

constant is appreciably lowered for  $N$  greater than  $7 \times 10^{16}/\text{cc}$  is not confirmed. Further experimental details and results will be presented in a later publication.

<sup>1</sup> M. W. Zemansky, Phys. Rev. **29**, 513 (1927).

<sup>2</sup> K. T. Compton, Phys. Rev. **20**, 283 (1922).

<sup>3</sup> E. A. Milne, J. Math. Soc. London **1**, 1 (1926).

<sup>4</sup> C. Kenty, Phys. Rev. **42**, 823 (1932).

<sup>5</sup> L. M. Bieberman, J. Exper. Theor. Phys. U.S.S.R. **17**, 416 (1947). The analysis of this paper is based on the same integro-differential equation as that of reference 6. Since it is applied only to the steady-state case of a continuously incident beam, the results cannot be used in the evaluation of decay experiments.

<sup>6</sup> T. Holstein, Phys. Rev. **72**, 1212 (1947).

<sup>7</sup> The formula used is:  $T = \frac{1}{2} k_0 R (\pi \log k_0 R)^{\frac{1}{2}}$ , where  $R$  is the cylinder radius and  $k_0$  the absorption coefficient at the center of a Doppler broadened line. For mercury vapor  $k_0$  is given in terms of vapor density  $N$  and absolute temperature  $\theta$  by the expression:  $k_0 = (2.19 \times 10^{-12} N) / \theta^{\frac{1}{2}}$  cm<sup>-1</sup>.

### Persistence of Band Fluorescence in Mercury Vapor

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WHEN mercury vapor is excited with 2537Å resonance radiation it emits not only the resonance line itself but also a continuous spectrum<sup>1</sup> whose main constituents are two bands in the visible and near ultraviolet regions. The visible band extends from 4000Å to 5300Å with a maximum intensity at 4850Å; the near ultraviolet band is contained in a range from 3000Å to 3700Å with maximum intensity at 3350Å.

The persistence of this band fluorescence after the removal of the exciting light, first discovered by Phillips,<sup>2</sup> was investigated rather extensively by Lord Rayleigh with the aid of a moving-vapor-stream technique. In an experiment<sup>3</sup> in which the pressure, although not measured, was presumably kept at a minimum, this author observed a decay time of 1.8 millise. for the fluorescence.

Interpretations of the different observations in terms of excited states of Hg<sub>2</sub> have been advanced by a number of authors. Of these, the most recent, due to Mrozowski,<sup>4</sup> is illustrated in Fig. 1. Optical transitions from the excited levels to the ground state give rise to the two bands previously mentioned, as well as to the 2540Å band, closely adjacent to the resonance line. Two of these transitions, (<sup>3</sup>1<sub>u</sub> - <sup>1</sup>Σ<sub>g</sub><sup>+</sup>) and (<sup>3</sup>0<sub>u</sub><sup>+</sup> - <sup>1</sup>Σ<sub>g</sub><sup>+</sup>), are presumed to occur with a probability of the same order as that of the corresponding atomic transitions (<sup>3</sup>P<sub>1</sub> - <sup>1</sup>S<sub>0</sub>), i.e., ~10<sup>7</sup> sec.<sup>-1</sup>. The transition (<sup>3</sup>0<sub>u</sub><sup>-</sup> - <sup>1</sup>Σ<sub>g</sub><sup>+</sup>) is forbidden for pure Case c classification of the molecular levels; the experimentally observed presence of the 4850Å band is to be attributed to a small deviation from Case c, presumably in the direction of Case b. Rough estimates indicate that the lifetime of the <sup>3</sup>0<sub>u</sub><sup>-</sup> state may well be of the order of the persistence time (1.8 millise.) observed by Lord Rayleigh. One is thus led to assume that the <sup>3</sup>0<sub>u</sub><sup>-</sup> state acts as the primary reservoir of long-lived molecular excitation; the identity of decay times of both the visible and near ultraviolet bands is explained as arising from the continual replenishment of the <sup>3</sup>1<sub>u</sub> level from the <sup>3</sup>0<sub>u</sub><sup>-</sup> level by collisions of the second kind.

In our experiment on imprisoned resonance radiation, described in the preceding letter, band fluorescence first showed up at densities of about  $N = 10^{16}/\text{cc}$ , giving rise to a composite trace on the oscilloscope. From this trace one could discern two decay processes, the shorter of which we associated with resonance radiation, the longer with molecular fluorescence. This interpretation was confirmed by the use of glass transmission filters with which we could eliminate resonance radiation and observe a simple exponential decay of the fluorescence alone; the near ultraviolet and visible bands were found to decay at the same rate. Measured values of the common time constant are given in Fig. 2 of the preceding letter. We note that the low pressure limit of  $T$  agrees quite well with Lord Rayleigh's value (1.8 millise.).

It might be supposed that the decrease in  $T$  with increasing density is actually due to the simultaneous increase of temperature according to the saturated vapor pressure curve of

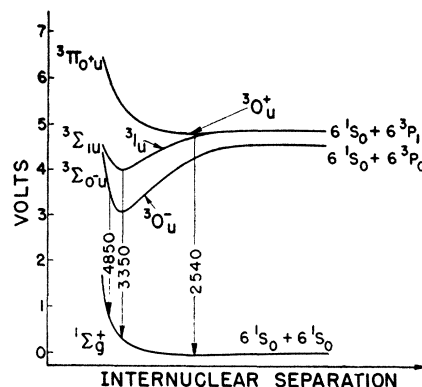


FIG. 1. Energy level diagram of Hg<sub>2</sub> according to Mrozowski (see reference 4(b), Fig. 1), with slight alterations. For large internuclear distances, the levels are described in terms of states of the separated atoms; for intermediate and small internuclear distances, this classification is replaced by those of Hund's Cases c and a, respectively.

mercury.<sup>5</sup> The absence of such an effect was demonstrated in a preliminary experiment in which, at a given pressure, two different observation temperatures were provided by the use of two furnaces of somewhat differing design. It was found that, at constant pressure, the time constant actually *increases* with temperature. This observation is in sharp disagreement with the interpretations based in Fig. 1, according to which a rise in temperature would enhance the probability of jumps from the <sup>3</sup>0<sub>u</sub><sup>-</sup> level to the <sup>3</sup>1<sub>u</sub> level by collisions of the second kind. An effect of this type would shorten the observed time constant since the <sup>3</sup>1<sub>u</sub> state is presumed to decay immediately (10<sup>-7</sup> sec.), emitting the 3350Å band.

According to Fig. 1, we would also expect the ratio of the intensities of the two bands,  $I_{4850}/I_{3350}$ , to decrease with increasing temperature. This has indeed been observed by Lord Rayleigh<sup>3</sup> and by Mrozowska.<sup>6</sup> The latter author, in addition, observed  $I_{4850}/I_{3350}$  to increase with pressure at constant temperature. In our experiments, in which the pressure and temperature varied interdependently according to the saturated vapor curve, an increase in  $I_{4850}/I_{3350}$  was also observed with increasing furnace temperature. The effect of pressure variation on the intensity ratio has not been explained in terms of the energy level scheme in Fig. 1.

Further experiments in which the pressure and temperature can be varied independently are now in progress.

<sup>1</sup> See, for example, W. Finkelburg, *Kontinuierliche Spektren* (Verlag. Julius Springer, Berlin, 1938), Section 60, for a short survey and bibliography.

<sup>2</sup> F. S. Phillips, Proc. Roy. Soc. **89**, 39 (1913).

<sup>3</sup> Lord Rayleigh, Proc. Roy. Soc. **114**, 620 (1927).

<sup>4</sup> S. Mrozowski, (a) Zeits. f. Physik **106**, 458 (1937); (b) Rev. Mod. Phys. **16**, 153 (1944), especially pp. 160, 161.

<sup>5</sup> Actually, the temperature of the furnace in the region of observation is somewhat higher than the temperature where the liquid mercury condenses.

<sup>6</sup> I. Mrozowska, Acta Phys. Polonica **2**, 81 (1933).

### Nuclear Magnetic Resonance Shift in Metals\*

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THE purpose of this letter is to report the observation of a shift in the nuclear magnetic resonance frequencies from expected values in five metals, Li, Na, Al, Cu, and Ga, in magnetic fields ranging from five to ten thousand gauss, using an automatic search type radiofrequency spectrometer.<sup>1</sup> The magnitudes of the signals observed were in all cases at least twenty times noise amplitude, and in all cases the resonance frequencies, for constant magnetic field, were higher by tenths of a percent than the resonance frequencies observed in salts of the corresponding metals. The absolute accuracy of the frequency measurements was about 0.01