Molecular Level-Crossing Spectroscopy*

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Classical and quantum formulations are presented for the effects of level crossings on the angular distribution of molecular resonance fluorescence. It is shown that a study of the "molecular Hanle effect," or its electric-field analog, may be used to determine the product of the radiative lifetime $\tau_{v'J'}$ with the magnetic moment μ_m, or the electric dipole moment μ_e, respectively, for the (v', J') excited state. The theory is developed for diatomic or polyatomic molecules characterized by symmetric-top wavefunctions. Order-of-magnitude estimates are performed, and the observation of zero-field molecular level crossings appears to be quite feasible.

INTRODUCTION

LEVEL-crossing spectroscopy[1] is a technique which exploits the interference phenomena that can occur in resonance fluorescence when two or more energy levels are nearly degenerate (i.e., within a natural linewidth of each other). So far it has been applied exclusively to resonance light scattering from atomic systems. If the Zeeman levels of an excited atomic state are distinct (i.e., separated by several natural linewidths), their contribution to the atomic resonance fluorescence may be treated independently by summing over the population of each excited level. However, when the Zeeman levels are nearly degenerate, we must take account of the existence of phase relations between the Zeeman levels (coherence) which have been "locked" into the excited state by its particular mode of formation. This results, in general, in interference terms arising from the "crossed" levels which alter the angular distribution of the resonance fluorescence while preserving the total resonance fluorescence rate.

The most commonly known example of this effect is the magnetic depolarization of atomic resonance fluorescence, the so-called Hanle effect.[2] In the absence of an externally applied field (zero field), the Zeeman levels of an excited atomic state are degenerate. These levels may then be excited coherently, for example, by a unidirectional beam of polarized light. If the excited state is undisturbed, it radiates to the ground state with a characteristic time constant for decay (the natural lifetime), and the fluorescence radiation is observed to be polarized much in the same way as the exciting light beam. When a magnetic field is applied along an arbitrary direction to this excited state, the degeneracy between the magnetic sublevels is removed. The coherence in general is partially destroyed and

the resonance fluorescence is depolarized. By measuring the change in the scattered intensity at a particular angle with magnetic-field strength, one can determine the natural radiative lifetime from a knowledge of the magnetic moment of the excited-state Zeeman levels and from the magnetic-field-dependent width of the resonance fluorescence intensity. This Hanle-effect technique is one with a long history, but it is presently experiencing an active renaissance in the accurate determination of atomic oscillator strengths.[3] Its increasing popularity and acceptance stems, in part, from the fact that absolute lifetimes may be determined without knowledge of the density of scatterers (i.e., no absolute intensity measurements need to be made).

It is the purpose of this paper to explore the applicability of level-crossing spectroscopy to molecular resonance fluorescence. Unlike most atoms, there is a wide class of molecular excited states which have permanent electric dipole moments. Under favorable conditions, we show that the magnitude of the electric dipole moment may be obtained by observing the change in the angular distribution of the molecular resonance fluorescence due to zero-field level crossings.

We present first a simple theory of the molecular Hanle effect, and its Stark-field analog, in terms of purely classical concepts. We do this in order to give as clearly as possible the physical basis for the level-crossing spectroscopy of molecules. The model we choose is based on the classical interpretation of the Hanle effect developed by Eldridge,[4] combined with the classical picture developed by Vavilov and Levshin[5] to explain the degree of polarization of molecular resonance fluorescence.

We develop next a generalized quantum treatment with the aid of a formula first derived by Breit,[6] and later rederived by Franken[7] and by Rose and

[1] F. D. Colegrove, P. A. Franken, R. R. Lewis, and R. H. Sands, Phys. Rev. Letters **3**, 420 (1959).
[2] W. Hanle, Z. Physik **30**, 93 (1924).

[3] For a review of early Hanle-effect measurements see A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, Cambridge, England, 1934). For more recent work see for example W. W. Smith and A. Gallagher, Phys. Rev. **145**, 26 (1966), and references cited therein.
[4] J. A. Eldridge, Phys. Rev. **24**, 234 (1924).
[5] S. I. Vavilov and V. L. Levshin, Z. Physik **16**, 135 (1923).
[6] G. Breit, Rev. Mod. Phys. **5**, 91 (1933).
[7] P. Franken, Phys. Rev. **121**, 508 (1961).

Carovillano,[8] to describe the interference effects in resonance fluorescence excited by broad-band optical pumping. We apply this formula with suitable modifications to molecules, the energy levels of which are described by symmetric-top wavefunctions to calculate the resonance fluorescence intensity (at a fixed angle) as a function of the total angular momentum J of the molecule. We find that the quantum formulation differs appreciably from the classical formulation at low rotational angular momentum, but rapidly approaches the classical expression with increasing J. Following a comparison between the classical and quantum treatments, we discuss the experimental feasibility of molecular level-crossing spectroscopy. The well-known resonance fluorescence series of Na_2 is considered as a prototype example.

THEORY

Classical Treatment

Consider a beam of polarized light incident upon a collection of randomly oriented molecules in the gas phase. Let the frequency of the light source correspond to the transition frequency between two energy states of the molecule. We assume that we can replace the electric dipole transition moment of a molecule by a classical Hertzian dipole oscillator pointed in the same direction and attached rigidly to the molecular framework. The probability of absorption of light by the molecule is proportional then to the square of the component of the electric vector ε along the axis of the classical dipole oscillator $\mathbf{\mu}$, i.e., $| \mathbf{\mu} \cdot \varepsilon |^2$. Thus, the transition dipole moments of the absorbing molecules are no longer expected to be isotropically distributed throughout the medium but will have a preferential direction of orientation along the electric vector ε of the light beam.

The extent of this initial directional alignment is readily formulated in terms of the Euler angles α, β, γ which relate the rotating, "molecule-fixed" set of coordinate axes xyz to the nonrotating, "space-fixed" system with axes parallel to the specified laboratory directions XYZ as pictured in Fig. 1. For both systems the origin is chosen to coincide with the center of mass of the molecule. The angles β, α are the ordinary polar coordinates θ, ϕ which locate the z axis relative to the Z axis and the XY plane, and γ is an azimuthal angle about the z axis.[9] Since all orientations of the molecule are equally likely,

$$(1/8\pi^2) d\alpha \, \sin\beta d\beta d\gamma \qquad (1)$$

is the (normalized) probability of an orientation with Eulerian angles in the range α, β, γ to $\alpha+d\alpha$, $\beta+d\beta$,

[8] M. E. Rose and R. L. Carovillano, Phys. Rev. **122**, 1185 (1961).
[9] We choose our definition of the Euler angles to agree with A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, N.J., 1957).
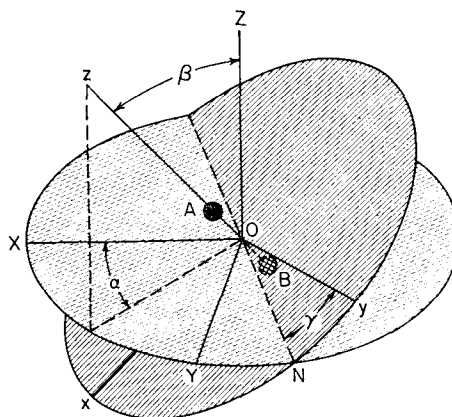
FIG. 1. Definition of Euler angles $\alpha\beta\gamma$ relating the space-fixed XYZ and rotating molecule-fixed xyz coordinates systems. The angle β is the included angle between Z and z: the angle α is measured from the X axis to the projection of z upon XY plane: and the angle γ is measured from the line of nodes N to the y axis. The internuclear axis of the molecule AB defines the z axis. The origin O of both coordinate systems coincides with the center of mass of the AB molecule.

$\gamma+d\gamma$. If the electric vector of the incident light has direction cosines λ_F along the space-fixed axes $F=X$, Y, Z, and if the transition dipole moment has direction cosines λ_g along the molecule-fixed axes $g=x$, y, z, the absorption probability is proportional to

$$| \mathbf{\mu} \cdot \varepsilon |^2 = \mu^2 \varepsilon^2 | \sum_F \sum_g \lambda_F \lambda_g \Phi_{Fg}(\alpha\beta\gamma) |^2, \qquad (2)$$

since

$$\varepsilon_F = \varepsilon\lambda_F,$$

$$\mathbf{\mu}_g = \mu\lambda_g,$$

and

$$\lambda_F = \sum_g \Phi_{Fg}\lambda_g,$$

where the angle-dependent factors Φ_{Fg}, summarized in Table I, are the direction cosine elements which describe the unitary transformation between the XYZ and xyz coordinate systems.

The probability that absorption occurs for orientations in the range specified by (1) is thus proportional to

$$(1/8\pi^2) | \sum_F \sum_g \lambda_F \lambda_g \Phi_{Fg}(\alpha\beta\gamma) |^2 d\alpha \, \sin\beta d\beta d\gamma. \qquad (3)$$

The intensity of absorption in the unit solid angle element, $(1/4\pi^2) \sin\theta d\theta d\phi = (1/4\pi^2) \sin\beta d\beta d\alpha$, is obtained from (3) by averaging over all azimuthal angles γ:

$$A(\beta, \alpha) = \frac{1}{2\pi} \int_0^{2\pi} | \sum_F \sum_g \lambda_F \lambda_g \Phi_{Fg}(\alpha\beta\gamma) | d\gamma. \qquad (4)$$

Once the molecule is pumped into the excited state, it will radiate to all other allowed states with a lifetime τ. Let us suppose a light detector (e.g., polarizer and photocell) has been set up to measure the molecular resonance fluorescence which has an electric vector

TABLE I. Direction cosine elements $\Phi_{Fg}(\alpha, \beta, \gamma)$ expressing the transformation between the laboratory coordinates $F=XYZ$ and the molecule-fixed coordinates $g=xyz$ in terms of the Euler angles α, β, γ defined in Fig. 1.

	X	Y	Z
x	$\cos\alpha \cos\beta \cos\gamma - \sin\alpha \sin\gamma$	$\sin\alpha \cos\beta \cos\gamma + \cos\alpha \sin\gamma$	$-\sin\beta \cos\gamma$
y	$-\cos\alpha \cos\beta \sin\gamma - \sin\alpha \cos\gamma$	$-\sin\alpha \cos\beta \sin\gamma + \cos\alpha \cos\gamma$	$\sin\beta \sin\gamma$
z	$\cos\alpha \sin\beta$	$\sin\alpha \sin\beta$	$\cos\beta$

with laboratory direction cosines $\lambda_{F'}$. At some time t after absorption the dipole oscillator described by the direction cosines $\lambda_{g'}$ in the molecular reference frame will radiate. In the same manner as we defined the absorption probability per unit solid angle $A(\beta, \alpha)$, so may we define the fluorescence intensity $F(\beta'\alpha')$ per solid angle at time t to be

$$F(\beta', \alpha') = \frac{1}{2\pi} \int_0^{2\pi} |\sum_{F'}\sum_{g'}\lambda_{F'}\lambda_{g'}\Phi_{F'g'}(\alpha', \beta', \gamma')|^2 d\gamma',$$
(5)

where unprimed variables refer to absorption and primed variables to emission.

Let the population of the excited state be denoted by N. The rate of resonance fluorescence is then given by

$$dN/dt = -\Gamma N,$$
(6a)

where $\Gamma = 1/\tau$ (reciprocal of lifetime), or, in terms of the initial population N_0 at $t=0$, by

$$dN/dt = -\Gamma N_0 \exp(-\Gamma t).$$
(6b)

The radiative lifetime is much longer than the rotational period of the molecule. However, although the rotational tumbling of the molecule reduces the initial directional alignment of the transition dipole moment, it does not succeed in completely "washing out" the preferred orientations. Consequently, the angular distribution of the molecular resonance fluorescence still shows a corresponding anisotropy.

The calculation of this anisotropy is performed (a) by compounding the probability of absorption per unit solid angle, given by Eq. (4), with the probability of fluorescence per unit solid angle at the time t, given by Eq. (5), and (b) by integrating this product over all possible molecular orientations, indicated in Eq. (1), and for all time t, with the help of Eq. (6). The resultant total intensity recorded by the fluorescence emission detector is given by

$$I(\lambda_F, \lambda_g; \lambda_{F'}, \lambda_{g'}) = -\frac{\Gamma N_0}{4\pi} \int_0^\infty dt \int_0^\pi \sin\beta d\beta$$

$$\times \int_0^{2\pi} \exp(-\Gamma t) A(\beta, \alpha) F(\beta', \alpha') d\alpha. \quad (7)$$

In the absence of an external field, $F(\beta', \alpha')$ does not implicitly depend on time and $\beta'=\beta$, $\alpha'=\alpha$. How-

ever, when a magnetic or electric field is applied, the corresponding excited-state magnetic moment or electric moment of the molecule precesses about the direction of the external field. For a magnetic field the angle of precession ω is related to the classical Larmor frequency L by

$$\omega = 2\pi g_J L t,$$
(8)

where g_J is the Landé g factor for the molecule in the Jth rotational state, and the Larmor frequency is related to the magnetic moment μ_m by

$$L = \mu_m H / 2\pi\hbar.$$
(9)

For an electric field, the same equations apply when first-order Stark splitting occurs in a molecule, provided we replace in (9) the Zeeman-effect constant, $\mu_m H = 9.2732 \times 10^{-21}$ (ergs/Bohr magneton) G^{-1}, by the Stark-effect constant, $\mu_e E = 3.3356 \times 10^{-21}$ (ergs/D) $(V/cm)^{-1}$.

If the direction of the magnetic or electric field differs from the direction of the electric vector $\mathcal{E}$ of the exciting light beam, the anisotropic distribution of molecular dipole oscillators which remains after averaging over the rotational motion of the molecule becomes more evenly distributed, and the resonance fluorescence is further depolarized. The extent of depolarization may still be calculated from Eq. (7), provided we consider that α', β' depend on time and are related to α, β in a complex manner depending upon the direction of the external field. However, much simplification is achieved by defining the laboratory Z axis to lie along the field direction. Precession occurs then in the XY plane, and the primed and unprimed polar angles are related to each other by

$$\alpha' = \alpha + \omega,$$

$$\beta' = \beta,$$
(10)

where ω is the angle of precession defined by Eq. (8). The degree of field-dependent depolarization is thus seen to depend physically on the ratio of the fluorescence rate to the precession rate. The precession rate in turn is shown by Eqs. (8) and (9) to be dependent upon the strength of the field and the magnitude of the corresponding magnetic or electric moment.

So far we have derived a generalized classical expression for the interference effects that appear in the angular distribution of molecular fluorescence

caused by the effects of zero-field level crossings. We wish now to apply this formulation to a specific (traditional) experimental setup and to focus our attention on diatomic systems. There are several possible ways of observing level crossings, and polarized light need not even be used. However, the simplest geometrical arrangement (and one often employed in practice) is to have a beam of plane-polarized resonance radiation incident along the X axis with its electric field $\mathcal{E}$ pointing along the Y axis, where the external field direction coincides with the space-fixed Z axis. The location of the fluorescence detector is chosen to lie along the Y axis and to measure the intensity $I_{\perp}$ of light plane polarized along the X axis, perpendicular to the electric vector of the incident light beam. We shall also consider a fluorescence detector placed along the X axis to measure the intensity $I_{||}$ of light plane polarized along the Y axis, parallel to the electric vector of the incident light beam. As a measure of the anisotropy of the fluorescence angular distribution, we define the *degree of polarization* P, to be given by

$$P = (I_{||} - I_{\perp})/(I_{||} + I_{\perp}). \tag{11}$$

The degree of polarization has the range $-1 \leq P \leq 1$, where P takes on the value zero when the radiation is completely isotropic. For the experimental configuration illustrated in Fig. 2, $\mathcal{E}_F = \mathcal{E}\lambda_Y$; and for $I_{\perp}$, $\mathcal{E}_{F'} = \mathcal{E}\lambda_{X'}$ or for $I_{||}$, $\mathcal{E}_{F'} = \mathcal{E}\lambda_{Y'}$. Thus the number of cross terms appearing in Eqs. (4) and (5) is considerably diminished, and the subsequent evaluation of Eq. (7) is much facilitated.

Let the z axis of the molecular reference frame be chosen to lie along the internuclear axis of the molecule. Based upon symmetry considerations, the transi-
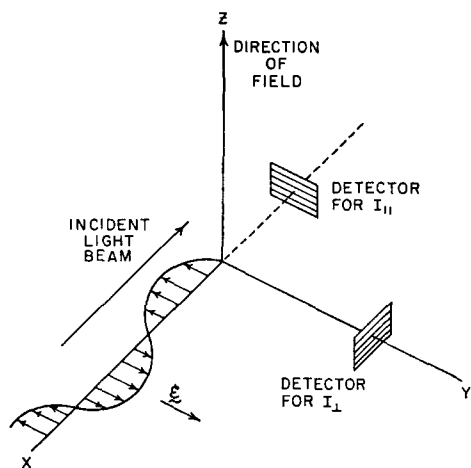

FIG. 2. Idealized geometrical arrangement for the observation of molecular level-crossing spectroscopy. The light beam is incident along the X axis with its electric vector $\mathcal{E}$ plane polarized along Y. Detectors are placed along the X and Y axes to measure the fluorescence intensity emitted which is plane-polarized parallel or perpendicular to the initial direction of $\mathcal{E}$, respectively. The direction of the static electric and/or magnetic field is along Z.

TABLE II. Degree of polarization for molecular level-crossing spectroscopy: classical treatment.

Orientation of transition dipoles (Absorption, emission)		Degree of polarization
(1)	$(||, ||)$	$P = \frac{1}{2} \dfrac{\Gamma^2}{\Gamma^2 + (2g_J\mu_m H/\hbar)^2}$
(2)	$(||, \perp)$	$P = -\frac{1}{3} \dfrac{\Gamma^2}{\Gamma^2 + (2g_J\mu_m H/\hbar)^2}$
(3)	$(\perp, ||)$	$P = -\frac{1}{3} \dfrac{\Gamma^2}{\Gamma^2 + (2g_J\mu_m H/\hbar)^2}$
(4)	$(\perp, \perp)$	$P = \frac{1}{7} \dfrac{\Gamma^2}{\Gamma^2 + (2g_J\mu_m H/\hbar)^2}$

tion moment of a diatomic molecule can have only two possible orientations: along the internuclear axis (parallel transition, $\mathbf{\mu}_g = \mu\lambda_z$), or at right angles to the internuclear axis (perpendicular transition, $\mathbf{\mu}_g = \mu\lambda_x + \mu\lambda_y$). Thus, we can distinguish four possible types of molecular fluorescence given by the combination of the two possible dipole orientations occurring in absorption and emission. Table II lists these transition types in order of increasing depolarization.

Using Eqs. (4), (5), (7), (8), and (10), and Table I, the polarization intensity, recorded by the detectors oriented as in Fig. 2, is readily evaluated for these four cases. As an example, we work out explicitly values of the $I_{||}$ and $I_{\perp}$ intensities for the case in which both the absorption and fluorescence dipole moment lie along the molecular axis $[(||, ||)$ transition]. Thus, $A(\beta, \alpha) = \sin^2\beta$, $F(\beta', \alpha') = \sin^2\beta \sin^2(\alpha+\omega)$ for $I_{||}$ or $F(\beta', \alpha') = \sin^2\beta \cos^2(\alpha+\omega)$ for $I_{\perp}$, and we find that

$$I_{||} = -\frac{\Gamma N_0}{4\pi} \int_0^{\infty} dt \int_0^{\pi} \sin\beta d\beta \int_0^{2\pi} d\alpha$$
$$\times [\exp(-\Gamma t) \sin^4\beta \sin^2\alpha \sin^2(\alpha+\omega)] \tag{12a}$$

and

$$I_{\perp} = -\frac{\Gamma N_0}{4\pi} \int_0^{\infty} dt \int_0^{\pi} \sin\beta d\beta \int_0^{2\pi} d\alpha$$
$$\times [\exp(-\Gamma t) \sin^4\beta \sin^2\alpha \cos^2(\alpha+\omega)] \tag{12b}$$

yield, upon integration, the values

$$I_{||} = N_0(3a^2+8)/15(a^2+4) \tag{13a}$$

and

$$I_{\perp} = N_0(a^2+8)/15(a^2+4), \tag{13b}$$

where

$$a = \Gamma/2\pi g_J L$$
$$= \hbar\Gamma/g_J\mu_m H.$$

The degree of polarization is thus found to be

$$P = \frac{1}{2} \frac{\Gamma^2}{\Gamma^2 + (2g_J\mu_m H/\hbar)^2}. \quad (14)$$

In a similar manner, the degree of polarization for the other molecular fluorescence cases are calculated, and the results are summarized in Table II. All the classical expressions have the same characteristic Lorentzian form as Eq. (14), giving isotropic fluorescence in the high field limit ($\Gamma \ll 2g_J\mu_m H/\hbar$) and giving a finite degree of polarization, *independent of J*, in the low field limit ($\Gamma \gg 2g_J\mu_m H/\hbar$). The latter results are found to agree with classical expressions obtained previously by Vavilov and Levshin,[5] and by Feofilov,[10] for the absence of external fields.

Quantum Treatment

The quantum counterpart of Eq. (7) is readily formulated by modifying an expression, first derived by Breit,[6] which provides a fully quantum-mechanical description of the interference effects arising from level crossings. Consider a symmetric-top molecule (of which a diatomic molecule is a special example) undergoing a transition $\alpha''v''J''K'' \rightarrow \alpha'v'J'K'$ from the ground state α'' to the excited state α' from which it spontaneously radiates to a third state $\alpha: \alpha'v'J'K' \rightarrow \alpha vJK$. Normally, the initial and final states are the same ($\alpha''=\alpha$), but this need not be introduced into the derivation.[11] Let the magnetic sublevels of the initial state α'' be denoted by m'', those of the excited state by M, M', and those of the final state by m. The quantum numbers vJK characterize, respectively, the vibrational energy level of the molecule, the total angular momentum of the molecule, and the projection of the total angular momentum on the molecular symmetry axis.[12] The general expression for the total rate $R(\mathbf{a}, \mathbf{b})$ that a molecule will absorb radiation with polarization vector $\mathbf{a}$ and subsequently emit radiation of polarization $\mathbf{b}$ will be proportional to

$$R(\mathbf{a}, \mathbf{b}) = \sum_M \sum_{M'} \frac{A_{MM'} F_{M'M}}{\Gamma - i(E_{v'K'M'} - E_{v'K'M})/\hbar}, \quad (15)$$

where $(E_{K'M'} - E_{K'M})$ is the energy difference between the upper-state magnetic sublevels and where the absorption and fluorescence matrices $A_{MM'}$ and $F_{M'M}$ have the form

$$A_{MM'} = \sum_{m''} \langle J'K'M \mid \mathbf{\mu} \cdot \mathbf{\mathcal{E}}_a \mid J''K''m'' \rangle$$

$$\times \langle J''K''m'' \mid \mathbf{\mu} \cdot \mathbf{\mathcal{E}}_a \mid J'K'M' \rangle \quad (16a)$$

[10] P. P. Feofilov, *The Physical Basis of Polarized Emission* (Consultants Bureau Enterprises, Inc., New York, 1961).
[11] It is also possible that $\alpha = \alpha' = \alpha''$, as in the case of vibration-rotation bands of molecules, usually observed in the infrared part of the spectrum.
[12] For diatomic molecules the projection of the total angular momentum on the molecular axis is more often denoted by Ω; for polyatomics, by P. However, we follow a common notation used for symmetric-top molecules.

and

$$F_{M'M} = \sum_m \langle J'K'M' \mid \mathbf{\mu} \cdot \mathbf{\mathcal{E}}_b \mid JKm \rangle$$

$$\times \langle JKm \mid \mathbf{\mu} \cdot \mathbf{\mathcal{E}}_b \mid J'K'M \rangle. \quad (16b)$$

On comparing the "molecular" Breit formula Eq. (15) with the classical expression Eq. (7), we see that we have replaced the average over all rotational orientations of the molecule in the classical treatment by a sum over all initial, intermediate, and final state magnetic sublevels; and we have replaced the classical Larmor precession frequency by the energy difference between excited-state magnetic sublevels:

$$\Delta U = E_{K'M'} - E_{K'M}.$$

Provided the symmetric-top molecule possesses electronic angular momentum, the latter substitution can be recast in much the same form as the classical expressions (8) and (9) except that the dependence on the quantum numbers J, K, M is made explicit. Thus, the Zeeman energy splitting of a symmetric-top molecule[13] with electronic angular momentum has the form

$$\Delta W = g_{J'K'}\mu_m HM,$$

where the molecular Landé g factor is given by

$$g_{J'K'} = K'/[J'(J'+1)]$$

and where the molecular magnetic moment (measured in Bohr magnetons) is

$$\mu_m = \Lambda + 2.002\Sigma.$$

Here Λ is the projection of the electronic orbital angular momentum and Σ the projection of the electronic spin angular momentum on the molecular axis ($K' = \mid \Lambda + \Sigma \mid$). The energy difference is thus given by

$$\Delta U = \mu_m HK'(M'-M)/J'(J'+1). \quad (17)$$

If Eq. (16) is small or vanishes, the magnetic moments of the nuclei as well as the rotational magnetic moment of the molecule give rise to Zeeman splittings, the magnitude of which are typically 1000 times smaller.

For the analogous electric-field case the energy difference is given by a formula of the same form as Eq. (16):

$$\Delta U = [-\mu_e EK'(M'-M)/J'(J'+1)], \quad (18)$$

where μ_e is the permanent electric dipole moment of the excited state. If $K'=0$, there is no longer a first-order Stark splitting, but rather a second-order Stark effect:

$$\Delta U = \frac{-3\mu_e^2 E^2(M'+M)(M'-M)}{B_{v'}J'(J'+1)(2J'-1)(2J'+1)}, \quad (19)$$

[13] For a review of the Zeeman and Stark effect in symmetric-top molecules see C. H. Townes and A. L. Shawlow, *Microwave Spectroscopy* (McGraw-Hill Book Co., Inc., New York, 1955).

TABLE III. Values of factors for the direction cosine matrix elements: $(\Phi_{F_g})_{JKM;J'K'M'}=\chi_{JK;J'K'}\phi_{JM;J'M'}$. Subscript capital letters XYZ refer to the laboratory coordinate system; subscript lower-case letters xyz refer to the coordinate system of the symmetric-top molecule.

Matrix-element factor	Value of J'		
	$J+1$	J	$J-1$
$(\chi_z)_{JK;J'K}$	$\dfrac{[(J+1)^2-K^2]^{\frac{1}{2}}}{[2(J+1)]^{\frac{1}{2}}[(2J+1)(2J+3)]^{\frac{1}{2}}}$	$\dfrac{K}{[2J(J+1)]^{\frac{1}{2}}}$	$\dfrac{(J^2-K^2)^{\frac{1}{2}}}{(2J)^{\frac{1}{2}}(4J^2-1)^{\frac{1}{2}}}$
$(\chi_x \text{ or } \pm i\chi_y)_{JK;J'K\pm1}$	$\dfrac{\mp[(J\pm K+1)(J\pm K+2)]^{\frac{1}{2}}}{2(J+1)^{\frac{1}{2}}[(2J+1)(2J+3)]^{\frac{1}{2}}}$	$\dfrac{[(J\mp K)(J\pm K+1)]^{\frac{1}{2}}}{2[J(J+1)]^{\frac{1}{2}}}$	$\dfrac{\pm[(J\mp K)(J\mp K-1)]^{\frac{1}{2}}}{2J^{\frac{1}{2}}(4J^2-1)^{\frac{1}{2}}}$
$(\phi_Z)_{JM;J'M}$	$\dfrac{[(J+1)^2-M^2]^{\frac{1}{2}}}{[2(J+1)]^{\frac{1}{2}}[(2J+1)(2J+3)]^{\frac{1}{2}}}$	$\dfrac{M}{[2J(J+1)]^{\frac{1}{2}}}$	$\dfrac{(J^2-M^2)^{\frac{1}{2}}}{(2J)^{\frac{1}{2}}(4J^2-1)^{\frac{1}{2}}}$
$(\phi_X \text{ or } \pm i\phi_Y)_{JM;J'M\pm1}$	$\dfrac{\mp[(J\pm M+1)(J\pm M+2)]^{\frac{1}{2}}}{2(J+1)^{\frac{1}{2}}[(2J+1)(2J+3)]^{\frac{1}{2}}}$	$\dfrac{[(J\mp M)(J\pm M+1)]^{\frac{1}{2}}}{2[J(J+1)]^{\frac{1}{2}}}$	$\dfrac{\pm[(J\mp M)(J\mp M-1)]^{\frac{1}{2}}}{2J^{\frac{1}{2}}(4J^2-1)^{\frac{1}{2}}}$

where $B_{v'}$ is the rotational constant of the v' vibrational level of the upper state. In general, the magnitude of second-order Stark splittings is much smaller than first-order Stark splittings for electric-field strengths readily produced in the laboratory. If the excited state has no permanent electric dipole moment, a splitting may still be produced due to the polarizability $\alpha_{v'J'K'}$ of the upper state. The energy difference for this effect is approximately given by

$$U=[\alpha_{v'J'K'}E^2(M'+M)(M'-M)/4J^4], \quad (20)$$

but in most cases Eq. (20) is about 10 000 times smaller than a second-order Stark splitting.

Further comparison between the classical and quantum equations indicates that the geometrical arguments based on different orientations of a classical dipole oscillator appear to have been disguised in the form of the transition dipole matrix elements appearing in Eqs. (16a) and (16b). The close similarity as well as important differences between these two formulations may be brought out, however, by substituting the identity

$$\mathbf{\mu}\cdot\mathbf{\mathcal{E}}=\mu\mathcal{E}\sum_{F}\sum_{g}\lambda_F\lambda_g\Phi_{F_g}(\alpha,\beta,\gamma) \quad (21)$$

into Eqs. (16a) and (16b). The resulting expressions do not directly contain the direction cosines Φ_{F_g} as in the classical treatment, but rather the matrix elements of Φ_{F_g} calculated between symmetric-top wavefunctions. These matrix elements, first worked out explicitly by Cross, Hainer, and King,[14] factor into a JK; $J'K'$ term independent of M and a JM; $J'M'$ term independent of K:

$$\langle JKM \mid \Phi_{F_g} \mid J'K'M' \rangle=\chi_{JK;J'K'}\phi_{JM;J'M'}. \quad (22)$$

Table III summarizes the values of the factors χ and ϕ for different allowed values of J', K', and M'.

The selection rules for symmetric-top spectra[15] are such that, for the transition moment parallel to the top axis ($\|$ band), the rotational quantum numbers can change by

$$\Delta K=0, \qquad \Delta J=0, \pm1, \qquad \text{if } K\neq0,$$

$$\Delta K=0, \qquad \Delta J=\pm1, \qquad \text{if } K=0;$$

whereas for the transition moment perpendicular to the top axis ($\perp$ band)

$$\Delta K=\pm1, \qquad \Delta J=0, \pm1.$$

To distinguish among the several optical pumping schemes for molecules, we adopt the following notation: a transition that increases by J by unity in absorption or decreases J by unity in emission is known as an R branch; a transition that decreases J by unity in absorption or increases J by unity in emission is a P branch; and a transition which leaves the value of J unchanged is a Q branch. In addition each branch may have three different subbranches corresponding to the possible changes in ΔK. These subbranches may be denoted by a superscript R, Q, or P placed to the left of the branch designation where the values of the superscript depend on the change in ΔK in the same way the branch designations depend on ΔJ. We shall use an arrow pointing upwards ($\uparrow$) for absorption or pointing downwards ($\downarrow$) for emission. Thus, the sequence of molecular transitions J, $K\rightarrow J+1$, K in absorption followed by $J+1$, $K\rightarrow J+2$, K in emission, for instance, is symbolized by ($^{Q}R\uparrow$, $^{Q}R\downarrow$).

At first glance it would appear that we must evaluate 81 different rotational cases given by the combination of the different values of ΔJ and ΔK in absorption and in emission. Upon closer inspection, however, we see that the value of ΔK in absorption or emission enters into the calculations as a multiplicative factor

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[14] P. C. Cross, R. M. Hainer, and G. W. King, J. Chem. Phys. **12**, 210 (1944).

[15] G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Co., Inc., Princeton, N.J., 1945).

TABLE IV. Degree of polarization for molecular level-crossing spectroscopy: quantum treatment.[a]

Transition sequence	Degree of polarization
(1) $(Q\uparrow, Q\downarrow)$	$P = \dfrac{4J'^2 + 4J' - 3}{8J'^2 + 8J' - 1} \dfrac{\Gamma^2}{\Gamma^2 + (2g_{J'K'}\mu_m H/\hbar)^2}$
(2) $(Q\uparrow, P\downarrow)$	$P = -\dfrac{2J'-1}{6J'+7} \dfrac{\Gamma^2}{\Gamma^2 + (2g_{J'K'}\mu_m H/\hbar)^2}$
(3) $(Q\uparrow, R\downarrow)$	$P = -\dfrac{2J'+3}{6J'-1} \dfrac{\Gamma^2}{\Gamma^2 + (2g_{J'K'}\mu_m H/\hbar)^2}$
(4) $(P\uparrow, Q\downarrow)$	$P = -\dfrac{2J'-1}{6J'+7} \dfrac{\Gamma^2}{\Gamma^2 + (2g_{J'K'}\mu_m H/\hbar)^2}$
(5) $(R\uparrow, Q\downarrow)$	$P = -\dfrac{2J'+3}{6J'-1} \dfrac{\Gamma^2}{\Gamma^2 + (2g_{J'K'}\mu_m H/\hbar)^2}$
(6) $(P\uparrow, P\downarrow)$	$P = \dfrac{2J'^2 - J'}{14J'^2 + 33J' + 20} \dfrac{\Gamma^2}{\Gamma^2 + (2g_{J'K'}\mu_m H/\hbar)^2}$
(7) $(P\uparrow, R\downarrow)$	$P = \dfrac{1}{7} \dfrac{\Gamma^2}{\Gamma^2 + (2g_{J'K'}\mu_m H/\hbar)^2}$
(8) $(R\uparrow, P\downarrow)$	$P = \dfrac{1}{7} \dfrac{\Gamma^2}{\Gamma^2 + (2g_{J'K'}\mu_m H/\hbar)^2}$
(9) $(R\uparrow, R\downarrow)$	$P = \dfrac{2J'^2 + 5J' + 3}{14J'^2 - 5J' + 1} \dfrac{\Gamma^2}{\Gamma^2 + (2g_{J'K'}\mu_m H/\hbar)^2}$

[a] The correspondence between the classical and quantum results (Tables II and IV) is as follows: $(\|, \|)$ with $(Q\uparrow, Q\downarrow)$; $(\|, \perp)$ and $(\perp, \|)$ with $(Q\uparrow, P\downarrow)$, $(Q\uparrow, R\downarrow)$, $(P\uparrow, Q\downarrow)$, and $(R\uparrow, Q\downarrow)$; and $(\perp, \perp)$ with $(P\uparrow, P\downarrow)$, $(P\uparrow, R\downarrow)$, $(R\uparrow, P\downarrow)$, and $(R\uparrow, R\downarrow)$.

$\chi_{JK;J'K'}$ which affects the over-all fluorescence rate, but not the angular distribution. Thus, we need only consider the nine possible ΔJ transitions shown in Table IV in characterizing the anisotropic forms possible for symmetric-top molecules.

The calculation of this anisotropy measured by detectors oriented as in Fig. 2 is readily performed for these nine cases by using Eq. (15) and related equations, and with the help of Table III. As an example, we work out explicit expressions for $I_{\|}$ and $I_{\perp}$ for the quantum analog of the $(\|, \|)$ transition sequence we previously treated. To be specific we consider the optical pumping cycle $({}^R Q\uparrow, {}^R Q\downarrow)$, which might represent, for instance, the $\Sigma\rightarrow\Pi\rightarrow\Sigma$ transition sequence of the resonance fluorescence of a diatomic molecule.

For this case $J' = J$, $K' = K+1$; and we find that the elements of the absorption matrix are given by

$$A_{MM'}\delta_{MM'} = 2\chi_{JK;JK+1}\chi_{JK;JK-1}[J(J+1) - M^2],$$
$$(23a)$$

$$A_{MM'}\delta_{M;M'=M+2} = -\chi_{JK;JK+1}\chi_{JK;JK-1}$$
$$\times[(J-M)(J+M+1)(J-M+1)(J+M+2)]^{\frac{1}{2}},$$
$$(23b)$$

and

$$A_{MM'}\delta_{M,M'=M-2} = -\chi_{JK;JK+1}\chi_{JK;JK-1}$$
$$\times[(J+M)(J-M+1)(J+M+1)(J-M+2)]^{\frac{1}{2}}.$$
$$(23c)$$

For $I_{\|}$ the fluorescence matrix elements are identical with the absorption matrix elements $(F_{M'M} = A_{M'M})$. By reference to Eqs. (23a), (23b), and (23c), it is easily shown that

$$F_{M'M}\delta_{M'M} = A_{MM}, \qquad (24a)$$

$$F_{M'M}\delta_{M'=M+2,M} = A_{MM+2}, \qquad (24b)$$

and

$$F_{M'M}\delta_{M'=M-2,M} = A_{MM-2}. \qquad (24c)$$

Let the magnetic moment of the molecule be denoted by μ_m. The evaluation of Eq. (15) is facilitated by summing over each different ΔM value:

$$I_{\|} = \sum_M \left[\frac{A_{MM}F_{MM}}{\Gamma} + \frac{A_{MM+2}F_{M+2M}}{\Gamma - (2ig_{J'K'}\mu_m H/\hbar)} + \frac{A_{MM-2}F_{M-2M}}{\Gamma + (2ig_{J'K'}\mu_m H/\hbar)} \right]. \quad (25)$$

After rationalizing the denominators of (25) and substituting explicit expressions involving M for the elements of the absorption matrix, Eq. (23), and the elements of the fluorescence matrix, Eq. (24), the final sum over M may be performed with the aid of the following identities:

$$\sum_{-J}^{J} M^n = 2J+1, \qquad \text{for } n=0;$$

$$\sum_{-J}^{J} M^n = \tfrac{1}{3}[J(J+1)(2J+1)], \qquad \text{for } n=2;$$

$$\sum_{-J}^{J} M^n = \tfrac{1}{15}[J(J+1)(2J+1)(3J^2+3J-1)],$$
$$\text{for } n=4;$$

and

$$\sum_{-J}^{J} M^n = 0, \qquad \text{for } n \text{ an odd integer.}$$

We obtain for $I_{\|}$ the expression

$$I_{\|} = \chi^2_{JK;JK+1}\chi^2_{JK;JK-1} \frac{2J(J+1)(2J+1)}{15}$$
$$\times \left[\frac{16J^2 + 16J + 2}{\Gamma} + \frac{(8J^2 + 8J - 6)\Gamma}{\Gamma^2 + (2g_{J'K'}\mu_m H/\hbar)^2} \right]. \quad (26)$$

Calculation of the $I_{\perp}$ fluorescence intensity proceeds in the same manner. Due to the different geometry we find that Eq. (24a) is valid as it stands for diagonal elements of the fluorescence matrix, but a minus sign

must be inserted in Eqs. (24b) and (24c). We thus obtain for $I_\perp$ the final expression

$$I_\perp = \chi^2_{JK;JK+1} \chi^2_{JK;JK-1} \frac{2J(J+1)(2J+1)}{15}$$

$$\times \left[\frac{16J^2+16J+2}{\Gamma} - \frac{(8J^2+8J-6)\Gamma}{\Gamma^2+(2g_{J'K'}\mu_m H/\hbar)^2} \right]. \quad (27)$$

The degree of polarization is then found to be, for a $(Q\uparrow, Q\downarrow)$ transition sequence,

$$P = \frac{4J'^2+4J'-3}{8J'^2+8J'-1} \frac{\Gamma^2}{\Gamma^2+(2g_{J'K'}\mu_m H/\hbar)^2}. \quad (28)$$

In a similar manner, the degree of polarization is calculated for the other optical-pumping transition sequences, and the results are presented in Table IV.

For $J'=1$ (the smallest value of J' that can occur), the polynomial fraction $f(J')$ in front of the characteristic Lorentzian function of Γ in Eq. (28) has the value of $\frac{1}{3}$; whereas in the limit of large J', $f(J')$ approaches $\frac{1}{2}$ which is in agreement with the classical result given in Eq. (14). Moreover, $f(J')$ rapidly attains the high J' limiting value, e.g., for $J'=5$ it differs from $\frac{1}{2}$ by 2.1% and for $J'=10$ by 0.6%. The same type of behavior is shown by the other transition sequences given in Table IV; namely, for very small values of J', the classical picture of a Hertzian oscillator either rigidly fixed in space or rotating in a prescribed plane is inadequate. But with increasing J' the quantum results rapidly approach their corresponding classical limiting expressions. For increasing external field strength, the degree of polarization is seen from Table IV to approach zero; whereas, for decreasing external field strength, P approaches the value of the polynomial fraction $f(J')$. Algebraic expressions for $f(J')$ have been derived previously by Feofilov[10] for atomic resonance fluorescence. Indeed, we note that the results of Table IV apply equally as well to atomic transitions. For example, the quantum treatment of Lurio, de Zafra, and Goshen[16] for the $^1S_0 \rightarrow {}^1P_1 \rightarrow {}^1S_0$ atomic transition sequence in a special case of $(R\uparrow, R\downarrow)$ for $J'=1$.

DISCUSSION

In principle, molecular level-crossing spectroscopy offers us a means of measuring the radiative lifetime, magnetic moment, and electric dipole moment of molecular excited states. The applicability and realization of this experimental technique will depend primarily on two factors: (1) whether molecular level-crossing interference effects can be observed in molecular resonance fluorescence with external field strengths readily achieved in the laboratory, and (2) whether suitable light sources can be developed for the optical pumping of molecules. The answer to these questions of course

can only be found through experiment. However, a calculation of the well-known Na_2 resonance fluorescence progression[17,18] excited by the Cd 4800-Å line has encouraged us to believe such experiments are feasible.

The Na_2 molecule has an excited $^1\Pi$ state lying about 20 320 cm^{-1} above its $^1\Sigma_g{}^+$ ground state, and emission from this excited electronic state is responsible for the characteristic blue-green bands of Na_2. Once the Na_2 molecule is excited to a particular (v', J') vibration–rotation level of the upper state, it might be thought that emission would occur from that state to all the allowed (v'', J'') levels of the ground state where $J''=J'$, $J'+1$, and $J'-1$ according to the selection rules $\Delta J=0$ and $\Delta J=\pm 1$ presented previously for symmetric-top transitions. However, the resonance fluorescence emission bands of the $^1\Sigma \rightarrow {}^1\Pi \rightarrow {}^1\Sigma$ transition sequence are observed to have a much simpler rotational branch structure, consisting entirely either of R- and P-branch lines or Q-branch lines, but not simultaneously of all three.[19] The explanation for this phenomena is due to the small Λ-type doubling of the $^1\Pi$ state which splits each rotational level into two components, one of which is a positive Λ-type doublet, the other of which is a negative Λ-type doublet. A given lower state can combine with one or the other upper-state doublet components according to the selection rule that positive levels combine only with negative levels, and vice versa. This accounts for the result that the resonance fluorescence from the $^1\Pi$ state of Na_2 consists either of a vibrational progression of closely spaced R and P doublets or a progression of Q singlets. By contrast a $^1\Pi \rightarrow {}^1\Sigma \rightarrow {}^1\Pi$ transition sequence can show all three possible rotational branch lines, although resonance fluorescence for this electronic transition type has not yet been reported.

Historically, the resonance spectra of Na_2 occupies a place of particular interest and irony, since the polarized fluorescence emission from Na_2 was observed by Wood[17,20] long before the polarization of atomic resonance fluorescence, and at the time was attributed to atomic sodium. Since then, atomic resonance fluorescence has been studied for a variety of systems in great detail, while our knowledge of molecular resonance fluorescence has depended upon those few fortuitous coincidences known in which an atomic line overlaps a molecular vibration–rotation line. However, the scant number of investigations of molecular fluorescence systems in the gas phase appears to be due more to the lack of interest in the past rather than to difficulty in the effort. For example, about 15

[16] A. Lurio, R. L. deZafra, and R. J. Goshen, Phys. Rev. **134**, A1198 (1964).

[17] R. W. Wood, *Physical Optics* (The Macmillan Co., New York, 1934), 3rd ed.

[18] P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1965), pp. 169–176.

[19] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Co., Inc., Princeton, N.J., 1950), pp. 251–256.

[20] R. W. Wood, Phil. Mag. **10**, 513, 521 (1905); **15**, 581 (1908); Physik. Z. **9**, 450 (1908).

different atomic lines have been reported to cause fluorescence in Na$_2$ vapor.[18,20]

In particular, the Cd 4800-Å line appears to excite Na$_2$ from the $v''=0$ level of the ground state to a high-lying rotational level of the $v'=5$ level of the upper state. From the latter excited state, the molecule emits a long progression of Q-branch lines (a spectrogram[21] of the fluorescence series is found in Herzberg's *Spectra of Diatomic Molecules*). The exact rotational level is uncertain, the difficulty being that energy levels cannot be calculated with reliability from tabulated spectroscopic constants for high values of J. It would appear though that the correct value[22] of J' is about $J'=40$.

The fluorescence transition sequence produced by the Cd 4800-Å line is the $(^RQ\uparrow, \ ^RQ\downarrow)$ case we have considered both by a classical and by a quantum treatment. For this sequence we found in both cases that the degree of polarization should be one-half. In 1938 Pringsheim,[23] using photographic plates with time exposures of several hours, measured the degree of polarization for this molecular fluorescence series. He reported the value of P to be about 0.42 which is in reasonable agreement with theory. He did not investigate the effect of a magnetic field on his measurements.

However, we are now in a position to estimate what field strength would be necessary to observe depolarization of the resonance fluorescence due to the destruction of coherence in the excited state. In particular, we wish to calculate the values of H or E for which the degree of polarization has been reduced to one-half its initial value, i.e., when

$$\Gamma = 2g_{J'K'}\mu_m H/\hbar \qquad (29a)$$

or

$$\Gamma = 2g_{J'K'}\mu_e E/\hbar. \qquad (29b)$$

For a $^1\Pi$ state, $K'=1$, $\mu_m=1$ Bohr magneton, and for Na$_2$ excited by the Cd 4800-Å line, $g_{J'K'} \simeq \frac{1}{1600}$. If the upper $^1\Pi$ state of Na$_2$ has a radiative lifetime ranging from 10^{-6} to 10^{-8} sec, Eq. (29a) will be satisfied for a magnetic field between slightly under 100 G to slightly under 10 000 G. The $^1\Pi$ electronic state of the Na$_2$ of course cannot possess a permanent electric dipole moment, but we might imagine for the moment that it does. This might be true, for example, for the chemically similar NaK molecule which also has a well-known $^1\Pi$ excited state lying in the visible (green).[18] Then for an electric dipole moment of 1 D and a

radiative lifetime ranging from 10^{-6} to 10^{-8} sec, Eq. (29b) will be satisfied for an electric-field strength between about 275 and 27 500 V/cm. Magnetic and electric fields of this strength are not uncommonly large or unusually difficult to achieve. Thus these calculations for Na$_2$ support the belief that molecular level crossings can produce readily measurable changes in the angular distribution of fluorescence intensity. Moreover, by finding a resonance fluorescence series originating from rotation–vibration levels with lower J' values, not only will less field strength be required for the same extent of depolarization, but more molecules can be pumped into the excited state due to the more favorable value of the rotational partition function which governs the fraction of the total number of molecules in each rotational level.[19] Based on these considerations, the following molecular resonance fluorescence series suggest themselves as promising candidates: the NO γ-band system $(X \ ^2\Pi_i \rightarrow A \ ^2\Sigma^+)$ excited by the Cd$_{II}$ 2144-Å resonance line to the thirteenth rotational level of the first vibrational level of the upper state[24]; the O$_2$ Shumann–Runge-band system $(X \ ^3\Sigma_g^- \rightarrow B \ ^3\Sigma_u^-)$ excited by the Hg 1849-Å resonance line to the twelfth rotational level of the third vibrational level of the upper state[25]; and the OH ultraviolet band system $(X \ ^2\Pi_i \rightarrow A \ ^2\Sigma^+)$ excited by the Bi 3068-Å resonance line to the 11th rotational level of the zeroth vibrational level of the upper state.[26] We are presently preparing to investigate these fluorescence series and other systems in hopes of observing molecular zero-field level-crossing effects.

The remaining problem is to develop a broad range of light sources for molecular optical pumping. However, the fact that molecular absorption spectra are so much richer in lines than atomic spectra offers promise that there are many other suitable molecular fluorescence series which can be found by using conventional atomic-resonance-line light sources or lasers. Moreover, it may be possible to develop suitably intense molecular-resonance-line light sources so that a molecule can be made to pump itself. Furthermore, it may also prove feasible to use excitation by white light (continuum source) over a suitable wavelength bandwidth. Then from a knowledge of the statistical distribution of the molecules in the various rotation–vibration states, the observed distribution in fluorescence intensity can be unfolded to determine the molecular parameters of interest.

[21] Reference 19, p. 52.
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