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Measurement of *g* Factors by Quantum Beats in the OH Free Radical

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Using pulsed optical excitation we have measured the *g* factors of twelve hyperfine levels ($K = 1$ through 6) of the $A^2\Sigma_{1/2}^+$ state of OH by observation of quantum beats. The results are consistent with Hund's case (b) coupling to within the experimental uncertainty of 0.35% (principally limited by magnetic field calibration). However, the ratios of the *g* factors of a given hyperfine doublet, which are independent of field and accurate to about 0.15%, show significant discrepancies from theory.

Because of the ubiquitous nature of the OH free radical, its properties are of interest to investigators in such diverse fields as astrophysics, combustion studies, atmospheric physics, and molecular spectroscopy. The decay of the lowest-lying electronic excited state via the ultraviolet transition ($A^2\Sigma_{1/2}$ to $X^2\Pi$) has been studied extensively.[1] Recently, the use of tunable dye lasers has introduced a new level of versatility and sophistication in the study of this molecule.[2] In this Letter we report the direct measurement of the *g* factors of the $v = 0$, $A^2\Sigma_{1/2}$ excited state of OH by time-resolved excited-state spectroscopy. This follows the lead of Wallenstein, Paisner, and Schawlow[3] and demonstrates the utility of time-resolved techniques, particularly quantum beats, in molecular spectroscopy. It also provides motivation for further calculations of the magnetic properties of molecules.

The experiment consists of exciting a sample of OH free radicals in a dc magnetic field with a short pulse of light from a dye laser and observing the oscillations superposed on the fluorescence. If the bandwidth of the laser is greater than the Zeeman splitting of the molecular levels, the molecule is excited to a superposition state of several Zeeman components and the resulting fluorescence exhibits quantum beats. The angular frequency of these beats is given by $\omega = 2g_F\mu_B B/\hbar$, where g_F is the *g* factor of the individual hyperfine states, μ_B is the Bohr magneton, and B is the applied magnetic field. Quantum beats in fluorescence have been carefully described[4] for atoms excited by a light pulse of finite duration θ and observed for a finite duration δ. The application of that work to molecules is simply one of extending the domain of the summation of Eq. (4) in Ref. 4 over all the (far more numerous) molecular states.

For the transition we study in the OH free radical, $\tau \sim 10^{-6}$ sec so that both θ ($\cong 5$ nsec) and δ ($\cong 2$ nsec) are much shorter than τ. We therefore expand the sine and cosine terms of slightly different frequencies in Eq. (4) of Ref. 4 and find that the rate of detected photons R is

$$R \propto \sum_{\mu\mu' mm'} f_{\mu m} f_{m\mu'} g_{\mu' m'} g_{m'\mu}(\theta\delta) \times e^{-\Gamma T} A_{\mu\mu'} \cos\omega_{\mu\mu'} T, \qquad (1)$$

where we have chosen the polarization of both exciting light and observed fluorescence so that all the f's and g's are real and we have taken only the real part of the expression for R. $A_{\mu\mu'}$ is an amplitude parameter slightly less than unity; for the values of θ, δ, and T in this experiment, it is typically within 10^{-3} of unity. The f's and g's are the excitation and fluorescence matrix elements for electric dipole transitions between the ground states (denoted by m and m') and excited states (denoted by μ and μ'). They contain all the geometric and angular momentum selection rules. The energy difference between the two excited states μ and μ' is $\hbar\omega_{\mu\mu'}$.

Some of the terms ($\mu = \mu'$) in Eq. (1) show no oscillations and only contribute to the exponential decay of the fluorescence, while others also oscillate at various frequencies $\omega_{\mu\mu'}$. The allowed values of $\omega_{\mu\mu'}$ correspond to the hfs splitting of the excited state and to the Zeeman splitting of each of the hyperfine sublevels because the laser selectively excites a single rotational transition but cannot resolve its hyperfine components. Because the bandwidth of our detection system ($\cong 50$ MHz) is not large enough to detect the oscillations at the hfs frequency, we see only the beats between Zeeman components of the individual hyperfine sublevels. The hfs of the $A^2\Sigma$ state of OH derives only from the nuclear spin of the H atom ($I = \frac{1}{2}$) resulting in two hfs states with g factors given approximately by

$$\begin{aligned} g_F &= g_J[F(F+1) + J(J+1) - I(I+1)]/2F(F+1) \\ &= g_J[1 \mp (2J+1)^{-1}], \quad F = J \pm \tfrac{1}{2}, \qquad (2) \end{aligned}$$

where g_J is the g factor associated with the molecular angular momentum J. We therefore see quantum beats at two nearly equal frequencies resulting in a signal which looks very much like the amplitude-modulated sine waves commonly demonstrated in elementary physics labs (see Fig. 1). From these signals we extract the magnitude of the g factors of the hfs states from which we calculate their ratio. Although the measured values of the g factors depend on the magnetic field, the ratio does not and can therefore be obtained much more accurately.

The molecules are excited by a frequency-doubled [angle-tuned KDP (potassium dihydrogen phosphate) crystal] tunable dye laser of the oscillator-amplifier configuration[5] pumped by a

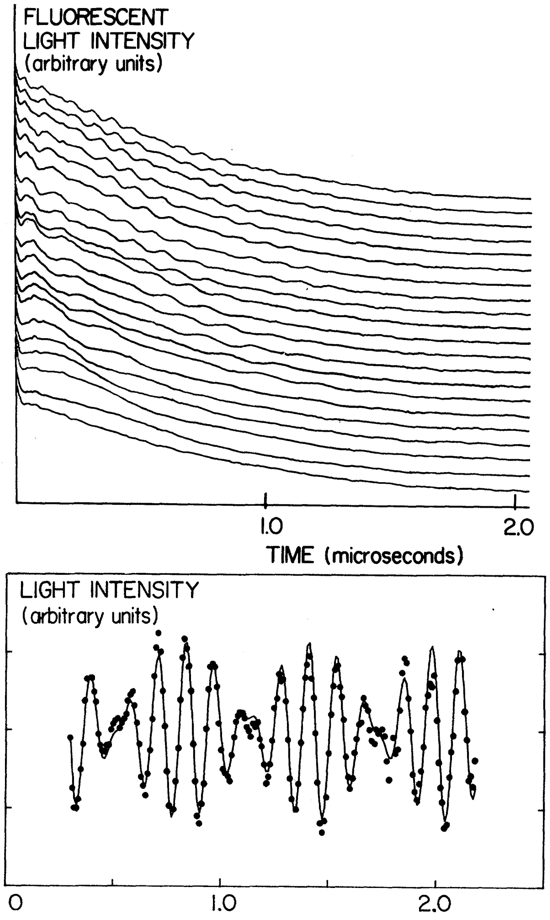

FIG. 1. (a) Fluorescent light intensity as a function of time for the $K=4$ rotational sublevel of the $A^2\Sigma_{1/2}$ state for different applied magnetic fields. The fields range from 20 G (top curve) to 0 G (bottom curve) in increments of 1 G. (b) One of these curves with the dominant decaying behavior divided out (see text). The uncertainties in the data points (depicted as dots) are on the order of the dot size. The solid line is fitted using a model of oscillations at two nearly equal frequencies.

home-built nitrogen laser.[6] The spectral width of the 3080-Å light is about 0.04 Å (≅12 GHz) in a 5-nsec pulse of 100–400-W peak power focused into a 1-mm-diam beam. The OH molecules are produced in a flow system upstream from the excitation region via the reaction $NO_2 + H \rightarrow OH + NO$.[1] Total pressure in the viewing region is less than 0.1 mTorr which corresponds to a mean free path of 1000 cm for kinetic cross sections. This is 100 times larger than the dimensions of the glass vacuum vessel.

The magnetic field is applied in the vertical (z) direction, the laser beam is incident along the x axis and linearly polarized in the y direction, and the photomultiplier (PMT) views light fluoresced into a 0.06-sr solid angle centered on the y axis. Scattered primary (6160 Å, red) light from the dye laser is attenuated by Corning glass No. 754 filters placed after the frequency doubler and in front of the PMT. Stray uv light from the N_2 laser is blocked by baffles. The PMT is an RCA 1P28 supplied with 1100 V and wired for fast pulse response. The fluorescence is focused through a 2-mm slit in front of the PMT with unit magnification by a 3.5-cm-diam, 6.5-cm–focal-length quartz lens.

The magnetic field is produced by orthogonal pairs of Helmholtz coils which cancel the Earth's field as well as provide the dc field for this experiment. The field homogeneity has been measured to be better than 1 part in 10^3 over the viewing region and is determined to 0.04 G with a Bell model 620 Hall-effect gaussmeter (data are taken with fields on the order of 10 G).

The PMT outfit, terminated in 50 Ω, is fed to a Biomation 8100 wave-form recorder which digitizes the fluorescence from each laser pulse into 2000 channels separated by 10 nsec. The output of the wave-form recorder is averaged over many laser pulses by Nicolet model 1072 signal averager.

A typical run consists of 30 min of data collection at a chosen magnetic field followed by a similar period at high magnetic field (≃75 G). Since the quantum beats from the high-field signal are at a frequency which cannot be detected, division of these two signals isolates the oscillatory signal at the field of interest from the dominating exponential decay as well as from spurious signals such as afterpulses from the PMT or cable reflections.

Figure 1(a) shows the time dependence of fluorescence from the $Q_1(4)$ excited $K = 4$ rotational level at various magnetic fields. The quantum beats appear as modulations on the exponential decay. Their amplitude is modulated by the interference of two signals at slightly different frequencies. At low fields the interference pattern spreads and shifts as the corresponding beat frequencies decrease. Figure 1(b) shows the data from one of these signals after division by a high-field signal. The solid line is a fit to this data of a model with two oscillations at slightly different frequencies. The results of the fits provide the g factors presented in Table I.

The g values in Table I represent an improvement of more than a factor of 10 in accuracy over the previous best measurements.[7] The

TABLE I. The experimental results and theoretical values for the g factors. Theoretical calculations based on Hund's case (b). The quantity r is $g_{F=J-1/2}/g_{F=J+1/2}$. The entries in the last two columns would all be 1.000 if theory and experiment agreed. The asterisk is the theory calculated without off-diagonal hfs terms and is equivalent to Eq. (2).

K	F	g_F^{theor}	g_F^{expt}	$r^{\text{expt}}/r^{\text{theor}}$	$r^{\text{expt}}/r^{\text{theor}*}$
1	1	0.8704	0.8777(0.0057)	1.0024(0.0034)	1.0460
	2	0.5002	0.5032(0.0035)		
2	2	0.4750	0.4753(0.0020)	1.0014(0.0013)	1.0193
	3	0.3335	0.3332(0.0014)		
3	3	0.3247	0.3243(0.0013)	1.0023(0.0018)	1.0116
	4	0.2501	0.2492(0.0011)		
4	4	0.2461	0.2459(0.0008)	1.0029(0.0010)	1.0098
	5	0.2001	0.1993(0.0007)		
5	5	0.1980	0.1976(0.0006)	1.0023(0.0016)	1.0068
	6	0.1667	0.1660(0.0005)		
6	6	0.1656	0.1644(0.0005)	1.0044(0.0015)	1.0069
	7	0.1429	0.1413(0.0004)		

statistical contribution to the uncertainty is less than 0.1% for most cases, and work is in progress to reduce further the systematic contribution. The major sources of systematic error are the accuracy of the magnetic field measurement and the accuracy of the time base. We have used a 2.000 000-MHz signal to calibrate our time base through the wave-form recorder to within 0.02%. The magnetic field calibration can be obtained to better than our present 0.3% accuracy with a Rb optical-pumping magnetometer.

The theoretical values of the g factors in Table I were found by using pure Hund's case (b) wave functions and solving for the field dependence of the energy. Each 4×4 part of the Hamiltonian matrix with fixed K and M_F, and with $J=K\pm\frac{1}{2}$ and $F=J\pm\frac{1}{2}$, is diagonalized at the appropriate field and the magnetic energy splittings for each M_F are averaged. We determined the hyperfine constants $b=723$ MHz and $c=162$ MHz by extrapolation from the measurements of German *et al.*[1] in OD. The off-diagonal Zeeman terms which link all but the $\Delta F=2$ states, the nuclear Zeeman effect, and the off-diagonal hfs terms which link states of different J but same F (separated by $\cong 10$ GHz) make important contributions (a few percent) at our level of precision ($\cong 0.3\%$).

Most of the data in Table I show agreement within the experimental uncertainty between the measured and calculated g factors. These measurements indicate that corrections to Hund's case (b) coupling for the $A^2\Sigma$ state of OH arising from various higher-order interactions do not affect the g factor by more than about 0.3%. It appears that there may be a small, systematic discrepancy between our measurements and the calculated ratios of g factors as indicated in Table I. Although the accuracy of the measured g factors reflects the field calibration uncertainty, the ratios are independent of that source of systematic error. The last column is the result of neglecting the two off-diagonal hfs matrix elements (obtained from Radford[8]) while the next-to-last column is the result of including them with a negative sign for the radical. (Use of the positive sign doubles the discrepancies shown in the last column.) The measured ratios for all six levels we have investigated are consistently higher than the calculated values by about 2 times the experimental uncertainty. We are led to a variety of speculations about the origin of the discrepancies. Excitation by satellite transitions [e.g., $Q_{21}(K)$] populates levels of different g factors, but a closer investigation makes this an unlikely source of the discrepancies. This supposition is substantiated by careful measurements which show no quantum beats of detectable amplitude (given the same statistics) when the $J=K-\frac{1}{2}$ levels are directly excited via the satellite transitions. Clearly more measurements are in order.

We expect to improve the precision of these measurements and to extend them to higher fields. When the Zeeman energy becomes comparable to the hfs splitting, the g factors of the various Zeeman levels are no longer equal, but reflect the curving and anticrossings of the various energy eigenvalues. This occurs at lower fields for OD than for OH. At sufficiently high fields, the level crossings of the different hfs states should be observable. We can then study the field-domain (level-crossing) signal to determine the hfs splitting.

We can extract the lifetime of the excited state from the exponential decay of the fluorescence. There are several systematic problems which affect the value of the lifetime determined this way, and we are presently studying them. Our current value for the lifetime is consistent with previously published results, but we hope that further study will provide a more reliable measurement.

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