

EXPERIMENTAL EVIDENCE OF THE INVERSION OF ANGULAR MOMENTUM  
DURING THE TRANSFER OF EXCITATION BY RESONANT COLLISIONS  
IN THE  $6^3P_1$  STATE OF MERCURY

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The zero-field level-crossing signal of even isotopes of natural Hg excited by resonant collisions from directly excited  $\text{Hg}^{198}$  atoms has been observed with circularly polarized light. The signal is proportional to the atomic "orientation" (mean value of the angular momentum of the excited atoms). The sense of this orientation is reversed when the excitation is transferred by collisions from  $\text{Hg}^{198}$  to other isotopes, as predicted by the theory.

At the time of a resonant collision between an atom excited in a resonant level and an atom of the same element in its ground state, the  $r^{-3}$  dipole electrostatic interaction potential gives rise to the transfer of the excitation from one atom to another.<sup>1</sup> The corresponding cross section has been measured by Holstein<sup>2</sup> in the  $6^3P_1$  level of mercury. There is also a perturbation of the phase of the electric dipole and the well-known Holtzmark broadening of the optical resonance line.<sup>1,3,4</sup> The same phenomenon is responsible for the broadening of double-resonance and level-crossing curves of resonance levels.<sup>4-6</sup> In general the collisions destroy all "polarization" or anisotropy of the excited state of the vapor; i.e., it mixes the populations of the Zeeman sublevels (diagonal elements of the density matrix), and destroys the off-diagonal elements.

The theory of these phenomena involves a detailed calculation of the collision matrix which describes the perturbation (due to the collision) in the wave function representing the internal state of the two atoms, and an average of the effect of the collisions over all the parameters associated with the collision.<sup>4-7</sup> The calculation is relatively simple since the matrix elements of the potential are all well known, and it is legitimate to use the semiclassical approximation with a straight-line trajectory. This theory predicts a relaxation time shorter for "orientation" (magnetic dipole moment) of the excited state of the vapor than for "alignment" (quadrupole moment). This has been verified by experiment.<sup>8,9</sup> In a vapor composed of many isotopes which one can distinguish optically, it is possible in certain cases to measure separately the orientation (or the alignment) of isotope *A*, initially optically excited, and that of isotope *B*, excited by resonant collisions with isotope *A*. If isotope *A* is present in trace amounts in a vapor composed of almost

pure isotope *B*, it is possible to use level-crossing techniques to study the relaxation of the orientation and alignment of isotope *A*.<sup>4</sup> We would like to report here the results of the observation of orientation transferred to other natural mercury isotopes by a given even isotope  $\text{Hg}^{198}$  which has been optically excited into the  $6^3P_1$  level.

The theory (Ref. 4) predicts that on the average the sense of orientation is reversed at the time of its transfer by resonant collisions of isotopes *A* and *B*. On the average, during such a process, 75% of the orientation is destroyed and 25% is transferred, with its sense reversed, i.e.,

$$\frac{d}{dt} \langle \vec{M}_B \rangle_{\text{coll}} = -\frac{1}{4} e g^0 \langle \vec{M}_A \rangle,$$

where  $\vec{M}_i$  represents the average value of the magnetic moment of the excited state of isotope *i* and  $e g^0$  the probability of transfer of excitation per unit time. A similar equation for the alignment does not involve a minus sign and hence alignment does not show any inversion. But it is difficult to observe this point since the theoretical transfer coefficient for alignment is only  $0.05 e g^0$ . A simple interpretation of these theoretical results is not easy since they are due essentially to the fact that the interaction potential is a rank-2 tensor.

From the experimental point of view, the essential difficulty encountered in the study of the effect of resonant collisions on level crossings or on the polarization of resonance light comes from the multiple diffusion of the resonance light in the vapor.<sup>10</sup> This appears at relatively low vapor pressures. However, at pressures where the effect of resonant collisions would be visible (atomic densities of about  $10^{15}$  atoms/cm<sup>3</sup>), the resonance light diffused laterally is completely depolarized by multiple diffusion.

It is possible to overcome this difficulty by ob-

servicing the light diffused not in a lateral direction as is usual, but in the backward direction.<sup>9,11</sup> This method permits observation at fairly high vapor densities of level-crossing curves which will consequently be considerably broadened.

To observe the inversion of orientation at the time of transfer of excitation, the following conditions must hold: The orientation of isotope *A*, initially optically excited, must be large; a non-negligible amount of the excitation of isotope *A* must be transferred by collisions to atoms *B* (this implies high vapor pressures of isotope *B*  $N_B \sim 10^{15}$  atoms/cm<sup>3</sup>); and the light re-emitted by isotope *B* must undergo a small number of multiple-diffusion processes before leaving the cell. These three conditions complicate the observation of transferred orientation, for laterally diffused light, regardless of the concentrations of isotopes *A* and *B*. However, these conditions can be fulfilled simultaneously for back-scattered light with  $N_A \sim N_B \sim 10^{15}$  cm<sup>-3</sup>. There is a high concentration of atoms *A*, excited and oriented in the excited state, near the wall of the cell containing the vapor. The atoms *B* excited by collisions with *A* are also near the cell wall, and the back-scattered light is only slightly depolarized by multiple diffusion.

In spite of the slight inconvenience due to the presence of odd isotopes, natural mercury contains even isotopes in quantities such that  $N_A \sim N_B$ . In the present experiment, isotope *A* was Hg<sup>198</sup> for the simple reason that it was the only isotope for which we had a lamp of very high purity (99.8%). This is necessary in order that the lamp does not excite directly other even isotopes in the scattering cell. We designate by "isotope *B*" all the other even isotopes in the cell.

The simplest way to observe the inversion of orientation would seem to consist in placing a scattering cell of mercury vapor in a fairly weak magnetic field (10-100 Oe) and illuminating the cell with a source of Hg<sup>198</sup> emitting circularly polarized light in a direction parallel to the field. One can then measure the rate of circularly polarized light back-scattered by isotopes other than Hg<sup>198</sup> which can be eliminated by placing a Hg<sup>198</sup> absorption filter in the detection arm. However, it is very difficult to eliminate enough of the background light, scattered by the walls of the cell, to make an accurate measurement of the rate of the circular polarization of light emitted by isotope *B*. It is much simpler to use the method of level crossing at zero field (Hanle effect). In this case, the excitation light parallel

to *OX* is perpendicular to the magnetic field  $H_0$ , and the rate of polarization is directly related to the intensity of the level-crossing signal. The background light does not depend on  $H_0$  and its influence is thus eliminated. The details of the experimental setup (Fig. 1) (rotating polarizer  $P_2$ , synchronous detection, multichannel analyzer, etc.) are described elsewhere.<sup>9,11</sup>

The level-crossing signal corresponding to circular polarization is distinguished from the classical signal corresponding to alignment by the choice of a convenient phase of the synchronous detection. In the absence of a Hg<sup>198</sup> filter in the detection beam, the signal is dominated by the Hg<sup>198</sup> light and has a Lorentzian shape [Fig. 2(a)]. In this case, one observes that

$$\begin{aligned} \langle M_x \rangle &= \langle M_{Ax} \rangle + \langle M_{Bx} \rangle = \text{Re} \langle M_{A+} + M_{B+} \rangle \\ &= \text{Re} \langle M_+ \rangle, \end{aligned}$$

where  $M_{\eta+} = M_{\eta x} + iM_{\eta y}$ , and one has

$$\begin{aligned} d\langle M_{A+} \rangle / dt &= -[\gamma + \alpha(1)N + i\omega] \langle M_{A+} \rangle \\ &\quad - \alpha(2)N_A \langle M_+ \rangle + \lambda, \end{aligned}$$

$$\begin{aligned} d\langle M_{B+} \rangle / dt &= -[\gamma + \alpha(1)N + i\omega] \langle M_{B+} \rangle \\ &\quad - \alpha(2)N_B \langle M_+ \rangle, \end{aligned}$$

$$N = N_A + N_B,$$

where  $\gamma$  represents the relaxation due to spontaneous emission, multiple diffusion, and wall collisions<sup>9,11</sup>;  $\omega$  is the Larmor frequency; and  $\lambda$  represents the excitation of the vapor by the Hg<sup>198</sup> lamp. Following the notation of Ref. 4, we have  $\alpha(i)N = \epsilon g^1(i)$ , where  $\alpha(1)$  refers to the destruction of orientation of the atom excited before the collision and  $\alpha(2)$  refers to the transfer of orientation to the other atom. Hence the rate equation for orientation involves three types of colli-

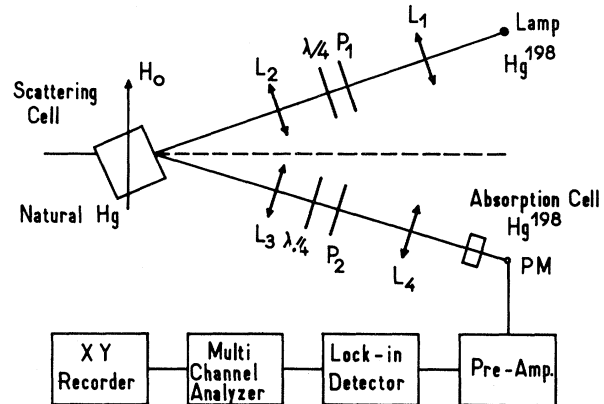


FIG. 1. Schematic diagram of the experimental setup.

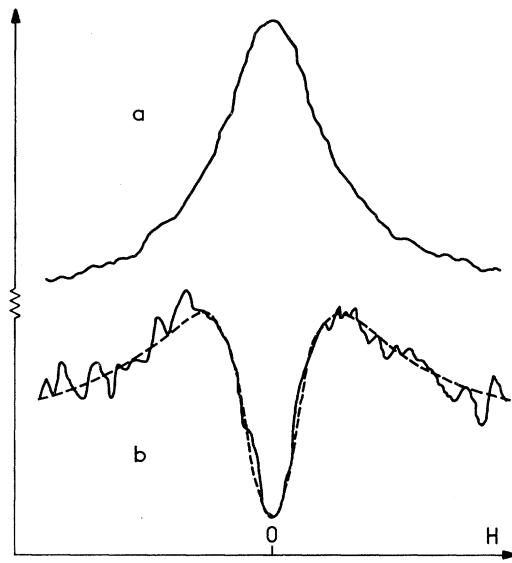


FIG. 2. Zero-field level-crossing curves of natural Hg (density  $N=3.5 \times 10^{15} \text{ cm}^{-3}$ ) excited by  $\text{Hg}^{198}$  light. (a) Experimental curve from all isotopes. (b) Solid line, experimental curve with a  $\text{Hg}^{198}$  filter on the detection arm; dashed line, theoretical curve  $\text{Re}[(1+i\omega/\Gamma_T)^{-2} - \eta(1+i\omega/\Gamma_T)^{-1}]$ ; The value of  $\Gamma_T$  is determined from the curve 2(a);  $\eta$  is taken equal to 0.7 to fit with the experimental curve. The vertical gain in Fig. 2(b) is 16 times that in Fig. 2(a).

sions. For example, let us consider the first equation which refers to the orientation of atom  $A$ . In collisions of the type  $A^*-A$ , the rate of destruction of the orientation of atoms  $A$  excited before the collision is  $\alpha(1)N_A \langle M_{A+} \rangle$ , and the rate of creation of orientation in atoms  $A$  unexcited before the collision is  $-\alpha(2)N_A \langle M_{A+} \rangle$ ; in collisions  $A^*-B$ , the rate of destruction of the orientation of atoms  $A$  is  $\alpha(1)N_B \langle M_{A+} \rangle$ ; and in collisions  $B^*-A$ , the rate of creation of orientation in atoms  $A$  is  $-\alpha(2)N_A \langle M_{B+} \rangle$ . At equilibrium,

$$\langle M_{+} \rangle = \frac{\lambda}{\gamma + N[\alpha(1) + \alpha(2)] + i\omega} = \frac{\lambda}{\Gamma_T} L\left(\frac{\omega}{\Gamma_T}\right),$$

$$\langle M_{B+} \rangle = \frac{-\alpha(2)N_B \langle M_{+} \rangle}{\gamma + \alpha(1)N + i\omega} \cong -\frac{\lambda \alpha(2)N_B}{(\Gamma_T)^2} L^2\left(\frac{\omega}{\Gamma_T}\right),$$

with  $\Gamma_T = \gamma + N[\alpha(1) + \alpha(2)]$ ,  $L(X) = (1 + iX)^{-1}$ , taking into account the fact that  $N_{\alpha}(2) \ll \Gamma_T$ .

In the presence of a 198 filter, if it absorbs all of the light emitted by the 198 atoms in the cell, one observes  $\langle M_{Bx} \rangle$  and hence a signal which has the form of the real part of  $L^2(\omega/\Gamma_T)$ . It is a particular case of the well-known shape which appears each time one observes a cascade or transfer phenomenon in level crossings.

In zero field [ $L(0) = -1$ ], the ratio of the signals

is  $\alpha(2)N_B/\Gamma_T$ .

The experimental results verify the theoretical prediction (Fig. 2). The signal obtained with a  $\text{Hg}^{198}$  filter has the two predicted characteristics; it has the opposite sign and falls off faster with increasing  $H_0$  than the signal without filter. However, the signal behaves as though the filter does not cut all the  $\text{Hg}^{198}$  light. It is possible also that the other isotopes are slightly excited by the  $\text{Hg}^{198}$  lamp. Hence the observed signal behaves as

$$\text{Re}[L^2(\omega/\Gamma_T) - \eta L(\omega/\Gamma_T)],$$

where  $\eta$  is a coefficient representing the relative importance of the 198 signal not absorbed by the filter. To take into account the form of the observed signals, the value of  $\eta$  varied from approximately 1 for low pressures of the vapor to 0 for high pressures. Once the correction was made the form of the signal was in agreement with the theory (Fig. 2).

As for the intensity of the signals, it is necessary to take into account all relevant corrections and approximations (absorptions by the walls of the filter, presence of odd isotopes in the cell, multiple diffusion, wall collisions, etc.). When the pressure increases,  $\alpha(2)N_B/\Gamma_T$  should tend to a limit that one can estimate to be  $\sim 15\%$ . This is verified in a satisfactory fashion by the experimental results. The experimental conditions of Fig. 2 ( $N_B \sim 2.5 \times 10^{15}$ ) predict  $\alpha(2)N_B/\Gamma_T \sim 0.1$ , which is in good agreement with the observed signals, after having subtracted the part attributed to  $\text{Hg}^{198}$  ( $\eta = 0.7$ ) and taking into account the different corrections.

The small value of  $\alpha(2)N_B/\Gamma_T$  explains the bad signal-to-noise ratio observed. Nevertheless the signal was observable from about  $N = 0.7 \times 10^{15}$  to  $N = 10^{16}$ .

The observations are a confirmation of the validity of the theory of resonant collisions<sup>4-7</sup> for states similar to the  $6^3P_1$  state of mercury.

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## EFFECT OF ELECTRIC FIELDS ON THE TEMPERATURE OF PHASE TRANSITIONS OF LIQUID CRYSTALS

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It is proposed that the temperature of mesomorphic-isotropic phase changes and of transitions between mesophases may be markedly shifted by manageable electric fields. First experiments demonstrating such a shift in the nematic-isotropic transition of *p*-ethoxybenzylidene-*p'*-aminobenzonitrile are reported.

The transitions between mesophases or between a mesophase and the isotropic liquid state are often associated with extraordinarily small heats of transition of the order of  $kT$  or less per molecule.<sup>1,2</sup> In the present note we wish to show that because of this property the transition temperatures can be influenced by electric fields of manageable strength and to report preliminary experimental observations confirming the prediction.

We start from the thermodynamic relation

$$\partial \Delta g / \partial T = -q / T_0, \quad (1)$$

valid in the absence of external fields and with constant pressure at the transition temperature  $T_0$ . Here  $q$  is the heat of transition per unit mass,  $\Delta g = g_2 - g_1$ , the difference between the Gibbs free energies per unit mass of the phases in question, and  $T$  is the absolute temperature. Since  $\Delta g = 0$  at  $T = T_0$ , Eq. (1) may be given the form

$$\Delta g = -\Delta T q / T_0, \quad (2)$$

where  $\Delta T = T - T_0$ . Equation (2) is a first-order approximation and of course only valid near  $T = T_0$ . In an electric field  $E$  (cgs units), one may include in  $\Delta g$  the difference of the polarization energies:

$$\Delta g = -\frac{q}{T_0} \Delta T + \frac{\epsilon_2 - \epsilon_1}{8\pi\rho} E^2,$$

where  $\epsilon_1$  and  $\epsilon_2$  are the dielectric constants below and above the transition and  $\rho$  the density.  $\Delta g$  being zero at the transition point, the temperature shift as a function of  $E$  at constant pressure

is

$$\Delta T = \frac{T_0}{q} \frac{\epsilon_2 - \epsilon_1}{8\pi\rho} E^2. \quad (3)$$

This relation has long been known but rarely mentioned,<sup>3</sup> probably because in most phase transitions  $(\epsilon_2 - \epsilon_1)/q$  is too small to permit a perceptible shift at practicable field strengths. The very small change of the polarization energy per mole associated with the volume jump (<1% in *p*-azoxyanisole) at the transition point is neglected in the above formulas.

As an example we consider the nematic-isotropic phase transition. A large  $\epsilon_2 - \epsilon_1$  may be expected from materials whose molecules possess a strong permanent electric dipole parallel to their long axes. In this case orientation and deformation polarization will, as a rule, cooperate, giving rise to a large difference  $\epsilon_{\parallel} - \epsilon_{\perp} > 0$  between the dielectric constants parallel and perpendicular to the unique axis in the nematic state. Also, because of the orientational restraints of the nematic order, one may expect  $\epsilon_{\parallel} - \epsilon_{is} > \epsilon_{is} - \epsilon_{\perp}$  with  $\epsilon_{\parallel} > \epsilon_{is} > \epsilon_{\perp}$  at the transition point where  $\epsilon_{is}$  is the dielectric constant of the isotropic liquid. The values<sup>4</sup>  $\epsilon_{\parallel} \approx 21$  and  $\epsilon_{\perp} \approx 7$  were measured for the material used in our experiments (see Fig. 1), so we may take  $\epsilon_2 - \epsilon_1 = \epsilon_{\parallel} - \epsilon_{is} \approx 10$  as a large but possible value for the jump in polarizability. The heat of the isotropic-nematic transition of *p*-cyanobenzylidene-*p'*-anisidine (see Fig. 1), a compound similar to that used by us, is known<sup>2</sup> to be  $q = 0.63$  cal/g. Nearly the same heat has been measured for *p*-azox-