TRANSITION PROBABILITIES IN OH $A^2\Sigma^+ - X^2\Pi_1$:
BANDS WITH v' = 0 AND 1, v" = 0 TO 4

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ABSTRACT

Experimental results for relative vibrational band transition probabilities for v' = 0 and 1, and v" = 0 to 4 in the A-X electronic system of OH are presented. The measurements, part of a larger set involving v' = 0 to 4 and v" = 0 to 6, were made using spectrally dispersed laser-induced fluorescence (LIF) in the burnt gases of a flame. These Einstein coefficients will be useful in dynamics experiments for quantitative LIF determinations of OH radical concentrations in high v".

LIF Determinations and Transition Probabilities for OH

The OH radical has been the subject of numerous studies, in part due to its important role in atmospheric and combustion chemistry, and in part due to its amenability to state-specific energy transfer and reaction studies. Laser-induced fluorescence (LIF) forms an especially sensitive means of detecting OH, and is extensively used for field measurements in the troposphere and stratosphere and for laboratory determinations in flames and in kinetics and dynamics experiments. For most such measurements, excitation and observation of the lower levels by means of the strongest bands -- viz., $(v',v") = (1,0)$, $(0,0)$ and $(1,1)$ -- has proven adequate.

More recently however, there has been increasing interest in the detection of OH in higher vibrational levels, most of which require LIF detection via weaker off-diagonal bands. Such experiments have included vibrational distributions from both nascent reaction products [1] and following collisional quenching of the electronically excited $A^2\Sigma^+$ state [2], and vibrational and rotational energy transfer in the ground state [3]. A two-laser scheme for tropospheric monitoring of OH also involves LIF of vibrationally excited radicals [4]. In all these experiments, quantitative determinations require well established transition probabilities for the vibrational band(s) used in excitation and observation. Absolute values can be obtained from relative intensity ratios for bands with a given v', combined with an overall theoretical framework and absolute radiative lifetimes for each v'.

A series of papers [5], describing experimental measurements, theoretical calculations and a critical review of previous work, dealt with the stronger bands having $\Delta v \equiv v'-v" = 1$, 0 and -1. Relative transition probabilities for those bands were measured and shown to be well described by an electronic

transition moment, $R_e(r)$, which varies linearly with internuclear distance, a form first proposed many years earlier [6]. For bands with $\Delta v = -2$ and -3, the intensity of only the (2,4) band has been measured; and none of these bands can be adequately described by means of a linear form of $R_e(r)$. Although ab initio computations of $R_e(r)$ have been performed [7], there is too much uncertainty in the calculated values for the weak bands with large r-centroids, and new experimental data are needed to provide a consistent picture.

We have made measurements of the intensities of 26 different vibrational bands, including several not previously observed, in the $A^2\Sigma^+ - X^2\Pi_i$ system of OH. The experimental method is spectrally dispersed LIF, using OH in the burnt gases of a flame. The bands include v' ranging from 0 to 4, and v" as high as 6. Many of the bands are extremely weak in fluorescence, due in part to their low inherent transition probability and in part to the predissociation of levels with v' > 2. Nonetheless, with the use of strong lasers which can approach optical saturation even for weak transtions, it will be possible to use these weak bands as sensitive monitors of ground state OH populations in high v". We have, for example, detected OH in v" = 4 via excitation in the (1,4) band [2].

Many of the bands with high v' and v" have r-centroids beyond the distance (~1.4 Å) where the linear moment becomes more and more negative, losing its meaning and usefulness. Consequently, they form a stringent test of the ab initio transition moment, and hence the ab initio wavefunctions, at large values of internuclear distance. We are currently proceeding with the data analysis of the bands with v' = 2 to 4, together with fits of various $R_e(r)$ in the same general functional form as those from the ab initio calculations. The full set of results and comparisons with theory will be published later [8]. Because of the desirability of measuring OH in v" as

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high as 4, we report here the experimental results for bands having v' = 0 and 1, in advance of that full analysis.

Experimental Details and Data Analysis

Most of the measurements are made in a flame, although one set is made in a low pressure flow system. We describe the flame experiments first. Methane and oxygen are burned at atmospheric pressure on a small laboratory burner; in the burnt gases there exist copious quantities ($> 10^{16}$ cm^{-3}) of OH radicals. The OH radical is excited using a frequency-doubled, excimer-pumped dye laser having 0.6 cm^{-1} bandwidth (about twice the OH Doppler width in the flame) and operated at typically 5 to 30μJ per pulse (levels where the fluorescence intensity was linear in laser power). The fluorescence is collected at right angles with either a one or two lens system, focussed onto the slit of a 0.35 m monochromator, and detected with a photomultiplier. In many cases, when measuring weak bands with high v", a WG335 Schott glass filter is used to block the strong background signals due to the (1,1) and/or (0,0) bands. The photomultiplier output is amplified and is measured by a boxcar integrator controlled by a laboratory computer; the resulting signals are normalized to a simultaneous measurement of laser intensity. The v' = 1 data are taken exciting in the (1,1) band either the $P_1(6)$ or $Q_1(4)$ transitions; for the v' = 0 measurements several different rotational transitions are excited in the (0,0) band.

Spectrometer scans for the weaker bands, Δv < -1, are shown in fig. 1. As plotted, these are all normalized to laser power and detection system response. The ratio of Einstein emission coefficients A_{02}/A_{01} for the (0,2) and (0,1) bands is determined with narrower slits than the ratio for (0,3) and the limit for (0,4); both scans are shown in the upper panel.

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The lower part of fig. 1 shows scans for bands with $v' = 1$. In addition to emission from this directly excited vibrational level, emission also occurs from nearby bands having $v' = 0$, a level populated by vibrational energy transfer in the flame [9]. Some of this emission underlies the nominal $v' = 1$ bands and must be accounted for in the data analysis. It is done so in the following manner. Higher resolution fluorescence scans are made of the (0,0) and (1,1) region following excitation in $v' = 1$ (see fig. 2). Here, the intensity of (0,0) and (1,1) is first obtained by taking the areas to each side of the R_1 head marked in fig. 2. The contribution of (0,0) in the region of (1,1) is estimated by a linear extrapolation of the tail of the P and Q branches of (0,0) at the R_1 head; this is subtracted from the (1,1) intensity and added to the (0,0) intensity. The average intensity ratio I_{00}/I_{11} is 0.55. (Note that this intensity ratio corresponds to a population ratio $N_0/N_1 = 0.32$, lower than the value $N_1/N_0 = 0.6$ found in ref. [9]. This apparent inconsistency is caused by a different flame composition; the present flame contains no nitrogen, whereas that in ref. [9] was an air flame containing N_2 which causes vibrational transfer but quenches poorly.) We then use ratios $A_{01}/A_{00} = 0.0045$ and $A_{02}/A_{01} = 0.026$ to compute the $v' = 0$ contributions to the $v' = 1$ emission in the other bands. The results are that in $\Delta v = 0$, 35% of the emission is from $v' = 0$; in $\Delta v = -1$ it is 18% and in $\Delta v = -2$ it is 5%. There is no observable contribution in the case of the (1,4) band.

The spectral response of the entire fluorescence detection system (including filters where appropriate) is calibrated using both tungsten and deuterium lamps. Such a calibration, covering a large wavelength region and thus a large range of lamp output, must be done with care; the procedure will be described in detail in ref. [8]. We note in particular that measurements

of the ratio A_{11}/A_{10} in the flow system (see below) are the same for either first or second order monochromator repsonse.

Tables 1 and 2 list the Einstein coefficient ratios determined from these scans. The quoted value is a weighted average over the number of runs indicated; the weights are the signal to noise ratio of the weaker band in each case. The 2-σ level errors listed are calcuated from the statistical deviations in the averaging. They include no systematic uncertainties, but we estimate those to be negligible in comparison with the statistical component.

In the flame we measure a ratio A_{11}/A_{10} significantly higher (~2) than the flow system measurement reported in ref. [5a] or considered [5] the best theoretical value. Because of this large discrepancy and the crucial nature of this ratio for many OH determinations, it was remeasured in a low pressure discharge flow system where there are considerably fewer OH radicals. Here, a discharge in H_2O vapor at about 50 mTorr serves as the OH source. Experiments are performed detecting the fluorescence in both the first and second order response of the monochromator; for second order a UG-5 filter (Schott) is used. This determination results in $A_{11}/A_{10} = 1.64 \pm 0.15$ (the value given in table 2), in excellent agreement with the result of ref. [5a].

The original flame measurements for this ratio are in error due to the optical depth for OH in the $v'' = 0$ level in the flame gases. At the point of observation in the flame, fluorescence back to this level is absorbed whereas fluorescence to higher v'' undergoes negligible absorption. This effect was confirmed by a subsequent series of relative measurements as a function of distance into the flame. Consequently, the ratio A_{01}/A_{00} measured in the

flame is also too high. The present results for that ratio vary between 0.004 and 0.0065, consistent with the value determined in ref. [5a].

Error bounds on the upper limits for the (0,4) and (1,5) bands are difficult to quantify. Our estimate of noise excursions is at about the $2-\sigma$ level; the lack of discernible features in the appropriate wavelength region can be seen in fig. 1.

Discussion

For only two of the ratios measured here are there previously determined values. Our result for A_{11}/A_{10} agrees well with both the experimental value 1.58 ± 0.16 $(2-\sigma)$ and the best [5] theoretical value of 1.75 using a linear $R_e(r)$. That for A_{12}/A_{11} is the same as determined in ref. [5a] (0.0104 ± 0.0004, $2-\sigma$). However, the error bars for this ratio in ref. [5a] were determined from only two runs, and are unrealistically low; the present 25% error in table 2 is a better estimate of the real uncertainty in this ratio. The ratio A_{01}/A_{00} = 0.0037 ± 0.0008 $(2-\sigma)$ from ref. [5a] is preferable to the current range of measured values due to the optical depth problems in the flame.

Because of the centrifugal distortion in OH, both the vibrational overlap and r-centroid for a given band vary with rotational level N'; thus the transition probabilities depend upon N'. This variation is in general different from band to band, and is quite marked for the weaker bands [5b]. In most of the present experiments, the OH is excited near the maxiumum of the rotational distribution at the flame temperatures; although rotational energy transfer in the flame is not fully complete, the intensity ratios should be quite close to those for a thermal distribution peaking near $N'=5$. In the case of $v' = 0$, several different N' levels are pumped and no variation is

observed. The anticipated [5] difference compared with the rotationless case is about 2%. Quantitative, N'-dependent transition probabilities are best determined from calcuation [5c], using an $R_e(r)$ established from the vibrational band ratios; this procedure will be discussed for these weaker bands in ref. [8]. In the meantime, we will ignore the rotational effects, which are smaller than the experimental errors.

For comparison of populations determined by LIF using bands with different upper state vibrational levels v', we must convert the transition probability ratios to a series of Einstein coefficients. This can be done readily for the levels v' = 0 and 1, using the measured absolute radiative lifetimes (for v' > 2, the levels are predissociated and the observed lifetime is not entirely radiative). We use the lifetime values determined by German [10] using LIF at very low total pressure, where collisional effects are absent. His value $\tau_{v'=0}$ agrees excellently with a later determination under beam conditions [11], and more recent single-level excited LIF measurements [12] are also consistent with that result. German found τ_1 to be 6% longer, in general accord with theoretical [5] expectations. We use the values for the rotationless, N' = 0, levels: τ_0 = 693 ± 20 ns, τ_1 = 736 ± 22 ns, with 2-σ error bars [10].

The results of this computation are given in table 3. The quoted uncertainties for the weaker bands arise only from the statistical uncertainties in the Einstein coefficient ratios given in tables 1 and 2; when more than one ratio enters into the computation the errors are added in quadrature. The error for the stronger bands — (0,0), (1,0) and (1,1) — also includes the 3% uncertainty in the lifetimes.

This set of experimental results thus provides the transition probabilities needed for quantitative detection of OH in $X^2\Pi_i$ ground state

vibrational levels as high as v″ = 4. Although some of the bands are very weak, as can be seen from table 3, the use of powerful lasers can saturate the transitions and yield strong signal levels per unit concentration in these quantum states. In a similar way, the results for v′ = 2, 3 and 4 [8] will permit measurements as high as v″ = 6. The OH molecule, of considerable practical importance and the subject of many interesting chemical studies, can now be detected quantitatively in high vibrational levels of the electronic ground state.

Acknowledgements

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Table 1: Measured Einstein Coefficient Ratios for $v' = 0$

Ratio	Number of Runs	Result (2σ errors)
A_{01}/A_{00}	-	0.0037 ± 0.0008[a]
A_{02}/A_{01}	22	0.026 ± 0.006
A_{03}/A_{02}	12	0.059 ± 0.037
A_{03}/A_{01}	6	0.0018 ± 0.0010
A_{04}/A_{03}	4	<0.4
A_{04}/A_{02}	4	<0.02

[a]from ref. [5a]; see text.

Table 2:   Measured Einstein Coeffient Ratios For $v' = 1$

Ratio	Number of Runs	Result (2σ errors)
A_{11}/A_{10}	25	1.64 ± 0.15[a]
A_{12}/A_{11}	8	0.0104 ± 0.0026
A_{13}/A_{12}	14	0.100 ± 0.017
A_{14}/A_{12}	8	0.0087 ± 0.0016
A_{14}/A_{13}	8	0.086 ± 0.015
A_{15}/A_{14}	2	<0.2

[a]flow cell result

Table 3: Absolute Einstein Coefficients, sec^{-1} (2σ errors in parentheses)
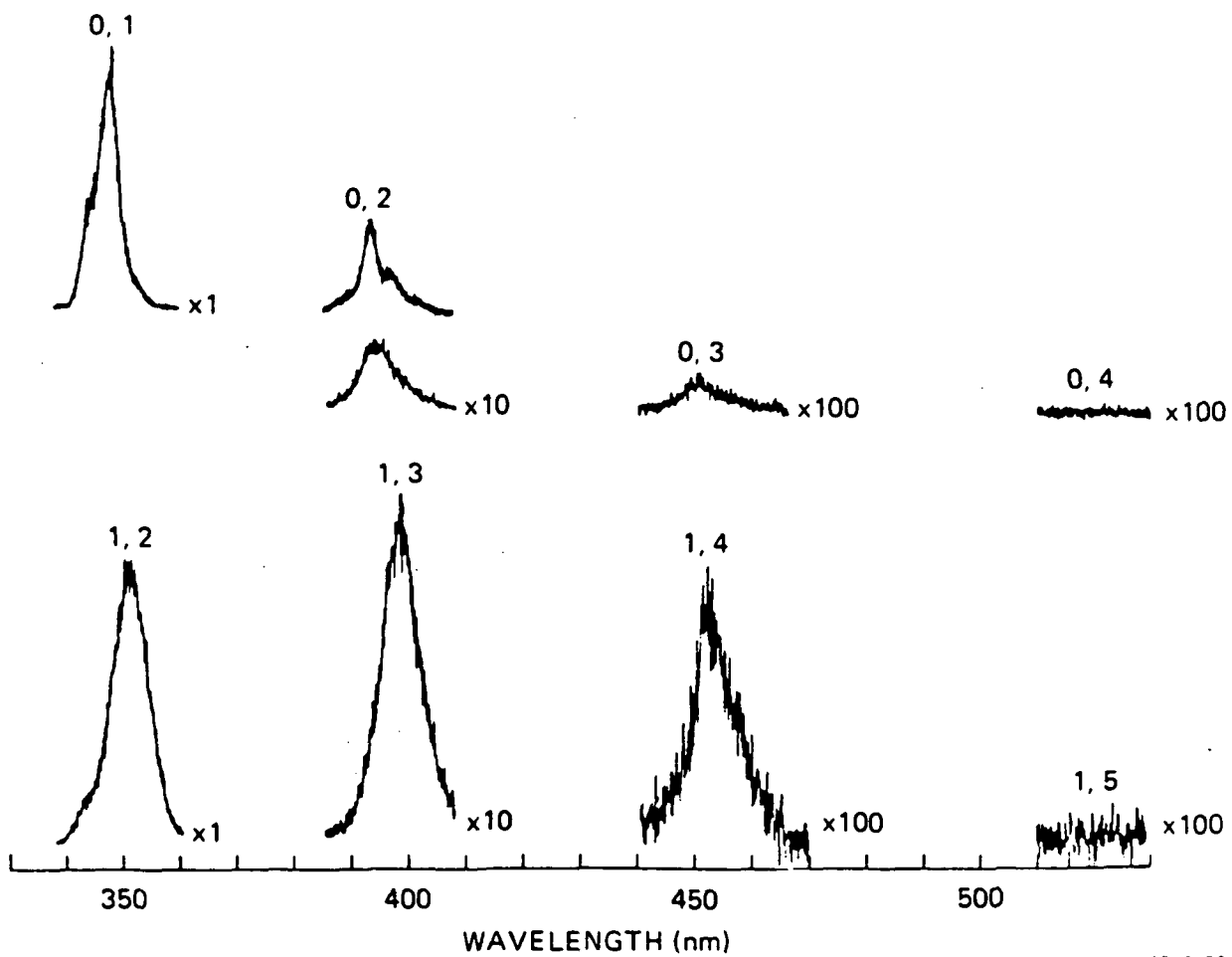
A_{00}	$1.44 \ (0.04) \times 10^6$
A_{01}	$5.3 \ (1.1) \times 10^3$
A_{02}	$1.4 \ (0.4) \times 10^2$
A_{03}	$9 \ (6)$
A_{04}	<3
A_{10}	$5.11 \ (0.49) \times 10^5$
A_{11}	$8.38 \ (0.81) \times 10^5$
A_{12}	$8.7 \ (2.3) \times 10^3$
A_{13}	$8.7 \ (2.8) \times 10^2$
A_{14}	$7.5 \ (2.5) \times 10^1$
A_{15}	$<1.5 \times 10^1$

Figure Captions

Figure 1. Laser-induced fluorescence spectra following excitation of the

v' = 0 (top) and v' = 1 (bottom) vibrational levels of the $A^2 \Sigma^+$

electronic state of OH. The two uppermost traces — that of the

(0,1) band and the (0,2) upper scan — are taken at 2 nm

resolution while all other bands are at 4 nm resolution. The area

of each band corresponds to the relative A-factor for each vibra-

tional transition when the indicated scale factors are taken into

account, except for the v' = 0 contribution to the v' = 1 bands as

described in the text. The (0,4) and (1,5) bands are not observed

above the noise level. These v' = 0 scans are taken following

(0,0) $P_2(5)$ excitation and the v' = 1 scans are taken following

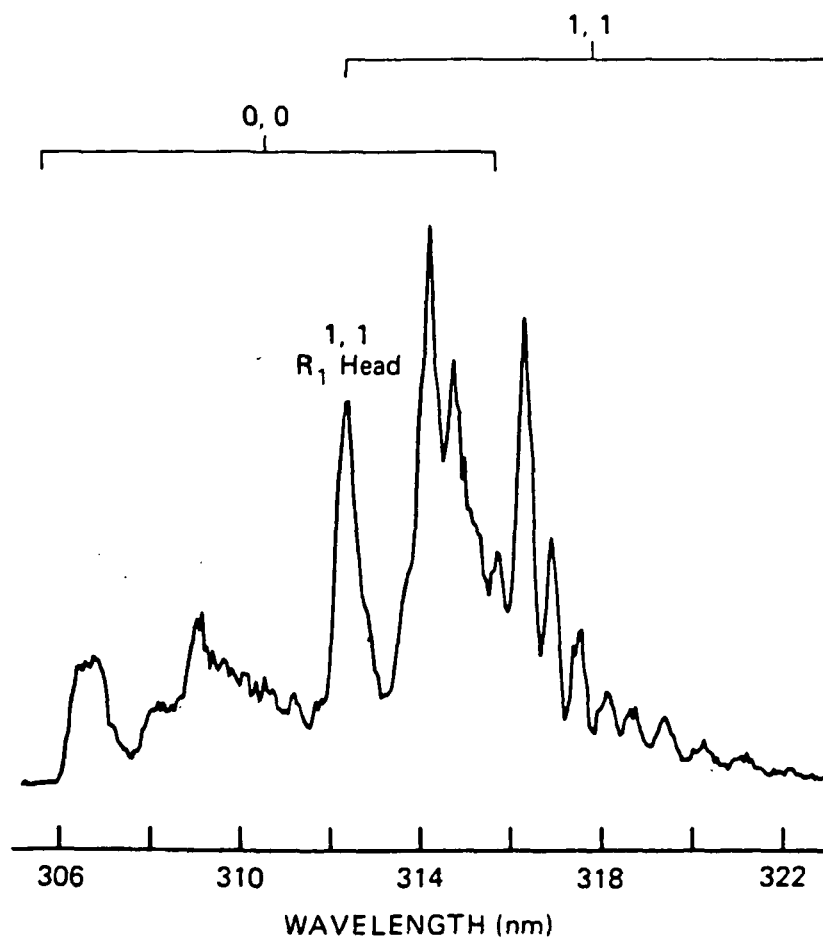excitation of the (1,1) $P_1(6)$ transition.

Figure 2. Fluorescence scan of the (0,0) and (1,1) vibrational bands of OH

following excitation of the (1,1) $P_1(6)$ transition in the burnt

gases of an atmospheric pressure CH_4/O_2 flame. The monochromator

slit width is 150 μm which corresponds to a resolution of about

0.5 nm. The spectrum is digitized at 0.06 nm/point, and each

point is the average of 50 laser shots. The large feature labeled

the (1,1) R_1 head divides the bands. All features to lower

wavelengths are due to the (0,0) band, while those at larger wave-

lengths are predominantly due to the (1,1) band with a small (0,0)

contribution. Scans such as these are used to determine the amount

of v' = 0 emission falling in the region of v' = 1 fluorescence

(see text).

Figure 1

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Figure 2