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Measurement of the Hanle Effect for the OH Radical*

K. R. German[†] and R. N. Zare[‡]

Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder, Colorado 80302

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We have used the coincidence of the Zn I 3072.06 Å line with the $R_{12}(1)$ line of the (0, 0) band in the OH $A^2\Sigma^+ - X^2\Pi$ ultraviolet system to perform a measurement of the molecular Hanle effect on the $K' = 2$, $J' = \frac{3}{2}$ rotational level of the excited state. The OH was formed by the reaction $H + NO_2 \rightarrow OH + NO$, and the Hanle linewidth is extrapolated to zero pressure of H₂ and NO₂. The half-width is found to be 258 ± 36 mG and the pressure broadening of the linewidth corresponds to 13 ± 7 mG/mTorr of NO₂ pressure and 5.2 ± 0.8 mG/mTorr of H₂ pressure. This linewidth gives a value of $g\tau = (2.20 \pm 0.27) \times 10^{-7}$ sec for this excited state of the OH molecule.

I. INTRODUCTION

The OH radical has long been a subject of intensive investigation because of its common occurrence in high-temperature sources such as flames, arcs, discharges, and even in our own sun.¹ Since the advent of microwave and ESR techniques the $X^2\Pi$ ground state of OH has been thoroughly studied,²⁻⁸ yielding precise measurements of such quantities as its magnetic moment, Λ -type doubling and hyperfine splitting constants. No comparable measurements have been obtained for the first excited $A^2\Sigma^+$ state of OH,^{9, 10} although recent observations of interstellar OH emission lines¹¹ have heightened interest in the detailed nature of the $A^2\Sigma^+$ state, which might explain the mechanism for population inversion found in the ground state.

Another related astrophysical application involving the $A^2\Sigma^+$ state of the OH molecule was pointed out by Crosley, Tango, and Zare¹² last

year. The magnitude of the magnetic field associated with a comet is a matter of some controversy. It is believed that the cometary plasma interacts with the solar wind to form a shock front in which the interplanetary magnetic lines of forces are compressed and "frozen in." There is also speculation on the existence of an intrinsic cometary magnetic field. Crosley *et al.* propose that the cometary magnetic field can be measured through magnetic depolarization studies (Hanle effect)^{13, 14} of molecular resonance fluorescence in comets. The half-width of the depolarization signal depends on the product $g\tau$, where g is the excited-state molecular g factor (analogous to the Landé g factor for atoms) and τ is the radiative lifetime. It was suggested that the OH $A^2\Sigma^+ - X^2\Pi_i$ ultraviolet-band system was particularly suitable for earth-based observation and might allow an upper limit of a few milligauss to be set.

Recently, Marshall, deZafra, and Metcalf^{15, 16} have determined $g\tau$ for several different rota-

tional levels of the $A \ ^2\Sigma^+$ state of OH. In their work, the OH molecules, formed by combining $H + NO_2$,¹⁷ are excited by light from a microwave-powered water discharge lamp. The fluorescence at right angles to the incident beam is dispersed through a monochromator and detected. Because of the widely spaced rotational-structure characteristic of hydride molecules, this technique permits observation of individual lines. In this manner, they have determined $g\tau$ for $K' = 2, 3, 4$, and 5.

We report here a measurement of $g\tau$ for the $K' = 2$ rotational level of the OH $A \ ^2\Sigma^+$ state. Although the OH molecules are produced by the same reaction, we have employed the coincidence¹⁸ of the Zn I 3072.06 Å line with the $R_{12}(1)$ molecular absorption line¹⁹ to excite OH. The fluorescence is detected simultaneously by two photomultipliers placed at 45° and 135° to the incident light beam, and the two signals are passed through a difference amplifier (optical bridge).^{20, 21} This technique is particularly advantageous for detecting weak signals in the presence of large lamp fluctuations and/or OH density fluctuations.

II. EXPERIMENTAL

A. Description of Apparatus

Figure 1 shows a block diagram of the experimental setup. The 3072.06 Å light is produced by a 2450-MHz microwave discharge in a cylindrical quartz tube containing argon (1 Torr) and a small but arbitrary amount of zinc metal. Spectra of the light from the lamp showed no traces of the OH uv emission bands. The lamp is enclosed in a quartz jacket through which heated air flows at about 290 °C. The 3072.06 Å light corresponds to the transition between two

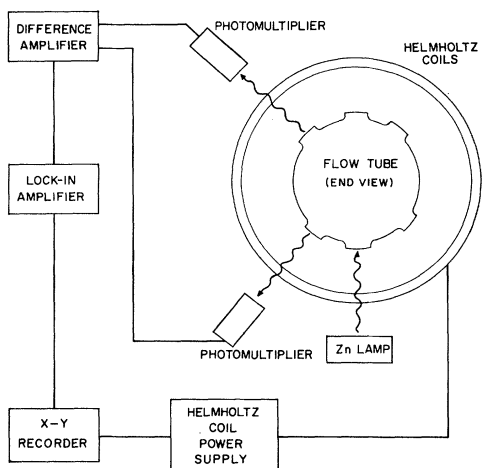


FIG. 1. Block diagram of apparatus.

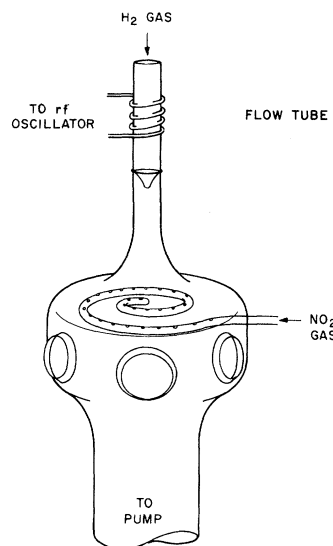
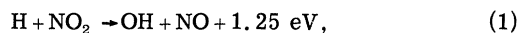


FIG. 2. Interaction region of the flow tube.

excited states of the Zn atom ($^3P_2^\circ - ^3S_1$). Unfortunately, an intercombination line ($^3P_1^\circ - ^1S_0$) occurs at 3075.90 Å with an intensity about ten times stronger than the desired line. Interference filters, placed in front of the two photomultipliers, cannot discriminate between these two lines, and most of the noise on the Hanle signal is caused by scattered light of this unwanted line. The stability of the lamp, which is primarily a measure of the stability of the stronger line, is approximately 0.25% per 15 min.

The OH radicals are produced by the chemical reaction



where at least 95% of the OH is in the $v'' = 0$ vibrational level. The H atoms are generated by a 90-MHz discharge in H_2 and are passed through a 1-mm nozzle into the interaction region. The nozzle prevents the discharge from propagating into the interaction region. The NO_2 is added through a multiperforated spiral, and its flow is directed against the hydrogen stream (see Fig. 2). Both gases were of commercial grade and were used without further purification.

The flow tube, made of Pyrex, measures 110 mm diam at the interaction region. All six windows are of optical II grade quartz and are attached to the flow tube with Torr Seal. Pressure readings are made with an NRC alphasatron gauge, which is placed approximately 170 cm downstream. A liquid-nitrogen trap is located between the pressure gauge and the mechanical pump (a Welch model 1397B with a pumping speed of 17.7 cfm).

The mechanical pump and cold trap together produce an ultimate vacuum of about 0.1 mTorr. This configuration is used for all runs in which the total pressure exceeds 15 mTorr. For lower pressures, however, an oil diffusion pump is inserted between the mechanical pump and the cold trap. This increases the pumping speed by a factor of 4. For these low-pressure measurements, the alphasatron gauge is replaced by a vacuum ionization gauge.

A magnetic field, produced by a pair of Helmholtz coils (shown in Fig. 1), is applied to the interaction region in a direction perpendicular to the plane of the detection system. Another pair of Helmholtz coils is used to apply an oscillating magnetic field for ac detection. Finally, the entire interaction region is located at the center of three orthogonal pairs of coils that cancel the local magnetic field. The residual field gradients are less than 2 mG over the interaction region. All magnetic-field measurements, both ac and dc, are made with a Bell model 620 Gaussmeter.

The detection system consists of two matched RCA 1P28A photomultiplier tubes, each mounted with an interference filter whose 100 Å passband is centered at 3080 Å. The two photomultiplier currents are subtracted by a difference amplifier whose output is adjusted to a null at zero field. By adjusting the relative cathode bias of the two photomultipliers, the dc balance is achieved. An important practical advantage of this technique is that a relatively inexpensive operational amplifier (Burr-Brown 3112) may be used as the difference amplifier.

The difference amplifier output is detected by an EMC model RJB lock-in amplifier whose output, in turn, drives the Y axis of a Moseley X-Y recorder. The X axis of the recorder is controlled by the voltage applied to the Helmholtz coils.

B. Theory of Operation

For the particular geometry chosen, the Hanle signals are dispersion shaped, but with opposite signs for the two detection directions.²¹ Hence, if both photomultipliers are positioned to see the same relative amount of scattered plus fluorescent light, the Hanle signal components will be added in the output of the difference amplifier, while the scattered light signals will be subtracted. This arrangement enhances the signal by a factor of 2 and greatly suppresses the variations due to fluctuations in the background light. This is especially useful in this experiment because of the presence of the strong unwanted Zn line at 3076 Å. In the extreme case where one photomultiplier sees only scattered light, the optical bridge then functions as a lamp monitor and acts to reduce the effect of lamp fluctuations.

A typical trace of the lock-in output is shown in Fig. 3. For small modulation amplitudes, this signal approaches the derivative of a dispersion shape. In this experiment, it is necessary to use modulation amplitudes that contribute as much as a 30% broadening to the actual linewidth of the Hanle signal. Consequently, all linewidth measurements are extrapolated to zero modulation amplitude.

Initially, the modulation-broadened linewidth was determined from the zero crossing points of the signal (see Fig. 3). A series of such measurements at different modulation amplitudes was extrapolated to yield the unbroadened linewidth. Subsequently, a computer program was used to perform a least-squares fit to the full line profile including the distortion effects caused by modulation broadening and the asymmetry caused by optical misalignment.

In order to check the linearity of the detection system, linear polarizers are placed in front of

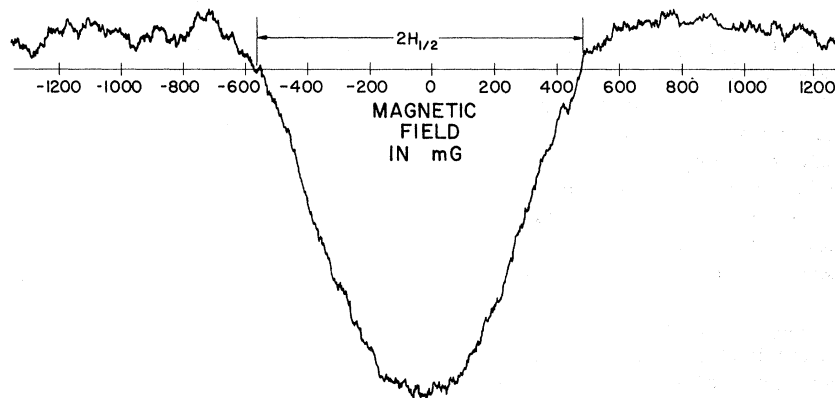


FIG. 3. Typical OH level crossing signal. The conditions are: $P(\text{H}_2) = 23$ mTorr; $P(\text{NO}_2) = 6.6$ mTorr; modulation field = 300 mG; and lock-in time constant = 30 sec.

the photomultipliers so that they cancel the Hanle signal and the magnetic field is swept from 0 to 20 linewidths. No variation of the output signal is observed.

A question may arise as to the identity of the fluorescing species. Since the Hanle signal disappears when the hydrogen dissociator is turned off, it is possible to rule out H_2 and NO_2 . In order to rule out the possibility of NO fluorescence, D_2 is substituted for H_2 under identical operating conditions. The Hanle signal is then observed to decrease by a factor of 50, which roughly corresponds to the H_2 impurity in the D_2 used. On the basis of this evidence we conclude that we are observing Hanle signals from the $A^2\Sigma^+$ state of OH .

III. DISCUSSION OF RESULTS

A theoretical expression for the linewidth ($\Delta M = 2$) in the absence of pressure broadening is given by

$$H_{1/2} = \hbar / 2\mu_0 g \tau, \quad (2)$$

where μ_0 is the electronic Bohr magneton, and $H_{1/2}$ is one-half the difference between the zero signal crossing points (see Fig. 3). The Hanle effect linewidth is found to vary with both H_2 and NO_2 pressure. The formation of OH , shown in reaction (1), is quite rapid and has a rate constant²² of $(4.8 \pm 0.5) \times 10^{-11}$ cm^3/sec . The primary destruction mechanism of OH is second order in the OH pressure:



and its rate constant¹⁷ has been determined to be about 2.5×10^{-12} cm^3/sec . Reaction (3) is followed by a more rapid destruction process:



with a rate¹⁷ of $(1-2) \times 10^{-11}$ cm^3/sec . Thus the effective rate of destruction of OH is about 13 times slower than the rate of formation. From these considerations reaction (1) goes to completion in the interaction region, and reactions (3) and (4) do not make appreciable inroads on the OH concentration. Thus, we can conclude that in the interaction region, pressure broadening can only be caused by the NO_2 , H_2 , OH , and NO present.

We have observed that the pressure in the system increases by as much as 1 mTorr out of about 20 mTorr when the rf dissociator is turned on while the NO_2 is flowing, but no such change is observed in the absence of NO_2 . This pressure increase should be due principally to the NO pro-

duced by reaction (1); hence we may estimate that the OH pressure is roughly comparable (~ 1 mTorr). Consequently, we would expect that the principal broadening of the Hanle signal is caused by collisions of OH with the excess H_2 and NO_2 which are present in much greater abundances than the OH and NO .

Maintaining the pressure of one of the reactants fixed and measuring the Hanle linewidth as a function of the other pressure, we obtain the results shown in Figs. 4 and 5 for H_2 and NO_2 , respectively. Note that the NO_2 pressure dependence cannot be carried out for partial pressures as large as for H_2 since excess NO_2 destroys the Hanle signal. Because the alphasatron gauge is not in the interaction region, pressure readings are corrected for the conductance of the connecting tubing.²³ For the pressure region studied, the flow is intermediate between molecular and viscous, but the pressure corrections are only of the order of 5%.

The linewidth broadening studies are analyzed by a linear least-squares fit to the H_2 and pressure variables:

$$H_{1/2} = a + bP(NO_2) + cP(H_2), \quad (5)$$

$$\text{where } a = 258 \pm 36 \text{ mG}, \quad (6a)$$

$$b = 13 \pm 7 \text{ mG/mTorr}, \quad (6b)$$

$$c = 5.2 \pm 0.8 \text{ mG/mTorr}. \quad (6c)$$

The quoted errors for the parameters a , b , c , represent 3 standard deviations (95% confidence limit). In addition to the data shown in Figs. 4 and 5, two other points were taken at lower pressures, 3.8 mTorr (total) and 1.12 mTorr (total) using the diffusion pump. It is interesting to note that the intercept obtained from the data in Figs. 4 and 5 alone is only 1 standard deviation higher than the intercept obtained using all the data.

To determine the value of the g factor and the collision cross sections for NO_2 and H_2 from these measurements, it is necessary to assume a value

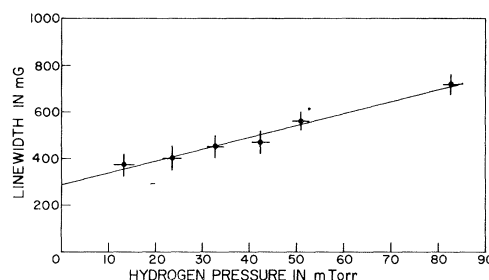


FIG. 4. $H_{1/2}$ as a function of H_2 pressure for constant NO_2 pressure at 2.0 mTorr.

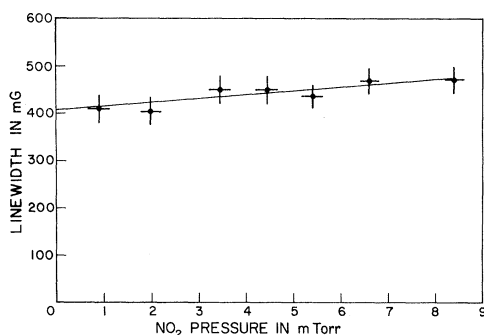


FIG. 5. $H_{1/2}$ as a function of NO_2 pressure for constant H_2 pressure at 23.0 mTorr.

for τ , the radiative lifetime for the ($v'=0$, $K'=2$, $J'=\frac{3}{2}$) state. Unfortunately, published results disagree by a factor of about 2: Bennett

and Dalby²⁴ quote an oscillator strength $f_{00} = (8.0 \pm 0.8) \times 10^{-4}$, while Anketell and Pery-Thorne²⁵ quote $f_{00} = (14.8 \pm 1.3) \times 10^{-4}$. We feel that we are in no position at present to decide between these values. Consequently, we will quote only the product $g\tau = (2.20 \pm 0.27) \times 10^{-7}$ sec.

Assuming a value of $\tau = 1.03 \times 10^{-6}$ sec for this state, based on the work of Bennet and Dalby, deZafra *et al.*¹⁶ determine the effective g factor to be 0.226 ± 0.043 (1 standard deviation).²⁶ For comparison, we obtain $g = 0.213 \pm 0.027$, assuming the same value of τ . Similarly, this value of τ gives $(1.2 \pm 0.7) \times 10^{-9}$ cm³/sec and $(5.1 \pm 0.8) \times 10^{-10}$ cm³/sec for NO_2 and H_2 depolarization rates (σv), respectively. On the other hand, if we accept the value of τ given by the work of Anketell and Pery-Thorne, the value of g we obtain agrees with the g value predicted for the $A^2\Sigma^+$ state of OH, assuming Hund's case (b) coupling.

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[†]Joint Institute for Laboratory Astrophysics Post-doctoral Research Associate, 1967-1969.

[‡]Alfred P. Sloan Fellow.

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