The Ultraviolet Spectra of Matrix Isolated Disulfur Monoxide and Sulfur Dioxide

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The absorption spectrum of disulfur monoxide was observed in matrices at 20°K. All 18 observed bands of the $(0, 0, v_3) - (0, 0, 0)$ progression fit the equation $G(v_{3}') = 29\ 070 + 426\ (v_{3}' + \frac{1}{2}) - 4.80\ (v_{3}' + \frac{1}{2})^2 + 0.075\ (v_{3}' + \frac{1}{2})^3$. The matrix data was used to reassign the reported gas-phase data and to deduce v_{2}' and v_{2}'' . The absorption spectrum of sulfur dioxide in a krypton matrix at 20°K is tentatively assigned to a progression $A(v_1, v_2, 0) \leftarrow X(0, 0, 0)$. The SO₂ *a*-X phosphorescence, excited by absorption of light in either the *C* or *A* system, is strongly enhanced in the matrix. T_{00} , v_1 and v_2 shifts are listed for solid argon, krypton, xenon, nitrogen, methane, SF₆, and C₄F₈. The phosphorescence intensity is strongly temperature dependent. The temperature-intensity curves are consistent with an energy transfer model involving interaction of the SO₂ triplet state with the lattice vibration.

This paper is part of a study of sulfur oxides. It is concerned with the low-lying electronic transitions of S_2O and SO_2 . Two systems will be described in two separate parts: (A) the absorption spectrum of S_2O in xenon, and (B) the absorption and phosphorescence of SO_2 in various solvents.

The gas phase spectra of both molecules are well studied and several transitions have been observed. It was our intention to observe the difference between gas phase and matrix spectra and learn more about the spectra by studying ab sorption and emission to and from the ground electronic and vibrational states.

PART A. ABSORPTION SPECTRUM OF S2O

Schenk (1), Cordes (2), Kondratieva and Kondratiev (3), and Jones (4) reported the spectrum of a sulfur oxide which was originally believed to be SO, then later S_2O_2 . The microwave studies of Meschi and Myers (5) identified the absorber as S_2O . The UV and IR work of Jones led to values for the vibrational frequencies ν_1 and ν_2 of the ground state molecule together with the vibrational frequency ν_3 for the upper state and a provisional value for the origin of the band

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system. Meschi and Myers (6) in a microwave study obtained an approximate value for the remaining ground state frequency ν_2 , and a more precise value for this frequency, referring, however, to the molecule in a solid film at 77°K, was reported from an infrared study by Blukis and Myers (7). The purpose of the present study was to analyze the matrix absorption spectrum and to confirm the origin of the system by observing the progression of bands with v'' = (000).

Experimental Methods

The molecular beam arrangement and the cryostat were described earlier (8). A Cryo-tip refrigerator AC-2L (Air Products and Chemicals, Allentown, Pa.) was used to cool the sapphire target, and a copper versus gold-cobalt thermocouple was used to measure the target temperature.

The S₂O-rare gas mixtures were prepared using a modification of Schenk's synthesis (θ). For this purpose SOCl₂ was premixed with the rare gas in a measured volume. The mixture was then expanded through a Teflon valve and the flow measured with a Fischer-Porter flowmeter equipped with a Teflon ball. The gas then passed through a U-tube containing silver sulfide which was kept at 160°C. From the reaction tube the gas stream now containing S₂O and rare gas was expanded through a jet and deposited on the sapphire target as a molecular beam. If freshly prepared granulated silver sulfide was used, and the flow system was purged with pure SOCl₂ prior to deposition, the S₂O-containing solids were spectroscopically pure and gave none of the strong SO₂ fluorescence. Solvent to solute ratios were commonly about 100:1, and a total of about 2 mmoles of material were deposited in each experiment.

The rare gas solvents were research grade (Linde), $SOCl_2$ was Eastman Kodak practical grade used after fractional condensation at $-78^{\circ}C$. The CH_4 , SF_6 , SO_2 , and C_4F_8 were Matheson high-purity products.

Absorption spectra were photographed on a Jarrell-Ash f/6.3 Czerny-Turner instrument with a 2160 lines/mm grating blazed for 3000 Å. Polaroid film and Kodak spectroscopic plates type 103a-F were used. Fluorescence and phosphorescence were recorded with a 0.3-m McPherson model 218 instrument with an 1100 lines/mm grating blazed for 5000 Å, and an E. M. I. 9502S photomultiplier.

Fluorescence and phosphorescence were excited with an AH-6 high pressure mercury arc, in conjunction with a Farrand f/3 monochromator. Exciting frequencies between 2500 and 6000 Å could be selected. The slits were chosen to give a bandwidth of about 50 Å. Absorption and fluorescence blanks were recorded throughout the entire range.

Results and Discussion

In the 2300–6000 Å region only one transition of S_2O is observed. The absorption spectrum of S_2O in argon, krypton, and xenon matrices consist of a long



FIG. 1. Absorption Spectrum of S₂O in xenon at 20°K

progression of vibrational bands. In nitrogen at 20°K the spectrum is so broad that vibrational structure is not well resolved. We report here only the results for xenon matrices, which gave the sharpest bands, with well resolved and clear absorption peaks. Figure 1 shows the absorption spectrum of SO₂ in Xe at 20°K. Although the absorption regions of S₂O, SO₂, and SOCl₂ overlap, and although the molecules are chemically related and could occur simultaneously in our system, it proved easy to prepare spectroscopically pure samples of S₂O solutions. The fact that we could prepare S₂O free of the very sensitive phosphorescence of the other two molecules indicates that our method of preparation leads to S₂O which is essentially 100 % pure (9).

In Table I are listed the positions of all the observed absorption peaks of S_2O in xenon at 20°K. Measurements are believed accurate to ± 20 cm⁻¹. The observed bands form a single progression obeying the formula

$$G(v_3') = 29\ 070 + 426(v_3' + \frac{1}{2}) - 4.80(v_3' + \frac{1}{2})^2 + 0.075(v_3' + \frac{1}{2})^3.$$
(1)

The last two columns of Table I contain values of G(v) calculated from Eq. (1) and of Δ , the difference between observed and calculated values.

Columns two and three of Table I list the corresponding band heads observed during the work of Cordes and Jones, respectively. The data of Cordes, up to $v_3' = 18$ can be fitted to

$$G(v_{3}') = 29 \ 026 + 436 \ (v_{3}' + \frac{1}{2}) - 4.00 \ (v_{3}' + \frac{1}{2})^{2} + 0.08 \ (v_{3}' + \frac{1}{2})^{3}, \quad (2)$$

ε'3 '	Gas phase band heads		Absorption	Calc from	T. 1.27
	Cordes ^a	Jones ^b	maxima matrix ^c	Eq. (1)	Difference
0			29 285	29 285	0
1			$29 \ 700$	29 700	0
2	$30 \ 091$	30 100	30 120	$30 \ 105$	15
3	30 503	$30 \ 506$	30 505	30 505	0
4	30 907	30 909	$30 \ 875$	30 890	15
5	$31 \ 303$	$31 \ 308$	$31 \ 270$	$31 \ 275$	ā
6	31 699		$31 \ 635$	$31 \ 655$	20
7	$32 \ 093$		$32 \ 040$	$32 \ 030$	10
8	32 488		$32 \ 375$	32 390	15
9	$32 \ 871$		32 715	32 750	35
10	$33 \ 251$		$33 \ 105$	$33 \ 100$	5
11	$33 \ 634$		$33 \ 435$	$33 \ 450$	15
12	$34 \ 006$		33 810	33 795	15
13	$34 \ 377$		$34 \ 145$	$34 \ 130$	15
14	$34 \ 745$		34 460	34 470	10
15	$35 \ 115$		34 835	34 800	35
1 6	$35 \ 472$		$35 \ 165$	$35 \ 130$	35
17	$35 \ 850$		$35 \ 450$	35 460	10
18	36 242		$35 \ 705$	35 735	30

TABLE I S2O Absorptions in the GAS Phase, and in Xenon at 20°K $(\rm cm^{-1})$

a Ref. (2).

ь Ref. (4).

 $^\circ$ ± 5 cm^{-1}.

while the limited but more precise data of Jones leads to

$$G(v_{3}') = 29\ 064.9 + 419.7\ (v_{3}' + \frac{1}{2}) - 2.425\ (v_{3}' + \frac{1}{2})^{2} + 0.05\ (v_{3}' + \frac{1}{2})^{3}.$$
(3)

Equations (1-3) indicate that the matrix spectrum is very similar to that of the gas phase. The ν_3 vibration is only slightly constrained in the matrix, even the rate of convergence changing only slightly, although significantly. The predissociation limit (2) is not apparent in the solid.

On the basis of the data of Jones, Herzberg (10) lists a T_{00} value of 30 099.8 cm⁻¹. Since the gas-phase spectra are complex, and also involve transitions from excited ground state vibrational levels, it is likely that Jones could not observe the weak bands which we have found to the red of the reported gas phase origin. We conclude, therefore, that the gas-phase numbering is incorrect. The numbering in Table I assumes that so far generally observed heavy atom effect holds, and that only a small shift of the transition energy is expected.

The occurrence of only a single upper state progression facilitates the analysis

of our data but reduces the amount of information that can be gained about the molecule. However, knowing that matrix transitions must originate from v'' = (000) we can now reconsider the gas phase data. The fundamental ground state vibrational frequencies of S₂O are listed as $\nu_1 = 1165$ and $\nu_3 = 679$ cm⁻¹ (2), and $\nu_2 = 388$ cm⁻¹ in a solid film at 77°K. For the upper state, on the basis of a figure of 415 cm⁻¹ for the ν_3 fundamental derived from Eq. (3), one can estimate $\nu_1 \sim 720$ and $\nu_2 \sim 240$. Jones distinguished three gas phase progressions of which A is given in Table I. Series B he assigned to a progression in ν_3' originating from $\nu_3'' = 1$. Series C would now appear to correspond to a progression of ν_3 with simultaneous excitation from $\nu_2' = 0$ to $\nu_2' = 1$. On this assumption one deduces by extrapolation to $\nu_3' = 0$ a value of 286 cm⁻¹ for the ν_2 fundamental in the gas-phase upper state. Cordes observed low-lying transitions which he listed in the same progression at 29 998 and 29 568 cm⁻¹; however, these bands do not really fit here and are better interpreted as involving ν_2 in both electronic states, since

$$29 \ 998 = 29 \ 243 \ - \ 377 \ + \ 428 \ + \ 420 \ + \ 284 \tag{4}$$

and

$$29 568 = 29 243 - 377 + 428 + 274 \tag{5}$$

where the separation of the zero vibrational levels and the v_3 spacings are as given by Eq. (2). The value $v_2'' = 377 \text{ cm}^{-1}$ that we have used in Eqs. (4) and (5) comes from the lower lying of the two pairs of transitions which Cordes lists at 29 998, 30 373 cm⁻¹ and 29 440, 29 817 cm⁻¹. This value is consistent with $v_2 = 388$ as found by Blukis and Myers in the solid (7) and 370 \pm 30 cm⁻¹ found by Meschi and Myers in the gas phase (6). The second column of Cordes Table 2 (2) contains transitions which differ by an average of 1174 cm⁻¹ from the transitions two places further down the v_3' progression; thus these transitions probably originate from the level $v_1'' = 1$. It is therefore likely that transitions including v_1 of the upper state are among those that remain unassigned (about one-third of the transitions in Cordes' table) but the low precision of the data makes identification ambiguous at present.

PART B. ABSORPTION AND PHOSPHORESCENCE OF SO2

The gas phase spectrum of SO_2 is well known (10). Transitions from the ground state to the states a and A are observed both in absorption and fluorescence. The gas phase triplet-singlet phosphorescence has been studied by Greenough and Duncan (11) and by Strickler and Howell (12). The latter analysed their observations in terms of collision induced intersystem crossing from the excited singlet, only singlet-singlet fluorescence being observed at low gas pressures. We hoped to compare the gas phase spectra with the matrix spectra and to study the triplet-singlet quenching in the solid phase.

Assignment v_1'', v_2'', v_3''	Band heads observed in gas ^a	Absorption peaks observed in matrix	Difference
2 4 0	32 198	32 180	18
$3 \ 2 \ 0$	$32 \ 377$	$32 \ 410$	33
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	32 713	$32 \ 685$	28
$\frac{1}{3}$ 4 0	32 850	32 895	45
$3 \ 5 \ 0$	33 080	33 110	30
3 6 0)	3 3 31 3	$33 \ 320$	7
4 3 0			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	33 547	33 540	7
5 2 0	33 760	33 780	20
$5 \ 3 \ 0$	33 960	33 970	10
$6 \ 1 \ 0$	34 240	$34 \ 240$	0
$6\ 2\ 0$	34 396	$34 \ 420$	24
$6 \ 3 \ 0$	34 620	$34 \ 645$	25
6 4 0	34 785	34 825	40
$7 \ 2 \ 0$	$35 \ 068^{\mathrm{b}}$	$35 \ 020$	
7 3 0	35 236 ^b	$35 \ 270$	
$8 \ 1 \ 0$	$35 556^{\mathrm{b}}$	35 530	
$8\ 2\ 0$	35 708 ^b	35 725	

TABLE II

Absorption Bands of SO2 in Krypton at 20°K (cm⁻¹)

^a Ref. (13).

^b Calculated from the formula given in Ref. (13).

Experimental Methods

The SO_2 samples were mixed with eight different solvents which were deposited in the usual manner. The U-tube containing silver sulfide was removed from the flow system.

Results and Discussion

Absorption. Only the spectral region between 2500 and 6000 Å was studied. The a-X transition is weak and was not further studied during this work. The A-X absorption appears as a long progression of bands which overlap. In krypton and xenon a series of bands show clear maxima. Table II lists these maxima and compares them with band heads listed by Metropolis (13). As in S₂O, the absorption forms a smooth Franck-Condon curve. Assuming small matrix interactions one can arrive at a tentative assignment which includes all observed peaks. However, it is dangerous to give such assignments too much credence since matrix shifts need not always be very small, as can be seen from the shifts of the more firmly assigned phosphorescence bands listed below.

Phosphorescence. No resonance fluorescence was observed. However, excitation

	1001	011	MIAAIMA	or u m	1 1001 1	ORESCEN		02 11 1	ARIOUS	SOLVENI	\sim
Assi	gnn	nent	Gas phaseª	Argon ^{be}	Kryp- ton ^{be}	Xenon ^{be}	Met- hane ^{be}	Nitro- gen ^{be}	SF6 ^{bc}	C4F8bc	C4F8° (80°K)
0 0	0 1	0 0	$25 \ 727$ $25 \ 214$	$\begin{array}{c} 25 & 375 \\ 24 & 830 \end{array}$	$25 \ 340 \\ 24 \ 830$	$\begin{array}{ccc} 25 & 145 \\ 24 & 660 \end{array}$	$\begin{array}{ccc} 25 & 170 \\ 24 & 670 \end{array}$	$25 \ 310 \\ 24 \ 840$	$25 535 \\ 25 020$	$\begin{array}{ccc} 25 & 620 \\ 25 & 085 \end{array}$	$25 580 \\ 24 995$
$\begin{array}{c} 1 \\ 0 \end{array}$	$\begin{array}{c} 0 \\ 2 \end{array}$	0 0	$\begin{array}{ccc} 24 & 602 \\ 24 & 706 \end{array}$	24 265	24 230	24 030	$24 \ 065$	24 240	24 445	24 515	24 455
1 0	$\frac{1}{3}$	0 0	$\begin{array}{ccc} 24 & 066 \\ 24 & 173 \end{array}$	23 760	23 710	23 535	23 600	23 805	23 905	23 975	23 870
$2 \\ 1 \\ 0$	$egin{array}{c} 0 \ 2 \ 4 \end{array}$	0 0 0	23 464 23 576 27 319	23 205	23 150	22 930	22 885	23 215	23 235	23 420	23 315
$2 \\ 1 \\ 0$	$1 \\ 3 \\ 5$	0 0 0	22 890 23 073 ^d	22 660	22 605	22 415	$22 \ 495$	22 775	22 825	22 875	22 805
${3 \\ 2 \\ 1}$	${0 \\ 2 \\ 4}$	0 0 0	22 462	22 080	22 025	21 845	21 925	22 215	22 255	22 305	22 235
${3 \\ 2 \\ 1}$	${1 \atop {3} \atop {5}}$	0 0 0		21 520	21 430	21 290	21 290	21 565	21 650	21 800	21 660
3	2	0			20 895	20 740			21 090	21 180	$21 \ 145$
4	т	U			20 360 19 805	$\begin{array}{ccc} 21 & 170 \\ 19 & 695 \end{array}$	_ _	-	$\begin{array}{ccc} 20 & 570 \\ 20 & 025 \end{array}$	20 655	-

TABLE III

Emission Maxima of a-X Phosphorescence of SO₂ in Various Solvents (cm⁻¹)

* Ref. (11) band heads.

^b Emission peaks at 20°K.

^c All rounded to nearest 5 cm⁻¹.

 $^{\rm d}$ Originally assigned to (050).

to both singlet states A and C leads to strong phosphorescence in the 3900 to 4800 Å region. The intensity of the phosphorescence seems greater for excitation in the first singlet than in the second, but this may be due to the relative intensity of the AH-6 excitation in the 2500 and 3100 Å regions if the exciting light source frequency is changed. The intensity of the phosphorescence follows the Franck-Condon absorption intensities of the excited singlet state.

Table III lists the observed vibrational bands for SO_2 emission in seven different solvents, along with the tentative assignments for the bands. The linewidth and the length of the progression varies considerably from solvent to solvent, but the Franck-Condon maxima are not greatly different. Figure 2



FIG. 2. Phosphorescence of SO₂ in krypton at 20°K



FIG. 3. Phosphorescence spectrum of SO₂ in SF₆ at 20°K after 30 min annealing at 77°K

shows the phosphorescence in krypton. It might appear to consist of one single progression, however the spectra in matrices with narrower bandwidth indicate line distortions, and, at least in SF₆, structure. Figure 3 shows the phosphorescence of SO₂ in SF₆ after annealing at 77°K. The annealing results in considerable sharpening and changes the originally broad progression to a more complex pattern. The analysis of the structure, as indicated in the Fig. 3 leads to an assignment similar to that of the gas-phase spectrum. However, the matrix environment strongly affects the origin of the transition, and the vibrational frequencies. Figure 4 shows the spectrum of SO₂ synthesized from the values measured for the first quanta of ν_1 and ν_3 with neglect of anharmonicity. Figure 4 shows that variational frequencies from solvent to solvent are ex-



Fig. 4. Phosphorescence spectrum of SO₂ in various solvents at 20°K, calculated from the observed first vibrational quanta.

pected to yield a different spread of emission peaks, leading in the case of argon to clearly separated groups of bands, and in the case of nitrogen to an almost equal spacing of bands. This grouping and distribution of peaks explains why argon and krypton spectra appear to consist of a single progression while nitrogen gives almost continuous emission with unresolved structure.

The observed linewidths are, therefore, primarily due to overlap of bands, and to the broadening of the spectrum. The matrix broadening between different solvents can be compared in the first vibrational transition, which is not overlapped in most solvents (Table IV).

Table V lists the matrix shift of T_{00} , ν_1 and ν_3 for seven solvents at 20°K and includes values for C₄F₈ at 80°K. The red shifts of T_{00} increase in the following order:

$$C_4F_8 < SF_6 < Ar < Kr < N_2 < CH_4 < Xe$$

while ν_1 increases in the order:

 $N_2 < CH_4 < C_4F_8 < Ar < Kr < Xe < gas phase < SF_6 < C_4F_8$ (80°K), and ν_2 in the order:

 $N_2 < Xe < CH_4 < Kr < gas phase < SF_6 < C_4F_8 < Ar < C_4F_8 (80^{\circ}K).$

Matrix	Half-width
Xenon	240
Argon	310
Krypton	210
SF6	150
SF_{6} annealed	75
C_4F_8	190

TABLE IV

TABLE V

GAS PHASE, MATRIX VALUES AND SHIFTS OF THE TRANSITION ENERGY To AND THE VIBRATIONAL MODES ν_1 AND ν_2 (cm⁻¹)

	T_{00}		ν_1		ν_2	
Medium	Value	Shift	Value	Shift	Value	Shift
Gas phase ^a	25 727		1125		513	
Argon ^b	$25 \ 375$	352	1110	15	544	31
Krypton ^b	$25 \ 342$	385	1112	13	511	2
Xenon ^b	25 144	58 3	1112	13	484	29
Methane ^b	$25 \ 169$	558	1103	22	497	16
Nitrogen ^b	$25 \ 309$	418	1068	57	471	42
SF6 ^b	25 536	191	1126	1	518	5
$C_4F_8^{b}$	$25 \ 621$	106	1106	19	534	21
C ₄ F ₈ (80°K)	25 581	146	1126	1	588	75

* Band head of Ref. (11).

^b Peaks at 20°K.

It is interesting to note that both ν_1 and ν_2 shifts are largest in nitrogen, while in SF₆ both shifts are very small and almost gas-like spectra are obtained. Is should also be noted that the "heavy atom effect" is different for ν_1 and ν_2 ; ν_1 it smallest in argon, and with increasing polarizability, approaches the gas-phase value. In contrast, ν_2 , showing generally larger matrix shifts, is smallest in xenon and largest in argon. In argon, ν_2 is actually larger than in the gas phase. This effect could be due to more pronounced solvent restrictions on the ν_2 vibrations, but seems small compared to the large shifts of the origin of the transition.

The assignment of the origin of the phosphorescence is unambiguous since the Franck-Condon maximum is close to the (000) band which is therefore strong. In view of the large shifts observed for nitrogen, methane, and xenon, caution seems in order if matrix vibrational numbering of heavy molecules is transfered to the gas-phase spectrum. Thus the numbering of the absorption bands of SO_2 in Table II might be in error, since assignment of the matrix transition to the closest lying gas phase band is not conclusive if several other bands are within the next 500 cm^{-1} .

Assignment v_1'', v_2'', v_3''	Calc frequency	Obs	Calc – obs
0 0 0		25 580	
$0 \ 1 \ 0$		25 070	
$0 \ 2 \ 0$	24 555	24 550	5
1 0 0	—	$24 \ 455$	_
0 3 0	24 040	$24 \ 030$	10
$1 \ 1 \ 0$	23 940	23 920	20
$1 \ 2 \ 0$	$23 \ 430$	23 400	30
$2 \ 0 \ 0$	23 330	23 295	35
$1 \ 3 \ 0$	22 915	22 920	5
$2 \ 1 \ 0$	22 815	$22 \ 785$	30
$1 \ 4 \ 0$	$22 \ 405$	$22 \ 395$	10
$2 \ 2 \ 0$	$22 \ 305$	$22 \ 265$	40
$3 \ 0 \ 0$	$22 \ 205$	$22 \ 155$	50
$2 \ 3 \ 0$	21 790	21 770	20
$3 \ 1 \ 0$	21 690	21 650	40

TABLE VI

Phosphorescence of SO_2 in SF_6 at 20°K after 1 hr Annealing at 77°K (cm⁻¹)

As in the gas phase, antisymmetrical stretching-vibration modes, ν_3 , are not observed. Anharmonicity seems to be small since the intensity maxima fit the synthetic spectra which neglect this effect (Table VI).

Temperature Dependence. Since trapping at 20°K may lead to multiple site formation we annealed all solids at a temperature corresponding to a vapor pressure of about 5×10^{-8} Torr. (This usually corresponds to about one-half of the melting point of the solid.) The SF₆ showed a strong annealing effect which resulted in sharpening of the vibrational bands, and in the separation of bands which before were blended.

During annealing drastic changes in phosphorescence intensity were observed. Two effects were noted: (i) the phosphorescence intensity increased during annealing for any given temperature, the increase being parallel to the progress of solvent annealing. After annealing was complete, the phosphorescent intensity stayed constant at constant temperature. We attribute this intensity enhancement to a decrease of scattering losses in the annealing solid, but a change of phosphorescence yield due to changes of the solute sites cannot be excluded at present.

(ii) A reversible intensity change was noted whenever the temperature was varied between 20° and the sublimation temperature. Figure 5 shows the intensity-temperature curves for six solvents. The intensity changes are roughly four times greater than the change in absolute temperature. The effect is so large and the reproducibility so high that it could be used to measure the temperature of an annealed solid to within 2° K. If better understood, this effect might be



Fig. 5. Intensity versus temperature plot of phosphorescence of SO_2 in six different solvents useful for the determination of temperatures in solids to which SO_2 was added as a temperature probe.

Although the peaks corresponding to individual vibrational transitions in the phosphorescence spectrum become broader when the temperature is raised, we find that the measured peak intensities of Fig. 5 remain proportional to the integrated intensity. The proportionality factor decreases by less than 10% on going from 20 to 77°; for our present purposes this variation may be neglected. The measured peak of Fig. 5 was assigned to the $(0, 0, 0) \rightarrow (1, 1, 0)$ transition near the Franck-Condon maximum. From the lack of observable singlet-singlet fluorescence at either high or low temperatures we conclude that the rate of intersystem crossing into the triplet state is always fast, so that the variation of intensity is due to changes in the relative rates of emission and deactivation from the triplet state, rather than to variations in the initial intersystem crossing yield. Thus the curves of Fig. 5 effectively show the temperature variation of a quantity $k_{R}/(k_{R} + k_{Q})$, where k_{R} is the rate of radiation and k_{Q} is the rate of nonradiative transitions from the lowest triplet level. There is no reason to expect a marked temperature dependence of k_R , so that with the presently available information we favor an explanation which assumes the temperature dependence to be due to k_q (14).

Hilpern *et al.* (14) account for effects of temperature on triplet state deactivation by supposing that the molecules require an activation energy to cross a barrier between the lowest triplet level and an accessible singlet level. On the basis of our present data this mechanism leads to values for the height of the energy barrier which are too low to correspond to excitation of SO₂ vibrations, and too high to correspond to lattice modes (14). Thus this mechanism does not satisfactorily account for the observations. Diffusion of mobile lattice defects, or quenching by impurities, should not be important at low temperatures. Triplettriplet interaction (16) is ruled out because SO₂ is not believed to diffuse appreciably under our conditons, and because the effect should be irreversible. We are therefore led to consider solute-lattice interactions as the source of the temperature dependence of k_q .

Two different mechanisms have been proposed as a basis for the effect of solute-lattice interactions on the rate of intersystem crossing. In the theory of Robinson and Frosch (16) the mixing of Born-Oppenheimer states of the isolated molecule, due partly or mainly to vibronic interaction, is such that Born-Oppenheimer states are not true stationary states and so more-or-less rapid transitions occur between them. When the molecule is placed in a crystal such factors as the coupling of the lattice modes with the molecular vibrations and the additional degeneracies created by the addition of the lattice energy levels alter the magnitude of the perturbation which mixes the Born-Oppenheimer states, and so change the rate of nonradiative transitions. This kind of mechanism can be regarded as strictly applicable in the limiting case of a large molecule in a weakly interacting solid. It predicts that there should be little temperature effect on the transfer of moderately large amounts of electronic energy, and so appears to be unable to account for our observations with SO₂. The theory of Bixon and Jortner (17), though differing in its quantum mechanical details, is based on the same physical model and is specifically intended to apply to isolated molecules.

In the theory of Gouterman (18) the rapid variations in the crystal field that accompany the lattice vibrations are assumed to interact directly with the transition moment of the molecule, and expressions for the corresponding Einstein Aand B coefficients are obtained by a derivation parallel to that which is commonly given for radiative transition probabilities. The effect of temperature on the energy density ρ in the lattice modes leads directly to a temperature dependence of the quantity $B.\rho$ which gives the rate of induced transitions. The A-coefficient, which arises from interaction between the transition moment and the zeropoint lattice vibrations, is independent of temperature. This is also an extreme mechanism, in that it cannot account for nonradiative transitions in an isolated molecule. Nevertheless it predicts temperature coefficients of the same order of magnitude as found for k_{ρ} in our experiments.

The gas-phase studies (12) indicate that intersystem crossing leading to phosphorescence does not occur in an isolated SO₂ molecule; thus it is likely that this process in the matrix is not entirely the result of intramolecular effects. However, because of the high density of energy levels near the excited singlet states, the intersystem crossing is probably much more efficient than any competing process, and so the observed rate of production of triplet molecules is not expected to con-

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tribute to the observed temperature dependence. The breakdown of the Born-Oppenheimer approximation is favored by a high density of molecular states, and it is possible that in SO₂ the initial intersystem crossing proceeds mainly by the intramolecular type of mechanism, while the reverse process that we have designated by $k_{\rm Q}$ proceeds mainly through interaction with the lattice modes.

Preliminary study of the relative quantum yield of phosphorescence, together with observations of the radiative life time in the matrix of T_1 - S_0 transitions at different temperatures (19) indicates that both intersystem crossing rates are affected by solvent and temperature.

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