

Accurate determination of the band oscillator strength for the (0,0) ultraviolet transitions of OH

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Various experimental results for the band oscillator strength of the (0,0) ultraviolet transitions of OH are examined in the light of a recent theory. A value of $(1.09 \pm 0.04) \times 10^{-3}$ and $0.79 \pm 0.03 \text{ \AA}^{-1}$ is confirmed for the band oscillator strength and its rotational constant, respectively. New experimental results which verify the spin-independent nature of both are also presented.

OH is an important molecule which has been studied extensively ever since the advent of quantum mechanics.¹ The interest^{2,3} in OH has been revived recently because of the pivotal role⁴ which OH plays in atmospheric sciences. For example, a determination of OH concentrations with an accuracy of 5–10% is needed in order to test the validity of various models for the clean and polluted atmospheres. With either the fluorescence technique² or the absorption technique,⁵ this requires that the band oscillator strength of OH be determined with an accuracy to better than 5%. The purpose of this paper is to examine various experimental results in the light of a recent theory, and to determine a sufficiently accurate value for the band oscillator strength and its rotational dependence. New experimental results which verify the spin-independent nature of these quantities will also be presented.

The precision with which our value for the band oscillator strength is determined approaches that limited by the accuracy of other molecular parameters such as the coupling constant¹ for spin-rotation coupling in the ground electronic state of the OH molecule. We believe this marks the first time when the theory of spin-rotation coupling for the intensity of molecular transitions is *quantitatively* verified.

The band oscillator strength of OH has been measured by various authors⁶ to be $\sim 1 \times 10^{-3}$ and slightly dependent on the rotational excitation. However, because of experimental difficulties, the accuracy of these measurements was rather limited, and serious discrepancies existed among various results. While recent lifetime measurements⁷ yield good results, analysis of these results was hampered for want of a clear understanding of the effect of rotation on the band oscillator strength of OH. With the development of a workable theory,⁸ it seems appropriate to review the available data, and to reanalyze them in the light of this theory.

The rotational dependence of the band oscillator strength of OH can be predicted quantitatively if it is recognized that rotational excitation brings about stretching of the internuclear spacing, and that the extent of stretching is determined by the restoring force derived from the quadratic term in the potential energy function. It follows that the rotational dependence should be insensitive to the anharmonicity of the potential energy function. While this point was demonstrated clearly in a recent publication,⁸ it was apparently not recognized at all in other works on OH to date. This lack of understanding has caused much frustration^{9,10} in the use of OH rotational distribution for diagnostic purposes, and has belabored many authors^{10,11} in performing extensive numerical computations which can now be replaced by simple closed-form solutions.

The band oscillator strength for the (0,0) transitions of OH is given by⁸

$$f(J'') = A q(J'J'') R_e^2(J'J''), \quad (1)$$

where A is a constant,

$$q(J'J'') = (\alpha_1 \alpha_2 / \alpha^2)^{1/2} \exp[-(\alpha_1 \alpha_2 / 2\alpha)(r_1 - r_2)^2] \quad (2)$$

is the Franck-Condon factor, and

$$R_e(J'J'') = R_e(0,0)[1 - \rho(\alpha_1 r_1 + \alpha_2 r_2)/2\alpha] \quad (3)$$

is the electronic transition moment with

$$r_i = r_{i0} + (D_i/B_i)r_{i0}J^i(J^i + 1). \quad (4)$$

Here J^i is the rotational quantum number; ρ is a constant; r_i and r_{i0} are, respectively, the equilibrium internuclear spacing with and without rotational excitation; $i=1,2$ for the excited and ground electronic states, respectively; D_i and B_i are spectroscopic constants; $\alpha = (\alpha_1 + \alpha_2)/2$; and α_i is a measure of the extent of the vibrational wave functions, which are all determined from spectroscopic data.⁹ For the (0,0) transitions under con-

sideration, $|r_1 - r_{10}| \ll r_{10}$ and Eqs. (1)–(3) can be simplified further to exhibit a linear decrease in the Franck-Condon factor and in the electronic transition moment with increasing rotational excitation. This linear dependence greatly facilitated the experimental determination of ρ , and thus the correction factors¹⁰ for the oscillator strength, as a function of rotational excitation.

With the aid of the analysis outlined above, it has been possible to deduce from recent absorption measurements⁸ that $f = (1.09 \pm 0.04) \times 10^{-3}$ for the band oscillator strength¹² without rotational excitation and $\rho = 0.79 \pm 0.03 \text{ \AA}^{-1}$ for its rotational constant in Eq. (3). When corrections are made according to Eq. (2) for the changes in the Franck-Condon factors, one also deduces from the lifetime measurements⁷ that $f = (1.085 \pm 0.035) \times 10^{-3}$ for a rotationless OH molecule, and $\rho = 0.78 \pm 0.03 \text{ \AA}^{-1}$ for the rotational constant. It follows that these results are in excellent agreement, and a reliable value with an accuracy of better than 4% for the band oscillator strength is thus confirmed.

It remains to be demonstrated that the band oscillator strength and its rotational dependence are spin independent. That this indeed is the case may be seen from Fig. 1 where results from accurate absorption measurements for the R_2 lines are shown and compared with those for Q_1 lines reported recently.⁸ We have also observed that the results for the Q_2 lines are the same as those of the Q_1 lines within about 1%. The results for R_2 lines seem to be consistently higher than their corresponding Q_1 lines $\sim (2 \pm 2)\%$. While this difference with the R_2 lines could be discounted as being within the experimental uncertainty, it is important to point out that this difference could be due to the uncertainty in the constant for the spin-rotation coupling,⁹ which is known to perhaps no

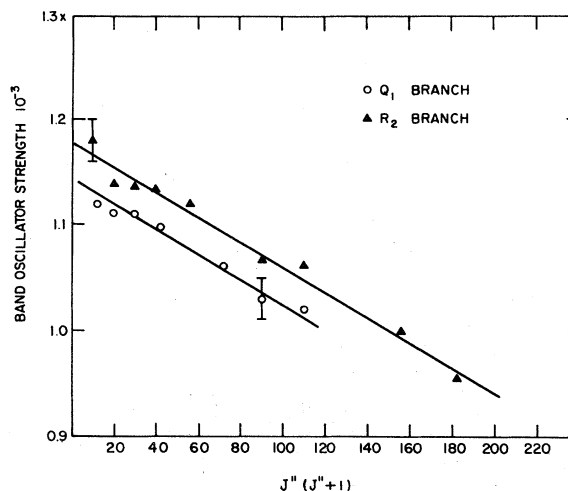


FIG. 1. Plot of the band oscillator strength for the R_2 -branch transitions as a function of the energy of the rotation level from which absorption originates. These results are obtained in a manner similar to that described in Ref. 8. Previous results for the Q_1 lines are also included for comparison.

better than 2%. R_2 lines are the weaker transitions, and their rotational transition probabilities are more susceptible to changes in the value for this coupling constant, particularly at lower rotational levels. It thus seems unlikely that the rotational transition probability for individual lines could be determined more accurately without a more accurate value for the spin-rotation coupling constant.

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¹²This value is different from the value of $(1.13 \pm 0.01) \times 10^{-3}$ deduced directly from the rotational dependence as described in Ref. 8. This difference reflects corrections for small experimental peculiarities and compounding of systematic errors such as experimental uncertainties (2%), lack of reproducibility (1%), and fitting errors (2%).