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Observation of Zeeman Quantum Beats in Molecular Iodine*

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Zeeman quantum beats have been observed in the fluorescent emission from individual rotational levels of the $B^3\Pi_{0u}{}^+$ state of $^{127}I_2$ after excitation by a short resonant dye-laser pulse. The derived Landé factors g_J and g_1 (chemical shift) are compared with the spin-rotation hyperfine coupling constants.

Despite the detailed spectroscopic analysis of the $B^3\Pi_{0u}{}^+$ excited state of molecular iodine, only little is known about the magnetic moments in the rotational vibrational substates.[1,2] This is primarily because of the small rotational Landé factors and the rich rotational spectrum, both prohibiting the measurement of Zeeman splittings by conventional optical spectroscopy. The high resolution of laser saturation spectroscopy has made possible the investigation of Zeeman splittings of single hyperfine (hf) transitions.[3] These measurements, however, could only provide the difference of the Landé factors of the ground and the excited levels.

With the development of narrow-band, pulsed tunable lasers, small hf or Zeeman splittings in atoms could be measured without Doppler broadening by recording hf[4] or Zeeman[5] quantum beats after pulsed optical excitation. Using this method we were able to excite a coherent superposition of magnetic substates within individual rotational levels of the $B^3\Pi_{0u}{}^+$ state of $^{127}I_2$ using short resonant dye-laser pulses of σ polarization ($\hat{\epsilon} \perp \vec{H}_0$). The σ component of the fluorescent light (I_σ) orthogonal to the incident polarization displayed Zeeman quantum beats, providing, to our knowledge, the first observation of transient coherence in the fluorescence from a molecular system. This method permitted the determination of the rotational Landé factors of the levels investigated. The experimental g_J values vary strongly with the rotational vibrational energy E in the excited state. These results are in excellent agreement with the energy dependence indicated by the variation of the measured hf coupling constants,[6] and allow an estimate of the g_J factors for the B-state levels.

In the absence of hf structure (nuclear spin $I = 0$) the Zeeman beat frequency should be twice the Larmor precession frequency. The amplitude of the beat signal depends on the rotational quantum number J. However, for high J in P and R transitions it is about 14% of the fluorescent intensity I_σ. In this approximation ($J > 10$) the time dependence of I_σ is given by

$$I_\sigma(t) \propto e^{-\Gamma t}[1 - \tfrac{1}{7}\cos(2g_J \mu_N H_0 t)]; \tag{1}$$

Γ is the reciprocal of the lifetime, $g_J\mu_N$ is the electronic magnetic moment of the excited state J, and H_0 is the external magnetic field.

The presence of the hf structure in $^{127}I_2$ requires the following factors to be considered.

(1) The B state of $^{127}I_2$ is a good example of Hund's case (c) with $\Omega_e = 0$.[7] In zeroth order the electronic magnetic moment along the rotation axis $\vec{J}$ vanishes. The molecular rotation, mixing the B state with nearby states with $\Omega_e \neq 0$, however, induces an electronic angular momentum

along the rotation axis.[8] The resultant magnetic moment ($g_J\mu_N$) is found to be small and comparable to that of the nucleus.

(2) The hf interaction ($I=\frac{5}{2}$, $g_I=1.123$) splits the rotational states with even (odd) J into 21 (15) hf components (F), having different Landé factors g_F.

(3) In a magnetic field, the nuclear magnetic moment is shielded (or antishielded) by the precession of the valence electrons. The required diamagnetic correction is taken into account by introducing an effective nuclear g factor[8] $g_{\rm eff}=g_I+g_1$.

Including the nuclear-spin contribution, the Zeeman Hamiltonian can be written

$$\mathcal{H}_Z=-g_J\mu_N\vec{J}\cdot\vec{H}-(g_I+g_1)\mu_N\vec{I}\cdot\vec{H}. \qquad (2)$$

The dipole selection rule $\Delta F=\Delta J$, valid for $J\gg I$, implies that coherence is created only within the magnetic substates of each hf level, the amplitude for hf beats being vanishingly small. Neglecting hf beats, the fluorescent decay intensity $I_\sigma(t)$ was calculated in terms of g_J and g_1 using wave functions which diagonalize the hf Hamiltonian $\mathcal{H}_{\rm hf}$.[6] The lifetime[9] can be measured independently, by observing the fluorescent light, $I_\pi(t)$, polarized parallel to the magnetic field. $I_\pi(t)$ displays no quantum beats and is purely exponential.

In rotational states with large J the contribution of the nuclear moment to the Zeeman splitting is small. Each of the hf components has nearly the same $g_F\approx g_J$ and the signal approaches $I_\sigma(t)$ given in Eq. (1). For levels with small J, as observed by Sorem,[3] the g_F values for the hyperfine components (F) are considerably different. Consequently, $I_\sigma(t)$ exhibits beats at 21 (15) different frequencies for even (odd) J. The resultant superposition tends to wash out the beat structure.

Individual rotational levels were optically excited by intense light pulses of 7 nsec duration and 1.5-GHz spectral width provided by a N_2-laser–pumped dye laser. The fluorescence was detected by a system similar to that described in Ref. 4. As the transition strengths are small, the fluorescent intensity is about 10^{-6} of that obtained in similar experiments on atoms.[4] Thus, an extremely high detection sensitivity is required. A detailed description of the experimental setup will be given in Ref. 9.

After excitation via the $R(78)$ 40-0 transition at $\lambda=5208$ Å, fluorescence from the level $(J,v)=(79,40)$ was observed. The decay intensity $I(t)$ is displayed in Fig. 1. The σ component, $I_\sigma(t)$, of the fluorescence is modulated because of the presence of Zeeman quantum beats. The π component, $I_\pi(t)$, is purely exponential, so that the difference $I_\sigma-I_\pi$ more clearly displays the beat structure. The dye laser was then tuned to the $R(26)$ 62-0 transition at $\lambda=5017$ Å. The decay intensity $I_\sigma(t)$ of the level $(J,v)=(27,62)$ shows a well pronounced beat structure only at the beginning of the fluorescent decay (Fig. 2, curve a) in agreement with the small J value. The theoretical fit to the experimental data was excellent (Fig. 2, curve a). The sensitive dependence of the fit on g_J and g_1 (Fig. 2, curve b) allowed the accurate determination of both parameters. The results are, for the level $(J,v)=(79,40)$, $g_J=-0.28(2)$, $g_1=0.6(1)$; and for the level $(J,v)=(27,62)$, $g_J=-2.6(2)$, $g_1=7.5(8)$. The sign of g_J is taken from the Hanle signal observed on the $R(26)$ 62-0 transition[2] but could easily be assigned

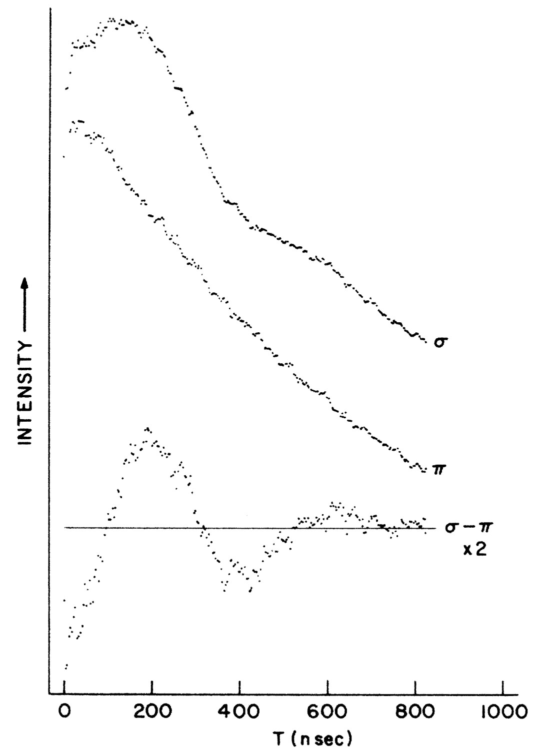

FIG. 1. Fluorescent decay of the level $(J,v)=(79,40)$ excited via the $R(78)$ 40-0 transition ($\lambda=5208$ Å). $H_0=5.6$ kG, $P_{I_2}=33$ mTorr (0°C). The σ- and π-polarized components of the fluorescence are displayed. The beat structure, modulating σ, is shown more clearly in the subtraction $\sigma-\pi$.

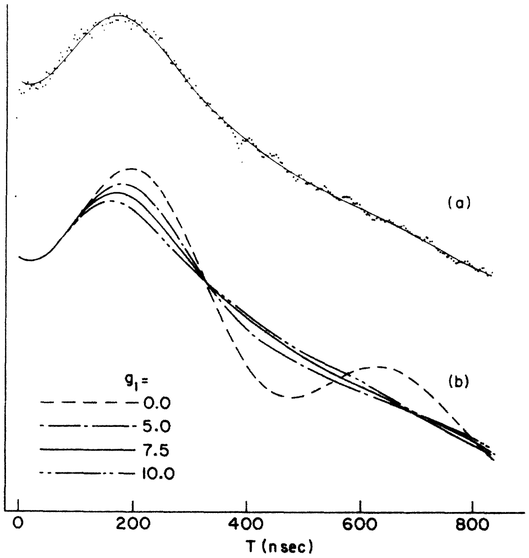

FIG. 2. Curve *a*: σ component of the fluorescent decay of the level $(J,v)=(27,62)$ excited via the $R(26)$ 62-0 transition ($\lambda = 5017$ Å). $H_0 = 565$ G, $P_{I_2}=33$ mTorr (0°C). The solid line represents the theoretical fit ($g_J = -2.6, g_1 = 7.5$). Curve *b*: Dependence of the calculated decay on g_1.

by observing the fluorescent decay intensity $I_\sigma(t)$ at 45 or 135° to the polarization of the incident light beam.

So far, collisional relaxation processes (T_2) of the induced coherence have not been investigated in great detail. However, in measuring the decay intensity $I_\sigma(t)$ for various pressures of iodine [2 mTorr (− 25°C), 33 mTorr (0°C), 200 mTorr (19°C)], no significant change in the beat amplitude has been observed ($T_2 \approx 1/\Gamma$), indicating preferential self-quenching rather than rotational or vibrational energy transfer in I_2*-I_2 collisions.

From microwave spectroscopy of ${}^1\Sigma_g^+$ electronic ground states, a close relationship is known between the Landé factors and the hf spin-rotation constant $g_I\mu_N G$.[8] This feature remains unaltered for the $B^3\Pi_{0u}^+$ excited state as long as it couples via Hund's case (c). Following the treatment by Levenson and Schawlow[6] of the spin-rotation interaction,

$$g_I\mu_N G/g_J = -(\mu_N/\mu_B)aK_1 \tag{3}$$

and

$$g_1/g_I\mu_N G = (\mu_B/\mu_N)K_2/2B, \tag{4}$$

where $B = 1/2\mu R^2$ is the rotational coupling constant and a is the molecular average of $2g_I\mu_N\mu_B/r^3$ over the excited valence electrons (r is the distance between the valence electrons and the nuclei). K_1 and K_2 are spectroscopic constants of order unity which depend only on the electronic radial wave functions and the coupling of the electronic angular momenta. For ${}^1\Sigma_g^+$ states Eqs. (3) and (4) hold with $K_1 = K_2 = 1$. These equations indicate that the spin-rotation constant and the Landé factors g_J and g_1 are proportional. The ratio $R_1 = g_I\mu_N G/g_J$ [Eq. (3)] as well as $R_2 = Bg_1/g_I\mu_N G$ should have a constant value for all rotational levels (J,v). With the experimental values of $g_I\mu_N G$ and the measured g_J and g_1 factors, the ratios are $R_1(79,40) = -5.4\times10^2$ kHz, $R_1(27,62) = -3.6\times10^2$ kHz, and $R_2(79,40) = R_2(27,62) = 7.9\times10^{-5}$ cm^{-1}/kHz. These values show a rather good agreement between the experimental data and the theoretical relationships expressed in Eqs. (3) and (4).

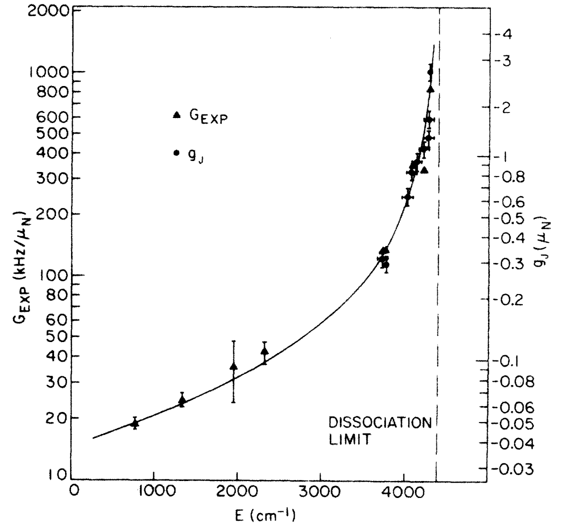

FIG. 3. Dependence of the spin-rotation constant G_{exp} and the Landé factor g_J on the energy of the excited level.

In an extensive treatment of the magnetic hf interaction in the B state, Levenson and Schawlow[6] show that the hf coupling constant G_{exp}[10] varies strongly with the energy E of the excited state, diverging at the dissociation limit, but little, if at all, with the rotational quantum number J (Fig. 3). According to Eqs. (3) and (4) the same strong energy dependence is expected for g_J and g_1. This motivated the measurement of the g_J factor of additional rotational levels. So far, the fluorescent decay intensities $I_\sigma(t)$ and $I_\pi(t)$ have been recorded for seven strong transitions picked randomly between 5208 and 5017 Å. Although the lines are not identified, the strength of the fluorescence and the beat structure observed ensured that these lines were excited from $v=0$, $J=40$–90 ground-state levels. The wave numbers of the transitions were measured to within 0.15 cm^{-1}. The analysis of $I_\sigma(t)-I_\pi(t)$ provided the g_J factors with an accuracy of about 8%. The seven values are plotted in Fig. 3 along with the g_J values of the $(J,v)=(27,62)$ and the $(J,v)=(79,40)$ levels. They are scaled to enable a comparison with the spin-rotation data $G_{\rm exp}$. Figure 3 displays an excellent agreement between the energy dependence of $G_{\rm exp}$ and g_J, demonstrating the proportionality between these coupling constants. Using a least-squares fit to the hf coupling data $G_{\rm exp}$, we find for the energy dependence of g_J in the energy range investigated $g_J=A/(E_c-E)$, with $A=-2.3(2)\times10^2\mu_N$ cm^{-1} and $E_c=4391(40)$ cm^{-1}.

The detection of Zeeman quantum beats has proven to be a valuable new spectroscopic tool for the direct measurement of Landé factors in molecular iodine. The only other method reported to measure g factors in the excited B state is the Hanle effect with modulated light.[2] Unlike quantum-beat spectroscopy, this technique is limited to levels with rather large g_J and long lifetime τ and therefore to investigations very close to the dissociation limit. Further investigations with these methods should provide a detailed survey of the magnetic interactions in the excited states of iodine and other molecules.

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[10] $G_{\rm exp}=G^1-G^0$; G^0 and G^1 are the hyperfine coupling constants of the ground and excited levels. Except for low energies E, G^0 is very small compared to G^1 (Ref. 6).

Precision Measurement of the Rydberg Constant by Laser Saturation Spectroscopy of the Balmer α Line in Hydrogen and Deuterium*

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We have determined a new Rydberg value, $R_\infty=109\,737.3143(10)$ cm^{-1}, with an order of magnitude improvement in precision, by measuring the absolute wavelengths of resolved fine-structure components of the Balmer α line in hydrogen and deuterium, excited in a dc gas discharge. Doppler broadening was eliminated by saturation spectroscopy with a pulsed dye laser. An iodine-stabilized He-Ne laser was the wavelength standard. Possible sources of systematic errors have been carefully investigated.

We have determined the Rydberg constant with an almost tenfold improvement in accuracy over recent other experiments,[1,2] by measuring the absolute wavelength of the optically resolved $2P_{3/2}$-$3D_{5/2}$ component of the red Balmer line H_α of atomic hydrogen and D_α of deuterium in a Wood discharge. Doppler broadening was eliminated by saturation spectroscopy[3] with a pulsed, tunable, dye laser. An iodine-stabilized He-Ne laser served as the wavelength standard.[4] The same measurements provide a new precise value for the H_α-D_α isotope shift. We have also determined the splittings between the stronger fine-structure components in the optical spectrum to within a few megahertz.

The Rydberg constant, an important corner-