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Collision and quenching cross sections in the $A^2\Sigma^+$ state of OH and OD

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A pulsed dye laser has been used to excite OH and OD radicals to the $A^2\Sigma^+$ state and the quenching and vibrational relaxation cross sections have been measured for several different buffer gases. It was found that the quenching cross sections were reasonably constant within a given vibrational level and tended to increase at higher vibrational levels. The vibrational relaxation cross sections decreased for higher rotational states and were generally smaller for collisions in which V' changes by two than for collisions where it changes by only one. Finally, the implications of these measurements to the detection of OH in the atmosphere are discussed.

INTRODUCTION

The advent of tunable ultraviolet lasers has resulted in renewed interest in measuring the rates of both radiative and nonradiative processes in the $A^2\Sigma^+$ state of the hydroxyl radical.¹⁻⁷ It has been observed that the A state has a significant cross section for a change of both rotational and vibrational quantum numbers upon collision with common diatomic molecules.^{1,5} The present measurements are the first to obtain cross sections both for quenching in $V' = 1$ and for direct collisional transfer from $V' = 2$ to $V' = 0$. Such cross sections are interesting from a theoretical standpoint in that they should prove more readily calculable than similar processes in more complicated molecules. From a more practical standpoint OH is an important catalyst in several atmospheric pollution cycles. Its proposed monitoring by fluorescence at atmospheric pressures as in the recent experiment by Wang and Davis³ requires a knowledge of both quenching and vibrational transfer cross sections in order to calculate the absolute sensitivity of the detection scheme, and our measurements indicate that they have overestimated their sensitivity by a factor of about 13.5.

EXPERIMENT

In the present experiment OH and OD were produced in the $^2\Pi$ ground state by means of the usual chemical reaction



in a flow system where the total reactant pressure was about 2 mTorr.

Selective excitation to the three lowest vibrational levels of the A state was achieved by pumping with a frequency doubled dye laser whose pulse width was about 3 nsec. The fluorescent light was dispersed through a spectrometer which isolated the various vibrational bands but not the rotational structure. A photomultiplier on the spectrometer was used with either a small load resistor to measure the time response of the fluorescence, or with a large resistor to measure the integrated intensity in an entire vibrational band. Both time domain and intensity measurements were performed with a two channel boxcar integrator operated in a ratio mode to normalize fluctuations in both laser intensity

and hydroxyl concentration. For more complete descriptions of the experimental apparatus, the reader is referred to the author's earlier publications on hydroxyl radiative lifetimes.^{5,6}

In the present experiment, the total decay rate was obtained by measuring the change in fluorescence lifetime with buffer gas pressure while the vibrational relaxation cross section was measured by comparing the relative fluorescent intensity of bands populated by collisions to that of the directly excited band. The difference of the rates for these two processes was then taken to be the quenching rate of the directly excited state. For the $V' = 2$ levels however, the fluorescent intensity was too small to permit time domain measurements and so only vibrational relaxation cross sections could be obtained.

An example of the data for the change of the fluorescent decay rate of OH as a function of pressure can be seen in Figs. 1 and 2 for the cases of both rapid and slow vibrational relaxation. In these measurements the two channels of the boxcar were operated from a single photomultiplier with a fixed relative sampling aperture delay of about 800 nsec and the change in the ratio of the intensities was measured for various buffer gas pressures. This two point sampling technique gave results which were indistinguishable from complete scans of the sampling gate over the same time interval. Even at the highest pressures used in the experiment (about 1 Torr of N_2) the decay was well represented by a single exponential indicating that analysis in terms of bimolecular rates is valid.

ANALYSIS

A. $V' = 1$ excitation

The experiment measures both the integrated intensity and the decay rate of fluorescence from an entire vibrational band. Rotational exchange collisions do not contribute to either measurement except as they excite states with different radiative and quenching decay rates than the initial state. Even in this case a single rate equation may still be written for the population of each vibrational level including the effects of radiative decay, quenching, and vibrational transfer where the various rates are now averages over the occupied rotational levels.^{1,5,6} In the present case very little rotational re-

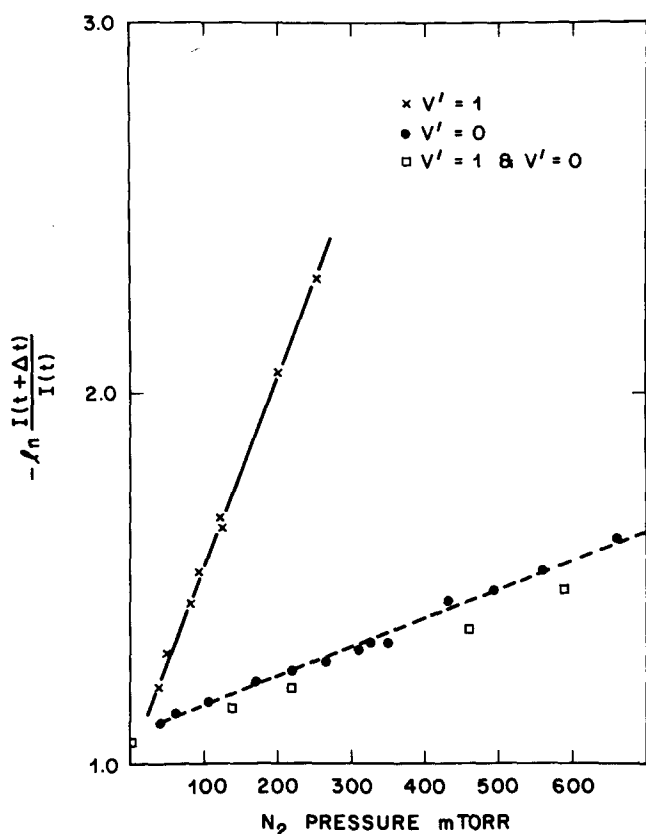


FIG. 1. Fluorescent decay rate of OH as a function of pressure for rapid vibrational relaxation.

distribution occurs in the upper state so that the measured vibrational transfer rate is essentially that of the initially excited state. The following analysis assumes that the quenching rate is the same for all rotational sublevels of a given vibrational state. For excitation to $V' = 1$ the probability $p_{v'}$ of a molecule being in a given vibrational state as a function of time is found to be

$$p_1(t) = e^{-t/\tau_1}, \quad (2a)$$

$$p_0(t) = \frac{n\sigma_{10}v}{\tau_1^{-1} - \tau_0^{-1}} (e^{-t/\tau_0} - e^{-t/\tau_1}), \quad (2b)$$

where the total decay rate τ_1^{-1} is a sum of the radiative decay rate τ_{rad}^{-1} , the quenching rate ($n\sigma_{QV}, v$), and the vibrational transfer rate ($n\sigma_{V_1V_0}, v$) from the level V'_1 to V'_0 . By integrating these equations one may obtain a value for the ratio of the integrated fluorescence intensity from the two states

$$\frac{I_0}{I_1} = \frac{A_{00}}{A_{11}} (n\sigma_{10}v) \tau_0, \quad (3)$$

where $A_{V,V'}$ is the radiative emission rate for a given band. From Eq. (3) one may obtain the vibrational transfer cross section σ_{10} by measuring the intensity in the adjacent (0,0) and (1,1) fluorescence bands as was recently done in the experiments by Lengel and Crosley.¹

In Figs. 1 and 2 the ordinate is proportional to the logarithm of the ratio of the fluorescent decay intensity at two times separated by an interval Δt . From Eq.

(2a) this quantity is just $\Delta t/\tau_1$ which is given by

$$\frac{\Delta t}{\tau_1} = \Delta t \left(\frac{1}{\tau_{rad}} + n\sigma_{10}v + n\sigma_{Q1}v \right), \quad (4)$$

so that the slope of the plot against pressure is proportional to $v(\sigma_{10} + \sigma_{Q1})$. The case described in the figures represent the extremes $\sigma_{10} \gg \sigma_{Q1}$ and $\sigma_{Q1} \gg \sigma_{10}$ which are illustrated by N_2 and O_2 , respectively. The data in these figures do not constitute the totality of measurements on the $N' = 1$ levels but merely serve to illustrate the significant differences in behavior for essentially identical experimental conditions. The gases used in the experiment were all commercially available dry gases with moisture contents of less than 10 ppm. The bandwidth of the spectrometer used in observing the $V' = 1$ decay rate was about 3.5 nm. Even at the highest pressures used in the experiment there was a broad null where only dark current was observable at wavelengths between the (1,0) and (0,0) fluorescence bands.

The results of the data analysis on the basis of the above equations are listed in Table I along with their one standard deviation errors. Values for the radiative lifetimes were taken from the measurements of German⁶ while the emission rates $A_{V,V'}$ were obtained from the work of Lengel and Crosley.⁸ The results for the quenching cross section in $V' = 0$ indicate that it does not vary significantly with N' at least in this region of the band thus confirming the assumption made in deriving Eq. (2). Furthermore, the quenching cross section seems to be generally larger for $V' = 1$ than for $V' = 0$. Although O_2 would be expected to be a reasonably effi-

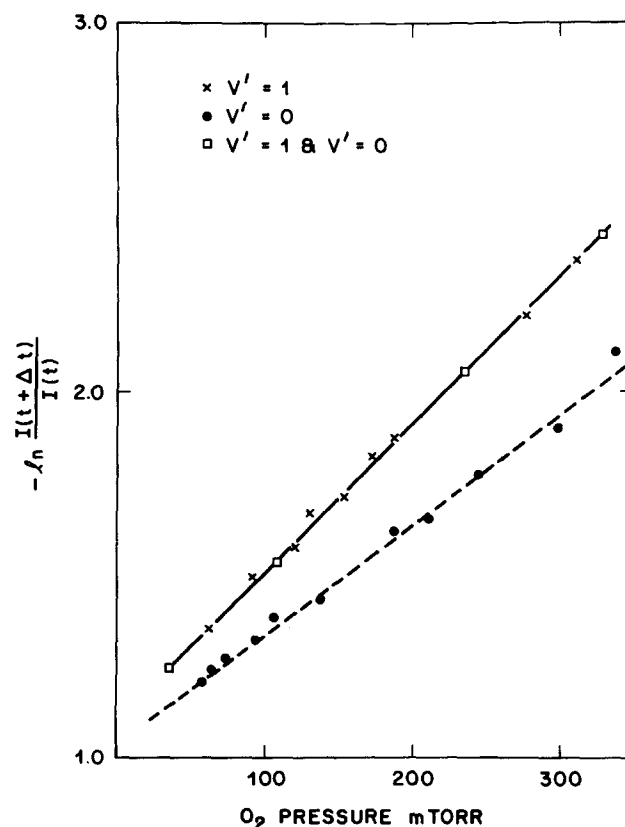


FIG. 2. Fluorescent decay rate of OH as a function of pressure for slow vibrational relaxation.

TABLE I. Quenching and relaxation cross sections (in units of 10^{-16} cm²).

OH	N	σ_{Q0}	σ_{Q1}	σ_{10}
OH	H ₂	1	7.4 ± 0.6	7.7 ± 0.6
		4	6.9 ± 0.6	5.7 ± 0.6
		5	6.8 ± 0.6	6.5 ± 0.5
	N ₂	1	3.4 ± 0.3	3.9 ± 0.5
		4	3.5 ± 0.3	4.9 ± 0.5
		5	5.3 ± 0.3	12 ± 1.1
	O ₂	1	13.9 ± 1	21.0 ± 1
		4	11.7 ± 1	15.9 ± 1
		5	11.3 ± 1	1.8 ± 0.2
OD	H ₂	1	8.3 ± 0.7	11.0 ± 1
		2	7.5 ± 0.7	9.8 ± 0.7
	N ₂	1	3.5 ± 0.5	5.6 ± 0.5
		2	17.5 ± 1.2	17.5 ± 1.2
	O ₂	1	12.0 ± 1	18.6 ± 1.2
		2	11.9 ± 1	4.2 ± 0.3

cient quencher because of its chemical activity it is surprising that it is so much less efficient than N₂ in inducing vibrational relaxation. The vibrational relaxation rate for O₂ is, however, reasonably, sensitive to the vibrational spacing as there is a reproducible factor of two increase from OH to OD, which is a bigger change than for any other vibrational cross section.

The results of the present experiment are in reasonable agreement with the work of Lengel and Crosley¹ who measured both σ_{Q0} and σ_{10} by fitting their fluorescence measurements to an expression like Eq. (3) and first observed the decrease in σ_{10} with increasing N' . Since the present experiment measures σ_{Q0} directly it should be the more sensitive technique particularly in the case of a large ratio of σ_{10} to σ_{Q0} .

Recently Hogan and Davis² claimed to have measured the quenching in $V' = 1$ by fitting a single exponential to their signal which was a linear combination of light from both $V' = 1$ and $V' = 0$, i.e., in their case a weighted sum of Eqs. (2a) and (2b). Such a procedure is wrong in principle and gives information about σ_{Q1} only in the limit $\sigma_{Q1} \gg \sigma_{10}$ which is definitely not the case for N₂ and H₂ which they measured. In the presence of strong vibrational relaxation their procedure must be rejected as too crude to give meaningful results for σ_{Q1} . The potential error inherent in such a procedure is effectively evidenced by the square data points on Fig. 1 which indicate the decay rate of the equally weighted sum of fluorescence from both $V' = 0$ and $V' = 1$ following excitation to $V' = 1$. The result is just what one would intuitively expect, namely, that for fast vibrational relaxation the decay is modulated only a quenching in the lowest vibrational level. Figure 2 illustrates the opposite extreme in the case of O₂. Here the quenching rate in $V' = 1$ is much more rapid than the vibrational relaxation rate. In this case a measurement of the decay rate of the total fluorescence (indicated by the square points on Fig. 2) would indeed be dominated by σ_{Q1} . Recently Davis has admitted that his measurements of σ_{Q1} were in error and that he is taking steps to correct his earlier results.⁹

Of course, OH quenching has been extensively studied before but not with the capability of state selection available since the development of lasers. Nonetheless, measurements^{10,11} based on techniques such as the flash photolysis of water also measured quenching cross sections which are consistent with the present values although a detailed comparison is inappropriate since such studies generally involved much higher rotational states and there is no reason in principle why such cross sections could not depend on the specific level measured although the dependence at low rotational values is small.

B. $V' = 2$ excitation

The expressions analogous to Eq. (1) for excitation to $V' = 2$ are more complicated and will not be presented here. In general, only the directly excited level has a single exponential behavior. However, expressions for the integrated intensity ratios of the fluorescence bands after initial excitation to $V' = 2$ are found to be

$$\frac{I_0}{I_2} = \frac{A_{00}}{A_{22}} \tau_0 [n\sigma_{20}v + (n\sigma_{21}v)(n\sigma_{10}v)\tau_1] \quad (5a)$$

$$\frac{I_1}{I_2} = \frac{A_{11}}{A_{22}} (n\sigma_{21}v)\tau_1, \quad (5b)$$

for the same assumptions used in deriving Eq. (3).

The use of the measured fluorescence intensities to extract σ_{20} and σ_{21} is subject to greater uncertainties than the analogous case for $V' = 1$ excitation. First of all Eq. (5) contains the measured quantities σ_{Q1} , σ_{Q0} , and σ_{Q10} which are known only to the precision listed in Table I. A more fundamental problem is that the $V' = 2$ to $V' = 1$ relaxation produces a distribution in N levels in the $V' = 1$ state and σ_{10} quite clearly depends on N . Thus some sort of a weighted average is implied in the use of Eq. (4). For instance the use of σ_{10} appropriate to $N' = 1$ in $V' = 1$ would tend to underestimate σ_{20} . From observations of the spectral distribution in $V' = 1$ it is felt that these effects probably give an additional 10% uncertainty to σ_{21} .

In any event the fluorescence data was analyzed according to Eq. (4) and using the same average σ_{10} for OH and OD. The results are listed in Table II where it can be seen that there is an appreciable cross section for direct $V' = 2$ to $V' = 0$ relaxation for N₂. The quenching of oxygen made observations of $V' = 2$ OH, which is already predissociated, too weak to be useful. From the similarities between OH and OD it will be assumed in the discussion in the following section that vibrational relaxation of OH $V' = 2$ by O₂ is comparably small. The precise numerical results are rather quali-

TABLE II. Vibrational relaxation cross sections for $V' = 2$ in units of 10^{-16} cm².

OH	N	σ_{21}	σ_{20}
OH	N ₂	1	17 ± 2
	O ₂	1	15 ± 3
OD	N ₂	1	24 ± 3
	O ₂	1	6 ± 1
			0.2 ± 0.3

tative, however, and could change appreciably with additional measurements.

DISCUSSION

In the aforementioned experiment of Wang and Davis³ fluorescence from the $V' = 0$ level of $A^2\Sigma^+$ was detected at atmospheric pressures following excitation into $V' = 1$. In estimating their experimental sensitivity they stated that the overall quantum efficiency η of this process was about 10^{-2} at 50% relative humidity, and that quenching was entirely due to water vapor. This is indeed not a bad value for the effect of water vapor as a measurement of the quenching cross section with the present apparatus yielded value of $(75 \pm 12) \times 10^{-16} \text{ cm}^2$ which gives a value for η of 5×10^{-3} due to water vapor alone. Later measurements by these authors¹² indicated that N_2 did indeed have a measurable cross section, but even their most recent publication¹³ on the ambient OH concentration uses the same value for η of 10^{-2} .

It is impossible to reconcile this value of η with the results of the present experiment. From the data in Table I it is straightforward to calculate that in dry air the efficiency for relaxation to $V' = 0$ of molecules initially excited to $V' = 1$ is 70%. In $V' = 0$ there is a distribution of N' values peaking about $N' = 5$ and assuming that σ_{00} is constant for these levels and is given by the mean of the measurements in Table I it follows that the quantum efficiency for fluorescence from $V' = 0$ is 1.35×10^{-3} . The total quantum efficiency for the process of vibrational relaxation followed by fluorescence in dry air is consequently $(9.4 \pm 0.6) \times 10^{-4}$. At the stated condition of 50% relative humidity this is lowered to $(7.4 \pm 0.7) \times 10^{-4}$.

The consequence of using this lower value for η is that the OH concentration measurements of Wang *et al.*¹² must be adjusted upwards by a factor of at least 13 so that the diurnal peak concentration is about $8 \times 10^8 \text{ cm}^{-3}$ and the average concentration is about $7 \times 10^7 \text{ cm}^{-3}$. Both of these are surprisingly high values and are dif-

ficult to reconcile with the value for the average OH concentration of $5 \times 10^6 \text{ cm}^{-3}$ derived by Weinstock.¹⁴ If these higher values are indeed real and not the result of calibration error then the contribution of OH reactions to atmospheric photochemistry would be much stronger than had been previously surmised.

Finally, it is worth noting that at atmospheric pressures the vibrational relaxation from $V' = 2$ would be much faster than the predissociation rate.⁶ Furthermore, in view of the large relaxation cross sections to $V' = 0$, both directly and through $V' = 1$, the quantum efficiency for fluorescence from $V' = 0$ after excitation to $V' = 2$ should be about 0.7 times the value for excitation to $V' = 1$, assuming that the unmeasured quenching cross sections in $V' = 2$ are about the same as in $V' = 0$ and 1. Of course the absorption cross section is about five times smaller but the shift of the excitation frequency would shift any Raman scattering background to the fluorescence and could result in improved overall sensitivity for this interesting technique.

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