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OPTICAL PUMPING OF MOLECULES

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I. Introduction

In 1949, a proposal by Brossel and Kastler first demonstrated that optical excitation opened the way to extending all the capabilities of magnetic resonance to thermally unpopulated states of atoms or molecules. Shortly thereafter, in 1950, Kastler proposed the famous "optical pumping" technique through which a transfer of angular momentum from a light beam to an atomic vapor permits a great number of fundamental experiments as well as exciting applications, such as atomic clocks and magnetometers. For

about two decades, these techniques were only used in atomic physics and ignored by molecular physicists. The main reason for this is: Any electronic excited state of a molecule contains a very large number of vibrational and rotational sublevels. It is therefore impossible to build a spectral lamp that would excite only one level at a time. Moreover, even if some circumstances did exist that permitted one to excite a very limited number of excited levels individually, there were very few of these and they did not offer any hope of studying series of vibrational and rotational states of an electronically excited molecule. It is therefore only with the recent development of tunable lasers in the visible and close ultraviolet range that systematic studies became possible and that optical pumping, in its broader meaning, became a very useful tool for molecular investigations.

Even for the simplest diatomic molecules, the electronic excited states are still virtually unknown. Conventional spectroscopy gives energy levels, and in several cases, it is now possible to understand to a large extent the many perturbations that take place in such states. However, simple parameters such as g factors, lifetimes, hyperfine structures, and so on, which can be very sensitive to these perturbations, are generally unknown or are known only very approximately. In this paper, we would like to present some techniques that in the near future will allow such parameters to be measured by rather simple experiments. They will certainly give, in many cases, a much deeper understanding of electronically excited molecular states.

In Section II, we describe briefly some experimental techniques. In Section III, a formalism is presented which must be used to interpret correctly the results of all the experiments that involve optical excitation and detection with polarized light. Since in many molecules high values of the rotational quantum number J are involved, we also develop a semiclassical theory that applies in the limiting case when $J \to \infty$. As we shall see, this theory permits one to interpret some of the saturation effects that take place when the large light fluxes of lasers are used. In Section IV, a brief review of the molecules that have been studied by these techniques is presented. Section V is specially devoted to the iodine molecule I_2, which is one of the few molecules for which systematic optical pumping investigations have been made. These investigations have allowed a much better understanding of the predissociation of this molecule to be obtained.

II. Experimental Methods

Optical pumping of molecules allows a great number of important molecular parameters to be measured. The most often studied are:

τ = lifetime of the molecular excited state

σ = collision cross sections for quenching, depolarization, etc.

g = Landé factors and also fine structure, λ or ρ doubling, hyperfine structure, chemical shifts, spectroscopic constants, electric dipole moment, etc.

Most of the techniques that we describe here take advantage of the fact that an optical excitation populates not just one excited state, but a set of Zeeman, Stark, or hyperfine levels; and the complexity of these systems requires the use of density matrix techniques in their analysis. Section III is devoted to this analysis.

In this section, we briefly review the most commonly used experimental techniques, some of which have been known for a very long time (Hanle effect, double resonance, etc.), while others have been developed for practical applications only recently, since they take advantage of the specific characteristics of lasers (resonances in a modulated light beam, quantum beats, etc.).

A. Selective Excitation

As compared to those of atoms, molecular excited states are very complicated due to their rotational and vibrational structures. However, "monochromatic" excitation allows a single rovibronic state to be investigated separately without the need for very high resolution spectroscopy. For low pressure diatomic molecular vapors (10^{-3} Torr to 1 Torr), the absorption lines are generally well resolved, the Doppler width ranging from 100 to 1000 MHz. Light sources with spectral width of about 1 GHz are quite convenient for selective excitation of the molecules; there is generally no need for narrower lines, except for saturated absorption spectroscopy. When a single level is excited, the first problem is to identify its vibrational v' and rotational J' quantum numbers. Since the molecules under study are generally well known from absorption spectroscopy, this is often very easy. In a number of cases, J' can be found by measuring the (R, P) frequency interval in the fluorescence spectrum, which is given to first order in J' and v' by:

$$\Delta\nu_{R,P} = 2B''(2J' + 1)$$

B'' being the ground state rotational constant. When J' is known, v' is generally easily found. The great sensitivity of laser-induced fluorescence can also be used to improve the determination of molecular spectroscopic constants; the first example of such progress may be found in the study of Na_2 by Demtroder *et al.* (1969) and Demtroder and Stock (1975). Even when several levels are simultaneously excited, a careful study of the fluorescence

progressions allows one to assign precisely the various excited levels and to select the fluorescence light coming from a single level (Vigué and Lehmann, 1972).

Due to the special structure of laser light, one should be somewhat careful. Because of the mode structure of the laser spectrum, only some molecules are excited, namely, those at locations on the Doppler profile corresponding to the mode frequencies. Moreover, the large intensities obtained with either cw or pulsed lasers may produce various types of saturation phenomena. Some saturation effects will be discussed in Section III. Others are presented and discussed by Dumont (1972), Ducloy (1973), and Lehmann (1976). In most cases, it is then necessary to extrapolate carefully the obtained results to zero light intensity, taking into account the fact that such an extrapolation is not always a linear one.

B. Exponential Decay and Quantum Beats

The advent of nitrogen laser-pumped dye lasers giving very short pulses (1 to 5 nsec) of tunable monochromatic light in all the visible and near uv range of the spectrum has prompted a new interest in the impulse response of molecules and atoms. Following the pulse, the fluorescence decays exponentially, as does the population of the excited state. This decay gives a direct measurement of the lifetime τ. The natural molecular lifetime τ_0 is obtained by an extrapolation to zero vapor pressure. Moreover, the decay probability $\gamma = 1/\tau$ being a linear function of the vapor pressure, the slope of the extrapolation curve gives the cross section σ_0 for depopulation of the excited state due to collisions:

$$(d\gamma/dp) = (4\sigma_0)/(\pi MkT)^{1/2} \tag{1}$$

where M = molecular mass and T = cell temperature.

Let us go a little further: a light pulse of duration θ has, owing to the uncertainty principle, a spectral width at least equal to $\Delta\nu = 1/\theta$. Two levels lying at a distance $\Delta E \leq h/\theta$ may then be excited *coherently*. If this is the case, the exponential decay is modulated at a frequency $\Delta E/h$, from which one can deduce ΔE. This technique is known as the "quantum beats" method (Corney and Series, 1964) and has recently been demonstrated with dye laser excitation (Gornik *et al.*, 1972 and Haroche *et al.*, 1973). It has been used by Paisner and Wallenstein (1974) to measure Landé factors in some excited levels in I_2. The pulsed excitation method has a number of very interesting features: first, one observes the fluorescence *after* the exciting light pulse has been turned off. It is therefore truly the *free* evolution of the molecules which is observed. Another advantage is purely experimental: the pulsed dye lasers at the present time cover a much wider spectral range than cw ones. Also very fast transient recorders are now available and allow a very efficient collection of data. A review paper on time resolved experiments is presently being written by Haroche (1976).

C. Hanle Effect and Resonances in a Modulated Light Beam

1. *Hanle Effect (or Magnetic Depolarization)*

One of the most widely used techniques to measure lifetimes and Landé factors of molecular excited states is the Hanle effect. A detailed theory of such experiments is given in Section III; we present here only the principle of such experiments: in a zero magnetic field the different Zeeman M sublevels are degenerate; if the molecule is excited by a σ linearly polarized light beam, the resulting σ fluorescence contains an interference term between two possible paths

$$\begin{cases} M \xrightarrow{\text{exc.}} M+1 \xrightarrow{\text{fluor.}} M \\ M \xrightarrow{\text{exc.}} M-1 \xrightarrow{\text{fluor.}} M \end{cases}$$

The interference term is destroyed when a magnetic field is applied provided that the excited sublevels $M+1$ and $M-1$ are separated by a distance larger than their natural width $1/\tau$. This appears as a change in the polarization and intensity diagram of the fluorescence light.

In general the Hanle effect curves have a Lorentzian shape; for $\Delta M = 2$ coherences, their full width at half maximum is given by:

$$\Delta H = \frac{\hbar}{\mu_B |g_J|}\left\{\frac{1}{\tau} + \frac{4}{(\pi MkT)^{1/2}} P\sigma_2\right\} \tag{2}$$

where σ_2 is the cross section for destruction of the $\Delta M = 2$ coherences.

For some polarizations, dispersion-shaped Hanle curves can be observed, the sign of which is related to the sign of the Landé factor in the excited state.

The study of ΔH versus P allows one to find the $g\tau$ product (by extrapolating to zero vapor pressure), and $\sigma_2/|g_J|$ (from the slope of the extrapolation curve).

Note that multiple scattering is generally not a problem in molecular vapor due to the small branching ratio of the fluorescence directed toward the absorbing state; however, this effect has nevertheless been observed in CS (Silvers and Chiu, 1972).

It must be emphasized that Hanle effect only gives the $g_J\tau$ product for the excited state. However, several different cases may occur allowing a further step to be made: first, if we suppose that the Landé factor is known, the Hanle effect gives a value of the lifetime. Another situation may arise (Broyer

et al., 1975a) when several hyperfine levels are simultaneously excited. If they have different Landé factors, the resulting superposition of Hanle curves is no longer Lorentzian; as the various hyperfine Landé factors g_F can be derived from a single rotational Landé factor g_J, a computer fit can be made to derive g_J and τ from the shape of the Hanle curve in this case. But in general, besides Hanle effect, one has to do a separate measurement of g_J or τ. It should be noted that the Landé factor being very sensitive to small perturbations of the wavefunction, expressions derived from simple angular momentum coupling schemes are not always reliable.

2. *Resonances in a Modulated Light Beam*

This technique is actually the Fourier transform of the quantum beats method. Instead of exciting by a short pulse of light and looking to the response of the molecular vapor, one uses an intensity modulated light beam at a frequency ω and looks at the modulation of the fluorescence light at the same frequency: $L_F(\omega)$. If $\omega \ll 1/\tau$ the fluorescence is fully modulated, but when $\omega \gg 1/\tau$ the molecules no longer "follow" the excitation and $L_F(\omega)$ goes to zero. Simultaneously, its phase is retarded with respect to the modulation of the laser; this is the basis of the well-known "phase shift" technique. If, however, ω, being $\gg 1/\tau$, goes through a Bohr frequency ω_0 of the excited molecule (a Zeeman frequency or a hyperfine frequency, for example), then the fluorescence is resonantly modulated at the frequency ω. (Fig. 1). If one is interested in measuring a Landé factor, it is better to keep the frequency fixed and scan the magnetic field; two resonances are then observed for symmetric values of the magnetic field $\pm H_0$ (Fig. 2). The measurement of H_0 gives g_J in the excited state by the relation $\hbar\omega = 2g_J\mu_B H_0$ for $\Delta M = \pm 2$ resonances. This technique was first proposed by Corney and Series (1964). The resonances have the width of the Hanle effect. It has been applied to measurement of Landé factor in I_2 (Keller *et al.*, 1973) and Se_2 (Gouedard and Lehmann, 1975).

It seems to be a very convenient experimental technique since intensity modulation of a cw laser beam is now rather easy to achieve using Pockels

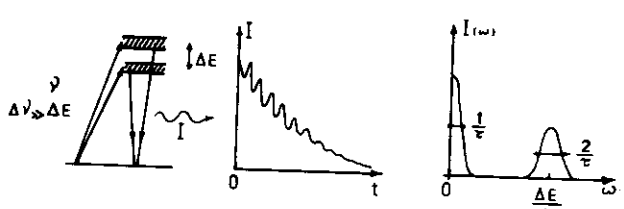

FIG. 1. Principle of quantum beats and resonances in a modulated light beam.

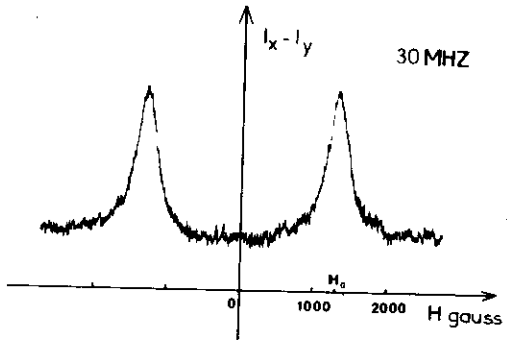

FIG. 2. Resonances in a modulated light beam in the B 1u $v' = 0$, $J' = 105$ state of Se_2 excited at 4727 Å.

cells or acousto-optic elements. This technique would compare very favorably with double resonance methods (see Section II, D), at least for resonance frequencies up to 100 MHz.

3. *Other Related Methods*

The physical principle of nonzero field *level crossings* is the same as for the Hanle effect, but one observes crossings between Zeeman sublevels originating from *different* (hyperfine or fine) levels. The signal amplitude is however generally rather weak since the number of crossings is of the order of J', the sum of their amplitudes being of the order of the Hanle effect amplitude.

Unlike level crossings, *anticrossings* (Levy, 1972) are only population effects; the exciting beam must therefore have an "incoherent" polarization. In many cases, one has to apply an external perturbation to mix the two levels which would otherwise cross each other. The mixing of the two wavefunctions then causes a change in the radiation pattern centered at the anticrossing point.

Generally speaking, crossings are observed between states of the same total parity. Anticrossings can either be naturally induced by some term of the Hamiltonian of the molecule or be induced by an external electric field.

Electric field level crossings, as well as mixed electric field and magnetic field level crossings have also been observed and used to measure electric dipole moments.

D. Double Resonance

The principle of double resonance is very simple: the exciting light populates the molecular excited level; during the lifetime τ a second "low frequency" (rf, microwave, or even IR) wave induces transitions between the

excited state sublevels or to nearby states. These transitions are recorded through changes in the fluorescence pattern. The theory of such experiments is very well established (German *et al.*, 1973, Silvers *et al.*, 1970), and we shall just recall some of their main features.

Let us only consider rf resonances between Zeeman sublevels of the excited state, used for instance, to measure Landé factors.

A condition required to observe a resonance is that the transition probability between the two states involved is not too small during the lifetime τ (ideally it should be of the order of unity). This requires:

$$\mu_B g_J H_{rf} \sim \frac{2\pi}{\tau} \tag{3}$$

This condition implies that H_{rf} must be large enough, i.e., $H_{rf} \sim H_{1/2}$, $H_{1/2}$ being the width of the Hanle effect curves. This is a rather troublesome limitation for double resonance experiments in diatomic molecular states: g_J being generally very small, and the lifetimes ranging from 10^{-6} to 10^{-9} sec, $H_{1/2}$ is often of the order of 100 to 1000 gauss. It is very difficult to obtain oscillating fields of this amplitude.

However, since double resonance experiments are noncoherent processes, they have found many applications in the study of zero field structures: hyperfine or fine structures (German *et al.*, 1973), or even rotational structures (Field *et al.*, 1973). These experiments give very high precision measurements of these structures, generally in the GHz range.

III. Theory

As we have seen, a molecular optical resonance is a three level process (Fig. 3): the molecule is optically excited from an initial state $|i\rangle$, to an

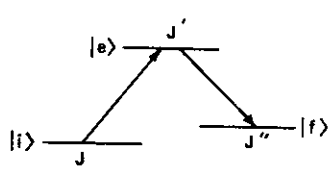

FIG. 3.

excited state $|e\rangle$, and the fluorescence observed is due to the spontaneous emission from state $|e\rangle$ to a final state $|f\rangle$. Let J, J', and J'' be the angular momentum of these three states. We neglect at first the hyperfine structures and the optical nonlinear effects through which the molecule would come back from $|e\rangle$ to $|i\rangle$ by stimulated emission. These problems are discussed at a later stage.

A. General Relations

1. Optical Excitation

The time-dependent perturbation theory gives the probability per unit time that a molecule absorbs a photon to reach state $|e\rangle$:

$$\frac{d}{dt}P(|e\rangle) = \sum_i \frac{1}{T_p} |\langle e|\mathbf{e}_{\lambda_0} \cdot \mathbf{D}|i\rangle|^2 \tag{4}$$

where $\mathbf{e}_{\lambda_0}$ is the polarization vector of the exciting light beam, $\mathbf{D}$ is the angular part of the electric dipole operator, T_p is a pumping time. This function depends on the spectrum of the exciting beam as compared to the absorption spectrum of the molecule. $1/T_p$ is also proportional to the intensity of the pumping beam (Barrat and Cohen-Tannoudji, 1961). If we introduce the *excitation operator*:

$$\boxed{\mathscr{E} = \sum_i (\mathbf{e}_{\lambda_0} \cdot \mathbf{D})|i\rangle\langle i|(\mathbf{e}_{\lambda_0} \cdot \mathbf{D})^\dagger} \tag{5}$$

we have

$$\frac{d}{dt}P(|e\rangle) = \frac{1}{T_p}\langle e|\mathscr{E}|e\rangle \tag{6}$$

The "pumping" term of the rate equation of the density operator in the excited state ρ_e is therefore found to be equal to

$$\left(\frac{d}{dt}\right)_p \rho_e = \frac{\mathscr{E}}{T_p} \tag{7}$$

2. Rate Equation of ρ_e

We now introduce the two other terms of this rate equation:

(a) The *free evolution* of ρ_e under the hamiltonian *He*. *He* is here the Zeeman Hamiltonian. Later on it will contain the hyperfine Hamiltonian or other terms like the Λ doubling or the spin–rotation terms.

(b) The *relaxation* term. We shall call γ the relaxation operator. It contains mainly the spontaneous emission operator but may include other effects like predissociation or quenching collisions (disorientation collisions are not taken into account by this expression).

The rate equation for ρ_e can then be written (taking $\hbar = 1$):

$$\boxed{\frac{d}{dt}\rho_e = -i[He, \rho_e] - \frac{1}{2}[\gamma, \rho_e]_+ + \frac{\mathscr{E}}{T_p}} \qquad (8)$$

$$[\gamma, \rho_e]_+ = \gamma\rho_e + \rho_e\gamma$$

3. Fluorescence

The intensity of the fluorescence light is proportional to:

$$L_F = \frac{3\gamma_r}{8\pi}\mathrm{Tr}(\rho_e \mathscr{D}) \qquad (9)$$

where $\mathscr{D}$ is the *detection operator*

$$\mathscr{D} = \sum_f (\mathbf{e}_\lambda \cdot \mathbf{D})|f\rangle\langle f|(\mathbf{e}_\lambda \cdot \mathbf{D})\dagger \qquad (10)$$

where $\mathbf{e}_\lambda$ is the polarization vector of the fluorescence observed. In expression (9), γ_r is the radiative relaxation rate.

B. The $\alpha_{m_1 m_2}$ Operators

In the Liouville vectorial space of the operators acting in the excited state, several basis sets are possible. We shall start with the set

$$\alpha_{m_1' m_2'} = |\tau' J' m_1'\rangle\langle\tau' J' m_2'| \qquad (11)$$

τ' stands for the quantum numbers of $|e\rangle$ other than J' and m'. We have the obvious relations:

$$|(\alpha_{m_1' m_2'})\dagger = \alpha_{m_2' m_1'} \qquad (12)$$

$$|\mathrm{Tr}\{(\alpha_{m_1' m_2'})\dagger \alpha_{m_3' m_4'}\} = \delta_{m_1' m_3'}\delta_{m_2' m_4'} \qquad (13)$$

The density operator ρ_e can be developed on this basis:

$$\rho_e = \sum_{m_1', m_2'} \rho^e_{m_1' m_2'} \alpha_{m_1' m_2'} \qquad (14)$$

with

$$\rho^e_{m_1' m_2'} = \langle\tau' J' m_1'|\rho_e|\tau' J' m_2'\rangle = \mathrm{Tr}(\rho_e \alpha_{m_2' m_1'}) \qquad (15)$$

Let us develop equation (8) on this set of operators:

$$\langle\tau' J' m_1'|[He, \rho_e]|\tau' J' m_2'\rangle = (m_2' - m_1')\omega_e \rho^e_{m_1' m_2'} \qquad (16)$$

where

$$\omega_e = g_{J'}\mu_0 H$$

μ_0 is the Bohr magneton, H the magnetic field, and $g_{J'}$ the excited state Landé factor taken positive if the magnetic moment is parallel to $\mathbf{J}'$.

If we assume an isotropic relaxation with a relaxation rate γ:

$$\tfrac{1}{2}\langle\tau' J' m_1'|[\gamma, \rho_e]_+|\tau' J' m_2'\rangle = \gamma\rho^e_{m_1' m_2'} \qquad (17)$$

Equation (8) therefore becomes:

$$\frac{d}{dt}\rho^e_{m_1' m_2'} = -\{\gamma + i(m_2' - m_1')\omega_e\}\rho^e_{m_1' m_2'} + \frac{\mathscr{E}_{m_1' m_2'}}{T_p} \qquad (18)$$

where

$$\mathscr{E}_{m_1' m_2'} = \sum_m \langle\tau' J' m_1'|\mathbf{e}_{\lambda_0} \cdot \mathbf{D}|\tau J m\rangle\langle\tau J m|(\mathbf{e}_{\lambda_0} \cdot \mathbf{D})\dagger|\tau' J' m_2'\rangle. \qquad (19)$$

The *stationary solution* of Eq. (18) is:

$$\boxed{\rho^e_{m_1' m_2'} = \frac{1}{T_p}\frac{\mathscr{E}_{m_1' m_2'}}{\gamma + i(m_2' - m_1')\omega_e}} \qquad (20)$$

In this expression, one clearly sees the resonant behavior of $\rho^e_{m_1' m_2'}$ when ω_e goes through zero.

Let us now evaluate the fluorescence signal:

$$L_F = \frac{3\gamma_r}{8\pi}\mathrm{Tr}(\rho_e \mathscr{D}) = \frac{3\gamma_r}{8\pi}\sum_{m_1' m_2'} \rho^e_{m_1' m_2'} \mathscr{D}_{m_2' m_1'} \qquad (21)$$

that is,

$$\boxed{L_F = \frac{3\gamma_r}{8\pi T_p}\sum_{m_1' m_2'}\frac{\mathscr{E}_{m_1' m_2'}\mathscr{D}_{m_2' m_1'}}{\gamma + i(m_2' - m_1')\omega_e}} \qquad (22)$$

More explicitly

$$L_F = \frac{3\gamma_r}{8\pi T_p}\sum_{\substack{m_1' m_2' \\ m m''}} \frac{\langle\tau' J' m_1'|\mathbf{e}_{\lambda_0} \cdot \mathbf{D}|\tau J m\rangle\langle\tau J m|(\mathbf{e}_{\lambda_0} \cdot \mathbf{D})\dagger|\tau' J' m_2'\rangle}{\gamma + i(m_2' - m_1')\omega_e}$$
$$\times \langle\tau' J' m_2'|\mathbf{e}_\lambda \cdot \mathbf{D}|\tau'' J'' m''\rangle\langle\tau'' J'' m''|(\mathbf{e}_\lambda \cdot \mathbf{D})\dagger|\tau' J' m_1'\rangle \qquad (23)$$

We shall come back to this expression later.

C. The T_q^k Operators

Instead of using the $\alpha_{m_1'm_2'}$ operators as a basis of the Liouville space, one may prefer the tensor operators T^k whose components are:

$$T_q^k = \sum_{m_1'm_2'} (-1)^{J'-m_2'} \langle J'J'm_1' - m_2' \,|\, kq\rangle \,|\tau'J'm_1'\rangle\langle\tau'J'm_2'\,| \tag{24}$$

$$= \sum_{m_1'm_2'} (-1)^{J'-m_1'} (2k+1)^{1/2} \begin{pmatrix} J' & J' & k \\ m_1' & -m_2' & -q \end{pmatrix} |\tau'J'm_1'\rangle\langle\tau'J'm_2'\,| \tag{25}$$

where $\langle J'J'm_1' - m_2' \,|\, kq\rangle$ is a Clebsch–Gordan coefficient and

$$\begin{pmatrix} J' & J' & k \\ m_1' & -m_2' & -q \end{pmatrix}$$

the corresponding $3j$ symbol (Racah, 1942; Fano and Racah, 1959; Judd, 1963).

It is easy to demonstrate the following relations:

$$(T_q^k)\dagger = (-1)^q T^k_{-q} \tag{26}$$

as compared to Eq. (12)

$$\mathrm{Tr}\{(T_q^k)\dagger T_{q'}^{k'}\} = \delta_{kk'}\delta_{qq'} \tag{27}$$

as compared to Eq. (13)

$$\rho_e = \sum_{kq} \rho_{kq}^e T_q^k \tag{28}$$

$$\rho_{kq}^e = \mathrm{Tr}\{(-1)^q \rho_e T^k_{-q}\} \tag{29}$$

as compared to Eqs. (14) and (15).

$\mathscr{E}$ and $\mathscr{D}$ can of course be similarly developed on the T_q^k:

$$\mathscr{E} = \sum_{kq} \mathscr{E}_{kq} T_q^k \qquad \mathscr{D} = \sum_{kq} \mathscr{D}_{kq} T_q^k \tag{30}$$

and

$$\mathrm{Tr}\{\rho_e \mathscr{D}\} = \sum_{kq} (-1)^q \rho_{kq}^e \mathscr{D}_{k-q} \tag{31}$$

as compared to Eq. (21).

If we go back to the rate equation of ρ_e, it is easy to show that since T_q^k is a linear combination of $\alpha_{m_1'm_2'}$ in which the only nonvanishing terms are those for which $m_1' - m_2' = q$:

$$[He, \rho_e]_{kq} = q\omega_e \rho_{kq}^e \tag{32}$$

and therefore, the *stationary solution* of Eq. (8), developed on the T_q^k basis is given by

$$\boxed{\rho_{kq}^e = \frac{1}{T_p} \frac{\mathscr{E}_{kq}}{\gamma + iq\omega_e}} \tag{33}$$

Hence

$$\boxed{L_F = \frac{3\gamma_r}{8\pi T_p} \sum_{kq} (-1)^q \frac{\mathscr{E}_{kq}\mathscr{D}_{k-q}}{\gamma + iq\omega_e}} \tag{34}$$

In this equation:

$$\left\{ \begin{aligned} \mathscr{E}_{kq} = \mathrm{Tr}\{(-1)^q \mathscr{E} T^k_{-q}\} = \sum_{m_1'm_2'} (-1)^{J'-m_1'+q} \\ \times (2k+1)^{1/2} \begin{pmatrix} J' & J' & k \\ m_1' & -m_2' & q \end{pmatrix} \\ \times \langle \tau'J'm_2' \,|\, \mathbf{e}_{\lambda_0} \cdot \mathbf{D} \,|\, \tau Jm\rangle \\ \langle \tau Jm \,|\, (\mathbf{e}_{\lambda_0} \cdot \mathbf{D})\dagger \,|\, \tau'J'm_1'\rangle \end{aligned} \right. \tag{35}$$

$$\left\{ \begin{aligned} \mathscr{D}_{k-q} = \sum_{\substack{m_1'm_2' \\ m''}} (-1)^{J'-m_1'-q} (2k+1)^{1/2} \begin{pmatrix} J' & J' & k \\ m_1' & -m_2' & -q \end{pmatrix} \\ \times \langle \tau'J'm_2' \,|\, \mathbf{e}_\lambda \cdot \mathbf{D} \,|\, \tau''J''m''\rangle \times \langle \tau''J''m'' \,|\, (\mathbf{e}_\lambda \cdot \mathbf{D})\dagger \,|\, \tau'J'm_1'\rangle \end{aligned} \right. \tag{36}$$

D. Calculation of L_F

1. Development of $\mathbf{e}_{\lambda_0} \cdot \mathbf{D}$

In both expressions (22) and (34) it appears matrix elements of the type $\langle \tau'J'm' \,|\, \mathbf{e}_{\lambda_0} \cdot \mathbf{D} \,|\, \tau Jm\rangle$. To calculate such matrix elements, one must develop both the polarization operator $\mathbf{e}_{\lambda_0}$ and $\mathbf{D}$ in standard components. Let α, β, γ be the director cosines of $\mathbf{e}_{\lambda_0}$:

$$\mathbf{e}_{\lambda_0} \cdot \mathbf{D} = \alpha D_x + \beta D_y + \gamma D_z = \frac{\alpha + i\beta}{\sqrt{2}} \frac{D_x - iD_y}{\sqrt{2}} + \frac{\alpha - i\beta}{\sqrt{2}} \frac{D_x + iD_y}{\sqrt{2}} + \gamma D_z$$

$$= \sum_p (-1)^p e^{\lambda_0}_{-p} D_p \tag{37}$$

where

$$\begin{aligned} D_{+1} &= -(D_x + iD_y)/\sqrt{2} & e^{\lambda_0}_{+1} &= -(\alpha + i\beta)/\sqrt{2} \\ D_0 &= D_z & e^{\lambda_0}_0 &= \gamma \\ D_{-1} &= (D_x - iD_y)/\sqrt{2} & e^{\lambda_0}_{-1} &= (\alpha - i\beta)/\sqrt{2} \end{aligned} \tag{38}$$

are the standard components of $\mathbf{D}$ and $\mathbf{e}_{\lambda_0}$. The $e^{\lambda_0}_p$'s are the σ^+, π, and σ^- components of the polarization. An "incoherent" polarization is a pure component $e^{\lambda_0}_p$ while an "coherent" one is a linear combination of different $e^{\lambda_0}_p$'s. Note that $\mathbf{e}_\lambda$ is a geometric vector, while $\mathbf{D}$ is a vector operator.

Using the Wigner–Eckart theorem, one finds:

$$\begin{cases} \langle \tau' J' m' | \mathbf{e}_{\lambda_0} \cdot \mathbf{D} | \tau J m \rangle = \sum_p (-1)^p e^{\lambda_0}_{-p} \langle \tau' J' || D || \tau J \rangle \\ \qquad \times (-1)^{J'-m'} \begin{pmatrix} J' & 1 & J \\ -m' & p & m \end{pmatrix} \qquad (39) \\ \langle \tau J m | (\mathbf{e}_{\lambda_0} \cdot \mathbf{D})^\dagger | \tau' J' m' \rangle = \sum_{p'} (-1)^{p'} (e^\star)^{\lambda_0}_{-p'} \langle \tau' J' || D || \tau J \rangle^\star \\ \qquad \times (-1)^{J'-m} \begin{pmatrix} J & 1 & J' \\ -m & p' & m' \end{pmatrix} \qquad (40) \end{cases}$$

Let us now develop the two expressions of L_F [Eqs. (22) and (34)].

2. *Use of the α Basis Set*

From expressions (23), (39), and (40) one obtains:

$$L_F = \frac{3\gamma_r}{8\pi T_p} \sum_{\substack{pop_0' \\ pp'}} \{ e^{\lambda_0}_{-p_0} (e^\star)^{\lambda_0}_{-p_0'} e^{\lambda}_{-p} (e^\star)^{\lambda}_{-p'} \} |\langle \tau' J' || D || \tau J \rangle|^2 \times |\langle \tau' J' || D || \tau'' J'' \rangle|^2 C^{pop_0'}_{pp'} \tag{41}$$

with

$$C^{pop_0'}_{pp'} = \sum_{\substack{m_1' m_2' \\ m, m''}} (-1)^{m_1' + m_2' + m + m''} \begin{pmatrix} J' & 1 & J \\ -m_1' & p_0 & m \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ -m & p_0' & m_2' \end{pmatrix} \times \begin{pmatrix} J' & 1 & J'' \\ -m_2' & p & m'' \end{pmatrix} \begin{pmatrix} J'' & 1 & J' \\ -m'' & p' & m_1' \end{pmatrix} \Big/ \gamma + i(m_2' - m_1')\omega_e \tag{42}$$

Since the 4, $3J$ symbols imply four relations between the p's and m's, the summation goes only over one parameter. However if J' is of the order of

100 as can be the case for a molecule, it contains 200 terms! However, using the formal expressions of the $3j$ symbols, one can obtain simple expressions for the C coefficients using the expressions of

$$\sum_{-J'}^{+J'} m_i'^n$$

with $n = 1, 2, 3, 4$.

Nevertheless, in many cases we prefer an expression in which the roles of the polarizations $\mathbf{e}_{\lambda_0}$ and $\mathbf{e}_\lambda$ and that of the angular momenta J, J', and J'' are more clearly separated. And this is what is obtained when using the $T^\star_q$'s.

3. *Use of the $T^\star_q$ Basis Set*

From Eqs. (35), (39), and (40), one obtains:

$$\mathscr{E}_{kq} = \sum_{\substack{m_1' m_2' \\ m}} (-1)^{J'-m_1'+q} (2k+1)^{1/2} |\langle \tau' J' || D || \tau J \rangle|^2 \sum_{popo'} e^{\lambda_0}_{-p} (e^\star)^{\lambda_0}_{-p_0'} \times (-1)^{p_0+p_0'+J'-m_2'+J-m} \begin{pmatrix} J' & 1 & J \\ -m_2' & p_0 & m \end{pmatrix} \times \begin{pmatrix} J & 1 & J' \\ -m & p_0' & m_1' \end{pmatrix} \begin{pmatrix} J' & J' & k \\ m_1' & -m_2' & q \end{pmatrix} \tag{43}$$

Using the general relation:

$$\sum_{\mu_1\mu_2\mu_3} (-1)^{l_1+l_2+l_3+\mu_1+\mu_2+\mu_3} \begin{pmatrix} J_1 & l_2 & l_3 \\ m_1 & \mu_2 & -\mu_3 \end{pmatrix} \begin{pmatrix} l_1 & J_2 & l_3 \\ -\mu_1 & m_2 & \mu_3 \end{pmatrix} \times \begin{pmatrix} l_1 & l_2 & J_3 \\ \mu_1 & -\mu_2 & m_3 \end{pmatrix} = \begin{Bmatrix} J_1 & J_2 & J_3 \\ l_1 & l_2 & l_3 \end{Bmatrix} \begin{pmatrix} J_1 & J_2 & J_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \tag{44}$$

where

$$\begin{Bmatrix} J_1 & J_2 & J_3 \\ l_1 & l_2 & l_3 \end{Bmatrix}$$

is a $6j$ coefficient, one obtains:

$$\mathscr{E}_{kq} = \left\{ \sum_{popo'} e^{\lambda_0}_{-p_0} (e^\star)^{\lambda_0}_{-p_0'} \begin{pmatrix} 1 & 1 & k \\ -p_0 & -p_0' & q \end{pmatrix} \right\} |\langle \tau' J' || D || \tau J \rangle|^2 \mathscr{A}_k(J', J) \tag{45}$$

where

$$\mathscr{A}_k(J', J) = (-1)^{J+J'}(2k+1)^{1/2}\begin{Bmatrix} 1 & 1 & k \\ J' & J' & J \end{Bmatrix} \tag{46}$$

The first factor of $\mathscr{E}_{kq}$ is characteristic of the polarization of the light, while $\mathscr{A}_k(J', J)$ depends on the angular characteristics of the $\tau J \to \tau' J'$ transition. The reduced matrix element of D is proportional to the square root of the oscillator strength of the transition. One can therefore write:

$$\mathscr{E}_{kq} = \mathscr{U}_{kq}^{\lambda_0} |\langle \tau' J' || D || \tau J \rangle|^2 \mathscr{A}_k(J', J) \tag{47}$$

where $\mathscr{U}_{kq}^{\lambda_0}$ is actually the kq component of a polarization operator. Similarly:

$$\mathscr{D}_{kq} = \mathscr{U}_{kq}^{\lambda} |\langle \tau' J' || D || \tau'' J'' \rangle|^2 \mathscr{A}_k(J', J'') \tag{48}$$

In the $3j$ coefficient which appears on $\mathscr{U}_{kq}^{\lambda_0}$, k can only take the values 0, 1, or 2. This is due to the electric dipole character of the transition. We have therefore:

$$L_F = \frac{3\gamma_r}{8\pi T_p} |\langle \tau' J' || D || \tau J \rangle|^2 |\langle \tau' J' || D || \tau'' J'' \rangle|^2$$
$$\times \sum_{k=0,1,2;\, q} \left| (-1)^q \frac{\mathscr{U}_{kq}^{\lambda_0} \mathscr{U}_{k-q}^{\lambda_0} \mathscr{A}_k(J', J) \mathscr{A}_k(J', J'')}{\gamma + iq\omega_e} \right| \tag{49}$$

Although equivalent to Eq. (41), this expression is much easier to evaluate.

E. Polarization Rates—Hanle Effect

1. Molecules Without Nuclear Spin

Using Eq. (49), we will give the expressions of the rate of polarization of the fluorescent light under a linearly polarized excitation: As shown in Fig. 4, $\mathbf{e}_{\lambda_0}$ is parallel to Oy and $\mathbf{e}_\lambda$ is either parallel to Ox or to Oy. The polarization rate is defined by

$$\mathscr{P} = \frac{L_y - L_x}{L_y + L_x} \tag{50}$$

The only nonvanishing components of ρ_e are those for which $q = 0$ or ± 2. When $H \to \infty$, all the $q \neq 0$ terms of ρ_{kq}^e vanish. Then L_x and L_y become equal and $\mathscr{P} \to 0$. When this is not the case:

$$\mathscr{P} = \frac{3\mathscr{A}_2(J', J)\mathscr{A}_2(J', J'')}{\mathscr{A}_2(J', J)\mathscr{A}_2(J', J'') + 10\mathscr{A}_0(J', J)\mathscr{A}_0(J', J'')} \cdot \frac{\gamma^2}{\gamma^2 + (2\omega_e)^2} \tag{51}$$

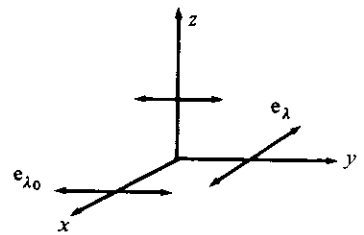

FIG. 4.

When H increases the polarization decreases as the $\rho_{k,\pm 2}^e$ components of ρ_e, which results in a *Lorentz-shaped* depolarization curve.

We shall now give the values obtained for $\mathscr{P}_0$, the zero field polarization, using the following notations:

$J = J' + 1$ is represented	by the symbol P↑
$J = J'$	by Q↑
$J = J' - 1$	by R↑
$J'' = J' + 1$	by P↓
$J'' = J'$	by Q↓
$J'' = J' - 1$	by R↓

The notations P, Q, R are the usual notations for such transitions in molecular spectroscopy.

Then, using the tabulated values for the $6j$ symbols, one finds for the polarization $\mathscr{P}_0$ the values shown in Table I.

TABLE I

Polarization Rates in Zero Magnetic Field

Transitions	$\mathscr{P}_0$	Limit when $J' \to \infty$
(P↑ P↓)	$\frac{J'(2J'-1)}{14J'^2+33J'+20}$	$\frac{1}{7}$
(P↑ Q↓) or (Q↑ P↓)	$-\frac{2J'-1}{6J'+7}$	$-\frac{1}{3}$
(P↑ R↓) or (R↑ P↓)	$\frac{1}{7}$	$\frac{1}{7}$
(Q↑ Q↓)	$\frac{(2J'+3)(2J'-1)}{8J'^2+8J'-1}$	$\frac{1}{2}$
(Q↑ R↓) or (R↑ Q↓)	$-\frac{2J'+3}{6J'-1}$	$-\frac{1}{3}$
(R↑ R↓)	$\frac{(2J'+3)(J'+1)}{14J'^2-5J'+1}$	$\frac{1}{7}$

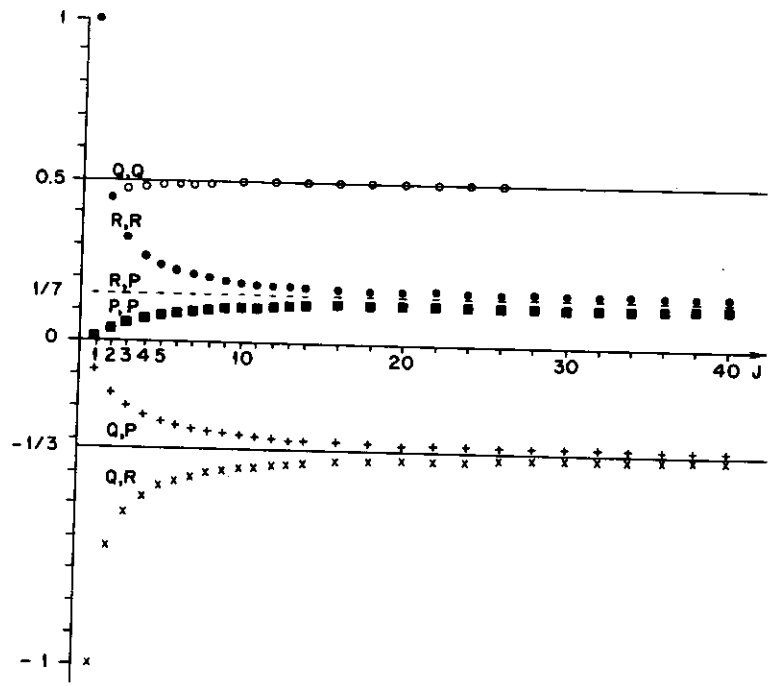

FIG. 5. Polarization rates of the fluorescence at $H = 0$.

Figure 5 shows the behavior of $\mathscr{P}_0(J')$ with J'. When $J' \gg 1$, $\mathscr{P}_0$ is higher when a Q transition is involved, its maximum value being for a (Q↑ Q↓) situation. The sign of the polarization is given by $(-1)^{J-J''}$.

2. *Molecules with Nuclear Spins*

If one or several of the nuclei of the molecule have a nuclear spin, then a hyperfine structure of $\{\tau' J'\}$ will exist. As we shall see, if this structure is much smaller than γ, then everything behaves as if it did not exist. On the other hand, if the hyperfine structure is much larger than the Doppler width of the lines, then one is able to excite a single hyperfine state with a total angular momentum F'. Then, all the above formulas are still valid just by changing J, J', J'' into F, F', F''.

We consider here the case when the hyperfine structure is much larger than γ but smaller than the exciting line spectral width, so that all the hyperfine states are equally excited. This is the "broad line" situation. I is the total nuclear spin of the nuclei. We also assume here that the applied magnetic field is small enough so that there is no hyperfine decoupling.

Under this assumption, the energies of the Zeeman sublevels are all linear in H and the zero field eigenstates are a good enough approximation.

If there is no quadrupole hyperfine coupling, the eigenstates of the excited molecule are the $|\tau' J' I F m_F\rangle$ states. However, if a quadrupole interaction is involved, I may not be a good quantum number and the eigenstates are called:

$$|\tau' J' \varepsilon F m_F\rangle = \sum_I \alpha^{\varepsilon}_{I,F} |\tau' J' I F m_F\rangle \tag{52}$$

ε is here a label but not a quantum number. Each of these states has a Landé factor given by:

$$g_{\varepsilon F} = \sum_I |\alpha^{\varepsilon}_{I,F}|^2 \left\{ g_{J'} \frac{F(F+1) + J'(J'+1) - I(I+1)}{2F(F+1)} + g_I \frac{F(F+1) - J'(J+1) + I(I+1)}{2F(F+1)} \right\} \tag{53}$$

Here, g_J is the rotational Landé factor of the molecule and g_I the nuclear Landé factor possibly corrected from the diamagnetic effect. The energy differences between sublevels can therefore be written:

$$\omega^{\varepsilon_1 F_1 \varepsilon_2 F_2}_{m_{F_1} m_{F_2}} = \Delta_{\varepsilon_1 F_1 \varepsilon_2 F_2} + m_{F_2} \omega_{\varepsilon_2 F_2} - m_{F_1} \omega_{\varepsilon_1 F_1}$$

In this expression $\Delta_{\varepsilon_1 F_1 \varepsilon_2 F_2}$ is either zero if $\varepsilon_1 F_1 = \varepsilon_2 F_2$ or much larger than

$$m_{F_2} \omega_{\varepsilon_2 F_2} - m_{F_1} \omega_{\varepsilon_1 F_1} \qquad \text{if } \varepsilon_1 F_1 \neq \varepsilon_2 F_2; \qquad \omega_{\varepsilon F} = g_{\varepsilon F} \mu_B H \tag{54}$$

The α operators are now given by:

$${}^{F_1 F_2}_{\varepsilon_1 \varepsilon_2}\alpha_{m_{F_1} m_{F_2}} = |\tau' J' \varepsilon_1 F_1 m_{F_1}\rangle\langle \tau' J' \varepsilon_2 F_2 m_{F_2}| \tag{55}$$

and the fluorescence light is:

$$L_F = \frac{3\gamma_r}{8\pi T_p} \sum_{\substack{\varepsilon_1 \varepsilon_2 \\ F_1 F_2}}^{m_{F_1} m_{F_2}} \times \frac{\left(\sum_J \alpha^{\varepsilon_1}_{JF_1} (\alpha^{\star})^{\varepsilon_2}_{JF_2} \mathscr{E}^{JF_1 JF_2}_{m_{F_1} m_{F_2}}\right)\left(\sum_{I'} (\alpha^{\star})^{\varepsilon_1}_{I'F_1} \alpha^{\varepsilon_2}_{I'F_2} \mathscr{Q}^{I'F_1 I'F_2}_{m_{F_1} m_{F_2}}\right)}{\gamma + i\omega^{\varepsilon_1 F_1 \varepsilon_2 F_2}_{m_{F_1} m_{F_2}}} \tag{56}$$

To write this expression, the fact that $\mathscr{E}$ and $\mathscr{Q}$ do not affect the nuclear spins has been taken into account.

We now expand the $\mathscr{E}$ and $\mathscr{Q}$ operators on tensor operators. Let us consider the case of a diatomic molecule with nuclear spins I_1 and I_2. It is then convenient to develop $\mathscr{E}$ and $\mathscr{Q}$ on a set of products of tensor operators: ${}_J T^{\star}_q \cdot {}_{I_1} T^{\star}_{q'} \cdot {}_{I_2} T^{\star}_{q''}$.

Each one of these operators being defined by relations similar to Eq. (25), the matrix element of such a product in an uncoupled basis set of state is given by:

$$\langle J_1 m_J I_1 m_{I_1} I_2 m_{I_2} |\, {}_{J'}T^{k}_{q} \cdot {}_{I_1}T^{k'}_{q'} \cdot {}_{I_2}T^{k''}_{q''} \,| J_2 m'_J I_1 m'_{I_1} I_2 m'_{I_2}\rangle = \delta_{J'J_1}\delta_{J'J_2}$$
$$((2k+1)(2k'+1)(2k''+1))^{1/2}(-1)^{J'-m_J+I_1-m_{I1}+I_2-m_{I2}}\begin{pmatrix} J' & k & J' \\ -m_J & q & m'_J\end{pmatrix}$$
$$\begin{pmatrix} I_1 & k' & I_1 \\ -m_{I_1} & q' & m'_{I_1}\end{pmatrix}\begin{pmatrix} I_2 & k'' & I_2 \\ -m_{I_2} & q'' & m'_{I_1}\end{pmatrix} \tag{57a}$$

so that they are orthonormalized in the sense:

$$Tr[({}_{J'}T^{k}_{q}\ {}_{I_1}T^{k'}_{q'}\ {}_{I_2}T^{k''}_{q''})\dagger({}_{J'}T^{K}_{Q}\ {}_{I_1}T^{K'}_{Q'}\ {}_{I_2}T^{K''}_{Q''})] = \delta_{kK}\delta_{k'K'}\delta_{k''K''}\delta_{qQ}\delta_{q'Q'}\delta_{q''Q''} \tag{57b}$$

Since $\mathscr{E}$ and $\mathscr{D}$ do not affect the nuclear spins of the molecule, these developments on this basis set of operators only involve ${}_{I_1}T^0_0$ and ${}_{I_2}T^0_0$ so that one can write:

$$\mathscr{E} = \sum_{kq}\sqrt{(2I_1+1)(2I_2+1)}\,\mathscr{E}_{kq}\ {}_{J'}T^k_q \cdot {}_{I_1}T^0_0 \cdot {}_{I_2}T^0_0 \tag{58a}$$

$$\mathscr{D} = \sum_{kq}\sqrt{(2I_1+1)(2I_2+1)}\,\mathscr{D}_{kq}\ {}_{J'}T^k_q \cdot {}_{I_1}T^0_0 \cdot {}_{I_2}T^0_0 \tag{58b}$$

The notations $\mathscr{E}_{kq}$ and $\mathscr{D}_{kq}$ actually stand for $\mathscr{E}^{koo}_{qoo}$ and $\mathscr{D}^{koo}_{qoo}$. From here on we shall not write explicitly ${}_{I_1}T^0_0$ and ${}_{I_2}T^0_0$ and write T^k_q for ${}_{J'}T^k_q$.

We now go back to the $|\tau' J' I F m_F\rangle$ basis set. However, for homonuclear molecules only ortho or para states exist for a given J'. To take that into account in the normalization procedures, one must change $(2I_1+1)\times(2I_2+1)$ into $\sum_I (2I+1)$.

Then:

$$\mathscr{E}^{IF_1F_2}_{m_{F_1}m_{F_2}} = \sum_{kq}\mathscr{E}_{kq}\langle\tau' J' I F_1 m_{F_1}|\,T^k_q\,|\tau' J' I F_2 m_{F_2}\rangle \tag{59a}$$

with:

$$|\tau' J' I F m_F\rangle = \sum_{m' m_I}(-1)^{J'-I+m_F}(2F+1)^{1/2}\begin{pmatrix} J' & I & F \\ m' & m_I & -m_F\end{pmatrix}|\tau' J' I m_I m'\rangle \tag{59b}$$

Hence, making use of formula (57a):

$$\langle\tau' J' I F_1 m_{F_1}|\,T^k_q\,|\tau' J' I F_2 m_{F_2}\rangle = \sum_{\substack{m_1' m_2' \\ m_I}}(-1)^{3J'-2I-m_1'+m_{F1}+m_{F2}}\left(\frac{(2k+1)(2F_1+1)(2F_2+1)}{\sum_I(2I+1)}\right)^{1/2} \times\begin{pmatrix} J' & I & F_1 \\ m'_1 & m_I & -m_{F_1}\end{pmatrix}\begin{pmatrix} J' & J' & k \\ m'_1 & -m'_2 & q\end{pmatrix}\begin{pmatrix} J' & I & F_2 \\ m'_2 & m_I & -m_{F_2}\end{pmatrix} \tag{60}$$

$$= (-1)^{J'+I-m_{F1}+F_1+F_2+k}\left[\frac{(2k+1)(2F_1+1)(2F_2+1)}{\sum_I(2I+1)}\right]^{1/2} \times\begin{Bmatrix} J' & F_1 & I \\ F_2 & J' & k\end{Bmatrix}\begin{pmatrix} F_1 & k & F_2 \\ -m_{F_1} & q & m_{F_2}\end{pmatrix} \tag{61}$$

Let us come back to the energy difference $\omega^{\varepsilon_1 F_1 \varepsilon_2 F_2}_{m_{F1}m_{F2}}$

Let us first consider in L_F the terms for which $\varepsilon_1 F_1 = \varepsilon_2 F_2$. They give a contribution:

$$L^R_F = \frac{3\gamma_r}{8\pi T_p}\sum_{\substack{kq \\ \varepsilon F}}(-1)^q\frac{\mathscr{E}_{kq}\mathscr{D}_{k-q}}{\gamma + iq\omega_{\varepsilon F}}\mathscr{B}(\varepsilon F k J') \tag{62}$$

with:

$$\mathscr{B}(\varepsilon F k J') = \frac{(2F+1)^2}{\sum_I(2I+1)}\left|\sum_I |\alpha^{\varepsilon}_{IF}|^2\begin{Bmatrix} J' & F & I \\ F & J' & k\end{Bmatrix}\right|^2 \tag{63}$$

L^R_F is called the "resonant" part of L_F. When the magnetic field goes through zero it appears as a linear combination of Lorentz curves of different widths. This results in a non-Lorentzian Hanle curve. Provided the $\alpha^{\varepsilon}_{IF}$ are known, one can compare this curve to theoretical curves with g_J/g_I taken as a fitting parameter. Then from the width of the curve one can obtain the width of the excited state γ. Let us now come back to the contribution of the terms of L_F for which $\varepsilon_1 F_1 \neq \varepsilon_2 F_2$. They are called the non-resonant terms of L_F since they do not vary with the magnetic field at least in the low field limit. They give the contribution:

$$L^{NR}_F = \frac{3\gamma_r}{8\pi T_p}\sum_{\substack{kq \\ \varepsilon_1 F_1}}^{\varepsilon_2 F_2}(-1)^q\frac{\mathscr{E}_{kq}\mathscr{D}_{k-q}}{\gamma + i\Delta_{\varepsilon_1 F_1 \varepsilon_2 F_2}}\mathscr{C}(\varepsilon_1 F_1 \varepsilon_2 F_2 k q) \tag{64}$$

where

$$\mathscr{C}(\varepsilon_1 F_1 \varepsilon_2 F_2 kq) = \frac{(2F_1+1)(2F_2+1)}{\sum_I (2I+1)} \left| \sum_I \alpha^{\varepsilon_1}_{IF_1} (\alpha^{\star})^{\varepsilon_2}_{IF_2} \begin{Bmatrix} J' & F_1 & J \\ F_2 & J' & k \end{Bmatrix} \right| \quad (65)$$

If $\Delta_{\varepsilon_1 F_1 \varepsilon_2 F_2} \gg \gamma$, L_F^{NR} is of the order of $(\gamma/\Delta) L_F^R$, that is, it is negligibly small. Moreover,

$$\begin{Bmatrix} J' & F_1 & I \\ F_2 & J' & k \end{Bmatrix}^2$$

behaves, when $J' \to \infty$, as $1/J'^2$ if $F_2 - F_1 = \pm 1$ and as $1/J'^4$ if $F_2 - F_1 = \pm 2$. This prevents the optical excitation of hyperfine coherences in this case and can be considered as an approximate selection rule $\Delta F = \Delta J$ valid only if $J \gg 1$.

If, however, $\Delta_{\varepsilon_1 F_1 \varepsilon_2 F_2} \lesssim \gamma$, then an hyperfine uncoupling occurs. The above formulas are then no more valid since: (i) one should introduce the change produced in the eigenstates by the magnetic field (hyperfine decoupling), and (ii) one should also introduce the hyperfine coherences. In the limiting case, when the hyperfine structure is much smaller than γ, these two modifications will give for $L_F^R + L_F^{NR}$ an expression similar to (34), that is, the molecule behaves as if it did not have any nuclear spin.

Let us now go back to the polarization $\mathscr{P}$ of the fluorescence when $L_F^{NR} \ll L_F^R$. In similar conditions to those in which $\mathscr{P}_0$ was calculated previously [formula (51)], one now finds:

$$\mathscr{P}'_0 = \frac{3a_2(J', J)a_2(J', J'') \sum_{\varepsilon F} \mathscr{B}(\varepsilon F 2J')}{a_2(J', J)a_2(J', J'') \sum_{\varepsilon F} \mathscr{B}(\varepsilon F 2J') + 10a_0(J', J)a_0(J', J'') \sum_{\varepsilon F} \mathscr{B}(\varepsilon F O J')} \quad (66)$$

Note that $\sum_{\varepsilon F} \mathscr{B}(\varepsilon F O J') = 1$.

For the $v' = 43 J' = 12$ and 16 levels of I_2 in the $B^3\Pi_{0_u^+}$ level, the $\alpha^{\varepsilon}_{IF}$ can be calculated and therefore $\mathscr{P}'_0$ can be explicitly evaluated. Table II shows the results obtained.

TABLE II

POLARIZATION RATES WITH AND WITHOUT HFS

Transitions	$\mathscr{P}_0$(%)	$\mathscr{P}'_0$(%)
P(13)↑ P(13)↓	11.35	8.9
P(13)↑ R(11)↓	14.3	11.3
R(15)↑ P(17)↓	14.3	12.2
R(15)↑ R(15)↓	17.0	14.4

These diminutions of 2 to 3% of the theoretical polarizations are characteristic of the effect of hyperfine structures.

F. A Semiclassical Theory

As we have already mentioned, the rotational quantum number J can be very high for a molecule (up to more than 100). It is then a temptation to use a quasi-classical theory for the rotation while keeping a quantum mechanical description of the other parameters. As we shall see, this will not only give us simpler expressions for the fluorescence polarization but also give us the basis for a complete analysis of the optical saturation effects, at least under some conditions. We present here a theory first developed by Ducloy (1975, 1976)

1. *The "Coherent" States of an Angular Momentum*

To go to the classical limit, it is convenient to introduce the coherent state of an angular momentum J by the definition:

$$|\Omega\rangle = e^{-i\phi J_z} e^{-i\theta J_y} |J, +J\rangle \quad (67)$$

Such states are the $m_J = +J$ state rotated by an angle θ around Oy and then by an angle ϕ around Oz (Fig. 6). They are in many respects similar to the coherent states $|\alpha\rangle$ of the linear harmonic oscillator. The $|\Omega\rangle$ states form a complete set of vectors, but unless $J \to \infty$ they are not normalized or orthogonal to each other:

$$\frac{1}{4\pi} \int |\Omega\rangle \, d\Omega \langle\Omega| = \frac{1}{2J+1} \quad (68)$$

$$\langle\Omega|\Omega'\rangle = \left\{ \cos\frac{\theta-\theta'}{2} \cos\frac{\phi-\phi'}{2} + i \cos\frac{\theta+\theta'}{2} \sin\frac{\phi-\phi'}{2} \right\}^{2J} \quad (69)$$

where $d\Omega = \sin\theta \, d\theta \, d\phi$.

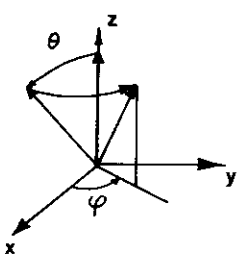

FIG. 6.

In the $|\Omega\rangle$ representation, we can project the density operator:

$$\rho(\Omega) = \langle\Omega|\rho|\Omega\rangle$$

When $J \to \infty$, *and only in this case*, $\rho(\Omega)\, d\Omega$ represents the number of molecules whose rotation axes point in the solid angle $d\Omega$ around the $\Omega = (\theta, \phi)$ direction.

It can also be shown quite easily that in this representation the operator J_z is equal to $-i(\partial/\partial\phi)$. We will not consider in this section any structure other than the Zeeman effect.

2. *The Rate Equation for* $\rho_e(\Omega)$

We now take Eq. (8) multiplied by $\langle\Omega|$ on its left side and $|\Omega\rangle$ on its right side. Assuming an isotropic relaxation rate γ, one finds:

$$\frac{d}{dt}\rho_e(\Omega) = \omega_e \frac{\partial}{\partial\phi}\rho_e(\Omega) - \gamma\rho_e(\Omega) + \frac{1}{T_p}\langle\tau'\Omega|\mathcal{E}|\tau'\Omega\rangle \tag{70}$$

$$\langle\tau'\Omega|\mathcal{E}|\tau'\Omega\rangle = \frac{(2J+1)(2J'+1)}{4\pi}\sum_i \iint d\Omega_1\, d\Omega_2 \langle\tau'\Omega|\mathbf{e}_{\lambda_0}\mathbf{D}|\tau\Omega_1\rangle \times \langle\tau\Omega_1|i\rangle\langle i|\tau\Omega_2\rangle\langle\tau\Omega_2|(\mathbf{e}_{\lambda_0}\mathbf{D})^\dagger|\tau'\Omega\rangle \tag{71}$$

At the limit $J \to \infty$, with $\Delta J = J - J'$ constant,

$$\langle\tau'\Omega|\mathbf{e}_{\lambda_0}\mathbf{D}|\tau\Omega_1\rangle = \mathbf{e}_{\lambda_0} \cdot \mathbf{n}_{\Delta J}(\Omega)\langle\Omega|\Omega_1\rangle \tag{72}$$

where

$$\mathbf{n}_{\Delta J}(\Omega) = R_\Omega(\mathbf{U}_{\Delta J}) \tag{73}$$

is the unit vector obtained by rotating by (θ, ϕ) a vector $\mathbf{U}_{\Delta J}$ which depends on the nature P, Q, or R of the transition ($\Delta J = J - J'$):

for a P transition

$$\mathbf{U}_P = -\frac{1}{\sqrt{2}}(\mathbf{U}_x + i\mathbf{U}_y)$$

for a Q transition

$$\mathbf{U}_Q = \mathbf{U}_z$$

for an R transition

$$\mathbf{U}_R = \frac{1}{\sqrt{2}}(\mathbf{U}_x - i\mathbf{U}_y) \tag{74}$$

$\mathbf{U}_x$, $\mathbf{U}_y$, and $\mathbf{U}_z$ are the unit vectors of the xyz axis. $\mathbf{n}_{\Delta J}(\Omega)$ is therefore, as expected classically, a unit vector pointing along the rotation axis of the molecule for a Q line and rotating clockwise or counterclockwise around this axis for a P or R line.

As is shown by Ducloy (1975), when $J \to \infty$:

$$\frac{1}{T_p}\langle\tau'\Omega|\mathcal{E}|\tau'\Omega\rangle = \gamma_L\, g(\Omega)\rho_i(\Omega) \tag{75}$$

where γ_L is a probability of excitation per unit time proportional to the intensity of the light beam [$\gamma_L = 1/(2T_p)$],

$$g(\Omega) = 2|\mathbf{e}_{\lambda_0}\mathbf{n}_{\Delta J}|^2$$

and $\rho_i(\Omega) = \langle\tau\Omega|\rho_i|\tau\Omega\rangle$ is the density matrix of the initial state projected on the $|\Omega\rangle$ basis. This density matrix was, until now, supposed isotropic [$\rho_i(\Omega) = 1$]. However, since later on in this section, we interpret some optical saturation effects for which $\rho_i(\Omega)$ may be anisotropic, we introduce here this more general notation.

Finally we obtain a rate equation, valid only when $J \to \infty$

$$\boxed{\frac{d}{dt}\rho_e(\Omega) = \omega_e \frac{\partial}{\partial\phi}\rho_e(\Omega) - \gamma\rho_e(\Omega) + \gamma_L\, g(\Omega)\rho_i(\Omega)} \tag{76}$$

Remarks:

i. This equation can only be obtained assuming a "broad band" excitation in the sense that the Doppler width of the absorption line is covered uniformly. This would not be the case for a single-mode laser beam. For a multimode laser, this is the case only if the Bennet holes burned by the various modes are larger than the intervals between the modes. This requires in principle that γ is larger than the mode interval.

ii. $\rho_e(\Omega)$ is only coupled to $\rho_i(\Omega)$. This means that $\rho_e(\Omega')$ is not coupled to $\rho_i(\Omega)$ if $\Omega' \neq \Omega$. This is due to the fact that for large values of J, the photon angular momentum, which is equal to 1, is negligible. The direction Ω of $\mathbf{J}$ is therefore not changed by the absorption or emission of a photon. This will prevent, for $J \to \infty$, any optical pumping of an individual molecule, as is observed for finite values of J (and especially for atoms, for which $J \sim 1$). However, since $g(\Omega)$ depends on the orientation Ω of the molecules, a statistical effect can be predicted in which an orientation results from differences in the pumping rates for different orientations Ω.

3. The Fluorescence Light

By projecting Eq. (9) on the $|\Omega\rangle$ basis, one can show that L_F is proportional to:

$$l_F = \int \rho_e(\Omega) g_F(\Omega)\, d\Omega \tag{77}$$

with

$$g_F(\Omega) = 2\,|\mathbf{e}_\lambda\, \mathbf{n}_{\Delta J}(\Omega)|^2 \tag{78}$$

where $\Delta J = J'' - J'$.

The *stationary solution* of Eq. (76) ($(d/dt)\rho_e = 0$) is the following:

$$\rho_e(\theta, \phi) = \frac{\gamma_L}{\omega_e} e^{\gamma\phi/\omega_e}\left\{\int_0^{\phi} g(\Omega)\rho_i(\theta, x) e^{-\gamma x/\omega_e}\, dx + \frac{1}{e^{-2\pi\gamma/\omega_e} - 1}\int_0^{2\pi} g(\Omega)\rho_i(\theta, x) e^{-\gamma x/\omega_e}\, dx\right\} \tag{79}$$

and an expression of l_F readily follows.

However another method of evaluation of l_F has been widely used for a long time and gives the same result while having an easier physical interpretation: (Zare, 1966; Gouedard and Lehmann, 1973).

In the resolution of Eq. (76) we at first neglect γ and γ_L. Then the *free evolution* of ρ_e is given by:

$$(d/dt)\rho_e = \omega_e(\partial/\partial\phi)\rho_e \tag{80}$$

which has as solutions:

$$\rho_e(\theta, \phi, t) = \rho_e(\theta, \phi_e + \omega_e t, 0) \tag{81}$$

This expression clearly shows that ρ_e is submitted to a Larmor precession around Oz at a speed $-\omega_e$.

We now introduce the excitation process by writing:

$$\rho_e(\theta, \phi, 0) \propto g(\theta, \phi)\rho_i(\theta, \phi) \tag{82}$$

and then we calculate l_F by integrating over Ω and over t from 0 to ∞ with a damping factor $e^{-\gamma t}$:

$$l_F = \gamma_L \int d\Omega \int_0^{\infty} \rho_e(\theta, \phi, t) g_F(\theta, \phi) e^{-\gamma t}\, dt \tag{83}$$

It is easy to show that (Ducloy, 1976)

$$\gamma_L \int_0^{\infty} g(\theta, \phi + \omega_e t)\rho_i(\theta, \phi + \omega_e t) e^{-\gamma t}\, dt$$

is exactly equal to the stationary expression of $\rho_e(\theta, \phi)$ given in (79), so that (83) and (77) give the same value for l_F.

4. Optical Nonlinear Effects

We shall now write the coupled rate equations of $\rho_i(\Omega)$ and $\rho_e(\Omega)$ under an intense illumination at the resonant optical frequency. Then not only does

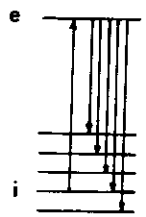

FIG. 7.

a transfer from $|i\rangle$ to $|e\rangle$ (Fig. 7) take place at a rate $\gamma g(\Omega)$, but also a similar transfer from $|e\rangle$ to $|i\rangle$ at the same rate. Hence:

$$\frac{d}{dt}\rho_e(\Omega) = \omega_e \frac{\partial}{\partial\phi}\rho_e(\Omega) - \gamma_e\rho_e(\Omega) + \gamma_L g(\Omega)\{\rho_i(\Omega) - \rho_e(\Omega)\} \tag{84}$$

γ_e is the total decay rate of the excited state. However only part of the excited molecules decays back to the $|i\rangle$ state by spontaneous emission. We shall call γ_{ei} the rate of spontaneous emission with a decay from $|e\rangle$ to $|i\rangle$.

Since some molecules are transferred by optical resonance to rotational or vibrational states of the ground electronic state other than $|i\rangle$, we must take into account the thermalization of this ground state through which state $|i\rangle$ is repopulated at a rate λ_i, but can also be depopulated at a rate γ_i. Hence, we can write the rate equation for ρ_i:

$$\frac{d}{dt}\rho_i(\Omega) = \omega_i \frac{\partial}{\partial\phi}\rho_i(\Omega) - \gamma_i\rho_i(\Omega) + \gamma_{ei}\rho_e(\Omega) + \lambda_i + \gamma_L g(\Omega)\{\rho_e(\Omega) - \rho_i(\Omega)\} \tag{85}$$

If T is the temperature of the vapor, we have a thermodynamic equilibrium without light:

$$\begin{cases} \rho_i^0 = \dfrac{\lambda_i}{\gamma_i} = Ne^{-E_i/kT} \\ \rho_e^0 = 0 \end{cases} \tag{86}$$

which does not depend on Ω. N is the total number of molecules.

Unfortunately, it is not possible to find exact stationary solutions of Eqs. (84) and (85). We can however find some simple results:

a. No Magnetic Field: $\omega_i = \omega_e = 0$. Then one has stationary solutions such as the following ones:

$$\begin{cases} \rho_e(\Omega) = \rho_i^0 \dfrac{1}{\gamma_e \tau} \dfrac{sg(\Omega)}{1 + sg(\Omega)} & (87) \\ \rho_i(\Omega) = \rho_i^0 \left\{ 1 - \dfrac{1}{\gamma_i^\star \tau} \dfrac{sg(\Omega)}{1 + sg(\Omega)} \right\} & (88) \end{cases}$$

where

$$\begin{cases} \gamma_i^\star = \dfrac{\gamma_i}{1 - \dfrac{\gamma_{ei}}{\gamma_e}} & (89) \\ \tau = \dfrac{1}{\gamma_e} + \dfrac{1}{\gamma_i^\star} & (90) \\ s = \gamma_L \tau & (91) \end{cases}$$

s is a saturation parameter proportional to the light intensity. At the limit $s \to 0$, one finds the solution of the "linear" equation (76). When $s \to \infty \rho_e(\Omega) \to (1/\gamma_e \tau)\rho_i^0$ which is isotropic. This result is different from the result obtained for low J where an anisotropy can be still found in infinitely intense light fields (Dumont, 1972 and Ducloy, 1973).

b. Infinitely High Magnetic Field. Let ω_e and ω_i become much larger than γ_e, γ_{ei} and γ_i. Then a stationary solution of Eqs. (84) and (85) can only exist if $(\partial/\partial\phi)\rho_e(\Omega) = (\partial/\partial\phi)\rho_i(\Omega) = 0$. This means that under a very fast Larmor precession ρ_e and ρ_i become independant of ϕ. One can therefore take an average over ϕ of Eqs. (84) and (85) without affecting ρ_e and ρ_i. One obtains then ϕ-independent stationary solutions:

$$\begin{cases} \rho_e(\theta) = \rho_i^0 \dfrac{1}{\gamma_e \tau} \dfrac{s\langle g(\Omega)\rangle_\phi}{1 + s\langle g(\Omega)\rangle_\phi} & (92) \\ \rho_i(\theta) = \rho_i^0 \left\{ 1 - \dfrac{1}{\gamma_i^\star \tau} \dfrac{s\langle g(\Omega)\rangle_\phi}{1 + s\langle g(\Omega)\rangle_\phi} \right\} & (93) \end{cases}$$

When $s \to \infty$, ρ_e and ρ_i go to the same isotropic limit as without a magnetic field.

From expressions (87) and (92), one can get the amplitude of the Hanle effect curves for any value of the saturation factor s. For example, one finds for the polarization rate in zero field $\mathscr{P}(s) = (I_y - I_x)/(I_y + I_x)$ the expressions given in Table III.

TABLE III

SATURATION EFFECTS ON POLARIZATION RATES

Transitions	$\mathscr{P}$	Transitions	$\mathscr{P}$
P↑ Q↓ or R↑ Q↓	$-\dfrac{(6s+9)B-9}{4s+3-(6s+3)B}$	Q↑ Q↓	$\dfrac{(6s+9)A-9}{8s-3-(6s-3)A}$
Q↑ P↓ or Q↑ R↓	$-\dfrac{(6s+9)A-9}{16s+3-(18s+3)A}$	P↑ P↓ or P↑ R↓ or R↑ R↓ or R↑ P↓	$\dfrac{(6s+9)B-9}{8s-3-(6s-3)B}$

where

$$A = \frac{1}{(2s)^{1/2}} \tan^{-1}(2s)^{1/2} \qquad B = \frac{1}{[s(1+s)]^{1/2}} \tanh^{-1}\left(\frac{s}{1+s}\right)^{1/2}$$

when $s \to 0$ these expressions tend to reach the asymptotic values given for $J \to \infty$ in Table I.

It can also be shown from Eqs. (87) and (92) that the π-polarized fluorescence changes with the magnetic field. This is a pure saturation effect since in the "linear" theory, no Hanle effect can be observed in an "incoherent" polarization. It is called a zero field saturation resonance.

5. *General Solutions*

Another way to deal with rate equations (84) and (85) is to use an iterative procedure in which $\{\rho_i(\Omega) - \rho_e(\Omega)\}$ in the last terms of these equations is at first taken equal to $\rho_i^0 - \rho_e^0$. This gives first-order stationary solutions ρ_i^1 and ρ_e^1 which can be reinjected in the $\{\rho_i(\Omega) - \rho_e(\Omega)\}$ terms and so on. This perturbation method gives interesting results if the saturation parameters is not too high.

If one wants to obtain results that are valid for any value of the magnetic field and for any value of the saturation parameter s, one can use the following procedure:

To have a physical meaning the stationary solutions $\rho_e(\Omega)$ and $\rho_i(\Omega)$ of Eqs. (84) and (85) must be periodic in ϕ with a period 2π. One can take advantage of this periodicity by expanding these density functions in Fourier series:

$$\rho_j(\Omega) = \alpha_0(\theta) + \sum_{n=1}^{\infty} \{\alpha_n^j(\theta) e^{in\phi} + \text{c.c.}\} \qquad (94)$$

where j stands for i or e.

Then, if one wants to evaluate the fluorescence signal polarized, for example, in π or in σ, one finds for a linear σ excitation:

$$I_\pi = 2\pi \int_0^\pi \alpha_0^e(\theta) h(\theta) \sin\theta \, d\theta \tag{95}$$

where $h(\theta) = \cos^2\theta$ or $\frac{1}{2}\sin^2\theta$ for Q or P–R lines, respectively, and for the anisotropic part of I_σ:

$$\Delta I_\sigma = 2\pi \int_0^\pi \mathrm{Re}\{\alpha_2^e(\theta)\} \sin^3\theta \, d\theta \tag{96}$$

Therefore, one needs only evaluate the coefficients α_0^e and α_2^e in development (94).

From Eqs. (84) and (85) it is possible to obtain recurrence relations between the α_n^i coefficients and then by numerical technique to obtain the required coefficients with any precision set in advance. This is especially possible since the lowest precision is obtained by this technique in zero magnetic field for which an exact solution has been found previously. By comparison one may therefore evaluate the precision obtained at any stage of the calculations. Figure 8 shows, for example, the shapes obtained for Hanle effect curves at various values of s, for a Q laser line and a system in which $\omega_i = \omega_e$ and $\gamma_i = \gamma_e/5$. At first the curve is Lorentzian. Then it starts to broaden and later on exhibits a dip denoting the coupling between Hanle effects in states e and i. Curiously enough, at higher intensities an additional narrow peak appears which seems to be the hexadecapolar Hanle effect due to ρ_{44}^i component of ρ_i. This was indeed observed for small values of J but was not expected when $J \to \infty$ before the calculations were made. Such very narrow resonances do not appear for P or R laser lines.

Remark: These results have been obtained in the "broad line approximation." When this is not the case, for example, when the laser is single mode or when it is multimode with the width of the Bennett holes smaller than the mode separation, then other saturation effects may occur. For instance γ_L is then dependent on the velocity v of the molecules. Hence, if one uses a linear σ polarization a single hole is burned in the velocity distribution for each mode in zero magnetic field. When a magnetic field is applied, the holes burned by the σ^+ and σ^- polarizations are shifted with respect to one another and therefore the total number of absorbing molecules is increased. This results in an increase of absorption (and consequently of the fluorescence) with the magnetic field.

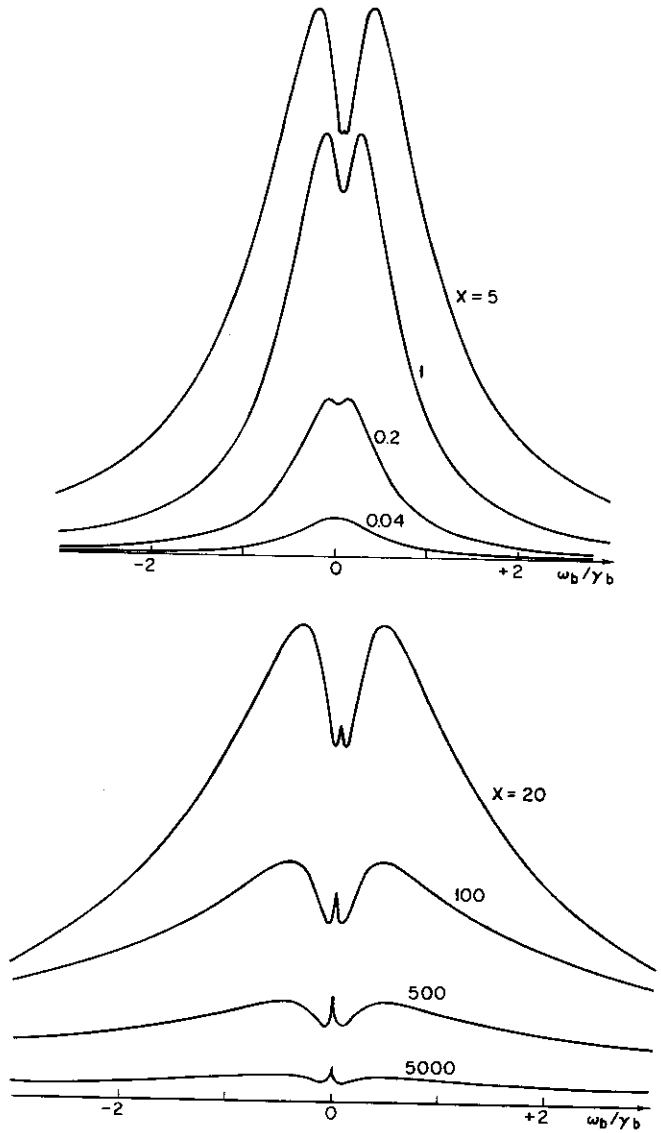

FIG. 8. Theoretical Hanle curves for various saturation parameters $x(x = s)$ (Q excitation and detection, $\omega_i = \omega_e$) (from Ducloy, 1976).

IV. Review of Molecules

In this section, we briefly review a series of diatomic molecules in which some optical pumping experiments were done. As will be seen, most of these works are concerned with very few levels, taking advantage of coincidences between laser or conventional light sources and molecular absorption. These experiments should therefore be considered as the forerunners of more systematic studies in which tunable light sources will permit a whole series of rovibronic states to be studied. Section V gives an example of such a work. Although only optical excitation is considered here, one should mention some very important works in H_2 (Pebay-Peyroula, 1974) and CN (Levy, 1973) in which electron impact excitation was used instead of optical excitation. However, such excitation is not a selective one and therefore can be applied only to light molecules for which a limited number of levels are thermally populated.

1. Na_2

Experiments on this molecule have been performed mainly by Zare and his co-workers (Demtroder *et al.*, 1969; Drullinger and Zare, 1969). Six lines of the Ar^+ laser excite the resonance fluorescence series of the Na_2 $B^1\prod_u - X^1\sum_g^+$ blue-green band system. From a spectroscopic analysis of the fluorescence light the v, J quantum numbers involved in these transitions have been measured and the set of spectroscopic constants for the $X^1\sum_g^+$ and $B^1\prod_u$ states have been revised and completed. From these constants, potential curves have been constructed for the B and X states of Na_2. This is a good example of molecular fluorescence spectroscopy.

The $v' = 10$, $J' = 12$ level of the $B^1\prod_u$ state excited by the 4765 Å laser line was studied by Hanle effect (McClintock *et al.*, 1969). The $g\tau$ product has been measured. If the g value is calculated assuming Hund's coupling case a, the lifetime can be determined. It is found to be $\tau = 6.41 \pm 0.38\ 10^{-9}$ sec. To obtain the $g\tau$ product, it is necessary to take into account the magnetic broadening of the absorption line. Although the natural line width is about 40 times smaller than the Doppler linewidth, this magnetic broadening is important in this experiment since J is equal to 12. It would be even larger for higher values of J. This difficulty is unknown in atomic physics.

Optical pumping of the $v'' = 3$, $J'' = 43$ level of the ground electronic state $X^1\sum_g^+$ was also studied using the 4880 Å Ar^+ laser line as a light source (Drullinger and Zare, 1973). The alignment of the ground state of the transition appears through a decrease of the fluorescence light polarization as the laser intensity increases. This experiment is, however, somewhat difficult to interpret due to the influence of stimulated emission. The relaxation of this alignment has been measured with addition of foreign gas. With the laser modes making holes in the Maxwell distribution, the velocity-changing collisions have been observed and studied.

Finally, cross sections for rotational transfers in the $Na_2B^1\prod_u$ state were measured by Bergmann and Demtroder (1971) and Bergmann *et al.* (1972) who found an interesting asymmetry: $\sigma(\Delta J = +1) \neq \sigma(\Delta J = -1)$. It is related to Λ doubling and a theoretical interpretation has been given by Bergmann and Demtroder (1972) and Poppe (1973).

2. NaK

Six lines of an Ar^+ laser excite the $D^1\prod$ state of NaK (Zare, 1973). By spectroscopic analysis of the fluorescence light, the (v', J') levels excited were assigned. Each rotational level of the $^1\prod$ state has two Λ components of opposite parities, and when an electric field is applied, it mixes these two states and a new Q line appears in the fluorescence spectrum. Once the Λ doubling separation was known, the excited state electric dipole moment of the molecule was determined.

3. Li_2

The work done on Li_2 is very similar to that in Na_2 but it is less detailed. The levels of the $B^1\prod_u$ state excited by six Ar^+ laser lines were assigned and rotational and vibrational collisions transfers studied. It is actually on this molecule that the asymmetry between rotational transfer probabilities $[\sigma(\Delta J = +1) \neq \sigma(\Delta J = -1)]$ was first observed.

4. OH–OD

de Zafra, Marshall and Metcalf (de Zafra *et al.*, 1971; Marshall *et al.*, 1969) have observed Hanle effect and double resonance signals in the $v' = 0$ $A^2\sum^+$ excited state of OH and OD. Optical excitation was performed by a molecular lamp. Rotational levels with $2 \leq N' \leq 5$ for OH and $2 \leq N' \leq 8$ for OD were excited. For these levels the g factors and the $g\tau$ products were measured. The g factors are in good agreement with what was expected from a pure case b coupling. The lifetime τ is almost the same in the whole set of investigated rotational levels. It is found to be $\tau = 660 \pm 22$ nsec for OH and $\tau = 598 \pm 20$ nsec for OD.

German, Bergeman, Weinstock and Zare (German and Zare, 1969; Weinstock and Zare, 1973; German *et al.*, 1973) have used atomic lines to excite

the $v' = 0$, $N' = 2$, $J' = 3/2$ level of the OH $A^2\sum^+$ state and the $v' = 0$, $N' = 1$, $J' = 3/2$ level of the OD $A^2\sum^+$ state. Like de Zafra *et al.* they perform Hanle effect and double resonance experiments, and they obtain g factors and lifetimes, in reasonable agreement with those of de Zafra *et al.* Zare and his co-workers also observed high field level crossing (HFLC) between hyperfine sublevels of OD: as was mentioned in Section II, the high values of J make such HFLC very weak and therefore difficult to observe. However in this experiment $J = 3/2$, so that such crossings are not too weak. From the positions of the crossings, the hyperfine structure of OD $A^2\sum^+$ $v' = 0$, $J' = 3/2$ was completely determined. Then, the dipole moment in the excited state was deduced from the shift of those crossings in the presence of an electric field parallel to the magnetic field.

Sutherland and Anderson (1973) have used the delayed coincidence technique in conjunction with an interrupted rf discharge through water vapor to measure lifetimes of individual rotational levels in the $A^2\sum^+$ state of OH. They report values of τ for $0 \leq N' \leq 29$ in $v' = 0$, and $0 \leq N' \leq 20$ in $v' = 1$. In $v' = 0$, τ increases from $\tau \approx 0.75$ μsec for $N' \lesssim 5$ to $\tau = 1.1$ μsec for $N' \approx 23$, then for higher values of N', it suddenly decreases to 0.1 μsec for $N' = 29$. Such observations agree reasonably well both with Hanle effect measurements of de Zafra *et al.* (for $N' \lesssim 5$) and with the results of Bennett and Dalby (1964) ($\tau \approx 1$ μsec), the lifetime measured by these authors corresponding to an average over several N' levels between 10 and 20. Similar results were obtained in the $v' = 1$, the decrease in the lifetime being observed above $N' = 14$. This increase of τ with N' is due to the variation of the transition moment with the internuclear distance. The sudden decrease is attributed to a second-order predissociation effect due to a dissociative $^4\sum^-$ state. The perturbations are probably spin–orbit, spin–spin, and spin–rotation interactions.

Recently, using a N_2 pumped dye laser, German (1975) measured by the decay technique the lifetimes for $1 \leq N' \leq 8$ in the $v' = 0$ $^2\sum^+$ state of OH and for $0 \leq N' \leq 9$ in the $v' = 0$ $^2\sum^+$ state of OD. Like Sutherland he found a slight lengthening of τ as N' increases. For low N' values he measured $\tau \approx 690 \pm 8$ nsec in slight disagreement with Sutherland. It seems that the measurements of German are the most precise. However, Brophy *et al.* (1974) using also a pulsed dye laser excitation measured $\tau \approx 788 \pm 12$ nsec for $N = 1$.

5. CS

The $A^1\prod$ state of CS can be excited by various atomic lines. At first, the spectral line MnII 2576, 1 Å pumps the R(7) transitions of the 0–0 band. In this level, Silvers *et al.* (1970) observed the zero electric field level crossing

signal and the Hanle effect. They also observed the level crossings that appear with both an electric and a magnetic field. These experiments give a good estimate of the lifetime τ, the dipole moment μ, and the Λ doubling δ. Then they performed double resonance experiments in zero and nonzero magnetic fields which provide precise measurements of μ and δ.

On the same transition, Silvers and Chiu (1972) studied in details the width of the Hanle effect as a function of pressure. They observed a narrowing of the linewidth as the pressure increases. This is attributed to radiation trapping. To our knowledge, it is the only observation of "coherence narrowing" by radiation trapping in molecules. Indeed, in molecules the light reemitted corresponds to transitions not only to the $v'' = 0$ level of the ground state but also to $v'' = 1, 2, 3, \ldots$, etc. Since many of these states (for high v'' values) are not thermally populated, no strong reabsorption takes place. However, in the case of the $v' = 0$ level of the $A^1\prod$ state of CS, the Franck–Condon factors are such that the emission takes place mainly toward the $v'' = 0$. The Pb 2577, 2 Å spectral line also excites the 0–0 Q(12) transition and the Hanle effect was observed.

The Pb 2446, 2 Å line pumps the 2–0 P(7) transition. The Hanle effect was observed as well as its pressure broadening. There is no radiation trapping in this case since from the $v' = 2$ state, the emission probabilities are equally distributed toward the $v'' = 0, 1, 2, 3, \ldots$ states.

For these three excited levels, the g factors can be theoretically calculated in the "case a" coupling scheme, by taking into account the mixing of the $A^1\prod$ state with neighboring $a'^3\sum^+$ and $k^3\prod$ states. Hence, from the zero vapor pressure $g\tau$ product, the lifetime can be deduced for these three levels.

6. BaO

The $A^1\sum$ and $X^1\sum$ states of BaO (Field *et al.*, 1972a,b, 1973) have been studied by microwave optical double resonance. The transition $X^1\sum$–$A^1\sum$ is strongly saturated by an Ar^+ laser or a cw dye laser. Microwave transitions can then be induced between adjacent rotational levels of the excited or fundamental state. The resonance is detected through a change in the intensity of the rotationally unresolved photoluminescence. About twenty transitions were observed and the constants B_v were deduced.

The $A'^1\prod$ state of BaO have been spectroscopically studied (Pruett and Zare, 1975) using a pulsed nitrogen-laser pumped dye laser. The weak long-lifetime A'–X fluorescence is separated from the strong short-lifetime A–X fluorescence by delaying the observation of the A'–X emission until the A–X emission dies away. This may be called "lifetime separated spectroscopy." The lifetime of the $A'^1\prod$ state is found to be 9 ± 1 μsec, and vibrational and rotational constants are deduced.

7. S_2

The ZnI 3075, 9 Å and the CdI 3261, 1 Å atomic lines (Meyer and Crosley, 1973) excite respectively the 4–1 P(41) $B^3\sum_u^- - X^3\sum_u^-$ and the 3–3 P(43)$B^3\sum_u^- - X^3\sum_u^-$ transitions of the S_2 molecule. For these two levels, the Hanle effect has been observed. The g factor of the B state was then calculated using a nonzero spin–spin interaction constant, and the lifetimes were deduced for the two levels from the Hanle effect signal.

8. NS–PN–CO

For these three molecules (Wells and Isler, 1970; Silvers and Chiu, 1974; Moeller *et al.*, 1975), all the rotational levels of one band were excited using a molecular lamp. Fluorescence and Hanle effect were then observed. The results were analyzed by making some assumptions about the contribution of different rotational levels and by theoretical evaluation of their g factors. A radiative lifetime estimate was then deduced.

9. NO

The CdII 2144 Å and the TeI 2147 Å spectral lines excite, respectively, the $v' = 1$, $N' = 13$ and the $v' = 1$, $N' = 10$ levels of the $A^2\sum^+$ state. On these two transitions, Hanle effect measurements were performed and permit one to deduce the product $g\tau$ (Gouedard and Lehmann, 1970; Gouedard, 1972; German *et al.*, 1971; Weinstock *et al.*, 1972). An optical rf double resonance (Weinstock *et al.*, 1972) confirmed that the angular momentum coupling scheme is very close to Hund's case $b_{\beta J}$. Using g values appropriate to this coupling scheme, the radiative lifetime was determined. It appears to be the same for both levels: $\tau \approx 180 \pm 20$ nsec.

The $v' = 3$, $N' = 1$, $J' = 3/2$ level of the $A^2\sum^+$ state can be excited by the SeI 1961 Å spectral line. Using this coincidence, Bergeman and Zare (1974) observed the zero field ρ-doubling hyperfine transition by optical rf double resonance. They also measured the Stark shift of one of the resonance component. They obtained by this technique the ρ-doubling constant, the hyperfine structure parameters, and the dipole moment. Their results are in agreement with theoretical calculations except for the dipole moment. Speculations are given on possible explanations of this discrepancy.

10. Se_2

Various lines of a Kr^+ and Ar^+ laser excite the $B^3\sum_u^- - X^3\sum_g^-$ band system of the Se_2 molecule. The spectroscopic analysis of the fluorescence spectra

and the assignment of the excited levels have been made mainly by Barrow *et al.* (1970) and Yee and Barrow (1972). Recently, Dalby *et al.* reported a Hanle effect measurement on three rotational levels of the $B^3\sum_u^-(1u)$ state (Dalby *et al.*, 1975). The $g\tau$ product, together with the sign of the g factor, has been determined for each of the levels. Very recently, Gouedard and Lehmann (1975), and Gouedard (1976) using the technique of resonance in modulated light beam have done a series of measurements of the g factor for all levels excited by the Ar^+ and Kr^+ laser. These experiments together with complementary Hanle effect provide g and τ for about 10 levels in the $B^3\sum_u^-$ state. Interpretation of the results is on its way by taking into account the different coupling scheme possibilities in a $^3\sum_u^-$ state and the possible perturbations.

11. CN

Very interesting level anticrossing experiments and optically detected gas phase magnetic resonance spectrum were observed on the CN radical (see Levy, 1972; Cook and Levy, 1972, 1973a, b). We won't describe in detail these experiments since they are beyond the scope of this paper, the excited states being populated by chemical reaction. However, the lifetime of the fifteen first rotational levels of the $v' = 0 B^2\sum$ state of CN were measured by the decay technique following pulsed dye laser excitation (Jackson, 1974). The lifetime is the same for all investigated levels except for the $N' = 4$ which is perturbed by the $A^2\prod$ state.

V. Iodine Investigations

We now present a brief survey of the results that laser investigation has given in the excited states of I_2. The precise choice of this molecule is due to several reasons.

The B state of iodine and the visible fluorescence due to the $B \rightarrow X$ transition have been studied for more than half a century by many different techniques. The spectroscopic knowledge of this transition is therefore quite good, and the most recent papers (Singh and Tellinghuisen, 1973; Leroy, 1970; Brown *et al.*, 1973) give a clear assignment of most of the absorption lines. This is a favorable condition for working with laser excitation since it provides a precise identification of the excited levels. Furthermore, since I_2 is a heavy molecule, the absorption spectrum is dense, and only rough or no results were obtained as long as the studies were carried out with wide band excitation. This explains why many parameters have been only recently

measured with accuracy and why at the same time several problems regarding the B state have been understood.

We will present here the different kinds of results that were obtained.

A. Hyperfine Structures of the B ↔ X Transitions

The techniques that were used are beyond the scope of this paper. However, the large number of results thus obtained deserve a short review.

Saturated absorption spectroscopy was extensively used on I_2, the laser sources being at first the Ar^+, Kr^+, HeNe lasers (Hanes and Dahlstrom, 1969; Hänsch *et al.*, 1971; Levenson and Schawlow, 1972; Hanes *et al.*, 1971) and now dye lasers (Couillaud and Ducasse, 1975).

Hyperfine structures of the excited and ground states are due to a coupling of the nuclear electric quadrupole with the molecular electric field gradient and also of the nuclear magnetic moment with the rotation of the molecule (Kroll, 1969). The same type of Hamiltonian applies for the excited and ground states:

$$\mathcal{H} = \sum_{i=1}^{2} \left(eQq \frac{3(\mathbf{I}_i \cdot \mathbf{J})^2 + \frac{3}{2}\mathbf{I}_i \cdot \mathbf{J} - (\mathbf{I}_i^2)(\mathbf{J}^2)}{2J(2J-1)2I_i(2I_i-1)} + C\mathbf{I}_i \cdot \mathbf{J} \right) \qquad (97)$$

the values of C, eQq, and J being different in the excited and ground states. As the nuclear spin is 5/2 for each of the ^{127}I nuclei, the number of hyperfine sublevels is 15 for para states and 21 for ortho states. The number of intense hyperfine transitions is equal to the number of levels, since an approximate selection rule $\Delta F = \Delta J$ holds. This selection rule is not strict, and some $\Delta F = 0$ transitions have a noticeable intensity if J is not too high.

The first experiments gave only the $\Delta F = \Delta J$ transitions from which can be deduced $\Delta(eQq) = eQq' - eQq''$ and $\Delta C = C' - C''$ (Kroll, 1969). If J is not too high, it is also possible to measure directly eQq although with a large error bar. The observation of $\Delta F = 0$ transitions has given precise values of both eQq'' and eQq' (Sorem *et al.*, 1972). This was made by intermodulated fluorescence, a technique related to saturated absorption spectroscopy.

Another experiment that gives the same kind of information is a measurement of the fluorescence excited on a molecular beam by a tunable monomode laser. The laser may then be of low intensity, and therefore no power broadening is produced. Since a molecular beam is used, no pressure broadening appears either (Hackel *et al.*, 1975). The line positions are precisely determined by an heterodyne technique, the error bar being 5 kHz. It is then possible to measure with precision eQq', eQq'', $C' - C''$, but also the tensor spin–spin interaction first introduced by Bunker and Hanes (1974) for

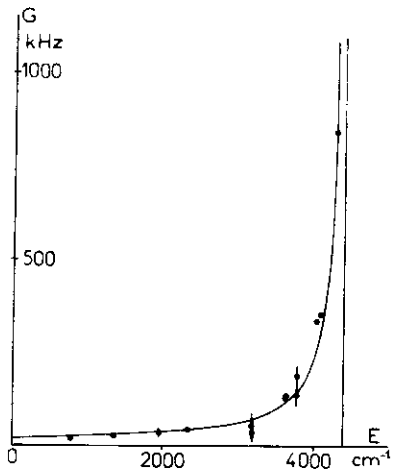

FIG. 9. Variation of the quantity $G = (C' - C'')/g_I$ as a function of the vibrational energy E. The solid curve is given by 87, 300/(4380-E) (the choice of G rather than $C' - C''$ is necessary in order to compare the results obtained with different isotopic species).

I_2. Hackel *et al.* (1975) have obtained a slightly better agreement by introducing scalar spin–spin and nuclear magnetic octupole interactions.

A survey of $\Delta(eQq)$ and $\Delta(C)$ values is presented by Levenson and Shawlow (1972). Figure 9 shows the drastic variation of $\Delta(C)$ with the vibrational excited state; such a variation appears for the Landé factor as well and is discussed later in this section.

B. Landé Factors

The first experiments were made by Hanle effect using Ar^+, Kr^+, and HeNe laser line (Broyer and Lehmann, 1972; Broyer *et al.*, 1975a). We shall present at first a simplified theoretical evaluation of these Landé factors: the rotational Landé factors for a molecular state without electronic angular momentum ($\Omega = 0$) are generally interpreted by second-order perturbation theory.

The perturbation Hamiltonian is:

$$V = V_1 + V_2 + V_3$$

$$V_1 = -\frac{\hbar^2}{\mu r^2}\mathbf{J} \cdot (\mathbf{L} + \mathbf{S})$$

being the off diagonal part of the rotational Hamiltonian

$$B(\mathbf{J} - \mathbf{L} - \mathbf{S})^2$$

$$V_2 = \mu_B \mathbf{H} \cdot (\mathbf{L} + 2\mathbf{S})$$

being the electronic Zeeman Hamiltonian

$$V_3 = a\mathbf{I} \cdot \mathbf{L} + \cdots$$

being the hyperfine Hamiltonian. L and S are the electronic angular momenta; $\mathbf{I} = \mathbf{I}_1 + \mathbf{I}_2$.

The second-order perturbation term of the energy of a given $|\tau, v, J, M_J\rangle$ state is:

$$\Delta E_{\tau, v, J, M_J} = \sum_{\alpha} \frac{|\langle \alpha | V_1 + V_2 + V_3 | \tau, v, J, M_J \rangle|^2}{E_{\tau, v, J, M_J} - E_{\alpha}} \tag{98}$$

Let us now look to the three cross products that appear when one calculates the squared matrix element:

(1) the $V_1 V_2$ term is proportional to $\mu_B(\hbar^2/\mu r^2)\mathbf{H} \cdot \mathbf{J}$ and represents the Zeeman effect $g_J \mu_N \mathbf{J} \cdot \mathbf{H}$,

(2) the $V_2 V_3$ term is proportional to $a\mu_B \mathbf{H} \cdot \mathbf{I}$ (if one only takes the first term of V_3) and represents the chemical shift $g_1 \mu_N \mathbf{I} \cdot \mathbf{H}$, and

(3) the $V_3 V_1$ term is proportional to $(a\hbar^2/\mu r^2)\mathbf{I} \cdot \mathbf{J}$ and represents the magnetic hyperfine structure $C'\mathbf{I} \cdot \mathbf{J}$.

Since the matrix elements of the various angular momenta involved are all of the same order of magnitude, one can show that the following approximate relations hold:

$$\frac{g_J \mu_N}{\mu_B B_{v'}} \sim \frac{g_1 \mu_N}{a\mu_B} \sim \frac{C'}{aB_{v'}} \tag{99}$$

where $B_{v'}$ is the rotational constant of the v' state.

These relations are rather well verified by the experimental results.

The magnetic Hamiltonian of the molecule can now be written in the form:

$$\mathscr{H} = -g_J \mu_n \mathbf{J} \cdot \mathbf{H} - (g_I + g_1)\mu_n \mathbf{I} \cdot \mathbf{H} \tag{100}$$

From this Hamiltonian, it is possible to calculate theoretical Hanle curves, using the Landé factors of the various hyperfine levels given by formula (53). As already mentioned, the Hanle effect curve is not Lorentzian if these Landé factors are very different from one another. This happens if $|g_J| \lesssim (g_I + g_1)(I/J)$. In this case, the shape of the Hanle curve gives the value of $g_J/(g_I + g_1)$. Then the width gives the value of $g_J \tau$. If one neglects g_1, g_J and τ can be obtained independently since g_I is known ($g_I = 1.12$).

However, in many cases, $g_J > (g_I + g_1)(I/J)$, and there is no strong deviation from a Lorentz shape. Then, the Hanle effect gives only the value of $g_J \tau$.

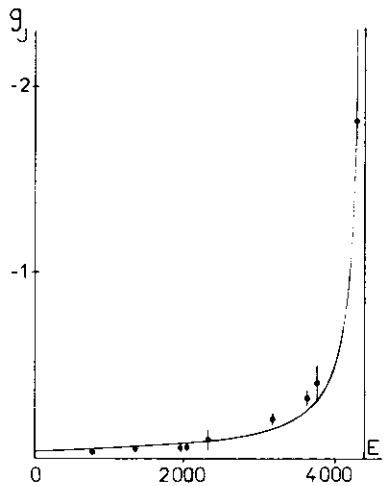

FIG. 10. Rotational Lande factors g_J as a function of the vibrational energy E measured in cm^{-1}. The solid curve is given by 190/(4380-E).

It is then necessary to obtain either g_J or τ directly. Resonances in a modulated light beam have been used to measure g_J. For example, in the $v' = 62$, $J' = 27$ level, the full spectrum of hyperfine Zeeman resonances was obtained. By fitting the position of these resonances, it became clear that g_1 could not be neglected and should be taken equal to 3.4 ± 0.5 for this level. This value of g_1 is in good agreement with the relation (99). This theory then permits to evaluate g_1 for other levels that were studied and to correct the value of g_J if necessary.

The resulting values of g_J are plotted on Fig. 10. The large variation with v is similar to that of $\Delta C = C' - C''$, as was predicted by Eq. (99). The experimental results for g_J and ΔC are well represented by $[1/(E_{v'} - E_I)]$ dependence (solid curves of Figs. 9 and 10), where E_I is the energy of the B state dissociation limit, and $E_{v'}$ the vibrational energy of the considered level. This suggests that the main perturbing level α [Eq. (98)] is a dissociative state sharing the B state dissociation limit.

Quantum-beat experiments (Wallenstein *et al.*, 1974) give results for the Landé factors in fair agreement with those of Fig. 10.

C. Electric Anisotropic Polarizability

Zero field Stark level crossing effect was performed on the $B^3\prod_{0_u^+}$ state using the 5145 Å Ar^+ laser excitation (Dalby *et al.*, 1973). The experiment can be easily interpreted in terms of the anisotropic polarizability.

D. Predissociations, Lifetimes, and Collisions

Different methods have been used recently to prove that the B state is naturally predissociated (Chutjian *et al.*, 1967; Wasserman *et al.*, 1968; Chutjian and James, 1969; Chutjian, 1969; Brewer and Tellinghuisen, 1972). It has also been known for a long time (van Vleck, 1932) that it is subject to a strong magnetic predissociation. Let us give here the present theory of these two predissociations.

We shall consider here (Broyer *et al.*, 1973; Vigué *et al.*, 1975) that both of them are due to the *same dissociative state* which must have a 1u symmetry. The perturbing Hamiltonian V is the same that was used in the theory of Landé factors; however V_3 is generally considered as negligible. The probability of predissociation is then given by the Fermi golden rule:

$$\gamma_p = \frac{2\pi}{\hbar}\rho(E)\sum_D |\langle B^3\Pi_{0_u^+} v, J, M_J | (V_1 + V_2) | D\rangle|^2 \qquad (101)$$

$|D\rangle$ stands for the final dissociative state.

The development of γ_p gives rise to three terms:

(1) one in V_1^2: $\alpha_v^2 J(J+1)$, the pure *natural* predissociation
(2) one in V_2^2: $\beta_V^2[(J^2 + M_J^2)/4J^2]H^2$, the pure *magnetic* predissociation
(3) an *interference term* between V_1 and V_2:

$$\sqrt{2}\alpha_V \beta_V M_J H$$

The lifetime τ of an energy level is therefore given by:

$$\frac{1}{\tau} = \gamma = \gamma_r(v) + \alpha_v^2 J(J+1) + \beta_v^2 \frac{J^2 + M_J^2}{4J^2} H^2 + \sqrt{2}\alpha_v \beta_v M_J H \qquad (102)$$

where γ_r is the probability of radiative decay.

τ is therefore dependent of all the quantum numbers of the state *including* M_J. This should affect the theory of Hanle effect, except if its field scale is much smaller than that of magnetic predissociation (usually, it is the case in iodine).

1. Natural Predissociation

If the magnetic field is zero, the only predissociation effect is the natural predissociation and:

$$\gamma = \gamma_r(v) + k_v J(J+1) \qquad (103)$$

where $(k_v = \alpha_v^2)$.

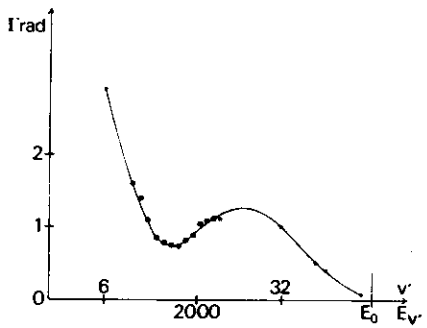

FIG. 11. Radiative decay rate in the B state versus the vibrational energy.

This expression has recently been experimentally verified in detail by fluorescence decay, using a very narrow band pulsed dye laser (Broyer *et al.*, 1975b). Measurements of γ for different v and J values have proved the validity of this formula; some values of k_v have been deduced, and a very large variation of γ_r with v observed (the variation of γ_r with v was already known through direct decay experiments using a few angstrom wide pulsed dye laser (Sakuraï *et al.*, 1971; Capelle and Broida, 1973). These results appear in Figs. 11 and 12.

2. Magnetic Predissociation

Pure magnetic predissociation has also been studied in detail; its consequence is a decrease of the fluorescence intensity when a magnetic field is applied. Experiments have given values of β_V^2 (Degenkolb *et al.*, 1969;

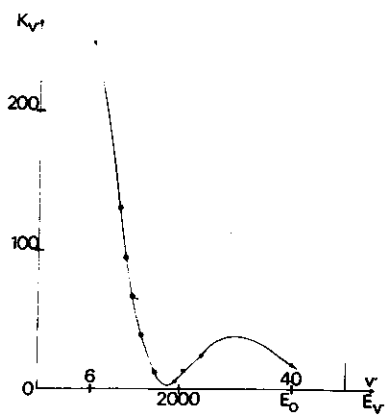

FIG. 12. $k(v)$ versus the vibrational energy in the B state.

Chapman and Bunker, 1972). The H^2 magnetic field dependence of the lifetime was proved by direct lifetime measurements (Capelle and Broida, 1972). The vibrational dependence of β_v^2 and k_v should be nearly identical since the Franck–Condon factors are the same. This is in fair agreement with the experimental results.

3. *Interference Effect Between the Two Predissociations*

It is clear that this effect gives a different lifetime for Zeeman sublevels of opposite M_J values. Therefore, a *strong orientation* of the excited molecule is produced and appears as a circular polarization of the fluorescence. Circular polarization rates up to 30% have been observed. For a given level, this rate is proportional to α_v. It is therefore possible to deduce $k_v = \alpha_v^2$ from this experiment, even if k_v is quite small. Some values of k_v have been obtained by this method and are shown on Fig. 12.

Moreover, lifetime measurements performed on circularly polarized fluorescence light (Fig. 13) are in nice agreement with formula (102); it is interesting to note that for each polarization (σ^+ or σ^-) the lifetime is maximum for nonzero values of the magnetic field (Vigué *et al.*, 1975).

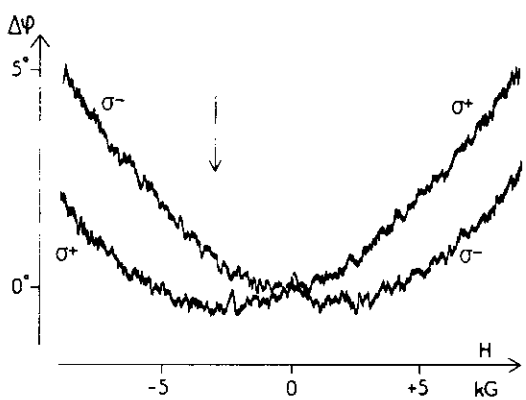

FIG. 13. Lifetime measurements obtained by the phase shift technique on σ^+ and σ^- fluorescence light. The curves show the variations $\Delta\varphi$ of the phase shift as a function of the magnetic field. The arrow points in the direction of increasing lifetimes.

E. Collision Effects

All the considerations above suppose that the experiment is made at zero vapor pressure. If it is not the case, the lifetime is reduced and various collision cross sections can be measured.

The variations of the lifetime with the pressure give the cross section for destruction of the population σ_0 (Sakuraï *et al.*, 1971; Capelle and Broida, 1973; Paisner and Wallenstein, 1974; Broyer *et al.*, 1975b). By an analysis of the fluorescence spectrum as a function of pressure, it is possible to measure the collision cross section for transfer from one energy level to another (Brown and Klemperer, 1964; Steinfeld and Klemperer, 1965; Steinfeld, 1967, 1970; Kurzel, 1970; Kurzel *et al.*, 1971, 1972).

Finally, the width of the Hanle effect as a function of the pressure gives the cross section for destruction of the alignment $\sigma^{(2)}$ (Broyer *et al.*, 1975a). Direct polarization measurements give the same kind of information (Kurzel and Steinfeld, 1972). All these quantities have been measured with I_2 as a collision partner, but some experiments were done with the following gases: He, Ne, Ar, Kr, Xe, H_2, D_2, N_2, O_2, NO, SO_2, CO_2, CH_3Cl, NH_3, etc.

F. Stepwise Excitation of I_2, E State

A stepwise excitation of the I_2, E state was performed (Rousseau and Williams, 1974). The excitation from X to B was obtained with a tunable rhodamine-6G dye laser and the transition from B to E by a uv line of a krypton ion laser. The fluorescence spectrum thus obtained was the first observation of Condon "internal diffraction" resulting from a single vibronic state. From this fluorescence spectrum, it was possible to measure precisely the equilibrium internuclear distance of the E state and to deduce the qualitative variation of the B ↔ E transition moment as a function of the internuclear distance (Tellinghuisen, 1975).

It is important to note that stepwise excitation could be applied to many molecules, and therefore optical pumping methods could be used for investigation of states that cannot be reached by single-photon excitation.

VI. Conclusion

In this paper, several optical techniques have been presented through which one can make measurements of excited states molecular parameters. A summary of the kinds of problems that can be studied by these methods would include the following:

(a) Measurements of molecular parameters: g_J, τ, g_1, C, etc. Such measurements may be of great help in the analysis of perturbations between electronically excited states.

(b) Predissociations and other dynamical effects, such as, simple chemical reactions. It should be emphasized that optical pumping is especially well adapted to the study of the angular aspect of these phenomena. For example,

photodissociation, using polarized light may produce an alignment of the remaining molecules (Dehmelt and Jefferts, 1962; Ling and Wilson, 1975). A detailed analysis of such an effect can give much valuable information on the dissociation process itself.

(c) Relaxation of electronically excited molecules. Since the lifetimes in the excited states are generally very short, one can study very fast relaxation processes that would be difficult to observe in the ground state. Among these processes, the disorientation of molecule, that is, relaxation between M_J sublevels, is of special interest and can be studied by such techniques.

(d) Laser–vapor interaction and saturation effects. The special properties of laser light have already been studied in many details. However, some problems still exist for which no complete theoretical understanding exists. The great number of molecular absoprtion lines makes it possible to study any experimental situation that one can imagine. Already several saturation effects have been observed and understood only in the case of molecular absorption (or dispersion).

Finally, one should mention further some of these techniques that have been either only briefly mentioned or omitted in this article:

(a) Two-step absorption has already been observed in molecules (Rousseau and Williams, 1974) and may become a very important technique both to study highly excited levels of the same symmetry as the ground state and also to measure molecular parameters in intermediate states through an analysis of the fluorescence spectrum reemitted.

(b) Two-photon excitation is a technique that has recently been developed to eliminate the Doppler width (Cagnac, 1975). Indeed, if the two photons simultaneously absorbed travel in opposite directions, no Doppler effect is observed whatever the speed of the molecule is. Although the molecules are somewhat less favorable than the atoms in that respect, due to the weaker oscillator strength and the fact that the nonresonant intermediate energy level is replaced by a set of rovibronic levels, two-photon absorption has already been observed in molecules (Bray *et al.*, 1974; Bischel *et al.*, 1975) and may become an interesting way to overcome the Doppler broadening of optical transitions.

Finally, we would like to mention the possibility of optical pumping of the ground state. Orientation and alignment of the ground state have already been observed by several authors (Drullinger and Zare, 1969, 1973; Ling and Wilson, 1975), but they were obtained by anisotropic excitation of this level. Similarly, ortho-para pumping was obtained by Letokhov (Bazhutin *et al.*, 1973) by selectively photodissociating the ortho or para molecules of I_2. This latter technique has also been demonstrated with different isotopes and might be used for isotope separation. However, it is also possible to obtain

an optical pumping of the Kastler type in which the molecules are first excited and then repopulate a vibrationally excited state of the ground electronic states which was initially empty. Although rather weak, such an effect has already been observed by one of the authors. Since in the electronic ground state, the relaxation times can be much longer than in the excited states, such techniques may be useful to study, as in atoms, very weak relaxation processes.

It is therefore reasonable to estimate that in the next few years, molecular optical pumping with its wide variety of different possibilities, in close connection with standard high resolution molecular spectroscopy, will be of great help for a better understanding of excited states of simple molecules as well as relaxations of molecules in the excited or ground electronic level.

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