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RELATIVE TRANSITION PROBABILITIES IN
THE A-X SYSTEM OF OD

David R. Crosley
Russell K. Lengel

August 1977

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INTRODUCTION

The OH radical is known or thought to occupy a central role in a wide variety of reaction networks, particularly those important in combustion processes, or upper atmosphere and air pollution chemistry. Absorption or emission intensity measurements on the A-X system are often used to probe such overall processes themselves or to detect OH in laboratory investigations of the rates of individual reactions. Thus it is necessary to have reliable values of transition probabilities for the several bands of this system.

Of particular importance in this regard is the oxidation of any hydrogen-containing compound. This includes the vast majority of all combustion processes, so that OH is a nearly ubiquitous participant in flames, shocks and explosions; it is the most prevalent of the transient, reactive species in many such systems. Consequently, measurements of its concentration and population distribution (temperature) profiles constitute important probes of individual systems and comparisons between systems. These measurements are made by spectroscopic means, facilitated by the existence of the A-X system in the 2800 to 3200 Å region. The bands are intense, observable in emission and absorption, and in a convenient range for study. Several recent experiments, carried out both under low-pressure conditions as well as in flames and ambient air, have demonstrated that OH is an eminently suitable candidate for detection by the sensitive method of laser excited fluorescence diagnostics. (Here, as with conventional spectroscopic detection, technological considerations

are important; the major bands of the A-X system fall serendipitously within the range of frequency doubled radiation from the prime laser dye, Rhodamine 6G.) Correct analysis of any of this spectroscopic data, but especially that involving thermometric measurements on either the A or the X states, require well determined values of transition probabilities. There exist in the literature several carefully executed spectroscopic temperature measurements on OH which are likely in error by many hundreds of degrees¹ due to the use of incorrect transition probabilities for this system.

Recently,¹ a series of new measurements of the relative transition probabilities was made using fluorescence of $A^2\Sigma^+$ OH excited by a tunable laser. These results were then combined with those of previous investigations in order to select the best overall set of normalized probabilities. In that study (referred to below as 1) it was concluded that the transition probabilities could be well characterized by a Morse oscillator model and an electronic transition moment $R_e(r)$ varying linearly with internuclear distance r (c is here a constant):

$$R_e(r) = c(1 - \rho r) \quad (1)$$

Here, the best value of the constant ρ is $0.75 \text{ \AA}^{-1}$, as first suggested by Shuler² in an early paper on the topic. Not only is this linear moment

¹D. R. Crosley and R. K. Lengel, Relative Transition Probabilities and the Electronic Transition Moment in the A-X System of OH," JQSRT 15, 579-591 (1975).

²K. E. Shuler, "Kinetics of OH Radicals from Flame Emission Spectra. I. Vibrational Transition Probabilities, Intensities, and Equilibrium in the $^2\Sigma^+ - ^2\Pi$ Transition," J. Chem. Phys. 18, 1221-1226 (1950).

preferable to one of exponential form,^{3,4} but it also generally reproduces the "good" experimental data^{*} to within experimental error.

The results reported here are an extension of these measurements and the application of a linear moment model to the OD molecule. Although OD clearly does not occupy as prominent a position as OH insofar as system diagnostics are concerned, an increasing number of experiments on the deuterated species is being carried out in conjunction with, and for comparison with, those on OH. In fact, our interest in the problem arose, as was the case for OH, due to a need for such transition probabilities for analysis of data in our $A^2\Sigma^+$ state energy transfer studies,⁵ which we are currently extending to OD. Most importantly, from the standpoint of the use of these transition probabilities for diagnostic purposes, these current results on OD form further confirmation of the correct choice of the electronic transition moment for the isotopic pair, strengthening the evidence for the previous results¹ for OH.

Within the framework of the Born-Oppenheimer approximation, one of course expects that, even for an isotopic pair differing as much as OH and OD, the electronic transition moment should be the same for both

³R. C. M. Learner, "The Influence of Vibration-Rotation Interaction on Intensities in the Electronic Spectra of Diatomic Molecules. I. The Hydroxyl Radical," Proc. Roy. Soc. A269, 311-326 (1962).

⁴J. Anketell and R. C. M. Learner, "Vibration Rotation Interaction in OH and the Transition Moment," Proc. Roy. Soc. A301, 355-361 (1967).

⁵R. K. Lengel and D. R. Crosley, "Rotational Dependence of Vibrational Relaxation in $A^2\Sigma^+$ OH," Chem. Phys. Lett. 32, 261-264 (1975).

^{*}*Part of the confusion and controversy surrounding the transition probabilities in OH has been due to a lack of recognition that not all of the experimental data is of uniform quality. In I, the data available were examined in some detail in this regard to select reliable values for comparison with the models.*

species. Indeed, as seen below, this is the case; differences in the actual transition probabilities are due to the mass dependencies of the nuclear wavefunctions. Consequently the comparisons among experiments and models on each species are properly inseparable for the purpose of assessing the best overall set of transition probabilities; the success of Equation (1) for OH is probably the best reason for using it for OD. However, although the data are much more sparse in the case of the deuterated molecule, the assessments made here will consider only those measurements directly.

The treatment follows essentially that in I. Although the rotational dependence of the transition moments is now well established for both OH and OD from lifetime measurements, the variation for low rotational quantum number is well within usual error bars on *intensity* measurements. Therefore, except for a section devoted to this topic, rotation will be neglected in comparing experimental results, and calculations will be made on rotationless molecules. Finally, we conclude the paper with a section updating the OH transition probability study to the present time.

We collect here definitions of quantities useful in the following discussion. The intensity $I_{v',v''}$ of the light ($\text{erg cm}^{-3}\text{sec}^{-1}$) emitted in the (v',v'') band by $N_{v'}$ molecules cm^{-3} in the v' level of the excited state is:

$$I_{v',v''} = N_{v'} h\nu_{v',v''} A_{v',v''} . \quad (2)$$

The Einstein emission coefficient $A_{v',v''}$ (sec^{-1}) is related, through the vibrational transition probability $p_{v',v''}$, to $R_e(r)$ and the vibrational wavefunctions $\psi_{v'}$ and $\psi_{v''}$:

$$A_{v',v''} = \frac{64\pi^4}{3hc^3} \nu_{v',v''}^3 p_{v',v''} ; \quad (3)$$

$$p_{v',v''} = \left| \int \psi_{v'} R_e(r) \psi_{v''} dr \right|^2 .$$

Other associated quantities are the oscillator strength* $f_{v',v''}$ and lifetime $\tau_{v'}$ of the v' level:

$$f_{v',v''} = 1.5 \times 10^{-16} \frac{c^2}{\nu_{v',v''}^2} A_{v',v''} \frac{g''}{g'} ; \quad (4)$$

$$\tau_{v'} = A_{v'}^{-1} \equiv \left(\sum_{v''} A_{v',v''} \right)^{-1} = \left(\sum_{v''} \nu_{v',v''}^3 p_{v',v''} \right)^{-1} .$$

Here, the g 's are the level degeneracies, and h and c have their usual meaning throughout these equations.

We reduce calculated $p_{v',v''}$ to $A_{v',v''}$ using for the $\nu_{v',v''}^3$ factor in Equation (3) the reciprocals of the band head wavelengths.** These are taken (when available) from the tabulation in Rosen⁶ or calculated (when necessary) using the vibrational constants⁷ for the A and X states. Though the band head wavelength does not represent even an average for

* A dimensionless quantity; the numerical factor refers to c in cm sec^{-1} , and A and ν in sec^{-1} units.

** Rounded to the nearest Å; see Table 3.

⁶ B. Rosen (Editor), Données spectroscopiques relatives aux molécules diatomiques (Pergamon, Oxford), 1970.

⁷ J. A. Coxon, "The $A^2\Sigma^+ - X^2\Pi$ System of OD: Determination of Molecular Constants by the Direct Two-State Fit Approach," *J. Mol. Spectrosc.* **58**, 1-38 (1975).

the band, its use introduces negligible* error for the present purposes of assembling and assessing a set of consistent Einstein transition probabilities. For measurements of high accuracy and over a large range of rotational levels, as for a rotationally hot sample, intensities should be reduced to populations through Equations (2) and (3) using the vibrational transition probabilities $p_{v',v''}$ (tabulated below) which represent the vibrational contribution over the entire band. These should then be combined with a correction for the rotational dependence of the transition probability (see below); into this correction can conveniently be woven the actual v^3 dependency for each line.

In the case of a linear transition moment as in Equation (1), one may directly use the Franck-Condon factor

$$q_{v',v''} = \left| \int \psi_{v'} \psi_{v''} dr \right|^2$$

and the $\bar{r}$ centroid

$$\bar{r}_{v',v''} = \int \psi_{v'} r \psi_{v''} dr / \int \psi_{v'} \psi_{v''} dr$$

to represent the vibrational transition probability as

$$p_{v',v''} = c q_{v',v''} (1 - \bar{r}_{v',v''})^2,$$

where c is here some constant.

* E.g., conversion using the Q_3 (Dieke and Crosswhite⁸ notation) line frequency yields shifts in the $A_{v',v''}$ of $\lesssim 0.5$ percent.

⁸ G. H. Dieke and H. M. Crosswhite, "The Ultraviolet Bands of OH," Bumblebee Report No. 87, Johns Hopkins University, 1948, republished in JQSRT 2, 97-199 (1962).

EXPERIMENTAL DETAILS AND RESULTS

The experimental method (see Figure 1) is identical to that used in I for the OH measurements, except for the obvious substitution of D_2O for H_2O as the atom source. Briefly, the OD is generated by the reaction $D+NO_2$ in a flow system with $\sim 3\ell \text{ sec}^{-1}$ pumping speed and at total pressures of $\sim 15 \text{ mTorr}$ (of D_2O and NO_2). A Chromatix system, comprised of a frequency doubled rhodamine -6G dye laser pumped by a doubled Nd^{+3} :YAG laser, is used to irradiate the OD, exciting individual v', J' levels of the $A^2\Sigma^+$ state. Emission at right angles to the exciting beam is focused into a 0.35 m spectrometer operated in second order* and with slits sufficiently narrow to permit identification of most of the individual rotational branches of the fluorescence. The photomultiplier output is fed through a pulse shaper and amplifier to one channel of a dual channel boxcar integrator. Input to the other channel is provided by a second monochromator monitoring total fluorescence. The ratio of the two channels then forms the output, yielding continuous normalization throughout a scan; such normalization is necessitated by drift** in both the OH concentration and the laser frequency. The output of a scan is electronically integrated; both the intensity versus wavelength and the integrated intensity versus wavelength are recorded. Figure 2 shows scan of the (1,1) and (1,0) band. The fluorescence from the initially

*Except for the search for the (2,4) band, made in first order.

**The normalization channel is also read out directly; those occasional runs having a single-channel drift greater than 10 percent over the 15 min scan time are discarded.

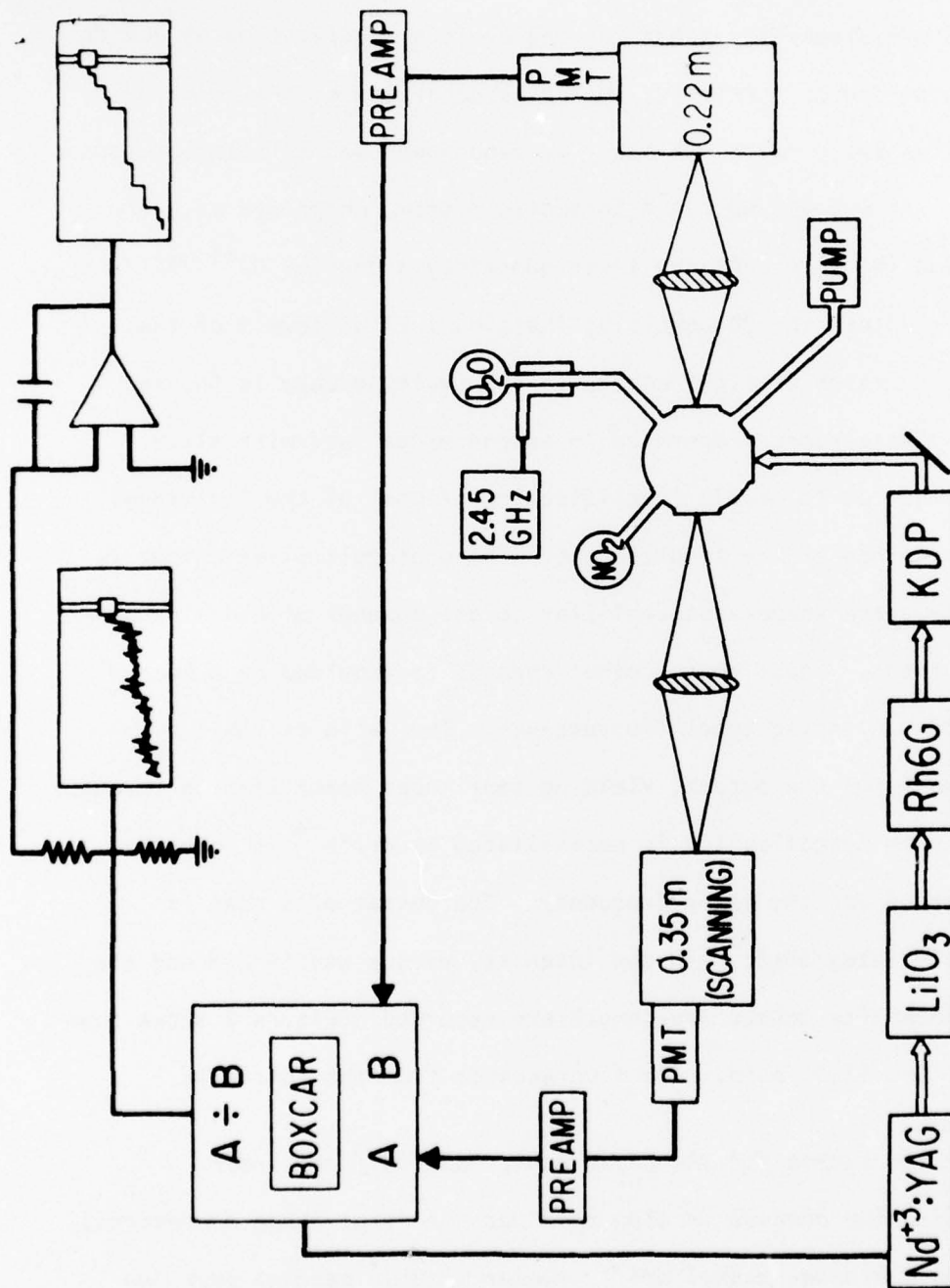


Figure 1. Experimental Setup. The microwave discharge in D_2O produces D atoms. Both the $\text{Nd}^{+3}:\text{YAG}$ and rhodamine-6G laser beams are doubled to ultimately provide tunable (pulsed) ultraviolet radiation. The smaller monochromator is operated at fixed wavelength to provide normalization and to act as a separate drift monitor. As the wavelength is scanned, both the spectrum and its integral are recorded.

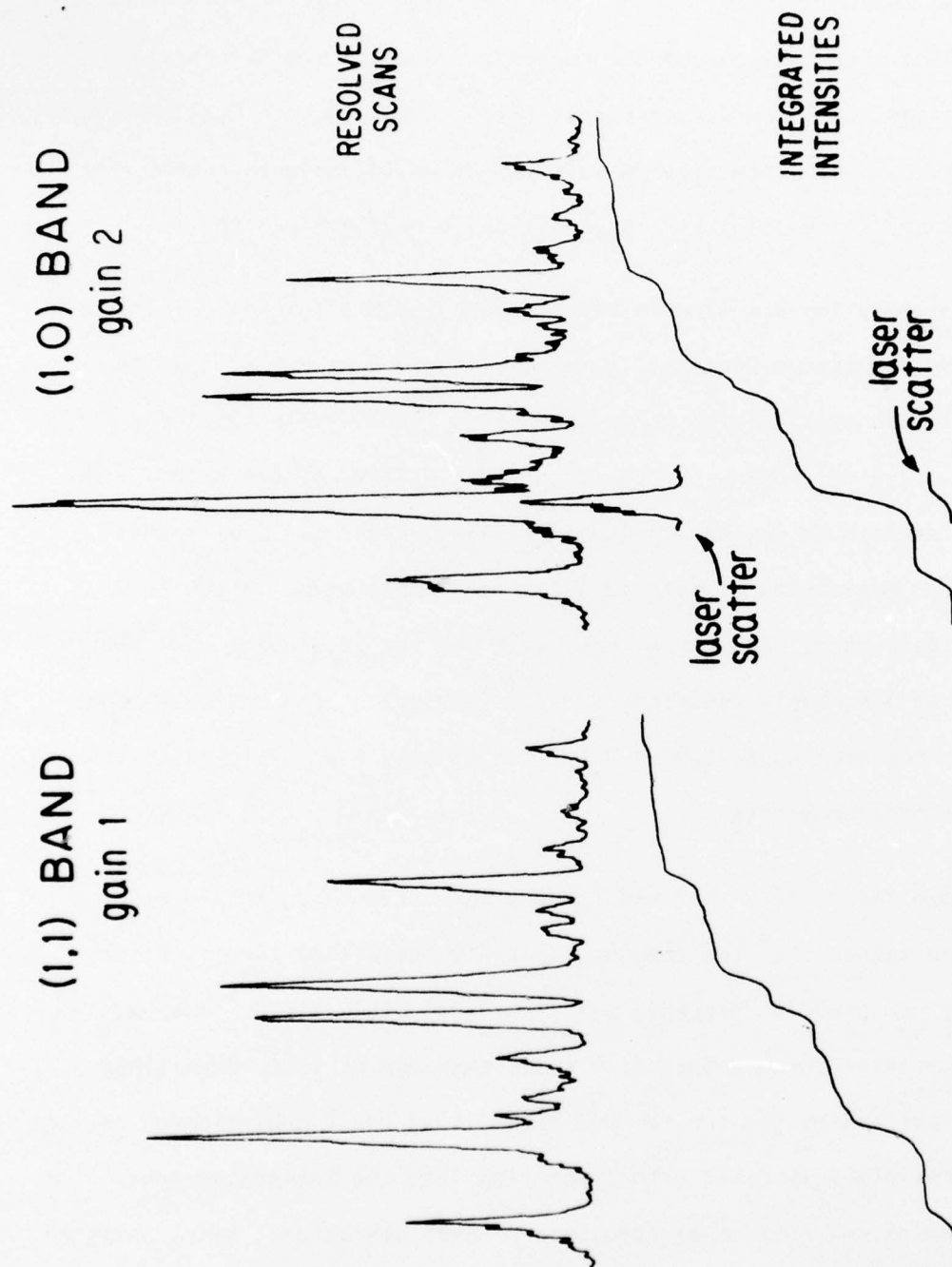


Figure 2. Experimental Results. These scans are made with slightly smaller slits (40 μ) than used for the measurements. The $N' = 4$, $J' = 4 \frac{1}{2}$ level of $v' = 1$ is pumped in the (1,0) band, yielding six rotational branches in fluorescence back to $v'' = 0$ and 1. Smaller lines are due to rotational energy transfer within $v' = 1$. These scans have a time constant of 1 s and scan time of ~ 7 min per band, and are uncorrected for spectrometer/photomultiplier efficiency. The laser scatter trace is obtained with the NO_2 flow shut off.

excited $F_1(4)$ level (i.e., $N' = 4$, $J' = N' + 1/2$) consists of six main lines. The remaining lines are due to rotational energy transfer caused by collisions with the D_2O and NO_2 present; since the vibrational bands are well separated in this experiment, this has no effect on the measured relative transition probabilities (within the valid assumption that the N' -dependence of the transition probability is negligible here).

In all runs the Q_14 line is used to pump the $F_1(4)$ level. This is because the absorption spectrum is relatively clean near Q_14 , that is, there is little overlap with other absorption lines within our laser linewidth of $\sim 5 \text{ cm}^{-1}$ FWHM. Further, the $N'' = 4$ level of the ground state is at the maximum of the excitation efficiency* under our experimental conditions. Excitation is carried out through absorption in the (0,0), (1,0) or (2,1) band. As was the case with OH, the (2,3) band does not appear to be previously reported; our low resolution (250- μ slits) scans here place the overlapped $Q_24' + P_15$ lines at 3435 Å as anticipated from the vibrational constants.

For excitation of $v' = 0$ and 1, data was taken using the integrated intensities rather than the resolved scans (subtracting laser scatter, separately measured, if present; see Figure 2). This yields somewhat better uncertainties on a per datum basis than use of individual lines. In 1 a comparison of the two methods established their equivalence, in the face of possible systematic errors entering into the integrated runs. For OD, the compressed rotational structure of each vibrational band, compared

* *Relative population times rotational line strength.*

to OH, leads to less concern with overlap problems, so such a comparison was not repeated for OD. Excitation of $v' = 2$ is carried out beginning from the $v'' = 1$ state; the lower population there leads to weaker fluorescence intensities and severe problems with laser scatter in determining the A_{21}/A_{22} ratio. Consequently this ratio was determined via peak heights of individual rotational branches in resolved scans (R_13 , the $Q_24' + P_15$ blend, and P_25' ; see Table 1). The other ratios involving $v' = 2$ are measured using integrated intensities.

The detection system calibration, using a GE DXW tungsten iodide lamp, was described in I. These measurements have a precision of 2 percent but it is difficult to assess their accuracy.

The results of these emission branching ratio measurements are presented in Table I. The uncertainties quoted are standard deviations taken from averaging the data from all the runs, except for the A_{12}/A_{11} ratio. Here, the statistical error bars calculated in this way are "too good," i.e., much better than we feel is warranted from the raw data. The quoted uncertainty is a more realistic assessment of the data signal/noise. The (2,4) band was searched for but not found within the upper limit quoted. Possible systematic errors (in particular, the spectrometer/detector response calibration) are not included in the uncertainties listed.

In a separate and different type of measurement, the ratio A_{10}/A_{00} was probed using fluorescence as a monitor of absorption strength. Again, the Q_14 line was pumped in each of the (1,0) and (0,0) bands. The

TABLE 1. EXPERIMENTAL RESULTS

Ratio	Mode ^a	Slits (μ)	n ^b	Result
A_{11}/A_{10}	I	50	12	1.65 ± 0.04
A_{12}/A_{11}	I	50	10	0.046 ± 0.004^c
A_{21}/A_{22}	R: $R_1 3$	250	8	1.58
	R: $Q_2 4' + P_1 5$	250	8	1.59
	R: $P_2 5'$	250	8	1.60
	average	-	24	1.59 ± 0.08
A_{20}/A_{22}	I	250	7	0.21 ± 0.01
A_{23}/A_{22}	I	250	5	0.089 ± 0.006
A_{24}/A_{22}	-	250	-	≤ 0.005
A_{01}/A_{00}	I	50	8	0.019 ± 0.001

^aI = integrated intensities; R = rotationally resolved, for which observed lines are listed in Dieke and Crosswhite⁸ notation.

^bNumber of runs.

^cEstimated error; see text.

incident laser power was monitored via the ultraviolet radiation reflected from the front surface of a Corning 7-54 filter, through another 7-54 filter and onto a sodium salicylate plate in front of a photodiode. The appropriate ratios from Table 1 are used to convert observed fluorescence into total emission from each of the $v' = 0$ and 1 levels, which is then divided by the incident laser intensity at the pump wavelength. The result is that $A_{10}/A_{00} = 0.25$ with a statistical error (four runs) of 0.05. The only assumption here is that the reflectivity of the reflecting 7-54 filter, and the efficiency of the sodium salicylate, are independent of wavelength. There is a small amount of overlap of $Q_1 4$ with $R_2 4$ and $P_1 2$ in (1,0) and of $Q_1 4$ with $R_2 4$ in (0,0), within the laser bandpass. Such overlap was not accounted for in the analysis; the presence of such overlap would tend to lower the measured ratio below the true value.* Further, as the laser is tuned from the (1,0) to the (0,0) absorption, the beam walks slightly, causing possibly a different deflection onto the photodiode; this effect, if present, cannot be directly gauged, and we must assume we correctly measure the incident laser power. We do not have much confidence in these assumptions and estimate an overall uncertainty of ~35 percent. The resulting value, 0.25 ± 0.09 , overlaps only at the limit of the error bars with that of Rouse and Engleman⁹ for the same ratio, which we recommend as being better determined (see below).

* Taking into account the line separations, laser bandwidth, and excitation efficiencies.

⁹P. E. Rouse and R. Engleman, Jr., "Oscillator Strengths from Line Absorption in a High Temperature Furnace. I. The (0,0) and (1,0) Bands of the $A^2\Sigma^+ - X^2\Pi$ Transition in OH and OD," JQSRT 13, 1503-1521 (1973).

DISCUSSION

1. The Choice of a Model

In I, an overall set of transition probabilities for OH was calculated using a linear transition moment and Morse oscillator wavefunctions, following the method originally applied by Shuler² to the data of Dieke and Crosswhite.¹⁰ The computed transition probabilities depend to some degree on the model chosen (both the analytical form of the wavefunctions as well as the spectral constants necessary to specify the actual molecular states involved). Thus it is important to delineate the method and parameters used.

For the calculations on OD, we again use a Morse oscillator model, taking the spectral constants from Coxon's recent determination⁷ using a direct two-state fit. Here we insert constants, so obtained from spectral line positions and the numerical diagonalization of Hamiltonian matrices, into a model of the molecular motion for the purpose of intensity calculations. To do so, one must ascertain that the constants do have the proper mechanical significance pertinent to the model chosen. Coxon addresses this point (which is discussed at more length by Zare *et al.*¹¹); his constants may properly be adapted to a Morse model. A more sophisticated treatment would use the RKR curves which Coxon calculates. Under the assumption that the transition moment is linear, Coxon's array of Franck-Condon factors and r-centroids (determined via these RKR curves) may be directly used for calculating transition probabilities.

¹⁰G. H. Dieke and H. M. Crosswhite, Quarterly Report NOrd-8036, JHB-3, Problem A(1 Oct - 31 Dec 49), as quoted in Reference 2.

¹¹R. N. Zare, A. L. Schmeltekopf, W. J. Harrop, and D. L. Albritton, "A Direct Approach for the Reduction of Diatomic Spectra to Molecular Constants for the Construction of RKR Potentials," J. Mol. Spectrosc. 46, 37-66 (1973).

Results using both Morse wavefunctions and Coxon's values have been obtained. The differences, at most about 1 percent, we consider insignificant in that either set is equally consistent with the experimental data available. With regard to the Morse oscillator fits, we have explored the sensitivity of the calculated transition probabilities to the input parameters, settling on the choice given in the Appendix. When considering the effectiveness of the model chosen (that is, a Morse, RKR or *ab initio* potential) to represent the actual OD molecule, the purposes of this study must be borne in mind. These are to provide a consistent, reliable set of $A_{v',v''}$ values useful to an experimentalist making measurements, and to check the idea of a linear dependence of the electronic transition moment on internuclear distance. Once the latter has been established, the form of the model loses physical importance here, becoming simply a mathematical prescription for combining the individually measured branching ratios to produce a smoothed set of transition probabilities. In this spirit, the use of the model collects all of the experimental data points so that an individual calculated $A_{v',v''}$ includes, as it were, a fit to data on other measured $A_{v',v''}$. Clearly one aspect of such input is the evidence for OD gained by considering the OH results, and *vice versa*, a link which can be established only after incorporation into a specific model.

2. Fits of the Present Experimental Data

The six independent transition probabilities determined as branching ratios and listed in Table I, can be used to calculate a value of ρ [Equation (1)] using the Franck-Condon factors and r-centroids from the

Morse model (see Appendix). The results for the ρ values so obtained are given in Table 2, where the quoted error bars come strictly from a propagation of error treatment of the uncertainties assigned the experimental results. An unweighted average of these results, excluding the A_{10}/A_{00} determination, yields $\rho = (0.752 \pm 0.008) \text{ \AA}^{-1}$. An examination of the ratios predicted using the three error-bar-limit values of $\rho = 0.74, 0.75, \text{ and } 0.76 \text{ \AA}^{-1}$ (see Table 2), together with evidence from other investigations described below, leads us to conclude that here, as with OH, the value $\rho = 0.75 \text{ \AA}^{-1}$ used in a Morse model forms the best overall set of transition probabilities. (For comparison, reduction of the experimental ratios with Coxon's $q_{v_1 v_2}$ and $\bar{r}_{v_1 v_2}$ yields an average $\rho = (0.750 \pm 0.009) \text{ \AA}^{-1}$.)

3. A Comparison of the Calculated Sets of Transition Probabilities

There exists no experimental investigation of intensities in OD providing the same scope of transition probabilities which is available for OH. Consequently, a comparison between experiments and models must here be made on the basis of the present work coupled with a few oscillator strength and lifetime ratios.

The overall set of $p_{v_1 v_2}$ and $A_{v_1 v_2}$ values, calculated with the Morse model and a linear moment having $\rho = 0.750 \text{ \AA}^{-1}$, and normalized to the intensity of the (0,0) band, is given in Table 3. A linear moment calculation is not applicable to the (2,4) band. Here, $\rho \approx (\bar{r}_{24})^{-1}$ so

TABLE 2. FIT TO PRESENT EXPERIMENTS

Ratio	ρ	Predicted Ratio			Experiment
		$\rho = 0.74$	$\rho = 0.75$	$\rho = 0.76$	
A_{11}/A_{10}	0.767 ± 0.005	1.80	1.73	1.65	1.65
A_{12}/A_{11}	0.750 ± 0.005	0.058	0.050	0.042	0.046
A_{21}/A_{22}	0.745 ± 0.011	1.61	1.68	1.77	1.59
A_{20}/A_{22}	0.751 ± 0.006	0.21	0.22	0.24	0.21
A_{23}/A_{22}	0.746 ± 0.003	0.107	0.089	0.070	0.089
A_{01}/A_{00}	0.751 ± 0.004	0.024	0.022	0.019	0.019
A_{10}/A_{00}	0.64 ± 0.19	0.33	0.34	0.35	0.25

TABLE 3. TRANSITION PROBABILITIES NORMALIZED TO
THE (0,0) BAND VALUE = 1000

Band (v', v'')	λ^a (Å)	$P_{v',v''}$ (Linear Moment)	$A_{v',v''}$ (Linear Moment)	$A_{v',v''}^b$ (Exponential Moment)
0,0	3068	1000	1000	1000
0,1	3332	28	22	34
1,0	2876	281	342	305
1,1	3109	615	591	640
1,2	3372	39	30	57
2,0	2712	47	68	61
2,1	2920	443	513	474
2,2	3153	331	305	363
2,3	3418 ^c	38	27	69
2,4	3719	-	-	-
3,0	2571 ^c	6	11	10
3,1	2759	127	175	162
3,2	2968 ^c	488	539	517
3,3	3302 ^c	146	128	157 ^d
3,4	3465	27	19	-

^aBand head (see text).

^bFrom Learner, Reference 3.

^cCalculated. Other bands have been observed previously.

^dTaking Learner's $p_{33} = 0.196$. (See text.)

that an $R_e(r)$ near zero would be predicted; rather the transition moment is probably decreasing more slowly, and asymptotically toward zero, as indicated by the *ab initio* calculation of Henneker and Popkie¹² for OH.

Also listed in Table 3 are the $A_{v',v''}$ obtained from the $p_{v',v''}$ calculated by Learner³ using Morse-Pekeris wavefunctions and a transition moment of exponential form:

$$R_e(r) = c \exp(-\alpha r), \quad (5)$$

with $\alpha = 2.5 \text{ \AA}^{-1}$. Anketell and Learner⁴ later preferred a faster fall-off of the transition moment ($\alpha = 5.97 \text{ \AA}^{-1}$). However, the lower α value yields a decidedly preferable fit to the better OH data, insofar as the exponential moment is applicable; a discussion of the choices here is presented in I. Consequently we consider the earlier calculations^{*} for comparison of the linear and exponential moment models for OD. The differences in the resulting $A_{v',v''}$ are not large, at most some 20 percent for intense bands, however differences in certain ratios important for data analysis purposes are larger (see below).

Compared with OH, the experimental data available for OD is relatively sparse. We choose to utilize, as criteria for assessing the overall sets of $A_{v',v''}$, experimental results in the form of ratios rather than absolute

¹²W. H. Henneker and H. E. Popkie, "Theoretical Electronic Transition Probabilities in Diatomic Molecules. I. Hydrides," J. Chem. Phys. 54, 1763-1778 (1971).

^{*}There is an apparent typographical error in the entry for p_{33} in Learner's Table 6; we here adopt the value 0.196.

values, in order to minimize the influence of systematic error. In addition to the present experimental results, we also consider oscillator strength measurements and recent lifetime studies. All such independently determined ratios of transition probabilities (or quantities derived therefrom) are collected in Tables 4 and 5.

Rouse and Engleman⁹ used a furnace at 1100°C to make photographic absorption strength measurements from which they determine absolute oscillator strengths. OD concentrations are determined by chemical equilibrium calculations. Although they assign an uncertainty of ~20 percent to their absolute f-values, the ratio f_{10}/f_{00} depends on no equilibrium assumptions and should be more accurate than this. Their measurements also permit an estimate of f_{11} and an upper limit on f_{21} . The $A_{v,v'}$ ratios derived from these oscillator strength ratios [see Equation (4)] are listed in Table 4.

Absolute lifetime measurements on the $A^2\Sigma^+$ state of OD do not suffer from as much dispute as those on OH, though there is some disagreement. We here consider only those investigations providing lifetime ratios for different vibrational levels obtained from the same experiment. Earlier work by Becker and Haaks¹³ using decay of fluorescence following a terminated radio-frequency discharge in D₂O vapor yields lifetimes averaged over rotational levels; extrapolations to low N' furnish the ratio $\tau_1/\tau_0 = 1.04 \pm 0.10$. A similar technique was combined with dispersion to provide lifetimes for individual N' levels, by Wilcox, Anderson and

¹³K. H. Becker and D. Haaks, "Measurement of the Natural Lifetimes and Quenching Rate Constants of OH ($^2\Sigma$, v = 0,1) and OD ($^2\Sigma$, v = 0,1) Radicals," Z. Naturforsch. 28a, 249-256 (1973).

TABLE 4. RATIOS OF EINSTEIN TRANSITION PROBABILITIES

Ratio	Present Experiment	Rouse & Engleman	Linear Moment	Exponential Moment
A_{11}/A_{10}	1.65 ± 0.04	1.87 ± 0.31	1.73	2.10
A_{12}/A_{11}	0.046 ± 0.004	-	0.051	0.089
A_{01}/A_{00}	0.019 ± 0.001	-	0.022	0.034
A_{10}/A_{00}	0.25 ± 0.09	0.33 ± 0.09^a	0.34	0.30
A_{21}/A_{00}	-	< 0.72	0.51	0.47
A_{11}/A_{00}	-	0.61 ± 0.10	0.59	0.64
A_{20}/A_{22}	0.21 ± 0.01	-	0.22	0.17
A_{21}/A_{22}	1.58 ± 0.08	-	1.68	1.31
A_{23}/A_{22}	0.089 ± 0.006	-	0.089	0.190

^aError in $\sqrt{2}$ times the 20 percent estimated by the authors for absolute f-values, and is probably too high (see text).

TABLE 5. LIFETIME RATIOS

	τ_1/τ_0	τ_2/τ_0
GERMAN	1.03 ± 0.02	1.07 ± 0.02
BECKER AND HAAKS	1.04 ± 0.10	-
WILCOX <i>et al.</i>	~ 0.96	-
LINEAR MOMENT	1.07	1.13
EXPONENTIAL MOMENT	1.03	1.07

Preacher.¹⁴ From Figure 4 and Table I of their paper we estimate a ratio τ_1/τ_0 , for low N' , slightly less than unity (~ 0.96). German¹⁵ has recently excited individual v', J' levels with a pulsed laser. The results for levels of low N' yield the ratios $\tau_1/\tau_0 = 1.03 \pm 0.02$ and $\tau_2/\tau_0 = 1.07 \pm 0.02$. (These error bars are obtained by combining, as uncorrelated, the 1- σ level errors obtained from German's quoted uncertainties on the absolute lifetimes.) In OH, all N' levels in $v' = 2$ exhibited predissociation and consequent lifetime shortening, rendering the τ_2/τ_0 ratio useless for comparison purposes. Because of the smaller vibrational spacing in OD, however, levels of low N' in $v' = 2$ are unaffected by the predissociation.

An examination of Tables 4 and 5 leads us to the conclusion that here, as with OH, a linear electronic transition moment better describes transition probabilities within the A-X system, compared to a moment of exponential form. The Rouse and Engleman oscillator strength ratios are consistent with either model, while German's lifetime ratios are better described by the exponential moment. We find this last result puzzling. For both OH and OD, the exponential model predicts a lifetime lengthening (for unpredissociated levels) of $\sim 3 \frac{1}{2}$ percent per vibrational level, and the linear model predicts lengthening at ~ 8 percent per level. German's result for OH agrees with the linear moment value at the limit of his error bars (see below) but those results for OD are in better accord with the exponential moment predictions. Since they are carried out on the same apparatus, systematic errors cannot be blamed.

¹⁴D. Wilcox, R. Anderson, and J. Preacher, "Rotational and Predissociation Lifetimes of the $A^2\Sigma^+$ State of OD," J. Opt. Soc. Am. 65, 1368-1370 (1975).

¹⁵K. R. German, "Radiative and Predissociative Lifetimes of the $v' = 0, 1$ and 2 Levels of the $A^2\Sigma^+$ State of OH and OD," J. Chem. Phys. 63, 5252-5255 (1975).

Nonetheless we feel that the current experimental intensity ratios can be used to conclude that the set of $A_{v',v''}$ values from the linear moment model is decidedly preferable, even with the disaccord with German's lifetimes. This is particularly important for the ratios of the more intense bands (A_{11}/A_{10} and A_{21}/A_{22}) which are of direct importance in the analysis of energy transfer or diagnostic experiments. Combined with a similar weight of evidence for the linear moment model in the case of the OH species, we feel confident in recommending the results of these calculations for the analysis of experiments on OD involving intensity measurements.

The current experimental results may be examined within the context of the overall set of transition probabilities. In particular, the ratio measured for A_{11}/A_{10} (1.65 ± 0.04) appears "too low," overlapping only at the 2- σ level with the recommended value of 1.73. A similar discrepancy for this same ratio (an experimental value of 1.58 ± 0.08 versus a model prediction of 1.75) was found for OH in I. This immediately suggests a systematic error concerned with the calibration of the spectrometer and photomultiplier. However, because of the disagreement in the OH ratio, the calibrations were carefully checked at the time of that study. Further, a miscalibration causing A_{11}/A_{10} to appear too low would make A_{20}/A_{22} and A_{21}/A_{22} too *high* (in opposition to what was stated in I). These latter ratios for OH and OD agree with the model to within their error bars, except for the A_{21}/A_{22} ratio for OD which if anything is slightly too low. The experimental traces for the calibration runs are smooth, showing no spikes or other odd features which might suggest

pathological behavior of either the standards lamp or detection system over a limited wavelength range. The correction^{*} from our measurements on the $N' = 4$ level to the rotationless molecule (see below) is quite different for the (1,0) band (4×10^{-4}) than the (1,1) band (1.16×10^{-2}). This does raise the ratio from 1.65 to 1.67 but it remains low.^{**} We thus are again unable to account for the discrepancy and again recommend a preferred a value of 1.7 for this ratio.

4. The Rotational Dependence of the Transition Probabilities in the (0,0) Band

The appreciable centrifugal stretching and vibration-rotation interaction in OH and OD, together with a transition moment dependence on internuclear distance, causes the transition probability to vary noticeably with rotational level. For a given vibrational band and values of the angular momentum quantum number^{***} J less than about 20 one may adequately express this dependence in a form linear in $J(J+1)$:

$$P_{v'J'}^{v''J''} = P_{v'J'} \left[1 - \beta_{v'J'}^{\Delta J} J(J+1) \right]$$

^{*} Not included in any of our quoted results.

^{**} Such corrections applied to other ratios are much less than the experimental error.

^{***} For these purposes, values of N and J , which differ by $\pm 1/2$, may be considered indistinguishable. In the face of some evidence both pro and con, we shall assume that F_1 and F_2 levels with the same value of N have the same transition probabilities. This equality is consistent with the models.

where $p_{v',v''}$ is the vibrational transition probability, for the rotationless molecule, as discussed earlier. $\beta_{v',v''}^{\Delta J}$ is a constant for a given branch P, Q or R. Calculations on the (0,0) band show that $\beta^R > \beta^Q > \beta^P$ (as expected from a simple physical picture); the differences are each about 3 percent and β^Q quite adequately represents the average. Since a 3 percent difference in β means about 0.6 percent difference in $p_{v',J'}^{v'',J''}$ at $J = 20$, we will ignore the variation with branch and rewrite

$$p_{v',J'}^{v'',J''} = p_{v',v''} \left[1 - \beta_{v',v''} J(J+1) \right] \quad (6)$$

where J represents *either* the excited or ground state total angular momentum quantum number.

In this section we focus our attention on the (0,0) band for which there exist some experimental results; also it is this most intense band which is often used for rotational temperature determinations.

Using Morse-Pekeris wavefunctions we have calculated $p_{v',J'}^{v'',J''}$ for the (0,0) band and for J values up to 20. Within the experimental errors involved in any intensity measurements, the results for the (more intense) Q-branches adequately represent the full transition probabilities associated with a given J' or J'' , and those actually compared here.* The calculations are performed using both a linear moment ($\rho = 0.752$), and exponential moments, repeating the calculations of Learner [$\alpha = 2.67$ in Equation (7)] and Anketell and Learner [$\alpha = 5.97$ in Equation (5)]. The results are then fitted to Equation (6) to extract a value of β ; these are collected

* We here ignore the v^3 dependence in comparing our results to experiment.

in Table 6. A β value (labeled RKR) obtained directly (see below) from calculations using Coxon's J-dependent Franck-Condon factors and $\bar{r}$ -centroids together with a linear moment ($\rho = 0.750 \text{ \AA}^{-1}$) is also included. Clearly the results from all the calculations except the steeper exponential are indistinguishable.

There are three existing studies of the rotational level dependence of $v' = 0$ lifetimes in OD. In two of these^{14,16} the variation with N' is much too irregular (and too large) to be fitted to a simple form such as Equation (6). The variation found in these two investigations is well outside the error bars quoted and in one case¹⁶ its reproducibility is specifically mentioned. The model, on the other hand, demands a much smoother variation, suggesting caution when using these relative lifetimes;^{**} however any discussion of possible errors would be entirely speculative.

German's¹⁷ lifetime measurements using pulsed laser excitation do provide a reasonably smooth variation of τ with N' ; the lifetime increases about 3 percent between $N' = 2$ and $N' = 9$, more than his (1- σ level) 1 percent error bars. The experimental value for β given in Table 6 is

¹⁶B. G. Elmergreen and W. H. Smith, "Direct Measurement of the Lifetimes and Predissociation Probabilities for Rotational Levels of the OH and OD $A^2\Sigma^+$ States," *Astrophys. J.* **178**, 557-564 (1972).

¹⁷K. R. German, "Direct Measurement of the Radiative Lifetimes of the $A^2\Sigma^+$ ($v=0$) States of OH and OD," *J. Chem. Phys.* **62**, 2584-2587 (1975).

*Lifetime results are typically quoted as a function of N' , not J' . Since, for our purposes, the two are indistinguishable, we shall use N' here in accord with the lifetime papers.

**The models are incapable of directly addressing the questions of absolute lifetimes or predissociation.

TABLE 6. VALUES OF B FOR THE 0,0 BAND

<u>Model/Moment</u>	<u>$B \times 10^4$</u>
Morse-Pekeris, $1 - 0.752r$	3.9
Morse-Pekeris, exp $(-2.67r)$	3.4
Morse-Pekeris, exp $(-5.97r)$	6.6
RKR, $1 - 0.75r$	4.0
Experiment (Lifetimes)	3.6

obtained from a fit of these^{*} lifetimes to Equation (6). Cognizance of the errors implicit in the experiment and thus the fit renders the good agreement between model and experiment fortuitous. It does, however, provide some confidence in the linear form for the representation of the rotational dependence. As discussed in I for OH, the β values obtained here are useful for applying corrections to rotational temperature determinations using the (0,0) band of OD; however caution regarding the quantitative limitations of the procedure are again advised.

5. The Rotational Dependence of the Transition Probability in Other Bands

As noted above, the centrifugal stretching in this light molecule is responsible for the rotational dependence of the transition probabilities (the centrifugal distortion coefficient D_e is 5×10^{-5} of the rotational constant B_e in OD). This increase in the effective average internuclear distance as J increases has two consequences bearing on the transition probability: the transition moment decreases, and the overlap between the vibrational wavefunction is also altered (often, but not always, decreasing).

An estimate of the anticipated magnitude of the effect may be obtained following the approach of German¹⁷ and using our value $\rho = 0.75 \text{ \AA}^{-1}$. This considers the change in $R_e(r)$ only and neglects any variation in the

^{*}*Inclusion of German's lifetimes for $N' = 0$ and $N' = 1$ yields a meaningless least squares fit to Equation (6) and they have been excluded. However, they do overlap the resulting straight line when their error bars are included.*

overlap, and hence should be more apt for the (0,0) band than for others. The effective internuclear distance r_J for a molecule in the J th rotational level is

$$r_J = r_e \left[1 - \frac{D_e}{B_e} J(J+1) \right]^{-1/2}.$$

Presuming that the r -centroid of the transition varies with J in the same fashion, this may be inserted into Equation (1). After expansion of the square root, keeping only terms linear in $J(J+1)$, a comparison to Equation (6) leads to the identification

$$\beta_{00} \sim \frac{D_e}{B_e} \rho \bar{r}_{00} (1 - \rho \bar{r}_{00})^{-1}.$$

Using averages of the A and X state constants yields estimates of $\beta = 3.4 \times 10^{-4}$ for OH and 1.8×10^{-4} for OD from this simple physical picture, which are of the proper magnitude. However the factor of 2 discrepancy with the Morse-Pekeris wavefunctions shows that a more complete treatment, including the variation in $q_{v,v'}$ with J , is necessary. This approach does however permit an estimate of the ratio of β for OH to β for OD in the (0,0) bands; from the recommended values one has a ratio of about 55 percent, compared to the 53 percent expected from the mass dependence of D_e and B_e .

Using RKR wavefunctions determined from his spectral constants, Coxon has calculated J -dependent Franck-Condon factors and r -centroids for a number of vibrational bands. We have used these results (his Table X) together with a linear moment having $\rho = 0.750 \text{ \AA}^{-1}$ to calculate

a number of $p_{v',J'}^{v'',J''}$. These resulting transition probabilities are then plotted vs $J(J+1)$ to assess the applicability of Equation (6). For $J \lesssim 20$, this linear form is acceptable except for the (1,0) and (3,0) bands. The values of $\beta_{v',v''}$ so obtained are tabulated in Table 7. The negative value of β for the (2,0) and (3,1) bands means that the transition probability is increasing, not decreasing, with increasing J'' . Here, as J'' increases, the overlap (Franck-Condon factor) is increasing faster than the transition moment decreases. These factors nearly balance for the (1,0) band such that there is only about a 1 percent change in the transition probability between $J = 0$ and $J = 20$. A linear fit is thus not meaningful here, and the transition probability may be considered essentially constant. For the (3,0) band, which is quite weak anyway, the variation is not linear with $J(J+1)$. The $\beta_{v',v''}$ values given in Table 7, together with Equation (6), represent (for J between 0 and 20) the calculations to an accuracy which varies with the band but which is in all cases better than that obtainable from lifetime or intensity measurements. Clearly the same (if not stronger) caveats concerning the application of these β values apply here as for the (0,0) band.

TRANSITION PROBABILITIES IN OH

In I, we assessed the available data on OH pertinent to relative transition probabilities and the extraction from them of an electronic transition moment. Since that time a few other studies have appeared which bear on the question; these are discussed briefly in this section.

TABLE 7. $\beta_{v',v''}$ VALUES FOR VARIOUS BANDS, USING
COXON'S FRANCK-CONDON FACTORS AND r -CENTROIDS,
AND $R_e(\bar{r}) = c(1 - 0.750 \bar{r})$

Band (v',v'')	$\beta_{v',v''} \times 10^4$
0,0	4.0
0,1	1.7
1,0	0.2 ^a
1,1	5.8
1,2	3.5
2,0	-3.6
2,1	1.4
2,2	8.4
2,3	6.3
3,0	-5 ^a
3,1	-2.6
3,2	3.0
3,3	12

^aCharacteristic, not quantitative; see text.

Smith, Elmergreen, and Brooks¹⁸ (SEB) have proposed a linear transition moment having a slope $\rho = 0.55 \text{ \AA}^{-1}$, which they have used to fit data¹⁶ on lifetimes as a function of rotational level. We find difficulty in discerning a regular enough variation in their lifetimes to extract such a moment, as noted in I. That notwithstanding, the range of r values covered by SEB (1.02 to 1.10 $\text{\AA}$) is much smaller than that which can effectively be considered via the $A_{v',v''}$, calculated using such this value of ρ . This smaller slope together with our Morse wavefunctions yields the following key ratios of transition probabilities, with the "best" experimental values (see I) in parentheses: $A_{10}/A_{00} = 0.20$ (0.30); $A_{11}/A_{10} = 3.42$ (1.7); and $A_{21}/A_{22} = 0.83$ (1.8). Other ratios for less intense bands show similar discrepancies. We find this sufficient to rule out such a moment, considering as untenable any possibility of a different slope in this region of internuclear distance than over the fuller range of r . However, it should be noted that the conclusions concerning predissociation, the primary subject of SEB, are unaffected by the choice of transition moment.

Hogan and Davis¹⁹ have made lifetime measurements in $v' = 0$ and 1 using pulsed laser excitation. Their results must be considered with some caution due to difficulties²⁰ in their pressure extrapolation. However, *if* the presence of 10 mTorr of O_3 does not cause appreciable

¹⁸W. H. Smith, B. G. Elmergreen, and N. H. Brooks, "Interactions Among the Lower Valence States of the OH Radical," J. Chem. Phys. 61, 2793-2799 (1974).

¹⁹P. Hogan and D. D. Davis, "OH Lifetime Measurements of Several K Levels in the $v'=1$ Manifold of the $A^2\Sigma^+$ Electronic State: Excitation via a Tunable uv Laser," Chem. Phys. Lett. 29, 555-557 (1974).

²⁰R. K. Lengel and D. R. Crosley, "Comment on 'Electronic Quenching and Vibrational Relaxation of the OH ($A^2\Sigma^+$, $v'=1$) State,'" J. Chem. Phys. 64, 3900-3901 (1976).

vibrational transfer,^{*} their quoted operating pressures of 30 mTorr H₂ and 1 Torr Ar should be low enough to yield reasonable results for the lifetime ratio. They obtain $\tau_1/\tau_0 = 1.06 \pm 0.02$, using their 1- σ level error bars.

German¹⁵ finds for this same ratio a value of 1.06 ± 0.03 (his 1- σ level uncertainties) using a similar technique but operating at lower pressures and a different mode of OH production. German's absolute lifetimes are some 10 percent lower than those of Hogan and Davis; whatever systematic errors are responsible for this continuing problematic discrepancy in OH lifetimes *might* not affect the ratio. From 1, a linear moment model predicts $\tau_1/\tau_0 = 1.09$ while Learner's exponential moment yields a ratio of 1.04.

German's preliminary values of lifetimes as a function of N' in $v' = 0$ were quoted in 1 as yielding a value $\beta = (13 \pm 5) \times 10^{-4}$. Now published in final form,¹⁶ they may be fitted to a $\beta = (12 \pm 2) \times 10^{-4}$, where these error bars are estimated considering (1- σ level) error bars of 1 percent on the lifetimes and a total variation of about 8 percent over the range of N' studied.

Implicit in the SEB¹⁸ fit discussed above is the existence, among the experimental data, of a smooth enough relationship to extract a value of β . We have used the SEB linear moment and the Morse-Pekeris model to calculate $\beta = 3.4 \times 10^{-4}$ which may be as representative of SEB's

^{*} We are not convinced that it is negligible, following our experience⁵ with NO₂ and H₂O.

assessment of the lifetime variation. Some variation of τ with N' as found by Hogan and Davis¹⁹ cannot be fit with a linear form such as Equation (6).

These results may be compared with values of β extracted from Morse-Pekeris calculations, as well as other experimental values, listed in Table 7 of I. We conclude that a variation linear in $J(J + 1)$ with a β of about 7×10^{-4} continues to form a sensible representation, at least for low J , but repeat that any quantitative use of this model should take into account its limitations.

Liu²¹ has used extended configuration interaction wavefunctions²² to calculate transition moments in OH. He finds a transition moment linear in internuclear distance, as well as absolute transition probabilities in better agreement with experiment than found in a previous theoretical calculation¹² (which yielded very good relative transition probabilities, however). Studies of other diatomics yields confidence²² in the results from the configuration interaction approach. We find pleasing the success of the linear moment model as a fitting tool, combined with its appearance in these *ab initio* studies.

We conclude by correcting some typographical errors and clarifying some minor discrepancies in I. In Table I, the pump lines for the six

²¹B. Liu, "Accurate Theoretical Oscillator Strengths for Diatomic Molecules, CH and OH," Symposium on Molecular Structure and Spectroscopy, Columbus Ohio, June 1975; private communication 1975.

²²S.-I. Chu, M. Yoshimine, and B. Liu, "Ab initio Study of the $X^2\Pi$ and $A^2\Sigma^+$ States of OH. I. Potential Curves and Properties," *J. Chem. Phys.* 61, 5389-5395 (1974).

Integrated intensity runs on the A_{11}/A_{10} ratio should be three runs each for the single line Q_13 and for the overlapped pair of lines $Q_21 + Q_23$. The unweighted average of the ρ values ($\ln A^{-1}$) from the experimental ratios is 0.748 ± 0.009 , not 0.749 ± 0.010 . The value of 0.748 was used to calculate the final set of transition probabilities (Table 2) and their ratios (Tables 5 and 6). However the predicted ratios listed in Table 4 are obtained using $\rho = 0.740$, 0.750, and 0.760, so that the set with $\rho = 0.75$ differs slightly from the values calculated with $\rho = 0.748$. The expression for γ , used in eqn. (14), should read $\gamma = k\beta/B_e$; the numerical value given for γ is correct. Finally, in Section 3 of the Appendix, $d = \left| \delta^2 + \epsilon^3 f(3\epsilon - 1) \right|^{1/2}$.

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APPENDIX A: OD SPECTROSCOPIC CONSTANTS

The mathematical forms of the Morse and Morse-Pekeris wavefunctions used here are described in the Appendix to I. For OD we use the recent set of spectroscopic constants determined by Coxon.⁷ He notes (his Table XII) that his quoted B_e is actually the Dunham coefficient Y_{01} ; it should probably be corrected by $Y_{01} = B_e - 2B_e^3/\omega_e^2$ for determination of r_e . Although the correction is smaller than the error bars, as Coxon points out, we have nonetheless applied it to yield $r_e'' = 0.9696 \text{ \AA}$ and $r_e' = 1.01227 \text{ \AA}$. Sensitivity calculations with a variety of constants show that this parameter (r_e) is the most critical. In Table 8 are listed the Franck-Condon factors $q_{v',v''}$ and r -centroids $\bar{r}_{v',v''}$ calculated with our model, together with Coxon's RKR-determined $q_{v',v''}$ and $\bar{r}_{v',v''}$.

Coxon's recent determination of the OD spectral constants likely leads to the set for this species as having slightly more accuracy than that for OH. We have recomputed the OH transition probabilities using Coxon's OD constants scaled by the appropriate reduced mass ratios. The differences from those given in I are minimal; the largest change is in A_{10} (less than 2 percent) yielding a predicted ratio $A_{11}/A_{10} = 1.71$ instead of 1.75. Although this is slightly closer to our troublesome experimental value for this quantity (1.58 ± 0.08), we do not consider that sufficient reason to necessarily prefer the model with these revised constants. The overall sensitivity of the models to the input parameters precludes attaching significance to the third figure of any calculated transition probabilities.

TABLE A1. FRANCK-CONDON FACTORS AND r-CENTROIDS

Band v', v''	$q_{v',v''}$		$\bar{r}_{v',v''}(\text{\AA})$	
	Morse	RKR ^a	Morse	RKR ^a
0,0	0.8734	0.8740	1.0024	1.0034
0,1	0.1195	0.1194	1.1846	1.1862
1,0	0.1148	0.1135	0.8491	0.8496
1,1	0.6317	0.6342	1.0282	1.0308
1,2	0.2293	0.2297	1.2052	1.2077
2,0	0.0108	0.0111	0.6903	0.6966
2,1	0.2095	0.2061	0.8839	0.8855
2,2	0.4075	0.4106	1.0547	1.0590
2,3	0.3177	0.3205	1.2273	1.2306
3,0	0.0091	0.0011	0.5137	0.5413
3,1	0.0343	0.0346	0.7374	0.7420
3,2	0.2714	0.2675	0.9189	0.9221
3,3	0.2199	0.2225	1.0817	1.0878

^aFrom Coxon, Reference 7.

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