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OPTICAL RADIO-FREQUENCY DOUBLE RESONANCE IN MOLECULES: THE OH RADICAL*

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The g values for the two hyperfine components of the $J'=\frac{3}{2}$, $K'=2$, $v'=0$ level of the $A^2\Sigma^+$ state of OH have been determined using the technique of optical radio-frequency double resonance. They are found to be $g(F=2)=0.301\pm0.0015$ and $g(F=1)=0.492\pm0.0045$ in agreement with the values calculated assuming Hund's case (b) coupling. From our earlier measurement of $g\tau$ for this state, the radiative lifetime is found to be $(7.7\pm0.8)\times10^{-7}$ sec, corresponding to a band oscillator strength $f_{00}=(9.3\pm1.0)\times10^{-4}$.

It is a sobering thought that although the $A^2\Sigma^+$-$X^2\Pi$ band system of OH has been studied by more workers in a wider variety of ways than any other diatomic molecule,[1-11] the oscillator strength or f value for this transition remains a matter of much controversy with a spread by a factor of 8 in the reported values. We report here a determination of the oscillator strength of the OH ultraviolet bands by a conceptually different technique whereby no corrections for thermochemistry, resolving power, or other parameters related to the OH concentration are necessary. This method, which is well known in its atomic applications,[12] uses the value of $g\tau$ determined from a level-crossing study, together with the value of g obtained from optical radio-frequency double resonance, to derive the radiative lifetime τ from which the oscillator strength is readily calculated.

Previously, we reported a measurement of the Hanle effect on the $v'=0$, $K'=2$, $J'=\frac{3}{2}$ vibrational-rotational level of the $A^2\Sigma^+$ state of OH using the coincidence with the Zn I 3072.06-Å line.[13] From the halfwidth of the Hanle signal we determined an average $g\tau$ of $(2.20\pm0.27)\times10^{-7}$ sec. We describe here the direct measurement of the g values for this state based on the technique of optical radio-frequency double resonance.

The experimental apparatus is basically the same as that in Ref. 13 with the exceptions that the incident light is π polarized and the two photomultipliers of the optical bridge detect π- and σ-polarized light, respectively (see Figs. 1 and 2 in Ref. 13). In addition, a linear rf field is applied in the plane perpendicular to the static magnetic field. In the experiment the frequency and amplitude of the rf field are held fixed and the static field, H_0, is swept. The static field is also modulated and lock-in detection is used.

The double-resonance signals are shown in Fig. 1. It is clear that there are present two signals of different g which become destinctly resolved at frequencies above 6 MHz. Figure 2 summarizes the magnetic field positions of the signals as a function of rf frequency. From a least-squares fit to the data the two g values are found to be 0.301 ± 0.0015 and 0.492 ± 0.0045. The errors (one standard deviation) in these measurements are caused by the uncertainty in locating the centers of the traces in Fig. 1; the rf frequency can be measured to a part in 10^5 and hence contributes no appreciable error. In addition to the above statistical error there is a systematic uncertainty of 1% in the magnetic field calibra-

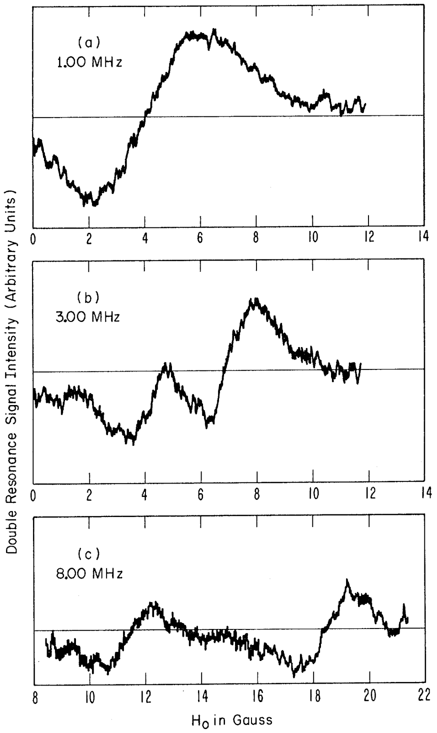

FIG. 1. The double-resonance signals as a function of frequency for Zn lamp excitation. The OH radical is formed at an H_2 pressure of 6.1 mTorr and an NO_2 pressure of 1.24 mTorr. Panel (c) was taken at one-third the rf field amplitude of (a) and (b).

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The two g values arise from the $F=1$ and $F=2$ hyperfine sublevels of the $K'=2$ level. For Hund's case (b) coupling the value of g_J is given by $g_{J=K-1/2}=-(K+\frac{1}{2})^{-1}$. To obtain g_F (the g value when the nuclear spin $\vec{I}$ is coupled to $\vec{J}$ to form the resultant $\vec{F}$), g_J must be multiplied by the factor $[F(F+1)+J(J+1)-I(I+1)]/2F(F+1)$. For $K=2$, $J=\frac{3}{2}$, $I=\frac{1}{2}$, the g_F values for $F=1$ and $F=2$ are 0.500 and 0.300, respectively. (We quote only absolute magnitudes since the experiment is not sensitive to the sign of g.) We conclude that this state obeys Hund's case (b) coupling within our experimental error.

In Ref. 13 the $g\tau$ value quoted ($g\tau=2.20\times10^{-7}$ sec) did not take into account the complications resulting from the hyperfine structure since no information on the hyperfine coupling was then available. Unfortunately, the two g values are not sufficiently different to permit an accurate experimental ratio of the two signals to be extracted from the data. A theoretical calculation has been made which indicates that the $F=2$ level contributes about 95% to the observed Hanle signal.[14] This calculation, however, did not include the complication of a variation of line strength with hyperfine level that may be significant for low rotational states. For this ratio of intensities the value of the radiative lifetime was determined to be $\tau=(7.7\pm0.8)\times10^{-7}$ sec. This corresponds to a band oscillator strength of $f_{00}=(9.3\pm1.0)\times10^{-4}$. The errors quoted for τ and f_{00} have been increased from the experimental uncertainties to reflect the uncertainty in the theoretical calculation of the ratio of the various hyperfine contributions.

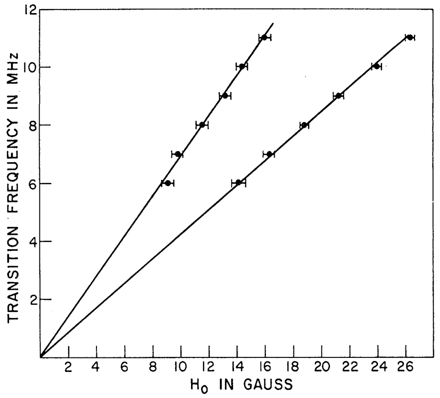

FIG. 2. Center of the double-resonance signal versus frequency for Zn lamp excitation of OH.

Recently, Marshall, de Zafra, and Metcalf[15,16] determined $g\tau$ for several different rotational levels of the $A^2\Sigma^+$ state of OH from a Hanle-effect measurement using a water discharge lamp for excitation and observing a single fluorescence line through a monochromator. While our value of $g\tau$ is consistent with theirs for the one (J', K') level at which they can be compared, they quote values of g quite different from ours based on an assumed $\tau=1.03\times10^{-6}$ sec. Although we are not in a position to reanalyze their data fully for the effects of hyperfine structure, if we take their value of $g\tau$ for the $K'=5$ level, where the effects of hyperfine structure are not as large, we obtain $\tau=6.8\times10^{-7}$ sec, assuming the average theoretical g value given in Table I, Ref. 15. This is in rough agreement with our value for the radiative lifetime.

An interesting variation on their technique is to perform the optical radio-frequency double-resonance experiment using the water discharge lamp, but omitting the monochromator. In this scheme, a resonance is obtained every time two or more Zeeman sublevels are separated in magnetic field by an energy corresponding to the rf frequency. Figure 3 shows the fairly complex double-resonance spectrum that we obtained.

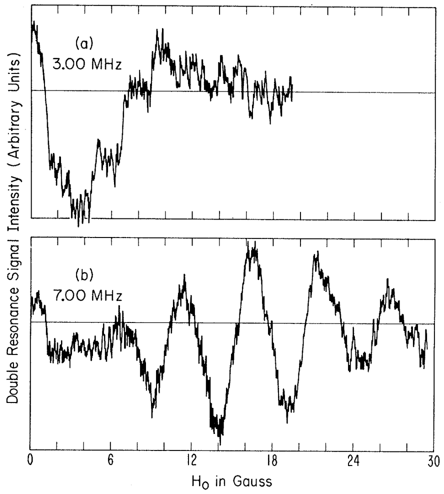

FIG. 3. The double-resonance signals as a function of frequency for water lamp excitation. The OH radical is formed at an H_2 pressure of 7.6 mTorr and an NO_2 pressure of 2.4 mTorr.

From the absence of resonances above 10 G in Fig. 3(a), it is apparent that we cannot detect any levels with g values between 0.20 and 0.10. This is consistent with the OH ground-state populations expected for the $T = 320°K$ Boltzmann distribution.[6] In Fig. 3(b), four signals are observed with g values of 0.48, 0.33, 0.24, and 0.20. A tabulation of the possible g_F values for the $K' = 2, 3, 4, 5$ sublevels shows a clustering about these values, assuming Hund's case (b) coupling. Thus to fully resolve all the components, much higher fields are required than are presently obtainable with our apparatus.

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DETERMINATION OF AN ISOTOPE SHIFT IN THE RATIO OF ATOMIC g_J VALUES OF HYDROGEN AND DEUTERIUM*

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The ratio $g_J(\mathrm{H})/g_J(\mathrm{D})$ in the electronic ground state has been determined using optical pumping of Rb and spin-exchange detection of H and D atomic Zeeman resonances. The result is $g_J(\mathrm{H})/g_J(\mathrm{D}) = 1 + (7.2 \pm 3.0) \times 10^{-9}$. The error includes an estimate of possible systematic effects.

Several unsuccessful attempts have been made in the past to observe a shift in the ratio of g_J values of hydrogen isotopes in the electronic ground state.[1-4] We report in this Letter an experimental determination of such an isotope shift for the ratio $g_J(\mathrm{H})/g_J(\mathrm{D})$. A mass dependence in the shielding of the electron magnetic moment in the atom is the origin of the effect according to a recent theory by Hegstrom.[5] It is now possible to compare theory with experiment.