constant is appreciably lowered for N greater than 7×10^{15}/cc is not confirmed. Further experimental details and results will be presented in a later publication.

[1] M. W. Zemansky, Phys. Rev. 29, 513 (1927).
[2] K. T. Compton, Phys. Rev. 20, 283 (1922).
[3] E. A. Milne, J. Math. Soc. London 1, 1 (1926).
[4] C. Kenty, Phys. Rev. 42, 823 (1932).
[5] 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.
[6] T. Holstein, Phys. Rev. 72, 1212 (1947).
[7] 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 θ by the expression: $k_0 = (2.19 \times 10^{-12} N)/\theta^{\frac{1}{2}}$ cm^{-1}.

Persistence of Band Fluorescence in Mercury Vapor

T. Holstein, D. Alpert, and A. O. McCoubrey

Westinghouse Research Laboratories, East Pittsburgh, Pennsylvania

August 29, 1949

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

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

Interpretations of the different observations in terms of excited states of Hg$_2$ have been advanced by a number of authors. Of these, the most recent, due to Mrozowski,[4] 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 2540A band, closely adjacent to the resonance line. Two of these transitions, $(^3 1_u - {}^1\Sigma_g^+)$ and $(^3 0_u^+ - {}^1\Sigma_g^+)$, are presumed to occur with a probability of the same order as that of the corresponding atomic transitions $(^3 P_1 - {}^1 S_0)$, i.e., $\sim 10^7$ sec.$^{-1}$. The transition $(^3 0_u^- - {}^1\Sigma_g^+)$ is forbidden for pure Case c classification of the molecular levels; the experimentally observed presence of the 4850A 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 $^3 0_u^-$ state may well be of the order of the persistence time (1.8 millisec.) observed by Lord Rayleigh. One is thus led to assume that the $^3 0_u^-$ 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 $^3 1_u$ level from the $^3 0_u^-$ 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 $N = 10^{16}$/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 millisec.).

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
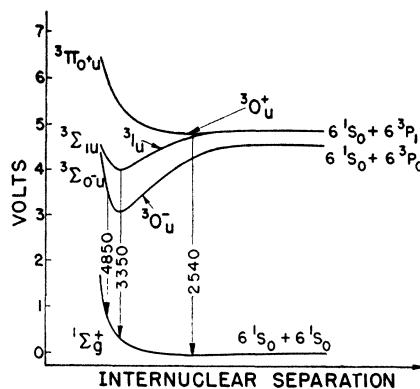

FIG. 1. Energy level diagram of Hg$_2$ according to Mrozowski (see reference 4(b), Fig. 1), with slight alterations. For large internuclear distances, the levels are described in terms of states of the separated atoms; for intermediate and small internuclear distances, this classification is replaced by those of Hund's Cases c and a, respectively.

mercury.[5] 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 $^3 0_u^-$ level to the $^3 1_u$ level by collisions of the second kind. An effect of this type would shorten the observed time constant since the $^3 1_u$ state is presumed to decay immediately (10^{-7} sec.), emitting the 3350A 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[3] and by Mrozowska.[6] 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.

[1] See, for example, W. Finkelnburg, Kontinuerliche Spektren (Verlag. Julius Springer, Berlin, 1938). Section 60, for a short survey and bibliography.
[2] F. S. Phillips, Proc. Roy. Soc. 89, 39 (1913).
[3] Lord Rayleigh, Proc. Roy. Soc. 114, 620 (1927).
[4] S. Mrozowski, (a) Zeits. f. Physik 106, 458 (1937); (b) Rev. Mod. Phys. 16, 153 (1944), especially pp. 160, 161.
[5] Actually, the temperature of the furnace in the region of observation is somewhat higher than the temperature where the liquid mercury condenses.
[6] I. Mrozowska, Acta Phys. Polonica 2, 81 (1933).

Nuclear Magnetic Resonance Shift in Metals*

W. D. Knight**

Brookhaven National Laboratory, Upton, Long Island, New York

September 1, 1949

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.[1] 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
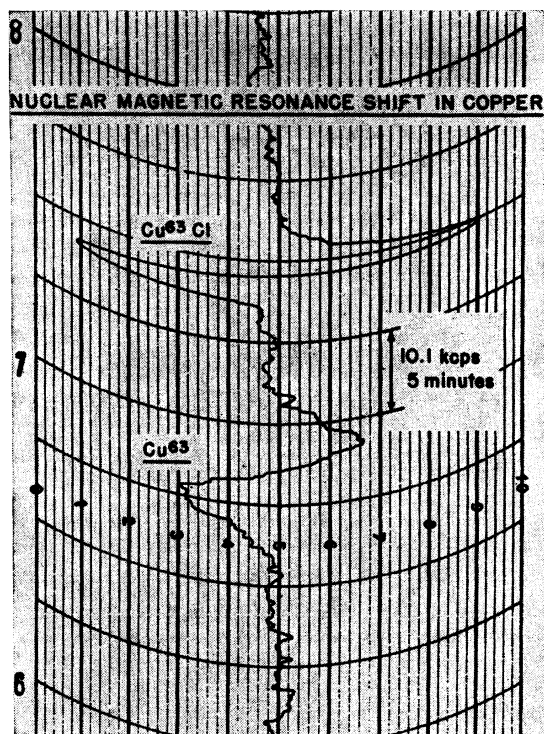
FIG. 1. The resonances are both due to the Cu^{63} isotope. The more intense line is due to CuCl powder. The broader line occurs in Cu metal powder at a frequency higher by about 25 kc.p.s. at a resonance frequency of about 10 mc.p.s. The two dry powders are mixed in the proportion of 100 parts CuCl to 64 parts Cu by weight.

percent, while small frequency differences were accurate to about 0.002 percent of the average frequency.

The lithium and sodium resonances were observed in shavings of the respective metals in kerosene, while the copper and aluminum resonances occurred in metal powders which had been suspended in melted paraffin and subsequently cooled in a mold. The gallium metal was sealed in several capillary tubes, each about one millimeter in diameter. These tubes were placed in the r-f coil with their axes parallel to the coil. The ambient temperature in the case of gallium was above the melting point of that metal. The gallium resonance was not observed when the temperature was lowered below the melting point.

This shift has been observed in separate samples of a particular metal and its salts and in samples of a metal mixed with its salt. In the latter situation, one could be certain that the resonances occurred in exactly the same applied field. Observations have been made on separate runs for precise frequency comparisons, and on single continuous runs (see Fig. 1) in order to display the effect qualitatively. The shift for a given isotope is proportional to the resonance magnetic field (or frequency) within the limits of error stated above. Values of the observed shifts and line widths are

TABLE I. Values of the observed shifts and line widths.

Isotope	Salt*	Resonance frequency in salt (mc.p.s.)	Frequency shift in metal (kc.p.s.)	Line width in metal (kc.p.s.)	Line width in salt (kc p.s.)
Li⁷	LiCl	9.436	+ 3.4 ±0.2	1.4 ±0.2	1.2 ±0.2
Na²³	NaCl	10.123	+10.5	0.5	1.4
Al²⁷	AlCl₃	10.145	+16.2	9.3	0.8
Cu⁶³	CuCl	10.321	+23.7	7.4	2.6
Cu⁶⁵	CuCl	11.050	+25.6	5.8	2.6
Ga⁷¹	GaCl₃	7.409	+33.3	1.5	3.0

* With the exception of CuCl, which was compressed powder, the samples were in aqueous solution.

given in Table I. It is to be noted that the shift is greater in the heavier metals, a trend which follows qualitatively that of the known values for hyperfine structure splitting.

C. H. Townes has suggested that the shift may be due to the paramagnetic effect of the conduction electrons in the vicinities of the metal nuclei. If this is true, the shift in the metal should be proportional to the hyperfine splitting of the ground state of the free atom. Suppose, then, for sodium that: 1. There is one conduction electron per nucleus on the average in the metal; 2. the value at the metal nucleus of the wave function of this average conduction electron is the same as of the valence electron of the normal free atom; 3. the bulk susceptibility (corrected to give the net paramagnetic part)[2] divided by the average density of conduction electrons is a measure of the number of conduction electrons which contribute to the shift. Then the product of the susceptibility per electron and the applied magnetic field should give the average effective magnetic moment per electron. The ratio of this quantity to the Bohr magneton should be equal to the ratio of the observed shift in the metal to the hyperfine splitting in the free atom, taken in energy units. Here it is to be noted that the total hyperfine splitting[3] should be modified before making the above comparison. First, for the sodium nucleus, three equal transitions are possible in the applied magnetic field, and, second there is a complete Paschen-Back effect when the field is applied to the metal. The effect of these considerations is to reduce the hyperfine splitting by a factor of four before comparing the above ratios.

The results of this simple calculation show that the predicted value of the shift in sodium to be larger than that observed by about fifty percent. A more detailed analysis is being made in an effort to improve this calculation. It is thought that a closer examination of the respective wave functions (see 2, above) will yield information which leads to a closer agreement.

Further experimental work is being done to determine the magnitude of this effect in these and other metals and alloys at varying temperatures, and to determine the possible existence of a shift in resonance frequency when comparing two or more salts of the same metal. Preliminary measurements show that the latter shift, if it exists, is certainly less than 0.001 percent among similar salts of a given metal (CuCl, CuBr, CuI). More accurate measurements are under way to confirm the existence of shifts of about 0.01 percent among some phosphorous compounds. The magnitude of this shift is of the order of the line width or slightly larger.

The author's thanks are due Dr. V. W. Cohen, who has directed this work, and Dr. C. H. Townes for many helpful discussions.

1 R. V. Pound, Phys. Rev. 72, 527 (1947).
2 F. Seitz, Phys. Rev. 58, 633 (1940).
3 M. Fox and I. I. Rabi, Phys. Rev. 48, 746 (1935).

A New Determination of the Relative Abundance of Rhenium in Nature*

HARRISON BROWN AND EDWARD GOLDBERG
Institute for Nuclear Studies, University of Chicago
AND
Argonne National Laboratory, Chicago, Illinois
August 29, 1949

IT has become generally recognized that a most peculiar discontinuity exists at $A = 185$ and $A = 187$ in the curve representing the relative abundances of nuclear species as a function of mass number.[1-3] It is of interest to determine whether the observed low abundances of Re^{185} and Re^{187} are real, or whether the discontinuity is the result of faulty determinations of rhenium concentrations in meteorites by previous investigators.[4]

In view of the chemical properties of rhenium, one would expect the element to be concentrated primarily in the metal phase of the earth and in the metal phase of meteoritic matter. Conse-
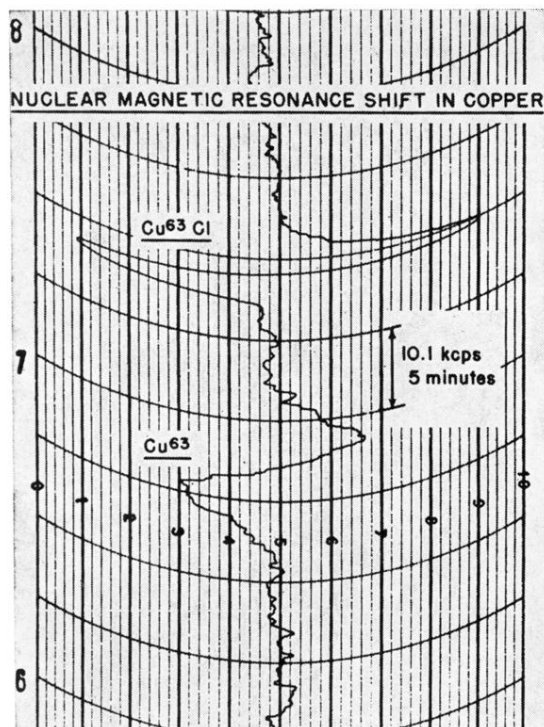
FIG. 1. The resonances are both due to the Cu^{63} isotope. The more intense line is due to CuCl powder. The broader line occurs in Cu metal powder at a frequency higher by about 25 kc.p.s. at a resonance frequency of about 10 mc.p.s. The two dry powders are mixed in the proportion of 100 parts CuCl to 64 parts Cu by weight.