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ABSTRACT

The spectrum of SnS and SnO was studied in the 14,000 to 50,000 cm^{-1} region in argon, krypton and xenon matrices at 20°K. The D $^1\Pi$ - X $^1\Sigma$ absorption system is reported. All SnO spectra show a vibrational band red of that earlier reported to be (0,0). This suggests that the numbering should be corrected to yield a new T_{oo} = 28,923 cm^{-1}. Excitation of the D state of both molecules leads to strong red fluorescence but not to the resonance fluorescence observed in the gas phase. The red fluorescence is attributed to the transition a - X where a is believed to be $^3\Pi$. The fluorescence results from matrix induced intersystem crossing, a process which is unusual in diatomic molecules. Absorption and fluorescence matrix shifts of T_{oo} and ω_o are consistent with the heavy atom effect.

INTRODUCTION:

The gas phase spectra of SnS and SnO have been studied by several workers (1). Both molecules contain ten valence electrons and are, therefore, isoelectronic with CO, for which all theoretically predicted levels and transitions have been observed (2).

The lowest vibrationally and rotationally analysed transition of SnS is the $D\ ^1\Pi - X\ ^1\Sigma$ system for which a thorough isotope study was made (3). Reference 3 also contains a listing of various, partially analyzed, vibrational transitions which have not yet been conclusively assigned. A vibrational study of the visible transitions indicates that many bands can be fitted into two progressions belonging to as yet unidentified states B and C (4).

In SnO the D - X system has also been analyzed (5). It has an upper state $^1\Pi$ which corresponds to the state D in SnS and the $a\ ^1\Pi$ state of CO. The D - X transition corresponds to the Fourth Positive System of CO. Various bands of lower lying, weak and irregular visible systems of SnO have been analyzed and were tentatively assigned to a transition involving the $^3\Pi_1$ and $^3\Pi_0+$ state (6).

The purpose of this work was to study the D - X transitions of SnS and SnO in matrices.

EXPERIMENTAL:

SnS was prepared from high purity elements and excess sulfur was removed through heating under vacuum; SnO was made from stannous chloride and sodium carbonate. Research Grade Rare Gases (Linde Division Union Carbide Co.) were used without further treatment. High purity SnS and SnO (7) vapors were made by heating the tin compounds in a carbon resistance furnace which

is described elsewhere (8). A natural mixture of tin isotopes was used.

The molecular beam arrangement and the cryostat were similar to those described earlier (8). For several experiments a Cryo-tip refrigerator AC-2L (Air Products and Chemicals Co.) was used.

In a typical experiment about 3 millimoles per hour of matrix gas were deposited on a sapphire window which was kept at $20^{\circ}K$. The molecular beam Knudsen cell was heated to $575-580^{\circ}C$ for SnS and for SnO, corresponding for each to a vapor pressure of about 10^{-3} torr. The matrix-molecule ratio was estimated to be about 1000. The pressure in the optical Dewar during deposition was $5x10^{-6}$ torr; during observation it was below $8x10^{-7}$ torr.

Spectra were recorded on a Jarell-Ash Czerny-Turner f/6.3 spectrometer equipped with gratings blazed for 3000Å, 5000Å, and 7500Å, giving a dispersion between 5 to 20Å/mm. Fluorescence was both photographed and photoelectrically recorded. For the latter, an f/5 McPherson spectrometer with a 1000 line grating blazed for 5000Å was employed, using an EMI photomultiplier tube 9502S as detector.

For fluorescence excitation the target was irradiated with monochromatized light from a General Electric AH-6 high pressure mercury arc. The monochromator was a Farrand f/3 instrument equipped with slits to give a band width of 50Å. The fluorescence frequency was both photoelectrically scanned and photographed for each 50Å interval over and beyond the entire absorption region of each molecule. For each experiment fluorescence blanks were recorded. Also, a spectrum of each pure matrix solvent was obtained.

The tin compound beams were always started later and stopped earlier than the rare gas flow so that SnS and SnO were only in contact with rare gas solvent. Deposition time ranged from 2 hours to 10 hours.

RESULTS:

In the 15,000 to 45,000 cm^{-1} region both SnS and SnO show only one clear and sharp absorption spectrum consisting of a progression of vibrational bands. No absorption corresponding to the weak gas phase absorption bands was found. Thicker samples than studied during this work would be needed to determine and observe such transitions.

Fig. 1 shows the absorption spectrum of SnS in Xe at $20^{o}K$. The absorption peaks of SnS and SnO in argon, krypton, and xenon solutions at $20^{o}K$ are listed in Table I. Fig. 1 indicates that SnS exhibits strong Franck-Condon intensity perturbations at $v'=4$ and $v'\geq 6$.

Several v' levels above those reported for the gas phase were found in both SnS and SnO. In SnS the furthermost red absorption corresponds well to the (0,0) gas phase band. However, if the gas phase numbering is used for SnO, a level to the red of the (0,0) band is observed in all matrices.

The half width of vibrational absorptions are given in Table II. The absorption bands have relatively symmetrical shapes and do not exhibit any obvious fine structure.

When the absorption regions of SnO and SnS were irradiated with monochromatized light no resonance fluorescence was observed. Instead, a strong fluorescence in the red was obtained for both molecules. The fluorescence consists of a sharp and well developed progression of bands with frequencies which are characteristic for the ground state of the two molecules. The absolute intensity, but not the relative intensity, of bands in the Franck-Condon curve changes as the exciting frequency is scanned. Fig. 2 shows the emission spectrum of SnO in krypton as a function of exciting light frequency. Table III lists the emission peaks of SnS and SnO for argon, krypton, and xenon. The relative intensities are not listed since both the

photomultiplier response and the plate response decrease toward the red. The Franck-Condon maximum appears, therefore, on Fig. 2 probably by one vibrational number too far to the blue.

DISCUSSION:

ABSORPTION:

Since both spectra of SnS and SnO are dependent on the presence of the tin compound beam the assignment of our bands to the D - X system seems reasonable. The vibrational assignment of the matrix bands is based on correlation of many distinct intensity perturbations which are preserved in all solids. This choice leads to matrix shifts which correspond to the expected heavy atom effect.

In SnS gas phase and matrix spectra show the same origin. The fact that bands to the red of (0-0) appear in SnO matrices suggest that the gas phase vibrational numbering is in error. A satisfactory analysis is found if the gas phase origin, T_{oo}, is shifted to the red and v' numbers are increased by one. A gas phase level earlier labelled (2,2) fits the intensity and frequency requirements for the new (0,0) band. If the earlier (2,3) level is now relabelled (0,1) a smooth Deslandres curve is obtained. This new vibrational numbering leads to the following set of corrected constants for the D $^1\Pi$ state of SnO:

$$T_{oo} = 28923 \text{ cm}^{-1} ; \quad \omega_o = 579.0 \text{ cm}^{-1}$$

This new assignment should be tested with $Sn^{18}O$ in the gas phase.

The T_{oo} and v' of the matrix absorption observed during this work fall well within 1% of the values for the gas phase constants of the D $^1\Pi$

states of the two molecules. Gas phase rotational analysis of the D states in SnS (3) and SnO (5) has shown that both are $^1\Pi$.

The absorption spectrum of SnS shows a strong intensity change at $v' \geq 6$. It is possible that the weak levels listed with $v' \geq 6$ in Table I belong to a different electronic system. SnS andSnO have so many states close to D $^1\Pi$ that strong perturbations may be expected. This region was not studied by earlier workers (3). In analogy with CO the vibrational energies of close-by levels are expected to be so similar to that of D that matrix measurements are not accurate enough to discriminate between transitions. The width of the absorption bands varies from 120 cm^{-1} to 150 cm^{-1}. This line width is similar to that found in transitions of other diatomics with other multiplicities, S_2, for example. Therefore it seems probable that the line width is due to effects of the matrix environment rather than due to overlapping unresolved sublevels, as was suggested earlier (9). A portion of the line width in the SnS and SnO is due to the large number of tin isotopes which are present in comparable concentrations in a natural mixture of the element. This effect contributes <10 cm^{-1} for $v'=1$ and <80 cm^{-1} for $v'=11$. It should be noted that it is not clear at this time why diatomics have sharper absorptions than atoms (10), but much broader absorptions than many larger molecules such as benzene and porphyrins (11, 12).

FLUORESCENCE:

In the gas phase resonance fluorescence has been reported for the system D - X of SnO (1). When the D levels of SnS and SnO are excited in matrices we observe fluorescence in the red part of the spectrum, but not in the resonance region. The strong red fluorescence progressions fall into a region where no absorption has yet been observed. Therefore the assignment of the transitions is not immediately obvious. Several facts make it likely that the fluorescent bands of SnS and SnO are both due to transitions between analogous electronic states: (1) the origin of the SnO system is somewhat more towards the blue than for SnS, as would be expected because of the lower molecular weight of SnO; (2) the vibrational frequency of the well developed progressions corresponds closely to the ground state frequency of the two respective molecules, and (3) the fluorescence appears only when the corresponding D - X absorption spectrum can be observed, and its intensity changes when the exciting frequency is changed over the Franck-Condon curve (Fig. 2 and Tab. IV).

Two processes could cause non-resonance fluorescence: (1) Emission from the D state to an intermediate state with subsequent quenching of the lower state to the ground state, or (2) radiationless relaxation of energy from the D state to a lower lying state from which fluorescence to the ground state is allowed. In order to discriminate between the two processes the low lying electronic states of row IV-VI ten electron diatomics must be shortly discussed: For CO, the lightest IV-VI ten electron diatomic, all theoretically predicted states have been observed and identified. The electronic transition energy and vibrational frequency of these low lying states are listed in Table V and compared with the known states of SnS and SnO. Transitions between the $^1\Pi$ and intermediate states and also between

intermediate states and the ground state are forbidden, but many have been observed in CO. These transitions become much more allowed yet in the heavier SnS and SnO which probably approach Hund's spin coupling case c.

Fluorescence from the D state to a forbidden intermediate state would have to compete against the fully allowed D - X resonance fluorescence, and would be very weak. Only the state analogous to state a of CO is low enough to correspond to the lower state of the fluorescence from the state D of SnS and SnO if one assumes that the relative position and the relative internuclear distance of electronic states within any one molecule does not normally change very drastically between different molecules with the same number of valence electrons. However even the a state is expected to lie 30% or more higher than the observed fluorescence energy suggests. Also the observed lower state vibrational frequency is too high for the (as yet unknown) a state in SnS and SnO.

Since resonance fluorescence was not detected in our experiments, and since the vibrational frequencies of the lower state in the fluorescence corresponds in both molecules to within 10% of the ground state, it seems more likely that the fluorescence involves the ground state of the molecules and does not originate from state D. As the fluorescence was excited via the D state this explanation necessitates rapid depopulation of the D state to a lower emitting state. Such electronic quenching is quite common in organic molecules in solid solutions (13), but is unexpected from what has been reported for the few other diatomics so far studied (9). SnS and SnO are, however, much heavier than diatomics such as S_2, and approach Hund's case c. This would make transitions to intermediate states $^3\Pi_1$ and $^3\Sigma_1$ more allowed. Such quenching would also be greatly enhanced since the four levels below D are all expected to be very close to each other and surely must cross.

An indication for such crossing is the strong vibrational perturbation in SnS at v'=4 and v' above 6 in the absorption system D.

In our work, effective vibrational quenching is demonstrated. Neither frequency nor relative intensity of the vibrational bands, but only the absolute intensity of the entire system changes when the exciting frequency is scanned through the range of the absorption. This fact might suggest that weak secondary fluorescence observed, for example, in S_2 is due to different sites rather than due to emission from v'=1 as was suggested earlier (9).

Of all intermediate electronic levels, the level analogousto a in CO is the lowest. It is $^3\Pi$ in CO and would in SnS and SnO presumably correspond to three states, of which the $^3\Pi_1$ would give allowed transitions to both the D andX state. The ratio of the energy of $A^3\Pi$ to $a^3\Pi$ in CO corresponds very well to the energy of the observed SnS and SnO fluorescence. Furthermore an internuclear distance of the order expected for the a state is consistent with the Franck-Condon curve of the fluorescence.

Assuming that all intermediate levels intersect and that, therefore, fluorescence occurs from the lowest level, it seems sensible to assign tentatively the observed transition to the Cameron analogue. This explanation allows also for earlier tentative assignments of weak bands. One fact remaining for discussion is the assignment of the higher lying A and B bands of SnO which, based on partial rotational analysis, were attributed to the same Cameron system. Our proposed assignment would necessitate reassignment of the A and B bands to the transition corresponding to a' $^3\Sigma$. However, it is possible that $^3\Pi$ and $^3\Sigma$ could reverse relative position between CO and the heavy SnO. In this case the fluorescence would originate from the a' $^3\Sigma$ state corresponding to the Hopfield-Birge bands. Matrix spectra do not show rotational structure since both transitions are equally allowed. A

conclusive choice between $^3\Pi$ and $^3\Sigma$ could only be made through analysis in the gas phase. Such an analysis might however not be available in the near future since the visible spectrum of SnS and SnO has proven to be complex.

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TABLE 1

Absorption Bands of SnS and SnO in argon, krypton and xenon (in cm^{-1})

	SnS				SnO		
v'	argon	krypton	xenon	gas	krypton	xenon	gas [a]
0	28360	28340	27990	28260	29210	29140	29023
1	28750	28670	28300	28588	29990[b]	29730[b]	29507
2	29100	29000	28620	28915	30420	30190	30085
3	29430	29300	28920	29238	31050	30730	30647
4	29780	29620	29240	29560	31620	31240	31192
5	30080	29940	29570	29878	32280	31780	
6	30370	30230	29880	30194			
7	30720	30550	30150	30512			
8		30850	30440	30824			
9		31140	30790				
10		31440	31130				

a corrected vibrational numbering ; b strong perturbation

TABLE II

Half Widths of Vibrational Bands of SnS and SnO Absorption and Fluorescence in Various Solvents (in cm^{-1})

	SnS			SnO		
	argon	krypton	xenon	argon	krypton	xenon
Absorption	120	150	130	a	130	130
Fluorescence	220	200	200	300	320	300

a not measured

TABLE III

Fluorescence Bands of SnS and SnO in Argon, Krypton and Xenon (in cm^{-1})

	SnS			SnO		
v"	argon	krypton	xenon	argon	krytpon	xenon
0			18290	21100	21050	20890
1		17960	17870	20300	20260	20110
2		17700	17380	19450	19430	19290
3	17500	17340	16920	18710	18630	18490
4	17070	16870	16460	17880	17840	17720
5	16610	16390	15970	17120	17050	16940
6	16110	15910	15550	16400	16290	16170
7	15650	15430	15020	15440	15520	15670
8	15210	14940	14650		14750	
9	14760	14580	14300		13920	
10	14380					

TABLE IV

Intensity Correlation between Absorption in the D - X system and Fluorescence in the a - X system

(in mμ)

	SnO			SnS		
	argon	krypton	xenon	argon	krypton	xenon
Region of Fluorescence Excitation	300-325	305-340	300-340	300-400	325-345	315-350
Excitation Yielding Maximum a - X Intenisty	304	320	330	345	335	340
Wavelength of Maximum Absorption in D - X	329	329	331	344	334	338

TABLE V

Low Lying Electronic Energy Levels of CO, SnO and SnS

CO [a]		SnO		SnS	
State	Energy	State	Energy	State	Energy
A $^1\Pi$	64747	D $^1\Pi$	29023[b]	D $^1\Pi$	28360
e $^3\Sigma$	63709				
d $^3\Delta$	60647	B (1)	24760	C ($^3\Sigma$)	23613
a' $^3\Sigma$	55354	A (0^+)	24200	B ($^3\Sigma$)	22756
a $^3\Pi$	48474	a ($^3\Pi$)	20900[c]	a ($^3\Pi$)	18300[c]
X $^1\Sigma$	0	X $^1\Sigma$	0	X $^1\Sigma$	0

a reference 2; b corrected vibrational numbering; c observed in matrix, $\pm$ 100 cm^{-1}

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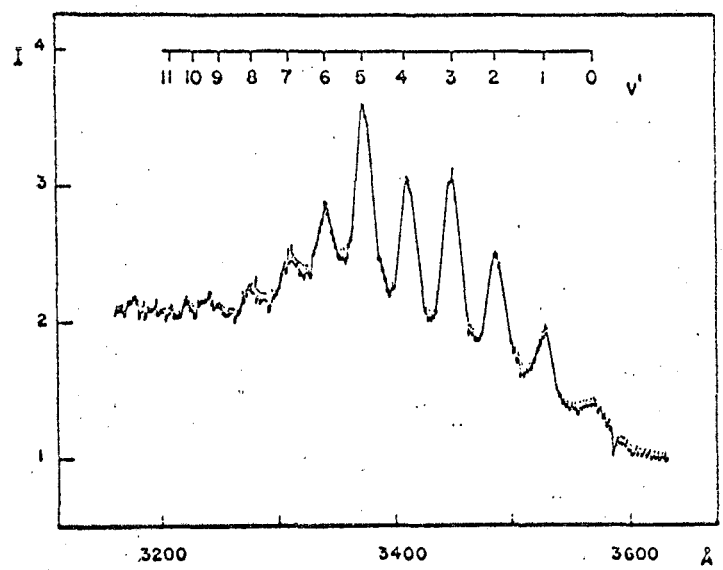

Fig. 1 Density tracing of D $^1\Pi$ - X $^1\Sigma$ absorption system of SnS in xenon at 20°K.

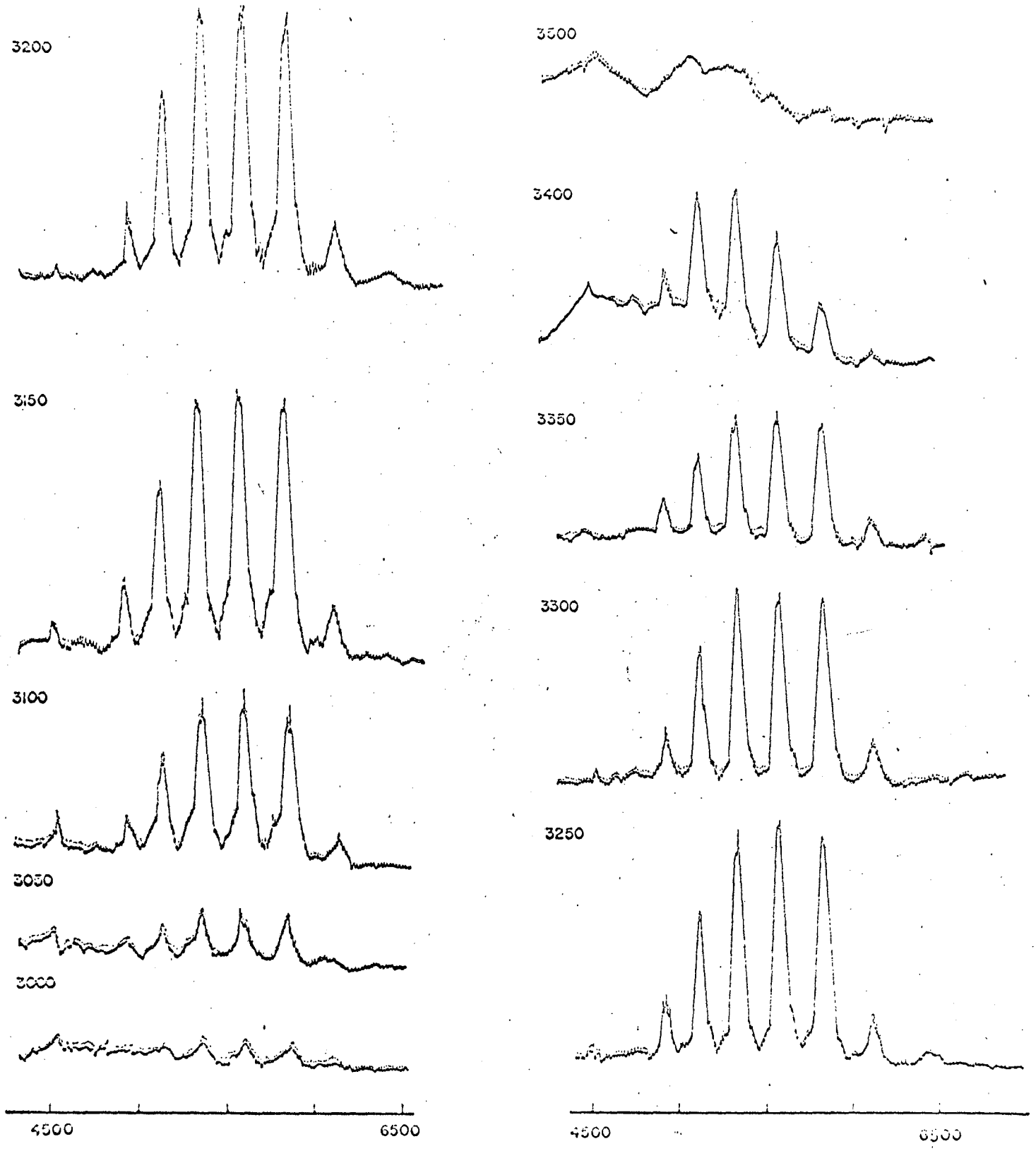

Fig. 2 Photoelectric tracing of fluorescence emission of SnO in argon at 20°K. The number in the upper left hand corner of each tracing indicates the wavelength of the center of the exciting band.

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