

Effect of rotational excitation on the band oscillator strength of OH

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Using a continuous-wave, single-frequency, tunable dye laser, the authors have made accurate absorption measurements of the band oscillator strength for various rotational-electronic lines in the ${}^2\Sigma^+(v' = 0) \leftarrow {}^2\Pi(v'' = 0)$ transitions of OH. The band oscillator strength is seen to decrease linearly with the energy of rotational excitation. It is established that this decrease results solely from lengthening of the internuclear distance due to rotation.

The ${}^2\Sigma^+ - {}^2\Pi$ ultraviolet transitions of OH have been the subject of many recent investigations.¹⁻⁷ These transitions belong to a system which is forbidden both in the united atom and in the separated atoms.⁸ For intermediate values of the internuclear spacing the electronic transition moment first increases to a maximum and then decreases with increasing internuclear spacing.⁹ Since the internuclear spacing and the electronic wave functions may be altered in the presence of rotational or vibrational excitation, the transition moment may be expected to depend upon rotational and vibrational excitation. Various attempts⁹⁻¹³ have been made to quantify this dependence. However, reliable experimental results^{4,5,14,15} have been difficult to obtain and numerical analyses^{9,12} generally provide little physical insight into the nature of the problem. Using a cw single-frequency tunable dye laser, we have made accurate measurements of the band oscillator strength for the ${}^2\Sigma^+(v' = 0) - {}^2\Pi(v'' = 0)$ transitions of OH as a function of the rotational quantum number. It is seen from our results that the band oscillator strength decreases linearly with the energy of rotational excitation. Our results are in excellent agreement with recent measurements of the lifetime⁴ of OH in the excited state and correlate well with the dependence of electron transition moment deduced from measurements of vibrational band intensities.⁵ These results are discussed in the light of a simple theory which we developed in closed forms. It is concluded that the decrease in oscillator strength, and thus in electron transition moment, can be explained solely in terms of the lengthening of the internuclear distance due to rotation, with negligible effect attributable to the distortion of the electronic wave functions.

The experimental setup used in our experiments was similar to that reported previously,^{2,16} but with many important improvements.¹⁷ As the light source, the frequency-doubled output from a Coherent Model 599-021 single-frequency dye laser was used. This output was tuned to sweep a-

cross various rotational-electronic lines in the (0,0) transitions of OH near 3080 Å and traversed an OH cell. The absorption signal thus generated was normalized, passed through a precision logarithmic amplifier, and recorded on a chart recorder. The absorption line-shape was deconvoluted with the aid of a computer to determine the base line and the homogeneous linewidth; the line oscillator strength was obtained by integrating the experimental line shape with the base line determined above, and was then normalized according to a thermalized rotational distribution to yield the value per molecule.³ Finally, the band oscillator strength was obtained from the line oscillator strength by equating the ratio of these two quantities to that calculated from the tabulated values of rotational transition probabilities.¹⁸

OH was generated by passing a stoichiometric mixture of water and oxygen gases through a 30.2-cm quartz cell placed in a high-temperature furnace.¹⁷ The temperature of the furnace was maintained at $(1040 \pm 1)^\circ\text{C}$ and was kept constant to within $\pm 0.5^\circ\text{C}$ over a length of 32 cm. Care was taken to ensure that the gas mixture was in thermal-equilibrium and that no OH was generated im-

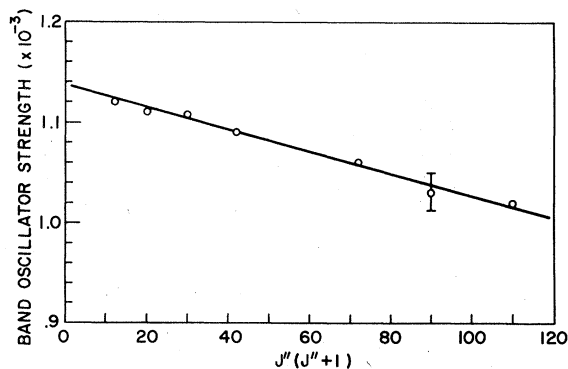


FIG. 1. Plot of the band oscillator strength as a function of the energy of the rotation level from which absorption originates.

mediately outside the quartz cell.¹⁹ With these arrangements the absorption signal was found to be reproducible well within 2%.

In Fig. 1 the band oscillator strength deduced from the Q_1 -branch transitions is shown as a function of the energy of the rotational level from which absorption originates. It is seen that the band oscillator strength decreases linearly with increasing energy of rotational excitation. A least-squares analysis taking into account the uncertainties of the individual data points yields a value of $(9.6 \pm 2) \times 10^{-4}$ for the normalized slope and a value of $(1.13 \pm 0.01) \times 10^{-3}$ for the oscillator strength of a rotationless molecule. These results are in excellent agreement with those obtained recently from lifetime measurements.⁴ In view of the fact that our technique is diametrically different from that employed in emission lifetime measurements, this agreement leaves little doubt that the observed rotational dependence was genuine.

Ignoring the effect of electron spin, the band oscillator strength associated with a group of rotational-electronic lines with a particular set of rotational and vibrational quantum numbers (v' , v'' , J' , J'') is given by

$$\begin{aligned} f &= A \sum_{J'} |R(v'v''J'J'')|^2 \\ &= A \sum_{J'} \left| \int \psi'(v'J') R(r) \psi''(v''J'') dr \right|^2 \frac{S_{J'J''}}{2J''+1} \\ &\cong A |R_e(v'v''J'J'')|^2 q(v'v''J'J''). \end{aligned} \quad (1)$$

Here A is a constant; $S_{J'J''}$ is the rotational transition probability¹⁸; $|R(v'v''J'J'')|^2$ and

$$p(v'v'') = \left| \int \psi'(v'J') R(r) \psi''(v''J'') dr \right|^2$$

are, respectively, the electronic and vibrational transition probabilities;

$$q(v'v''J'J'') = \left| \int \psi'(v'J') \psi''(v''J'') dr \right|^2 \quad (2)$$

is the Franck-Condon factor and

$$|R_e(v'v''J'J'')| = \frac{\left| \int \psi'(v'J') R(r) \psi''(v''J'') dr \right|}{[q(v'v''J'J'')]^{1/2}} \quad (3)$$

is the electronic transition moment. Note that

$$T_{J'J''} = |R_e(v'v''J'J'')|^2 / |R_e(v'v''OO)|^2$$

is the correction factor due to rotation-vibration interaction.¹²

Based on the results of an *ab initio* calculation,⁹ the transition moment of OH decreases linearly with increasing internuclear spacing. Thus

$$R(r) = C(1 - \rho r), \quad (4)$$

where C and ρ are constants and r is the internu-

clear spacing. Crosley and Lengel⁵ analyzed the vibrational band intensities within the framework of r -centroid approximation,¹¹ and found that $\rho \approx 0.75 \text{ \AA}^{-1}$ over a wide range of values for r . With Eq. (4) and known vibrational wave functions, the vibrational transition probabilities can be calculated to yield the correction factors due to rotation-vibration interaction.¹²

In previous analyses^{5,9-13} for the (0,0) transitions of OH, Morse-Pekeris wave functions were often used and resort had to be made to numerical computations to obtain the correction factors. We have found, however, that these correction factors can be obtained in closed forms by using simple harmonic wave functions⁸ modified to include changes in the internuclear spacing due to rotational excitation. It may be shown by explicit integration that the vibrational transition probability is given by

$$\begin{aligned} p(v'v'') &= (\alpha_1 \alpha_2 / \alpha^2)^{1/2} \exp[-(\alpha_1 \alpha_2 / 2\alpha)(r_1 - r_2)^2] \\ &\quad \times [1 - \rho(\alpha_1 r_1 + \alpha_2 r_2) / 2\alpha]^2, \end{aligned} \quad (5)$$

with

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

Here r_i and r_{i0} are, respectively, the equilibrium internuclear spacing with and without rotational excitation in the i th electronic-vibrational manifold, $i=1,2$ for ${}^2\Sigma^+(v'=0)$ and ${}^2\Pi(v''=0)$, respectively; D_i and B_i are spectroscopic constants¹⁸; $\alpha = \frac{1}{2}(\alpha_1 + \alpha_2)$ and α_i is a measure of the extent of the vibrational wave functions,⁸ which may be determined from band spectroscopic data.¹⁸ In Eq. (5) the Franck-Condon factor and electronic transition moment are given, respectively, by

$$\begin{aligned} q(v'v''J'J'') &= (\alpha_1 \alpha_2 / \alpha^2)^{1/2} \exp[-(\alpha_1 \alpha_2 / 2\alpha)(r_1 - r_2)^2] \end{aligned} \quad (6)$$

and

$$R_e(r) = 1 - \rho(\alpha_1 r_1 + \alpha_2 r_2) / 2\alpha. \quad (7)$$

For the (0,0) transitions of OH, $\alpha_1 \approx \alpha_2$, Eq. (7) may then be simplified to become

$$R_e(r) = [1 - \rho(r_{10} + r_{20})/2](1 - \beta \Delta r), \quad (8)$$

where

$$\beta = \rho[1 - \rho(r_{10} + r_{20})/2]^{-1}, \quad (9)$$

$$\begin{aligned} \Delta r &= \frac{1}{2}[(D_1/B_1)r_{10} + (D_2/B_2)r_{20}] J''(J'' + 1) \\ &\quad + 2(D_1/B_1)r_{10}G, \end{aligned} \quad (10)$$

and $G = -J''$, O , and $J'' + 1$ for P , Q , and R branches, respectively.

It is seen in Eqs. (8)–(10) that the electron transition moment decreases linearly with the energy of rotational excitation. For the Q -branch transitions this decrease is simply proportional

to $J''(J''+1)$, thus allowing ready experimental verification.

Before comparing the above results with our experiments, it is important to note that the correction factors as computed numerically by Learner^{12,13} are for an electron transition moment of the form

$$R(r) = \text{const } e^{-\beta(r-r_0)} = \text{const } e^{-\beta\Delta r},$$

with $\beta=2.5$ and 5.97 \AA^{-1} . For small changes in internuclear spacing this exponential form can be approximated as

$$R(r) \cong \text{const}(1 - \beta\Delta r + \frac{1}{2}\beta^2\Delta r^2). \quad (11)$$

Except for the presence of a quadratic term, Eq. (11) is equivalent to Eq. (8) and the value of β may be related to that of ρ through Eq. (9). We have found that Learner's numerical results can be reproduced with precision from our Eqs. (8)–(10) when our equations are modified by including such a quadratic term in the derivation. Since Morse-Pekeris wave functions used by Learner are quite different from the harmonic wave functions employed in our derivation, this precise agreement suggests very strongly that the validity of Eqs. (8)–(10) is more general than what the simplifying assumptions, under which these equations are derived, might seem to indicate.

The Franck-Condon factor obtained from Eq. (6) is also in excellent agreement with the results of numerical computation.¹² With the appropriate values for D_i/B_i and α_i , it is seen that our values from Eq. (6) are the same within 0.6% of the results of numerical computation obtained with Morse-Pekeris wave functions. For small changes in internuclear spacing due to moderate rotational excitation ($J'' < 20$), Eq. (6) may be expanded to give

$$q(v'v''J'J'') \cong q_0 \left(1 - (\alpha_1\alpha_2/\alpha)(r_{10} - r_{20}) \right. \\ \left. \times \left\{ [(D_1/B_1)r_{10} - (D_2/B_2)r_{20}] \right. \right. \\ \left. \left. \times J''(J''+1) + 2(D_1/B_1)r_{10}G \right\} \right), \quad (12)$$

where

$$q_0 = (\alpha_1\alpha_2/\alpha^2)^{1/2} \exp[-(\alpha_1\alpha_2/2\alpha)(r_{10} - r_{20})^2].$$

Thus the Franck-Condon factor also varies linearly with rotational excitation. However, the rate of change is proportional to $\alpha_1\alpha_2/\alpha$, and is independent of the assumed form for the electronic transition moment.

We believe the above analysis adequately explains the experimental results presented in Fig. 1. For the Q_1 -branch transitions one calculates

TABLE I. Values of the Franck-Condon factors $q(0, 0, J', J'')$ and the correction factor $T_{J', J''}$ for the P-, Q-, and R-branch transitions of OH. The following spectroscopic data are used: $D_1/B_1=1.20 \times 10^{-4}$, $D_2/B_2=1.01 \times 10^{-4}$, $r_{10}=1.0121 \text{ \AA}$, $r_{20}=0.9706 \text{ \AA}$, $\alpha_1=0.897 \times 10^{18} \text{ cm}^{-2}$, $\alpha_2=1.056 \times 10^{18} \text{ cm}^{-2}$.

J''	$q(0, 0, J', J'')$			$T_{J', J''}$		
	P	Q	R	P	Q	R
1	0.9145	0.9136	0.9118	1.0002	0.9982	0.9943
2	0.9150	0.9132	0.9105	0.9986	0.9947	0.9889
3	0.9154	0.9127	0.9091	0.9953	0.9894	0.9817
4	0.9156	0.9120	0.9074	0.9902	0.9825	0.9728
5	0.9156	0.9111	0.9056	0.9834	0.9738	0.9623
6	0.9155	0.9101	0.9036	0.9749	0.9634	0.9500
7	0.9151	0.9088	0.9013	0.9647	0.9513	0.9362
8	0.9147	0.9074	0.8989	0.9528	0.9377	0.9208
9	0.9140	0.9058	0.8962	0.9393	0.9224	0.9038
10	0.9131	0.9039	0.8933	0.9242	0.9056	0.8853
11	0.9121	0.9109	0.8902	0.9076	0.8873	0.8654
12	0.9109	0.8997	0.8868	0.8894	0.8675	0.8441
13	0.9095	0.8972	0.8832	0.8698	0.8464	0.8215
14	0.9079	0.8946	0.8794	0.8488	0.8239	0.7976
15	0.9061	0.8917	0.8753	0.8265	0.8001	0.7725
16	0.9041	0.8886	0.8709	0.8028	0.7751	0.7463
17	0.9020	0.8852	0.8660	0.7780	0.7491	0.7190
18	0.8996	0.8816	0.8613	0.7520	0.7219	0.6908
19	0.8970	0.8778	0.8561	0.7250	0.6938	0.6617
20	0.8941	0.8737	0.8506	0.6970	0.6648	0.6319
21	0.8911	0.8693	0.8447	0.6681	0.6351	0.6014
22	0.8878	0.8646	0.8386	0.6384	0.6046	0.5703
23	0.8842	0.8597	0.8321	0.6080	0.5736	0.5387
24	0.8805	0.8545	0.8254	0.5770	0.5421	0.5068
25	0.8764	0.8490	0.8182	0.5456	0.5102	0.4747

from Eq. (10) that

$$\Delta r = 1.1 \times 10^{-12} J''(J''+1).$$

With this value for Δr , and correcting for the small change in the Franck-Condon factor, one deduces from the slope in Fig. 1 that $\beta=4 \pm 1 \text{ \AA}^{-1}$ and $\rho=0.79 \pm 0.03 \text{ \AA}^{-1}$. This latter value may be compared directly with the value of about 0.75 \AA^{-1} obtained from an analysis of vibrational band intensities.⁵ In view of the approximate nature of the values for r centroids employed in Ref. 5, we consider the agreement between these two values to be very satisfactory. It follows that the electron transition moment indeed decreases linearly with increasing internuclear spacing, and that changes in the electronic transition probability associated with rotational excitation are a result of lengthening of the internuclear distance due to rotation. It is particularly gratifying that this effect of rotation can be described quantitatively through the use of Eqs. (7)–(10).

For easy reference we have compiled in Table

I values for the Franck-Condon factors $q(00J'J'')$ and the correction factors $T_{J'J''}$ using $\beta = 4 \text{ \AA}^{-1}$ deduced above. These values should supersede the numerical results of Learner.¹² This is because Learner's results were computed with $\beta = 2.5 \text{ \AA}^{-1}$, a value which is too low according to the experimental information presently available, and with an assumed exponential dependence which is inconsistent with the linear relationship observed in the vibrational band intensities.⁵ Although the correction factors for $J'' < 10$ as computed by Learner are approximately the same as those predicted from a linear dependence with the same β value, they become significantly larger for $J'' > 10$ because of the second-order term discussed in Eq. (11).

It was suggested that additional effects of rotational-electronic interaction not accounted for in Eq. (7) may also be operative.¹³ However, this is contrary to the result of explicit calculation.⁵ It

is also contrary to physical intuition since the effect of rotation on the electronic wave functions is, like that of vibration,⁸ largely through changes in the internuclear spacing. Our agreements noted above make it all the more unlikely that this conjecture is valid.

We are in the process of extending the analysis to other bands of the ${}^2\Sigma^+ - {}^2\Pi$ transitions. Preliminary results indicate that the correction factors for rotation-vibration interaction may be altogether different, and the concept of Franck-Condon factor may have to be abandoned for some of these bands.

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