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Level-Crossing Spectroscopy in 7 $^2S_{1/2}$ Thallium. II. Theory of Self-Broadening and Tl*-Tl–Foreign-Gas Collisions

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The experimental results for the self-broadening of pure Tl of the previous paper are shown to be in good agreement with the theory of resonant collisions, taking into account the effects of the hyperfine structure. Wall collisions are nearly negligible in that case. The decrease of the self-broadening observed with the addition of a foreign gas is explained in terms of three-body collisions (Tl-He collisions occurring during a Tl*-Tl collision) which broaden the optical transitions of Tl and decrease the resonance effect in the transfer of excitation between Tl atoms. The quantitative agreement obtained with the experimental results shows that these three-body collisions must be responsible for the major part of the observed reduction in self-broadening.

I. INTRODUCTION

In the previous paper[1] on zero-field level crossing in atomic thallium (Hanle effect) several observations were made. Among these were (a) the resonance-broadening cross section for thallium-thallium excitation-transfer collisions and (b) the fact that in the presence of a foreign gas, either helium or argon, the resonance-broadening cross section was reduced. In the first case, agreement with theory was less than expected and in the second case there existed no suitable theoretical description. It is the purpose of this paper to present a theoretical explanation of these two effects.

The theories of D'Yakonov and Perel',[2] Byron and Foley,[3] Omont and Meunier,[4] Kazantsev,[5] and Berman and Lamb[6] on resonance-broadening line shapes are based on several assumptions among which are (i) a spherical geometry of the radiating atoms, (ii) a large hyperfine separation so that the hfs levels may be treated independently, (iii) transitions having angular momenta $J=0$, 1, and (iv) binary collisions. Some of these assumptions are relaxed for the special case of the $7\,^2S_{1/2}$ state of thallium. The resonance-broadening cross section for Tl*-Tl excitation transfer is calculated and found to be in good agreement with experiment. With the reasonable physical model for three-body collisions that assumes that during a Tl*-Tl collision there is a large probability that at least one He-Tl collision takes place, it is found that a reduction in the resonance-broadening cross section occurs. This reduction in the probability of the excitation-transfer process occurs because of a broadening of the thallium-atom levels, due to helium-thallium collisions, and a concomitant loss of resonance between the energy of the initial state and the final state where the excitation has been transferred.

In Sec. II we discuss the self-broadening of pure-thallium atoms in the level-crossing experiment; and in Sec. III we present a study of the relaxation of thallium atoms caused by resonant collisions in the presence of a foreign gas. Section IV contains discussion and conclusions.

II. SELF-BROADENING OF PURE THALLIUM

A. Resonant Collisions

Relaxation rates caused by resonant collisions between an excited state with $J_e=1$ and a ground state having $J_g=0$ have been calculated by several authors.[2-6] For transitions with $J_e=\frac{1}{2}$ and $J_g=\frac{1}{2}$ the same calculations have been performed by Stacey and Cooper.[7] In their case the S matrix can be expressed in terms of the S matrix elements for a $J_e=1$, $J_g=0$ transition and the final results written in the form

$$g^\alpha = 10^{-2} C^\alpha N \lambda^3 \Gamma B \, , \tag{1}$$

where N is the atomic density, λ is the wavelength of the transition, $1/\Gamma$ is the lifetime of the upper level, and B is the total branching ratio from the upper level to the lower level. g^α denotes the relaxation rate of the observable α and C^α is a constant. For a $J=\frac{1}{2}$ level the only observables are the total population and the orientation (magnetic dipole). The relaxation rate of the total orientation of the vapor is (in the notation of Ref. 4)

$$g^1 = g^1(1+2) = g^1(1) + g^1(2)$$

for observation, after the collision, of atom 1 initially excited and atom 2 initially unexcited. The corresponding values for C^α are[7]

$$C^0 = 1.06, \quad C^1 = 1.91 \, . \tag{2}$$

To evaluate the effect of the hyperfine structure in the 3776-Å line in atomic thallium (see Fig. 1), one may consider two possibilities. The first is the ideal case of a nuclear spin with $I=\frac{1}{2}$ and a small hfs such that all hyperfine shifts satisfy $\Delta E_{hf} \ll \hbar/T_c$, where T_c is the mean duration of a Tl*-Tl collision. The hyperfine coupling is thus negligible during a collision, but large compared to the natural width Γ. The second possibility is the opposite hypothesis, $\Delta E_{hf} \gg \hbar/T_c$.

We may, in this first approximation, compute the relaxation rate of the orientation, g^1_{11}, of the $F=1$ excited state using the classical procedure (see Ref. 4). This is done by writing the density matrix in a basis in which the electronic and nuclear angular momenta $\vec{J}$ and $\vec{I}$ are uncoupled, computing the mean effect of a collision on the electronic part, assuming that the nuclear part is unaffected, and going back to the representation where $\vec{I}$ and $\vec{J}$ are coupled. In the present case, since the values of the angular momenta are small, it is simpler to write some elements of the density matrix and compute their evolution by an elementary procedure instead of using the general method with $9j$ Wigner coefficients. The result is

$$g^1_{11} = \tfrac{1}{2}(g^0 + g^1) \, . \tag{3}$$

In this case $\langle \vec{J} \rangle = \langle \vec{I} \rangle = \frac{1}{2} \langle \vec{F} \rangle$, and the electronic orientation $\langle \vec{J} \rangle$ relaxes with the rate g^1 and the nuclear orientation $\langle \vec{I} \rangle$ is destroyed at a rate g^0 when the excitation is transferred from atom 1 to atom 2. It is also assumed that the ground state is completely disoriented.

Equations (2) and (3) give

$$C^1_{11} = \tfrac{1}{2}(C^0 + C^1) = 1.485 \, . \tag{4}$$

For the 3776-Å line of thallium, with[1,8] $1/\Gamma = 7.55 \times 10^{-9}$ sec and $B=0.463$, the relaxation rate is

$$g^1_{11} = 4.90 \times 10^{-8} N \, . \tag{5}$$

This result is derived under the hypothesis that $\Delta E_{hf} T_c \ll \hbar$, where all the transitions $1F_1, 2F_2' \to 1F_1'$,

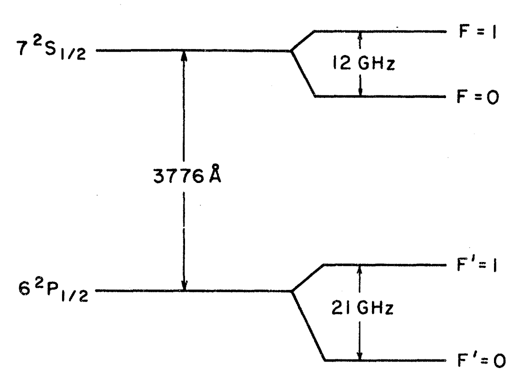

FIG. 1. Hyperfine structure of 3776-Å resonance line of thallium.

$2F_2$ are equally possible. If one takes as the definition of T_c

$$T_c = \bar{v}_{\mathrm{Tl-Tl}}^{-1}(\sigma/\pi)^{1/2} , \tag{6}$$

where[1] $\sigma = 1.2\times10^{-12}$ cm^2 and $T = 970\,^\circ$K, one has

$$T_c^{-1}/2\pi = 11.6 \text{ GHz} . \tag{7}$$

This frequency is not large compared to the hyperfine splittings of the various FF' transitions (Fig. 1). Accordingly, certain transitions $1F_1$, $2F_2' \to 1F_1'$, $2F_2$ will have a smaller probability and the value of Eq. (4) is probably too large.

To obtain a lower limit to g_{11}^1 we assume the second and opposite hypothesis, namely, $\Delta E_{\mathrm{hf}}\, T_c \gg \hbar$, where only the transition $1F_1$, $2F_2' \to 1F_2'$, $2F_1$ is allowed.[9] For this case,

$$g_{11}^1 = 10^{-2} N\lambda^3 \Gamma (\tfrac{1}{4}\,{}^{10}C^1 B_{10} + \tfrac{3}{4}\,{}^{11}C^1 B_{11}) , \tag{8}$$

where the partial branching ratios are[1,9] $B_{10} = \frac{1}{3}B$ and $B_{11} = \frac{2}{3}B$. ${}^{10}C^1$ is the constant for an isolated $F = 1 \leftrightarrow 0$ transition[2–6] and equals 3.44. There is no exact calculation for the constant ${}^{11}C^1$ for an isolated $F = 1 \leftrightarrow 1$ transition. It is a simple matter to compute this in the Anderson approximation[10] using a cutoff parameter for strong collisions which gives ${}^{11}C^1_{\mathrm{app}} = 2.28$ [Ref. 4(b), Eq. (1.146) and (1.138)] but the accuracy of this approximation is known to be poor. Nevertheless, using this result yields $C_{11}^1 = 1.43$ from Eq. (8). The difference between this value and the value in Eq. (4) is seen to be small.

Furthermore, ΔE_{hf} is not much larger than $\hbar T_c^{-1}$. A comparison between experimental results in the ${}^3P_1$ state of mercury[4(b),4(c)] and with theory[4(b),11] shows that the influence of ΔE is nearly negligible for $\Delta E = 12$ GHz, and small for $\Delta E = 21$ GHz. Since the influence of the situation in which $\Delta E = 31$ GHz is expected to be very small in the thallium case, it seems reasonable to think that the exact value of C_{11}^1 is not very different from 1.485 and perhaps a bit smaller. We shall adopt for the theoretical value

$$C_{11}^1 = 1.46 \pm 0.15 . \tag{9}$$

Taking into account the uncertainty in B and Γ this gives

$$g_{11}^1 = (4.80 \pm 0.80)\times 10^{-8} N . \tag{10}$$

B. Wall Collisions

For an $F = 1 \leftrightarrow 0$ transition the broadening of level-crossing curves by wall collisions of excited atoms has been discussed by Dodsworth, Gay, and Omont.[12] Under the experimental conditions of I, Eq. (20) of Ref. 12 would give an approximate broadening rate

$$\Gamma_{w_i} = \tfrac{1}{2}\Gamma_M \simeq 0.8\times10^{-2} N\lambda^3\Gamma , \tag{11}$$

which is generalized for a transition $i = F_i \to F_i'$ to

$$\Gamma_{w_i} = 0.8\times10^{-2} N_i \lambda^3 \Gamma B_i \, \frac{(2F_i+1)}{3(2F_i'+1)} , \tag{12}$$

where B_i is the branching ratio and N_i the number of atoms in the F_i' ground state.

In natural thallium, with isotopic concentrations $C_{203} = 0.295$ and $C_{205} = 0.705$, the Hanle signal comes from four different transitions: $F = 1 \leftrightarrow 0$ and $F = 1 \leftrightarrow 1$ of both isotopes. The contribution of each isotope to the signal depends upon the intensity emitted by the lamp in each set of transitions. Assuming an equal intensity in these four lines, we shall take for the broadening rate

$$\Gamma_{W\,T} = \sum p_i \Gamma_{W_i} , \tag{13}$$

where p_i is the relative contribution of the excitation by the ith transition to the Hanle signal ($\frac{1}{3}$ for each $F = 1 \leftrightarrow 0$ transition, $\frac{1}{6}$ for each $F = 1 \leftrightarrow 1$ transition). This gives

$$\Gamma_{W\,T} = 0.045\times10^{-2} N\lambda^3 \Gamma B , \tag{14}$$

which is about 3% of the value for resonance collisions, Eq. (9). If the intensity emitted by the lamp is greater in the components for which the absorption coefficients are largest, this value will be a little enhanced, but 5% seems a safe upper limit. The total broadening constant is then

$$C_{11\,T}^1 = 1.50 \pm 0.18 \tag{15}$$

and

$$g_{11\,T}^1 = g_{11}^1 + \Gamma_{WT} = (5.0 \pm 0.9)\times10^{-8} N , \tag{16}$$

in excellent agreement with the experimental value[1,9] for pure thallium:

$$g_{\mathrm{expt}} = (5.38 \pm 0.49)\times 10^{-8} N . \tag{17}$$

III. RELAXATION BY RESONANT COLLISIONS IN PRESENCE OF FOREIGN GAS

The experimental results of I show that the boradening of thallium Hanle signals caused by resonant collisions is reduced in the presence of roughly half an atmosphere of helium or argon. The efficiency of resonant collisions is lessened by the interaction of thallium atoms with the foreign gas. In this section we propose a quantitative interpretation of this effect in terms of three-body collisions Tl*-Tl-He.

The description of such three-body collisions is greatly simplified by the fact that a Tl-Tl* collision lasts much longer than a Tl-He or Tl-Ar collision. We have seen in Sec. II, Eq. (7), that the mean duration of a Tl-Tl* collision is of the order of

$$T_c = 1.4\times10^{-11} \text{ sec} . \tag{18}$$

In the case of a Tl-He collision the broadening cross section for the 3776-Å line is[13] $\sigma' = 1.2\times10^{-14}$

cm^2 and

$$T_c' \simeq T_c/50 \tag{19}$$

(for Tl-Ar collisions $T_c/T_c' \simeq 10$). It is thus reasonable to consider Tl-He or Tl-Ar collisions as occurring instantaneously during a Tl-Tl* collision and to therefore describe the thallium–rare-gas collisions in terms of the parameters of the collision-broadening theory.

The collision-broadening rate of thallium by helium is

$$\gamma = \sigma' N_{\mathrm{He}} v_{\mathrm{He\text{-}Tl}} = 4.0\times 10^{10}\ \mathrm{sec}^{-1} \tag{20}$$

for $N_{\mathrm{He}} = 1.5\times 10^{19}\ \mathrm{cm}^{-3}$ ($p = 426$ torr) and $T = 920\ ^\circ\mathrm{K}$. Since this value is the same order of magnitude as T_c^{-1} there is a large probability that the phase of the electric dipole of one of the thallium atoms will be destroyed by He-Tl collisions during a Tl-Tl* collision. In other words, the He-Tl collisions perturb the probability of excitation transfer between the thallium atoms through the dipole-dipole interaction. In fact, we shall see in Sec. III C that some functions appear in the theoretical expressions that are characteristic of nonexactly resonant transfer of the excitation.[4,11,14]

Let us point out that this *reduction* of broadening by the addition of a foreign gas is only observable for S levels or isolated $J = \frac{1}{2}$ levels such as the $7\,^2S_{1/2}$ state of thallium for which depolarization by collisions with a foreign gas is very small ($\sigma_D \simeq 3 \times 10^{-18}\ \mathrm{cm}^2$ for Tl-He collisions[1]). In the usual case, foreign-gas broadening of the level-crossing curves would completely obscure this reduction of resonant broadening.

A. General Equations

To compute the effect of resonant collisions perturbed by foreign-gas broadening we shall use the formalism of Ref. 4. The potential appearing in the self-broadening theory is the dipole-dipole interaction

$$V(\vec{R}) = -(1/R^3)\left[3(\vec{P}_1\cdot\vec{u})(\vec{P}_2\cdot\vec{u}) - \vec{P}_1\cdot\vec{P}_2\right], \tag{21}$$

where $\vec{R} = R\vec{u} = \vec{b} + \vec{v}t$ is the interatomic vector with relative velocity $\vec{v}$ and impact parameter $\vec{b}$ (Fig. 2), and $\vec{P}_i$ is the electric-dipole operator for atom i.

The state vector of the two thallium atoms system is

$$|\Psi\rangle = \sum a(i_1, i_2)\,|i_1\rangle\,|i_2\rangle \tag{22}$$

and a classical straight-line trajectory is taken for the motion of the atoms. To describe the statistical effects of the foreign-gas collisions we use the density matrix for the two-thallium-atom system,

$$\rho = \sum a(i_1, i_2)\,a^*(i_1', i_2')\,|i_1\rangle\,|i_2\rangle\langle i_1'|\,\langle i_2'|\,, \tag{23}$$

or in the irreducible representation for each atom,

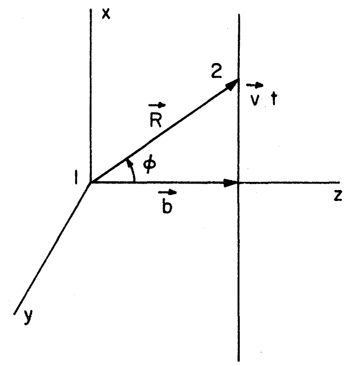

FIG. 2. Collision axis and parameters.

$$\rho = \sum{}^{\alpha_1\alpha_2}\,\rho^{k_1k_2}_{q_1q_2}\,|\,\alpha_1k_1q_1\rangle\rangle\,|\,\alpha_2k_2q_2\rangle\rangle\,, \tag{24}$$

where $|\,\alpha k q\rangle\rangle = {}^{\alpha}T_q^{(k)}$ is both a component of an irreducible tensor acting in the atomic-state space, and a vector of the so-called Liouville space.[4] We assume that there is no hyperfine structure or that the hyperfine structure is small and negligible during the collision. For one atom excited, the electronic states of interest belong to the subspace EE of Liouville-space spanned by the following vectors:

$$|\,eek_1q_1\rangle\rangle\,,\quad |\,ggk_2'q_2'\rangle\rangle\,, \tag{25}$$

$$|\,egK_1Q_1\rangle\rangle\,,\quad |\,geK_2'Q_2'\rangle\rangle\,, \tag{26}$$

and the symmetric vectors obtained by exchange of atoms 1 and 2 (e denotes the resonance excited state and g the ground state). In fact, we will be concerned only by vectors having $k_2' = 0$.

The master equation[15] during a Tl-Tl collision is

$$\dot{\rho} = -i[V, \rho] - G\rho = -iL\rho - G\rho\,, \tag{27}$$

where G is the relaxation matrix describing the effect of He-Tl collisions. G operates independently on atoms 1 and 2:

$$G\,|\,eek_iq_i\rangle\rangle = -{}_e\gamma^{k_i}\,|\,eek_iq_i\rangle\rangle\,, \tag{28}$$

$$G\,|\,egK_iQ_i\rangle\rangle = -(\gamma + id)\,|\,egK_iQ_i\rangle\rangle\,, \tag{29}$$

where ${}_e\gamma^{k_i}$ is the relaxation rate of the k_i observables of the excited state, and γ and d are the broadening and shift constants of the optical line which must be the same for every value of K_i for Tl–noble-gas collisions.[16]

We have

$$\sigma = e^{Gt}\rho \tag{30}$$

and use a perturbation expansion solution for Eq. (27):

$$\sigma(\tau) = \sigma(-\infty) - i\int_{-\infty}^{\tau} d\tau'\, e^{G\tau'}\, L(\tau')e^{-G\tau'}\,\sigma(-\infty)$$
$$-\int_{-\infty}^{\tau} d\tau' \int_{-\infty}^{\tau'} d\tau''\, e^{G\tau'}\, L(\tau')$$

$$\times e^{-G(\tau'-\tau'')} L(\tau'') e^{-G\tau''} \sigma(-\infty) . \quad (31)$$

The first-order term will disappear in angular averages ($\langle L\rangle = \langle V\rangle = 0$) so we will discuss only the second-order term.

As we are interested in computing the effect of He-Tl collisions on the self-relaxation of the observables of the excited state which belong to the EE subspace, we shall restrict our analysis to this subspace.

If we take

$$\sigma(-\infty) = | eek_1 q_1 \rangle\rangle \; | gg00 \rangle\rangle , \quad (32)$$

then

$$\langle\langle eek_1 q_1 , gg00 \,|\, \sigma(\infty)\rangle\rangle$$
$$= 1 - \int_{-\infty}^{+\infty} d\tau' \int_{-\infty}^{\tau'} d\tau'' e^{-h^{k_1}(\tau'-\tau'')}$$
$$\times \langle\langle eek_1 g_1 , gg00 \,|\, L(\tau') L(\tau'') \,|\, eek_1 g_1 , gg00 \rangle\rangle , \quad (33)$$

where

$$h^{k_1} = 2\gamma - {}_e\gamma^{k_1} . \quad (34)$$

[Note that in developing the product $L(\tau')L(\tau'')$ the intermediate states are of the type $| egK_1 Q_1, geK_2 Q_2\rangle\rangle$.] A similar term corresponding to transfer of excitation to the $| gg00, eek_1 q_1\rangle\rangle$ vector contains the same exponential factor. All the other components of $\sigma(\infty)$ become zero when the angular average is performed. For the $7\,{}^2S_{1/2}$ state of thallium, ${}_e\gamma^k$ is very small, and $h^k \simeq 2\gamma$.

In Sec. III B we shall evaluate the angular average of the matrix elements of

$$Y(\gamma, \vec{b}, \vec{v}) = 1 - \int_{-\infty}^{\infty} d\tau' \int_{\infty}^{\tau'} d\tau'' e^{-2\gamma(\tau'-\tau'')} L(\tau') L(\tau'') . \quad (35)$$

B. Angular Averages

Writing $V(\tau)$ [Eq. (21)] in the form (see Fig. 2)

$$V(\tau) = \sum_q V_q^{(2)} r_{q0}^{(2)}(\phi) , \quad (36)$$

where $r_{q0}^{(2)}$ is the rotation matrix about the y axis and $V^{(2)}$ is an irreducible tensor of rank 2, it can easily be shown that all the quantities appearing in the average of $L(\tau')L(\tau'')$ over the angles of $\vec{b}$ and $\vec{v}$ can be expressed in terms of

$$g(x, x') = \sum_q r_{q0}^{(2)}(x) \, r_{q0}^{(2)}(x') (1+x^2)^{-3/2} (1+x'^2)^{-3/2} , \quad (37)$$

where

$$x = \tan\phi = v\tau/b . \quad (38)$$

The angular average of Y is then given by

$$\langle Y(\gamma, b, v)\rangle - 1 = [\langle Y(0, b, v)\rangle - 1]$$
$$\times \int_{-\infty}^{\infty} dx' \int_{-\infty}^{x'} dx'' e^{-\eta(x'-x'')} g(x', x'') /$$
$$\int_{-\infty}^{\infty} dx' \int_{-\infty}^{x'} dx'' g(x', x'') , \quad (39)$$

where

$$\eta = 2\gamma b/v . \quad (40)$$

The upper integral of Eq. (39) can be written as a sum of terms of the type

$$I_F = \int_{-\infty}^{\infty} dx\, F(x) \int_{-\infty}^{x} dx'\, F(x') e^{-\eta(x-x')}$$
$$= \int_{-\infty}^{\infty} dx\, F(x) \int_{-\infty}^{0} du\, F(x+u) e^{\eta u} , \quad (41)$$

which is easily expressed in terms of the Fourier transform of F:

$$\phi(\omega) = \int_{-\infty}^{\infty} dx\, F(x) e^{i\omega x} \quad (42)$$

$$I_F = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{\eta}{\eta^2+\omega^2} \, |\phi(\omega)|^2 . \quad (43)$$

The explicit form for the different $F(x)$ are given in Refs. 4(b) and 11. Finally, one obtains

$$\langle Y(\gamma, b, v)\rangle - 1 = (\langle Y(0, b, v)\rangle - 1) h_1(\eta) , \quad (44)$$

where

$$h_1(\eta) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\eta}{\eta^2+\omega^2} f_1(\omega) \, d\omega . \quad (45)$$

The function $f_1(\omega)$ is defined by Tsao and Curnutte[14] in their study of nonexactly resonant collisions:

$$f_1(\omega) = \tfrac{1}{4} \omega^4 [K_2^2(\omega) + 4K_1^2(\omega) + 3K_0^2(\omega)] , \quad (46)$$

where the K_i are modified Bessel functions. Of course,

$$h_1(0) = f_1(0) = 1 . \quad (47)$$

The interpretation of Eq. (45) is clear: h_1 is the average of $f_1(\omega)$ with a weight $\pi^{-1}\eta(\eta^2+\omega^2)^{-1} d\omega$ equal to the probability that the distance of a point in the profile of atom 1 (broadened by He collisions) to a point in the profile of atom 2 is equal to ω.

The variation of h_1 with x is shown in Fig. 3. Notice that unlike f_1, which as an exponential decay, h_1 decays as x^{-1} for large x. The weight of the portions of the two profiles which are in resonance decreases slowly when the width increases.

C. Integrations over b and v

Equation (44) is only valid for large values of b; one has to introduce a cutoff[10] for close (strong) collisions. Furthermore, the result must be averaged with respect to the distribution $W(v)$ of the relative velocity v that we assume to be Maxwellian.[17]

To simplify, we shall only discuss the relaxation rate g_{11}^1 of the orientation of the $7\,{}^2S_{1/2}$ state of thallium (the result for the other relaxation rates of interest would be exactly the same). The mean

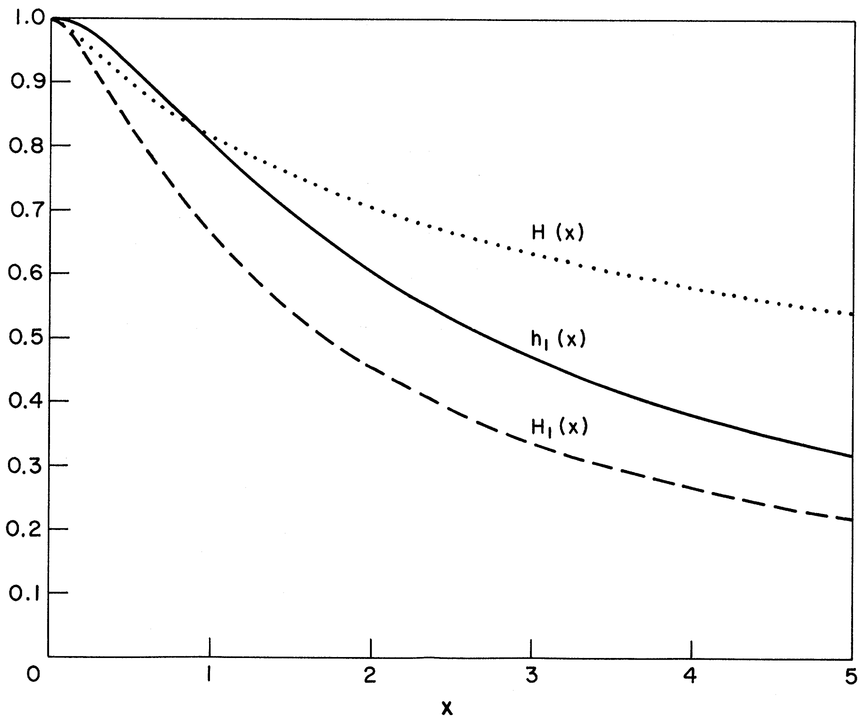

FIG. 3. Functions $h_1(x)$ [Eq. (45)], unbroken line; $H_1(x)$ [Eq. (56)], broken line; and $H(x)$ [Eq. (54)], dotted line.

"probability" of destruction of the orientation by a collision with parameters b and v is, written from Eq. (44), for large impact parameter

$$\Pi_{as}(b, v) = (\mu/b^4v^2)h_1(2\gamma b/v) , \tag{48}$$

where μ is a constant that depends on the electronic angular momenta J_e and J_g, the nuclear spin, and the total angular momentum of the excited state.[4]

To evaluate the relaxation rate [see Eq. (3) for the meaning of the indicies]

$$\bar{g}^1_{11} = \int_{-\infty}^{\infty} W(v)g(v)\,dv = 2\pi N \int_{-\infty}^{\infty} v\,W(v)\,dv \int_0^{\infty} \Pi(b, v) b\,db , \tag{49}$$

one uses the classical approximation[4,10]

$$g(v) = \pi N v[b_0^2 + 2\int_{b_0}^{\infty} \Pi_{as}(b, v) b\,db] , \tag{50}$$

where $b_0(v)$ is the Weisskopf radius defined by

$$\Pi_{as}(b_0, v) = 1 . \tag{51}$$

After some rather tedious transformations, it is straightforward to show that the relaxation rate can be put in the form

$$\bar{g}^1_{11} = g^1_{11}H(a) , \tag{52}$$

where g^1_{11} is the relaxation rate in the absence of a foreign gas, calculated using the same cutoff approximation. a is a dimensionless parameter of the order of magnitude of $\gamma b/v$,

$$a = 4\pi^{-5/4}\gamma\sqrt{\sigma}/\bar{v} , \tag{53}$$

where $\bar{v}$ is the mean relative velocity of two thallium atoms, $g^1_{11} = \sigma N\bar{v}$, and

$$H(a) = \frac{2}{\sqrt{\pi}} \int_0^{\infty} dx\, x^3 e^{-x^2} \times \left[\beta^2(x) + \frac{1}{x^2\beta^2(x)} H_1\left(\frac{a\beta}{x}\right)\right], \tag{54}$$

where the function $\beta(x)$ is defined from Eq. (51) by

$$h_1(a\beta/x) = \beta^4 x^2 . \tag{55}$$

The function H_1 is

$$H_1(x) = 2\int_1^{\infty} \frac{h_1(zx)}{z^3}\,dz = \frac{2}{\pi}\int_0^{\infty} \frac{x}{x^2+y^2} F_1(y)\,dy , \tag{56}$$

where $F_1(y)$ is the function introduced by Tsao and Curnutte[14] and which can be expressed in terms of modified Bessel functions.

The function $H(x)$ is tabulated in Table I. The functions $H_1(x)$ and $H(x)$ are shown in Fig. 3. As with $h_1(x)$, these functions decrease slowly for large x (as x^{-1} for H_1 and $x^{-2/5}$ for H).

Finally, let us point out that Eq. (52) is also valid for some other g^{α} rates and, in particular, for the rate of excitation transfer from atom 1 to atom 2.

D. Numerical Values for He-Tl and Ar-Tl and Discussion

The values of a [Eq. (53)] and of $H(a)$ for the different experimental conditions of Refs. 1 and 9 are given in Table II, together with the experimental ratios $\Delta\tilde{w}/\Delta w$ of the broadening rates of the Hanle signals in the presence of, and in the absence of, foreign gas. It is seen that the values of this ratio agree with $H(a)$ within the limit of *experimental* uncertainties in γ, Δw, and $\Delta\tilde{w}$. Nevertheless, the reduction of the relaxation rate by resonant collisions seems a little more important than the theoretical value of Eq. (52). This small discrepancy, if real, can be accounted for in several ways: It is well known that the cutoff procedure used for strong collisions can bring some nonnegligible errors, nevertheless, these errors must be less important for the ratio $\tilde{g}_{11}^1/g_{11}^1$ than for the absolute value of g_{11}^1. Furthermore, the effects of the hyperfine structure are not properly taken into account. In addition, kinetic collisions between excited thallium atoms and foreign-gas atoms can reduce the diffusion of excited thallium atoms and the probability of wall collisions.

To see the order of magnitude of this latter effect, we compare the mean distance traveled by a thallium atom during its excitation ($T = 970\ ^\circ\mathrm{K}$),

$$l_e = 2.4\times 10^{-4}\ \mathrm{cm}\ , \qquad (57)$$

to the "transport mean free path" l_g representing the mean distance an excited thallium atom travels before the direction of its velocity is randomized (see for instance, Ref. 18):

$$l_g = \alpha_G l_s\ . \qquad (58)$$

In this expression l_s is the mean free path

$$l_s^{-1} = N_G\sigma_s(1 + M_{\mathrm{Tl}}/M_G)^{1/2}\ ,$$

where $M_{\mathrm{Tl}}/M_G \gg 1$ is the ratio of the atomic mass of thallium to the atomic mass of the foreign gas, N_G ($\gg N_{\mathrm{Tl}}$) is the foreign-gas density, and σ_s is the Tl*-foreign-gas-scattering cross section. α_G is a coefficient depending upon the ratio M_{Tl}/M_G: $\alpha_{\mathrm{He}} \simeq 30$, $\alpha_{\mathrm{Ar}} \simeq 4.5$.

Taking $\sigma_s = 5\times 10^{-15}\ \mathrm{cm}^2$ as an order of magnitude for the cross section, one gets the values for l_g shown in Table II. It is seen that at 400 torr both buffer gases must almost completely prevent wall collisions. Helium at 113 torr must also reduce the wall effect. Since the order of magnitude of the wall effect is $\sim 4\times 10^{-2}\Delta w$ (Sec. II B) it is seen that the buffer-gas correction brings the experimental results into better agreement with $H(a)$ (Table II) for buffer-gas pressures of ~ 400 torr.

TABLE I. Tabulation of the function $H(x)$ [Eq. (54)].

x	$H(x)$	x	$H(x)$	x	$H(x)$	x	$H(x)$	x	$H(x)$
0.0	1.000	0.5	0.897	1.0	0.816	2.0	0.706	4.0	0.583
0.1	0.986	0.6	0.879	1.2	0.789	2.4	0.674	4.4	0.566
0.2	0.962	0.7	0.862	1.4	0.765	2.8	0.647	5.0	0.543
0.3	0.934	0.8	0.845	1.6	0.744	3.2	0.623		
0.4	0.917	0.9	0.830	1.8	0.724	3.6	0.602		

TABLE II. Comparison of theory and experiment for the reduction of self-broadening by buffer gas.

Foreign gas	He	He	Ar
Pressure (torr)	113	426	419
a [Eq. (53)][a]	0.25 ± 0.08	0.93 ± 0.30	0.78 ± 0.22
$H(a)$ [Eq. (54)][b]	0.95 ± 0.02	0.83 ± 0.04	0.85 ± 0.04
$(\Delta\tilde{w}/\Delta w)_{\mathrm{expt}}$[c]	0.97 ± 0.06	0.75 ± 0.04	0.76 ± 0.07
l_g [Eq. (58)](10^{-4}cm)[d]	2.1	0.56	0.25
$(\Delta\tilde{w}/\Delta w)_{\mathrm{th}}$[e]	0.93 ± 0.04	0.79 ± 0.05	0.81 ± 0.05

[a] a [Eq. (53)] is of the order of magnitude of the probability $2\gamma T_c$ that a He dephasing collision occurs during a Tl-Tl* collision.

[b] $H(a)$ is the corresponding theoretical decrease of the self-broadening rate [Eq. (52) and Table I].

[c] $(\Delta\tilde{w}/\Delta w)_{\mathrm{expt}}$ is the observed decrease (Refs. 1 and 9), the "transport mean free path."

[d] l_g [Eq. (58)] is to be compared to the mean distance traveled by an excited Tl atom, $l_e = 2.4\ 10^{-4}$ cm, to see whether the buffer gas prevents wall collisions.

[e] $(\Delta\tilde{w}/\Delta w)_{\mathrm{th}}$ is a combination of $H(a)$ and of the estimated reduction in wall-collision broadening.

IV. CONCLUSIONS

We see that the theory is able to account for all the experimental features[1,9] of self-broadening of Hanle signals of thallium and of the effects of a buffer gas.

For pure thallium, since wall effects are very small, this provides evidence, once again, of the very good accuracy of the theory of resonant collisions[2-6] when hyperfine effects have been treated properly.

The decrease in self-broadening due to buffer gases is well explained in terms of three-body collisions (Tl-He collisions occurring during a Tl*-Tl collision) which broaden the optical transitions of thallium and decrease the resonance effect in the transfer of excitation between thallium atoms. The quantitative agreement obtained with the experimental results shows that these three-body collisions are certainly responsible for the major part of the observed decrease in self-broadening, although the prevention of wall collisions by the buffer gas is probably the origin of a small part of the effect.

A similar reduction should be expected in the self-broadening of level-crossing signals of $J = \frac{1}{2}$ resonance states of heavy alkalis, and in the probability of exchange of excitation by resonant collisions ($X^* + X \to X + X^*$) for any element; but this last effect is probably more difficult to observe.

It is also reasonable to think that the same kind of three-body collisions should enhance the probability of collisional transfer of excitation ($X^* + Y \to X + Y^*$) in the case of nonperfect resonance matching. In this situation the atomic levels are broadened by collisions with the buffer gas thus causing a partial overlapping of the levels. If the cross section for this transfer is large then the same treatment above should be applicable.

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