Study of the electronic ground state of molecules by polarization-spectroscopy methods

M. P. Auzinsh

The possibility of using polarization-spectroscopy methods for determining the relaxation rates and magnetic moments of selected vibrational–rotational levels of the electronic ground state of diatomic molecules is discussed. Expressions are derived for the expected signals for different ways of setting up the experiments and different types of molecular transition.

Several methods are known for studying the relaxation characteristics and magnetic moments of selected vibrational-rotational (VR) levels of the electronic ground state of diatomic molecules: the ground state Hanle effect,[1] study of transient kinetics,[2] detection of quantum beats in transient kinetics in the ground electronic states of diatomic molecules,[3] study of quantum beat resonance in the electronic ground state of diatomic molecules.[4] However, all these methods assume that the molecule in the optically pumped[5] level studied absorbs light, and goes over to the VR level of the excited electronic state with subsequent deexcitation on one of the radiative transitions of the fluorescence progression. Thus, the signal being recorded is laser-induced fluorescence (LIF). As a result of such an observation process, the VR characteristics of the level of the excited state impose limitations on the applicability of the methods.[1-4] Successful observation of the signal requires that the condition $g''/\gamma \gg g'/\Gamma$ be satisfied, where g'' and g' are the Landé factors, and γ and Γ are the relaxation rates of the VR levels of the ground and excited states, respectively.

To preclude the influence of the VR level of the excited state, it is necessary to record the absorption from the level studied. However, under actual experimental conditions, the molecular concentration in the VR level studied is low, $N \sim 10^9$ cm^{-3}, and in principle, cannot increase. For this reason, in the study of the magnetic moments and relaxation rates of VR levels of the electronic ground state of diatomic molecules, polarization spectroscopy methods may prove to be promising.

Essentially, these methods consist in the following. As a result of the action of intense laser radiation on a rarefied gas-phase medium of atoms or molecules, the medium becomes optically anisotropic. Such a medium is characterized by induced dichroism and gyrotropy. If such an anisotropic medium is placed between crossed polarizers and exposed to a weak probing wave, the signal at the exit will be determined by the anisotropic properties of the gas. Such a method, involving the use of a split beam of a signal-frequency dye laser used as the intense and weak probing beams, made it possible to obtain high-resolution spectra both in atoms[6] and in molecules.[7] The polarization spectroscopy methods also make it possible to obtain the polarization decay times of atomic levels.[8,9] Reference 10 derived expressions for the polarization of a medium exposed to a strong light wave for molecular transitions where the states of angular momentum can be described classically; the effect of an external magnetic field on polarization-spectroscopy signals was studied in Ref. 11.

The object of this work is to explore the possibilities of using lasers in multimode operation for the purpose of studying the relaxation and magnetic properties of the VR levels of the electronic ground state of molecules.

To obtain the expressions for the expected signals, we shall use convenient methods of matrix optics.[12,13] We shall first assume that a strong light wave propagates along the x axis and has circular polarization. Circular dichroism and gyrotropy are then induced in the medium. Dichroism is characterized by different absorption coefficients α_- and α_+ for the light wave polarized clockwise and counterclockwise, respectively, and gyrotropy is characterized by two refraction coefficients: n_- and n_+. Using known methods[13] for such a medium, one can find the Mueller matrix M_m, which, when multiplied by the Stokes vector S of the probing wave, gives the Stokes vector S' of the light wave transmitted through the medium. Multiplying this vector by the Mueller matrix for the analyzer M_a, we obtain an expression for the signal at the light receiver of the recorder. The light receiver will be assumed sensitive only to the intensity, not to the polarization of the transmitted wave. The Stokes vector S_p for the polarization signal can hence be obtained as

$$S_p = M_a M_m S. \tag{1}$$

The first element of vector S_p characterizes the intensity of the transmitted signal. If the probing wave with intensity I_0 propagates along the x axis and is linearly polarized at an angle θ to the y axis, then its Stokes vector is

$$I_0 \begin{pmatrix} 1 \\ \cos 2\theta \\ \sin 2\theta \\ 0 \end{pmatrix}. \tag{2}$$

The matrix M_m can be written

$$M_{m1} = \begin{pmatrix} \frac{1}{2}(E_- + E_+) & 0 & 0 & \frac{1}{2}(E_- - E_+) \\ 0 & F\cos\delta & F\sin\delta & 0 \\ 0 & -F\sin\delta & F\cos\delta & 0 \\ \frac{1}{2}(E_- - E_+) & 0 & 0 & \frac{1}{2}(E_- + E_+) \end{pmatrix}, \tag{3}$$

where

$$E_i = \exp(-l\alpha_i), \qquad F = \exp\left[-\frac{l}{2}(\alpha_- + \alpha_+)\right],$$

l is the light path in an optically anisotropic medium, $\delta = (n_- - n_+)l\,2\pi/\lambda$, and λ is the wavelength of the probing light. The Mueller matrix for an analyzer whose transmission plane makes an angle $(\pi/2) + \varepsilon$ with the plane of polarization of the wave incident on the sample is

$$M_s = \frac{1}{2}\begin{pmatrix} 1 & -\cos(2\theta+\varepsilon) & -\sin(2\theta+\varepsilon) & 0 \\ -\cos(2\theta+\varepsilon) & \cos^2(2\theta+\varepsilon) & \cos(2\theta+\varepsilon)\sin(2\theta+\varepsilon) & 0 \\ -\sin(2\theta+\varepsilon) & \cos(2\theta+\varepsilon)\sin(2\theta+\varepsilon) & \sin^2(2\theta+\varepsilon) & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \tag{4}$$

Now, considering that $l\alpha_-$, $l\alpha_+$, δ, ε are small parameters, we expand E_- and E_+ and the trigonometric functions as a series in these parameters. Then from Eq. (1) we obtain for the intensity of transmitted light

$$I_1 = I_0\left[\frac{\varepsilon^2}{4} + \frac{l^2}{16}(\alpha_- - \alpha_+)^2 + \frac{l^2\pi^2}{4\lambda^2}(n_- - n_+)^2 + \varepsilon\frac{l\pi}{2\lambda}(n_- - n_+)\right]. \tag{5}$$

Equation (5) is written up to second-order terms.

Assuming that the anisotropy in the medium is produced by a strong light wave of not circular but linear polarization, with the vector **E** along the y axis, we can write the Mueller matrix for the medium

$$M_{c2} = \begin{pmatrix} \frac{1}{2}(E_x+E_y) & \frac{1}{2}(E_x-E_y) & 0 & 0 \\ \frac{1}{2}(E_x-E_y) & \frac{1}{2}(E_x+E_y) & 0 & 0 \\ 0 & 0 & F\cos\delta & F\sin\delta \\ 0 & 0 & -F\sin\delta & F\cos\delta \end{pmatrix}, \tag{6}$$

where in this case, the expressions for E_i, F, and δ include the absorption coefficients α_x and α_y and refractive indices n_x and n_y for the light wave polarized along the z and y axes, respectively. Proceeding as in the previous case, we can obtain for the intensity of the transmitted test wave

$$I_2 = I_0\left[\frac{\varepsilon^2}{4} + \sin^2\theta\,\frac{l^2}{16}(\alpha_x - \alpha_y)^2\right.$$
$$\left. + \sin^2 2\theta\,\frac{\pi^2 l^2}{\lambda^2}(n_x - n_y)^2 - \varepsilon\frac{l}{4}(\alpha_x - \alpha_y)\sin 2\theta\right]. \tag{7}$$

Equations (5) and (7) do not take into account the presence, in the windows of the cell containing the gas studied, of birefringence, which is due to the difference between the pressure inside the cell and the outside pressure. However, by compressing the cell windows, this birefringence can be compensated so that its influence on the signal becomes less than that of the remaining terms of Eqs. (5) and (7).[14]

The dependence of the absorption coefficients on the frequency of the incident light for atoms or molecules at rest has a Lorentzian shape, and the dependence of the refractive index has a dispersion shape, but the amplitude of the change in $\alpha_i l$ and $\pi l n_i/2\lambda$ for actual experimental conditions is of the same order of magnitude, $\sim 10^{-3}$.[7] Thus, by appropriately selecting the angle ε one can achieve a situation in which a decisive role in the signals (5) and (7) is played by the last terms.

In the case of a linearly polarized strong wave, this term can be calculated rather simply even in the case of excitation by a multimode laser.

In the study of the effect of multimode laser radiation on a rarefied gas, in many gases of practical importance use may be made of the broad-line approximation.[15] The action of strong radiation on the VR level of the electronic ground state of dimers gives rise to optical pumping by emptying.

This leads to anisotropy of light absorption from this level. The obtained optical pumping of the VR level can be described by means of the polarization moments (PM) φ_Q^K, produced by a strong field.[16] The absorption coefficient of the weak test wave with polarization e for a state with a large angular momentum can be written, on the basis of the results of Ref. 17.

$$\alpha(e) = A\sum_K (-1)^{K+\Delta}\sqrt{2K+1}\,C_{1\Delta1-\Delta}^{K0}\sum_Q(-1)^Q\,\Phi_Q^K(e)\,\varphi_{-Q}^K, \tag{8}$$

where $C_{1\Delta1-\Delta}^{K0}$ is the Clebsch-Gordan coefficient; $\Delta = J' - J''$ is the difference between the angular momenta of the excited and ground states; Φ_q^K is a tensor introduced in Ref. 16 for describing the polarization of absorbed light.

We shall assume that the strong field is directed along the x axis and polarized along the y axis. In the presence of an external magnetic field, for the probing light, which is polarized in the xy plane, the principal absorption axes x' and y' coincide with the polarization directions for which absorption is of the greatest importance. They are rotated through an angle β relative to the x and y axes. This angle can be found by using Eq. (8)

$$\beta = \frac{1}{2}\arctan\frac{\mathrm{Im}\,\varphi_2^2}{\mathrm{Re}\,\varphi_2^2}. \tag{9}$$

For the probing light, polarized in the zy plane, the principal absorption axes for any magnetic field strength coincide with the z and y axes.

The difference between the absorption coefficients for two polarizations of light along the principal absorption axes for probing light with polarization vector $\mathbf{E}_{v1}$ (Fig. 1) can be written

$$\Delta\alpha_1 = \alpha_{x'} - \alpha_{y'} \sim C_t\,\mathrm{Mod}\,\varphi_2^2, \tag{10}$$

where the coefficient C_i depends on the type of molecular transition $C_Q = 2\sqrt{2}/\sqrt{3}$, and for the P and R types $C_{PR} = -\sqrt{2}/\sqrt{3}$.

The corresponding expressions for probing light with polarization vector $\mathbf{E}_{v2}$ can be written

$$\Delta\alpha_2 = \alpha_y - \alpha_z \sim C_t\left(\frac{\sqrt{2}}{\sqrt{3}}\,\mathrm{Re}\,\varphi_2^2 + \varphi_0^2\right), \tag{11}$$

where $C_Q = -1$, $C_{PR} = 1/2$.

We shall consider a few variants of the experimental setup.

Let us assume that the strong light field is switched on in pulses with a pulse of arbitrary length. The external magnetic field is switched off. Then the PM φ_2^2 produced by the strong-field pulse in the geometry of Fig. 1 are real quantities (the imaginary parts of the PM are zero), which after cessation the action of the light pulse at time t_0 undergo relaxation to the equilibrium at a rate γ_2 (Ref. 18).

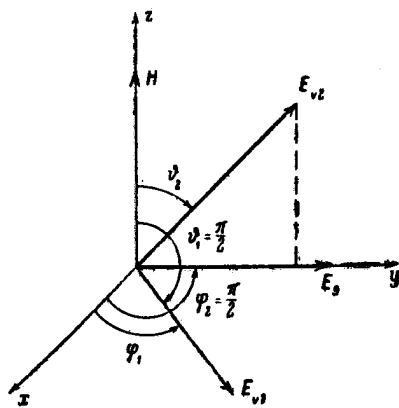$$\varphi_2^2(t) = \varphi_2^2(t_0)e^{-\gamma_2(t-t_0)}. \tag{12}$$

M. P. Auzinsh   617

FIG. 1. Geometry of calculation of polarization signals.

Then the temporal dependence of the light intensity behind the analyzer can be written.

$$I_1^Q \sim \frac{2\sqrt{2}}{\sqrt{3}}\ \varphi_2^2(t_0)\ e^{-\gamma_2(t-t_0)}I_\varepsilon \sin 2\varphi_1 + \frac{\varepsilon^2}{4},$$

$$I_2^Q \sim -\left(\frac{\sqrt{2}}{\sqrt{3}}\ \varphi_2^2(t_0) + \varphi_0^2(t_0)\right)$$

$$\times e^{-\gamma_2(t-t_0)}I_\varepsilon \sin 2\theta + \frac{\varepsilon^2}{4},$$

$$I_1^{PR} \sim -\frac{\sqrt{2}}{\sqrt{3}}\ \varphi_2^2(t_0)\ e^{-\gamma_2(t-t_0)}I_\varepsilon \sin 2\varphi_1 + \frac{\varepsilon^2}{4},$$

$$I_2^{PR} \sim \left(\frac{1}{\sqrt{6}}\ \varphi_2^2(t_0) + \frac{1}{2}\ \varphi_0^2(t_0)\right)e^{-\gamma_2(t-t_0)}I_\varepsilon \sin 2\theta + \frac{\varepsilon^2}{4}. \tag{13}$$

The recording of the signals (13) in the experiment makes it possible to determine the alignment relaxation rate γ_2 of the VR level studied. Methods used earlier[2] did not permit us to obtain the rates of population relaxation γ_0 and of alignment γ_2 separately.

If the strong field has the shape of δ pulses (pulse duration much shorter than γ_2^{-1}), and the external magnetic field H is switched on (Fig. 1), then the signal at the detector is harmonically modulated, i.e., quantum beats are recorded. In this case, after passage of a strong light pulse, which gives rise to anisotropic absorption, the principal absorption axes for probing light with polarization vector E precess in the magnetic field at an angular frequency $\omega = g''\mu_B H/\hbar$, where μ_B is Bohr magneton. The principal absorption axes for light with polarization vector E_{v2} are stationary. The PM φ_2^2 after a strong light pulse evolve with time as[3]

$$\text{Mod}\ \varphi_2^2(t) = \text{Mod}\ \varphi_2^2(t_0)\ e^{-\gamma_2(t-t_0)},$$

$$\text{Re}\ \varphi_2^2(t) = \text{Mod}\ \varphi_2^2(t_0)\ e^{-\gamma_2(t-t_0)}\cos[2\omega(t-t_0)+2\beta]. \tag{14}$$

In the geometry of Fig. 1, in the presence of a strong field in the form of a δ pulse $\beta = 0$, since φ_2^2 is a real quantity. Then the following signals can be expected behind the analyzer:

$$I_1^Q \sim \frac{2\sqrt{2}}{\sqrt{3}}\ \varphi_2^2(t_0)\ e^{-\gamma_2(t-t_0)}I_\varepsilon \sin(2\varphi_1 + 2\omega(t-t_0)) + \frac{\varepsilon^2}{4},$$

$$I_2^Q \sim -\left(\frac{\sqrt{2}}{\sqrt{3}}\ \varphi_2^2(t_0)\cos 2\omega(t-t_0) + \varphi_0^2(t_0)\right)e^{-\gamma_2(t-t_0)}I_\varepsilon \sin 2\theta + \frac{\varepsilon^2}{4},$$

$$I_1^{PR} \sim -\frac{\sqrt{2}}{\sqrt{3}}\ \varphi_2^2(t_0)\ e^{-\gamma_2(t-t_0)}I_\varepsilon \sin(2\varphi_1 + 2\omega(t-t_0)) + \frac{\varepsilon^2}{4},$$
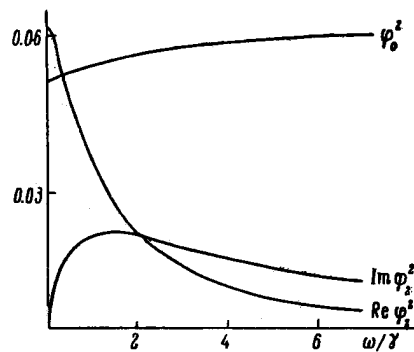
FIG. 2. The PM φ_q^2 as a function of the dimensionless parameter ω/γ, obtained by the method of Ref. 17.

$$I_2^{PR} \sim \left(\frac{1}{\sqrt{6}}\ \varphi_2^2(t_0)\cos 2\omega(t-t_0) + \frac{1}{2}\ \varphi_0^2(t_0)\right)e^{-\gamma_2(t-t_0)}I_\varepsilon \sin 2\theta + \frac{\varepsilon^2}{4}. \tag{15}$$

The magnitude of the PM $\varphi_2^2(t_0)$ and $\varphi_0^2(t_0)$ that enter into Eqs. (15) can be calculated by the method of Ref. 3. In particular, for a Q-type molecular transition $\varphi_0^2(t_0)$ $= \varphi_0^2(t_0) = (G/15) - 2(G^2/35) + (G^3/21)$, and φ_2^2 $(t_0) = \sqrt{6}(G/30) - \sqrt{6}(G^2/35) + \sqrt{6}(G^3/42)$, where G is the probability of light absorption by a molecule during the action of a δ pulse. Recording of the signals (15) makes it possible to determine the value of the Lande factor g'' of the selected VR level, whose value for diatomic molecules often does not lend itself to theoretical calculation.

Finally, if the strong light field is stationary and the molecule ensemble is placed in a magnetic field, the angle of rotation of the principal absorption axes is constant with time and depends on the strength of the external magnetic field. Then, in view of Eqs. (9), (10), and (11), the expected signals can be written

$$I_1^Q \sim \frac{2\sqrt{2}}{\sqrt{3}}\ I_\varepsilon\ (\sin 2\varphi_1\ \text{Re}\ \varphi_2^2 + \cos 2\varphi_1\ \text{Im}\ \varphi_2^2) + \frac{\varepsilon^2}{4},$$

$$I_2^Q \sim I_\varepsilon\left(\frac{\sqrt{2}}{\sqrt{3}}\ \text{Re}\ \varphi_2^2 + \varphi_0^2\right)\sin 2\theta + \frac{\varepsilon^2}{4},$$

$$I_1^{PR} \sim -\frac{\sqrt{2}}{\sqrt{3}}\ I_\varepsilon\ (\sin 2\varphi_1\ \text{Re}\ \varphi_2^2 + \cos 2\varphi_1\ \text{Im}\ \varphi_2^2) + \frac{\varepsilon^2}{4},$$

$$I_2^{PR} \sim \left(\frac{1}{\sqrt{6}}\ \text{Re}\ \varphi_2^2 + \frac{1}{2}\ \varphi_0^2\right)I_\varepsilon \sin 2\theta + \frac{\varepsilon^2}{4}. \tag{16}$$

The specific dependence of φ_0^2 and Re φ_2^2, Im φ_2^2 on the magnetic field can be found by computer, using the method described in Ref. 17. For a Q-type transition with $\gamma_x = \gamma = 0.3\ \mu\text{sec}^{-1}$, $\Gamma_p = 3.0\ \mu\text{sec}^{-1}$, neglecting the stimulated transitions, such a dependence is shown in Fig. 2. Using the signals (16) and knowing the magnetic moment of the state studied, one can determine its relaxation rate, or, conversely, knowing the relaxation rate, one can determine the magnetic moment.

[1] R. S. Ferber, O. A. Shmit, and M. Ya. Tamanis, Chem. Phys. Lett. 61, 441 (1979).

[2] M. P. Auzinzsh, R. S. Ferber, and I. Ya. Pirags, J. Phys. B 16, 2759 (1983).

[3] M. P. Auzinsh, M. Ya. Tamanis, and R. S. Ferber, Zh. Eksp. Teor. Fis. 90, 1182 (1986) [Sov. Phys. JETP 63, 688 (1986)].

[4]M. P. Auzinsh, K. A. Nasyrov, M. Ya. Tamanis, R. S. Ferber, and A. M. Shalagin, Zh. Eksp. Teor. Fiz. 92, 1590 (1987) [Sov. Phys. JETP 65, 891 (1987)].

[5]W. Happer. Rev. Mod. Phys. 44, 619 (1972).

[6]C. Wieman and T. W. Hansch, Phys. Rev.Lett. 36, 1170 (1976).

[7]R. Feinberg, T. W. Hansch, A. L. Schawlow, R. E. Teets, and C. Wieman, Opt. Commun. 18, 227 (1976).

[8]A. M. Shalagin, Zh. Eksp. Teor. Fiz. 73, 99 (1977) [Sov. Phys. JETP 46, 50 (1977)].

[9]V. M. Arutyunyan, G. G. Adonts, and E. G. Kanetsyan, Opt. Spektrosk. 53, 792 (1982) [Opt. Spectrosc. (USSR) 53, 472 (1982)].

[10]K. A. Nasyrov and A. M. Shalagin, Zh. Eksp. Teor. Fiz. 81, 1649 (1981) [Sov. Phys. JETP 54, 877 (1981)].

[11]J. Mlynek, Phys. Rev. Lett. 40, 1373 (1978).

[12]W. A. Shurchliff, *Polarized Light* (Harvard Univ. Press, Cambridge, 1962; Moscow, 1965).

[13]A. Gerrard and J. M. Burch, *Introduction to Matrix Methods in Optics* (Wiley, New York, 1975; Moscow, 1978).

[14]W. Demtroder, *Laser Spectroscopy; Basic Concepts and Instrumentation* (Springer-Verlag, New York, 1981; Moscow, 1985).

[15]B. DeComps, M. Dumont, and M. Ducloy in *Laser Spectroscopy of Atoms and Molecules*, (H. Walther, Ed. (Springer-Verlag, Berlin, 1976; Moscow, 1979).

[16]M. I. Dyakonov, Zh. Eksp. Teor. Fiz. 47, 2213 (1964) [Sov. Phys. JETP 20, 1484 (1964)].

[17]M. P. Auzinsh, Izv. Akad. Nauk LatvSSR Ser. Fiz. Tekh. Nauk 1, 9 (1984).

[18]M. P. Auzinsh and R. S. Ferber, Izv. Akad. Nauk LatvSSR Ser. Fiz. Tech. Nauk 1, 16 (1984).