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MEASUREMENT OF THE LIFETIME OF THE $A^1\Pi$ STATE OF CO BY LEVEL-CROSSING SPECTROSCOPY*

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The lifetime of the $v=2$ level of the $A^1\Pi$ state of CO has been measured by molecular level-crossing spectroscopy. Unlike previous experiments with molecules in which the Hanle effect has been analyzed for individual rotational states, the present results are obtained from analysis of the composite level-crossing signal from all of the rotational states which are excited by the entire $A\rightarrow X(2,0)$ resonance band. Our experimental result is $\tau(v=2)=9.0\pm1.0$ nsec in good agreement with Hesser's value of 10.5 ± 1.0 nsec obtained from phase-shift experiments.

Measurements of the oscillator strengths of the CO molecule have received much attention in the last few years not only because of increasing interest in the fundamental properties of molecules, but also because such measurements have astrophysical applications.[1,2] Integrated oscillator strengths of the $A^1\Pi \leftarrow X^1\Sigma$ system have been reported by Hesser[3] and by Lassettre and Silverman.[4] Individual f values between bands have also been tabulated by Hesser, by Rich,[5] and by Meyer, Skerbele, and Lassettre.[6] Hesser has measured the lifetime of the $A^1\Pi$ state by the phase-shift technique and used this lifetime in conjunction with relative intensities of the various bands excited by electron impact in order to obtain his results. The values reported by Rich have been obtained from an absorption experiment in shock-heated CO. Lassettre and his co-workers have extracted optical f values from the generalized oscillator strengths for inelastic collisions of electrons with CO. The oscillator strengths reported for the (2, 0) band reveal the typical disparity of the results; the three experiments yield 0.022, 0.033, and 0.051, respectively.

In an effort to establish the oscillator strengths of the fourth positive system more firmly, we have measured the lifetime of the $v=2$ level of the $A^1\Pi$ state from a level-crossing experiment in which we have exploited a technique that has not been used previously. Other level-crossing experiments on diatomic molecules have employed the Hanle effect to obtain g factors through the observation of spectrally resolved lines from single rotational states which have been excited either by a molecular source[7] or by an accidental overlap of an atomic line.[8] The present experiment is illustrative of a method which we believe will prove useful in certain situations for which atomic overlaps cannot be found and for which resolution of rotational lines is not possible. The entire (2, 0) resonance band (1478 Å) has been employed for excitation of the upper electronic state, and the observed level-crossing signal is the summation of signals which originate from all of the excited rotational states. The data are analyzed by fitting them to a model which accounts for the individual contributions to the total Hanle effect.

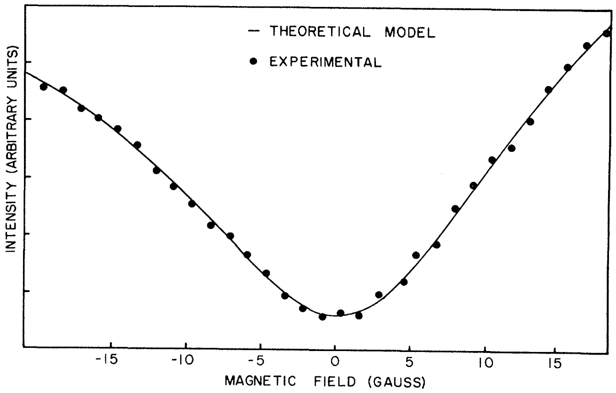

FIG. 1. Hanle-effect signal for the $v=2$ level of the $A^1\Pi$ state of CO. Experimental data from the signal averager have been plotted at intervals of eight channels.

The source of light for the excitation is a 30-MHz rf discharge in a mixture of helium and carbon dioxide. The band used for excitation is selected with a McPherson model 225 vacuum monochromator operating with a resolution of 15 Å in order to obtain the most intense beam possible without a large fraction of background light from nearby bands. This beam is used to excite the gas in the scattering cell, which is situated between the pole pieces of a magnet. The ultraviolet light scattered from the gas is shifted to a wavelength of about 4000 Å by a sodium salycilate coating on the end of a Lucite rod 1 cm in diam. The rod is oriented at 90° to the incident beam and acts as a light pipe to a cooled photomultiplier tube. The magnetic field is swept through a complete range of about 50 G every 20 sec, and the intensity of the scattered light is recorded in 256 channels of a Fabri-Tek model 1060 instrument computer which is used as a signal averager. The variation of the intensity as a function field strength is shown in Fig. 1. Most of the data have been obtained with the pressure of the target gas at 5 mTorr. No broadening of the signal was observed up to 100 mTorr, within the limits of experimental uncertainty.

The fluorescence which results from optical excitation of a single rotational level of the $A^1\Pi$ state and subsequent emission into a given branch of the fourth positive system is calculated from the Breit[9,10] formula

$$B_{J,J',J''} \propto \sum_{uu',m'm''} \frac{\langle J\mu|\vec{f}\cdot\vec{r}|J'm'\rangle\langle J'm'|\vec{f}\cdot\vec{r}|J\mu'\rangle\langle J\mu'|\vec{g}\cdot\vec{r}|J''m''\rangle\langle J''m''|\vec{g}\cdot\vec{r}|J\mu\rangle}{[1+i(\mu-\mu')g_J\tau_J H/\hbar]}. \tag{1}$$

The polarization vectors for excitation and re-emission are denoted by $\vec{f}$ and $\vec{g}$, respectively; J', J'', m', and m'' are the quantum numbers related to the total angular momenta of the ground states and their projections on the z axis, and J, μ, and μ' are the quantum numbers for the excited states. The lifetime and Landé g factor of the excited rotational level are denoted by τ_J and g_J, and H is the magnetic field strength. Terms are listed in Table I for different possible modes of excitation and decay if unpolarized light is used. The symmetry selection rule for electric dipole transitions in heteronuclear molecules, $+ \leftrightarrow -$, prohibits routes which couple the Q branch in excitation to the P and R branches in decay and vice versa. The field-independent part of the fluorescence comes from terms for which $(\mu-\mu')=0$; the field-dependent part arises only from terms for which $|\mu-\mu'|=2$.

If the band under observation could be completely resolved, it would be an easy matter to assess the relative contributions of scattered light from the different rotational levels by means of the relative intensities of individual lines. However, Figs. 2(a) and 2(b) demonstrate the spectrum of light observed directly from the lamp and the spectrum observed from the scattering cell at a resolution of 0.3 Å. Only at high rotational levels are individual peaks distinct, and even these are composites of lines from P, Q, and R branches of the band. A two-step procedure is followed, therefore, in order to construct a model which describes the relative intensities of individual rotational lines from the

Table I. $B_{J,J',J''}$ for permitted modes of excitation and decay of the $A^1\Pi$ state of CO. Both excitation and observation are assumed to take place with unpolarized light, and the angle between the two directions is φ. $A=(\cos 2\varphi+R\sin 2\varphi)/(1+R^2)$, with $R=2g_J\tau_J\mu_B H/\hbar$.

J'	J''	$B_{J,J',J''}$
J	J	$\frac{(2J+1)}{J(J+1)}[(28J^2+28J-1)+A(2J+3)(2J-1)]$
$J-1$	$J-1$	$\frac{(J+1)^2}{J(2J-1)(2J+1)}[(54J^2-25J+1)+A(J+1)(2J+3)]$
$J-1$	$J+1$	$\frac{J(J+1)}{2J+1}[27+A]$
$J+1$	$J-1$	$\frac{J(J+1)}{2J+1}[27+A]$
$J+1$	$J+1$	$\frac{J^2}{(2J+3)(2J+1)(J+1)}[(54J^2+133J+120)+AJ(2J-1)]$

scattering gas. The intensities and shapes of lines from the lamp are first obtained by assuming uniform excitation along the discharge and calculating the output from the following equations, which assume that if a photon is absorbed within the lamp it is completely lost from the beam entering the monochromator:

$$I_{JJ'}{}^{L} \propto \int_0^\infty S_{JJ'} d\nu, \tag{2}$$

$$S_{JJ'} = [N_u{}^L(J,J')/N_l{}^L(J',J)\alpha_L]\{1-\exp[-\alpha_L N_l{}^L(J',J)\exp(-\beta\nu^2)]\}. \tag{3}$$

The quantities $N_u{}^L(J,J')$ and $N_l{}^L(J',J)$ are products of Hönl-London factors and Boltzman factors for the upper and lower levels of a spectral line in the source, α_L is an absorption parameter for the lamp, and β is the usual coefficient of the frequency ν of a Doppler profile which varies inversely as T_L, the temperature of the gas in the lamp. Both α_L and T_L are treated as variable parameters and adjusted to obtain the best fit to the envelope of the spectrum shown in Fig. 2(a). The spectrum of the scattered light is fitted in much the same manner,

$$I_{JJ'J''}{}^{S} \propto \int_0^D dz \int d\Omega \int_0^\infty d\nu\, S_{JJ'} A_{JJ'} B_{JJ''}, \tag{4}$$

where

$$A_{JJ'} = \alpha_S M_{J'} \exp(-\gamma\nu^2)\exp[-\alpha_S N_l{}^S(J',J)z\exp(-\gamma\nu^2)]. \tag{5}$$

The gas in the scattering cell is assumed to be at room temperature, the absorption parameter is α_S, and the Boltzman factor is $M_{J'}$. The length of the scattering cell is D, and $d\Omega$ is the differential of solid angle subtended by the detector at the point of the scattering. Only single scattering is considered because approximately 80% of the detected intensity is from optically thin bands which terminate on levels for which $v>0$. An uncertainty of only 3% is introduced into the lifetime if α_S is uncertain by a factor of 2.

If the shape of the level-crossing signal was very sensitive to the relative line intensities, the procedure outlined for obtaining these amplitudes would be inadequate, owing to the inherent uncertainties in the calculation. However, the influence of these uncertainties is minimized because the coupling scheme for unperturbed levels of the $A^1\Pi$ state of CO is closely represented by Hund's case (a)[11,12] for which $g_J = [J(J+1)]^{-1}$. Because the signal from a given rotational level depends upon $g_J{}^2$, the variation of the total level-crossing signal at low fields strongly reflects the variation of the $J=1$ level.

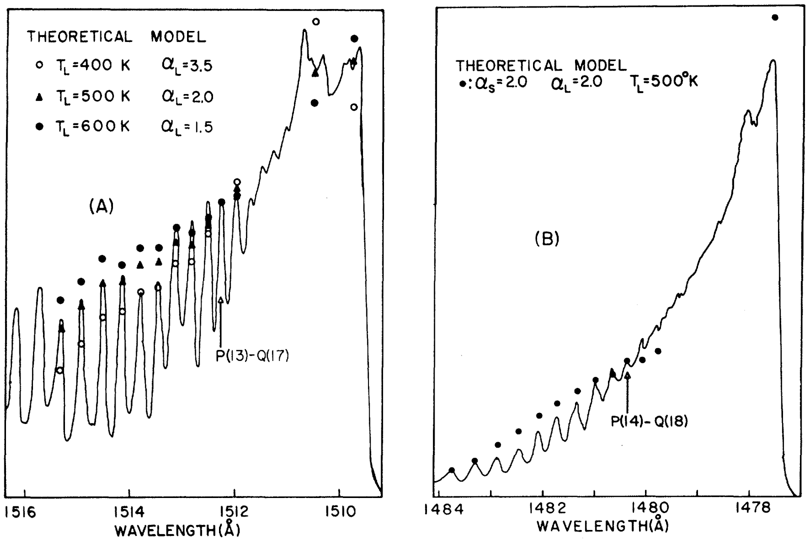

FIG. 2. (a) Spectrum of the lamp in the region of the region of the (1, 0) band of the fourth positive system of CO. The theoretical model is normalized to the experimental spectrum at the $P(13)$-$Q(17)$ peak. This band is used to establish the lamp parameters because it is relatively free from overlapping bands. (b) Resonance fluorescence spectrum of the (2, 0) band. The theoretical model is normalized to the experimental spectrum at the $P(14)$-$Q(18)$ peak.

Within one half-width of the $J=1$ crossing only about 23 % of the signal arises from higher rotational levels; as a result, a very accurate weighting of these higher rotational levels is not critical. In the final analysis, a 20% uncertainty in the magnitude of the contribution from the $J=2$ level leads to an uncertainty of about 5 % in the lifetime of the state. Crawford[13] and Kemble, Mulliken, and Crawford[14] have measured g_J for some of the rotational states in the $v=2$ level; the results are slightly smaller than those predicted strictly for a case (a) coupling scheme. We have, therefore, employed Crawford's average value of 0.482 for g_1 rather than 0.50 and scaled the other g factors by the same ratio. Data are analyzed by obtaining the best least-squares fit to a sum of field-dependent terms calculated from Eq. (4). Our result for four independent experimental curves is

$$\tau(v=2)=9.0\pm1.0 \text{ nsec}.$$

The uncertainty includes the standard deviation of the experimental results and an estimate of the possible systematic error for relative weighting of the various contributions of the Hanle effect. Within the limits of experimental error our present result overlaps Hesser's value for the lifetime, 10.5 ± 1.0 nsec, and implies agreement with his results for the oscillator strengths of the $A^1\Pi$ system.

Analyses similar to those discussed for the $v=2$ level are currently being performed for other vibrational levels of the $A^1\Pi$ state. However, the strong perturbations which exist in these levels can produce states for which g_J is not given by Hund's case (a) coupling scheme and for which the lifetimes may be far different from unperturbed states. The results of these analyses cannot, therefore, be used at the present time to corroborate the value of τ stated for the $v=2$ level.

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