Fluorescence of Diatomic Molecules of Antimony

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The phenomenon of fluorescence has been found for diatomic molecules of antimony excited by the lines 2967, 3022, 3126 and 3132 of a mercury arc. The formulas for these resonance series give for the equilibrium interatomic separation 2.21A and for the moment of inertia 489×10^{-40} g·cm^2.

THE phenomenon of molecular fluorescence excited by monochromatic light has formerly been studied for relatively few homopolar molecules. In particular, for the elements of the fifth column of the periodic table, only the fluorescence of phosphorus[1] and of bismuth[2] are known. The first has its maximum intensity near λ2050A, while for the second it occurs in the visible.

From the position of antimony in the periodic table, one would expect, if fluorescence of the molecule Sb_2 exists, to observe it in the ultraviolet between λ3000 and λ3500. Unfortunately, the absorption spectrum of antimony has not yet been studied and it has been impossible until the present time to know experimentally (1) if it has absorption bands and (2) if so, where they are to be found.

I have indirectly solved this problem by studying the fluorescence of Sb_2 excited by the ultraviolet radiation from a Hg arc.

APPARATUS

The preparation of the antimony vessel is classical. The vessel of fused quartz consisted of two tubes of different diameter in which pressure and temperature could be independently varied by two electric furnaces.

The quartz vessel was cleaned by prolonged heating to eliminate gas occluded in the walls. The antimony was introduced by successive distillations; liquid air was used to prevent impurities from entering the fluorescence vessel.

A very intense Hg arc in a quartz tube shaped so as to surround almost completely the antimony vessel was used.

The quartz spectrograph gave a dispersion of 20A/mm in the region in which fluorescence occurs.

CONDITIONS OF EXCITATION

At 700°C and a pressure corresponding to 550°C weak fluorescence began to appear in the neighborhood of the lines 3126 and 3132. The maximum intensity was always found at a temperature of 950°C and a pressure equivalent to 650°C. The emission was then in the region between λ2900 and λ3400A. In spite of the great intensity of the exciting light, exposures of four hours were necessary to obtain good plates.

RESULTS

It is easy to identify on the plates four resonance series excited respectively by the lines: λλ2967.6, 3021.7, 3125.8, 3132 of Hg I. The lines of each are generally quite distinct and without mutual superposition. In addition to these four lines, it is probable that the lines λλ2925 and 3342 also give rise to resonance. Unfortunately, the small intensity did not permit me to arrange them in series.

In Table I are given the numerical values of the resonance series. The first column contains the values of the "order number"; the second, those of the measured wave-lengths; the third, the measured frequencies corrected to vacuum from Kayser's tables; the fourth, the frequency intervals.

A resonance series may be empirically represented by the formula

$$\nu = \nu^* - a(N+\tfrac{1}{2}) + b(N+\tfrac{1}{2})^2,$$

[1] Jakowlewa, Zeits. f. Physik **69**, 548 (1931).
[2] Parys, Zeits. f. Physik **71**, 807 (1931).

TABLE I. *Fluorescence lines excited by λλ2967.6, 3021.7, 3125.8, 3132 of Hg. I.*

N	λ	ν (vac.)	$\Delta\nu$	ν (calc.)	N	λ	ν (vac.)	$\Delta\nu$	ν (calc.)
		Series 2967.6					*Series 3125.8*		
−1	2944.5	33952		33959	−2	3074.5	32516		32521
0	2967.6	33687	265	33687	−1	3100	32249	267	32252
1	2991.5	33418	269	33417	0	3125.8	31983	266	31983
2	3016	33147	271	33148	1	3153	31707	276	31715
3	3040.5	32880	267	32880	2	3179.5	31442	265	31448
4	3065.5	32612	268	32614	3	3206	31183	259	31183
5	3090.5	32348	264	32349	4	3233.5	30917	266	30918
6	3116	32083	265	32086	5	3261	30656	261	30655
7	—	—	—	—	6	3289	30395	261	30393
8	3167	31567	—	31564					
9	3193	31309	258	31305			*Series 3132*		
10	3220	31047	262	31048	−3	3055	32724		32726
11	3247	30789	258	30791	−2	3080.5	32453	271	32456
					−1	3106	32186	267	32187
		Series 3021.7			0	3132	31919	267	31919
−2	2973.5	33621		33627	1	3159	31646	273	31652
−1	2997.5	33351	270	33355	2	3186	31378	268	31385
0	3021.7	33084	267	33084	3	3213	31115	263	31120
1	3047	32810	274	32814	4	3240	30855	260	30855
2	3072.5	32537	273	32546	5	3267.5	30596	259	30592
3	3098	32270	267	32279	6	3296	30331	265	30329
					7	3325	30067	264	30067

where N is the "order number," a and b are two coefficients, and the frequency of the exciting radiation corresponds to $N=0$.

The method of least squares gives the following expressions

Series 2967.6: $\nu=33822-271.7(N+\frac{1}{2})+0.70(N+\frac{1}{2})^2$

Series 3021.7: $\nu=33219-271.1(N+\frac{1}{2})+0.68(N+\frac{1}{2})^2$

Series 3125.8: $\nu=32117-268.7(N+\frac{1}{2})+0.53(N+\frac{1}{2})^2$

Series 3132: $\nu=32053-268.2(N+\frac{1}{2})+0.46(N+\frac{1}{2})^2$.

The values of the frequencies calculated from these formulae are given in the fifth column of Table I. Further, the theoretical formula for resonance series derived by wave mechanics may be written in the form

$$\nu=\nu_e-\omega_e''(v''+\tfrac{1}{2})+\omega_e''x_e''(v''+\tfrac{1}{2})^2,$$

in which ν_e represents the "system origin"; ω_e'' the fundamental frequency of vibration; x_e'' the correction for anharmonicity and v'' the quantum number of the vibration in the normal state.

It is easily seen that the numerical value of ω_e'' is, in general, much the same as the different coefficients a. If we take as an approximate value of ω_e'' the quantity $\omega_e''=277$, the formula of Morse

$$\omega_e''\cdot r_e''^3=3000$$

gives the value of the interatomic equilibrium distance in the normal state, i.e.,

$$r_e''=2.21\text{A}.$$

It is easy to deduce from this the moment of inertia in the normal state

$$I''=489\times10^{-40}\ \text{gc}\cdot\text{m.}^2$$

A variation of some units in the value of ω_e'' changes the value of the moment of inertia by only a few percent.