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Temperature Dependence of Quantum Yield and Lifetime of Phosphorescence of Matrix Isolated SO<sub>2</sub>

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OF PHOSPHORESCENCE OF MATRIX-ISOLATED SO<sub>2</sub>

J. J. Smith and Beat Meyer

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TEMPERATURE DEPENDENCE OF QUANTUM YIELD AND LIFETIME  
OF PHOSPHORESCENCE OF MATRIX ISOLATED SO<sub>2</sub>

J. J. Smith and Beat Meyer

July 1968

TEMPERATURE DEPENDENCE OF INTERSYSTEM CROSSING;  
LIFETIME AND INTENSITY OF  $\text{SO}_2$  PHOSPHORESCENCE IN LOW-TEMPERATURE SOLIDS\*

B. Meyer, L. F. Phillips,\*\* and J. J. Smith

University of Washington, Seattle, Washington, and Lawrence Radiation  
Laboratory, University of California, Berkeley

Communicated by Leo Brewer, July , 1968

Energy absorbed by a molecule in an allowed transition can be re-emitted as fluorescence, degraded to heat, or re-emitted as phosphorescence by way of a spin-forbidden transition. The likelihood of phosphorescence depends on both the size of the molecule that absorbs the light and the nature of its environment. Atoms and diatomic molecules in the gas phase exhibit only fluorescence, while large molecules such as naphthalene in the solid state can give both fluorescence and phosphorescence. The diatomic molecules  $\text{SnO}$  and  $\text{SnS}$  phosphoresce strongly in rigid low-temperature solutions.<sup>1</sup> Gaseous  $\text{SO}_2$  gives pure fluorescence at low pressures, but strong phosphorescence above a few torr.<sup>2</sup>

In Fig. 1 are illustrated the electronic relaxation processes which are expected to be important following absorption of light by a phosphorescent molecule. For a molecule embedded in a solid, vibrational relaxation is usually rapid in comparison with radiative transitions from either the excited singlet level  $S_1$  or the triplet level  $T_1$ , so that transitions originate from the lowest vibrational levels of the excited states. Current theoretical models<sup>3-5</sup> assume that non-radiative electronic relaxation is favored in the solid by a variety of effects, which include the broadening of vibrational levels as a result of interaction with the lattice modes, change in intramolecular Franck-Condon factors, and

\* Work performed partly in Seattle, partly in Berkeley.

\*\* On leave from the University of Canterbury, Christchurch, New Zealand

increased mixing of singlet and triplet levels. Experimentally it has appeared up to now that where phosphorescence is observed the rate constant  $k_{ST}$  for  $S_1 \rightarrow T_1$  intersystem crossing is so large that any variation of  $k_{ST}$  with such parameters as temperature or pressure would not be expected to affect the lifetime or intensity of emission from  $T_1$ . Changes in  $T_1$  lifetimes have therefore been interpreted in terms of processes involving only  $T_1$  and  $S_0$ .<sup>6</sup> In this paper we report observations on the effect of temperature on the intensity and lifetime of  $SO_2$  phosphorescence, in solid solutions between 4° and 100°K, which result from a strong variation of the intersystem crossing rate with temperature in this range.

## EXPERIMENTAL

Two micromoles of  $\text{SO}_2$  were deposited on a sapphire window, either alone or as a  $10^{-3}$  mole-fraction mixture in neon, argon, krypton, xenon, nitrogen,  $\text{CH}_4$ ,  $\text{CD}_4$ ,  $\text{SF}_6$  or  $\text{C}_4\text{F}_8$ . The condensation temperature was either  $4^\circ$  in a helium glass dewar,<sup>7</sup> or  $20^\circ$  in a Cryo-Tip cryostat.<sup>8</sup> With this equipment the temperature can be raised, maintained, or lowered at will over the range from  $4^\circ$  to  $100^\circ\text{K}$ . Warm-up and cool-down rates were ordinarily about  $2^\circ\text{K}$  per minute. Temperatures were measured with gold-iron or gold-cobalt versus copper thermocouples. Samples were normally annealed for one hour at  $1/3$  of the melting point of the solvent. All reported data were measured during both warm-up and cool-down, and were fully reproducible. The optical system for exciting phosphorescence consisted of an A4/T medium-pressure mercury lamp, minus the outer jacket, and an  $f/3$  monochromator, with liquid and glass filters, giving a band width of  $50\text{\AA}$ . The phosphorescent emission was analyzed with a monochromator and photomultiplier. For lifetime measurements a rotating chopper was used to modulate the exciting light, with rise and fall times of  $0.05$  msec. Phosphorescence decay curves were photographed as oscilloscope traces.

## RESULTS

Figure 2 shows the phosphorescence spectrum of  $\text{SO}_2$  in  $\text{SF}_6$  at  $20^\circ\text{K}$ . Other solid solutions give comparable spectra; the spectrum of pure solid  $\text{SO}_2$  shows relatively little vibrational structure. The emission spectrum consists of the progression  $\underline{a}(0,0,0) \rightarrow \underline{X}(v_1, v_2, 0)$ , and is readily excited through absorption in either the  $\text{A} \leftarrow \text{X}$  or  $\text{C} \leftarrow \text{X}$  system, with maximum phosphorescence intensity upon irradiation at  $2900\text{\AA}$  and  $2500\text{\AA}$ , respectively.<sup>9</sup>  $\text{A} \rightarrow \text{X}$  fluorescence was not observed.

During annealing of the solids two temperature effects on the phosphorescence intensity were noted. First, the intensity increased during annealing for any given temperature. After annealing was complete the intensity remained constant at constant temperature. This effect was probably due to decreases in scattering losses. Second, after annealing, marked intensity changes occurred with changes in temperature. These changes were fully reproducible and reversible over any number of cycles in the temperature range between  $4^\circ\text{K}$  and  $0.4$  of the melting point of the solvent. Above  $0.4$  of the melting point diffusion became important and irreversible effects set in.

Figure 3 is a plot of the phosphorescence intensity (in arbitrary units) versus temperature for  $\text{SO}_2$  in various solvents. The values plotted were obtained by measuring the intensity of the peak near  $4175\text{\AA}$ , corresponding to the transition  $\underline{a}(0,0,0) \rightarrow \underline{X}(1,1,0)$ . Although the individual peaks in the spectrum broadened to some extent as the temperature was increased, the factor connecting the measured peak intensity to the integrated intensity remained constant to within 10%.

No attempt was made to determine precise relative intensities



for different solutions. The curves in Fig. 3 show large changes of intensity with temperature, and all the curves appear to have similar shapes.

Table I lists measured lifetimes of SO<sub>2</sub> phosphorescence in different solvents at various temperatures. The value for 300°K is the gas-phase value reported by Caton and Duncan,<sup>10</sup> and refers to the pressure range between 10<sup>-3</sup> torr and 1 torr. The value for the solid at 77°K was measured by Greenough and Duncan.<sup>11</sup> The entire range of lifetime values, with the exception of the reported value for pure SO<sub>2</sub> at 77°K, is within a factor of 2.5 of the gas-phase value. The lifetime of pure solid SO<sub>2</sub> obtained from our measurements is about intermediate in the observed range, and decreases significantly with increasing temperature, at least to 60°K.

All the decay curves appeared exponential, although small deviations might have escaped observation. In our concentration range the temperature dependence of intensity and lifetime were independent of concentration. The lifetime in all solvents studied to 60°K or above showed a shallow minimum at an intermediate temperature. It is noteworthy that the heavy atom effect on the lifetime, although observed, is not as pronounced as has been reported for other molecules.<sup>12</sup>

## DISCUSSION

The strong dependence of intensity on temperature is unexpected. Also, it is striking that while the phosphorescence intensity varies by a factor of up to 100 the lifetime of the  $\underline{a}$ -state ( $T_1$ ) in any given solvent varies by less than 50%, and that the lifetime in all solvents over the entire range of temperatures remains within a factor of 2.5 of the value for  $SO_2$  in the gas phase.

Several types of process might account for the dependence of intensity on temperature. Considering experimental factors first, we can exclude several possibilities. For example, the results do not depend on the formation of aggregates of  $SO_2$ , since the measured lifetime of phosphorescence is in some solvents larger than for pure  $SO_2$ , and in other solvents smaller. Additional evidence against aggregate formation is provided by the observation of a different characteristic spectrum for each solvent.<sup>9</sup> Temperature-dependent quenching, arising from diffusion of  $SO_2$  or impurity molecules like  $O_2$ , or from triplet-triplet interaction, is ruled out by factors which include the lack of a marked temperature variation of the triplet state lifetime and the observation that temperature effects are strong and smooth over a range from 5 to 40% of the melting point - a region where  $SO_2$  or impurities cannot migrate. Therefore the observed effects must be due to intramolecular, or solute-solvent interactions.

Since the lifetime of the  $T_1$  state is relatively insensitive to temperature and little affected by the presence or absence of a solvent, either  $k_T$  must be small (Fig. 1), or  $k_P$  and  $k_T$  must have equal and opposite temperature coefficients. The second alternative is possible, but seems an unlikely coincidence. If the observed change in quantum yield

of phosphorescence is to be due to processes between  $T_1$  and  $S_0$  alone,  $k_p$  and  $k_T$  must both change strongly with temperature. However, the small lifetime variation between the gas phase and  $4^\circ\text{K}$  makes it more likely that  $k_p$  is independent of temperature, and that  $k_T$  is always small. Consequently the explanation for the variation of intensity with temperature must be sought in the population mechanism, rather than the decay mechanism, for  $T_1$ . This also enables us to rule out varying Franck-Condon factors between  $T_1$  and  $S_0$  as a primary cause of our observations. The minimum lifetime values obtained in the intermediate temperature range suggest that  $k_T$  does change with temperature, but the change is too small to account for the observed intensity variations.

The population of  $T_1$  results from intersystem crossing from  $S_1$ , with a rate coefficient  $k_{ST}$ . This process competes with fluorescence and internal conversion ( $k_F$  and  $k_S$ ) and the observed variation of intensity with temperature must therefore reflect variations in the ratio  $k_{ST}/(k_S + k_F)$ . The population of  $T_1$  might also be affected by the thermally activated process described by  $k_{-ST}$ , leading to delayed fluorescence. In relation to our experiments this effect seems unimportant because it would affect both the intensity and lifetime, because of the large activation energy ( $4000\text{ cm}^{-1}$ ), and because we observe phosphorescence only from the (0,0,0) level of  $T_1$ . Delayed fluorescence has not previously been assumed to occur, even in the gas phase. If it did occur its long lifetime component might contribute to the unusually long lifetime which is reported for the fluorescence,<sup>11,13</sup> and which is inconsistent with calculations of integrated absorption intensity.<sup>14</sup>

Considering the rate coefficients  $k_{ST}$ ,  $k_S$ , and  $k_F$ , it is unlikely that the large temperature variation is associated with  $k_F$ . The quantity

$k_S$  is analogous to  $k_T$ , for which it was suggested that the temperature coefficient is small; thus a variation in  $k_S$  is not likely to account for the observed temperature effect. Finally,  $k_{ST}$  itself may be temperature sensitive, possibly as a result of interaction between the solvent field and the extent of  $S_1 - T_1$  mixing. As would be expected for such a case, different solvents appear to yield significantly different emission intensities. Variation of  $k_{ST}$  with temperature and solvent at present provides the most plausible explanation for our results.

## SUMMARY

We observe large temperature dependent changes in intensity of  $\text{SO}_2$  phosphorescence in weakly-interacting, low-temperature, solid solutions, accompanied by small changes in the radiative lifetime. We conclude that the rate of  $S_1 \rightarrow T_1$  intersystem crossing, relative to the rates of fluorescence and internal conversion, is a strong function of temperature. The rate of quenching from  $T_1$  to  $S_0$  shows only a small temperature dependence.

## ACKNOWLEDGMENT

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Table I. Phosphorescent lifetimes of SO<sub>2</sub>, pure or in various solvents.<sup>a</sup>  
 Values are in milliseconds; values obtained in the present  
 work are believed to be accurate to + 1 msec.

Temperature °K	Xe	Kr	Ar	Ne	CH <sub>4</sub>	CD <sub>4</sub>	SF <sub>6</sub>	Pure SO <sub>2</sub>
4	-	-	-	17.5	10.1	9.6	13.5	9.6
20	5.2	8.4	9.0	-	10.0	-	11	8.5
45	3.5	6.6	-	-	9.8	-	9.0	-
55	4.4	7.1	-	-	-	-	9.4	5.0
60	5.0	7.2	-	-	-	-	-	3.8
77	-	-	-	-	-	-	11	0.5 <sup>b</sup>
300	-	-	-	-	-	-	-	7 <sup>c</sup>

(a) lifetime not affected by annealing

(b) reference 10

(c) gas phase, reference 11

## FIGURE CAPTIONS

- Fig. 1 Electronic relaxation processes following absorption of light by a phosphorescent molecule. Rate coefficients are indicated for fluorescence ( $k_F$ ), internal conversion ( $k_S$ ),  $S_1 \rightarrow T_1$  intersystem crossing ( $k_{ST}$ ), delayed fluorescence ( $k_{-ST}$ ), phosphorescence ( $k_P$ ), and non-radiative triplet-state deactivation ( $k_T$ ).
- Fig. 2 Phosphorescent spectrum of  $SO_2$  in  $SF_6$  at  $20^\circ K$ .
- Fig. 3 Phosphorescent intensity of  $SO_2$  as a function of temperature in various solvents. (Intensity in arbitrary units.)



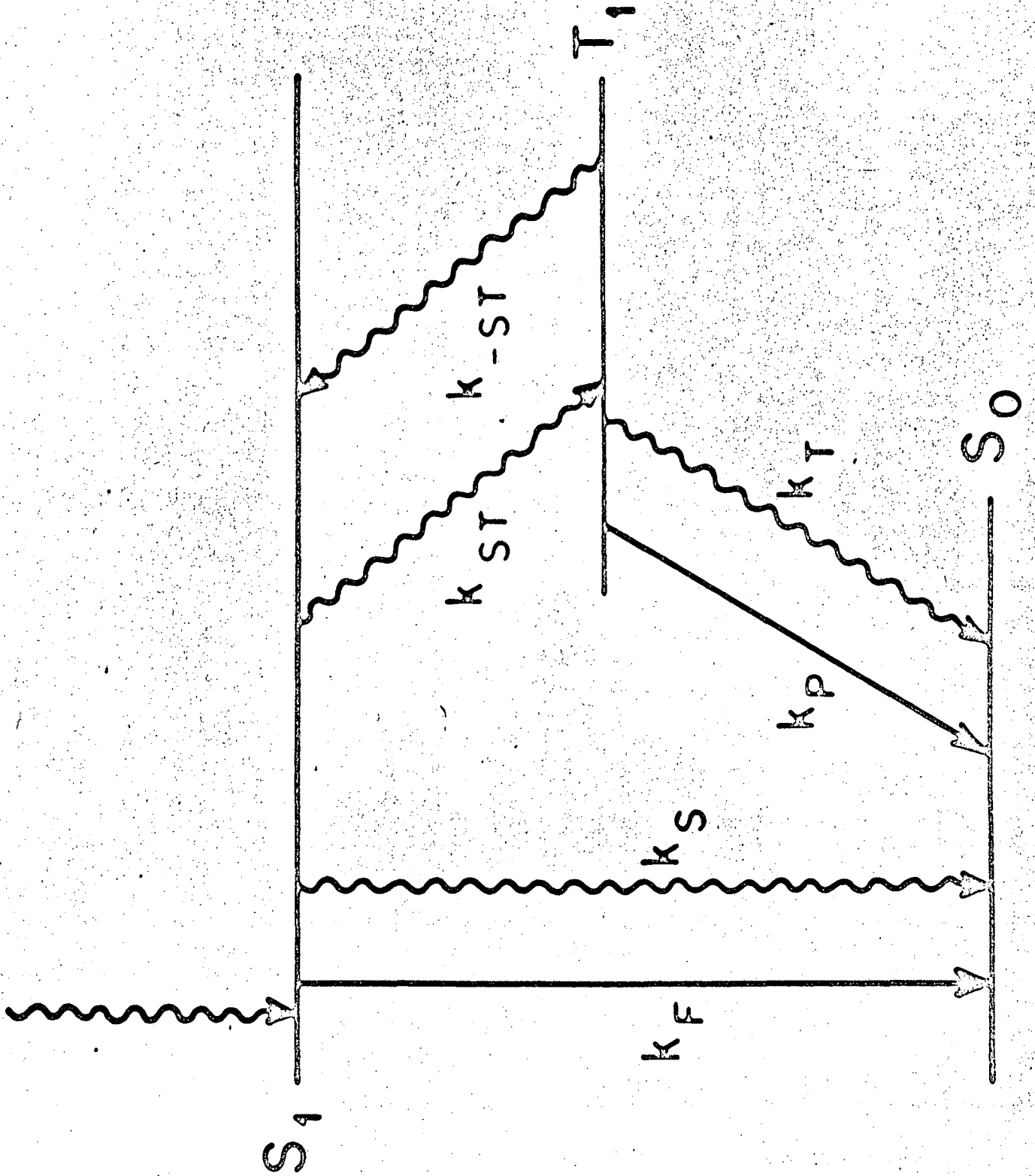
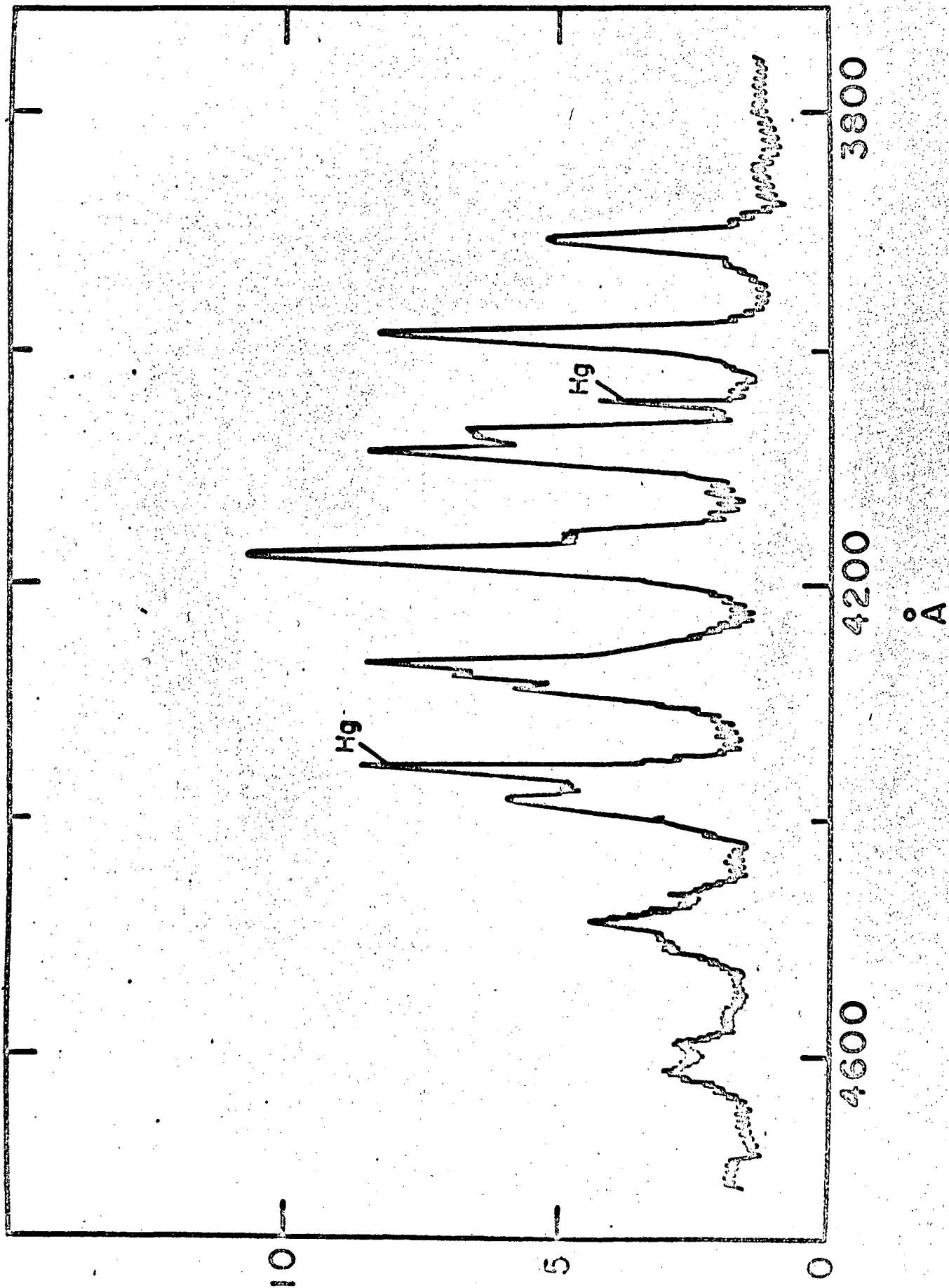


Fig. 1



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RELATIVE EMISSION

Fig. 2

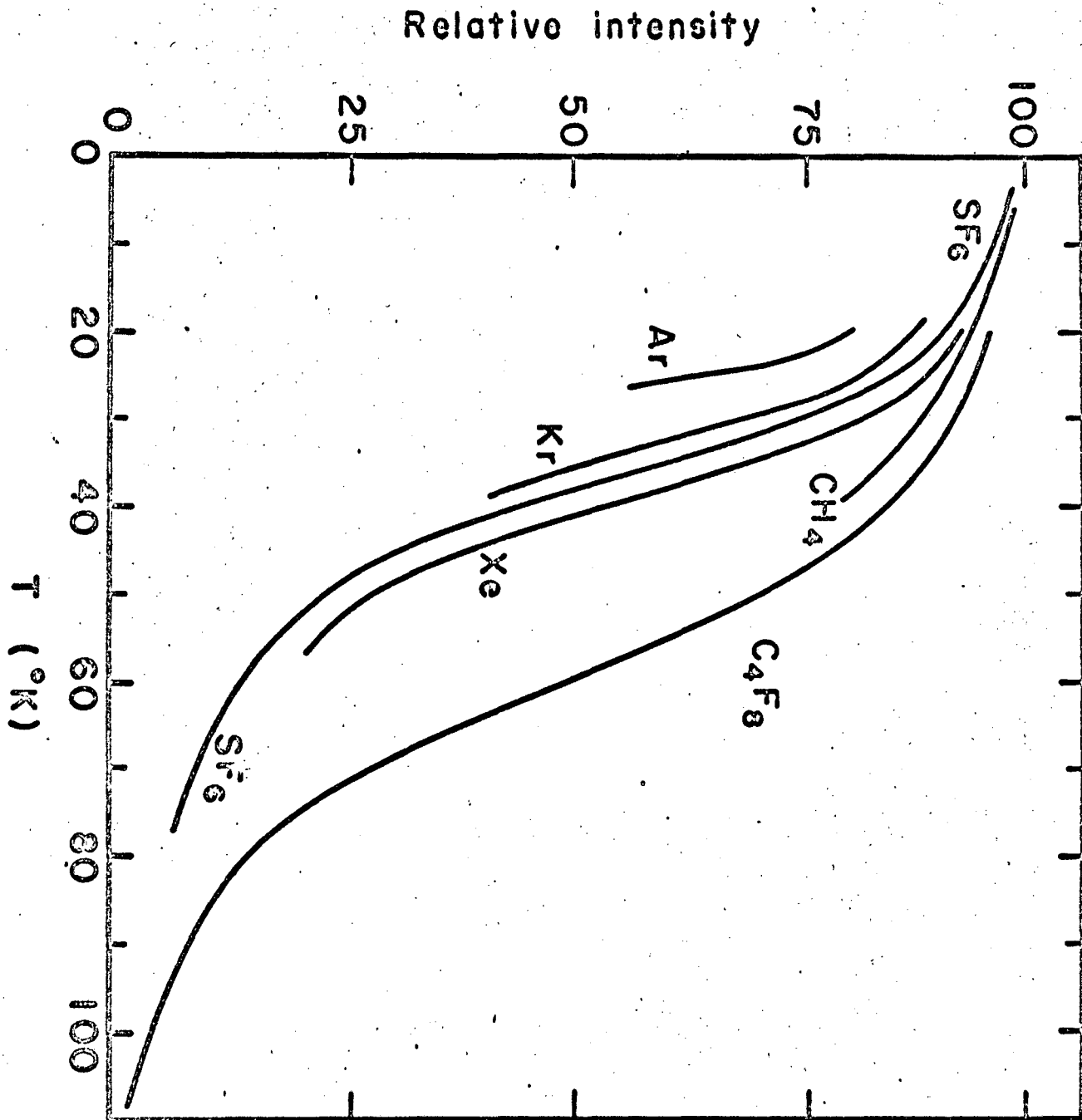


Fig. 3

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