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J. J. Smith and Beat Meyer

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TEMPERATURE DEPENDENCE OF INTERSYSTEM CROSSING: LIFETIME AND INTENSITY OF SO_2 PHOSPHORESCENCE IN LOW-TEMPERATURE SOLIDS*

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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 SnO and SnS phosphoresce strongly in rigid low-temperature solutions.[1] Gaseous SO_2 gives pure fluorescence at low pressures, but strong phosphorescence above a few torr.[2]

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[3-5] 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.
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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.[6] 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 SO_2 were deposited on a sapphire window, either alone or as a 10^{-3} mole-fraction mixture in neon, argon, krypton, xenon, nitrogen, CH_4, CD_4, SF_6 or C_4F_8. The condensation temperature was either 4° in a helium glass dewar,[7] or 20° in a Cryo-Tip cryostat.[8] With this equipment the temperature can be raised, maintained, or lowered at will over the range from 4° to 100°K. Warm-up and cool-down rates were ordinarily about 2°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 50Å. 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 SO_2 in SF_6 at 20°K. Other solid solutions give comparable spectra; the spectrum of pure solid SO_2 shows relatively little vibrational structure. The emission spectrum consists of the progression $\underline{a}(0,0,0) \rightarrow X(v_1, v_2, 0)$, and is readily excited through absorption in either the A←X or C←X system, with maximum phosphorescence intensity upon irradiation at 2900Å and 2500Å, respectively.[9] A → 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°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 SO_2 in various solvents. The values plotted were obtained by measuring the intensity of the peak near 4175Å, corresponding to the transition $\underline{a}(0,0,0) \rightarrow X(1,1,0)$. 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_2 phosphorescence in different solvents at various temperatures. The value for 300°K is the gas-phase value reported by Caton and Duncan,[10] and refers to the pressure range between 10^{-3} torr and 1 torr. The value for the solid at 77°K was measured by Greenough and Duncan.[11] The entire range of lifetime values, with the exception of the reported value for pure SO_2 at 77°K, is within a factor of 2.5 of the gas-phase value. The lifetime of pure solid SO_2 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.[12]

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 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.[9] 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°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 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,[11,13] and which is inconsistent with calculations of integrated absorption intensity.[14]

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 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.

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Table I. Phosphorescent lifetimes of SO_2, pure or in various solvents.[a] 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_4	CD_4	SF_6	Pure SO_2
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[b]
300	-	-	-	-	-	-	-	7[c]

(a) lifetime not affected by annealing

(b) reference 10

(c) gas phase, reference 11

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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°K.

Fig. 3 Phosphorescent intensity of SO_2 as a function of temperature in various solvents. (Intensity in arbitrary units.)

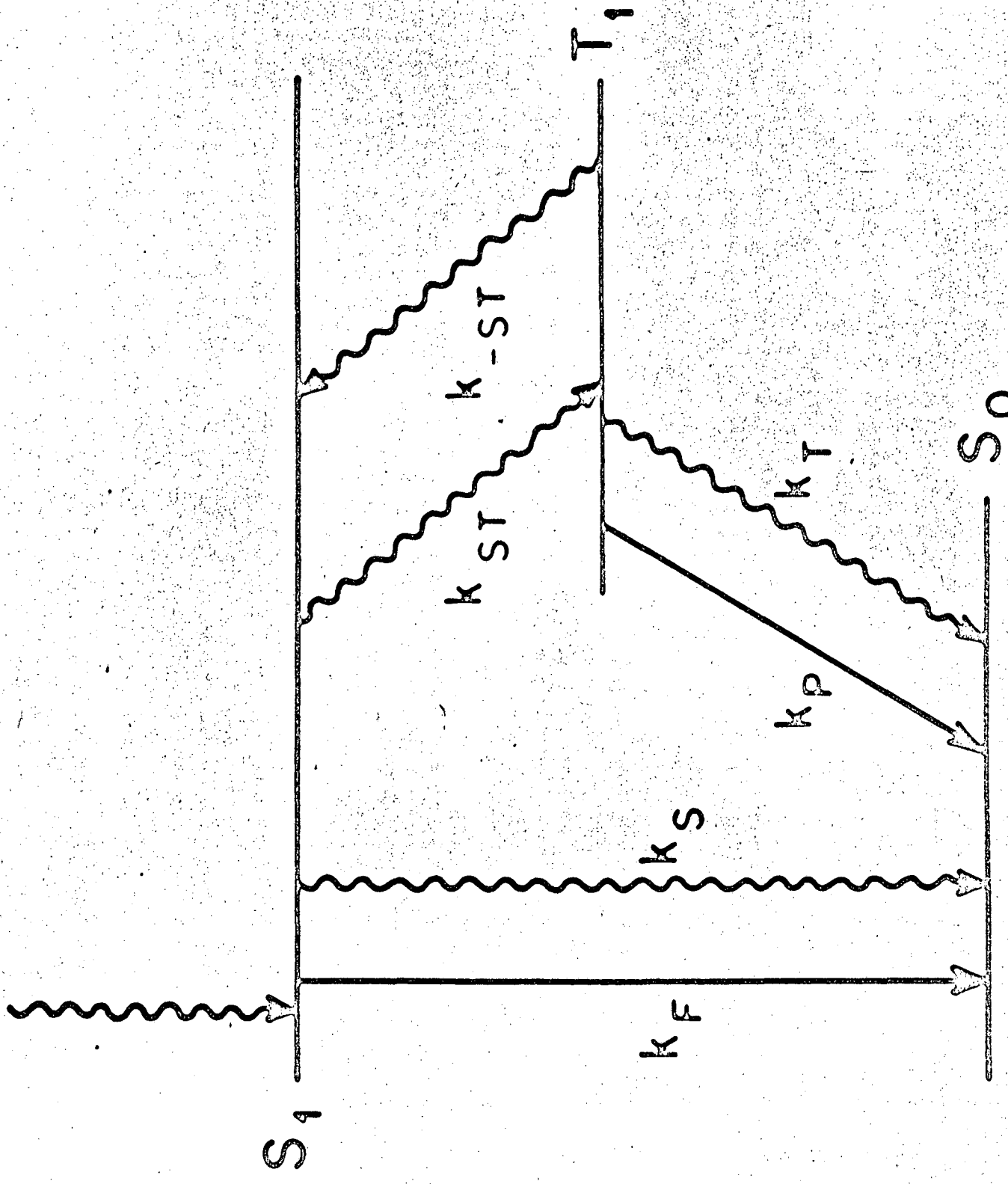

Fig. 1

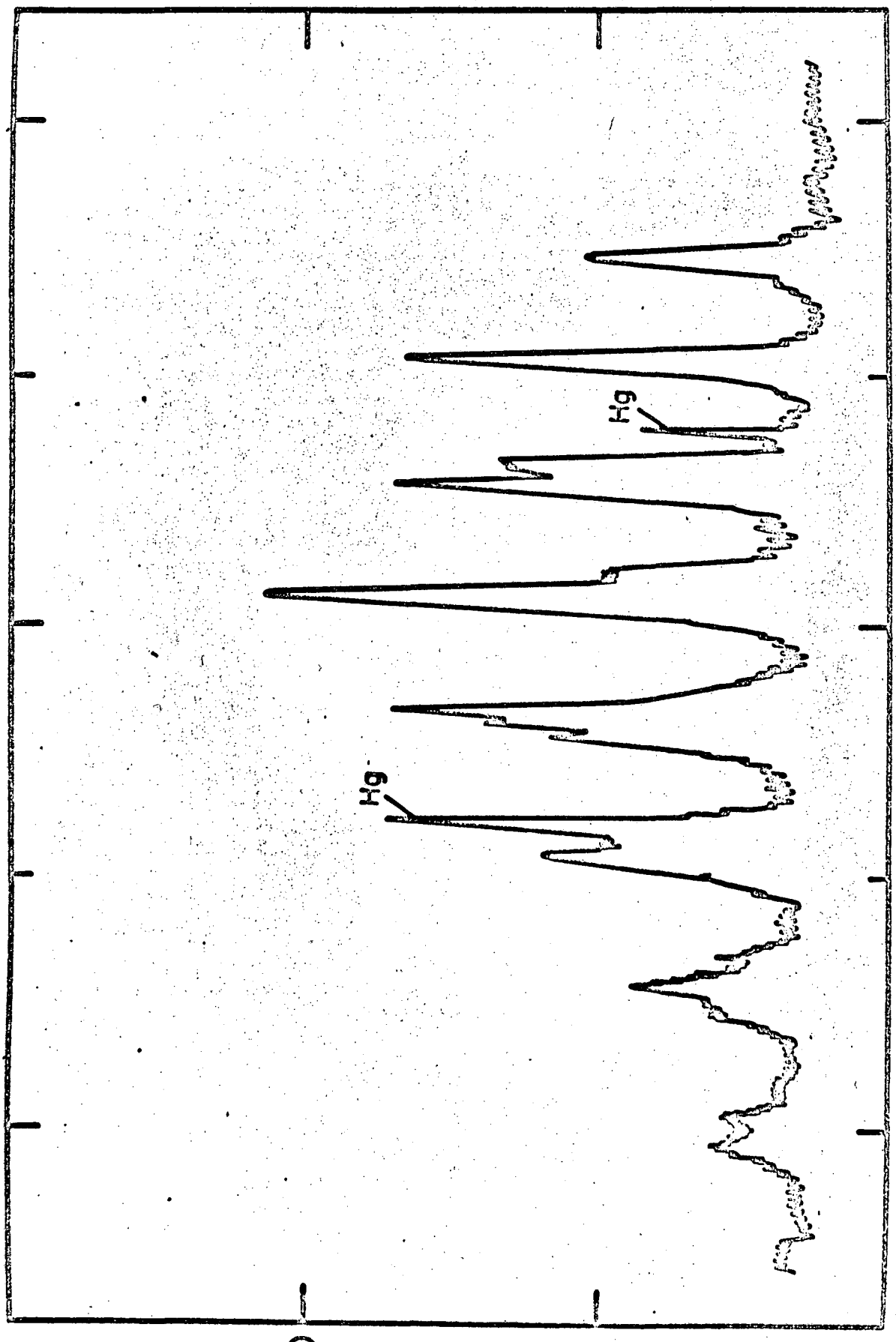

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Fig. 2

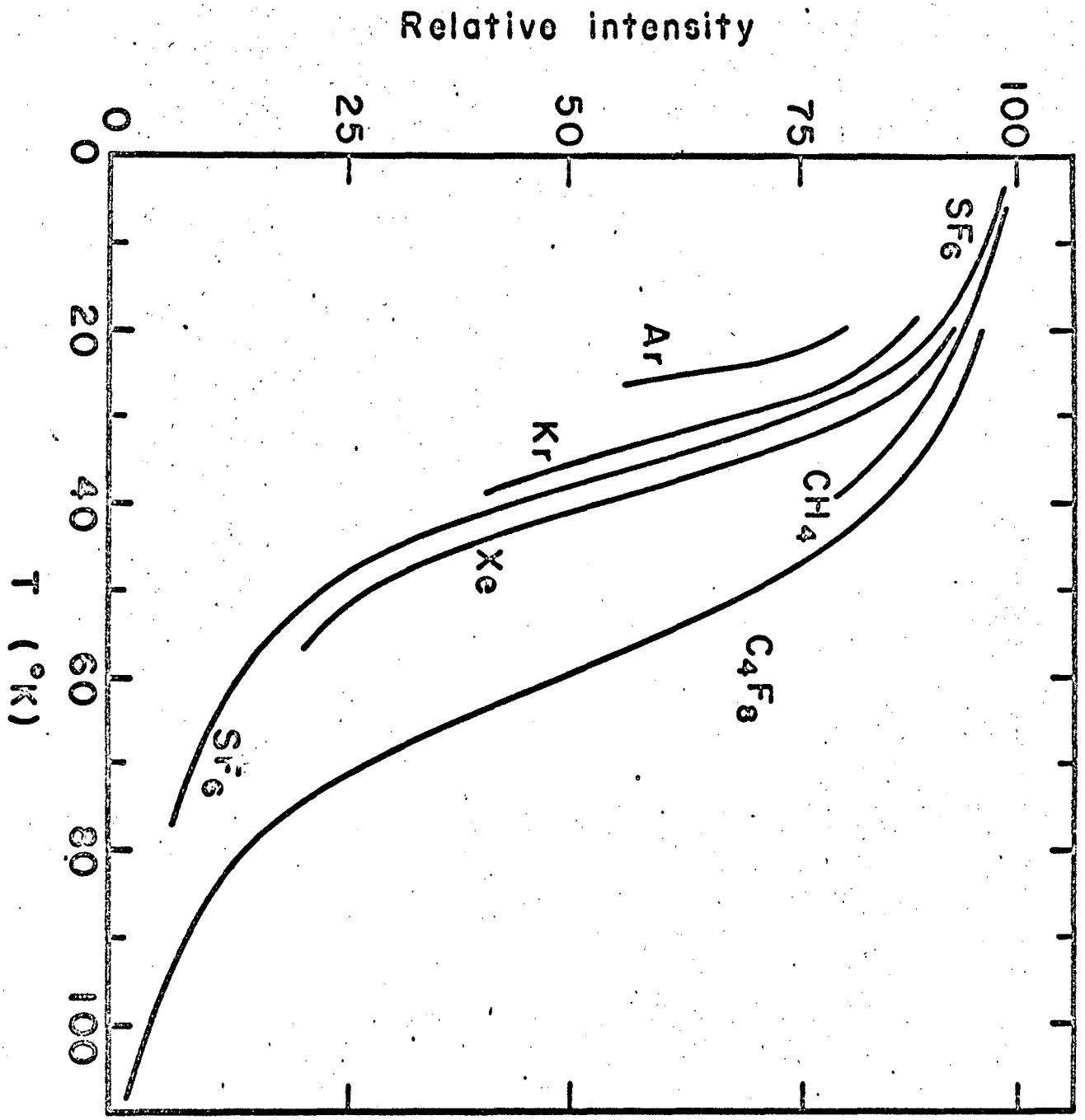
Relative intensity
0
25
50
75
100
T (°K)
0
20
40
60
80
100
SF6
Ar
Kr
Xe
CH4
C4F8
SF6
XBL697-3194

Fig. 3

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