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DOI:

[10.1063/1.458851](https://doi.org/10.1063/1.458851)

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Document Version

Publisher's PDF, also known as Version of record

Citation for published version (Harvard):

Irvine, AML, Smith, I & Tuckett, RP 1990, 'A laserinduced fluorescence determination of the internal state distribution of NO produced in the reaction:  $H+NO_2OH+NO$ ', *Journal of Chemical Physics*, vol. 93, no. 5, pp. 3187-3195. <https://doi.org/10.1063/1.458851>

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A laserinduced fluorescence determination of the internal state distribution of NO produced in the reaction:  $H+NO_2OH+NO$ . Alistair M. L. Irvine, Ian W. M. Smith, and Richard P. Tuckett. *The Journal of Chemical Physics* 1990 93:5, 3187-3195

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

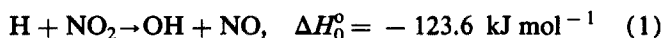
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(Received 12 December 1989; accepted 8 May 1990)

Laser-induced fluorescence (LIF) spectra have been recorded of NO produced when H atoms and NO<sub>2</sub> react in thermal energy collisions in the region where two uncollimated jets containing the reagents intersect. Spectra of the (0,0), (1,1) and (2,2) bands and the (0,2) and (1,3) bands of the  $A^2\Sigma^+ - X^2\Pi$   $\gamma$ -band system have been observed. Distributions of NO over rovibrational levels have been determined by matching the experimental spectra to simulated spectra. The high  $J$  tail of the rotational distributions fit a linear surprisal plot. The analysis leads to average fractional yields of vibration and rotation energy,  $\langle f_{\text{vib}} \rangle_{\text{NO}} = 0.056$  and  $\langle f_{\text{rot}} \rangle_{\text{NO}} = 0.10$ , as well as branching ratios into vibrational ( $v = 0-3$ ), spin-orbit and  $\Lambda$ -doublet states. Preferences are found for the lower  $^2\Pi_{1/2}$  spin-orbit substate and for the  $\Pi(A')$   $\Lambda$ -doublet levels. Combined with results from the preceding paper, the data indicate that  $\sim 31\%$  of the energy released in the reaction should appear as relative translational motion of OH and NO. The reaction appears to proceed via the ground state HONO surface but the complex does not survive sufficiently long for complete energy randomisation: OH is more excited, NO less excited, than would be expected on a purely statistical basis.

## I. INTRODUCTION

In the paper<sup>1</sup> immediately preceding this one, experiments are described in which the complete nascent internal state distribution of OH formed in the reaction



was deduced from measurements of laser-induced fluorescence (LIF) spectra of OH with the reaction taking place under near single collision conditions. The results of those experiments indicate that the average yields of vibrational and rotational energies in OH are  $\langle f_{\text{vib}} \rangle_{\text{OH}} = 0.23$  and  $\langle f_{\text{rot}} \rangle_{\text{OH}} = 0.29$  when reaction occurs in thermal energy collisions. These yields are both larger than expected on purely statistical grounds, using a prior that takes into account only conservation of energy.<sup>2</sup> The results for OH also indicate a mild preference for the  $^2\Pi_{3/2}$  lower spin-orbit component of the electronic ground state of OH, as well as some propensity for the  $\Pi(A')$   $\Lambda$ -doublet states to be formed in preference to the  $\Pi(A'')$  components, a finding which is consistent with reaction via an HONO transient species which is weakly constrained to planarity.

The present paper describes the complementary and similar LIF measurements that we have made on the NO product of reaction (1). Characterization of the internal state distribution of NO is especially valuable for two reasons. First, a direct check is made on estimates,<sup>3</sup> relying on energy balance arguments, that approximately 30% of the energy released in the  $\text{H} + \text{NO}_2$  reaction excites the vibration and rotation of NO. Second, the release of energy into the vibration of NO corresponds to excitation of the "old bond" in the reaction. Such excitation is only likely in non-direct reactions, and it therefore serves as a clear in-

dication that the potential well corresponding to the bound HONO molecule in its ground electronic state exerts some influence on the reaction dynamics.

Although there have been quite a number of studies<sup>4</sup> of the nascent states of OH formed in reaction (1), there have been far fewer experiments on the NO product. Setser's group<sup>3,5</sup> have managed to observe infrared chemiluminescence (IRC) from vibrationally excited NO and have estimated that the rate constants for formation of NO( $v = 1$ ) and NO( $v = 2$ ) are in the ratio 70:30. Very recently, Sauder and Dagdigan<sup>6</sup> have reported LIF measurements on NO in vibrational levels from  $v = 0$  to  $v = 2$ . In the work which we now describe, NO has been observed in vibrational levels up to and including  $v = 3$ . As NO, like OH, has a  $^2\Pi$  electronic ground state, experiments utilizing LIF enable one to determine branching ratios into spin-orbit components and into  $\Lambda$ -doublet levels, as well as distributions over rovibrational states.

## II. EXPERIMENTAL

In order to determine NO state distributions, laser excitation spectra have been recorded of bands in the  $A^2\Sigma^+ - X^2\Pi$   $\gamma$ -band system using a frequency-doubled, pulsed dye laser. The tunable output from the laser probed the region in a low pressure reactor where uncollimated jets containing NO<sub>2</sub> and H atoms intersected. The apparatus and general experimental method were the same as in our experiments on the OH product<sup>1</sup> and only differences between those measurements and the present ones on NO will be described here.

In most experiments on the NO product, mixtures of 5% NO<sub>2</sub> in He were used with a pressure of ca 1 bar

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TABLE I. Data on NO  $A^2\Sigma^+ - X^2\Pi$  bands used to determine populations of NO  $X^2\Pi(v=0-3)$ .

Band	Band origin/nm	Franck-Condon factor	Details of dye laser operation
(0, 0)	226.3	0.162	Coumarin 2 dye in methanol. Frequency doubling in KPB. Fluorescence observed without filtering.
(1, 1)	223.8	0.107	
(2, 2)	221.6	0.155	
(0, 2)	247.0	0.237	Coumarin 102 dye in methanol. Frequency doubling in KPB. Fluorescence observed without filtering.
(1, 3)	243.9	0.069	

behind the nozzle source. Early attempts to suppress NO impurity by adding 5% O<sub>2</sub> to this mixture were abandoned when this action was found to make little difference to the concentration of impurity that was detected.

In order to induce fluorescence from NO, the output from a Lambda-Physik FL2002 dye laser was frequency-doubled in KPB (potassium pentaborate), the crystal used depending on the wavelength required. Two series of experiments were performed. In the first, the laser radiation was tuned through the range  $\sim 225$ – $220$  nm to excite NO in its (0,0), (1,1), and (2,2) bands. In other experiments, the laser was scanned between  $\sim 247$  and  $242$  nm, and the (0,2) and (1,3) bands of the  $\gamma$  system of NO were excited. The origins of these bands, their oscillator strengths and the dyes employed in our experiments are listed in Table I. Checks were made to ensure that the laser intensities were low enough to avoid saturating any lines in the spectra. The laser beam was not focused, its pulse energy was estimated to be less than  $5 \mu\text{J}$  in all experiments, and comparison of lines from the main and satellite branches confirmed the absence of saturation effects.

The fluorescence induced by the laser was collected by a single  $f/1$  Spectrosil lens and directed on to an uncooled photomultiplier tube (Hamamatsu R821). In contrast to the situation for OH, fluorescence from NO  $A^2\Sigma^+(v')$  occurs to several vibrational levels in the  $X^2\Pi$  state and therefore over a relatively wide range of wavelengths. Fortunately, it was found that the emission could be observed without optical filtering. In all the experiments on NO, spectra were recorded digitally on a microcomputer. The signals both from the photomultiplier observing the fluorescence and from a photodiode monitoring variations in the laser intensity were processed in a gated integrator/signal averager (Stanford Research Systems, model SRS 250) before being passed to the microcomputer.

### III. SPECTROSCOPY AND DATA ANALYSIS

The spectroscopy of the  $A^2\Sigma^+ - X^2\Pi$  system in OH and the application of LIF to obtain the distribution of OH product species over individual quantum states has been described in the preceding paper. The general method employed in our studies of the NO product of reaction (1) is

broadly similar, but the spectroscopy of the NO  $A^2\Sigma^+ - X^2\Pi$  system differs in a number of significant respects from that of the corresponding system in OH. For example, in the electronic ground state of NO the two spin-orbit components are normal in that the  $^2\Pi_{1/2}$  component, with levels designated  $F_1$ , lies below the  $^2\Pi_{3/2}$  component, with levels designated  $F_2$ . Furthermore, in contrast to the situation in OH  $X^2\Pi$  which rapidly approximates to a Hund's case (b) species as  $J, N$  is increased, the behavior of NO  $X^2\Pi$  is best described by the case (a) coupling scheme, so that individual levels are identified in terms of their quantum numbers  $J$ , which can take values  $\Omega, \Omega + 1, \Omega + 2$ , etc. As with OH, each vibrational sub-band gives rise to three main plus three satellite branches.

In principle, the relative populations in different  $\Lambda$ -doublet levels, i.e., in either  $\Pi(A')$  or  $\Pi(A'')$  states,<sup>7</sup> can again be estimated by measuring relative intensities in the  $Q$  and  $P/R$  branches of the spectrum. However, the correlation of these  $\Lambda$ -doublet levels with the different orientations of the  $p\pi$  orbital containing the unpaired electron with respect to the plane of rotation of the  $^2\Pi$  radical only becomes complete in the limit of high  $N$  or  $J$ . Andresen and Rothe's calculations<sup>8</sup> show that in NO the degree of electron alignment only approaches this limiting behavior slowly, reaching values of  $\sim 0.5$  at  $J = 20\frac{1}{2}$  and  $\sim 0.8$  at  $J = 48\frac{1}{2}$ .

The general expression relating the measured intensity of a resolved line in an LIF spectrum to the population in the level responsible for absorption is given in Eq. (2) in the preceding paper. In the case of NO, the Einstein absorption coefficients  $B_{v'J',vJ}$  can acceptably be expressed in terms of separable Franck-Condon and Hönl-London factors. The variation of electronic transition moment over the bands which are directly compared in this work is slight<sup>9</sup> and could be ignored in our analysis. In contrast to the situation for OH, the band strengths are not concentrated in the diagonal bands. Franck-Condon factors were calculated for the bands excited in our experiments and are listed in Table I. These values are very close to those given by Piper and Cowles.<sup>9</sup>

Because the rotational constants in the  $A^2\Sigma^+$  and  $X^2\Pi$  states of NO are considerably smaller than those in the corresponding states of OH, far more rotational levels in NO are energetically accessible and the  $A^2\Sigma^+ - X^2\Pi$  band system is far more congested for NO than for OH. In addition, the six main and six satellite branches in each band, as well as lines from neighboring bands, overlap. The resultant high density of spectral lines, combined with the limited linewidth of our probe laser ( $\sim 1 \text{ cm}^{-1}$ ) leads to many blends in the spectrum, particularly in the region of the band heads. Consequently, populations could not be extracted directly from the spectra, as was the case for OH. Instead, relative state populations were determined by simulating spectra computationally, trial distributions of populations being varied until good agreement was obtained between the simulated and observed spectra. Line positions for the simulations were calculated using the expressions of Mallard *et al.*<sup>10</sup> with the improved molecular constants of

Atkins<sup>11</sup> for  $X^2\Pi(v=0-3)$  and  $A^2\Sigma^+(v=0)$ . Constants for  $A^2\Sigma^+(v=1,2)$  were taken from Huber and Herzberg.<sup>12</sup>

In order to simulate a complete LIF spectrum four pieces of data relating to the product state distributions were input to the program: rotational populations, vibrational populations, a spin-orbit branching ratio within each vibrational level, and the  $\Lambda$ -doublet propensity in the limit of high  $J$ . In practice, the population of every fifth rotational level of each spin-orbit substate of each vibrational level was selected, the populations in intermediate levels then being estimated computationally via a cubic spline interpolation. Spin-orbit and vibrational level branching ratios were also chosen for each simulation, the former serving to fix the sum of the rotational state populations in each of the two spin-orbit substates associated with a given vibrational level.

In order to complete the simulation of an LIF spectrum arising from a distribution in an  $X^2\Pi$  ground state which may display a preference for one set of  $\Lambda$ -doublet states over the other, it was necessary to allow for the effects of incomplete  $p\pi$  orbital alignment, as considered in detail by Andresen and Rothe<sup>8</sup> and discussed in relation to the OH product of reaction (1) in the preceding paper.<sup>1</sup> Because of the incomplete degree of electron alignment (DEA) for finite  $J$  in NO, it is necessary to distinguish between the observed ratio  $W$  of populations ( $N_A/N_{A'}$ ) in a pair of  $\Lambda$ -doublet components and the propensity  $R$  [ $= (N_A/N_{A'})_{J \rightarrow \infty}$ ] in the limit of high  $J$ . Using the equations of Andresen and Rothe,<sup>8</sup> it is easy to calculate DEA for each value of  $J$  and to show that

$$W = \frac{(1 - \text{DEA}) + (1 + \text{DEA})R}{(1 + \text{DEA}) + (1 - \text{DEA})R} \quad (2)$$

This expression can be used to simulate how  $W$  varies with  $J$  assuming that the dynamics of collisions in which NO is formed do not lead to a correlation between  $R$  and  $J$ . In the computer program used to simulate spectra, a value of  $R$  was input and  $W$  calculated for each  $J$  using Eq. (2). The rotational population assigned to a particular  $J$  was then divided between the two  $\Lambda$ -components according to the calculated value of  $W$ . The rotational populations reported correspond to the sum of those in the two  $\Lambda$ -components. Hönl-London factors were calculated using the formulas of Earls.<sup>13</sup>

The program also made allowance for differences in the detection sensitivity for fluorescence originating from different vibrational levels in the  $A^2\Sigma^+$  excited state. This was done using the standard expression of Levine and Bernstein:<sup>14</sup>

$$N_v = I_{v',v} / \left( q_{v',v} \sum_{v''} \nu_{v',v''}^A q_{v',v''} S_{v',v''} \right) \quad (3)$$

Here  $I_{v',v}$  is the measured fluorescence intensity associated with laser absorption in the  $(v', v)$  band corrected for variations in laser intensity, and  $N_v$  is the population in the level  $v$ . The factors in the denominator of this expression are  $q_{v',v}$ , the Franck-Condon factor associated with the absorption band (as listed in Table I); and  $\nu_{v',v''}$ ,  $q_{v',v''}$  and

$S_{v',v''}$  which are the frequency, Franck-Condon factor, and detection sensitivity for the  $(v', v'')$  emission band, the summation being over all vibrational bands contributing to the fluorescence from level  $v'$ . The values of  $S_{v',v''}$  were estimated from the specification for the photomultiplier tube with a small correction for losses in transmission through the collection optics.

Spectra were simulated assuming each line had a Gaussian line shape. The full-width half-maximum line-width was usually set to  $5 \times 10^{-3}$  nm ( $\equiv \sim 1$  cm<sup>-1</sup>) to correspond to the observed widths of fully resolved lines. The various parameters describing the distributions of population over states was systematically varied until satisfactory agreement between experimental and computed spectra was achieved.

#### IV. RESULTS

One difficulty in our measurements on the NO product of reaction (1), which had no parallel in the experiments on OH, was the presence of signal from NO which was not formed in the reaction. It was straightforward to show that these signals were not due to the presence of NO which had been formed from NO<sub>2</sub> admitted in previous openings of the pulsed valve. This was demonstrated by triggering the laser to fire just *before* each opening of the pulsed valve. Under these conditions, any signal would have been due to the presence of "background" NO reaction product but no LIF signals were observed.

Spectra were then recorded in the absence of H atoms; that is, without the discharge on the hydrogen flowline. NO was detected but only in its  $v=0$  level, and the bulk of the population was concentrated in the lowest rotational levels, suggesting that the NO being observed must have been cooled in the supersonic expansion. The corollary of this observation is that most of the NO not formed by reaction must have been present as impurity in the NO<sub>2</sub>/He mixture in the pulsed source. However, some population was observed in higher rotational levels and it was greater than would have been expected on the basis of a comparison with NO LIF spectra obtained when a mixture of 2% NO in Ar was expanded through the pulsed valve.

A possible explanation for the existence of a small amount of NO in relatively high rotational levels of the  $v=0$  level is that the probe laser, despite its low pulse energy, caused some photodissociation of the NO<sub>2</sub>.<sup>6,15</sup> Whatever the cause, these background signals interfered with our observations of reactively produced NO, but only in  $v=0$  and in rotational levels below about  $J=25\frac{1}{2}$ . Consequently, we only made use of that part of the (0,0) band spectrum at wavelengths  $< 222.5$  nm, where lines with  $J'' > 25\frac{1}{2}$  predominate.

Use was made of the spectra of NO impurity in checking whether there were any significant effects of polarization anisotropy. The approach was to derive a rotational state distribution in  $v=0$  from the measured intensities of lines in the  $R_{11}$  branch. This set of populations then served as input to the simulation program and a complete spectrum was simulated assuming no effects of polarization anisotropy. This simulation closely corresponded to the

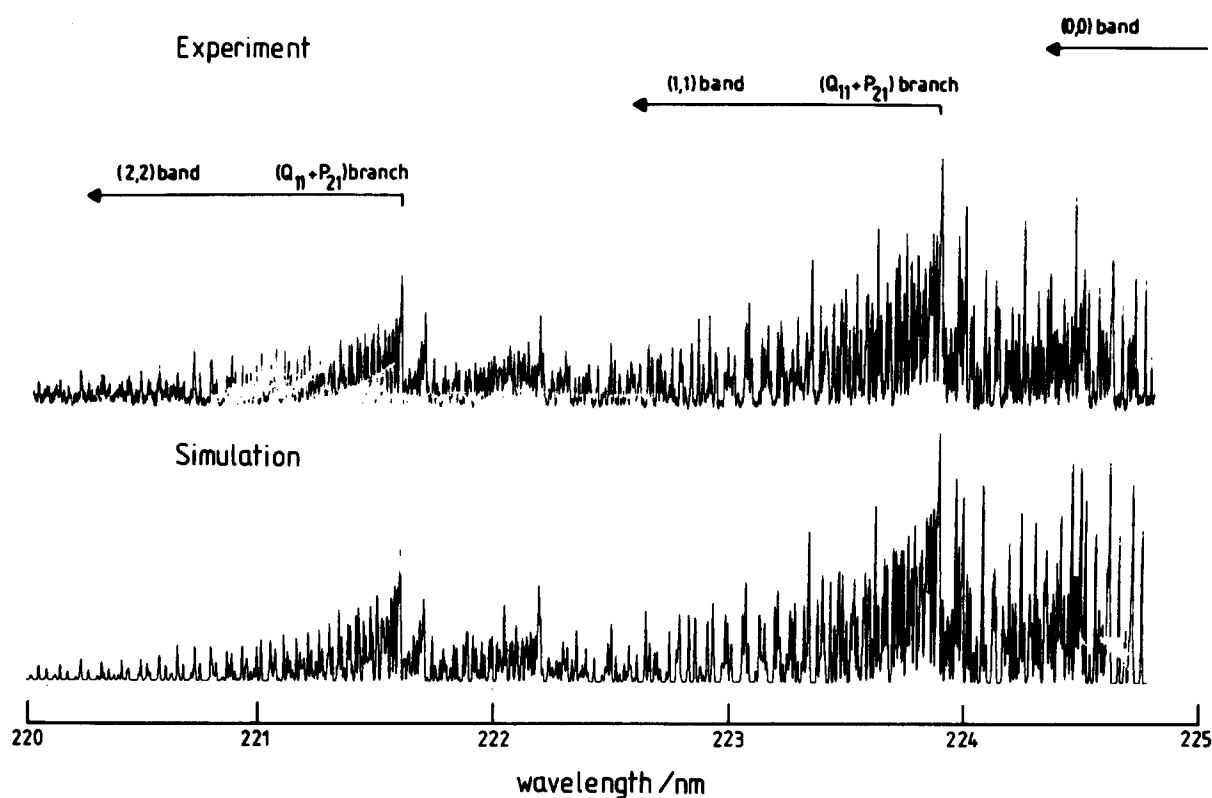


FIG. 1. LIF spectrum of the  $A^2\Sigma^+ - X^2\Pi$  band system of NO between 220 and 225 nm from NO produced in the  $H + NO_2$  reaction. The upper, experimental spectrum is compared with a computer simulated spectrum generated by the procedure described in the text.

observed spectrum. In particular, intensities in the  $Q_{11}$  branch were accurately predicted, implying that our spectra are not significantly influenced by polarization effects.

Typical LIF spectra of NO formed in the  $H + NO_2$  reaction, and each recorded in a single experiment, are compared with their simulated counterparts in Figs. 1–3. The agreement between experiment and simulation is generally quite good, although some discrepancies can be de-

tected in each spectrum. These differences are, in part, due to inaccuracies in the rotational constants of NO which lead to significant errors when the positions of high  $J$  lines are calculated. As a result, simulated spectra can differ notably from the experimentally observed spectra in the regions where high  $J$  transitions predominate.

The simulated band profiles were found to be relatively insensitive to variations in individual level populations

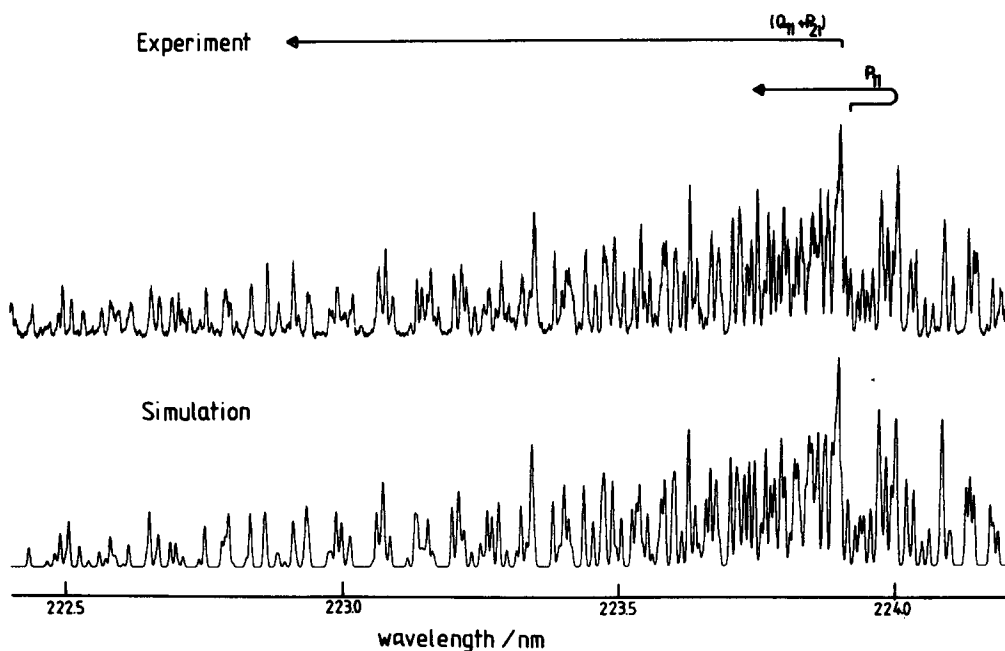


FIG. 2. Comparison between expanded experimental and simulated spectra in the range between 222.4 and 224.2 nm, where the NO  $A^2\Sigma^+ - X^2\Pi$  (1, 1) band predominates.

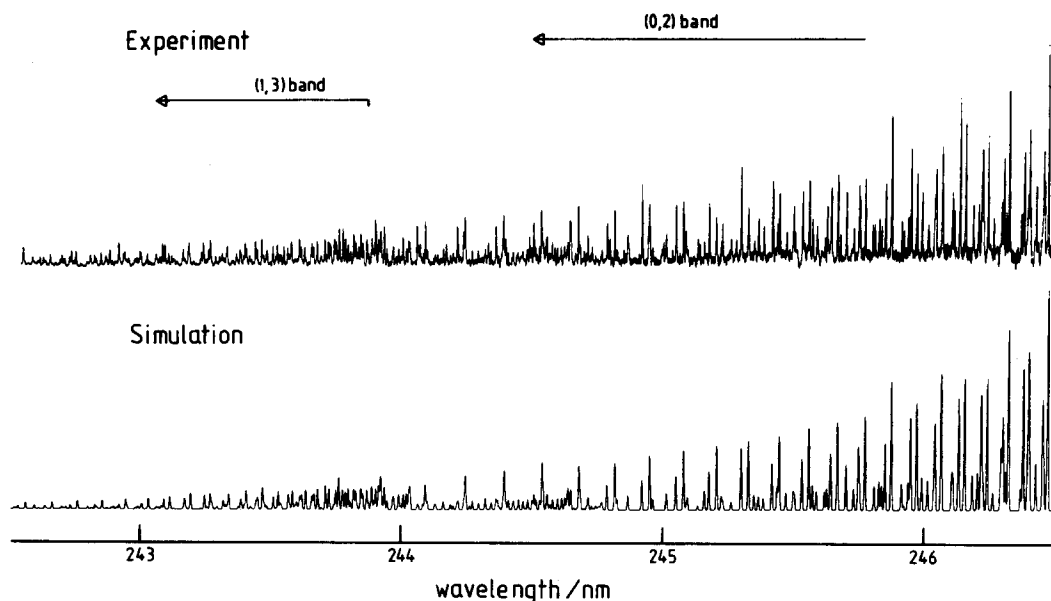


FIG. 3. Comparison between experimental and simulated spectra for the (1, 3) and (0, 2) bands of NO formed in the H + NO<sub>2</sub> reaction.

within the limits of experimental reproducibility. However, the profiles were sensitive to the position chosen for the maximum in each rotational distribution. In the case of the distributions within the  $v = 1, 2,$  and  $3$  levels, it was fairly easy to converge on an acceptable simulation by making successive changes to the selected level populations. However, the strong interference with the lines from lower  $J$  levels of NO( $v = 0$ ) made this approach unsuccessful in the case of the (0,0) band. Consequently, we chose to accept the rotational distribution for  $v = 0$  determined by Sauder and Dagdigian,<sup>6</sup> and we used this as input for our simulation of the (0,0) bands. It provided an acceptable match between the simulated spectrum and the uncontaminated part of the observed spectrum above  $J = 22\frac{1}{2}$ . It was on the basis of comparisons between the intensities of high  $J$  lines in the (0,0) band and those of lines in the (1,1) and (2,2) that we obtained estimates of the vibrational branching ratios.

The rotational state distributions derived from analysis of our spectra are shown in Fig. 4. For NO( $^2\Pi_{1/2}, v = 1$ ) our distribution is compared with that deduced by Sauder and Dagdigian. At high  $J$ , the match is quite good but our distribution peaks to lower  $J$  reflecting the higher degree of rotational relaxation in our experiments. For NO( $v = 2$ ) our distributions appear to extend to somewhat higher  $J$  than those obtained by Sauder and Dagdigian. They made no measurements on bands from NO( $v = 3$ ).

A surprisal analysis was carried out on the derived  $v = 1$  rotational distribution using the simple statistical model described in the previous paper.<sup>1</sup> The result is shown in Fig. 5. At high  $J$ , the surprisal varies linearly with  $g_J$  the fraction of available energy going into NO rotation for a particular rotational level  $J$ , but there is an enhanced population of lower rotational levels consistent with there being partial rotational relaxation under our experimental conditions. A rotational surprisal parameter of  $\theta_{v=1, \text{rot}} = 5.6$  was derived from the linear portion of the surprisal plot. This was then used to reconstruct complete rotational distributions for each NO vibrational level in the

manner described for OH in the preceding paper. These distributions closely matched the form of the observed rotational distributions in  $v = 0, 2,$  and  $3$  at high  $J$  but gave

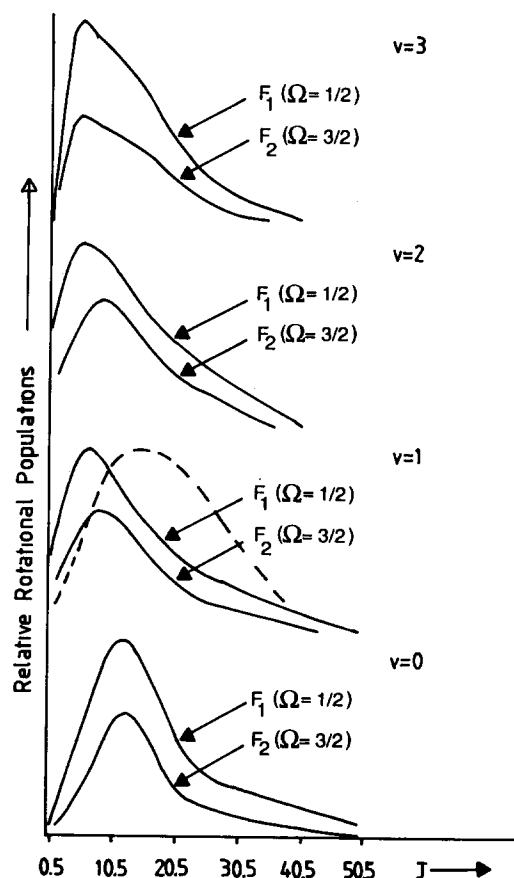


FIG. 4. Rotational distributions for each of the NO vibrational levels  $v = 0-3$  derived by matching computed simulated spectra with those obtained experimentally. The marked preference for production of the  $\Omega = \frac{1}{2}$  spin-orbit component is clearly shown. The dashed curve represents the rotational distribution for the  $F_1$  component NO( $v = 1$ ) determined by Sauder and Dagdigian (Ref. 6).

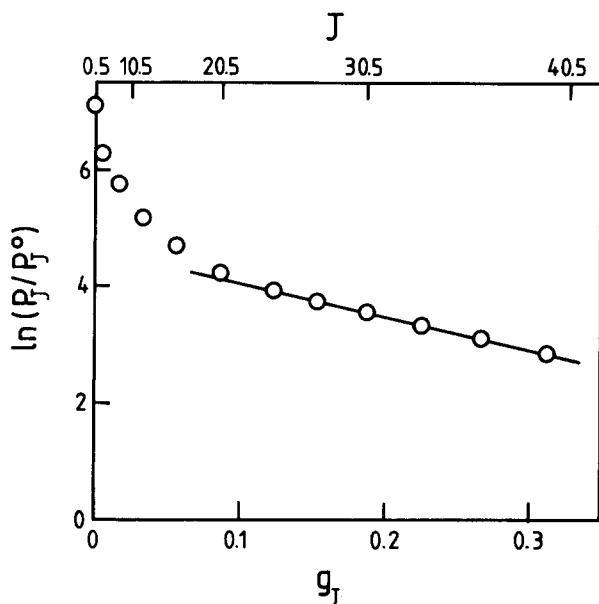


FIG. 5. Results of a surprisal analysis on the rotational populations in NO ( $v=1$ ). The parameter  $g_j$  is the rotational energy divided by the difference between the total energy available to the products and the energy of the  $v=1$  level in NO.

much lower populations than observed at low  $J$ , presumably due to relaxation.

The slope of the surprisal plot indicates that the NO rotation is much less excited in reaction (1) than would be expected on statistical grounds based on a simple prior model considering only conservation of energy. This is in contrast to the result found for OH. It should be noted that the fractional yield of NO rotational energy given later is based on the surprisal analysis and the assumption that the value of  $\theta_{\text{rot}}$  estimated for  $v=1$  is appropriate for all the vibrational levels of NO populated in the reaction.

Vibrational branching ratios were also derived, by successively adjusting the estimates of these quantities until simulated and experimental spectra agreed in respect of the relative intensities of bands in the same  $\Delta v$  sequence. Our results are compared in Table II with statistically predicted values and with the results of Sauder and Dagdigian.<sup>6</sup> The error limits quoted with our measurements represent the range of values over which the simulations remained acceptable, bearing in mind the experimental reproducibility. The large uncertainty associated with the estimate of the relative population in  $v=0$  reflects the difficulty of char-

TABLE II. Relative populations of the vibrational states of NO formed in the H + NO<sub>2</sub> reaction.

$v$	This work	Sauder and Dagdigian	Statistical prior
0	1.0 ± 0.4	1.0	1.00
1	0.25	0.17 ± 0.04	0.55
2	0.07 ± 0.01	0.05 ± 0.02	0.27
3	0.014 ± 0.004	...	0.11

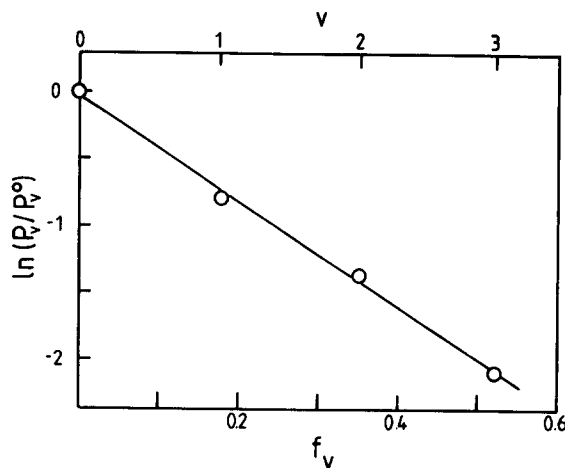


FIG. 6. Surprisal plot for the NO vibrational populations, including for each  $v$  contributions from both spin-orbit levels.

acterizing the rotational distribution in  $v=0$ . Figure 6 shows a vibrational surprisal plot. It yields a well-defined straight line with  $\lambda_{\text{vib}} = 3.9$ , indicating less vibrational excitation of NO than predicted by the simple statistical model.

Matching the simulated spectra to experimental ones also yielded branching ratios into the spin-orbit substates associated with each vibrational level. These ratios are compared in Table III with prior values predicted by our usual model assuming energy conservation as the only constraint.

Having established the product state distributions of NO over spin-orbit, vibrational, and rotational states it was possible to estimate the average yields of available energy into these degrees of freedom. The results of the calculations for  $\langle f_{\text{vib}} \rangle$  and  $\langle f_{\text{rot}} \rangle$  are shown in Table IV. The yield of NO in the  $^2\Pi_{3/2}$  upper spin-orbit substates corresponds to a fractional yield of 0.4%. The results for NO are compared with those for the OH product in Table V. Discussion of these data are deferred until Sec. V.

Defining any propensity for the production of one set of  $\Lambda$ -doublet states over the other was difficult, because the degree of electron alignment in NO is appreciably less than one until high  $J$  levels are reached (see above), and because the appearance of spectra at high  $J$  was affected both by relatively poor signal to noise and by inaccuracies in the simulated spectra resulting from uncertainties in the molecular constants. These factors meant it was difficult to

TABLE III. Ratios of populations in the spin-orbit substates of NO formed in the H + NO<sub>2</sub> reaction.

$v$	$N(^2\Pi_{3/2})/N(^2\Pi_{1/2})$ (Experiment)	$N(^2\Pi_{3/2})/N(^2\Pi_{1/2})$ (Statistical prior)
0	0.5 ± 0.3	0.944
1	0.6 ± 0.1	0.937
2	0.6 ± 0.1	0.928
3	0.5 ± 0.1	0.913

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

$v$	$P_v = N_v / \sum N_v$	$P_v E_v / E_{\text{rot}}$	$\langle f_{\text{rot}} \rangle_v^b$	$P_v \langle f_{\text{rot}} \rangle_v$
0	0.75	0	0.102	0.076
1	0.19 ± 0.06	0.033	0.089	0.017
2	0.05 <sub>2</sub> ± 0.02	0.018	0.073	0.007
3	0.01 <sub>0</sub> ± 0.003	0.005	0.054	0.0005
4	(1.8 × 10 <sup>-3</sup> ) <sup>a</sup>	...	...	...
5	(1.3 × 10 <sup>-4</sup> ) <sup>a</sup>	...	...	...
		$\langle f_{\text{vib}} \rangle = 0.056 \pm 0.012$	$\langle f_{\text{rot}} \rangle = 0.100$	

<sup>a</sup>Estimated from the vibrational surprisal analysis.

<sup>b</sup>Assumes a rotational surprisal parameter of  $\theta_{\text{rot}} = 5.6$  for all vibrational levels.

choose the correct value for the limiting  $\Lambda$ -doublet propensity simply by comparing the intensity of  $Q$  and  $P/R$  lines associated with high  $J$  states. Instead spectra were simulated with different values of  $R$  and the best estimate was chosen by comparing the appearance of the merged ( $Q_{11} + R_{21}$ ) and ( $R_{11} + Q_{21}$ ) branches over a wide range of  $J$ . Our experimental spectra were simulated best using a single value of  $R = 2.0 \pm 0.5$ , for all vibrational sub-bands. This indicates a significant overpopulation of the  $\Lambda$ -doublet component in NO which, in the limit of high  $J$ , has the unpaired electron in the  $p\pi$  orbital in the plane of molecular rotation.

## V. DISCUSSION

The only experiments providing data on the product state distributions in NO formed in the H + NO<sub>2</sub> reaction, which are comparable in detail and scope to those reported in the present paper, are the very recent measurements of Sauder and Dagdigian.<sup>6</sup> They observed LIF spectra of the NO created when two beams of H atoms and NO<sub>2</sub> crossed. In most respects, our results are in satisfactory agreement with theirs. First, they report that the  $\Pi(A')/\Pi(A'')$  population ratio reached a value of  $2.0 \pm 0.5$  by  $N = 30$ . Taking into account the degree of electron alignment, this corresponds to a limiting high  $J$  value of  $R = 3.5 \pm 0.9$ , in reasonable agreement with the value which we deduce. Second, Sauder and Dagdigian<sup>6</sup> found that production of NO in the lower  $^2\Pi_{1/2}$  spin-orbit state is significantly preferred over formation in  $^2\Pi_{3/2}$ . They report the ratio of populations to be independent of vibrational level and  $N(^2\Pi_{3/2})/N(^2\Pi_{1/2})$  to be equal to  $0.49 \pm 0.11$ , which agrees very well with our result.

Sauder and Dagdigian discuss in a general but detailed way how the  $F_1$  spin-orbit manifold might be populated in

TABLE V. Average fractional yields of electronic, vibrational and rotational energy in the OH and NO products of the H + NO<sub>2</sub> reaction.

	OH	NO
$\langle f_{\text{elec}} \rangle$	0.006	0.004
$\langle f_{\text{vib}} \rangle$	0.23	0.056
$\langle f_{\text{rot}} \rangle$	0.29	0.100
$\langle f_{\text{elec}} \rangle + \langle f_{\text{vib}} \rangle + \langle f_{\text{rot}} \rangle$	0.526	0.160

preference to the  $F_2$  manifold, and why such a relatively strong preference can be found for NO but not for OH. We do not reproduce their arguments here but do note that they make two crucial distinctions between NO and OH. First, and probably of primary importance, the electron spin in NO, which is well-described by Hund's case (a) coupling, is more strongly coupled to the internuclear axis than in OH which rapidly approximates to a case (b) species as  $N, J$  increases. Second, OH generally rotates faster than NO on account of its smaller moment of inertia. This will lead to a greater tendency to destroy any preferred alignment as the HONO intermediate complex dissociates and OH and NO separate. The observation that the ratio of spin-orbit populations in OH only differs markedly from the statistical prior for  $v = 3$  may be significant in this regard.<sup>1</sup> Only low  $N$  states in OH ( $v = 3$ ) can be populated and these are closer to case (a), resulting in relatively slow product rotation.

Sauder and Dagdigian estimate an average rotational energy yield in NO of  $\langle f_{\text{rot}} \rangle = 0.056 \pm 0.01$ . Our own estimate of this quantity is strongly affected by what we assume for the rotational distribution in NO ( $v = 0$ ), since 75% of the NO is formed in this vibrational level. If we assume that the rotational surprisal parameter  $\theta_{\text{rot}}$  measured for  $v = 1$  is appropriate for all vibrational levels, then we find  $\langle f_{\text{rot}} \rangle = 0.10$ . On the other hand, the uncontaminated part of our (0,0) band spectrum is acceptably matched by the distribution over high  $J$  deduced by Sauder and Dagdigian. If we accept their rotational energy yield in NO ( $v = 0$ ) and use our result only for higher levels, then we find  $\langle f_{\text{rot}} \rangle = 0.06$ .

It may be that the rotational energy yield in NO is much less than that in OH as a result of the need for conservation of total angular momentum. The H + NO<sub>2</sub> collisions in our system will generate complexes of limited total angular momentum: partly because the collisional reduced mass and therefore the initial angular momentum is small, and partly because the NO<sub>2</sub> is rotationally cooled in the jet expansion. Even allowing for the existence of final orbital angular momentum, there may be some propensity for the products to be formed in similar rotational states with their directions of rotation opposed so that little net angular momentum is generated. Of course, the very different moments of inertia for OH and NO ensures much higher rotational energy in OH for similar rotational angular momentum.

The vibrational state branching ratios which we have determined are compared with those of Sauder and Dagdigian in Table II. The relative vibrational state densities observed by Sauder and Dagdigian are in the ratio  $N(v=0): N(v=1): N(v=2) = 1.0: 0.21 \pm 0.04: 0.08 \pm 0.03$ . However, they corrected these numbers to relative fluxes, yielding the figures in Table II, by allowing approximately for the different residence times in the viewing zones of species in different internal states. In view of the evidence for some collisional rotational relaxation of both OH and NO in our experiments we have chosen not to do this. This is tantamount to an assumption that there are sufficient collisions in the region where our uncollimated



jets intercept to ensure roughly equal residence times for all species. This assumption is one invariably used in infrared chemiluminescence experiments of the "arrested relaxation" type.<sup>16</sup> Sauder and Dagdigian's distribution after correction in the way described above corresponds to an overall energy yield in the NO vibration of  $\langle f_{\text{vib}} \rangle = 0.039$ , in contrast to our value of 0.056 with an estimated error of 0.012. It should be emphasised that the likelihood of collisional relaxation of vibrationally excited NO in either set of experiments is negligible. The main gases in the crossing point of our two streams of gas are H<sub>2</sub> and He, both of which are known to be inefficient at relaxing NO( $v=1$ ).<sup>17</sup>

The only other estimate of energy disposal into the NO product of reaction (1) is based on infrared chemiluminescence experiments performed by Setser's group.<sup>3,5</sup> Observing infrared emission from NO formed in a fast flow experiment, they deduced a ratio  $N(v=2)/N(v=1)$  of 0.43, substantially higher than that determined from analysis of LIF spectra by either ourselves or Sauder and Dagdigian.<sup>6</sup>

Table V reports the average yields of energy into the electronic, vibrational, and rotational degrees of freedom of both products of the H + NO<sub>2</sub> reaction as determined in the experiments that are described in this and the preceding paper.<sup>1</sup> These yields account for 69% of the total energy available to the OH + NO formed in the reaction. Energy balance therefore suggests that the remaining 31% of the energy must be deposited in the relative translational motion of the separating OH and NO.<sup>20</sup> However, this result is appreciably higher than estimates based on molecular beam experiments<sup>18</sup> (at enhanced collision energies) or on the analysis of OH Doppler line profiles.<sup>19</sup> Both these studies suggested a value of  $\langle f_{\text{tr}} \rangle \approx 0.20$ . It was these results coupled with earlier studies of the OH internal state distribution<sup>4</sup> which led to suggestions<sup>3,18</sup> that the internal modes of NO must absorb 25%–30% of the energy released in the H + NO<sub>2</sub> reaction. The results reported in the present paper and by Sauder and Dagdigian<sup>6</sup> appear to show that this figure is a substantial overestimate of the energy absorbed by NO.

The reasons for the apparent "loss" of about 10% of the energy released in the reaction are not clear. It may be that the translational energy yield depends on collision energy, so that both Haberland's<sup>18</sup> and our own estimates of  $\langle f_{\text{tr}} \rangle$  are correct but they are not transferable to the conditions of the other experiment. This would still leave the apparent discrepancy between our estimate and Kinsey's result<sup>19</sup> to be explained. Murphy *et al.*<sup>19(d)</sup> measured product translational energy distributions associated with several specific internal states of OH by measuring Doppler line shapes. Over a restricted range of internal energies it appeared that there was a linear relationship between the OH internal energy and the translational energy yield and, assuming this relationship held over the full range of energies, Murphy *et al.* estimated an average translational energy yield. It is possible that this assumption leads to an overestimate of  $\langle f_{\text{tr}} \rangle$ .

A second possible explanation is that our methods for extracting nascent rotational state distributions from the partially relaxed distributions which we actually observe

underestimate  $\langle f_{\text{rot}} \rangle$  for either OH or NO, or both. However, we note that our values of  $\langle f_{\text{rot}} \rangle$  are close to those found in experiments performed under conditions where no significant relaxation can occur.<sup>6,19</sup> As already stated there seems very little likelihood of vibrational relaxation in our experiments. Moreover, allowing for any effects due to species in different internal states having different residence times for observation would lead to *colder* internal state distributions, and hence widen the gap between our estimated  $\langle f_{\text{tr}} \rangle$  and the values of this quantity which have been estimated previously.

Finally, we consider what our data on the product internal state distributions tell us about the dynamics of collisions in which reaction (1) occurs. It is clear that energy is not partitioned in an entirely statistical manner between the degrees of freedom of the OH and NO products, and this seems to rule out the formation of *long-lived* HONO collision complexes in which energy randomisation is complete. This is scarcely surprising. The formation of HONO in its  $\tilde{X}^1A'$  electronic ground state is 331 kJ mol<sup>-1</sup> exothermic, while reaction (1) is 123.6 kJ mol<sup>-1</sup> exothermic. Hence, any HONO complex formed from H + NO<sub>2</sub> will have energy 1.6 times the minimum that it requires to dissociate to OH + NO. An RRKM estimate of the lifetime of such a complex<sup>6</sup> gives a value of 0.1 ps.

On the other hand, the extent of NO excitation is greater than might be expected in a purely direct reaction. The most likely explanation for the dynamics is that reaction does occur over the surface of the HONO ground state but that any complex lasts, on average, for only a few vibrational periods. This allows some partial transfer of energy to internal motions associated with the NO moiety. The complex is only weakly constrained to be planar, because of its high internal energy exciting out-of-plane motions, so that when the complex dissociates there is only a fairly weak preference for one set of  $\Lambda$ -doublet states over the other. Further light may be shed on the collision dynamics by examining how the internal state distributions of the reaction products depend on the reagents' collision energy. Such studies will be difficult but now appear to be technically feasible.

*Note added in proof:* Professor J. B. Halpern has pointed out that estimating the average fractional yield as  $\langle f_{\text{trans}} \rangle = 1 - \langle f_{\text{int,OH}} \rangle - \langle f_{\text{int,NO}} \rangle$  does not give the true value of this quantity, which is strictly defined as  $\langle f_{\text{trans}} \rangle = \langle (1 - [f_{\text{int,OH}} + f_{\text{int,NO}}]) \rangle$  where  $f_{\text{int,OH}}$  and  $f_{\text{int,NO}}$  are the reduced internal energies of OH and NO formed in the same reactive event. If  $f_{\text{int,OH}}$  and  $f_{\text{int,NO}}$  are strongly correlated, the values of  $\langle f_{\text{trans}} \rangle$  calculated in these two ways could differ significantly. We believe however that this is unlikely to be the major source of the difference between the values of  $\langle f_{\text{trans}} \rangle$  estimated by us and those estimated in Refs. 18 and 19.

## ACKNOWLEDGMENTS

It is a pleasure to record valuable advice from a number of friends and colleagues. These include P. Dagdigian, R. N. Dixon, R. A. Kennedy, B. J. Orr, C. Wittig, and

X.-F. Yang. We are also indebted to SERC and the University of Birmingham for research grants, SERC for a research studentship (A.M.L.I.) and for loans of equipment from the Laser Loan Pool.

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