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Isotope Effect in the Imprisonment of Resonance Radiation

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On theoretical grounds it is expected that the decay time of imprisoned resonance radiation in the vapor of a single even isotope of mercury should be some six times larger than that observed with the natural samples of mixed isotopic constitution. To investigate this effect experimentally, decay measurements were carried out with samples of Hg^{198} (3 percent Hg^{199} and 0.1 percent Hg^{200}). For vapor densities $N \lesssim 10^{14}$/cc, the predicted effect was verified. For $N > 10^{14}$/cc, the observed decay time drops below that predicted theoretically for pure Hg^{198}. This secondary effect is here attributed to the transfer of excitation from Hg^{198} to Hg^{199} and Hg^{200} by collisions of the second kind. Comparison of experimental data with an appropriately generalized theory permits estimation of the cross section for such collisions. The value so obtained is 10^{-13} cm^2, some twenty times the gas-kinetic cross section, and in order-of-magnitude agreement with theoretical expectations.

ACCORDING to theory,[1] the persistence of imprisoned resonance radiation in gases is strongly dependent upon the line shape of the radiation. In particular, it is found that a correct description of the phenomenon necessitates taking into account the hyperfine structure of the resonance line.[2] For example, the persistence time of the 2537A line of Hg, which in naturally occurring samples consists of five hyperfine components, is theoretically some six times smaller than that associated with a pure even isotope, which does not possess hyperfine structure. Measurements carried out with samples of Hg^{198} (3 percent contamination of Hg^{199}, 0.1 percent of Hg^{200}) not only confirm this marked difference, but also exhibit in a striking manner additional effects arising from small admixtures of isotopic impurities.

The measurements of the persistence time T of imprisoned radiation, as a function of vapor density N, were carried out in a manner previously described.[3] A special procedure[4] was required for the preparation of resonance tubes of Hg^{198} from two 2-milligram samples, kindly supplied to us by Dr. Meggers of the National Bureau of Standards. The experimental points are shown in Figs. 1(I) and 1(II) (black circles). By way of comparison, the corresponding data for natural mercury, presented in reference 3, are reproduced in both Figs. (black squares).

The dashed curves labeled "natural mercury," also reproduced from reference 3, represent upper and lower limits of the theoretical prediction for that case. The curves coincide in the region of Doppler broadening ($N < 10^{15}$/cc); in this region T is given analytically by the expression[3,5]

$$T = \tfrac{5}{8} k_0 R (\pi \log k_0 R)^{\frac{1}{2}} \tau, \tag{1}$$

where τ, the lifetime of the isolated atom, is 1.08×10^{-7} sec, R is the radius of the resonance tube, and k_0 is the absorption coefficient at the center of the Doppler-broadened line. k_0 is given by the formula

$$k_0 = 2.19 \times 10^{-12}\, N/\theta^{\frac{1}{2}} \text{ cm}^{-1}, \tag{2}$$

where θ is the absolute temperature. Equation (2) results from the assumption that the five hyperfine com-

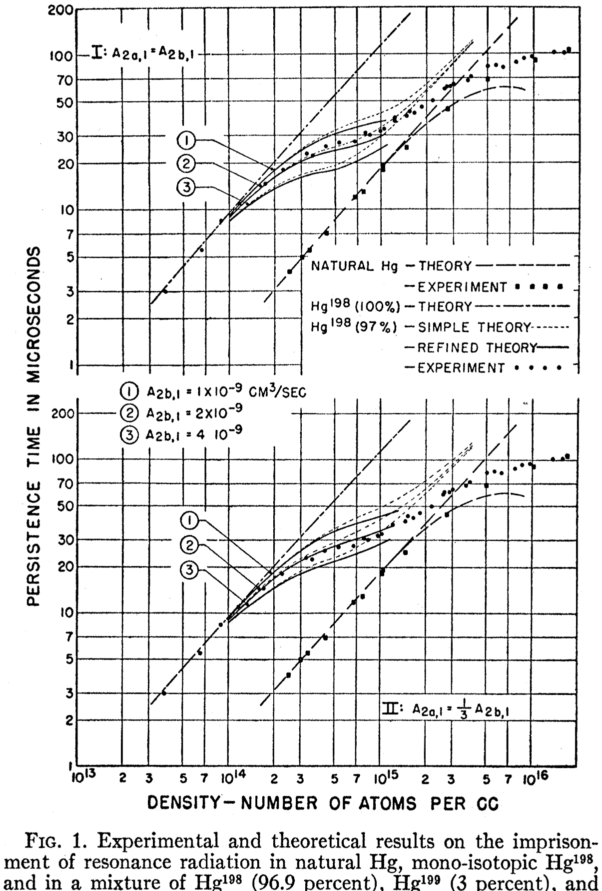

FIG. 1. Experimental and theoretical results on the imprisonment of resonance radiation in natural Hg, mono-isotopic Hg^{198}, and in a mixture of Hg^{198} (96.9 percent), Hg^{199} (3 percent), and Hg^{200} (0.1 percent). In the latter case the theoretical curves depend on the transfer coefficients, $A_{2a,1}$ and $A_{2b,1}$. Figure 1(I) is for the case $A_{2a,1} = A_{2b,1}$; Fig. 1(II) for the case $A_{2a,h} = \frac{1}{3} A_{2b,1}$.

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[1] T. Holstein, Phys. Rev. **72**, 1212 (1947).

[2] Reference 1, Sec. 5.

[3] Alpert, McCoubrey, and Holstein, Phys. Rev. **76**, 1257 (1949). Footnote 7 of this reference contains the theoretical expression for T given in Eqs. (1) and (2) of the present paper. For the derivation of the result see T. Holstein, Phys. Rev. **83**, 1159 (1951).

[4] To be reported by D. Alpert and C. G. Matland in Rev. Sci. Instr.

[5] T. Holstein, Phys. Rev. **83**, 1159 (1951).

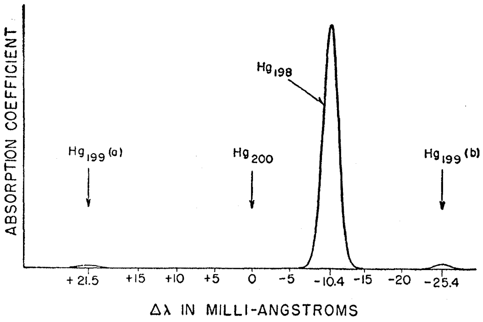

FIG. 2. Absorption spectrum of experimental Hg samples. On the scale of the figure the contribution of the Hg^{200} line is too small to be shown. In the case of Hg^{199} there are two hyperfine components, (a) and (b), corresponding to two excited states of total angular momentum $\frac{1}{2}$ and $\frac{3}{2}$, respectively.

ponents of the line are all of equal intensity; the more exact treatment,[2] which takes account of the actual intensity ratios of the different components, yields substantially the same result for T as (1) and (2).

The broken curve labeled "single isotope" is also given by an expression of the form of (1), in which, however, k_0 has to be multiplied by a factor of five, i.e.,

$$k_0 = 10.95\times 10^{-12}\, N/\theta^{\frac{1}{2}}. \tag{2'}$$

The factor of five arises from the coalescence of the hyperfine components into the single line characteristic of Hg^{198}. It is immediately evident that for $N < 10^{14}$/cc the curve is in agreement with experiment. It will now be shown that the deviations for $N > 10^{14}$/cc can be explained in terms of nonradiative transfer of excitation between atoms of Hg^{198} and the other isotopic constituents.

The absorption spectrum of our samples is illustrated in Fig. 2. The maxima of the absorption lines are, in this case of Doppler broadening, proportional to the "line intensities," i.e., to the areas under the curves. Each line intensity, in turn, is proportional to the product of (a) the concentration of the absorbing isotope, and (b) the ratio of the statistical weights of excited and ground states of the line in question. The separations of the hyperfine components are large enough so that the absorption bands[2] of the different lines do not overlap; hence, radiative transfer of excitation between different isotopes or between different hyperfine states of the same isotope can be ignored. Then, at sufficiently low vapor densities, where nonradiative transfer is also absent, each line decays independently with its own characteristic persistence time. We may thus expect a very rapid decay[6] of the radiation from Hg^{199} and Hg^{200}, followed by a relatively long persistence of the Hg^{198} line. This is actually what is observed by visual examination of the oscillographic traces of light intensity *vs* time; the time constants given in Figs. 1(I) and 1(II) are taken from the terminal portion of these traces and hence represent the longest time constant, which is associated with Hg^{198}.

As the vapor density is increased, it becomes necessary to take into account collisions involving nonradiative transfer of excitation between the different hyperfine states. These collisions have essentially the effect of transferring excitation from the slowly decaying Hg^{198} line to the much more rapidly decaying lines of Hg^{199} and Hg^{200}, with the result that the over-all decay rate is speeded up.

A quantitative description of the phenomenon is afforded by the following set of equations for the time variation of the densities n_i of the different excited states:

$$dn_1/dt = -n_1/T_1 - n_1[A_{1,2a}N_2 + A_{1,2b}N_2 + A_{1,3}N_3] + [n_{2a}A_{2a,1} + n_{2b}A_{2b,1} + n_3A_{3,1}]N_1, \tag{4a}$$

$$dn_{2a}/dt = -n_{2a}/T_{2a} - n_{2a}A_{2a,1}N_1 + n_1A_{1,2a}N_2, \tag{4b}$$

$$dn_{2b}/dt = -n_{2b}/T_{2b} - n_{2b}A_{2b,1}N_1 + n_1A_{1,2b}N_2, \tag{4c}$$

$$dn_3/dt = -n_3/T_3 - n_3A_{3,1}N_1 + n_1A_{1,3}N_3. \tag{4d}$$

In these equations the subscripts 1, 2, 3 refer to isotopes Hg^{198}, Hg^{199}, and Hg^{200}; in the case of Hg^{199} the additional subscripts a and b are used to specify the two excited states of angular momentum $\frac{1}{2}$ and $\frac{3}{2}$, respectively. Terms of the form $-n_i/T_i$ describe the radiative decay of the ith excited state,[7] with time constants T_i characteristic of the isolated lines. Terms of the type $n_iA_{i,j}N_j$ represent the transfer of excitation from the ith to the jth excited state; each "transfer coefficient" $A_{i,j}$ is the gas-kinetic average of the cross section $Q_{i,j}$ for the process multiplied by the relative velocity of the colliding atoms.

Equations (4) are actually a simplified version of the more exact formulation which is given in the appendix of this paper. The simplification is twofold. Firstly, the radiative decay is not a straightforward emission process, as implied by the terms $-n_i/T_i$, but actually involves transport of radiation between different parts of the enclosure. Secondly, all excitation transfers among the isotopic impurities have been ignored; the collision terms in Eqs. (4) represent transfers either to or from Hg^{198}. The applicability of these simplifications to our problem is also discussed in the appendix.

Before solving Eqs. (4) we take advantage of the principle of detailed balancing to establish relationships between the different $A_{i,j}$. We consider the situation in which the enclosure is surrounded by perfectly reflecting walls. In this case both dn_i/dt and n_i/T_i are zero in

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[6] For these lines, the values of k_0 to be inserted in (1) are smaller than (2′) by factors of 50 to 1000.

[7] The subscripts i and j are here used primarily to enumerate the excited states, i.e., they take on the values 1, $2a$, $2b$, and 3. In the case of the isotopic densities N_i of normal atoms, however, the distinction between the notations $2a$ and $2b$ is meaningless; in this case, then, i and j assume the values 1, 2, and 3, which enumerate the isotopes.

Eqs. (4) and one obtains from (4b), (4c), (4d)

$$\begin{aligned} n_{2a}/n_1 &= (N_2/N_1)(A_{1,2a}/A_{2a,1}), \\ n_{2b}/n_1 &= (N_2/N_1)(A_{1,2b}/A_{2b,1}), \\ n_3/n_1 &= (N_3/N_1(A_{1,3}/A_{3,1}). \end{aligned} \tag{5}$$

On the other hand, we have from general statistical considerations a kind of local thermodynamic equilibrium involving the ratios of the densities of the different excited states such that

$$\begin{aligned} n_1/N_1 &= Cw_1e^{-\epsilon_1/k\theta}, \quad n_{2a}/N_2 = Cw_{2a}e^{-\epsilon_{2a}/k\theta}, \\ n_{2b}/N_2 &= Cw_{2b}e^{-\epsilon_{2b}/k\theta}, \quad n_3/N_3 = Cw_3e^{-\epsilon_3/k\theta}. \end{aligned} \tag{6}$$

Here ϵ_i is the energy of the ith excited state and w_i its statistical weight relative to the ground state of the isotope involved. In the case at hand $w_1=w_3=3$, $w_{2a}=1$, and $w_{2b}=2$. Finally, C is a constant which, in the absence of complete thermodynamic equilibrium, is not determined.

Comparing Eqs. (5) and (6) and noting that, in the case at hand, $|\epsilon_i-\epsilon_j|\sim 10^{-4}$ ev$\ll k\theta$, we obtain

$$A_{1,2a}=\tfrac{1}{3}A_{2a,1}, \quad A_{1,2b}=\tfrac{2}{3}A_{2b,1}, \quad A_{1,3}=A_{3,1}. \tag{7}$$

The solution of Eqs. (4) is achieved by the standard technique of substituting $n_i=c_ie^{-t/T}$, where the c_i and T are constants to be determined. Elimination of the c_i then yields an algebraic equation of the fourth degree in T. The roots, T_α, of this equation characterize the "decay modes" of the n_i in the sense that each n_i, in general, can be written as a superposition of exponential decay terms e^{-t/T_α}. As pointed out in the text preceding Eqs. (4), the experimental observations refer to the terminal portion of the decay curve, for which the largest T_α is alone significant. For the case at hand, where N_2, $N_3\ll N_1$, the largest T_α (which we henceforth denote simply as T), may be approximated sufficiently accurately by the expression[8]

$$\frac{1}{T}=\frac{1}{T_1}+\frac{\frac{1}{3}(N_2/N_1)}{T_{2a}+1/(A_{2a,1}N_1)}+\frac{\frac{2}{3}(N_2/N_1)}{T_{2b}+1/(A_{2b,1}N_1)}+\frac{(N_3/N_1)}{T_3+1/(A_{3,1}N_1)}. \tag{8}$$

For low vapor densities such that $T_{2a}\ll 1/(A_{2a,1}N_1)$, $T_{2b}\ll 1/(A_{2b,1}N_1)$, and $T_3\ll 1/(A_{3,1}N_1)$, (8) reduces to a relation which with the use of (7) can be written as

$$1/T\cong 1/T_1+(A_{1,2a}+A_{1,2b})N_2+A_{1,3}N_3. \tag{8$'$}$$

In this case the isotopic impurities act essentially as quenching agents; whatever excitation is transferred to them is for the most part radiated from the enclosure and hence constitutes a net loss.

At the other extreme of high densities such that

$$T_{2a}\gg 1/(A_{2a,1}N_1), \quad T_{2b}\gg 1/(A_{2b,1}N_1),$$

and $T_3\gg 1/(A_{3,1}N_1)$, we obtain

$$\frac{1}{T}\cong\frac{1}{T_1}+\frac{\frac{1}{3}(N_2/N_1)}{T_{2a}}+\frac{\frac{2}{3}(N_2/N_1)}{T_{2b}}+\frac{N_3/N_1}{T_3}. \tag{8$''$}$$

In this limit the predominance of the collision terms in Eqs. (4) gives rise to a thermodynamic equilibrium of the same type as described by (5) or (6). The right-hand side of (8″) may then be regarded as a weighted average of the decay rates, $1/T_i$, of the different excited states, each weighting factor being equal to the equilibrium fraction of excited atoms occupying the state in question.[8]

The first numerical calculations of T, based on (8) were carried out under the assumption that the 0.1 percent Hg^{200} impurity could be neglected. Results were obtained for various values of $A_{2b,1}$ and for different ratios[9] of $A_{2a,1}$ to $A_{2b,1}$; unity and $\frac{1}{3}$; they are represented by the light-dashed curves of Figs. 1(I) and 1(II), respectively. The behavior of these curves in the limits of high and low vapor density, in accordance with the remarks of the preceding paragraphs, is to be noted.

More recent computations have taken into account two refinements. Firstly, it was found that the presence of Hg^{200}, even in the small concentration of 0.1 percent, could not be ignored at densities (of the main isotope) $\sim 10^{15}$/cc. A second complication which manifests itself at high densities is the incipient effect of pressure broadening. Relegating the detailed calculation of this effect to the appendix (Sec. 4), we here write down the result. Namely, one adds to (8) the term

$$\Delta_p\equiv 1.01\times 10^{-10}\, N/(\theta \log k_0R)^{\frac{1}{2}}\ \mathrm{sec}^{-1}. \tag{9}$$

The results obtained by the inclusion of these refinements are shown in Figs. 1(I) and 1(II) as solid curves for the cases of $A_{2a,1}/A_{2b,1}=1$ and $\frac{1}{3}$, respectively. The computations were performed only for vapor densities less than 10^{15}/cc; it was found by sample calculations that, for $N_1>10^{15}$/cc, the complicating effects of the overlap of the different hyperfine components rapidly become important. The limited results presented here, nevertheless, provide at least a qualitative understanding of the high density deviation of the experimental points from the simple theory as represented by the light-dashed curves.

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[8] A simple way of deriving (8) is to assume that $T\gg T_{2a}$, T_{2b}, T_3. One may then take the left-hand sides of (4b), (4c), and (4d) equal to zero, thereby obtaining the appendix Eqs. (15A) for the ratios $n_{i\neq 1}/n_1$. Inserting the latter into (4a) and employing (7), we immediately arrive at (8). The assumption that $T\gg T_{i\neq 1}$ can then easily be justified *a posteriori* for the case of $N_{i\neq 1}/N_1\ll 1$ by inspection of (8″), which provides a lower limit for T.

[9] From the considerations of Sec. 5 of the appendix, the relative magnitudes of $A_{2a,1}$ and $A_{2b,1}$ are seen to depend upon the energy differences $|\epsilon_{2a}-\epsilon_1|$, and $|\epsilon_{2b}-\epsilon_1|$ of the excited levels involved in the excitation transfer. These are given in Table I of that section in wave-number units. Since $|\epsilon_{2a}-\epsilon_1|>|\epsilon_{2b}-\epsilon_1|$, the qualitative indication, based in Eq. (24A), is that $A_{2a,1}<A_{2b,1}$. Hence, the assumption $A_{2a,1}/A_{2b,1}=1$ doubtlessly represents an upper limit for the ratio. The other choice, namely $\frac{1}{3}$, appears to us, on the basis of Eq. (24A) and Table I, to be a reasonable lower limit.

Before proceeding further with the comparison of theory with experiment, we must point out that in the intermediate region of vapor densities ($\sim 5\times 10^{14}$/cc), for which $T_{2a}\sim 1/A_{2a,1}N_1$ and $T_{2b}\sim 1/A_{2b,1}$, the quantitative results are subject to some error. Namely, in this region it turns out that T_{2a} and T_{2b} are not much greater than the lifetime τ of the isolated atom; in other words, the lines of Hg^{199} are only moderately imprisoned. Unfortunately, our imprisonment formulas of the type of (1) are not quantitatively accurate for $T_i \lesssim 10\tau$. This inaccuracy is carried over, by virtue of (8), to the final values for T; some crude estimates indicate that the error thus incurred may be $\sim$20 percent. With decreasing vapor densities, the errors in the T_i increase; however, as shown by (8′), T becomes essentially independent of the T_i.

With these considerations in mind, we have not attempted a detailed comparison of experiment with theory; it is nevertheless apparent that one can make an order of magnitude estimate for $A_{2b,1}$ which will give the best fit with the experimental points. Thus

$$A_{2b,1}\sim 2\times 10^{-9}\ \mathrm{cm}^3/\mathrm{sec}. \tag{9}$$

This estimate is not radically affected by different assumptions as to the ratio $A_{2a,1}/A_{2b,1}$.

Further comparison indicates that of the two choices for $A_{2a,1}/A_{2b,1}$ analyzed here, namely unity and $\frac{1}{3}$, the latter provides somewhat the better agreement with experimental facts. However, in view of the above remarks on the errors in the quantitative theory, we do not regard this indication as conclusive.

The order of magnitude of the transfer coefficient, as given by (9), deserves some comment. If we divide (9) by the mean relative velocity ($\sim 2\times 10^4$ cm/sec), we obtain an effective cross section,

$$Q\sim 10^{-13}\ \mathrm{cm}^2, \tag{10}$$

which is some 20 to 30 times the gas-kinetic cross section (depending on the definition of the latter quantity). Actually, this result is not too surprising; in fact, cross sections for transfer of excitation can exceed gas-kinetic cross sections, especially when the energy levels of the colliding atoms are nearly coincident, as is the case with different isotopes of the same element.

An upper limit to $A_{2b,1}$ can be estimated by considering the transfer of excitation between identical atoms. For this case of exact resonance, the approximate theory presented in a paper by Furssov and Vlassov[10] may be employed. The calculation which is carried out in the appendix, Sec. V, yields the result

$$A_{2b,1}\sim 3.4\times 10^{-9}\ \mathrm{cm}^3/\mathrm{sec}, \tag{11}$$

which is in good order-of-magnitude agreement with (9).

There remains the question as to the effect of the energy-level discrepancy between Hg^{198} and Hg^{199}. The estimation of this effect, on the basis of a simplified theory of transfer of excitation, is also presented in Sec. V of the appendix; the conclusion therein reached is that the level discrepancy is too small to cause any order-of-magnitude diminution of $A_{2b,1}$ from the resonance value given in (11).

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APPENDIX

I. Formulation of the Decay Problem in Terms of Integro-Differential Equations

In this section, we seek a formulation which takes into account not only the collision-induced transfer of excitation in a given volume element (which is presented explicitly in Eqs. (4) of the text) but also the radiative transport of excitation between different volume elements of the enclosure. This goal is achieved by a straightforward generalization of the integro-differential Eq. (3.4) of reference 1,

$$\tau\partial n(\mathbf{r})/\partial t=-n(\mathbf{r})+\int n(\mathbf{r}')G(\mathbf{r}',\mathbf{r})d\mathbf{r}', \tag{1A}$$

which describes the radiative transport of excitation for the case of a simple resonance state without hyperfine structure. In this equation the key quantity determining the time variation of the density of excited atoms, $n(\mathbf{r})$, is the kernel, $G(\mathbf{r}',\mathbf{r})$, of the integral term; it is defined as the probability that a resonance quantum emitted at $\mathbf{r}'$ is captured in a unit volume element centered at $\mathbf{r}$.

The required generalization to the case of present interest reads

$$\tau\partial n_i(\mathbf{r})/\partial t=-n_i(\mathbf{r})+\int n_i(\mathbf{r})G_i(\mathbf{r}',\mathbf{r})d\mathbf{r}' \\ +\tau\textstyle\sum_j\left[A_{j,i}N_in_j(\mathbf{r})-A_{i,j}N_jn_i(\mathbf{r})\right], \tag{2A}$$

where the subscripts i and j each take on the values 1, $2a$, $2b$, and 3. In these equations, the $G_i(\mathbf{r}',\mathbf{r})$ characterize the radiative transport for the different excited states. The relationship of Eqs. (2A) to Eqs. (4) of the text is treated in the following section.

II. Variational Treatment of the Basic Integro-Differential Transport Equations (2A)

For the purposes of the present paper we are interested in steady-state solutions, $n_i(\mathbf{r},t)=n_i(\mathbf{r})e^{-t/T}$, of (2A). For this case (2A) reduces to

$$-\tau n_i(\mathbf{r})/T=-n_i(\mathbf{r})+\int n_i(\mathbf{r}')G_i(\mathbf{r}',\mathbf{r})d\mathbf{r}' \\ +\tau\textstyle\sum_j\left[A_{j,i}N_in_j(\mathbf{r})-A_{i,j}N_jn_i(\mathbf{r})\right]. \tag{3A}$$

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[10] W. Furssov and A. Vlassov, Physik. Z. Sowjetunion 10, 378 (1936).

Now, by virtue of the text Eqs. (7), which are readily generalized to[11]

$$A_{i,j}=a_{ij}w_i, \tag{4A}$$

where

$$a_{ij}=a_{ji}, \tag{5A}$$

and, introducing the notation

$$F_i\equiv N_i w_i, \tag{6A}$$

we are able to establish the equivalence of (3A) to the following variational problem

$$\frac{\tau}{T}=1-\frac{\sum_i F_i^{-1}\int\int n_i(\mathbf{r}')G_i(\mathbf{r}',\mathbf{r})n_i(\mathbf{r})d\mathbf{r}d\mathbf{r}'}{\sum_i F_i^{-1}\int n_i^2(\mathbf{r})d\mathbf{r}}+\tau\sum_{ij}a_{ij}\frac{F_jF_i^{-1}\int n_i^2(\mathbf{r})d\mathbf{r}-\int n_i(\mathbf{r})n_j(\mathbf{r})d\mathbf{r}}{\sum_i F_i^{-1}\int n_i^2(\mathbf{r})d\mathbf{r}}; \tag{7A}$$

$$\delta(1/T)=0, \tag{8A}$$

as is easily verified.

The positive-definiteness of $1/T$ can be demonstrated by a procedure analogous to that used in reference 1, p. 1217. Namely, we can write (7A) in the alternate form

$$\frac{\tau}{T}=\frac{\sum_i F_i^{-1}\left[\int n_i^2(\mathbf{r})E_i(\mathbf{r})d\mathbf{r}+\frac{1}{2}\int\int[n_i(\mathbf{r})-n_i(\mathbf{r}')]^2G(\mathbf{r},\mathbf{r}')d\mathbf{r}d\mathbf{r}'\right]}{\sum_i F_i^{-1}\int n_i^2(\mathbf{r})d\mathbf{r}}+\tfrac{1}{2}\sum_{ij}\tau A_{ij}\frac{\int[F_j^{\frac{1}{2}}F_i^{-\frac{1}{2}}n_i(\mathbf{r})-F^{\frac{1}{2}}F^{-\frac{1}{2}}n_j(\mathbf{r})]^2d\mathbf{r}}{\sum_i F_i^{-1}\int n_i^2(\mathbf{r})d\mathbf{r}}, \tag{9A}$$

where

$$E_i(\mathbf{r})=1-\int G_i(\mathbf{r},\mathbf{r}')d\mathbf{r}'. \tag{10A}$$

In (9A) all the integrals are positive definite. The eigenvalues of $1/T$ can thus be arranged in a series of ascending positive numbers; the lowest of these, which is the one of interest to us, is an absolute minimum. Use of the Ritz variational procedure will therefore provide for $1/T$ an upper limit which will converge toward the true value as the number of adjustable parameters in the assumed functional forms for the $n_i(\mathbf{r})$ is increased.

We now choose

$$n_i(\mathbf{r})=n_i f(\mathbf{r}), \tag{11A}$$

when n_i denotes the value of $n_i(\mathbf{r})$ at a convenient reference point in the enclosure. In the case of infinite cylinders we assume a parabolic form for $f(\mathbf{r})$:

$$f(\mathbf{r})=1-\rho^2/R^2, \tag{12A}$$

where ρ is the distance of the point $\mathbf{r}$ from the cylindrical axis; the reference point is, then, any point on the cylindrical axis.

Inserting (11A) into (9A), we obtain

$$\frac{1}{T}=\frac{\sum_i F_i^{-1}n_i^2/T_i}{\sum_i F_i^{-1}n_i^2}+\frac{1}{2}\frac{\sum_{ij}A_{ij}[F_j^{\frac{1}{2}}F_i^{-\frac{1}{2}}n_i-F_i^{\frac{1}{2}}F_j^{-\frac{1}{2}}n_j]^2}{\sum n_i^2F_i^{-1}}, \tag{13A}$$

where

$$\frac{1}{T_i}=\frac{1}{\tau}\frac{\int f^2(\mathbf{r})E_i(\mathbf{r})d\mathbf{r}+\frac{1}{2}\int\int[f(\mathbf{r})-f(\mathbf{r}')]^2G_i(\mathbf{r},\mathbf{r}')d\mathbf{r}d\mathbf{r}'}{\int f^2(\mathbf{r})d\mathbf{r}},$$

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[11] w_i is the ratio of the statistical weight of the *i*th state divided by the statistical weight of the ground state, as employed in Eqs. (6) and subsequent text.

$1/T_i$ is actually the variational expression for the decay rate of an isolated line, as shown by comparison with Eq. (3.10) of reference 1.

An absolute minimum for (13A) is achieved by differentiation with respect to the n_i. The resulting equations are

$$n_i/T=n_i/\tau+\sum_j A_{ij}(F_jn_i-F_in_j), \tag{14A}$$

which, with the aid of (4A) and (6A), are seen to be just the equations one obtains by substituting the steady-state solutions

$$n_i(i)=n_i(0)e^{-t/T}$$

into Eqs. (4). In other words, our text procedure based on Eqs. (4) provides a variational approximation for $1/T$.

There remains the question as to how accurate a value of $1/T$ is obtained variationally by use of the $n_i(\mathbf{r})$ defined by (11A) and (12A). In this connection it should be pointed out that (a) the presence of the collision terms in (3A) or (7A) tends to equalize the spatial forms of the different $n_i(\mathbf{r})$; if, in particular, one passes to the high-density limit, where the collision terms dominate, the $n_i(\mathbf{r})$ bear constant ratios to each other [as given by the text Eqs. (5)] independent of position. (b) In the case of a single resonance state whose radiation is strongly imprisoned, reference 1 has shown that the assumption of a parabolic form for the density function yields a sufficiently accurate value for the decay time; in fact, Eq. (1) was derived[5] on this basis. (c) In the case of a weakly-imprisoned line, for which the parabolic function does not give good results, computational errors may be quite appreciable. These errors arise from the use of approximations, at various stages of the calculation, which are only asymptotically valid for the case of large optical opacities ($k_0R\gg1$). It is these errors, in fact, which, as remarked in the second paragraph after Eq. (9), prevent us from achieving quantitative accuracy at intermediate vapor densities $\sim5\times10^{14}$/cc. Refinements in the variational treatment will not improve the situation unless they are accompanied by a reduction of the computational errors; this undertaking, however, promises to be exceedingly difficult and tedious.

III. Neglect of Collision Terms $A_{i,j}N_iN_j$, Where Neither i Nor j Are Equal to 1

In our treatment these terms are neglected relative to the terms $A_{i,1}n_1N_j$ and $A_{1,j}n_1N_j$; the reason is simply that both $N_{i\neq1}/N_1\ll1$ and $n_{i\neq1}/n_1\ll1$. The first inequality is valid "by construction," i.e., by virtue of the isotopic constitution of our samples. To demonstrate the validity of the second inequality, we observe the following: (a) In the limit of large vapor densities, where the collision terms become dominant, the ratios $n_{i\neq1}/n_1$ are given by the text relations (6) which, apart from the weight factors and Boltzmann exponentials, are equal to the ratios $N_{i\neq1}/N_1$, and are hence $\ll1$. (b) In obtaining the approximate solution (8) of Eqs. (4) according to the prescription of reference 8, we find

$$n_{i\neq1}/n_1=A_{i,1}N_1/(1/T_i+A_{i,1}N_1), \tag{15A}$$

which is even less than the high density limit as given by (6). Thus, in this case the inequality is *a fortiori* valid.

IV. Pressure-Broadening Effects

The initial manifestation of pressure broadening, with which we are alone concerned, have been treated in reference 1, pp. 1223–1224. In our case, we consider only the broadening of the Hg^{198} component and ignore the absorption of this line arising from the other hyperfine components. The effect of pressure broadening may then be represented quite simply by adding to the right-hand side of (8) the term

$$\Delta_p=2a_p/\pi(\log k_0R)^{\frac{1}{2}}\tau; \tag{16A}$$

(16A) is derived in much the same way as Eq. (5.14) of reference 1, which describes the effect of natural broadening in plane-parallel enclosures. The correspondence between the two expressions arises from the assumption that the pressure-broadened line shape is of the dispersion type $\sim[\frac{1}{4}\gamma_p{}^2+(\omega-\omega_0)^2]^{-1}$, which differs from the shape of the naturally broadened line, $\sim[\frac{1}{4}\tau^2+(\omega-\omega_0)^2]^{-1}$ only in the line width constant. The main differences between (16A) and (5.14) are (a) in the logarithmic factors, which are characteristic of enclosure geometries and (b) the replacement of the factor $a_N=(\lambda_0/4\pi)\tau(2R\theta/M)^{\frac{1}{2}}$ by $a_p=a_N\tau\gamma_p$; the absence of the factor $1/\tau$ from (5.14) is due to the circumstance that the time unit is there taken to be the natural lifetime of the isolated atom.

For γ_p we take the theoretical result of Furssov and Vlassov,[10] which, as shown in reference 1, p. 1224, may be written as

$$\gamma_p\tau=N\lambda_0{}^3/2\pi^2=0.83\times10^{-15}N. \tag{17A}$$

Combining (16A), (17A), and the expressions for a_p and a_N given above, and inserting numerical values, we obtain the text expression (9) for Δ_p.

V. Transfer of Excitation between Atoms

For the case of transfer of excitation between two identical atoms an approximate expression for the cross section may be derived from the results of Furssov and Vlassov.[10] These authors treated the case in which the atomic ground and excited states involved in the collision are S and P states. The expression which they obtain for the probability of excitation transfer in a binary encounter (Eq. 28 of their paper) may be written as

$$P(\rho)=\tfrac{2}{3}e^4f^2/m^2\omega_0{}^2\rho^4v^2. \tag{18A}$$

Here, $P(\rho)$ (in the notation of Furssov and Vlassov, $\Delta|a|^2/|a|^2$) is a function of impact parameter ρ, the frequency ω_0 associated with an optical transition from the excited level to the ground state—in our case the frequency of the resonance line—the oscillator strength f of the line, the relative velocity v of the colliding atoms and fundamental constants; the numerical factor, $\frac{2}{3}$, present in our version comes from the averaging of the quantity $\sin^2\gamma_1$ occurring in the original equation.

Equation (18A) holds only for ρ large enough so that $P(\rho)\ll 1$. We shall nevertheless apply it up to that impact parameter, ρ_1, such that $P(\rho_1)=\frac{1}{2}$. For $\rho<\rho_1$, $P(\rho)$ oscillates between zero and unity; we assume that its effective value is $\frac{1}{2}$. With these simplifications, the cross section for excitation transfer becomes

$$Q=\tfrac{1}{2}\pi\rho_1^2+2\pi\int_{\rho 1}^{\infty}P(\rho)\rho d\rho,$$

which is readily evaluated. The result is

$$Q=\pi\rho_1^2=(4/3)^{\frac{1}{2}}\pi e^2 f/mv\omega, \tag{19A}$$

or

$$A=Qv=(4/3)^{\frac{1}{2}}\pi e^2 f/m\omega,$$

which, by virtue of a well-known relationship[12] between f and the radiative lifetime of the excited state τ, may be written as

$$A=\sqrt{3}\lambda_0^3/8\pi^2\tau, \tag{20A}$$

where λ_0 is the wavelength of the atomic resonance line. Substituting appropriate numerical values, we find

$$A=3.4\times10^{-9}\ \text{cm}^3/\text{sec},$$

as quoted in the text.

The foregoing considerations apply only to collisions between identical atoms. In the case of interest, however, we have to do with excitation exchange between different isotopes, and have therefore to take into account the effect of the energy level discrepancy of the colliding atoms. This problem has been investigated by Stückelberg[13] and, more recently, by Dr. Bernstein and one of the present authors (T.H.).[14] Both treatments employed a simplified model in which the excited and ground atomic states were assumed nondegenerate; the interaction responsible for excitation transfer was taken to be of the form K/R^3, suggestive of dipole-dipole coupling. It was found that the dependence of Q on the energy discrepancy ΔE between the excited states of the two colliding atoms is characterized by the parameter,

$$\delta=(\Delta E/\hbar)(R_c/v), \tag{21A}$$

where R_c, a "critical radius," is given by the formula

$$R_c=(2K/\Delta E)^{\frac{1}{3}}. \tag{22A}$$

TABLE I. Values of the parameter δ.

$\lvert\mu\rvert$	1	2
$\delta_{1,\,2a}$	0.85	1.07
$\delta_{1,\,2b}$	0.58	0.72

In our treatment of the problem the following results were obtained:

(a) for $\delta\ll 1$

$$Q=(\pi^2K/\hbar v)[1-(2\delta^3/\pi)(\log^2(\delta^3/2)+0.705\log(\delta^3/2)+48)], \tag{23A}$$

(b) for $\delta\ll 1$

$$Q=\pi^2K/\hbar v(3.2/\delta^2)e^{-1.12\delta}. \tag{24A}$$

These results, while qualitatively similar to those of Stückelberg, differ in quantitative detail.

One may conclude that in the region $\delta\simeq 1$ the order of magnitude of Q is that of the resonance value, π^2K/hv. On the other hand, for $\delta>2$, Q lies appreciably below the resonance value and diminishes rapidly with increasing δ.

The difficulty in applying these results to the transfer of excitation between Hg isotopes (as well as to any other actual transfer problem) is that either the excited or ground states are degenerate. One of the consequences of this degeneracy is that the magnitude of the dipole-dipole coupling term is not constant, but depends upon the component of electronic angular momentum Ω parallel to the axis of figure. For example, if the two colliding atoms both possess ground and excited states with angular momenta zero and unity, respectively, the dipole-dipole interaction constant K is given by the expression[15]

$$K=\mu e^2 f\hbar/2m\omega_0, \tag{25A}$$

where $\mu=1$ or -2 for $\Omega=\pm 1$ or zero.

Despite this ambiguity, the theory should still be capable of yielding an order-of-magnitude estimate of the energy-discrepancy effect. We limit ourselves to the aforementioned case of angular momenta zero and unity for atomic ground and excited states; while this situation is not the one encountered in our most important reaction—excitation transfer between Hg^{198} and Hg^{199}—we believe that it is sufficiently illustrative for order-of-magnitude considerations.

Inserting (25A) into (21A), and utilizing the above-quoted[12] relation between f and τ, we obtain

$$\delta=(c/2v)\lambda_0(3\mu/\pi c\tau)^{\frac{1}{3}}(\Delta\bar{\nu})^{\frac{2}{3}}, \tag{26A}$$

where λ_0 is the wavelength of the composite resonance line, $\Delta\bar{\nu}$ is the wave-number discrepancy corresponding to the energy difference of the excited levels of the colliding atoms, and c the velocity of light. For Hg,

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[12] Reference 1, equation subsequent to (5.17). The right-hand side of this equation is incorrect; it should contain an extra factor of π in the numerator.

[13] E. G. G. Stückelberg, Helv. Phys. Acta **5**, 369 (1933).

[14] T. Holstein and I. B. Bernstein, Phys. Rev. **83**, 201 (1951); Bulletin of the Conference on Gaseous Electronics, November 3–5 (1949), paper D3.

[15] H. Margenau and W. W. Watson, Revs. Modern Phys. **8**, 22 (1936), Sec. 5, Eq. (1).

taking $v=2\times 10^4$ cm/sec, we obtain

$$\delta=2.8\mu^{\frac{1}{3}}(\Delta\bar{\nu})^{\frac{2}{3}}. \tag{27A}$$

Now the relevant wave-number separations in our case are (in the subscript notation of the excited states employed in the text)

$$\begin{aligned}\Delta\bar{\nu}_{1,\,2a}&=0.47\ \text{cm}^{-1},\\ \Delta\bar{\nu}_{1,\,2b}&=0.26\ \text{cm}^{-1}.\end{aligned} \tag{28A}$$

The values of the δ's corresponding to (28A) and to the two different values of $|\mu|$ are given in Table I.

From these numbers and from the remarks subsequent to Eq. (25A) we arrive at the conclusion stated in the text subsequent to Eq. (11); namely, the energy-level discrepancy is too small to cause any order-of-magnitude diminution of the cross section from its resonance value.

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The Response of Anthracene Scintillation Crystals to High Energy μ-Mesons*,†

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The response of an anthracene scintillation counter to high energy charged particles which lose only a small fraction of their energy in traversing the crystal was determined, using μ-mesons in the cosmic radiation at sea level with energies from 29 Mev to greater than 1 Bev. The light output was found to have a sizeable fluctuation for mesons of the same initial energy, due to ionization loss straggling. The scintillation efficiency of the phosphor was found to decrease for increasing specific ionization, in agreement with the work of others on electrons and protons. The response of the crystal showed no rise within 2 percent for relativistic meson energies, which agrees with calculations of the density effect reduction in ionization loss for anthracene.

THE light output of scintillation crystals has been shown to be approximately proportional to the total ionization energy loss for low energy particles which spend their entire range in the crystal.[1] Such proportionality between energy loss and light output would also be expected to be true for high energy charged particles which pass completely through the crystal and lose only a small fraction of their total energy by ionization in the crystal. It was the purpose of this work to find the light output of an anthracene crystal as a function of the energy of the traversing particle. Anthracene was used for this investigation because it has the largest light output of the known organic phosphors. μ-mesons from the cosmic radiation at sea level provided a good source of particles for such an experiment, because a wide range of energies is available and absorption by radiation losses and by nuclear collisions is negligibly small. The results which would be found for other charged particles should be the same as for μ-mesons, except for a simple change of scale.

I. THEORY

For the case of a charged particle traversing a thin absorber, a large fluctuation in the ionization energy loss is to be expected. This "straggling" has been calculated by Williams[2] and, later, more accurately by Landau[3] and Symon.[4] The straggling is essentially caused by the fact that large energy transfers to single electrons can occasionally occur. These electrons, which are seen as "δ-rays" in nuclear emulsions or as "knock-on electrons" in cosmic-ray work, lose their energy in the crystal in most cases; hence, the light output is increased. For high energy particles, where

$$W\gg\xi, \tag{1}$$

with

$$\begin{aligned}W&\cong 2mc^2\beta^2/(1-\beta^2)\ \text{(mesons and protons)},\\ \xi&=2\pi ne^4x/mc^2\beta^2,\end{aligned} \tag{2}$$

the energy loss distribution approaches a form which can be expressed in terms of a universal function. Here n is the electron density, m is the electron mass, e is the electronic charge, c is the velocity of light, β is v/c for the incident particle, and x is the absorber thickness in cm. W is the maximum energy loss possible in a single collision, and ξ is a parameter with the dimensions of energy which is a measure of the thickness of the absorber. If the probability of an energy loss between ϵ and $\epsilon+d\epsilon$ is $P(\xi,\epsilon)d\epsilon$ in an absorber with a thickness parameter ξ, then it was shown by Landau[5] that

$$P(\xi,\epsilon)=\frac{1}{\xi}\phi\left(\frac{\epsilon-\epsilon_{\text{prob}}(\xi)}{\xi}\right). \tag{3}$$

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[1] W. H. Jordan and P. R. Bell, Nucleonics 5, 30 (1949); R. Hofstadter and J. McIntyre, Nucleonics 7, 32 (1950); R. W. Pringle, Nature 166, 11 (1950); and S. A. E. Johansson, Ark. Fys. 2, 171 (1950).

[2] E. J. Williams, Proc. Roy. Soc. (London) 125, 420 (1929).

[3] L. Landau, J. Phys. (U.S.S.R.) 8, 201 (1944).

[4] K. R. Symon, Harvard University thesis (1948).

[5] See reference 3, Eq. (18).