

that overlap forces contribute to the formation of the potential hump also must be taken into account. The height of the potential maximum will depend critically on the interaction. We hope that our experimental determination of the magnitude of the potential barrier will encourage a full theoretical treatment to elucidate

the relative contributions of the three different interactions we have described.

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Optical Pumping of Molecules*

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A technique is described for the optical pumping of gas-phase molecules based on the orientation dependence of their absorption cross section. It is shown that when the rate of excitation exceeds the relaxation rate of a ground-state (v'' , J'') level, the magnetic sublevels are preferentially "burned away" and the steady-state M -level population is altered appreciably. An experiment to demonstrate molecular alignment has proved successful using the 4880-Å line of a cw argon-ion laser to cause the transition ($v''=3$, $J''=43$) \rightarrow ($v''=6$, $J''=43$) in the $B^1\Pi_u-X^1\Sigma_g^+$ blue-green band system of the Na_2 molecule. The establishment of an unequal magnetic sublevel population is detected by monitoring the degree of polarization P of the fluorescence as a function of laser intensity. It is found that P first remains constant then decreases by about 50% as the laser-beam power increases from 0.1 to 150 mW. In addition, the absorption becomes nonlinear with a power threshold corresponding to the onset of the decrease in P . This optical pumping technique is applicable to a wide class of molecules, and both simple classical and quantum mechanical theories of the pumping process have been formulated. These theories relate the degree of polarization to both the pumping rate and the relaxation time of the pumped level. The time-dependent as well as steady-state behavior of P is examined. Under conditions of strong optical pumping it is predicted that the degree of polarization as a function of time will overshoot its steady-state value, and as the pumping rate increases large negative transients in P will appear.

I. INTRODUCTION

In 1950, Kastler¹ proposed a method for altering the relative population of the Zeeman levels or hyperfine levels of ground state atoms with optical irradiation. He visualized a two-step process whereby atoms in sublevel A are raised to the excited state B from which they decay by spontaneous emission back to A or to a new sublevel C (See Fig. 1). If the rate of depopulation of C to A by relaxation (through collisional or radiative means) is slower than the rate of population of C , then level C becomes appreciably populated at the expense of level A and the atomic system is said to be optically pumped. Successful optical pumping experiments were first carried out on the ^{23}Na ground state in a beam by Brossel, Kastler, and Winter² and by Hawkins and

Dicke,³ and in a bulb by Margerie,⁴ by Bender,⁵ and by Hartmann, Rambosson, Brossel, and Kastler.⁶

Since these early experiments a number of attempts have been made to achieve optical pumping in other atomic systems and these investigations have led to very accurate determinations of atomic magnetic moments, hyperfine interactions, pressure shifts, light shifts, disorientation cross sections, diffusion constants, and other quantities.⁷ However, almost without exception,⁸ it has been found that only in atomic S states does the spin orientation persist for a sufficient length of

³ W. B. Hawkins and R. H. Dicke, *Phys. Rev.* **91**, 1008 (1953).

⁴ J. Margerie, *Compt. Rend.* **241**, 865 (1955).

⁵ P. L. Bender, thesis, Princeton University, Princeton, N.J., 1956 (unpublished).

⁶ F. Hartmann, M. Rambosson, J. Brossel, and A. Kastler, *Compt. Rend.* **246**, 1522 (1958).

⁷ For a review see R. A. Bernheim, *Optical Pumping: An Introduction* (W. A. Benjamin, Inc., New York, 1965) and C. Cohen-Tannoudji and A. Kastler in *Progress in Optics*, E. Wolf, Ed. (North-Holland Publ. Co., Amsterdam, 1966), Vol. 5, pp. 3-81.

⁸ Recently, L. D. Schearer [*Phys. Rev. Letters* **21**, 660 (1968); *Phys. Rev.* **180**, 83 (1969)] has succeeded in optically pumping metastable Ne (3P_2) atoms as well as other rare-gas metastable atoms (private communication) having an outer s electron and an inner p electron hole. See also H. M. Gibbs, B. Chang, and R. C. Greenhow, *Phys. Rev. Letters* **22**, 270 (1969).

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¹ A. Kastler, *J. Phys. Radium* **11**, 225 (1950).

² J. Brossel, A. Kastler, and J. Winter, *J. Phys. Radium* **13**, 668 (1952).

time in the gas phase to make optical pumping practical. For non- S -state atoms the relaxation rate caused by collisions dominates the pumping process and prevents the build up of a significant non-Boltzmann distribution in the atomic sublevels.

The reason for this appears to be quite simple. If both orbital and spin angular momentum are present in an atom, they couple together by their mutual magnetic interaction (spin-orbit interaction). Then each collision tends to change the direction of the orbital angular momentum and thus subjects the electron spin to what appears to be a randomly varying magnetic field. At reasonable gas pressures this causes a rapid destruction of orientation in the non- S -state atoms which cannot be overcome by the pumping rate available from conventional atomic light sources.

The extension of traditional optical pumping techniques to molecular radicals appears to be an even more formidable task.⁹ For such species optical pumping is severely impeded not only by the molecular spin-rotation interaction (analogous to the spin-orbit interaction in atoms) which causes collisional destruction of orientation, but also by the inefficient pumping inherent in the molecular fluorescence process (as compared to atomic fluorescence). When a molecule absorbs (monochromatic) optical radiation it makes a transition to some particular vibrational-rotational level (v', J') of an excited electronic state. The subsequent fluorescence corresponds to transitions to all those ground state (v'', J'') levels that are populated according to the Franck-Condon principle and according to the rotational selection rules appropriate to the molecular transition. Because of the multiplicity of possible transitions, the pumping rate for any particular (v'', J'') level is considerably slower than the pumping rate in atomic systems.

Consequently, it is not surprising that there have been no reports of optical pumping of molecules in the gas phase, and indeed it has been suggested by some that it is impossible to prepare assemblies of oriented or aligned molecules¹⁰ except in the absence of collisions. Some extremely elegant experiments have been performed on the H_2^+ molecule under collision-free conditions following a suggestion of Dehmelt and Jefferts¹¹ based on what they called "selective photodissociation." They proposed that the ions be created by pulsed electron bombardment and contained in an rf quadrupole

⁹ R. J. McNeal, R. A. Bernheim, R. Bersohn, and M. Dorfman, *J. Chem. Phys.* **40**, 1678 (1964).

¹⁰ We distinguish between orientation and alignment as follows: Consider a system of total angular momentum J with magnetic sublevels M . If the population of $+M$ and $-M$ are unequal, the system has a net magnetization and is said to be *oriented*. If the population of the magnetic sublevels are such that the $+M$ and $-M$ levels are equally populated, but different $|M|$ levels have different populations, the system has a net polarization but no net magnetization and is said to be *aligned*.

¹¹ H. G. Dehmelt and K. B. Jefferts, *Phys. Rev.* **125**, 1318 (1962).

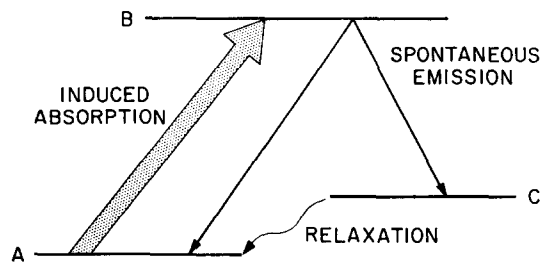


FIG. 1. Schematic of the conventional optical pumping process.

trap¹² which is illuminated by an intense source of linearly polarized light with a wavelength sufficient to photodissociate a number of the vibrational levels ($v'' \geq 3$) of the H_2^+ molecule. Since the probability of photodissociation is proportional to the square of the cosine of the angle between the polarization vector of the light beam and the dipole transition moment direction of the molecule, the magnetic sublevels are destroyed at different rates causing an alignment in the remaining M levels. In this manner magnetic resonance transitions have been observed¹³ among several Zeeman sublevels of the hyperfine states of the H_2^+ molecule (averaged over the vibrational levels populated by electron impact ionization).

We describe here a variant procedure, which might be called "selective excitation," that is capable of achieving optical pumping in a particular (v'', J'') level of a gas phase molecule through the orientation dependence of its photoabsorption cross section. In Sec. II we present a simplified theoretical model for the optical pumping process. Classical and quantum mechanical formulations are compared and it is shown that for $J'' \geq 5$ the classical treatment is fully adequate. Both the steady-state and time-dependent behavior of an optically pumped molecular system are developed. In Sec. III we describe some experiments using laser-induced fluorescence of the Na_2 molecule which demonstrate the attainment of optical pumping for this molecular system. Following the presentation of some experimental results, we discuss briefly in Sec. IV some of the implications and possible extensions of this new technique.

II. THEORY

Consider a beam of plane-polarized light incident upon an assembly of randomly oriented molecules in the gas phase. We assume that the bandwidth of the light source overlaps a single molecular absorption line causing the molecule to make an electronic transition

¹² H. G. Dehmelt, in *Advances in Atomic and Molecular Physics* D. R. Bates and I. Estermann, Eds. (Academic Press Inc., New York, 1967), Vol. 3, pp. 53-72.

¹³ K. B. Jefferts and H. G. Dehmelt, *Bull. Am. Phys. Soc.* **7**, 432 (1962); C. B. Richardson, K. B. Jefferts, and H. G. Dehmelt, *Phys. Rev.* **165**, 80 (1968) [Erratum: **170**, 350 (1968)].

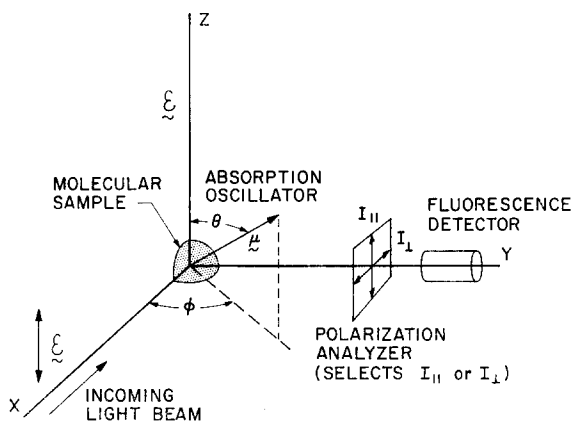


Fig. 2. Geometrical arrangement used for the measurement of fluorescence polarization.

from some ground state vibration-rotation level (v'', J'') to some excited state level (v', J'). In the absence of collisions molecules in the (v', J') level lose their energy by spontaneous emission, making radiative transitions to all those (v'', J'') levels of the ground state which satisfy the Franck-Condon principle and the appropriate selection rules for ΔJ . This gives rise to an extended series of emission lines commonly called a molecular resonance fluorescence progression.¹⁴ We wish to develop an expression for the polarization of the radiation originating from the (v', J') level as a function of the intensity of the incident light beam.

For this purpose it is convenient to introduce a geometrical arrangement, shown in Fig. 2, which is conventionally used in experimental polarization measurements. Here a plane-polarized light beam travels along the X axis with its electric vector \mathbf{E} parallel to the Z axis. The molecular sample is located at the origin of the coordinate system and a fluorescence detector views the molecular sample along the Y axis. A polarization analyzer (commonly a sheet of polaroid) is placed between the detector and the molecular scattering gas. The analyzer may be oriented in either of two positions so that the detector can measure I_{\parallel} , the intensity of fluorescent light plane-polarized with its electric vector parallel to the electric vector of the incident light, or I_{\perp} , the intensity of fluorescent light plane-polarized with its electric vector perpendicular to the electric vector of the incident light. With such an experimental setup the *degree of polarization* P is traditionally^{14,15} defined as

$$P = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp}). \quad (1)$$

The degree of polarization can assume the values $-1 \leq P \leq 1$, where $P=0$ corresponds to isotropic radiation, i.e., completely unpolarized light.

¹⁴ P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1965).

¹⁵ P. P. Feofilov, *The Physical Basis of Polarized Emission* (Consultants Bureau Enterprises, Inc., New York, 1961).

Previously, both classical and quantum mechanical expressions have been derived for the degree of polarization which illustrate its dependence on the various types of rotational branches possible in absorption and emission.¹⁵⁻¹⁷ The change of P with external applied field and the influence of hyperfine structure on the value of P have been considered as well. However, for clarity, we restrict our attention here to one special but often encountered case, that of a Q -branch transition ($\Delta J=0$) in absorption followed by a Q -branch transition in emission, symbolized by ($Q\uparrow, Q\downarrow$). The results for other rotational branches are readily generalized from this simple case. From symmetry considerations it is clear that the electronic transition moment for a diatomic molecule must lie along the molecular axis or in a plane perpendicular to the molecular axis. For Q -branch fluorescence ($Q\uparrow, Q\downarrow$) the absorption and emission transition moments coincide, and for large J they may be assumed to be directed along the angular momentum vector \mathbf{J} at right angles to the internuclear axis of the molecule.

A. Classical Treatment

We suppose that the molecular transition moment $\boldsymbol{\mu}$ may be replaced by a classical Hertzian dipole oscillator pointed in the same direction and attached rigidly to the molecular framework. The orientation of the Hertzian oscillator $\boldsymbol{\mu}$ can then be described by the ordinary polar coordinates, θ and ϕ , shown in Fig. 2, which locate $\boldsymbol{\mu}$ relative to \mathbf{E} and to the plane defined by the light beam and the fluorescence detector. The calculation of the degree of polarization for a ($Q\uparrow, Q\downarrow$) fluorescence series proceeds as follows.

Let $n(\theta, \phi)d\Omega$ denote the fraction of molecules with absorption oscillators oriented about θ, ϕ in the solid angle element $d\Omega = \sin\theta d\theta d\phi$. The probability for the absorption of light by the molecule is proportional to $|\boldsymbol{\mu} \cdot \mathbf{E}|^2$, the square of the component of the electric vector \mathbf{E} along the axis of the absorption oscillator $\boldsymbol{\mu}$, i.e., $\cos^2\theta$. For a ($Q\uparrow, Q\downarrow$) fluorescence series the emission oscillator is pointed in the same direction as the absorption oscillator. The fluorescent light originating from the emission oscillator may be resolved into two orthogonal plane-polarized components. The probability that the emitted light is plane-polarized parallel to \mathbf{E} is given by the square of the projection of the axis of the emission oscillator upon the Z axis, i.e., $\cos^2\theta$. The probability that the emitted light as viewed by the fluorescence detector is plane-polarized perpendicular to \mathbf{E} is given by the square of the projection of the axis of the emission oscillator upon the X axis, i.e., $\sin^2\theta \cos^2\phi$. Expressions for I_{\parallel} and I_{\perp} are then obtained by compounding these joint probabilities and

¹⁶ R. N. Zare, *J. Chem. Phys.* **45**, 4510 (1966).

¹⁷ M. McClintock, W. Demtröder, and R. N. Zare, *J. Chem. Phys.* **51**, 5509 (1969), this issue.

averaging over all possible molecular orientations:

$$I_{||} = \int_0^{2\pi} \int_0^\pi n(\theta, \phi) \cos^4\theta \sin\theta \, d\theta d\phi \quad (2)$$

and

$$I_{\perp} = \int_0^{2\pi} \int_0^\pi n(\theta, \phi) \cos^2\theta \sin^2\theta \cos^2\phi \sin\theta \, d\theta d\phi. \quad (3)$$

If the random distribution of oscillators is undisturbed by the presence of the incident light beam, then $n(\theta, \phi)$ may be taken to be a constant n_0 for all directions, and the evaluation of the integrals in Eqs. (2) and (3) are readily performed to yield

$$I_{||} = 4\pi n_0/5 \quad (4)$$

and

$$I_{\perp} = 4\pi n_0/15. \quad (5)$$

The degree of polarization, obtained from Eq. (1), then has the value $P = \frac{1}{2}$, in agreement with the results of previous calculations.¹⁵⁻¹⁷

Suppose, however, that the light beam illuminating the molecular sample is so intense that it is able to deplete the (v'', J'') level through the radiative transition $(v'', J'') \rightarrow (v', J')$ more rapidly than collisions can replenish the population of the (v'', J'') ground state level. Because the upper state level (v', J') has, in general, a very short radiative lifetime, and because it primarily reradiates to ground-state vibrational-rotational levels other than the one from which it is excited, it follows that the light beam pumps away (reduces) the population of the (v'', J'') level until a balance is achieved between the absorption rate and the rate of repopulation. As we have mentioned before, certain molecular orientations are preferentially destroyed (pumped away). Under conditions of intense illumination, the angular distribution of the ground-state oscillators, $n(\theta, \phi)$, becomes nonrandom and this anisotropy will alter the degree of polarization of the molecular fluorescence.¹⁸

In the same spirit that Bloch¹⁹ proposed phenomenological equations to describe the magnetic relaxation of ensembles of nuclei, we may write a master rate equation for the rate of change of the number of oscillators $n(\theta, \phi, t)$ having axes at time t pointing into the solid angle element $\sin\theta \, d\theta d\phi$ about (θ, ϕ) :

$$dn(\theta, \phi, t)/dt = -\beta I n(\theta, \phi, t) \cos^2\theta + \alpha [n_0 - n(\theta, \phi, t)], \quad (6)$$

where we have assumed that only one parameter, α , is sufficient to describe the rate at which equilibrium is

restored in the ensemble of molecules. In Eq. (6) the population loss rate, $-\beta I n(\theta, \phi, t) \cos^2\theta$, depends on (1) the intensity, I , of the light beam; (2) the population $n(\theta, \phi, t)$ of oscillators whose axes are described by the polar angles, (θ, ϕ) at time t ; (3) the square of the cosine of the angle between the electric vector \mathbf{E} of the light beam and the axis $\boldsymbol{\mu}$ of the absorption oscillator; and (4) a rate constant, β , which in turn depends on the line strength of the molecular transition, the overlap of the molecular absorption line with the incoming radiation, etc. The population gain term in Eq. (6) is simply the population difference between the initial population $n(\theta, \phi, 0) = n_0$ and the instantaneous population $n(\theta, \phi, t)$ multiplied by the rate constant α , the reciprocal of the relaxation time. From the solution of Eq. (6) the degree of polarization may be determined from Eqs. (1)-(3) as a function of time.

Suppose the light beam has been incident on the molecular sample for a long period of time. A steady-state solution of Eq. (6) results and we may set

$$dn(\theta, \phi, t)/dt = 0.$$

The steady-state population of absorption oscillators $n(\theta, \phi, \infty) = n(\theta, \phi)$ is then given by

$$n(\theta, \phi) = \alpha n_0 / (\alpha + \beta I \cos^2\theta). \quad (7)$$

In the limiting case in which the relaxation rate dominates the pumping rate ($\alpha \gg \beta I$), $n(\theta, \phi)$ approach n_0 , the initial random distribution of absorption oscillators. In the other extreme ($\beta I \gg \alpha$), the remaining absorption oscillators approach a $\sec^2\theta$ distribution.

If the expression for $n(\theta, \phi)$ given in Eq. (7) is substituted into the integrals of Eqs. (2) and (3), we obtain

$$I_{||} = 4\pi n_0 \gamma^2 [\gamma^3 \arctan(\gamma^{-1}) - \gamma^2 + \frac{1}{3}] \quad (8)$$

and

$$I_{\perp} = 2\pi n_0 \gamma^2 [-\gamma(\gamma^2 + 1) \arctan(\gamma^{-1}) + \gamma^2 + \frac{2}{3}] \quad (9)$$

from which the degree of polarization is found to be²⁰

$$P = \frac{3\gamma(3\gamma^2 + 1) \arctan(\gamma^{-1}) - 9\gamma^2}{3\gamma(\gamma + 1)(\gamma - 1) \arctan(\gamma^{-1}) - 3\gamma^2 + 4}. \quad (10)$$

In Eqs. (8)-(10) we have introduced for convenience the quantity γ^2 which is the ratio of the relaxation rate to the pumping rate

$$\gamma^2 = \alpha / \beta I. \quad (11)$$

¹⁸The optical pumping of atomic systems corresponds to "pumping" population into selected atomic energy levels. In contrast, the optical pumping of molecular systems we have described here depends on "pumping away" (depumping) population from selected molecular energy levels.

¹⁹F. Bloch, Phys. Rev. **70**, 460 (1946).

²⁰Equation (10) is equivalent to the polarization formula given in Ref. 15, p. 168, to explain the results of B. J. Sveshnikov [Compt. Rend. (Doklady) **51**, 675 (1946)] on the effect of the intensity of exciting light upon the polarization of the phosphorescence of fluorescein in a boric acid "glass" phosphor. The mechanism of course is quite different. See as well B. I. Stepanov and V. P. Gribkovskii, Opt. Spektrosk. **8**, 224 (1960) [Opt. Spectrosc. **8**, 114 (1960)]. R. Bersohn (private communication) has suggested the use of the asymmetry parameter $R = (I_{||} - I_{\perp}) / (I_{||} + 2I_{\perp})$ in place of the degree of polarization P . Equation (10) would then take the more compact form $R = \frac{3}{2} [\gamma(\gamma^2 + 1) \arctan(\gamma^{-1}) - \gamma^2] / [1 - \gamma \arctan(\gamma^{-1})]$.

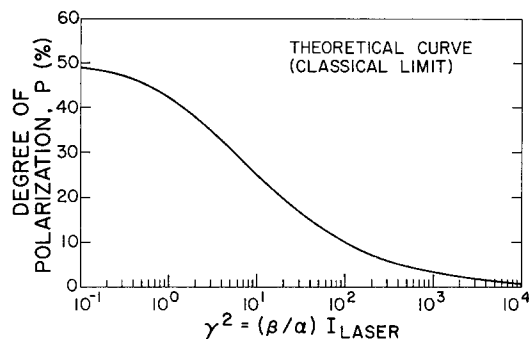


FIG. 3. The degree of fluorescence polarization (theoretical) as a function of the optical pumping parameter γ^2 , which is proportional to the intensity of the incident beam.

Figure 3 illustrates how the degree of polarization P is a function of $\gamma^2 = \beta I / \alpha$. We have chosen to plot P as a function of γ^2 so that the decrease of P with increasing intensity I of the light beam is clearly evident. For the case of weak illumination ($\alpha \gg \beta I$), γ^2 approaches infinity and the degree of polarization in Eq. (10) approaches the value of $P = \frac{1}{2}$, as expected. This limiting behavior may not be readily apparent from a cursory inspection of Eq. (10) since the ratio of the numerator to the denominator in Eq. (10) is indeterminate. However, the proper limiting value of P as $\gamma^2 \rightarrow \infty$ may be obtained by successive applications of L'Hospital's rule or by replacing $\arctan(\gamma^{-1})$ with the first three terms of its power series expansion, $\gamma^{-1} - \frac{1}{3}\gamma^{-3} + \frac{1}{5}\gamma^{-5}$. When the pumping rate equals the relaxation rate ($\alpha = \beta I$), $\gamma^2 = 1$ and P has the value $3(\pi - 3)$, i.e., $P = 0.425$, which corresponds to a small decrease from the limit of no optical pumping, $P = 0.500$. However, when the pumping rate exceeds the relaxation rate, the degree of polarization starts to fall off rapidly, as shown in Fig. 3. In the extreme case of intense illumination ($\alpha \ll \beta I$), γ^2 tends toward zero, $\arctan(\gamma^{-1})$ approaches $\pi/2$, and the degree of polarization has the limiting value $P = 0$. This has a simple physical interpretation. In the limit of large pumping rate, a molecule is removed by light absorption from the (v'' , J'') level as fast as it arrives. Such molecules enter the (v'' , J'') level with random orientations of their absorption oscillator. Consequently, the emission oscillators of the excited (v' , J') level [which coincide with the direction of the absorption oscillator for a ($Q \uparrow$, $Q \downarrow$) transition] are also randomly distributed (isotropic) and the molecular fluorescence is completely unpolarized ($P = 0$).

B. Quantum Treatment

The quantum counterpart to the classical model presented above is readily formulated by introducing the populations $n_M(t)$ of the discrete magnetic sublevels M in place of the population $n(\theta, \phi, t)$ of the continuously variable absorption oscillator orientations. Accordingly,

the integrals over $\sin\theta d\theta d\phi$ must be replaced by a summation over all final M' states and an average over all initial M states. Let us consider the resonance fluorescence process ($Q \uparrow$, $Q \downarrow$) caused by plane-polarized light incident upon a molecular sample with the light's polarization vector $\mathbf{\epsilon}$ taken as the axis of quantization (the Z axis). In absorption we have $\Delta J = 0$, $\Delta M = 0$ and the probability that a dipole transition occurs for each M level is proportional to the square of the Clebsch-Gordon coefficient, $C^2(J1J; M0)$. In emission either $\Delta J = 0$, $\Delta M = 0$, corresponding to fluorescent light plane-polarized parallel to $\mathbf{\epsilon}$, or $\Delta J = 0$, $\Delta M = \pm 1$, corresponding to fluorescent light plane-polarized perpendicular to $\mathbf{\epsilon}$. The probabilities for these two processes are proportional to $C^2(J1J; M0)$ and

$$\frac{1}{2}[C^2(J1J; M, +1) + C^2(J1J; M, -1)],$$

respectively. The quantum analogs of Eqs. (2) and (3) are obtained by compounding these joint probabilities weighted by the population of each M state and summing over all initial and final M states,

$$I_{||} = \sum_M n_M C^4(J1J; M0) \quad (12)$$

and

$$I_{\perp} = \frac{1}{2} \sum_M n_M C^2(J1J; M0) [C^2(J1J; M, +1) + C^2(J1J; M, -1)]. \quad (13)$$

Once again if the illumination is weak, n_M will be the same for each M state and it may be removed from the sum over M in Eqs. (12) and (13). With the help of explicit algebraic expressions²¹ for the squares of the Clebsch-Gordon coefficients,

$$C^2(J1J; M0) = M^2/J(J+1) \quad (14a)$$

and

$$C^2(J1J; M1) + C^2(J1J; M, -1) = 1 - [M^2/J(J+1)] \quad (14b)$$

and by introducing the identities¹⁶

$$\sum_M M^0 = 2J+1, \quad (15a)$$

$$\sum_M M^2 = \frac{1}{3}J(J+1)(2J+1), \quad (15b)$$

and

$$\sum_M M^4 = (1/15)J(J+1)(2J+1)(3J^2+3J-1), \quad (15c)$$

²¹ M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

the quantum mechanical degree of polarization is found to be

$$P = (4J^2 + 4J - 3) / (8J^2 + 8J - 1), \quad (16)$$

in agreement with previous results.^{15, 16} Note that as J increases, P rapidly approaches the classical limiting value, $P = \frac{1}{2}$.

However, for the case of intense illumination, the populations n_M of the different magnetic sublevels M may not be equal to each other and we must solve the corresponding quantum expression for the rate of change of the populations n_M

$$dn_M(t)/dt = -\beta IC^2(J1J; M0)n_M(t) + \alpha[n_0 - n_M(t)]. \quad (17)$$

Under steady-state conditions ($t \rightarrow \infty$)

$$n_M = \frac{\alpha n_0}{\alpha + \beta IC^2(J1J; M0)} = \frac{\alpha n_0}{\alpha + \beta IM^2/[J(J+1)]}. \quad (18)$$

Note that from the vector model for angular momenta,²² $M^2/[J(J+1)]$ approaches $\cos^2\theta$ with increasing J . Thus in the classical limit Eq. (18) becomes identical to Eq. (7).

By substituting the expression for n_M in Eq. (18) into Eqs. (12) and (13), and using the algebraic expressions for the Clebsch-Gordon coefficients given in Eq. (14) we obtain the steady-state expression for the quantum mechanical degrees of polarization

$$P = \left(\sum_{M=-J}^J \frac{3M^4 - J(J+1)M^2}{\gamma^2 + M^2/[J(J+1)]} \right) / \left(\sum_{M=-J}^J \frac{M^4 + J(J+1)M^2}{\gamma^2 + M^2/[J(J+1)]} \right). \quad (19)$$

Equation (19) is the quantum counterpart of the expression for the classical degree of polarization given in Eq. (10). We have introduced again in Eq. (19) the dimensionless quantity γ^2 for the ratio of the relaxation to the pumping rate [see Eq. (11)].

In Fig. 4 we examine the approach, with increasing J for different values of the parameter γ , of the quantum degree of polarization, P_Q [Eq. (19)], to the classical degree of polarization, P_C [Eq. (10)]. What is most remarkable about Fig. 4 is how rapidly P_Q tends to P_C . For $J=1$, $P_Q = \frac{1}{3}$, independent of the value of γ . With increasing J , P_Q approaches P_C as shown in Fig. 4 but not as a monotonic function of J for each value of γ . For $J=5$, P_Q has drawn within 2% of P_C for all the values of γ shown, and for $J>5$, P_Q and P_C become indistinguishable from each other (correspondence limit). Most molecular fluorescence progressions encountered in practice¹⁴ involve molecular states of high rotational angular momentum ($J>5$). For such states the quantum description differs so slightly from the classical description that we may henceforth restrict ourselves to the classical model with little loss in accuracy or generality.

C. Time-Dependent Behavior

Based on a simple model involving a single relaxation rate to describe the optical pumping of molecules, we have obtained both the classical and quantum mechanical steady-state degree of polarization and we have shown that they agree in the classical limit of "large" J . This then permits us to relate the parameter γ to the steady-state polarization P using the results of Figs. 3 and 4. However, in principle, more information about the optical pumping process may be obtained by investigating how the degree of polarization ap-

proaches its steady-state value as a function of time. By determining the manner in which the molecular system responds to the impressed light signal we can devise a means of measuring the rates α and βI separately, rather than just their ratio, γ^2 .

Let us suppose that the light beam of constant intensity I is suddenly switched on a time $t=0$. The general solution to the first-order differential equation given in (6) is

$$n(\theta, \phi, t) = [n_0 / (\gamma^2 + \cos^2\theta)] \times \{\gamma^2 + \cos^2\theta \exp[-\beta I(\gamma^2 + \cos^2\theta)t]\} \quad (20)$$

and the corresponding expressions for the parallel and perpendicular fluorescence intensity components as a function of time are

$$I_{||}(t) = \int_0^{2\pi} \int_0^\pi \frac{\cos^4\theta n_0}{\gamma^2 + \cos^2\theta} \times \{\gamma^2 + \cos^2\theta \exp[-\beta I(\gamma^2 + \cos^2\theta)t]\} \sin\theta d\theta d\phi \quad (21)$$

and

$$I_{\perp}(t) = \int_0^{2\pi} \int_0^\pi \frac{\cos^2\theta \sin^2\theta \cos^2\phi n_0}{\gamma^2 + \cos^2\theta} \times \{\gamma^2 + \cos^2\theta \exp[-\beta I(\gamma^2 + \cos^2\theta)t]\} \sin\theta d\theta d\phi. \quad (22)$$

We were unable to express $I_{||}(t)$ or $I_{\perp}(t)$ in closed analytic form except as an infinite series. Accordingly, Eqs. (21) and (22) were evaluated numerically for different arguments of α , β , and t using a simple com-

²² D. M. Brink and G. R. Satchler, *Angular Momentum* (The Clarendon Press, Oxford, England, 1962).

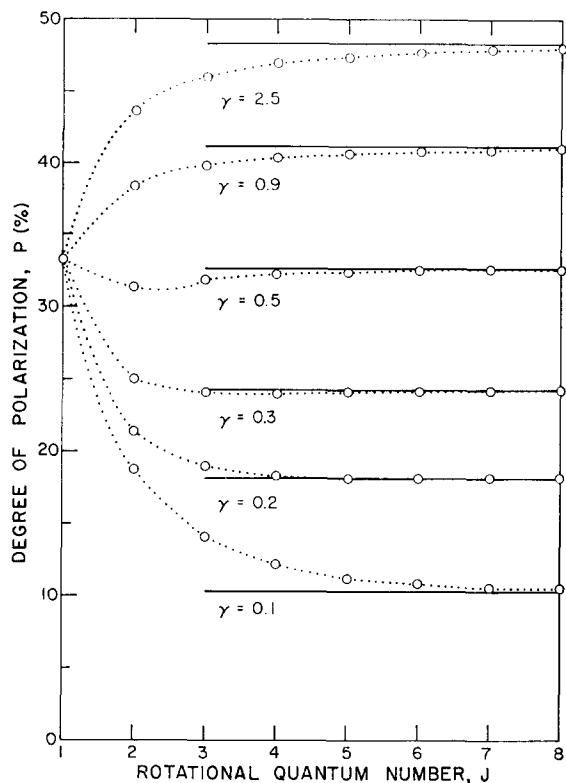


FIG. 4. Approach of the quantum mechanical degree of polarization to the classical limit (solid line) as a function of increasing rotational quantum number, J .

puter program to obtain the time-dependent degree of polarization, $P(t)$.

For the case of weak optical pumping we found that $P(t)$ smoothly joins onto its steady-state value $P(\infty)$ as a function of time. However, with increased optical pumping, $P(t)$ tends to overshoot its steady-state limit and may even become negative for a short period of time. This behavior is illustrated in Fig. 5 which presents $I_{\parallel}(t)$, $I_{\perp}(t)$, and $P(t)$ for $\gamma=0.1$ and for one particular value of $\alpha=2.4 \text{ sec}^{-1}$, corresponding to a relaxation time of about 417 msec. The upper half of Fig. 5 shows how $P(t)$ approaches its steady-state value of $P(\infty) = 10.4\%$ following an initial overshoot to about -18.5% ; the lower half of Fig. 5 illustrates the change in the parallel and perpendicular intensity components which accompanies the change in the degree of polarization with time. Note that $P=0$ occurs at the same instant of time $I_{\parallel}(t)$ crosses over $I_{\perp}(t)$.

The origin of this overshoot in $P(t)$ has a simple physical explanation in terms of the rates of change of $I_{\parallel}(t)$ and $I_{\perp}(t)$. Under conditions of strong illumination ($\alpha \ll \beta I$), absorption oscillators which have orientations nearly parallel to the electric vector of the incident light beam and hence are the main contributors to the parallel component of the intensity, are pumped away much more rapidly at first than oscillators which

contribute primarily to the perpendicular component of the intensity. Consequently before the relaxation rate can restore the system to its steady-state equilibrium, the decay of $I_{\parallel}(t)$ exceeds that of $I_{\perp}(t)$, resulting in a crossover of the two intensity components if the illumination is sufficiently intense. After a length of time, usually shorter than $1/\alpha$, the molecular relaxation rate drives $I_{\parallel}(t)$ and $I_{\perp}(t)$ toward their steady-state values. This "inertia" in the response of the molecular system to the impinging radiation causes an overshoot in the resulting degree of polarization as a function of time. The overshoot becomes more pronounced as the optical pumping becomes more vigorous, i.e., as the value of γ becomes smaller.

Another point of interest is how $P(t)$ varies with time for the same ratio of relaxation rate to pumping rate, γ^2 , but for different values of the relaxation rate, α . Figure 6 presents a family of curves for the same value of $\gamma=0.045$, corresponding to a limiting steady-state polarization of 5%, for four different values of α ranging from 0.6 to 2.4 sec^{-1} . In Fig. 6 the overshoot in $P(t)$ is close to -46.5% , compared to an overshoot in $P(t)$ of about -18.5% in Fig. 5. As we have mentioned, this behavior is to be expected for the more optically pumped system. However, the most remarkable feature

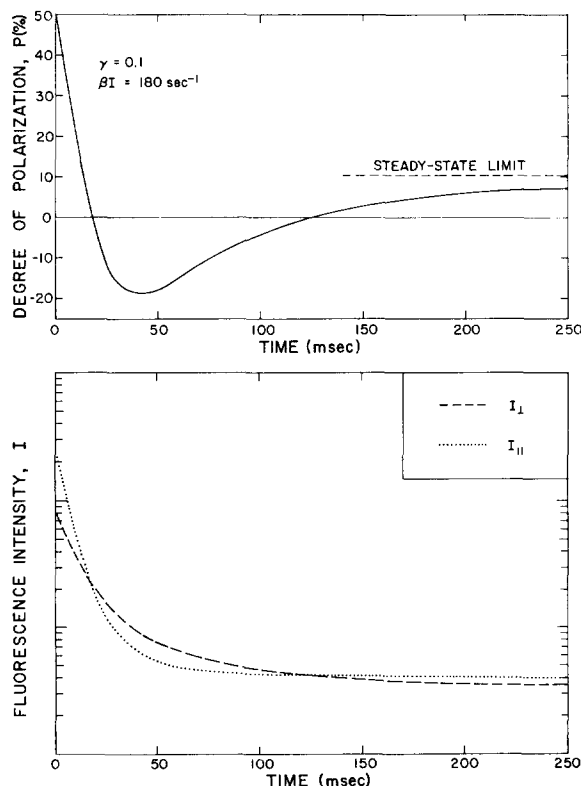


FIG. 5. The time evolution of the selective excitation optical pumping process. The upper half shows an overshoot in the degree of polarization; the lower half shows the corresponding decay in I_{\parallel} and I_{\perp} which causes this overshoot.

of Fig. 6 is the fact that the minimum value of the polarization is determined by the parameter γ and is *invariant* to the value of α , whereas the time at which the minimum polarization occurs depends sensitively on the value of α . We have seen previously how the steady-state value of the degree of polarization determines the optical pumping parameter γ . Figure 6 clearly shows that a measurement of the time evolution of $P(t)$ permits the individual rates α and βI to be determined as well.

We have presented a phenomenological model for the optical pumping of molecules based on the orientation dependence of their photoabsorption cross sections.²³ This model has the virtue that it is conceptually quite simple and is easily modified to include more complex considerations involving molecular diffusion, wall effects and other different relaxation processes. However, further elaboration must await the accumulation of reliable experimental data. We describe below

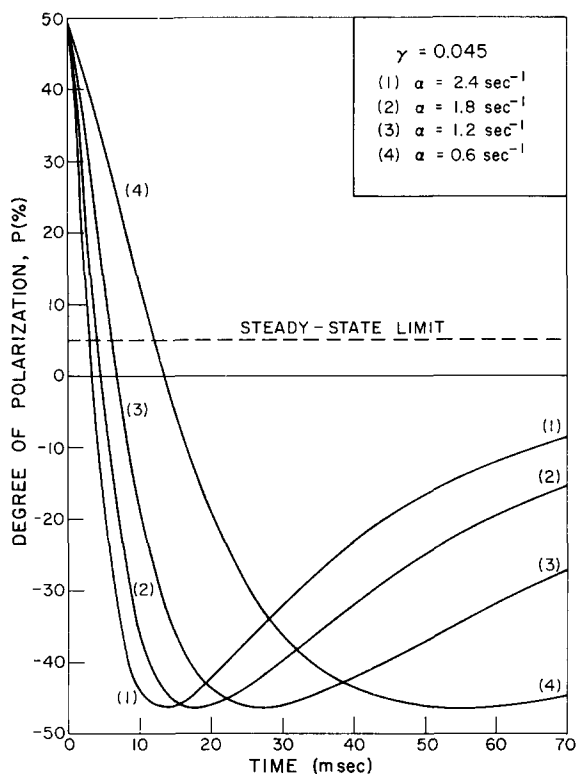


FIG. 6. Degree of polarization as a function of time for a given optical pumping parameter γ and for several values of the relaxation rate α .

²³ We have avoided the words "optical saturation" reserving their use to describe the situation in which the upper state and ground state populations are comparable, analogous to power saturation in the fields of infrared, microwave, ESR, and NMR. See A. Abragam, *The Principles of Nuclear Magnetism* (The Clarendon Press, Oxford, England, 1961) and E. U. Condon, Proc. Natl. Acad. Sci. U.S. 52, 635 (1964).

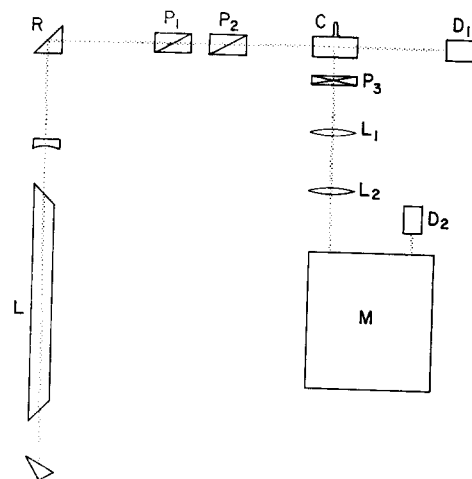


FIG. 7. Schematic diagram of the experimental setup: L=laser; R=prism; P₁, P₂, P₃=polarizers; C=cell; L₁, L₂=lenses; M=monochromator; and D₁, D₂=detectors.

the first observation of this optical pumping process for molecules.

III. EXPERIMENTAL

The 4880-Å line of a cw argon-ion laser has been found to excite five resonance fluorescence series in the Na₂ B ⁴Π_u-X ¹Σ_g⁺ band system. Demtröder, McClintock, and Zare have performed an interferometric analysis of the resulting fluorescence spectrum shown in Figs. 3 and 4 of their paper, and they have been able to perform the (v', J') → (v'', J'') assignments for each series.²⁴ It is clear from their Fig. 3 that the Q-line series (v'=6, J'=43) → (v'', J''=43) is the most prominent fluorescence progression and is over 10 times stronger than the other fluorescence series. This Q-line progression originates from the (v''=3, J''=43) → (v'=6, J'=43) transition and consists of 22 lines which span the wavelength region 4700–5600 Å. We have utilized this laser-induced fluorescence series to study the optical pumping of the (v''=3, J''=43) ground state level of the Na₂ molecule.

A schematic diagram of the experimental setup is shown in Fig. 7. The geometrical arrangement is the same as that described in Fig. 2. The laser (L) is a rare gas ion type of local origin,²⁵ 1.2 meters long with a 3-mm bore. The dc discharge (typically less than 10 A at 300 V) runs through a water-cooled quartz capillary that is coaxial with a solenoid magnet capable of producing a 1000-G field. Various cw laser lines can be selected by means of the internally reflecting prism that forms one end of the laser cavity. At the other end

²⁴ W. Demtröder, M. McClintock, and R. N. Zare, J. Chem. Phys. 51, 5495 (1969), this issue.

²⁵ We thank Dr. W. Demtröder who helped us in the construction of this laser.

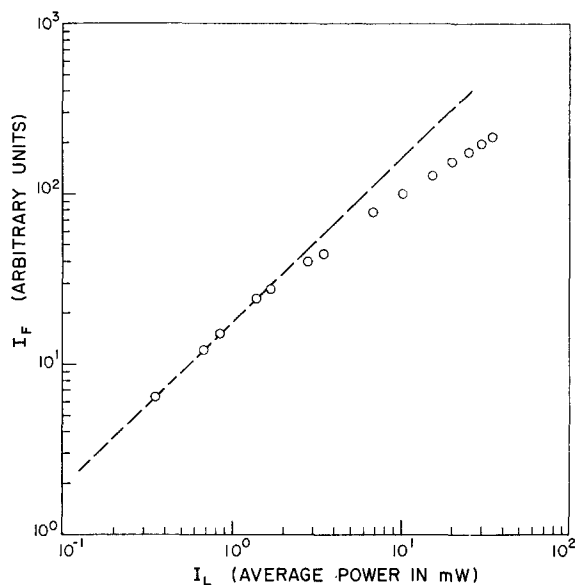


FIG. 8. Plot of I_F vs I_L . The dashed line represents behavior conforming to the Beer-Lambert law.

of the laser cavity is a dielectric-coated mirror (1%–5% transmission). The power output of the laser is about 700 mW for the 4880-Å laser line.

The laser beam passes through an external prism (R) which ensures the spectral purity of the laser output and also facilitates a more convenient arrangement of the rest of the apparatus. The laser beam then passes through two calcite polarizers²⁶ (P_1) and (P_2), which when “crossed” reduce the intensity of the beam more than six orders of magnitude. Because Brewster angle windows are used on the discharge tube, the laser output is plane-polarized to a high degree. Rotation of (P_1) relative to (P_2) attenuates the laser beam *without altering its spot size or its line profile*. The second calcite crystal (P_2) defines the plane of polarization of the light beam incident on the cell (C).

The alkali vapor cell is constructed from Corning 1720 aluminosilicate glass²⁷ to prolong its useful life. The cell is 1 in. in diameter and 3 in. long with a small sidearm for a reservoir in the middle. The cell’s main body and reservoir are heated separately (using nichrome wire wrapped in asbestos tape) and the reservoir is maintained at a temperature about 10°C below that of the main body in order to prevent condensation of sodium vapor on the cell windows. In addition, the heater coils are extended beyond each window to prevent local cool spots from forming. The temperature of both the main body and the reservoir are measured

by Chromel–Alumel thermocouples which are embedded in the asbestos in contact with the glass cell.

The transmitted light intensity is monitored by a selenium photovoltaic detector (D_1) and a correction for the transmission of the windows is applied to obtain the value of the light beam intensity in the cell. This intensity measurement represents the total light power and does not take into account the intensity distribution across the laser spot size (which can be assumed to be Gaussian if the laser operates in the TEM₀₀ mode).

The Na₂ fluorescence is observed at right angles to the incident laser beam and to its polarization vector. An analyzing polarizer (P_3) selects the intensity component of the fluorescence, $I_{||}$ or I_{\perp} , to be measured. The lenses (L_1) and (L_2) image the fluorescent light on the entrance slit of a $\frac{3}{4}$ -meter SPEX monochromator (M), which disperses the light and permits various lines of the fluorescence series under study to fall on the photomultiplier (D_2). In this manner we observed the $I_{||}$ and I_{\perp} components of the fluorescence lines²⁸ (Q1), (Q7), (Q10), (Q13), and (Q14) (See Fig. 3 of Ref. 24 for the identification of these lines) as a function of the intensity of the laser beam incident upon the alkali vapor cell.

The first evidence we had that we might be observing the optical pumping of the Na₂ molecule was the departure we detected from the Beer-Lambert law. The well-known Beer-Lambert law states that each layer of a material of equal thickness absorbs an equal fraction of the light which is transmitted through it. From this law is derived the exponential attenuation of the light beam

$$I = I_0 \exp(-\epsilon cl), \quad (23)$$

where I_0 is the incident intensity, I is the transmitted intensity, ϵ the extinction coefficient, c the concentration, and l the path length. For the sodium vapor cell we can assume that for each photon absorbed one is emitted in fluorescence (the vapor pressures are so low and the Na₂ lifetime is so short¹⁵ that quenching collisions may be neglected). Then a measure of the fluorescence intensity, I_F , should be proportional to the incident laser intensity I_L if the Beer-Lambert law is valid.

In Fig. 8 we have made a log-log plot of I_F vs I_L . For laser intensities below 1.4 mW the measurements fall on a straight line, but deviate appreciably for greater laser powers, showing that I_F cannot keep pace with increasing I_L . The failure of the Beer-Lambert law in the optical region is normally caused by the use of polychromatic light, in which different wavelength

²⁶ Absorbing polarizers (Polaroid, Polacoat, etc.) could not be used in the laser beam since they bleach at the high intensities employed.

²⁷ W. J. Tango, J. K. Link, and R. N. Zare, *J. Chem. Phys.* **49**, 4264 (1968).

²⁸ The entire detection optics system is calibrated for its response to parallel or perpendicular plane-polarized light at each wavelength using both a standard tungsten lamp and a medium-pressure mercury lamp. The calibration was performed for various lamp orientations to minimize the effects of residual polarization of these light sources.

components are absorbed at different rates. Clearly this is not applicable to the measurement we have described. Failure of the Beer-Lambert law in the infrared and radio-frequency region is often encountered and attributed to saturation in which the population of the upper level can no longer be considered to be negligible under the influence of the radiation field because of its extremely slow relaxation rate. In the optical region the primary relaxation process for the upper state is its radiative decay. At sufficiently high powers optical saturation will certainly occur. However, for the Na_2 molecule, with an estimated lifetime¹⁵ of

$$6.41 \pm 0.38 \times 10^{-9} \text{ sec,}$$

optical saturation cannot explain the deviation from the Beer-Lambert law at the low laser power levels shown in Fig. 8. A more likely interpretation of the deviation we have observed is the selective excitation of the ($v''=3, J''=43$) level of the ground state whereby the laser beam depletes this level more rapidly than collisions or radiative processes²⁹ can repopulate it.

Moreover, our model for selective excitation predicts that certain molecular orientations are preferentially "burned away" by the laser beam, resulting in an unequal population of the magnetic sublevels of the state which should affect the polarization of the fluorescence. Indeed, this effect has been observed, and Fig. 9 shows some typical data illustrating the variation in the degree of polarization of the molecular fluorescence with laser intensity. With increasing laser power, it is apparent from Fig. 9 that the fluorescence polarization P at first remains constant with an initial value of about 50%, as expected. However, P then decreases to about one half its value as the laser power increases to approximately 300 mW. We note that P begins to diverge from its constant value at the same laser power level (1.4 mW) for which the absorption, shown in Fig. 8, starts to deviate from the straight line predicted by the Beer-Lambert law. The variation of P with I_L has been determined for several members of the Q -line progression with the same cell operating conditions. The degree of polarization should not be a function of the initial or final state vibrational quantum numbers. In each case we have obtained the same dependence of P on I_L within the accuracy of our polarization measurements. Figure 9 also shows data taken for two cell temperatures, 260°C and 300°C. At the higher cell temperature the pressure is greater, and the population

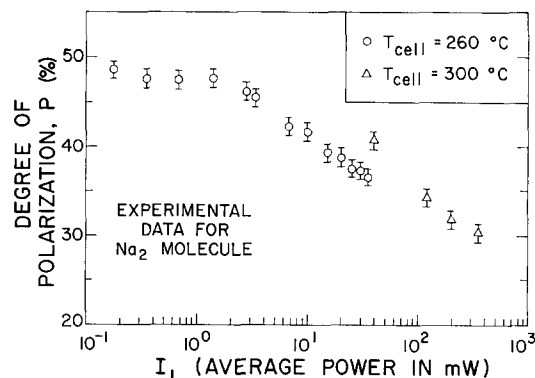


Fig. 9. The degree of fluorescence polarization (experimental) as a function of the incident laser power, which is proportional to the optical pumping parameter γ^{-2} . The 4880-Å line of a cw argon-ion laser is used to optically pump the ($v''=3, J''=43$) vibrational-rotational level of the Na_2 ground state.

of the (v'', J'') level which is pumped has increased. It is not surprising then to find that for the same laser light intensity a higher degree of optical pumping is achieved in the more rarefied vapor, resulting in a lesser degree of polarization of its fluorescence. We believe Figs. 8 and 9, taken together, constitute a demonstration that the Na_2 ($v''=3, J''=43$) level has been optically pumped using the 4880-Å line of the argon-ion laser.

From the preliminary data obtained for the Na_2 system it is not possible to assess quantitatively how well the theory in Sec. II matches these experimental findings. However, a comparison of Fig. 3 with Fig. 9 shows that the observed change of P with I_L has the correct form and features predicted by the simple phenomenological model we have presented. A more stringent test of theory must await the subsidiary determination of the pumping rate βI or the relaxation rate α by some other means. Nevertheless, we are encouraged by the qualitative agreement between Figs. 3 and 9, and experiments are now underway to study the time dependence of the degree of polarization in an attempt to further characterize the nature of this optical pumping process for molecules.

We have described an optical pumping experiment using a linearly-polarized laser beam to cause alignment in the magnetic sublevels of the ($v''=3, J''=43$) level of the $\text{Na}_2 X^1\Sigma_g^+$ ground state. It should be clear that orientation of the magnetic sublevels of the same system could have been achieved as well by using a beam of circularly polarized light, although the relaxation process might be expected to be different than for alignment, analogous to the Bloch equations.¹⁹ Suppose the molecule under study possesses a hyperfine structure, as indeed Na_2 does. Using a single-mode laser beam it should be possible to tune the laser to excite only one particular hyperfine component (hyperfine pumping). In addition to producing strong population

²⁹ For a homonuclear diatomic molecule, such as Na_2 , vibrational-rotational transitions to the pumped (v'', J'') level can be ignored since such molecules have no permanent electric dipole moment. However, for heteronuclear molecules such radiative transitions may contribute significantly to the relaxation rate of the optically pumped (v'', J'') level. Indeed, this opens the possibility of exploiting the population inversion between (v'', J'') levels of the ground state to obtain coherent amplification (infrared laser).

differences between molecular hyperfine levels the technique of selective excitation should permit "fine-structure pumping" as well if the molecule is a free radical.

In the foregoing we have concentrated much of our attention on the Na_2 molecule. However, the generalization to other gas-phase diatomic and polyatomic molecules is quite straightforward. Moreover, this optical pumping technique of selective molecular excitation should be applicable to molecules in solution.³⁰ In condensed media, the rotational motion of the molecule is usually no longer that of a free rotor but rather that of a drunkard's walk on the surface of a sphere or, more generally, an ellipsoid of revolution. Nevertheless, the existence of certain favorable orientations for light absorption can be exploited to selectively remove those orientations and optically pump the molecular system. Such a medium should then exhibit photoinduced dichroism.

IV. CHEMICAL APPLICATIONS

Once it is possible to prepare ensembles of optically pumped molecules, it will be possible to perform numerous kinds of experiments on such systems to gain information about molecular structure and molecular collisions. Although a detailed discussion of these possibilities would become a matter of much speculation, we can nevertheless sketch some of the general areas in which we believe future developments may be realized.

Optical pumping is a powerful method for creating and maintaining a nonequilibrium population of molecules in different specified quantum states. By applying a radio-frequency field to cause resonance transitions between these quantum states, the energy separations between levels may be precisely determined, the resonance being detected by its effect on the optical pumping signal (which may be monitored conveniently by the optical emission or absorption of the molecule). The study of radio-frequency resonances by this optical pumping technique should permit us to measure the magnetic moment, the electric dipole moment, the polarizability, the fine and hyperfine structure, etc., of the (v'', J'') level of the ground state. Moreover, optical pumping permits us to systematically study the interaction of an electromagnetic field with a molecular system. New features of this interaction can be investigated, such as multiple quantum transitions, light shifts, and coherence effects.

³⁰ This represents a natural extension of the method of photo-selection whereby the act of photoselection induces anisotropy into the initially random sample. See A. C. Albrecht, *J. Mol. Spectry*, **6**, 84 (1961).

It might be wondered how the radio-frequency study of optically pumped molecular systems compares with molecular beam resonance spectroscopy.³¹ The instrumentation is certainly simpler in the former case. Moreover, optical pumping by selective excitation permits the study of one unique (v'', J'') level of the molecule, whereas molecular beam resonance work is normally restricted to molecules in low rotational quantum states. However, a possible drawback to the study of optically pumped assemblies of molecules is the fact that the rf resonance is subject to pressure broadening and pressure shifts. Although this may impair the ultimate accuracy of this technique, at the same time it offers the possibility of investigating the detailed nature of intermolecular potentials, which would be of great interest in itself.

Indeed, the information optically pumped molecular ensembles can provide about collision phenomena and relaxation processes is perhaps an even richer source of knowledge. From the width of the resonance lines and from the time response of the pumped system, orientation and alignment relaxation rates can be evaluated for individual (v'', J'') levels, and the dependence of the relaxation mechanism on vibration, rotation, temperature, etc., can be investigated. If the relaxation of optically pumped molecules is studied in solution, it may be possible to learn about rotational diffusion constants and the influence of the solvation "cage"; if the relaxation of optically pumped molecules is studied in the gas phase under very low pressures, wall collisions may be the dominant source of relaxation so that the interaction of molecules with surfaces may be investigated.

The technique of selective excitation of molecular levels also creates the opportunity to prepare oriented or aligned samples which may be used as targets for subsequent chemical kinetics studies in gas flow systems or in crossed molecular beams.

Another appealing class of experiments involves the use of various physical means to probe the molecular system while it is undergoing optical pumping. For example, it might be possible, using absorption measurements, to monitor as a function of time the population of molecular levels nearby to the pumped (v'', J'') level after the laser beam has been suddenly turned off. In this way we might hope to observe directly how equilibrium is restored in the molecular ensemble through collisions and/or radiative transitions, and thus elucidate the bulk relaxation mechanism in terms of competing microscopic energy transfer steps.

³¹ See N. F. Ramsey, *Molecular Beams* (The Clarendon Press, Oxford, 1956).