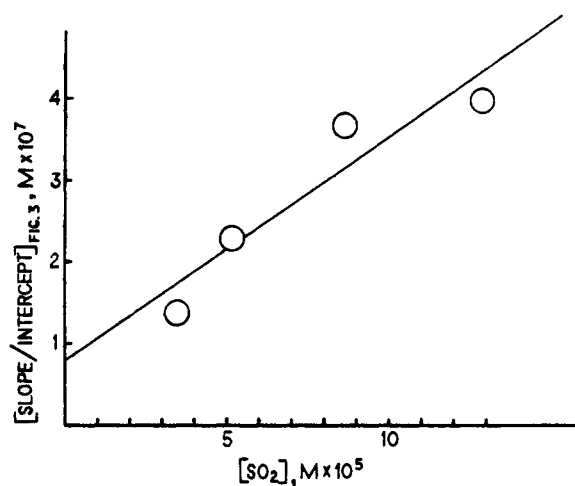

Figure 4. Plot of the (slope/intercept) ratio from the least-squares lines of Figure 3; the slope and intercept of this plot are used to derive estimates of k_8 and k_9.
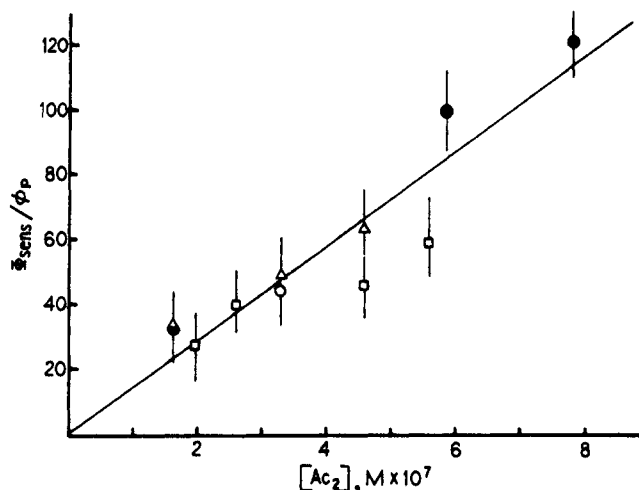

Figure 5. Plot of the ratio of the quantum yield of SO$_2$-sensitized phosphorescence from biacetyl to that for phosphorescence from SO$_2$ vs. [Ac$_2$]; the different symbols designate the given [SO$_2$] used in the runs: ●, $12.93 \times 10^{-5} M$; △, $8.62 \times 10^{-5} M$; ○, $3.45 \times 10^{-5} M$. In theory the slope of the line is equal to $[k_{10}k_9/k_6(k_{10} + k_{11})]$.

Accepting the estimate of $k_1 + k_2$ derived above, we can estimate the individual constants.

$$k_2 = (0.18 \pm 0.08) \times 10^{10} \text{ l./(mole sec)}$$

$$k_1 = (2.0 \pm 1.0) \times 10^{10} \text{ l./(mole sec)}$$

It can be seen that quenching collisions of $^1SO_2$ with SO$_2$ result in spin inversion with $^3SO_2$ formation about 8% of the time, and 92% of the quenching collisions cause relaxation to the ground state and/or chemical change which does not involve excited sulfur dioxide states. One can gain some additional confidence in these data and the interpretation by checking the consistency of the slopes observed in Figure 3. In theory the slope to intercept ratios in this plot should be given by relation 14.

$$\left[\frac{\text{slope}}{\text{intercept}}\right]_{\text{Fig 3}} = \frac{[SO_2]k_8 + k_6 + k_7}{k_9} \quad (14)$$

The slope to intercept ratios, derived by a least-squares treatment of the results in Figure 3, are plotted vs. [SO$_2$] in Figure 4. From this plot we estimate from the slope, $k_8/k_9 = (2.7 \pm 1.4) \times 10^{-3}$, and from the intercept, $(k_6 + k_7)/k_9 = (0.79 \pm 1.2) \times 10^{-7}$ mole/l. Taking the Caton and Duncan[6] value of $k_6 + k_7$, we estimate $k_9 = (1.8 \pm 2.7) \times 10^9$ l./(mole sec), and $k_8 = (4.9 \pm 13.5) \times 10^6$ l./(mole sec). The value of k_9 is in reasonable agreement with that expected for a triplet energy-transfer reaction. The estimate of k_8 is a fair check on the value calculated from the Strickler and Howell[7] data for phosphorescence intensity at low pressures, $k_8 = (2.5 \pm 0.5) \times 10^7$ l./(mole sec).[19] Probably the best estimate

(19) We have considered the Strickler and Howell data[7] in terms of the more complete sulfur dioxide photolysis mechanism outlined in this work. The function 6 of Strickler and Howell becomes $A(I_p^\infty/I_p) - 1 = [(k_6 + k_7)/k_8](1/[SO_2])$. The factor A is equal to $\{[SO_2](k_1 + k_2) + k_3 + k_4 + k_5)/[SO_2](k_1 + k_2)\}\{[SO_2]k_2/([SO_2]k_2 + k_5)\}$; for the conditions employed by Strickler and Howell A is near to, but not equal to, unity. Using the data from this work for $k_1 + k_2$, k_2, and k_5, and the Greenough and Duncan estimate of $k_3 + k_4 + k_5$, we have calculated A and $A(I_p^\infty/I_p) - 1$ from the Strickler and Howell data. The least-squares treatment of the plot of the function $A(I_p^\infty/I_p) - 1$ vs. $1/[SO_2]$ gave a slope $= (0.577 \pm 0.084) \times 10^{-5} M$ and an intercept $= -0.011 \pm 0.050$. The value of k_8 given was derived from the ratio of Caton and Duncan's[6] estimate of $k_6 + k_7$ and the slope of this plot.

of k_9 which we can derive from our data is made through the use of the k_8/k_9 ratio derived here and the value of k_8 from the data of Strickler and Howell.[7,19]

$$k_9 = (9.3 \pm 5.2) \times 10^9 \text{ l./(mole sec)}$$

Thus the SO$_2$-sensitized quantum yield data are seen to be consistent, and one can gain some confidence in the k_1 and k_2 estimates which we have derived.

The Unimolecular Decay Reactions of the Excited $^3SO_2$ Molecule. An Estimation of the Rate Constants, k_6 and k_7. It is possible to derive an estimate of the rate constant for the radiative decay of $^3SO_2$, reaction 6, through a consideration of the sulfur dioxide phosphorescence quantum yields (ϕ_p) and the SO$_2$-sensitized biacetyl phosphorescence quantum yields (Φ_{sens}) as determined in biacetyl-SO$_2$ mixtures. One expects relation 15 to hold, provided that all the quenching which results from the $^3SO_2$-Ac$_2$ encounters leads to excited biacetyl.
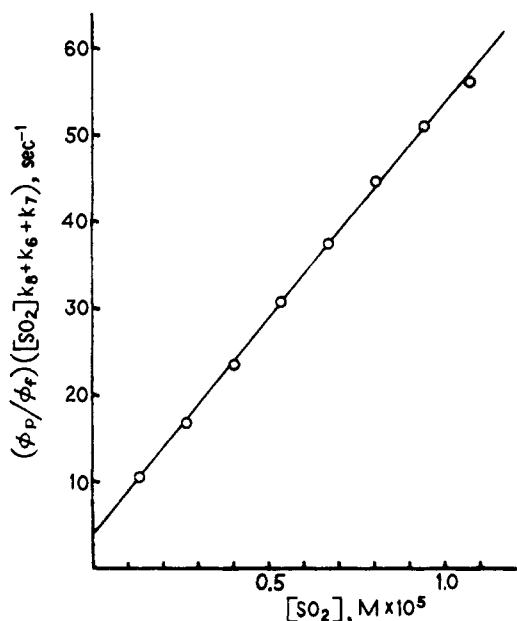
Figure 6. Plot of a function of ϕ_p/ϕ_f and [SO_2]; ratios of ϕ_p/ϕ_f are from data of Mettee;[8] the value of k_8 was taken from the study of Strickler and Howell;[7] the slope to intercept ratio is equal to k_2/k_5 in theory.

$$\frac{\Phi_{sens}}{\phi_p} = \frac{k_{10}k_9}{(k_{10} + k_{11})k_6} [Ac_2] \qquad (15)$$

This provision is probably met since collisional quenching of the $^3SO_2$ molecule by SO_2,[6,7,9,20] O_2,[6,20] and CO_2[20] is extremely inefficient. In each case it is smaller by a factor of 10^3 than that for biacetyl quenching. It is highly probable that the special efficiency of $^3SO_2$ quenching by biacetyl lies in the efficiency of biacetyl as an electronic energy acceptor. Since all rate constants in eq 15 but k_6 have been estimated, a path to the evaluation of this constant is evident. The data of Table II were used to test the form of relation 15 in Figure 5. The considerable scatter of the data reflect the experimental inaccuracy in the determination of the ratio Φ_{sens}/ϕ_p; ϕ_p data are the major source of scatter. However, within the large experimental error, the data from runs at several concentrations of sulfur dioxide are consistent with the theoretically expected linear function.

The intercept of the least-squares line is zero (3.3 ± 16.6) within the error limits, as relation 15 demands. From the slope of the line we derive

$$\frac{k_{10}k_9}{(k_{10} + k_{11})k_6} = (1.4 \pm 0.4) \times 10^8 \text{ l./mole}$$

Taking $k_{10}/(k_{10} + k_{11}) = 0.149 \pm 0.009$,[16] $k_9 = (9.3 \pm 5.2) \times 10^9$ l./(mole sec), and $k_6 + k_7 = (1.43 \pm 0.16) \times 10^2$ sec^{-1},[6] we estimate

$$k_6 = (0.10 \pm 0.06) \times 10^2 \text{ sec}^{-1}$$
$$k_7 = (1.33 \pm 0.17) \times 10^2 \text{ sec}^{-1}$$

The value of k_6 represents a maximum value since any inefficiency in the triplet energy transfer reaction would

(20) T. N. Rao, S. S. Collier, and J. G. Calvert, submitted for publication.

result in a low estimate. It is interesting to compare the radiative lifetime calculated from our k_6 estimate, $\tau^0 = 100 \pm 60$ msec, with that estimate from the integrated absorption of the triplet band. Caton and Duncan,[6] using values of the oscillator strength of the $^1A_1 \rightarrow {}^3B_1$ transition derived by Mulliken[21] from two independent sets of measurements, estimated lifetimes of 2.6 and 15.5 msec. Caton and Duncan assumed the ratio of degeneracies of the triplet to singlet states to be unity in this calculation following the conclusion of Sidman[22] that on the average only one of the three components of spin is responsible for the spin–orbit coupling which allows the $^1A_1 + h\nu \rightarrow {}^3B_1$ transition in sulfur dioxide. However, it has been pointed out to the authors that as long as there is rapid interconversion between the three triplet states before emission, as seems highly likely, then the appropriate ratio of triplet to singlet state degeneracy to be used is three.[23] This results since at any given instant only one-third of the molecules are in the proper triplet state from which emission is allowed, and the measured lifetime would be three times the true lifetime of the single triplet component. Taking the degeneracy factor of 3, the integrated absorption data suggest a lifetime of the triplet state in the range 7.8–46.5 msec. Within the large error limits there is agreement between the estimated lifetime from our $1/k_6$ data and that from integrated absorption data. It is possible in theory that a small increase in the radiative lifetime of the triplet results from some mixing of the vibronic levels of the triplet with those of the ground-state singlet. However, the number of such levels which could mix is small[7] and the effect would be expected to be small if present. One must await a redetermination of k_6 with greater precision and more accurate $^3B_1 \leftarrow {}^1A_1$ absorption data before speculating on the possible significance of this result.

The Unimolecular Decay Reactions of the Excited SO_2 State. An Estimation of the Rate Constants k_3, k_4, and k_5. The rate constants for reactions 3 and 5 can be derived from a consideration of the variation of the ratio of the quantum yield for phosphorescence to that for fluorescence in sulfur dioxide. Relation 16 is expected to describe ϕ_p/ϕ_f from the mechanism given.

$$\frac{\phi_p}{\phi_f} = \frac{k_6}{k_3} \left[\frac{[SO_2]k_2 + k_5}{[SO_2]k_8 + k_6 + k_7} \right] \qquad (16)$$

At high concentrations of sulfur dioxide, (16) reduces to

$$\phi_p/\phi_f = k_6k_2/k_3k_8 \qquad (17)$$

Both the studies of Strickler and Howell[7] and Mettee[8a] showed ϕ_p/ϕ_f to be independent of [SO_2] for [SO_2] $\geq 1 \times 10^{-5} M$. Using the limiting value of $\phi_p/\phi_f = 0.14 \pm 0.02$ for the high concentration conditions at 2875 and 2850 Å derived both in this work and by Mettee,[8a] and estimates of k_2, k_6, and k_8 derived above, we find

$$k_3 = (5.1 \pm 4.0) \times 10^3 \text{ sec}^{-1}$$

It is possible for us to estimate k_5 from the results of Mettee[8a] on the variation of the ϕ_p/ϕ_f ratio with [SO_2] in the region of rapid change. Since both our work and that of Mettee give essentially the same value for ϕ_p/ϕ_f in the high-pressure limit, the use of Mettee's ϕ_p/ϕ_f data for

(21) R. S. Mulliken, Can. J. Chem., 36, 10 (1958).
(22) J. W. Sidman, J. Chem. Phys., 29, 644 (1958).
(23) S. J. Strickler, private communication to the authors.

low pressure of sulfur dioxide should not introduce any inconsistency in our treatment. From the curve of ϕ_p/ϕ_f vs. pressure in Mettee's work at 2850 Å, we estimated ϕ_p/ϕ_f for every 25-μ pressure interval. From these data and the rate constant estimates for $k_8 = (2.5 \pm 0.5) \times 10^7$ l./(mole sec)[7,19] and $k_6 + k_7 = (1.43 \pm 0.16) \times 10^2$ sec^{-1},[6] we calculated the function, $[SO_2]k_8 + k_6 + k_7$, for the corresponding pressure of sulfur dioxide. The product of $(\phi_p/\phi_f)([SO_2]k_8 + k_6 + k_7)$ was then determined and plotted vs. $[SO_2]$ in Figure 6. The expected linear relationship between the variables is observed. The least-squares treatment of these data gives the slope

$$k_6 k_2/k_3 = (4.91 \pm 0.16) \times 10^6 \text{ l./(mole sec)}$$

and the intercept

$$k_5 k_6/k_3 = 4.0 \pm 1.1 \text{ sec}^{-1}$$

The ratio of slope to intercept gives

$$k_2/k_5 = (1.2 \pm 0.3) \times 10^6 \text{ l./mole}$$

Coupling this with our estimate for k_2 we find

$$k_5 = (1.5 \pm 0.8) \times 10^3 \text{ sec}^{-1}$$

Since the sum $k_3 + k_4 + k_5$ is known,[4] we can estimate k_4.

$$k_4 = (1.7 \pm 0.4) \times 10^4 \text{ sec}^{-1}$$

It is instructive to test the consistency of the k_3 estimate by comparison of the experimentally measured value of the limiting quantum yield of fluorescence at $[SO_2] = 0$, reported in this work, with the ratio expected from our rate constant estimates; at $[SO_2] = 0$ we would expect in theory ϕ_f to be given by

$$\phi_f = k_3/(k_3 + k_4 + k_5)$$

The calculated limiting ϕ_f is 0.21 ± 0.16. Within the rather large error limits this is in reasonable agreement with the value of ϕ_f at $[SO_2] = 0$ which we obtain from an extrapolation of the experimental data, $\phi_f = 0.14 \pm 0.06$. We must conclude that ϕ_f at $[SO_2] = 0$ is much less than unity. This is a surprising result in view of the present theories related to intramolecular radiationless transitions in simple molecules.[24] In theory two of the important factors which determine the rate of intramolecular radiationless transitions are: (1) the density of the vibrational levels of the ground-state molecule which lie in the vicinity of the occupied levels of the electronically excited molecule; and (2) the extent of coupling which occurs between these states. The density of states in triatomic molecules such as SO_2 is very low. However, the coupling between the states of sulfur dioxide may be very efficient. The present work suggests that the radia-

tive lifetime of the $^1SO_2$ state ($1/k_3$) is 2×10^{-4} sec. There is even a greater anomaly in the lifetime than has been thought previously; it is 300–1000 times longer than that calculated from the integrated absorption coefficient data.[4,5,7] The abnormally long radiative lifetime of $^1SO_2$ suggests that there is very efficient coupling between the vibronic levels of the excited and ground states in sulfur dioxide which overrides the intrinsic low density of states. This efficient coupling may be the origin of the significant participation of raditionless transitions which our results suggest for sulfur dioxide.

It is interesting to compare the ratio of the second-order rate constants for intersystem crossing and internal conversion with the ratio of the first-order rate constants for these same processes derived in this work.

$$k_2/k_1 = \frac{(0.18 \pm 0.08) \times 10^{10}}{(2.0 \pm 1.0) \times 10^{10}} = 0.090 \pm 0.060$$

$$k_5/k_4 = \frac{(1.5 \pm 0.8) \times 10^3}{(1.7 \pm 0.4) \times 10^4} = 0.088 \pm 0.051$$

The ratio of $^1SO_2$ molecules which form triplet to those that form ground-state singlet molecules is about the same whether the processes are collisionally induced or whether they occur in the isolated molecule. Strickler has estimated[7] (assuming harmonic vibrations) that within the width of one of the vibrational bands in SO_2 absorption near 3000 Å, there should be around 200 vibrational levels of the ground state and about 20 levels of the triplet state. The relative density of vibrational levels in the two states suggests that the maximum value of the ratio k_2/k_1 or k_5/k_4 would be 0.10. This is surprisingly near to the experimental values found here. One would expect some significant degree of discrimination against the spin inversion steps 2 and 5. Apparently the extent of reaction by alternative paths 1 and 2 or 4 and 5 is determined largely by the density of states in this case.

The rate constants derived in this work provide some substantial progress toward an understanding of the photophysical primary processes which occur in sulfur dioxide photochemistry at 2875 Å. Of major interest in our continuing research in this area is an attempt to correlate the photophysical primary processes with photochemical changes which can be observed in sulfur dioxide containing systems. Specifically we are attempting to determine the reaction rate constants for $^1SO_2$ and $^3SO_2$ species with various reactive molecules such as oxygen and the olefinic and paraffinic hydrocarbons.

(24) (a) G. W. Robinson, *J. Chem. Phys.*, **47**, 1967 (1967); (b) G. W. Robinson, "The Triplet State," Cambridge University Press, London, 1967, p 213; (c) M. Bixon and J. Jortner, *J. Chem. Phys.*, **48**, 715 (1968); (d) D. P. Chock, J. Jortner, and S. A. Rice, *ibid.*, **49**, 610 (1968).