

# A Shock Tube Study of Recombination in the Hydrogen-Oxygen Reaction Using Infrared Emission from Water Vapor\*

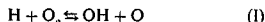
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Recombination in the hydrogen-oxygen reaction has been studied by monitoring the growth of infrared emission at  $2.7 \mu$  from water vapor formed during the shock-initiated combustion of dilute  $H_2$ - $O_2$ -Ar mixtures. Experiments were carried out with hydrogen/oxygen ratios between 2.2 and 0.33 and temperatures between 1435 and 1868°K. The proportionality between emission intensity and  $[H_2O]$  was confirmed under these conditions by shocking mixtures of water vapor in argon. In  $H_2$ -lean mixtures analysis of the recombination emission profiles gave a value for the rate coefficient of the dominant termolecular reaction,  $H + O_2 + Ar \rightarrow HO_2 + Ar$  ( $3.0 \times 10^{13} \text{ cc}^2/\text{mole}^2 \text{ sec}$ ), that is in good agreement with other shock tube determinations. Profiles in near-stoichiometric mixtures agreed quite well with predictions based on recent ultraviolet absorption measurements of the time dependence of the OH concentration during combustion. These results provide convincing evidence of the validity of the present understanding of recombination in the hydrogen-oxygen reaction.

## Introduction

This paper reports time-resolved measurements of infrared radiation at  $2.7 \mu$  emitted by reacting hydrogen-oxygen-diluent gas mixtures initiated by incident shock waves. The data provide information about the rate of the slow approach of the system to equilibrium via termolecular recombination reactions. The interpretation has made use of the assumption of the essential equilibration of the bimolecular chain steps



at all times during the recombination period (i.e., the *partial equilibrium* approximation) [1,2]. Comparison of the results with others obtained under comparable experimental conditions by following the absorption by OH in the ultraviolet ( $^2\Sigma^+ \rightarrow ^2\Pi$ ) [3-6] has made it possible—particularly in hydrogen-lean mixtures—to test the present understanding of recombination in this system. The experiments reported here appear to constitute the first *in situ*

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quantitative investigation of the hydrogen-oxygen reaction kinetics carried out in the infrared.

At the temperatures and gas densities used in this investigation contributions to the thermal radiation intensity at  $2.7\ \mu$  could have come from both  $\text{H}_2\text{O}$  and  $\text{OH}$ , both of which have infrared-active vibration-rotation bands in that spectral region ( $\nu_1$ ,  $2\nu_2$ , and  $\nu_3$ , and 1, 0, respectively). However, for reasons given later, it is evident that at least during the recombination period any contribution from  $\text{OH}$  was negligible. As far as can be determined, the measured intensity came solely from  $\text{H}_2\text{O}$ .

Considerable thermal emission is observed even before significant recombination has occurred in the present experiments as a result of the formation of water vapor during the initial, rapid combustion preceding the attainment of partial equilibria I-III. Thereafter the radiation intensity changes in a manner determined primarily by (a) the increase in temperature accompanying the release of thermal energy in highly exothermic termolecular steps, and (b) adjustments in mixture composition imposed by equilibria I-III in the presence of both (a) and a reduction in the total number of moles present in the system. The nature of the equilibria I-III is such that the increase in mole fraction  $\text{H}_2\text{O}$  during recombination is strongly dependent upon the initial  $\text{H}_2/\text{O}_2$  ratio; it is greatest in near-stoichiometric mixtures, somewhat less in hydrogen-lean mixtures, and near zero in hydrogen-rich mixtures [3]. Since high dilution minimizes the influence of (a) in these experiments, the sensitivity of our IR method to recombination rates is determined largely by (b). Consequently, this study has been limited to near-stoichiometric and hydrogen-lean mixtures.

### Experimental Procedures

Data relating infrared emission at  $2.7\ \mu$  to elapsed time behind incident shock waves were obtained in hydrogen-oxygen-argon and, for

calibration purposes, in water vapor-argon mixtures. The 10-cm-diameter shock tube with appropriately positioned piezoelectric sensors for velocity measurements, and the apparatus for flow-filling the shock tube with unshocked gas mixtures containing water vapor, have been described previously [3, 5, 6]. Emission was viewed through a sapphire window located 1.3 cm downstream of the fourth piezoelectric sensor. Collimation was provided by two 5-mm slits separated by 51 cm, the first being 3.2 cm from the window. Radiation transmitted through a Kodak interference filter (peak transmission: 88 per cent at  $2.72\ \mu$ ; half-peak width:  $0.7\ \mu$ ) located between the two slits was focused by a slightly off-axis spherical mirror (focal length: 11 cm) onto the 2-mm-diameter sensitive element of a room-temperature, photovoltaic indium arsenide detector. The entire emission detection setup, from the shock tube window to the detector, was placed in a Plexiglas enclosure flushed continuously with dry nitrogen gas to prevent absorption of the infrared radiation by  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the atmosphere. Signals from the detector were amplified and displayed on either one or two oscilloscopes. The time resolution of the detection system is determined by the spatial resolution within the shock tube and for these experiments was approximately  $4\ \mu\text{sec}$ .

Calibration experiments were performed with this apparatus in water vapor-argon mixtures containing 1.44 per cent and 2.86 per cent  $\text{H}_2\text{O}$  at postshock temperatures and pressures of 1338–1982°K and 2.3–3.6 atm. Partial pressures of water vapor in the unshocked gas mixtures were 1.7 and 3.3 mm Hg. Emission-time profiles, which were essentially step functions at the appropriate oscilloscope sweep speeds, were obtained for the range of water vapor concentrations and temperatures used in the recombination experiments. In this manner it was possible to test for and to verify the proportionality between emission intensity and  $[\text{H}_2\text{O}]$ , and to determine the temperature dependence of the appropriately normalized emission intensity.

Useful recombination rate information was obtained from IR emission profiles measured during the shock-initiated combustion of the  $\text{H}_2\text{-O}_2\text{-Ar}$  mixtures listed in Table 1. In these

Table 1. Composition of Experimental Mixtures

Designation	Per Cent $\text{H}_2$	Per Cent $\text{O}_2$	Per Cent Ar
A-1	1.00	2.00	97.00
A-2	1.00	1.00	98.00
A-3	2.00	4.00	94.00
A-4	2.00	2.00	96.00

experiments, which were carried out at mean reaction zone temperatures and pressures of 1435–1650°K and 1.0–3.3 atm, two oscilloscopes were used to record the emission data. Different sweep speeds, and identical vertical gains, were used so that both the ultimate full equilibrium emission level (often visible only on the slow-sweep-speed traces) and the earlier region of relatively rapid recombination could be accurately measured.

A few emission-time profiles were also obtained in 1.66%  $\text{H}_2$ -0.75%  $\text{O}_2$ -97.59% Ar (2.2:1), 4.00%  $\text{H}_2$ -4.00%  $\text{O}_2$ -92.00% Ar (1:1), and 1.00%  $\text{H}_2$ -3.00%  $\text{O}_2$ -96.00% Ar (1:3) mixtures. Reduction of these data to recombination rates was hampered by additional limitations on the IR technique that will be discussed later in this paper.

## Analysis and Results

The procedure for reducing shock front position-time data to a shock velocity at the observation window has been described [6]. Standard Hugoniot computations were performed using this shock velocity to determine the conditions of interest behind the shock front.

The results of the calibration experiments are summarized in Fig. 1, which is a graph of the time-independent emission signal following the incident shock wave, normalized by the no-reaction water vapor concentration, against the

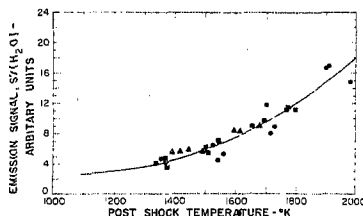


Figure 1. Calibration curve relating normalized emission signal to the postshock temperature. Curve drawn is a least-squares fit of the data from 24 experiments in the following mixtures: ● 1.44%  $\text{H}_2$ -98.56% Ar; ■ 2.86%  $\text{H}_2$ -97.14% Ar. Also plotted are normalized emission levels determined at complete equilibrium in this mixture: ▲ 1.00%  $\text{H}_2$ -3.00%  $\text{O}_2$ -96.00% Ar.

corresponding postshock temperature. Within the experimental scatter no difference is seen between the two sets of calibration experiments carried out with water vapor concentrations differing by a factor of 2. We interpret this as confirmation of the direct proportionality between the observed IR emission from water vapor and the  $\text{H}_2\text{O}$  concentration in these experiments. Also included in Fig. 1 for comparison are points relating the full equilibrium emission level, normalized by the equilibrium  $\text{H}_2\text{O}$  concentration, from seven experiments in the 1:3 hydrogen-oxygen-argon mixture and the corresponding equilibrium temperature. The proportionality between emission signal level,  $S$ , and  $[\text{H}_2\text{O}]$ , demonstrated in Fig. 1 for a total variation of more than a factor of 3 in the concentration, is believed to be a strong indication that the experimental gas mixtures are optically thin in the infrared.

The curve drawn in Fig. 1 is a least-squares computer fit of the calibration data, using the form

$$\beta(T) = S/[\text{H}_2\text{O}] = A(1 + BT + CT^2)$$

where  $B$  and  $C$  are  $-1.638 \times 10^{-3}$  and  $+7.558 \times 10^{-7}$ , respectively.  $\beta(T)$  is required in the analysis of the recombination data.

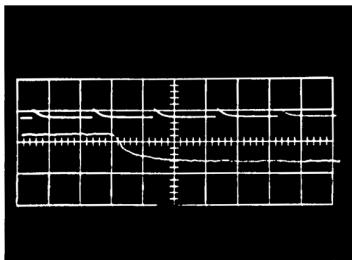


Figure 2. Fast-sweep-speed emission-time recombination oscillogram. Emission is downward. Time increases from left to right. Time marks: 100  $\mu$ sec. Mixture: A-4. Initial pressure: 10 cm Hg. Mean reaction zone temperature: 1435°K.

A fast-sweep-speed oscillogram taken in one of the recombination experiments is presented in Fig. 2. On this particular record are seen both the recombination region and the ultimate full equilibrium emission level,  $S_\infty$ . The initial deflection from the base line occurs immediately after the arrival of the shock wave at the observation window as  $H_2O$  is rapidly formed during the propagation of the main  $H_2-O_2$  chain. Later there is a fairly sharp discontinuity in the slope of the emission profile as the system passes into the recombination-limited approach to complete equilibrium.

Recombination rate data were deduced from the region following the discontinuity in slope by deriving a curve of  $S/S_\infty$  versus relative laboratory time,  $\tau$ , for each experiment. The use of  $S_\infty$ , the only observed emission level that could be readily related to known values of  $[H_2O]$  and temperature, that is,  $[H_2O]_\infty$  and  $T_\infty$ , as an internal calibration standard was required because of variations between experiments in the absolute value of  $S$  at any extent of reaction. This variation is illustrated in Fig. 1 by the scatter in the equilibrium emission levels obtained in the 1:3 experiments. A graph of  $S/S_\infty$  versus  $\tau$  for the experiment represented in Fig. 2 appears in Fig. 3. Calculations described

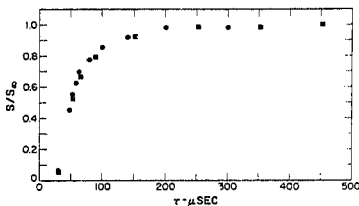


Figure 3. Time dependence of the normalized emission,  $S/S_\infty$ , for the experiment shown in Fig. 2. Abscissa is relative time in laboratory coordinates.  $\circ$  Data from fast-sweep record in Fig. 2.  $\blacksquare$  Data from slow-sweep record (200  $\mu$ sec/division) for same experiment.

below indicate that in this experiment the slope of the curve is controlled by the recombination rate only in the region of  $S/S_\infty$  between about 0.48 and 1.0.

It was not possible to deduce normalized emission profiles from the oscillograms obtained in a few experiments. For example, in the lowest density experiments in mixture A-2 and in all experiments in the 1.66%  $H_2$ -0.75%  $O_2$ -97.59% Ar mixture mentioned earlier, the time-independent level,  $S_\infty$ , was still being approached at large distances behind the shock front where interfering factors normally present became significant. On the other hand, in the 1.00%  $H_2$ -3.00%  $O_2$ -96.00% Ar mixture recombination at normal densities was so rapid that, although  $S_\infty$  was well determined, it was difficult to resolve satisfactorily the approach to equilibrium. Finally, in a few experiments  $S_\infty$  and the entire recombination profile were obscured by large oscillations in the emission level as the reaction proceeded. This phenomenon, which was quite reproducible, was observed only when relatively large concentrations of hydrogen and oxygen were present in the reaction zone (i.e., the highest-density experiments in mixture A-3 and all experiments in the 4.00%  $H_2$ -4.00%  $O_2$ -92.00% Ar mixture) and is believed due to the appearance of detonation-like behavior under these particular experi-

mental conditions. These observations and limitations on the IR method will be given additional consideration in the section headed "Discussion and Conclusions."

Recombination rates were determined from the  $S/S_\infty$  profiles described above by employing the partial equilibrium approximation in a manner closely paralleling the treatment used in the earlier OH absorption investigations [3-5]. As described below,  $S/S_\infty \tau$  data were converted into profiles relating  $v$ , a nondimensional progress variable decreasing from 1 to 0 as the system approaches complete equilibrium [3], and  $\tau$ . The rate of change of  $v$  with  $\tau$ ,  $dv/d\tau$ , as determined numerically by a quadratic least-squares fit of the  $v$ - $\tau$  information and differentiation at any  $v$ , was then used to compute the rate of recombination at any given  $v$  value from the fundamental relationship [3]

$$-\frac{p_0}{RT_0} (1 - N_{eq}) \frac{dv}{d\tau} = R_{rec} \quad (1)$$

In Eq. 1,  $p_0$  and  $T_0$  are the pressure and temperature of the initial, unshocked  $H_2$ - $O_2$ -Ar gas mixture.  $N_{eq}$  is the ratio of the number of moles in the system at complete equilibrium to the number present before the reaction began (typically in the range 0.9980-0.995 for these mixtures), and  $R_{rec}$  is the net rate of recombination at  $v$  (moles disappearing/cc-sec).

The value of  $v$  corresponding to the experimental  $S/S_\infty$  at any  $\tau$  was obtained by interpolation on graphs prepared for each experiment, showing the computed monotonic increase of  $S/S_\infty$  with decreasing  $v$ . These graphs in turn were produced by combining (a) partial equilibrium Hugoniot computations (i.e., those using the restrictive condition provided by the assumption that reactions I-III are in equilibrium at all  $v \leq 1$ ) to obtain all of the concentrations, the temperature, and the density at various  $v$ 's, and (b) the temperature dependence of  $S/[H_2O]$ ,  $\beta(T)$ , determined from Fig. 1. The procedural details are given in the reference thesis [8].

As a final step in the analysis, the recombination rates,  $R_{rec}$ , computed from Eq. 1 have been expressed as termolecular rate coefficients for the dominant recombination reaction in hydrogen-lean mixtures [3, 5]



to facilitate a comparison with previous OH results. Thus, at any  $v$ ,  $R_{rec}$  is equal to the rate of the substantially irreversible reaction IV, or

$$R_{rec} = k^{eff} [H][O_2][Ar] \quad (2)$$

As noted in an earlier paper [3], the equality expressed in Eq. 2 is independent of the fate of  $HO_2$ , provided the reaction(s) consuming  $HO_2$  (a) do not change the total number of moles present in the system, and (b) are sufficiently rapid that  $[HO_2]$  is kept quite small.

To a good approximation in dilute mixtures like A-1 to A-4, only argon and water vapor contribute significantly as third bodies to the effective coefficient,  $k^{eff}$ , in Eq. 2 [3, 5]:

$$k^{eff} = k^{Ar} \left\{ 1 + a_{H_2O} \frac{[H_2O]}{[Ar]} \right\} \quad (3)$$

where  $a_{H_2O}$  is the ratio  $k^{H_2O}/k^{Ar}$ .

Equations 1-3 have been solved for  $k^{Ar}$  at various  $v$  values in each experiment. The slopes  $dv/d\tau$  and concentrations corresponding to each  $v$  were determined in the manner described above. The correction required to reduce  $k^{eff}$  to  $k^{Ar}$  assumed [5]  $a_{H_2O} = 25$  and amounted to, at most, approximately one third of  $k^{eff}$ .

The results of these computations at  $v = 0.40$  are presented in Table 2. This particular value of  $v$ , which corresponds to  $S/S_\infty = 0.76$  in Fig. 3, was chosen because it consistently fell in the region where the experimental data provide the most accurate determination of  $dv/d\tau$ , and hence  $R_{rec}$ . It should be pointed out, however, that no systematic variation in  $k^{Ar}$  with  $v$  was observed. The essential independence of these two quantities is illustrated in Fig. 4 for the experiment shown previously in Figs. 2 and 3.

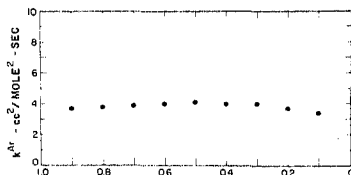
The average value of  $k^{Ar}$  for the twenty-six

Table 2. Summary of Experimental Results

Mixture	$\bar{T}$ , °K	$P_{O_2}$ , cm Hg	$R_{rec}^a$ , 10 <sup>-5</sup> mole/cc-sec	$k^{eff a}$ , 10 <sup>15</sup> cc <sup>2</sup> /mole <sup>2</sup> -sec	$[H_2O]/[Ar]^a$	$k^{Ar a}$ , 10 <sup>15</sup> cc <sup>2</sup> /mole <sup>2</sup> -sec
A-1	1559	10.01	28.2	3.8	0.009	3.1
	1573	5.00	2.86	3.1	0.009	2.5
	1605	4.99	4.75	5.2	0.009	4.3
	1650	5.01	5.20	5.7	0.009	4.6
A-2	1521	15.01	29.7	2.6	0.009	2.1
	1536	10.00	10.8	3.2	0.008	2.7
	1554	10.00	11.1	3.4	0.008	2.8
	1561	15.01	34.7	3.1	0.009	2.5
A-3	1444	10.01	127.2	4.8	0.019	3.3
	1539	5.00	11.3	3.4	0.019	2.3
	1587	5.01	9.02	2.7	0.019	1.8
	1601	5.01	10.6	3.2	0.019	2.2
	1622	12.01	86.1	1.9	0.018	1.3
	1634	10.01	70.1	2.7	0.019	1.8
	1647	9.99	86.3	3.4	0.018	2.3
A-4	1435	10.01	64.3	5.9	0.017	4.1
	1519	10.00	58.3	5.2	0.017	3.6
	1555	14.99	76.8	2.1	0.017	1.5
	1576	14.99	50.3	1.4	0.017	1.0
	1603	5.00	8.08	5.9	0.017	4.2
	1604	5.00	6.03	4.4	0.017	3.1
	1612	4.99	6.34	4.7	0.017	3.3
	1615	9.99	37.6	3.4	0.017	2.4
	1620	5.00	14.7	10.8	0.017	7.6
	1632	15.01	142.9	3.8	0.017	2.7
	1650	9.99	62.5	5.8	0.017	4.0

<sup>a</sup> Evaluated at  $v = 0.40$ .

experiments in mixtures A-1 to A-4 listed in Table 2 is  $3.0 \times 10^{15}$  cc<sup>2</sup>/mole<sup>2</sup> sec with a standard deviation of  $1.3 \times 10^{15}$  cc<sup>2</sup>/mole<sup>2</sup> sec. As expected for a termolecular rate coefficient,  $k^{Ar}$  is independent of temperature over the narrow range covered by the experiments.

Figure 4. Relationship between computed  $k^{Ar}$  and  $v$  for the experiment shown in Figs. 2 and 3.

## Discussion and Conclusions

Before comparing these results with earlier measurements it will be helpful to consider in more detail the important limitations on, and the opportunities provided by, the infrared method presented here for studying recombination in dilute hydrogen-oxygen mixtures. It is evident from the foregoing that the usefulness of this technique is quite restricted. This is so primarily because of (a) the relative insensitivity of mole fraction  $H_2O$ , and hence emission intensity, to changes in  $v$ , and (b) the requirement that  $S_{\infty}$  be determined in each experiment. In contrast, the OH absorption method [3-6] provides a considerably increased sensitivity with  $[OH]$  decreasing several orders of magnitude between  $v = 1$  and  $v = 0$  (the first two decades

or so of which can be followed quantitatively) and an absolute, although somewhat uncertain, calibration [5]. As seen earlier, (a) and (b) impose relatively severe composition and gas density limitations on the IR method.

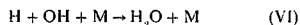
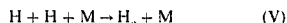
On the other hand, under conditions where this method is applicable it provides the opportunity to test fundamental aspects of the recombination process. In particular, the partial equilibrium approximation, the supposed recombination mechanism, and the accuracy of previously reported termolecular rate coefficients can be checked by comparing the IR results with earlier independent measurements. Previously, such tests have been confined largely to recombination in hydrogen-rich mixtures where independent data were available from both OH absorption shock tube experiments and numerous flame studies. Partial equilibrium in near-stoichiometric and hydrogen-lean mixtures has been tested previously by (a) comparing the maximum mole fraction of OH observed during reaction in OH absorption shock tube experiments [2] with the value computed for  $\nu = 1$ , and (b) determining both  $[\text{OH}]$  and  $[\text{O}]$  in several slightly lean flames at  $\nu$ 's very nearly equal to zero [9]. Limitations on flame stability have made it difficult to obtain unambiguous recombination rate information in flame studies in lean mixtures [10, 11].

The average value  $3.0 \pm 1.3 \times 10^{15} \text{ cc}^2/\text{mole}^2 \text{ sec}$  for  $k^{\text{Ar}}$  obtained in these experiments compares quite favorably with the value  $2.2 \times 10^{15} \text{ cc}^2/\text{mole}^2 \text{ sec}$  recently determined in experiments at comparable temperatures in which OH absorption was measured behind incident shock waves [5]. This most recent OH number is believed to be more accurate than an earlier, somewhat lower value [3] determined by using a semiempirical absorbance- $[\text{OH}]$  calibration that did not take into account suitable features of the relationship since recognized as important. The IR result is in excellent agreement with the value  $3.3 \times 10^{15} \text{ cc}^2/\text{mole}^2 \text{ sec}$  determined by Gutman et al. at 1100°K in a shock tube study

of the inhibiting effect of reaction IV on chain branching in the hydrogen-oxygen reaction [12].

The agreement with the OH coefficient is particularly significant since it provides a means of testing the assumptions involved in the reduction of the two types of reaction profiles to rate coefficient values. It should be noted that the independently determined recombination rates themselves could not be compared directly because of unavoidable differences in experimental conditions. Expressing the IR rates as effective coefficients,  $k^{\text{eff}}$ , or as  $k^{\text{Ar}}$ , for the dominant termolecular reaction IV, made such a direct comparison possible. The observed agreement between the two essentially independent sets of results over the range of temperatures, densities, initial  $\text{H}_2/\text{O}_2$  ratios, and  $\nu$  values covered in the various experiments is convincing evidence of the essential correctness of our present understanding of the recombination process in lean hydrogen-oxygen mixtures. As such it constitutes excellent, albeit indirect, confirmation of the validity of the concept of partial equilibrium over nearly the entire extent of recombination,  $1 \geq \nu \geq 0$ . In this sense it is believed to be the most complete experimental test of partial equilibrium yet reported.

A further comparison of OH and IR rate data is possible at those limiting conditions, that is,  $\text{H}_2/\text{O}_2$  ratios and densities, where the IR emission profiles cannot be reduced to recombination rate information. In these cases the experimental IR profiles have been compared with ones predicted by numerical computations using a reasonable set of bimolecular reactions and rate coefficients, and values for the rate coefficients for the important termolecular reactions, IV-VI,



recently determined in OH experiments [5]. As anticipated from partial equilibrium consid-

erations, the predicted profiles in the recombination region are independent of the values of the bimolecular coefficients. The qualitative agreement between the predicted and experimental recombination profiles over a wide range of conditions, including  $2.2 \geq (H_2/O_2)_0 \geq 0.33$ , is quite striking. For this reason we believe that the IR results provide confirmation of the significant features of recombination in the hydrogen-oxygen system over a considerably wider range of conditions than those reported in Table 2.

All of the preceding discussion presumes that emission from OH at  $2.7 \mu$  did not influence the results of this study in any significant way. It is readily apparent from the experimental profiles themselves that the bulk of the emission measured at any  $\tau$  in these experiments came from  $H_2O$ . This is so because, in contrast to the time variation of  $[H_2O]$ ,  $[OH]$  peaks at  $v=1$  and then decays to nearly zero at long times. Typically, the ratio  $[H_2O]/[OH]$  is about 5 at  $v=1$ , 10 at  $v=0.40$ , and  $10^3$  at  $v=0$ . Contributions from OH to the total emission intensity would, therefore, be expected to be greatest at  $v$  values close to 1. We interpret the absence of any systematic dependence of  $k^{Ar}$  on  $v$ , as demonstrated in Fig. 4, to mean that emission from OH is of negligible importance at even  $v$  values approaching 1.

Finally, it should be mentioned that in the present investigation of recombination in hydrogen-oxygen mixtures IR experiments were carried out throughout the range of conditions where the technique could profitably be utilized. It is possible that, in the analysis of profiles obtained near the limiting conditions imposed by particularly slow recombination rates, the quantity called  $S_v$  was not equal, as it should have been, to the equilibrium value  $S_{v=0}$ . In particular, in the lowest density experiments the slow approach of  $S$  to  $S_{v=0}$  at long times might have produced a positive slope,  $dS/d\tau$ , that would be too small to detect on the oscillograms. Choosing a value  $S_\infty < S_{v=0}$  in these experi-

ments would have led to calculated recombination rates and hence  $k^{eff}$ 's at any  $v$  value that were too large. Numerical reaction profile computations have demonstrated that a small effect of this type may have been the cause of the generally larger values of  $k^{Ar}$  obtained in the lowest density ( $p_0 = 5$  cm Hg) experiments listed in Table 2. Similarly, a value  $S_\infty > S_{v=0}$  would yield rate coefficients that were too small. Evidence that this may have happened in a few of the experiments containing the highest concentration of reactants (i.e., those most susceptible to the detonation-like behavior described earlier) was seen in the generally larger ratios  $S_\infty/[H_2O]_\infty$  and lower  $k^{Ar}$ 's (Table 2) in the  $p_0 = 12$  and 15 cm Hg experiments in mixtures A-3 and A-4.

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