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# A laser-induced fluorescence determination of the complete internal state distribution of OH produced in the reaction: $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$

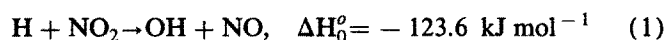
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Laser-induced fluorescence (LIF) spectra have been recorded of OH radicals produced when H atoms and NO<sub>2</sub> react in thermal energy collisions in the region where two uncollimated beams containing the reagents intersect. Spectra of the (0,0) and (1,1), (0,1) and (1,2), and (0,2) and (1,3) bands of the  $A^2\Sigma^+ - X^2\Pi$  system have been observed. Distributions of OH over the whole energetically accessible range of rovibrational levels have been determined using surprisal analysis to deduce complete rotational distributions from the observed distributions over high rotational levels ( $N \geq 10$ ). Both the vibration and rotation of OH are more excited than expected on a purely statistical basis, the average fractional yields of energy being  $\langle f_{\text{vib}} \rangle_{\text{OH}} = 0.23$  and  $\langle f_{\text{rot}} \rangle_{\text{OH}} = 0.29$ . Mild preferences are also found for the lower  $^2\Pi_{3/2}$  spin-orbit component and for the  $\Pi(A')$   $\Lambda$ -doublet levels. The last finding is consistent with reaction via a short-lived HONO complex with some consequent constraint to planarity. The paper immediately following this one describes experiments on the energy disposal into the NO product of the H + NO<sub>2</sub> reaction and the collision dynamics of this radical-radical reaction are discussed in that paper.

## I. INTRODUCTION

There are still rather few definitive experimental results on the dynamics of radical-radical reactions which proceed over a potential energy surface with a deep "well" and with attractive potentials between both the reagents and the products. The reaction



has become established as a prototype for this kind of reaction, since it can be studied relatively easily and it can—and the evidence is that it does—proceed across a potential energy surface corresponding to the ground state of the nitrous acid, HONO, molecule. The reaction (and its deuterated counterpart) are also important because they can be investigated by an unusually wide variety of experimental methods: molecular beams,<sup>1</sup> electron paramagnetic resonance spectroscopy,<sup>2</sup> infrared chemiluminescence (IRC),<sup>3-6</sup> and laser-induced fluorescence (LIF),<sup>7-9</sup> allowing results obtained from the applications of these different techniques to be critically evaluated.

In principle, both IRC and LIF observations can provide complete information about the internal state distributions in the  $^2\Pi$  electronic ground states of both OH and NO. In practice, results on the NO product have proved difficult to obtain. Setser's group<sup>5</sup> have observed rotationally unresolved IRC from vibrationally excited NO and estimated a ratio of rate constants into the ( $v=1$ ) and ( $v=2$ ) levels of NO of 70:30. More recently, LIF spectra of the nascent NO product have been recorded. Sauder and Dagdigian<sup>9</sup> have reported observations on NO in levels from  $v=0$  to  $v=2$ . In work in our own laboratory, reported in the paper<sup>10</sup> following this one, we have observed

NO in vibrational levels up to and including  $v=3$ . Measurements on NO are valuable for two reasons. First, they provide a direct check on estimates,<sup>5(a)</sup> made by energy balance, that approximately 30% of the energy liberated in reaction (1) is released into the vibration and rotation of NO. Second, the release of energy into the vibration of NO corresponds to the excitation of the "old bond" in the reaction. This would not be expected to occur in a direct reaction, so the observation of vibrationally excited NO is evidence for the importance of collision complexes in reaction (1).

IRC and LIF methods have already been used quite extensively to examine the internal state distributions of the OH produced in reaction (1). To some degree, the two methods provide complementary information. IRC experiments have been performed in both the low pressure, "arrested relaxation" mode where near nascent rotational level populations are observed and in fast flow reactors, in which rapid rotational, but not vibrational, relaxation takes place. In the most recent studies by Setser's group,<sup>5</sup> agreement between the OH vibrational distributions (for  $v=1-3$ ) derived from use of the two different apparatuses has been excellent. Earlier uncertainties regarding the calculated values of the Einstein emission coefficients<sup>11</sup> for the vibration-rotation transitions of OH appear to have been resolved recently<sup>12</sup> and can no longer be viewed as a possible source of error in the populations derived from IRC spectra.

In contrast to IRC experiments, studies using LIF can determine the population of OH produced in the  $v=0$  vibrational level. However, LIF measurements on OH encounter two difficulties. First, the  $\Delta v=0$  diagonal transitions in the  $A^2\Sigma^+ - X^2\Pi$  system of OH are very much

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stronger than the off-diagonal bands.<sup>13</sup> Second, all the rotational states above  $A^2\Sigma^+$  ( $v=0, N=25$ ;  $v=1, N=17$ ;  $v=2, N=4$ ) have very low fluorescence quantum yields on account of strong predissociation. Before the study reported here, LIF measurements on OH produced in the  $H + NO_2$  reaction had been restricted to products in  $X^2\Pi$  ( $v=0$  and  $1$ ), use being made of the strong  $\Delta v = 0$  diagonal transitions in the  $A^2\Sigma^+ - X^2\Pi$  band system. In our experiments, following the lead of Wiesenfeld and his co-workers,<sup>14</sup> we have observed OH in all the vibrational levels,  $v=0-3$ , accessible via reaction (1), by exciting the much weaker  $\Delta v = -1$  and  $\Delta v = -2$  bands using the output from a tunable pulsed dye laser. A second novel feature of our experiments is that the  $NO_2$  reagent is diluted in a noble gas and admitted to the reaction chamber through a pulsed nozzle. Consequently, the rotational excitation of the gas is very low. As the reduced mass of the colliding reagents is also small, the overall angular momentum in the system is quite restricted, and, in principle, the interpretation of the collision dynamics should be simplified.

Finally, we note that because both OH and NO have  $^2\Pi$  electronic states, high resolution spectroscopic methods, such as LIF, allow one to determine, in addition to the vibrational and rotational state distributions, branching ratios into the different spin-orbit components of each ground state species and any preference for one or other of the  $A'$  or  $A''$   $\Lambda$ -doublet levels.<sup>15</sup>

## II. EXPERIMENTAL

In order to determine OH state distributions, laser excitation spectra have been recorded of bands in the  $A^2\Sigma^+ - X^2\Pi$  system using a pulsed dye laser. The tunable output from the laser probes the region in a low pressure reactor where uncollimated jets containing  $NO_2$  and H atoms intersect.

The central part of the apparatus is shown schematically in Fig 1. The reaction chamber, constructed from brass, is cylindrical in shape with a diameter of 30 cm and a height of 10 cm. A 9 in. oil diffusion pump is mounted directly below this vessel and is backed by a combination of a  $700 \text{ l min}^{-1}$  rotary pump (Edwards, model E2M40) and a mechanical booster, or Roots blower (Edwards, EH250). These pumps can evacuate the reaction chamber to below  $10^{-6}$  mbar.

In the experiments reported here, a mixture of H atoms and  $H_2$  entered the reaction chamber from a separate discharge-flow system which is pumped by a  $450 \text{ l min}^{-1}$  rotary pump (Edwards, ISC450B). In this system hydrogen at ca 1 mbar flowed from a cylinder (BOC, zero grade; min. purity, 99.99%) through a 2450 MHz microwave discharge which was operated at 120 W (Electromedical Supplies, Microtron 2000). Before reaching the discharge the hydrogen was bubbled through water at room temperature to maximize the extent of its dissociation to atoms.<sup>16</sup> Standard gas-phase titrations with  $NO_2$  (Ref. 17) established that ca 10% dissociation of the  $H_2$  was achieved under our conditions. A small fraction of the total flow of discharged hydrogen was admitted to the main reaction

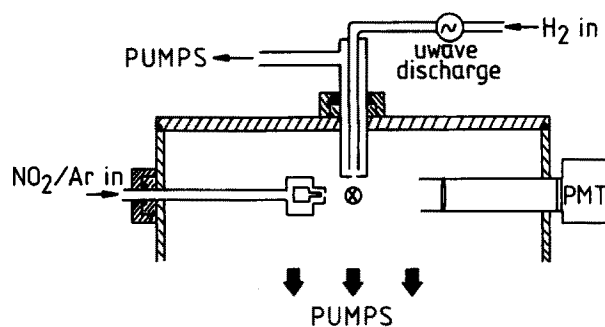


FIG. 1. Schematic diagram of the central part of the apparatus. The laser beam is perpendicular to the plane of this representation, probing the region indicated by the symbol  $\otimes$ .

vessel via a 1 mm diam hole in the base of an injector which is mounted through the top plate of the chamber (see Fig. 1). This hole is approximately 15 mm above the region probed by the laser beam.  $NO_2$  was admitted to the reaction chamber through an unskimmed pulsed nozzle, which was similar in design to those based on fuel injector valves.<sup>18</sup> It was pulsed at 10 Hz, the same repetition rate as the laser.

LIF spectra of OH were recorded using a variety of mixtures and total pressures in the nozzle source. The gas mixture contained 2.5–5 %  $NO_2$  diluted in He or Ar, and the total pressure “behind” the nozzle was usually in the range 650–950 mbar. Sometimes  $O_2$  was added in an attempt to suppress any NO impurity. In other experiments, the composition and pressure of the gas was varied to examine whether any significant contribution to the observed OH spectra resulted from the reaction of H atoms with weakly bound,  $NO_2$ -containing, complexes which might be formed in the gas expansion. To check this possibility spectra were recorded: (i) with the Ar diluent replaced by He, (ii) with reduced  $NO_2$  content and reduced total pressure of the mixture behind the nozzle, and (iii) with the  $O_2$  omitted from the gas mixture. To prepare the standard gas mixture, an equimolar mixture of  $NO_2$  (BDH; min. purity, 99.5%) and  $O_2$  (BOC, zero grade; min. purity, 99.97%) was first prepared at approximately 1 bar pressure and, after at least several hours, part of this mixture was withdrawn and diluted in argon.

The conditions in the pulsed nozzle produced substantial cooling in the expanded gas (see below). The gas jet propagates horizontally and the nozzle assembly is mounted inside the reaction chamber so that the 0.5 mm diam exit orifice is ca 30 mm from the volume probed by the laser beam. The gas pulses last ca 1 ms and the 500  $\mu$ s delay between the signal which opens the nozzle and the laser firing was selected to optimize the LIF signals. With both discharged hydrogen and the  $NO_2/O_2/Ar$  mixture being admitted to the chamber, the total background pressure was about  $2 \times 10^{-4}$  mbar, as measured by an ionization gauge mounted on the top plate of the reaction chamber.

The laser radiation passed through the center of the region where the two gas jets crossed in a direction perpendicular to both of them. The laser beam enters through

TABLE I. Origins and oscillator strengths of the OH( $A^2\Sigma^+ - X^2\Pi$ ) bands observed by LIF. Method of excitation and observation are given together with an estimate of the laser pulse energy.

Band	Band origin nm	$f$ -number	Methods of excitation and observation	Pulse energy $\mu\text{J}$
0,0	308.6	$1.1 \times 10^{-3}$	DMQ dye in <i>c</i> -hexane plus 1 anti-Stokes Raman shift	< 1
1,1	314.2	$6 \times 10^{-4}$	in $\text{H}_2$ , No filtering of the fluorescence	
0,1	346.8	$5 \times 10^{-6}$	TMQ dye in 10% methanol/ <i>p</i> -dioxane solution; PTP	< 200
1,2	351.9	$6.5 \times 10^{-6}$	dye in dioxane for shortest wavelengths. To observe both bands, (0,0) and (1,1) fluorescence was observed through a combination of broadband filters and interference filter centered at 310 nm. To observe (1,2) only, (1,0) emission was observed through an interference filter centered at 280 nm.	
0,2	393.3	$1 \times 10^{-7}$	PPBO dye in dioxane solution. Filtering as for observations	< 500
1,3	397.1	$7 \times 10^{-7}$	on (0,1) and (1,2) bands.	

one 30 cm long sidearm containing conical-shaped baffles and after passing through the reaction zone it exits the chamber through a similar baffle arm. Before the laser enters the reaction chamber, a small percentage of the laser radiation is reflected off a quartz plate through a piece of frosted quartz, and on to an ultraviolet-sensitive photodiode. The signal from this photodiode was used to observe how the laser intensity varied as its frequency was scanned and an LIF spectrum of OH was recorded.

Part of the fluorescence from OH induced by the laser was collected by a single  $f/1$  Spectrosil lens and was directed, through appropriate filters, on to an uncooled photomultiplier tube (EMI 9781 B). The dye laser is a Lambda-Physik model FL2002, pumped by a Lumonics model 420 excimer laser operating at 10 Hz on XeCl at 308 nm. Signals from the photomultiplier passed through a gated integrator/signal averager (Stanford Research Systems, model SRS 250) to either a chart recorder or, in later experiments, a microcomputer. The time constant of the electronics was set at 3 s, during which time the laser scanned ca  $0.25 \text{ cm}^{-1}$ . Signals from the photodiode were recorded simultaneously so that the LIF intensities could be corrected for variations in laser intensity.

In each series of experiments, a pair of bands in the OH ( $A^2\Sigma^+ - X^2\Pi$ ) system was excited. The two bands in each pair came from neighboring vibrational levels in the  $X^2\Pi$  ground state and have the same value of  $\Delta v$ . The  $\Delta v = -1$  and  $\Delta v = -2$  bands could be accessed directly using fundamental output from the dye laser. To reach the shorter wavelengths of the (0,0) and (1,1) bands, radiation from the dye laser was focussed through a stainless steel cell containing 8 bar of  $\text{H}_2$ . The first anti-Stokes Raman-shifted output was then used to excite the OH (0,0) and (1,1) bands. The bands which were excited, together with the laser dyes and the optical filters used to isolate fluorescence, are listed in Table I. In all cases, fluorescence in the strong (0,0) and (1,1) bands was observed.

Care was taken to ensure that spectra were recorded in the absence of saturation effects. Table I lists the oscillator strengths of the bands of OH which were excited in the

present experiments. For the relatively strong (0,0) and (1,1) bands, the Raman-shifted dye laser output was passed through a quartz cuvette containing a dye solution which reduced the laser intensity by 100–1000 times to below  $1 \mu\text{J}$  per pulse. For the much weaker (0,1) and (1,2) bands, the laser energy was reduced to  $\leq 200 \mu\text{J}$  and for the very weak (0,2) and (1,3) bands to  $\leq 500 \mu\text{J}$ . In all cases, checks for saturation were made by comparing the observed relative intensities of lines from the strong, main branches and from weak, satellite branches with the ratios of intensities predicted theoretically. These tests confirmed that the laser powers used to record spectra were too small to cause saturation effects.

### III. SPECTROSCOPY AND DATA ANALYSIS

In the present work, OH state populations have been derived by measuring relative LIF intensities of lines in the  $A^2\Sigma^+ - X^2\Pi$  electronic band system. The two spin-orbit components of the  $^2\Pi$  ground state of OH are "inverted". The  $F_1$  levels belong to the lower  $^2\Pi_{3/2}$  component and have  $N = J - \frac{1}{2}$ , whereas the  $F_2$  levels belong to the upper  $^2\Pi_{1/2}$  component and have  $N = J + \frac{1}{2}$ . For a given vibrational sub-band (i. e., from  $^2\Pi_{3/2}$  or  $^2\Pi_{1/2}$ ), there are six branches. For example, transitions to  $A^2\Sigma^+$  from the  $F_1$  levels give rise to three main branches,  $P_{11}$ ,  $Q_{11}$ , and  $R_{11}$ , together with an equal number of "satellite" branches,  $^qP_{21}$ ,  $^rQ_{21}$ , and  $^sR_{21}$ .<sup>19</sup>

In addition, each rotational level of the  $^2\Pi$  electronic ground state is split into a closely spaced  $\Lambda$ -doublet, the two levels corresponding to different linear combinations of the  $+\Lambda$  and  $-\Lambda$  projections of the electronic orbital angular momentum.<sup>15</sup> The magnitude of the  $\Lambda$ -doublet splitting increases with increasing  $N$ , and is accompanied by a transition from Hund's case (a) to case (b). Here, we follow the recent recommendation<sup>15</sup> that the  $\Lambda$ -doublet levels of OH should be labelled  $\Pi(A')$  or  $\Pi(A'')$  according to whether, for a given series of levels, the electronic wave function at high  $J$  is symmetric or antisymmetric with respect to reflection of the spatial coordinates of the electrons in the plane of rotation. In this notation, the main  $Q$

branch transitions in the  $A^2\Sigma^+ - X^2\Pi$  transition originate from the  $\Pi(A'')$  components, the main  $P$  and  $R$  branch lines from the  $\Pi(A')$  components and therefore any propensity for reaction (1) to populate one or other  $\Lambda$ -doublet can be determined by comparing the intensity in different branches of the spectrum. The important distinction in regard to the dynamics of photodissociation or reaction is that they correspond to different directions of the  $p\pi$  orbital containing the unpaired electron with respect to the rotation plane of the OH radical. However, this distinction only becomes entirely clear in the limit of high  $N$  or  $J$ , i.e., in pure Hund's case (b). Then the  $\Pi(A')$  state is that with the unpaired electron in the  $p\pi_x$  orbital in the plane of rotation, and  $\Pi(A'')$  has the unpaired electron in the  $p\pi_y$  orbital perpendicular to the plane of rotation. The situation at low  $J$ , where each  $\Lambda$ -component is associated with a linear combination of the two  $p\pi$  orbital functions and the degree of electron alignment falls below its limiting high  $J$  value, has been considered in detail by Andresen and Rothe.<sup>20</sup>

The measured signal for any resolved line in the LIF spectrum is related to the population  $N_{v,J,p}$  of the  $p$ th fine-structure component (spin-orbit and  $\Lambda$ -doublet) of a rovibrational ( $v,J$ ) level by the expression<sup>21</sup>

$$Sg(v',J',p';v,J,p) = C\rho(\lambda_{v',J',p';v,J,p})B_{v',J',v,J}N_{v,J,p} \times \sum_{v'',J'',p''} A_{v',J',p';v'',J'',p''} R_{JJ''} P(\lambda_{v',J',p';v'',J'',p''}), \quad (2)$$

where  $C$  is a proportionality constant which includes geometric factors,  $\rho$  is the density of the laser energy at the wavelength  $\lambda_{v',J',p';v,J,p}$  of the  $v',J',p';v,J,p$  transition, and  $B_{v',J',v,J}$  is the Einstein  $B$  coefficient of the  $v',J';v,J$  transition. In the summation for  $Sg$ , the summation over the states  $v'',J'',p''$  and the detector polarizations  $\hat{n}_d$  takes account of the fact that the polarization and wavelength of the fluorescence are not resolved.  $A_{v',J',p';v'',J'',p''}$  are the Einstein spontaneous emission coefficients for individual lines in the  $A^2\Sigma^+ - X^2\Pi$  spectrum,  $R_{JJ''}$  expresses the dependence of the LIF signal on the laser and detector polarizations and  $P(\lambda_{v',J',p';v'',J'',p''})$  allows for variation in the sensitivity of the photomultiplier plus filter(s) over the range of fluorescing wavelengths.

Individual lines in recorded spectra were assigned by comparison with a table of line positions which was prepared using the equations given by Dieke and Crosswhite.<sup>22</sup> Because of the relatively wide bandwidth of the laser, not all lines were resolved. First, some lines originating from different rovibrational levels were blended. This occurred wherever line positions were less than about  $1\text{ cm}^{-1}$  apart but was particularly troublesome in the congested regions near bandheads. Second, main and satellite branch lines overlapped at low  $N$ . This problem decreased for higher  $N$  as the main and satellite lines diverge and as the intensity of the latter decrease. Pairs of main and satellite lines were adequately resolved for  $N \geq 6$ .

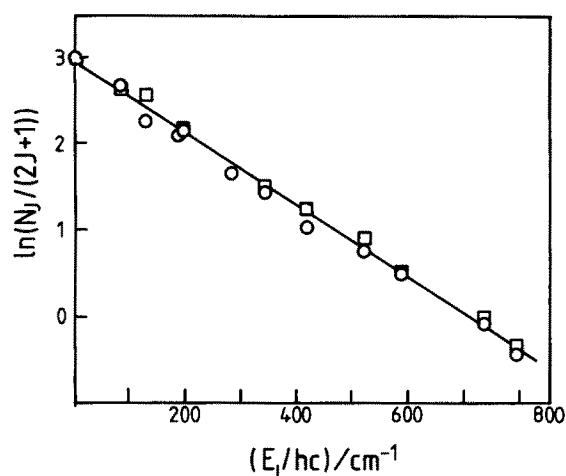


FIG. 2. Boltzmann plot of rotational populations in OH( $v=1$ ) under conditions where complete relaxation was to be expected. Populations derived from measurements in the  $Q$  branches ( $\square$ ) fall on the same line as those from the  $P$  and  $R$  branches ( $\circ$ ) indicating the absence of any effects from polarization anisotropy.

As already indicated, in most experiments the spectrum of a pair of bands (0,0 and 1,1; 0,1 and 1,2; or 0,2 and 1,3) was recorded. The variation of laser intensity was measured simultaneously and used to provide values of the factor  $\rho(\lambda_{v',J',p';v,J,p})$  in Eq. (2). The factor  $C$  was assumed to be the same for all wavelengths. The last two factors that had to be applied in order to convert the observed signals to relative populations arise from variations in the absorption line strengths and in the measurement of fluorescence intensities from different  $A^2\Sigma^+$  rovibrational levels. When the diagonal (0,0) and (1,1) bands are excited, fluorescence is overwhelmingly concentrated in the same, resonant, vibrational transitions. In such experiments, the fluorescence was observed unfiltered, the photomultiplier response was assumed to be constant over the narrow wavelength range of fluorescence, and no correction was made for different efficiencies of fluorescence detection. If polarization anisotropy was important in our experiments, its effects would be most pronounced (i.e., differences between the  $R_{JJ''}$  for different lines would be greatest) when comparing  $Q$ -branch transitions with  $P$ - and  $R$ -branch lines. Such comparisons are made principally to derive the relative populations in the  $\Pi(A')$  and  $\Pi(A'')$   $\Lambda$ -doublet components (see above). Therefore, it was important to test whether such effects were significant under our conditions. This was done by recording spectra with the distribution of OH over rotational levels clearly thermalized. Appropriate conditions were achieved by switching off the diffusion pump to the main chamber so that background pressure rose to ca 0.2 mbar. Figure 2 shows a "rotational Boltzmann plot" for OH( $v=1$ ) derived from a spectrum recorded under these conditions, assuming the  $R_{JJ''}$  factors to be unity for all lines. It is clear that the rotational distribution is thermalized ( $T_{\text{rot}} = 350 \pm 10\text{ K}$ ), and that populations derived from  $Q_{11}$ ,  $P_{11}$  and  $R_{11}$  branches all fall on the same line. This finding demonstrates that no significant effects arise as a result of any polarization of the laser

radiation combined with observation of the fluorescence over a restricted range of solid angles. We have therefore assumed that there are no effects of polarization anisotropy in our low pressure measurements, and have calculated populations of individual  $v, J, p$  states by dividing the corrected line intensities  $(Sg/C\rho)_{vJ,p;v,J,p}$  by the Einstein  $B$  coefficients for individual lines tabulated by Crosley and Chidsey.<sup>23</sup>

To derive populations from the (0,1), (1,2) and (0,2), (1,3) spectra, it was necessary to allow for the variation of the filter transmission over the wavelength range of the (0,0) and (1,1) fluorescing bands. To do this, the transmission curve of the filter was measured and then matched to a spline function determined computationally. This allowed us to calculate a factor for each absorption line which corresponded, in effect, to a weighted mean of the transmission of the filter over all the possible fluorescing transitions. In estimating this factor, it was assumed, as before, that the response of the photomultiplier tube was constant, which is reasonable as it was used close to the maximum of its sensitivity. Line intensities were divided by these factors and also by Einstein  $B$  coefficients.<sup>14(b)</sup>

As part of our data treatment, and in order to obtain information about populations which could not be measured directly because the corresponding spectral lines were blended, we have carried out information— theoretical or surprisal analyses<sup>24</sup> of our results.

The first requirement for a surprisal analysis is a statistical prior distribution. This was calculated using an exact computer count of quantum states, the energy levels of  $\text{OH}(^2\Pi_i)$  being calculated according to the formulas of Dieke and Crosswhite.<sup>22</sup> The expression for the prior population,  $P^0(v, N, \Omega; E_{\text{tot}})$  in a given OH vibrational, angular momentum, and spin-orbit state  $|v, N, \Omega\rangle$  at a total energy  $E_{\text{tot}}$  is then

$$P^0(v, N, \Omega; E_{\text{tot}}) = (2J_{\text{OH}} + 1) \sum_{v_{\text{NO}}} \sum_{J_{\text{NO}}} \sum_{\Omega_{\text{NO}}} (2J_{\text{NO}} + 1) \times (E_{\text{tot}} - E_{\text{OH}} - E_{\text{NO}})^{1/2} / Q, \quad (3)$$

where the summations are over the vibrational, rotational, and spin-orbit states of NO.  $E_{\text{OH}}$  and  $E_{\text{NO}}$  are the energies of internal states of  $\text{OH}(v, N, \Omega)$  and  $\text{NO}(v_{\text{NO}}, J_{\text{NO}}, \Omega_{\text{NO}})$ .  $Q$  is the sum of the  $P^0(v, N, \Omega; E_{\text{tot}})$  over all energetically accessible  $(v, N, \Omega)$  states of OH at the given total energy  $E_{\text{tot}}$ , and acts therefore as a normalizing factor.

Spectra have been recorded of the NO impurity in the gas mixture from the pulsed nozzle source,<sup>10</sup> with the discharge on the  $\text{H}_2$  flow line switched off. These experiments established that there was considerable rotational cooling of the NO (the low  $J$  distribution corresponded to a temperature of  $< 10$  K) and presumably the  $\text{NO}_2$  was at least as cold. Therefore,  $E_{\text{tot}}$  in Eq. (3) was assumed to be the sum of  $-\Delta H_0^\circ$  for the reaction and  $E_{\text{tr}}$ , the collision energy. Although the velocity of the  $\text{NO}_2$  reagent would be enhanced in the jet expansion, the kinematics are such (mass of  $\text{H} \ll$  mass of  $\text{NO}_2$ ) that this will have little effect

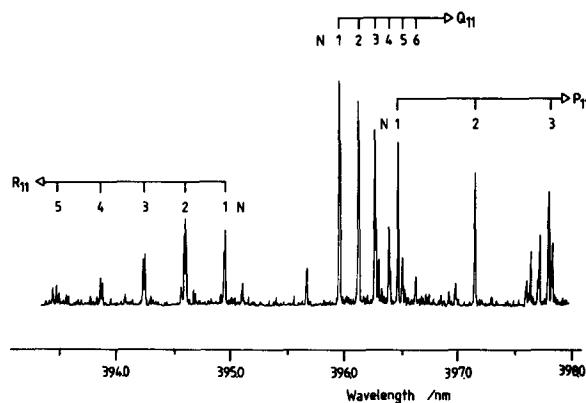


FIG. 3. LIF spectrum of the  $A^2\Sigma^+ - X^2\Pi(1,3)$  band of OH produced in the  $\text{H} + \text{NO}_2$  reaction.

on the distribution of energies in reactive collisions. We therefore assumed that the reactive collision energies corresponded to a thermal distribution at 300 K and calculated distributions of  $P^0(v, N, \Omega; E_{\text{tot}})$  at ten different values ( $E_i$ ) of  $E_{\text{tr}}$  such that  $\int_0^{E_i} f(E_{\text{tr}}) dE_{\text{tr}} = 0.5, 0.15, 0.25, \dots$  for  $i = 1, 2, 3, \dots$ , where  $f(E_{\text{tr}})$  is the normalized distribution function for collision energies at 300 K. A  $P^0(v, N, \Omega; E_{\text{tot}})$  distribution properly averaged over collision energies could then be computed by simply giving the individual results an equal weighting.

The prior distribution that was generated by this calculation is a function of vibrational, rotational, and spin-orbit states of the OH product. These fully detailed results could be summed in appropriate ways to yield vibrational and/or spin-orbit prior branching ratios. The surprisal associated with a given quantum state (or set of quantum states) is given by

$$I = -\ln(P/P^0), \quad (4)$$

where  $P^0$  is the appropriate prior probability and  $P$  is the observed probability.

#### IV. RESULTS

Examples of LIF spectra recorded during the course of our experiments are presented in Figs. 3 and 4. Figure 3 shows the spectrum of the (1,3) band, the low extent of rotational excitation reflecting the limited amount of energy available for disposal into other degrees of freedom when OH is produced in its  $v = 3$  level. In Fig. 4, the lower spectrum was recorded with only broadband filtering of the  $\Delta v = 0$  fluorescence, so that lines resulting from laser excitation of rotational components of both the (0,1) and (1,2) bands are obtained. To record the upper spectrum a narrow band filter was inserted in front of the photomultiplier tube. It transmitted only the (1,0) band, with the result that the (0,1) spectrum is suppressed and the rotational structure of the (1,2) band is seen more clearly than in the "compound" spectrum. High rotational excitation is evident in this band, as in all others emanating from  $v \leq 2$ . In all cases, the rotational excitation extends essentially out to the energetic limit: i.e.,  $N \approx 24$  in  $v = 0$ ,  $N \approx 19$  in  $v = 1$ ,

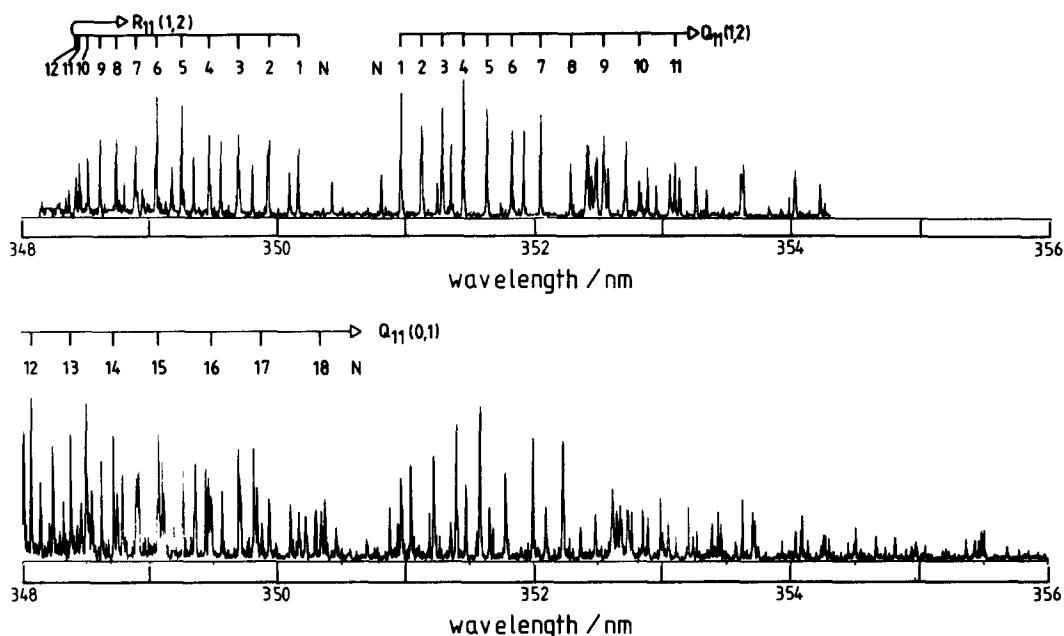


FIG. 4. Spectra of the  $A^2\Sigma^+ - X^2\Pi(0,1)$  and  $(1,2)$  bands of OH produced in the  $H + NO_2$  reaction. In recording the lower trace, only broadband filtering of the fluorescence was employed and both bands were observed. To record the upper spectrum, a filter transmitting only emission lines in the  $(1,0)$  band was placed in front of the photomultiplier tube.

$N \approx 13$  in  $v=2$ , and  $N \approx 6$  in  $v=3$ . The uncertainty in the highest accessible  $v, N$  levels reflects the fact that the  $H + NO_2$  collisions leading to reaction are not monoenergetic but have an approximately thermal spread of relative translational energies.

The relative rotational level populations derived from our spectra in  $OH(v=0, 1, \text{ and } 2)$  and both spin-orbit components are presented in Fig. 5. They are compared with data obtained in "arrested relaxation" IRC experiments for  $OH(v=1 \text{ and } 2)$  and in molecular beam-LIF experiments for  $v=1$ .

We have carried out surprisal analyses of the rotational distributions in each vibration/spin-orbit state. The results of these analyses for  $OH(^2\Pi_{3/2}, v=0, 11 \leq N < 21)$  and

$OH(^2\Pi_{3/2}, v=1, 10 \leq N < 18)$  are shown in Fig. 6. It is evident that these plots are linear:

$$I_{v,rot} = -\ln[P(v, N, p)/P^o(v, N, p)] = \lambda_{v,rot}^o + \theta_{v,rot} g_{v,N}, \quad (5)$$

where  $g_{v,N} = E_N / (E_{tot} - E_v)$  and the gradients yield rotational surprisal parameters of  $\theta_{v=0,rot} = -2.5 \pm 0.3$  and  $\theta_{v=1,rot} = -3.0 \pm 0.3$ . No significant difference was found between the values of  $\theta_{v,rot}$  for the  $F_1(^2\Pi_{3/2})$  and  $F_2(^2\Pi_{1/2})$  components.

At values of  $N$  below ca 11, it becomes more difficult to extract populations because of overlapping spectral transitions, but it is clear that the observed populations lie above those expected from a linear extrapolation of the surprisal plots to lower  $N$ . This effect has been observed by others,<sup>7,8</sup>

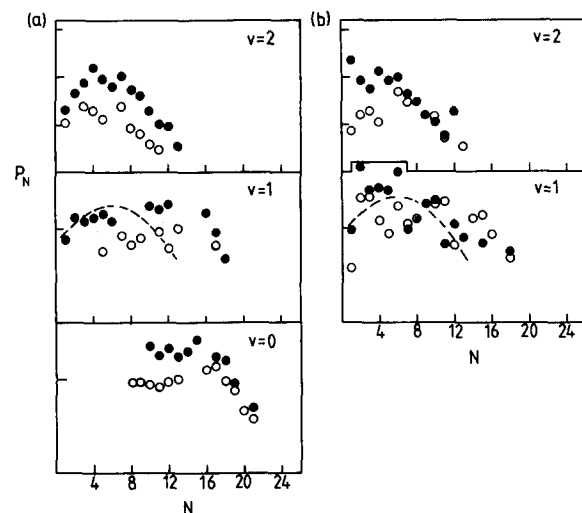


FIG. 5. Distributions of  $OH(v)$  produced in the  $H + NO_2$  reaction over rotational levels: (a) measured in the present work for  $v=0, 1, \text{ and } 2$ ; (b) derived from "arrested relaxation" IRC experiments for  $v=0$  and  $1$  and reported in Fig. 3(a) of Ref. 5(b). Filled and unfilled data points correspond to populations in  $^2\Pi_{3/2}$  and  $^2\Pi_{1/2}$ , respectively. The dashed curve for  $v=1$  represents data from molecular beam-LIF experiments [Refs. 7(c) and 7(d)].

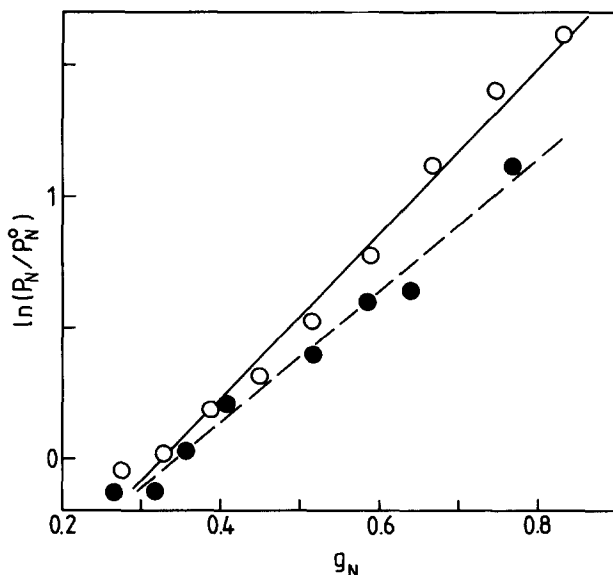


FIG. 6. Surprisal plots for the  $F_1$  rotational levels in  $OH(v=0)$  with  $11 < N < 21$  ( $\bullet$ ) and  $OH(v=1)$  with  $10 < N < 18$  ( $\circ$ ).

TABLE II. Vibrational branching ratios and yields of vibrational and rotational energy in the OH product from the H + NO<sub>2</sub> reaction.

$v$	$N_v/N_{v-1}$	$P_v=N_v/\sum N_v$	$P_v E_v/E_{\text{tot}}$	$\langle f_{\text{rot}} \rangle_v$	$P_v \langle f_{\text{rot}} \rangle_v$
0	...	0.47	0	0.365	0.172
1	0.9	0.42	0.157	0.252	0.106
2	0.23	0.10	0.065	0.143	0.014
3	0.14	0.01	0.008	0.059	$9 \times 10^{-4}$
		$\langle f_{\text{vib}} \rangle = 0.23$			$\langle f_{\text{rot}} \rangle = 0.29$

and attributed to partial rotational relaxation. Like them we assume that the *relative* populations in the ranges covered by the linear surprisal plots are unaffected by relaxation and a full rotational distribution is synthesized on the basis of the linear surprisal analysis for high rotational levels. Thus for  $v=0$  and  $v=1$ , we use the derived values of  $\theta_{v,\text{rot}}$  and  $\lambda_{v,\text{rot}}^0$  and Eq. (5) to calculate  $P(v,N,p)$ . This procedure yields values of  $P(v,N,p)$  for all  $N,p$  in a particular vibrational level  $v$ , smoothing the distribution in the range where  $P(v,N,p)$  can be observed and extending the distribution to the lower levels where populations are difficult to determine and may be affected by relaxation.

By comparing the synthesized rotational distributions for both spin-orbit states of OH( $v=0$ ) and OH( $v=1$ ), it was possible to determine the branching ratios into (a) the  ${}^2\Pi_{3/2}$  and  ${}^2\Pi_{1/2}$  components of the spin-orbit doublet, and (b) the vibrational levels  $v=0$  and  $v=1$ , summed over both components of the  ${}^2\Pi$  term. These ratios were found to be 1: 0.87 and 1: 0.78 for the  $F_1$  and  $F_2$  component of  $v=0$  and  $v=1$ , respectively, and 1: 0.9 for the ratio  $N_{v=0}/N_{v=1}$ .

The rotational distributions in the  $v=2$  and  $v=3$  levels of OH did not yield linear surprisal plots over a significant range of  $g_{v,N}$ . This finding is not surprising since the energetics of the process limits the formation of OH( $v=2$ ) to rotational levels  $N \leq 13$  and OH( $v=3$ ) to  $N \leq 6$ . It was therefore necessary to adopt a different approach in order to estimate the rotational energy yields in these levels, and the vibrational and spin-orbit branching ratios into  $v=2$  and  $v=3$ .

Experimentally, relative populations in OH  ${}^2\Pi_{3/2}$  ( $v=2,3;N$ ) levels were determined from measurements of line intensities within the  $Q_{11}$  branches of the (0,1), (1,2) and the (0,2), (1,3) bands. The distributions over  $N$  were then fitted to a polynomial function using a NAG Library Routine (EO2 ACF). The relative populations in each spin-orbit level associated with a particular  $v$  were obtained by summing these distributions over  $N$ , and the total relative populations in vibrational levels  $v=1, 2$ , and 3 were then estimated by further summing up the populations in the interpolated product state distribution over both spin-orbit components. This procedure yielded the vibrational and spin-orbit branching ratios which are given, along with those for production of OH in  $v=0$ , in Tables II and III.

Table II also gives the fractions of OH observed in different vibrational levels and the overall fractional yield of vibrational energy:  $\langle f_{\text{vib}} \rangle = \sum_v P_v E_v/E_{\text{tot}}$ . Our conclu-

TABLE III. Spin-orbit branching ratios  $N({}^2\Pi_{1/2}):N({}^2\Pi_{3/2})$  for different vibrational levels of OH formed in the reaction: H + NO<sub>2</sub> → OH + NO.

$v$	Experimental	Statistical <sup>a</sup>	Statistical <sup>a</sup>
0	0.87	0.87	0.91
1	0.78	0.84	0.89
2	0.58	0.79	0.86
3	0.40	0.50	0.85

<sup>a</sup>The bases for the two different priors are described in the text.

sion is that, in thermal energy reactive collisions between H atoms and NO<sub>2</sub>, 23% of the total energy available is channeled into the vibrational degree of freedom of the OH product. Figure 7 shows a surprisal analysis of the OH vibrational level populations. The data for  $v=0, 1$ , and 2 fall on a straight line yielding a vibrational surprisal parameter<sup>24</sup>  $\lambda_v = -3.0$ .

In order to estimate the overall yield of rotational energy in the OH product, it was necessary to devise some method of estimating the nascent rotational distributions in  $v=2$  and  $v=3$ . We chose to do this by finding  $N_{v,\text{max}}$ , that is the most populated rotational level in a given vibrational state, and then synthesizing a rotational distribution based on  $N_{v,\text{max}}$  and the assumption that the nascent rotational distribution would have a linear surprisal analysis with the average value of  $\theta_{v,\text{rot}}$  as had been found for  $v=0$  and  $v=1$ . Although this procedure is only approximate, the error introduced in the overall yield of  $\langle f_{\text{rot}} \rangle$  is small, because, as the numbers in Table II show, the contributions to  $\langle f_{\text{rot}} \rangle$  from  $v=2$  and  $v=3$  are small since almost 90% of the OH product is formed in levels  $v=0$  and  $v=1$ .

The branching ratios in spin-orbit states show a slight preference for the lower  ${}^2\Pi_{3/2}$  component which increases with vibrational quantum number. The observed spin-orbit branching ratios are compared in Table III with statistical priors based on two hypothesis. First, the branching ratios were estimated on the basis that all states were populated statistically in accord with Eq. (3) with conservation of energy being the only constraint. This amounts to summing the prior rotational distributions for the  $F_1$  and

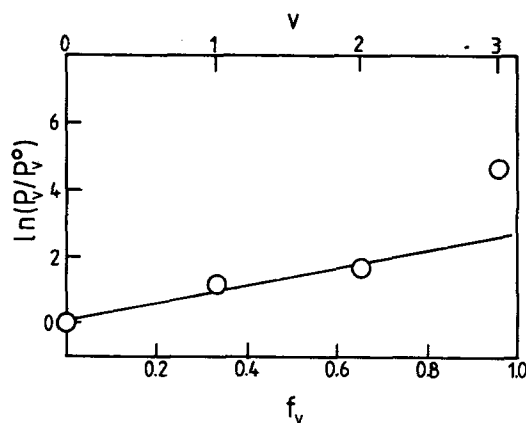


FIG. 7. Surprisal plot for the OH vibrational populations, including for each  $v$  contributions from both spin-orbit levels.



for the  $F_2$  components. This procedure gave the branching ratios listed in the third column of Table III. A second prior was calculated on the basis of the *observed* rotational distributions. This can be looked on as an additional constraint on the system. We then found the branching ratios given in the fourth column of Table III. They are in rather worse agreement with the experimental results than those given by the less constrained model.

For OH( $v=0$ ) and OH( $v=1$ ), the rotational level populations ( $N \geq 10$ ) derived from measurements on the  $P$  or  $R$  branches of bands from each spin-orbit component exceeded those deduced from the corresponding  $Q$  branch lines by a constant factor of  $1.7 \pm 0.2$ . For these levels, the degree of electron alignment defined by Andresen and Rothe<sup>20</sup> has an almost constant value of 0.85, so the results demonstrate a small but significant propensity for OH to be formed in the  $\Pi(A')$   $\Lambda$ -doublet states rather than the  $\Pi(A'')$  states. The implications of this result are considered in Sec. V.

As indicated in Sec. II, in view of the observed rotational cooling in the NO<sub>2</sub>/Ar expansions, an important concern in our experiments was whether we were also observing OH produced in reactions between H atoms and NO<sub>2</sub> clustered either with one or more Ar atom or with NO<sub>2</sub>. To examine this possibility, experiments were performed under four sets of widely differing conditions. Spectra were recorded using stagnation pressures of ca 1.2 and 0.4 bar, and with both Ar and He as the diluent gases in mixtures containing 5% of NO<sub>2</sub>. Both the change to a lower stagnation pressure and the replacement of Ar by He would have greatly lowered the degree of complexation, and these experiments should span a degree of complexation varying by one to two orders of magnitude. In each of these experiments, part of the (0,1) band was recorded and relative rotational populations calculated. There was no significant change in the rotational distributions. Since rotational relaxation is relatively facile, the observed rotational state distributions should be particularly sensitive to the presence of a complexing species. We conclude that the measured OH distributions are the result of reaction between H atoms and uncomplexed NO<sub>2</sub>.

## V. DISCUSSION

A problem which is common to all experiments that are performed under "near single collision" conditions is how the observed relative state populations should be transformed into the relative rates of reaction or relative reactive cross sections into those states. Laser-induced fluorescence experiments, like those employing infrared chemiluminescence, measure the *densities* of molecules in specific quantum states whereas rate coefficients or cross sections are related to fluxes. In "arrested relaxation" IRC experiments, it has been customary to assume that there are sufficient collisions to ensure that all product molecules remain within the observation zone for the same time, irrespective of their initial internal energy state (and hence their initial translational velocity). In consequence, the relative state densities are assumed to reflect directly the relative rate coefficients. In true crossed beam experiments,

the same assumption cannot be made. The state densities (measured, for example, at the crossing point of the beams by LIF) must be corrected to yield relative cross sections.

Our experiments are, we believe, somewhat closer to those of an infrared chemiluminescence experiment. The overpopulation in low rotational states of OH (and NO<sup>10</sup>) compared with what would be expected on the basis of the surprisal analysis of higher state populations indicates that *some* collisions occur in the region probed by the laser. We have therefore chosen to interpret our experiment by assuming that measured OH state densities directly reflect the relative rates at which the H + NO<sub>2</sub> reaction populates the different levels.

The experiments which are reported in this paper are the first single set in which the complete state distribution has been determined for OH formed in the H + NO<sub>2</sub> reaction. Earlier LIF measurements yielded the vibrational branching ratio for just the  $v=1$  and  $v=0$  pair of levels. Kinsey and co-workers<sup>7</sup> found OH( $v=1$ )/OH( $v=0$ ) = 0.8 and Luntz's group<sup>8</sup> determined OH( $v=1$ )/OH( $v=0$ ) = 0.72, both results being in reasonable agreement with our own value of 0.90. EPR measurements on the H + NO<sub>2</sub> reaction occurring in a flow tube gave<sup>2</sup> relative populations into the first three levels, OH( $v=2$ ): OH( $v=1$ ): OH( $v=0$ ) = 0.29: 0.71: 1.0, again in quite good agreement with our result, 0.21: 0.90: 1.0.

There have also been several studies<sup>3-6</sup> employing infrared chemiluminescence (IRC) techniques to characterize the distribution of OH over excited ( $v > 0$ ) vibrational levels. The earliest such measurements<sup>3</sup> gave OH( $v=3$ ): OH( $v=2$ ): OH( $v=1$ ) = 0.03: 0.4: 1.0 which compares quite favorably with our ratio, 0.03: 0.23: 1.0. Polanyi and Sloan<sup>3</sup> suggested that their results might have been affected by very rapid vibrational relaxation of the OH with retention of rotational state. However, the correction which they applied to allow for this effect has been questioned by several later investigators,<sup>3-6</sup> partly on the grounds that Polanyi and Sloan's observed (and uncorrected) distribution agrees quite well with others obtained under different experimental conditions where vibrational relaxation might be expected to be even more important.

The two most recent IRC studies are those by Klenerman and Smith<sup>6</sup> and by Wategoankar and Setser.<sup>5(c)</sup> Our distribution over levels  $v=1$  to  $v=3$  is close to that found by Klenerman and Smith. The results of successive thorough studies by Setser's group have consistently indicated higher rates into the levels  $v > 1$  than are reported here. Wategoankar and Setser<sup>5(c)</sup> report OH( $v=2$ )/OH( $v=1$ ) = 0.6 and demonstrate that this result is independent of which of two sets of Einstein coefficients<sup>11</sup> for the fundamental infrared transitions are used to derive populations. Although the discrepancy in the  $v=2/v=1$  branching ratio is the most serious difference between our results and those derived from previous experiments and there is no obvious explanation, the effect on the estimate of  $\langle f_{\text{vib}} \rangle$  the overall fractional yield of vibrational energy in OH, is fairly small. A surprisal analysis based on the results of Wategoankar *et al.*<sup>5(c)</sup> yields  $\langle f_{\text{vib}} \rangle = 0.25$  in contrast to our value of 0.23.

We believe that it is highly unlikely that our results are affected by vibrational relaxation. The major species in our reaction zone are Ar (or He) and H<sub>2</sub>. These gases are known<sup>25,26</sup> to be inefficient at relaxing vibrationally excited OH but are likely to cause much more rapid rotational relaxation.<sup>27</sup> The observation of markedly non-Boltzmann rotational distributions means that our observed vibrational distributions should be close to nascent.

Our measurements provide a rather direct estimate of the overall disposal of energy into OH rotation. By recording the nondiagonal ( $\Delta v \neq 0$ ) bands, it has been possible to avoid problems caused by predissociation in the  $A^2\Sigma^+$  state and hence to extend observations on rotational populations to the maximum values of  $N$  that can be populated in the reaction. As is partially shown in Fig. 5, the distributions over rotational levels which we measure are similar to those found in two different sets of "arrested relaxation" IRC experiments.<sup>5(b)</sup> The rotational surprisal parameter that we find for OH( $v=0$ ), i.e.,  $\theta_{\text{rot},v=0} = -2.5 \pm 0.3$ , is in good agreement with the values ( $-2.7 \pm 0.6$ ) and ( $-2.3 \pm 0.2$ ) obtained from previous LIF studies<sup>7,8</sup> using surprisal analyses with similar priors. The position in regard to the rotational distribution in OH( $v=1$ ) is less satisfactory. Mariella *et al.*<sup>8</sup> essentially assumed that  $\theta_{\text{rot}}$  would be the same for the  $v=1$  as for  $v=0$ ; their rotational surprisals for  $v=1$ , like ours, show appreciable scatter and could undoubtedly be fitted to a lower value of  $|\theta_{\text{rot}}|$  than the one they assumed. The rotational surprisal analysis for OH( $v=1$ ) of Silver *et al.*<sup>7(a)</sup> was based on rather few states ( $N$  between 8 and 14 with some values missing) and gave  $\theta_{\text{rot}} \sim 0$ . Despite the discrepancies in  $\theta_{\text{rot}}$ , the estimates of  $\langle f_{\text{rot}} \rangle$ , i.e., the overall OH rotational energy yield agree well. Our value of 0.29 compares with previous estimates of 0.2–0.3,<sup>3</sup> 0.20,<sup>7</sup> and 0.26.<sup>8</sup> It is, of course, possible that the observed rotational level distributions closely mirror the nascent distributions; i.e., there is less relaxation than is suggested by the surprisal analysis. Estimating the rotational energy yield directly from our observed distribution leads to a value of  $\langle f_{\text{rot}} \rangle = 0.24$ , close to that obtained (0.22) from a direct interpretation of the "arrested relaxation" IRC experiments of Setser's group.<sup>5(b)</sup> The two values of 0.24 and 0.29 represent lower and upper bounds to the value of  $\langle f_{\text{rot}} \rangle$  determined in our experiments.

Our results indicate that ca 52% of the total energy available to the products of the reaction is released into rovibrational motion of the OH product. Furthermore, our study confirms that OH populates the two spin-orbit states,  $^2\Pi_{1/2}$  and  $^2\Pi_{3/2}$ , almost in accord with statistical expectation. The mean electronic excitation of OH accounts for 0.6% of the energy released. We postpone a full discussion of the dynamics of the H + NO<sub>2</sub> reaction until the end of the succeeding paper<sup>10</sup> which reports measurements on the energy disposal into degrees of freedom of the NO product.

Measurements on the  $Q$  and  $R$  branches of the (0,0) band for values of  $N$  between 11 and 21 indicate a propensity for populating one  $\Lambda$ -doublet such that  $\Pi(A')/\Pi(A'') = 1.7 \pm 0.2$ . A similar result was obtained for OH( $v=1$ ). Despite the small splitting between  $\Lambda$ -doublet

levels, it appears that cross sections for transfer between such levels are comparable to those for rotational and spin-orbit relaxation.<sup>28</sup> Therefore, the spin-orbit and  $\Lambda$ -doublet population ratios that we determine should be close to the nascent distributions. Our results are similar to those made by Mariella *et al.*<sup>8</sup> who also showed that the  $\Lambda$ -doublet propensity was independent of collision energy. The interpretation of  $\Lambda$ -doublet propensities in terms of dynamical preferences has been discussed at length by Andresen and Rothe.<sup>20</sup> The  $\Pi(A')$  levels are those which in the limit of high  $N$  have the  $p\pi$  orbital containing the odd electron in the plane of rotation of the OH  $X^2\Pi$  species. In the fragmentation of planar HONO species in which OH acquires rotational excitation only as a result of repulsion along the separating HO–NO bond, one might expect to find OH rotating in the plane originally defined by the HONO species and hence a high propensity for the  $\Pi(A')$  states, since the odd electron in the OH fragment would be the one which had been associated with the HO–NO  $\sigma$ -bond.

In practice, two effects will tend to lower the  $\Lambda$ -doublet preference observed from that expected on the simplistic model which has just been described. First, the HONO collisional system contains considerable internal energy. As a consequence, it is very unlikely either that product formation results simply from an intermediate tightly constrained to a plane or that product rotation results only from repulsion along the HO–NO bond as the products separate. The second effect arises because, for finite values of the quantum number  $N$ , the electronic wave functions associated with pairs of different  $\Lambda$ -doublet states do not simply correspond to the wave functions associated purely with the  $x$  or  $y$  alignment of the  $p\pi$  orbital containing the odd electron. Rather the wave functions of  $\Pi(A')$  and  $\Pi(A'')$  are linear combinations of wave functions describing the perfectly aligned states, and only as  $N$  approaches infinity do the coefficients go to 1 and 0 (or 0 and 1). Only then does the correlation of the  $\Lambda$ -components with a state with a well-aligned  $p\pi$  orbital become valid.

Andresen and Rothe<sup>20</sup> show that for OH the degree of electron alignment which can be achieved for states with  $J = 10.5$ – $20.5$  [covering the range used to determine  $\Pi(A')/\Pi(A'')$  in our experiments] is approximately constant at 0.85. What this means in practice is that however strong the dynamical preference for production of OH with the odd electron in the  $p\pi$  orbital in the plane of molecular rotation, the population ratio  $\Pi(A')/\Pi(A'')$  could not exceed  $(1 + 0.85)/(1 - 0.85) \approx 12$ . The equations of Andresen and Rothe<sup>20</sup> can be used to evaluate a preference for formation of OH with the odd electron in a  $p\pi_x$  orbital over that of OH with the odd electron in  $p\pi_y$ , based on the measured population ratio  $\Pi(A')/\Pi(A'')$  and the (maximum) degree of electron alignment. This procedure yields  $p\pi_x/p\pi_y = 2$ . That is, if the definition of the  $\Pi(A')$  and  $\Pi(A'')$  states which holds at infinitely high  $N$  were applicable at all finite  $N$ , then the preference from the chemical dynamics for formation of OH with the odd electron in an orbital in the plane of rotation would be ca 2:1.

## VI. SUMMARY

The disposal of reaction energy into OH vibration, rotation, and spin-orbit excitation has been observed using the LIF technique. The measured yields,  $\langle f_{\text{vib}} \rangle = 0.23$ ,  $\langle f_{\text{rot}} \rangle = 0.29$ ,  $\langle f_{s-o} \rangle = 0.006$ , are in satisfactory agreement with other measurements. Some detailed discrepancies do remain, however, notably the difference in yield of OH( $v > 1$ ) indicated by the present LIF experiments and by the most thorough IRC measurements, and the question to what extent OH is rotationally relaxed under low pressure, "arrested relaxation" conditions. The second question is difficult to resolve. The source of the first disagreement may be identified if LIF measurements are made in a fast flow reactor where rotational relaxation is essentially complete but vibrational relaxation will be insignificant.

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