ABSORPTION OF RESONANCE RADIATION IN MERCURY VAPOR

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(Received April 8, 1930)

Abstract

The theories of absorption in mercury vapor of mercury resonance light of wave-length 2536.7A as formulated by Malinowski and H. A. Wilson are briefly reviewed. It is well established that the absorption coefficient for resonance radiation increases as the number of absorbing atoms decreases. This is probably due to a Doppler effect in the radiating vapor. To diminish the influence of the Doppler effect a jet of mercury vapor was used, and the resonance radiation coming from it was investigated. A series of measurements of the absorption coefficient of this light is given. The maximum atomic absorption coefficient observed is 10.22×10^{-13}, nine times as large as any previously observed. It is shown that Malinowski's assumptions are not in accord with the observed effects.

Introduction

A NUMBER of people[1,2,3,4,5,6] have investigated the properties of mercury resonance light of wave-length 2536.7A since it was first discovered by R. W. Wood.[7] The writer[8] assisted in one such investigation in which the atomic absorption coefficient was measured. The atomic absorption coefficient, γ, is defined by the equation

$$I = I_0 e^{-\gamma n_a} \qquad (1)$$

where I_0 is the intensity of the light as it enters the cell, I the intensity as it leaves it and n_a is the number of absorbing atoms per cm^2 of the cell. As the number of absorbing atoms changed from 1.35×10^{12} to 87.6×10^{12} per cm^2 of the absorption cell the atomic absorption coefficient changed from 11.2×10^{-14} to 2.53×10^{-14}. Several investigators have observed this variation in the absorption coefficient. The cause appears to be the non-homogeneity of the resonance line for in the case of a perfectly homogeneous radiation γ should be constant. Consequently, the values of γ are to be regarded only as average values for the atoms involved.

[1] A. v. Malinowski, Ann. d. Physik **44**, 935 (1914).
[2] C. Füchtbauer, G. Joos, and O. Dinkelacker, Ann. d. Physik **71**, 222 (1923).
[3] W. Orthmann, Ann. d. Physik **78**, 601 (1925).
[4] F. Goos and H. Meyer, Zeits. f. Physik **35**, 803 (1926).
[5] M. Schein, Ann. d. Physik **85**, 257 (1928).
[6] P. Kunze, Ann. d. Physik **85**, 1013 (1928).
[7] R. W. Wood, Phil. Mag. **23**, 696 (1912).
[8] A. L. Hughes and A. R. Thomas, Phys. Rev. **30**, 466 (1927).

Former Theories

The Doppler effect predominates among the various effects[9] proposed to account for the width of spectrum lines, particularly when the pressure is low, as it is in mercury vapor at room temperature. It has been shown that the visibility in interference patterns[10,11] is the same as one would expect if the entire width were due to the Doppler effect.

The shift in wave-length $\delta\lambda$ due to the Doppler effect is given by

$$\frac{\delta\lambda}{\lambda}=\frac{v}{c} \tag{2}$$

from which we get that

$$v=\frac{c\delta\lambda}{\lambda}=\beta\delta\lambda \tag{3}$$

where β is a constant. The number of atoms with any particular component of velocity along the line of emission is given by the formula from kinetic theory,

$$dn = Ke^{-v^2/\alpha^2}dv. \tag{4}$$

The intensity, dI, of the light at any particular wave-length, separated from the center of the line by a wave-length difference $\delta\lambda$, is proportional to the

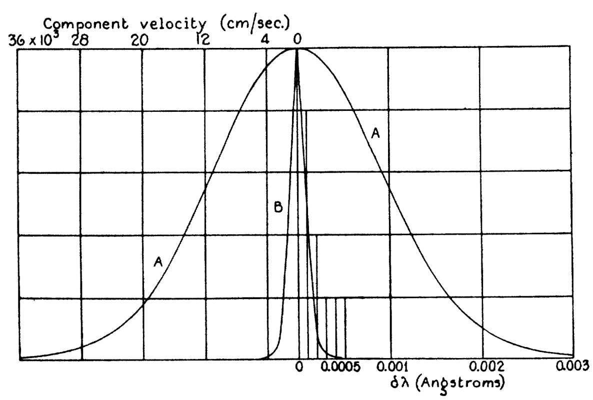


Fig. 1. Distribution of energy in the resonance line. Curve A shows the distribution in the ordinary resonance line, curve B, the distribution in the line used in this experiment.

number of atoms, dn, which have the proper component of velocity, v, to give this wave-length. We then have that

$$dI \propto dn \propto e^{-v^2/\alpha^2}dv \propto e^{-(\beta\delta\lambda)^2/\alpha^2}d(\delta\lambda) \tag{5}$$

[9] Rayleigh, Phil. Mag. **29,** 274 (1915).

[10] A. A. Michelson, Astrophys. J. **3,** 251 (1896).

[11] Buisson and Fabry, Jour. d. Physique **2,** 442 (1912).

where v and also $\delta\lambda$ varies from $-\infty$ to $+\infty$. This distribution is shown graphically in Fig. 1, curve A, when the emitting vapor is at a temperature of 293°K.

Malinowski[1], assuming this line form, has worked out an expression for I/I_0 in terms of n_a (see Eq. (1)). He also assumes that the ability of the atoms in an infinitely thin layer to absorb light of any particular wave-length will be given by

$$k_v = k_0 e^{-v^2/\alpha^2} \tag{6}$$

where k_0 represents the ability of the atoms to absorb the very center of the line. This equation results from assuming that an atom in the absorption cell can absorb light only near the wave-length which it, itself, can emit, and also that this band over which it can absorb light is very narrow with respect to the entire line. (If, in accordance with the strict quantum theory, we suppose that the correspondence between $\delta\lambda$ and v must be exact it is evident that there can be no absorption for as we narrow down the velocity range in which an atom must be in order to absorb light of a particular wave-length the number of atoms available for such absorption approaches zero.[12]) On these assumptions Malinowski shows that the absorption coefficient for the very center of the line is the square root of two times the observed value for a cell which is infinitely thin. The atomic absorption coefficient for the very center of the line should, then, also be the square root of two times the observed value for a very thin cell. A reasonable extrapolation of the values secured by Hughes and Thomas gives $\gamma = 12\times 10^{-14}$ for an infinitely thin layer of vapor and $\gamma_0 = 17\times 10^{-14}$. If his ideas are correct, it is evident that, if the importance of the Doppler effect could be reduced greatly, the observed atomic absorption coefficient should approach γ_0, that is, the square root of two times the former value observed for an infinitely thin layer of atoms. Also the coefficient should remain constant for all cell thicknesses.

H. A. Wilson[13] has also proposed a theory which is applicable in this case. He assumed that the atom absorbs as a simple linear oscillator, the equation of motion of which may be taken to be

$$n\ddot{x} + k\dot{x} + \mu x = Fe \tag{7}$$

where m is the mass of the vibrating particle, k the viscous resistance to the motion at unit velocity, μ a constant, F the electric intensity in the light at the atom, which may be taken as equal to $F_0 \cos pt$, e the charge on the particle and x the displacement of the particle. From this he deduces that

$$\gamma = \frac{\gamma_0}{1 + (4m^2/k^2)q^2} \tag{8}$$

where γ_0 is the atomic absorption coefficient for exact resonance, γ that for a departure from exact resonance given by a frequency difference q (which

[12] A. L. Hughes and A. R. Thomas, Phys. Rev. **30**, 472 (1927).

[13] H. A. Wilson, Proc. Roy. Soc. **A118**, 362 (1928).

corresponds to $\delta\lambda$ as used above). He then assumed that the energy distribution in the incident line was given by $Ae^{-\beta^2 q^2}$ which is the form appropriate for a Doppler effect but does not demand this explanation for the finite width of the line. With this added he shows that

$$\gamma_G = \frac{1}{(n_a)^{1/2}}\left(\log\frac{I_0}{I}\right)\frac{m}{\beta k} \tag{9}$$

when n_a is not too small. Wilson showed that this fitted Hughes and Thomas' results when n_a was greater than about 10^{13}. It is implied in the derivation of Eq. (8) that the emission line is broader than the absorption line.

Both theories predict that if the width of the resonance line could be reduced the observed absorption coefficient should increase and Malinowski's work specifies the amount of this increase. Also according to Malinowski the absorption coefficient should not change with cell thickness. An experimental test of these predictions is described on the following pages.

Distribution of Energy in Incident Light

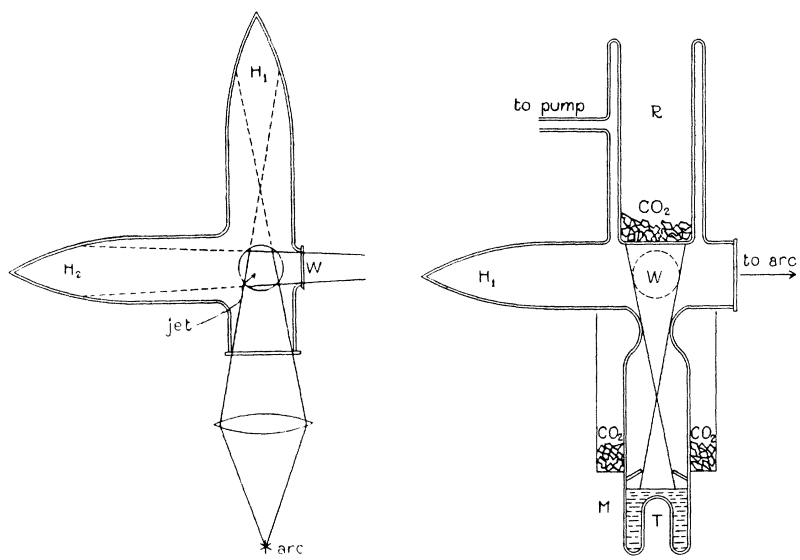
The most feasible method of reducing the width of the resonance line which presented itself was to use a jet of mercury vapor as a source of resonance light. If the light is taken out at right angles to the jet the component velocities of the atoms in the line of emission will be quite small. The jet was diaphragmed so that five degrees was the maximum angle that any atom's path could make with the line of centers of the diaphragms. The distribution of energy in the radiation from such a jet was computed and the results plotted graphically in Fig. 1, curve B. While this distribution curve cannot be represented accurately by a curve of the form e^{-v^2/α^2}, we may, however, find a curve of this form which is roughly superposable on the distribution curve, and so find a value for the "most probable velocity," α, in a direction perpendicular to the jet. This turns out to be about one tenth of the value of the most probable velocity in isotropic mercury vapor at room temperature. This means that laterally its effective temperature as measured by the component velocity of the atoms is about 0.31 times its real temperature, that is 90°K.

Apparatus and Procedure

The source of light was a vertical quartz mercury arc. It was kept cool by circulating distilled water around it. Ice was kept in the water most of the time to prevent heating. The current for the arc was supplied by a generator floating across a bank of storage batteries. A preliminary test showed that about four amperes through the arc gave the greatest amount of light from the resonance lamp. The central part of the arc was deflected to the front of the tube by an electro-magnet excited by the same current that was used in the arc. Under these circumstances the arc ran very steadily. No fluctuations could be noticed in the course of an entire day's work.

The light from this arc was focused into a resonance lamp constructed of Pyrex glass shown in Fig. 2. A is a cross section, B is a vertical section.

Light, not absorbed in the jet, continued into the horn, H_1, (see Fig. 2*A*) where it was lost by multiple reflection. The resonance light taken out through the window, *W*, had the horn H_2 as a background so that any stray light returning from H_1 could not get out in the same direction as the resonance light. The most careful tests made showed no light of this sort whatever. An intensity much less than one percent of the resonance light could have been detected. The jet (see Fig. 2*B*) was diaphragmed as shown, the upper diaphragm being merely a slight constriction in the tube. The walls of the tube were cooled with solid CO_2 as was the reentrant tube, *R*, on which the mercury in the jet condensed. A heater, *T*, to increase the strength of the jet was not used as the jet proved to be quite strong enough without it.



A *B*

Fig. 2. The resonance lamp used. *A* is a cross section, *B*, a vertical section.

Moreover the amount of stray vapor, the atoms of which were moving at random, was greatly increased by heating the mercury. In the final experiment practically the whole of the lamp was surrounded by solid CO_2 in order to diminish the amount of stray vapor as much as possible. In a former unpublished investigation[14] with potassium a method for securing quite strong jets was developed. A diaphragm was placed very near the liquid metal surface, *M*, and the walls of the tube were kept cool as close down to this diaphragm as possible. By this method it was possible to secure jets several times as strong as is possible with the metal in the bottom of just a straight tube with no diaphragm near the surface of the liquid metal.

The remainder of the apparatus was arranged as in Fig. 3. The resonance light passed through the absorption cell *C*, on through a quartz lens *L*, a

[14] Done with L. C. Van Atta.

variable rotating shutter S, and into a photoelectric cell. The active material in the photoelectric cell was aluminum. It was filled with helium to about one mm pressure after the surface had been sensitized by a discharge through hydrogen as is done in making an alkali hydride surface. A potential of 200 volts was used on the cell. The sensitivity to mercury resonance radiation was about seventy five times that of the untreated vacuum cell. The absorption cell, C, consisted of a glass tube 1.622 cm long to which quartz windows were sealed. A side tube contained a drop of mercury. The pressure in the cell and thus the number of absorbing atoms was controlled by cooling the side tube. The absorption cell was fixed so that it could be shifted

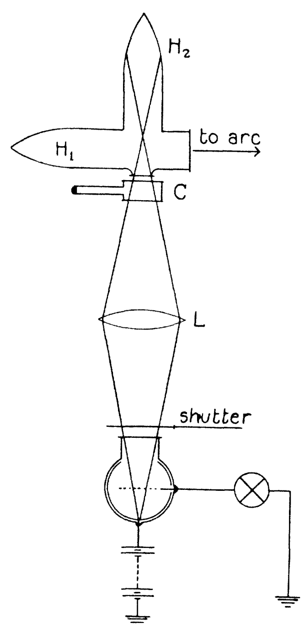


Fig. 3. Arrangement of the apparatus.

out of the beam and the electrometer current secured without the cell. The transmission of the cell was approximately matched by the variable rotating shutter and the actual transmission secured by interpolation. The mercury was all frozen out of the cell and its transmission secured by the same method as well as by comparing it with a previously calibrated screen. The transmission was 0.69. Calling the amount of light getting through the cell with the side tube cooled by solid CO_2 I_0, and the amount at any other temperature I then the fraction transmitted by the vapor will be I/I_0.

Results

The experimental values for I/I_0 are shown in Fig. 4 plotted against the temperature of the side tube. A smooth curve was drawn through the experimental points and values read off this for purposes of computation. These values are listed in Table I. The temperatures of the side tube are listed in column one and the corresponding values for I/I_0 in column two. The next column gives the values of the natural logarithms of I_0/I.

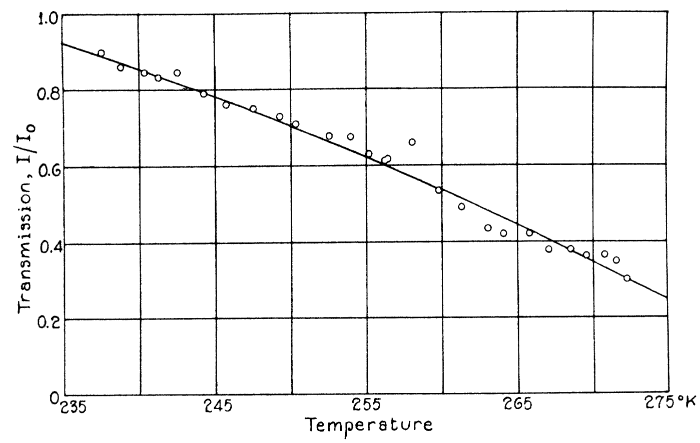


Fig. 4. Ratio of transmitted to incident radiation for various temperatures of mercury vapor.

To determine the atomic absorption coefficient we have to calculate the number of atoms involved in the absorption in each case. This must be calculated from the pressure. The fourth column gives the pressures of the

TABLE I.

Temp. °K	I/I_0	log I_0/I	p in side tube in mm	p in cell in mm	n_a	γ
235	0.915	0.0888	1.45×10^{-6}	1.62×10^{-6}	8.71×10^{10}	10.22×10^{-13}
240	0.862	0.1484	3.09	3.41	18.36	8.08
245	0.792	0.2332	6.30	6.89	34.06	6.29
250	0.715	0.3355	12.3	13.3	71.63	4.68
255	0.628	0.4652	23.2	24.9	133.8	3.48
260	0.538	0.6200	42.8	45.4	244.4	2.54
265	0.444	0.8118	76.2	80.1	431.0	1.88
270	0.344	1.0671	133.	139.	745.3	1.43
275	0.240	1.4271	228.	235.	1266.	1.13

mercury vapor in the side tube for the corresponding temperatures recorded in the first column. The vapor pressures of mercury at different temperatures given in the International Critical Tables were used in this computation. As the same absorption cell was used which Hughes and the writer used in their former investigation the relations deduced at that time can be used. The pressure, p, in the absorption cell and the pressure, p_m, in the side tube are connected by the relation

$$\frac{p}{p_m}=\left(\frac{T}{T_m}\right)^{1/2} \tag{10}$$

where T and T_m are the temperatures of the absorption cell and the side tube respectively. The pressures in the absorption cell, as corrected by this equation, which takes care of thermal transpiration, are listed in column five.

The number of absorbing atoms, n_a, per cm^2 of the cell is connected with the pressure, p, by the equation

$$n_a = (5.38 \times 10^{16})p. \tag{11}$$

The values of n_a are listed in column six. The atomic absorption coefficient, γ, is calculated according to Eq. (1) and listed in column seven. This is an average value for all the atoms present in the absorption cell although it is not absolutely certain that they are all active in absorbing the light.

The atomic absorption coefficient which, according to Malinowski's theory, should have been almost constant for all values of n_a, is shown plotted against n_a in Fig. 5, curve A, along with the values of the atomic

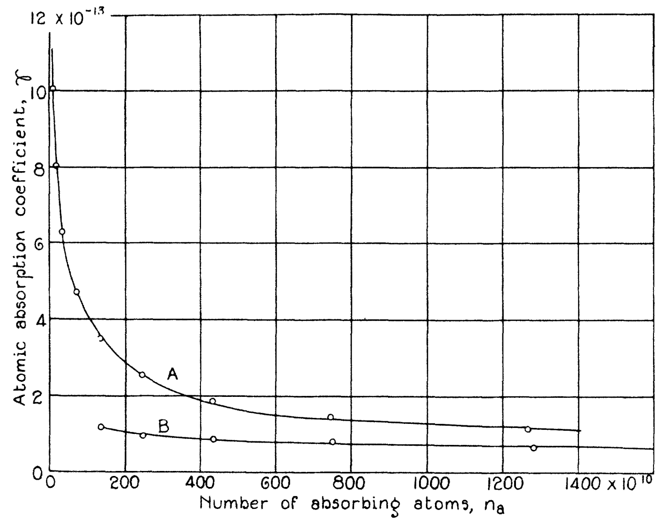


Fig. 5. Variation of the atomic absorption coefficient with the number of absorbing atoms. A is the curve secured in this experiment, B, that secured by Hughes and Thomas.

absorption coefficient from the previous work, curve B. The coefficient is definitely not a constant and it is certainly several times greater than the square root of two times any possible extrapolation of the former curve to an infinitely thin cell.

TABLE II.

n_a	$\frac{1}{(n_a)^{1/2}} \log_e \frac{I_0}{I}$	$\frac{(n_a+6\times 10^{10})^{1/2}}{n_a} \log_e \frac{I_0}{I}$
8.71×10^{10}	3.01×10^{-7}	3.91×10^{-7}
18.36	3.46	3.99
34.06	3.83	4.13
71.63	3.96	4.13
133.8	4.02	4.11
244.4	3.97	4.01
431.0	3.91	3.94
745.3	3.91	3.92
1266.	4.01	4.02

According to H. A. Wilson's theory, $1/(n_a)^{1/2} \log I_0/I$ should be constant for values of n_a which are not too small. These values are tabulated in Table II column 2. It is seen that they are practically constant for values of n_a greater than about 50×10^{10}. Wilson also proposed an empirical expression which is constant for all values of n_a and by means of which γ for an infinitely thin cell can be deduced. It is

$$\frac{(n_a + K)^{1/2}}{n_a} \log_e \frac{I_0}{I} = C. \tag{12}$$

It is seen that it goes over into the theoretical relation when n_a is large. Values of C are tabulated in Table II, column 3. From it γ for the infinitely thin cell is given by $C/K^{1/2}$ which for this case is 16.33×10^{-13}. This is thirteen times greater than the value secured (1.25×10^{-13}) when the same relation is applied to the results of Hughes and Thomas and about sixty per-cent greater than the maximum experimental value obtained in this experiment, (viz. 10.22×10^{-13}).

Discussion

As the light from the jet is much more absorbable than that from an ordinary resonance lamp the distribution of energy in the line must be very different from the ordinary distribution, certainly the line must be much more homogeneous, probably as homogeneous as light from a discharge tube cooled in liquid air (disregarding, for the moment, the fact that actually all the atoms would be condensed). It would seem from this that the Doppler effect controls emission for no other effect presents itself which will be affected by the jet sufficiently to explain, even qualitatively, the observed effects. It is evident that Malinowski's assumption that the absorption and emission lines have the same width is not justified for we do not get his predicted results. A consideration of these results points to the conclusion that the emission line must be wider than the absorption line, otherwise the absorption coefficient would not increase rapidly as the number of atoms, n_a, diminishes. Since there are good reasons, already mentioned, for believing that the width of the emission line is determined by the Doppler effect, we must, therefore, conclude that, because the absorption line is apparently narrower than the emission line, the width of the absorption line is not controlled by the Doppler effect. It appears, since H. A. Wilson's theory applies to these results, that we may consider the mercury atoms, as far as absorption goes, behaving like simple linear oscillators. It does not seem possible, at present, to interpret the results of these absorption experiments in such a way as to give a satisfactory and consistent picture of the processes involved in emission and absorption of resonance radiation.

The above work was done at Washington University, St. Louis, Mo. The writer wishes to thank Dr. A. L. Hughes for especial assistance and advice given during the course of the experiment. Also he wishes to thank Mr. C. A. Reinhart, instrument maker, for help in the construction of apparatus.