Vibrational state specificity and selectivity in the reactions N+OH→NO(**v)+H and N+NO(v**)→N2+O

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Vibrational state specificity and selectivity in the reactions N+OH→NO(v)+H and N+NO(v)→N₂+O

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The vibrational state distribution of NO formed in the radical–radical reaction N+OH→NO($v'\leqslant 9$)+H; $\Delta H_0^0 = -204.0$ kJ mol^{-1} has been determined using a pulse-and-probe technique. OH radicals were generated by pulsed laser photolysis of H$_2$O$_2$ at 266 nm in a flow of N$_2$ which had been passed through a microwave discharge to produce N atoms. The vibrational distribution of NO, measured by laser-induced fluorescence (LIF) spectroscopy, is similar to that predicted by phase-space theory and corresponds to an average yield of ca. 31% of the energy available to the reaction products. Experiments in which LIF signals were observed as the pulse–probe time delay was varied showed that populations within different vibrational levels ($v=0$–8) displayed similar kinetics, consistent with rapid removal of NO(v) by reaction with N atoms, N+NO(v)→N$_2$+O, at rates which exhibit a mild dependence on v.

I. INTRODUCTION

Early investigations of the dynamics of bimolecular reactions, and in particular of the energy disposal in such reactions,[1] were mainly carried out on systems like F+H$_2$→HF+H, in which a radical atom attacks a saturated, diatomic molecule. Such reactions almost invariably proceed directly across a potential energy surface on which there is no significant potential energy well, and they usually lead to nonstatistical energy partitioning: that is, the energy released can excite some product degrees of freedom preferentially.

More recently, experiments in reaction dynamics have widened their scope in at least two directions. First, reactions involving more atoms are being subjected to detailed scrutiny. For example, examination of reactions involving two diatomic species, like $AB+CD→ABC+D$, allows one to probe questions of (i) vibrational *selectivity* and (ii) vibrational *specificity*: that is, (i) is reaction selectively promoted by exciting CD or AB vibrationally;[2–4] and (ii) is energy channelled preferentially into some, rather than other, modes of ABC?[5–7] Likewise, results are starting to be reported on (iii) energy partitioning among the products of exothermic $A+BCD→AB+CD$ reactions,[8] and (iv) the energy requirements for endothermic reactions of the $A+BCD→AB+CD$ type, especially whether such reactions are vibrationally selective.[9,10]

A second major point of focus, frequently overlapping with that described in the previous paragraph, is the dynamical study of reactions between two radicals or between a radical and unsaturated molecule in which collision complexes may form, since the lowest electronic surface connecting reagents to products adiabatically is known or expected to include a deep potential energy well. In these circumstances, the reaction may be considered to proceed by successive steps of bimolecular association and unimo-

lecular fragmentation, and one can envisage two limits to the collision dynamics. At one extreme, the complex could last sufficiently long for energy randomization to be complete. The distribution of product molecules over rovibrational states would then be *statistical*; that is, it would be determined only by the requirement to conserve total energy and angular momentum. In the other limit, the potential energy well might exert little influence on the dynamics, they are *direct*, and some product degrees of freedom are excited preferentially. A number of factors, such as the exothermicity of the reaction, the depth of the potential well, and the number and mass of the participating atoms, might be expected to influence the dynamics. However, as yet there have been too few detailed studies of reactions of this kind for general dynamical rules or propensities to emerge.

Among reactions which might proceed via a collision complex and whose dynamics have been studied recently in this laboratory and elsewhere by spectroscopic measurements on the product state populations are H+NO$_2$→OH +NO,[8] CN+O$_2$→NCO+O,[5] and OH+CO→CO$_2$+H.[6] In all these three cases, one of the reagents (NO, O$_2$, or CO) is relatively stable, simplifying the experiments. This is also true of studies that have been made of the nascent state distributions of OH from the reactions of translationally "hot" H atoms with CO$_2$ (Ref. 11) and O$_2$.[12] Several studies of energy disposal in reactions between two unstable radicals have also been performed using the time-resolved infrared chemiluminescence technique.[13,14]

In the present paper, we report the results of laser-induced fluorescence (LIF) measurements on the vibrational state product distribution from the reaction

$$N+OH→NO(v\leqslant 9)+H; \quad \Delta H_0^0 = -204.0 \text{ kJ mol}^{-1}, \quad (1)$$

which is an example of the simplest class of radical–radical reaction; that is, one involving only three atoms. As such, it should be amenable to detailed and high quality theoretical calculations. Moreover, the results of our experiments

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can be compared with those on two closely related processes: (i) the promotion of NO to vibrationally excited states in collisions with translationally hot H atoms;[15] and (ii) the product state distribution of NO when it is formed in the reaction between $O(^3P)$ atoms and $NH(^3\Sigma^-)$.[16] Potential energy surfaces for HNO/NOH have been calculated by *ab initio* methods of various degrees of sophistication[17–19] and Colton and Schatz[20] have computed quasiclassical trajectories designed to simulate the collisions between NO and hot H atoms which were studied experimentally by Wight, Donaldson, and Leone.[15] The results of these various investigations and their connection with our own results will be discussed later.

The experimental method which has been adopted to study the NO product state distribution from reaction (1) is based on that used, several years ago, by Howard and Smith[21] to establish the rate constant for the same reaction and its variation with temperature. Their results yielded the following expression: $(k_1/cm^3\ molecule^{-1}\ s^{-1}) = 5.3 \times 10^{-11}\ (T/298)^{-0.25}$ and were confirmed by independent measurements by Lewis and Watson.[22] If it is assumed that reaction occurs only over one triplet surface that adiabatically connects reagents and products, then the value of the rate constant at 298 K corresponds to a thermally averaged cross section for reaction on that single surface of ca. 23 Å^2.

As in Howard and Smith's experiments,[21] N atoms were generated by passing a flow of molecular nitrogen through a microwave discharge, causing 0.1%–1.0% of the N_2 molecules to dissociate. HNO_3 or H_2O_2 was then added downstream of the discharge and photolyzed, in our experiments with the frequency-quadrupled output ($\lambda = 266$ nm) from a Nd:YAG laser. Under these conditions, the concentration of OH created by photolysis is much less than the steady-state concentration of N atoms present in the flowing gas. Consequently, OH radicals disappear in a pseudo-first-order process generating NO in a range of vibrational levels which can then be observed via laser-induced fluorescence spectroscopy. A special, and interesting, feature of studying reaction (1) under the conditions which have just been outlined is that the NO product is rapidly removed by subsequent reaction with NO

$$N + NO(v) \rightarrow N_2 + O, \quad \Delta H_0^0 = -313.8 \text{ kJ mol}^{-1}. \quad (2)$$
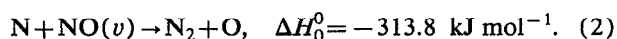
Between 200 and 400 K, the rate constant for this reaction under thermal conditions [i.e., for $NO(v=0)$] is given by $[k_2(v=0)/cm^3\ molecule^{-1}\ s^{-1}] = 3.1 \times 10^{-11}$, with an uncertainty in log (k_{298}) of 0.15.[23] The value of this rate constant is many times greater than that for relaxation of $NO(v=1)$ by N_2 (which is, together with argon, the most abundant species in our gas mixtures),

$$NO(v=1) + N_2 \rightarrow NO(v=0) + N_2 \quad (3)$$
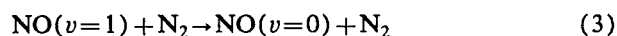
$(k_3/cm^3\ molecule^{-1}\ s^{-1}) = 1.4 \times 10^{-16}$.[24] Consequently, it was anticipated that under the conditions of our experiment, NO formed in specific vibrational levels by reaction (1) would be removed completely by reaction (2), rather

than relaxed to lower levels. Under conditions where the concentration of NO in any given vibrational level, i.e., $[NO(v)]$, is determined only by reactions (1) and (2), it will vary according to the simple rate equation

$$\frac{d[NO(v)]}{dt} = f_v k_1[N][OH] - k_{2,v}[N][NO(v)], \quad (i)$$

where f_v is the fraction of NO produced in level v by reaction (1) and $k_{2,v}$ is the rate constant for reaction between N atoms and NO in the specific vibrational level v. Evidence that this expectation was very largely fulfilled will be given later.

In this paper, the results of two kinds of experiments are reported. In the first kind, LIF spectra were recorded for several bands of the NO $A\ ^2\Sigma^+ - X\ ^2\Pi$ electronic system using a pulsed, tunable dye laser which was fired at a fixed time delay after the photolysis laser produced OH radicals. The distribution of NO over vibrational levels at the selected time delay can be inferred from the relative intensities of features in these spectra. In the second type of experiment, the frequency of the "probe" dye laser was fixed to correspond to an absorption in a particular band of the NO spectrum and the intensity of the LIF signal was recorded as the time delay between photolysis and probe lasers was systematically varied. These traces show how the concentration of NO in a particular vibrational level evolved with time.

II. EXPERIMENT

The reaction cell was constructed from Pyrex in the shape of a cross. The main tube, internal diameter 40 mm and ca. 60 cm long, carried the gas flow and was evacuated by a high speed rotary pump (Edwards, model E2M40) yielding a pumping speed of ca. 1 m s^{-1} in the flowtube. Nitrogen gas entered the flowtube via a sidearm close to its upstream end. This gas had already passed through a microwave discharge (2450 MHz, 60 W; Electromedical Supplies, Microtron 200, mk 2) which dissociated 0.1%–1% of the nitrogen to atoms. The flowtube was equipped with a centrally positioned, movable injector. In the main experiments, HNO_3 or H_2O_2 diluted in Ar was admitted through this injector which had its tip positioned just upstream of where the sidearms were attached to the main tube. In subsidiary experiments, the injector could be used to admit NO, so that titrations using the nitrogen, "air," and nitric oxide afterflows could be performed to establish the flow, and hence the steady-state concentration, of N atoms.[25]

The photolysis and probe laser beams entered the apparatus in counterpropagating directions via the two sidearms. These sidearms were 30 mm internal diameter and ca. 30 cm long, and they carried baffles to reduce scattered laser light and fluorescence from the Spectrosil windows mounted, at Brewsters angle, at their ends. Photolysis of HNO_3 or H_2O_2 to produce OH radicals was effected by the frequency-quadrupled output at 266 nm of a Nd:YAG laser (Spectron Lasers, model SL803) providing ca. 30 mJ per pulse and operating at 10 Hz. The probe radiation was

provided by a pulsed dye laser (Lambda-Physik, model 2002) pumped by an excimer laser (Lumonics, model 420) operating at 308 nm. The probe pulses were delayed with respect to the photolysis pulses using a delay generator (Stanford Research Systems, DG 535), which could also scan the delay time in kinetics experiments.

Fluorescence induced by the probe laser was collected by a 3.8 cm focal length lens and directed onto a photomultiplier tube (EMI, 9635QB). This telescope-detector assembly was mounted directly above the center of the cross formed by the flowtube and the baffle arms. It was unnecessary to use a filter to limit the wavelengths reaching the photomultiplier tube. However, a slit placed in front of the photomultiplier was employed to discriminate against scattered light. Photodiodes monitored any variation in the pulse energies from the Nd:YAG laser and from the dye laser. Boxcar integrators (Stanford Research Systems, model 250) digitized the transient signals from the photomultiplier and from the photodiodes and the resulting signals were passed to a microcomputer (Opus, model PCV). The signals from the photodiodes were then used to correct the LIF signals for variations in the pulse energies from the two lasers. The probe laser pulse energy was kept low to avoid saturation effects.

In order to obtain information about the populations in the wide range of vibrational levels ($0 \leqslant v \leqslant 9$) in which NO can be produced in reaction (1), it was necessary to record LIF spectra over a wide range of ultraviolet wavelengths, necessitating the use of several dyes and doubling crystals in the dye laser. Details of the bands observed, their wavelengths and relative strengths, and the dyes and doubling crystals used are given in Table I.

The reaction cell was connected to a standard gas-handling apparatus. Nitrogen was taken directly from a cylinder (BOC, "white spot") and used without purification. Its flow was controlled with a needle valve and monitored using a "floating-ball" flowmeter. Preliminary experiments were performed with HNO_3, diluted in argon, as the source of OH radicals. The flow of this mixture was controlled by a needle valve, monitored by a rotameter, and adjusted to yield a partial pressure of 50–100 mTorr of HNO_3 in the gas mixture irradiated by the lasers. For the main experiments, HNO_3 was replaced by H_2O_2 as the photochemical precursor of OH. A different method was required for introducing H_2O_2. The gas flowline leading to the movable injector was adapted to incorporate a 100 ml round-bottomed flask. About 30 ml of concentrated H_2O_2 was admitted to this flask and Ar was flowed over it. The temperature of the flask and the flowrate of gas was adjusted until satisfactory LIF spectra could be obtained.

All the experiments reported in this paper were performed at room temperature (295 ± 4 K) and a total pressure of ca. 2.5 Torr.

III. RESULTS

Although preliminary experiments were performed using HNO_3 as the photochemical source of OH radicals, the

TABLE I. Details of the observations of NO(v) populations via LIF spectroscopy in the $A\ ^2\Sigma^+-X\ ^2\Pi$ system.

v',v''	$\lambda_{v',v''}$ (nm)[a]	Rel. $B^b_{v',v''}$
(i) dye: coumarin 2; crystal: KPB		
2,2	221.6	0.96
1,1	223.9	0.62
0,0	226.2	1.00
3,4	228.4	0.67
2,3	230.9	0.44
(ii) dye: coumarin 503; crystal: KPB		
0,2	247.1	1.46
1,4	255.1	0.86
(iii) dye: coumarin 153; crystal: KPB		
1,4	255.1	0.86
0,3	258.7	1.07
2,6	263.1	0.60
1,5	267.1	0.94
(iv) dye: fluorol 75A; crystal: KDP		
3,8	271.0	0.46
0,4	271.3	0.67
2,7	275.4	0.79
1,6	280.1	0.78
3,9	283.7	0.72
0,5	284.9	0.38
2,8	288.8	0.77

[a]Wavelength of the Q_{11} head.
[b]The numbers in this column correspond to the product of the Franck–Condon factor and the square of the electronic transition moment divided by the same quantity for the (0,0) band. This procedure yields relative values of the Einstein B coefficients. Data were taken from L. G. Piper and L. M. Cowles, J. Chem. Phys. 85, 2419 (1986). For the $v'=3$ bands we calculated Franck–Condon factors using Morse wave functions and estimated values of the electronic transition moment by interpolation of values from Piper and Cowles' paper.

experiments which were analyzed to yield the results reported here were all obtained using H_2O_2

$$H_2O_2 + h\nu(\lambda = 266 \text{ nm}) \rightarrow 2OH.$$
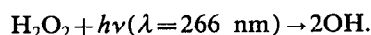
Hydrogen peroxide has two advantages over nitric acid as a source of hydroxyl radicals for our experiments. First, with H_2O_2 there is no possible "prompt" source of NO, either as an impurity or from one- or two-step photolysis of the precursor itself[26] (cf. $HNO_3 + h\nu \rightarrow HO_2 + NO$; $HNO_3 + h\nu \rightarrow OH + NO_2$, $NO_2 + h\nu \rightarrow NO + O$) or of impurities (cf. $NO_2 + h\nu \rightarrow NO + O$). Second, the yield of OH for the same concentration of precursor and the same laser fluence is ca. five times greater from H_2O_2 than from HNO_3, on account of a higher quantum yield (at least a factor of 2) and a higher absorption cross section (a factor of ca. 2.4).[23] There are, however, some disadvantages in using H_2O_2. Notably, its reaction with OH is faster ($k_{298} = 1.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) than the reaction between OH and HNO_3 ($k_{298} = 1.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}).[23] Second, with H_2O_2 it is more difficult to establish the concentration of the photochemical precursor, since it could not be admitted to the reaction cell as a component of a pre-prepared gas mixture at a known flowrate.

In order to estimate the concentration of H_2O_2 present in our experiments, a few measurements were made on the kinetic decays of the concentration of OH. This was ac-
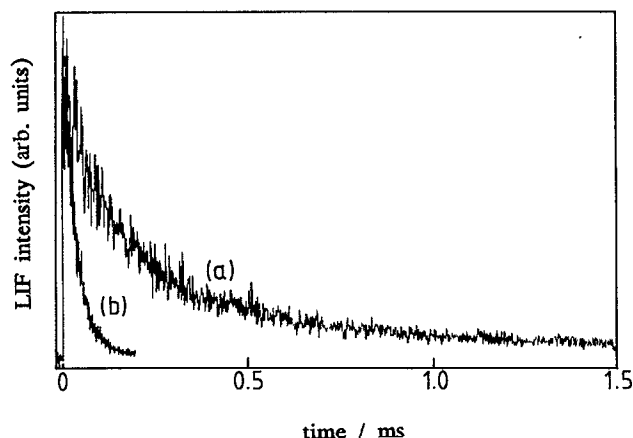
FIG. 1. Decay of LIF signal with the probe laser tuned to the $A\,^2\Sigma^+$–$X\,^2\Pi$ (2,0) band of OH: (a) with no N atoms present in the gas mixture, and (b) with the microwave discharge on producing N atoms in the gas.

TABLE II. Reactions included in the modeling calculations and their rate constants.[a]

Reactions	$k/10^{-11}$ cm^3 molecule^{-1} s^{-1}
$N+OH \rightarrow NO+H$	4.9
$N+NO \rightarrow N_2+O$	3.2
$OH+H_2O_2 \rightarrow HO_2+H_2O$	0.17
$N+HO_2 \rightarrow NO+OH$	2.2
$OH+HO_2 \rightarrow H_2O+O_2$	10.0
$NO+HO_2 \rightarrow NO_2+OH$	0.83
$O+OH \rightarrow O_2+H$	3.3
$O+HO_2 \rightarrow O_2+OH$	6.0
$H+HO_2 \rightarrow 2\,OH$	7.0

[a]Rate constants were taken from Ref. 23, except that for reaction between N and HO$_2$ which is from Ref. 28.

complished by observing LIF signals from OH via absorption in lines of the $A\,^2\Sigma^+$–$X\,^2\Pi$ (2,0) band at 260.6 nm. Despite strong predissociation in the upper state of this transition and its small Franck–Condon factor,[27] the LIF signals were strong and could be recorded as a function of the time delay between the 266 nm laser pulse generating OH and the probe pulse from the dye laser. Figure 1 shows two such traces: one with no N atoms present in the gas mixture, the other with the microwave discharge switched on to produce N atoms.

By analyzing the LIF traces recorded in the absence of N atoms, it was possible to estimate the partial pressure of H$_2$O$_2$ present in the gas mixture under typical experimental conditions. This estimate was made by dividing the first-order rate constants obtained by fitting the decay curves by the second-order rate constant for reaction between OH and H$_2$O$_2$ which was quoted earlier. The calculations indicated a partial pressure of H$_2$O$_2$ of ca. 70 mTorr ($\equiv 2.3\times10^{15}$ molecule cm^{-3}). This estimate neglects any contribution to the decay of the OH signal as a result of OH radicals diffusing out of the region irradiated by the probe laser, but this is reasonable since the diffusional loss rate was very much less than the rate of reaction with H$_2$O$_2$ under our experimental conditions. The partial pressure of H$_2$O$_2$ estimated in this way is consistent with what would be expected if the Ar used to transport H$_2$O$_2$ into the reaction cell became saturated with H$_2$O$_2$ vapor. The estimate of [H$_2$O$_2$], together with the known absorption cross section for H$_2$O$_2$ at 266 nm ($\sigma=4.0\times10^{-20}$ cm^2)[23] and an estimate of the laser fluence in photons cm^{-2}, could be used to calculate an approximate value for the concentration of OH produced in our experiments by the photodissociation of H$_2$O$_2$. These calculations indicated initial concentrations of OH in the range $0.2\text{–}1.0\times10^{13}$ molecule cm^{-3}.

The procedure which has just been described could be adapted to estimate the concentration of N atoms present under normal experimental conditions. To do this, the differences between first-order decay constants obtained with

and without N atoms present were divided by k_1, the rate constant for reaction between OH radicals and N atoms. Such calculations indicated partial pressures of N atoms in the range 10–15 mTorr ($\equiv 3.2\text{–}4.9\times10^{14}$ molecule cm^{-3}). These estimates were in good agreement with those made by titrating the steady-state concentration of N atoms in the flowing gas against NO admitted via the central injector.

It should be emphasised that an *accurate* knowledge of the concentrations of N, OH, and H$_2$O$_2$ is not required for the interpretation of the present experiments, where the aim is to establish the relative rates of NO(v) production in reaction (1) and the influence of NO vibrational excitation on the rate of reaction (2). On the other hand, *approximate* concentrations of the species present were required to assess the possible effect of side reactions. Comparison of pairs of OH LIF traces like those shown in Fig. 1 demonstrates that, under the conditions of our experiments, at least 80% of the OH radicals initially produced reacted with N atoms to produce NO. Reaction of some fraction of the remaining OH radicals with H$_2$O$_2$ produced HO$_2$ radicals

$$OH+H_2O_2\rightarrow HO_2+H_2O \qquad (4)$$

which would then react with N atoms ($k_{298}=2.2\times10^{-11}$ cm^3 molecule^{-1} s^{-1})[28]

$$N+HO_2\rightarrow NO+OH; \quad \Delta H_0^0=-328 \text{ kJ mol}^{-1}. \qquad (5)$$
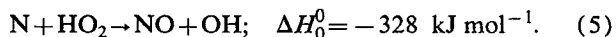
Reaction (5) could have two effects on the analysis of our experiments. First, it could serve as a secondary source of NO; second, it could regenerate OH radicals.

To examine the possible effects of these complications quantitatively, some calculations were performed using the kinetics modeling package FACSIMILE.[29] Table II lists the full scheme of reactions which was employed in these calculations and their rate constants. NO is produced in two reactions, (1) and (5). The modeling calculations allowed us to estimate what fractions of the NO present at any time delay were created in reaction (1) and how much in reaction (5). Thus at 4 μs delay, only 0.5% of the total NO present had been produced in reaction (5), whereas this
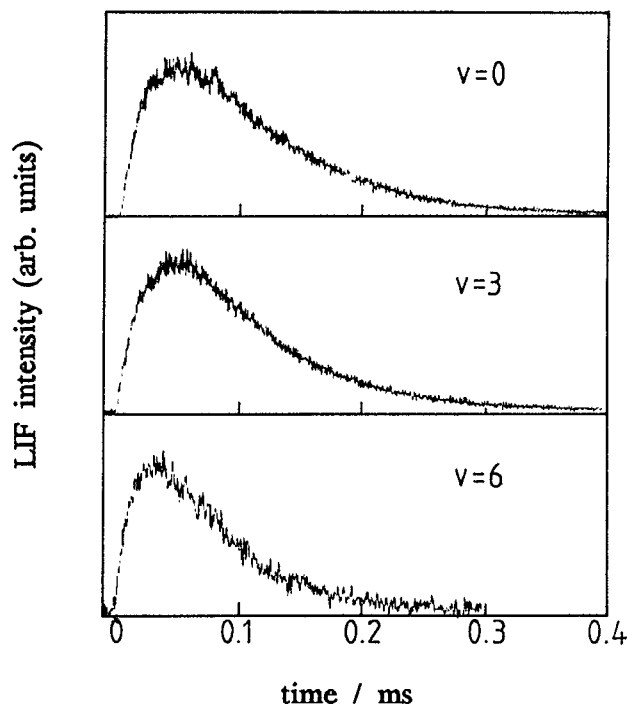
FIG. 2. Traces of LIF signal against time showing the variation of NO populations in $v=0$, $v=3$ and $v=6$.

amount increased to 7% at 50 μs. In the spectroscopic experiments designed to determine the vibrational distribution of the NO product of reaction (1), the time delay was set at either 10 or 16 μs. At these delays, the calculations showed that only ca. 1%–2% of the NO present would have been formed in reaction (5). Any distortion of the NO vibrational state population distribution from that produced in reaction (1) would therefore be negligible.

Solution of rate equation (i) for the concentration of NO within a particular vibrational level, modified to allow for loss of OH by reaction (4) but neglecting reaction (5) and diffusive loss of OH and NO(v), yields

$$[NO(v)]_t = [OH]_0 A[\exp(-k_{2,v}[N]t) - \exp(-k_{1st}t)],$$
(ii)

where $[OH]_0$ is the concentration of OH produced by pulsed laser photolysis of H_2O_2; $k_{1st} = (k_1[N] + k_4[H_2O_2])$; and $A = f_v k_1[N]/(k_{1st} - k_{2,v}[N])$. To examine how [NO($v$)] actually varied with time a number of experiments were performed in which the wavelength of the probe laser was fixed and the delay time between photolysis and probe pulses was scanned systematically. Experiments of this kind have been carried out on NO in all levels from $v=0$ to $v=8$. Figure 2 shows traces reflecting variations in [NO($v=0$)], [NO($v=3$)], and [NO($v=6$)]. The rise in [NO(v)] at short time delays is largely determined by k_{1st}, and the decay at long times by $k_{2,v}$. The $v=0$ and $v=3$ traces in Fig. 2 are clearly very similar, demonstrating that to a good degree of approximation the kinetics for NO($v=0$) and NO($v=3$)—and indeed in all levels from $v=0$ to

$v=4$—are controlled only by reactions (1), (2), and (4), and that the rate of reaction (2) is virtually independent of v.

Computer fits of such traces to an expression of the form, $B\{\exp(-\lambda_1 t) - \exp(-\lambda_2 t)\}$, yields values of the exponents λ_1 and λ_2. These values can be compared with estimated values of $k_{2,v=0}[N]$ and k_{1st} using the known values of the rate constants k_2, k_1, and k_4 and the estimated values of the concentrations [N] and [H_2O_2]. Agreement between the calculated first-order rate constants and the values derived from the experimental traces is fair, and this quantitative analysis indicates that the value of $k_{2,v}$ increases by ca. 15% from $v=0$ to 4. Two factors would be expected to detract from the agreement between experiment and calculation. The first is the occurrence of the secondary chemistry described earlier. The second is the fact that photolysis of H_2O_2 at 266 nm yields OH radicals with very high translational energy. At 266 nm, H_2O_2 is promoted to its $\widetilde{A} {}^1A$ repulsive state. Experiments on the subsequent photodissociation dynamics show that ca. 90% of the excess energy goes into translational motion of the two OH fragments, each acquiring ca. 110 kJ mol^{-1} of energy.[30] Despite the fact that N atoms are heavily diluted in N_2 and Ar, there is likely to be significant delay before the OH radicals are fully thermalized.

LIF traces from NO in levels with $v \geqslant 5$ show some increase in the value of λ_1, the smaller of the two first-order rate constants and the one which characterizes the signal decay. The increase is illustrated in Fig. 2 by the third trace, reflecting the kinetics of NO($v=6$). This effect could be caused by an acceleration of reaction (2) for $v \geqslant 5$. An alternative and interesting possibility is that the reaction, $N' + NO \rightarrow N'O + N$, in which the O atom is transferred between the two N atoms, becomes rapid and provides a mechanism for efficient vibrational relaxation.[31] Whatever the cause of the slight increase in the rate at which NO(v) is removed at high v, it can safely be stated that any enhancement of the rate constant for reaction between N atoms and NO(v) is negligible for $v \leqslant 4$ and is less than a factor of 2 for $5 \leqslant v \leqslant 8$.

The main purpose of our experiments was to measure the nascent vibrational state distribution of the NO formed in the reaction between N atoms and OH. As these molecules are removed completely by reaction (2) at a rate almost independent of v, instead of by a "cascading" process of relaxation, it was not necessary to work at very low pressure or short time delays to eliminate the effects of relaxation. Most of the LIF spectra used to determine the relative vibrational populations were recorded with a delay of 16 μs between photolysis and probe lasers and at a total pressure of 2.5 Torr. This was adequate to ensure complete rotational relaxation, as was confirmed by examining the rotational structure of the LIF spectra.

As the rotational distribution in each vibrational level was completely equilibrated, it was not necessary to observe each band in its entirety. Figure 3 shows spectra typical of those that were used to find the relative vibrational populations. Portions of several bands in the same wavelength region, and in each case close to the Q_{11} band-
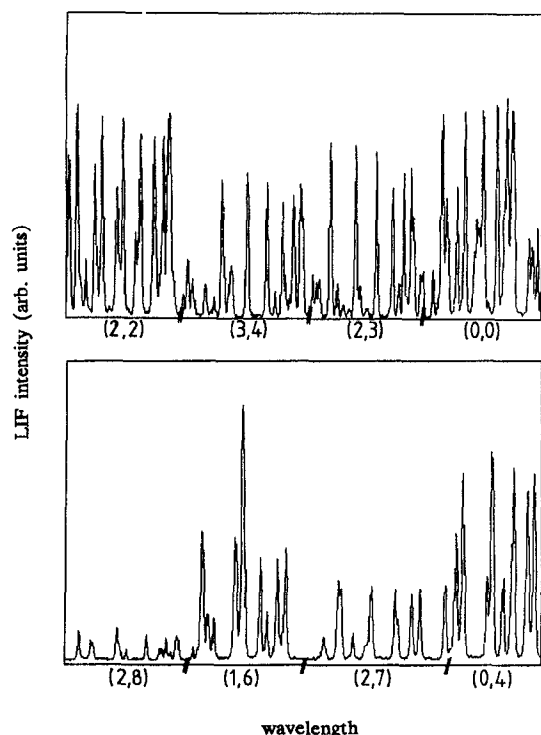
FIG. 3. Examples of NO $A\,^2\Sigma^+$-$X\,^2\Pi$ spectra recorded with 16 μs delay between photolysis and probe laser pulses. The spectra in each panel were recorded in the same scan. As the spectra were recorded under conditions of complete rotational relaxation, only a portion of each band was recorded and the oblique lines on the horizontal axes indicate discontinuities in the wavelength.

FIG. 4. Comparison of the experimental vibrational distribution ($\bullet$) of NO formed in the reaction between N atoms and OH with three calculated distributions: (a) the *prior* distribution according to the equations of Levine and Bernstein [Ref. 1(c)]; (b) the *prior* distribution according to the model of Quack and Troe (Ref. 32); and (c) a distribution based on the application of phase space theory (Ref. 33).

head, were recorded using the same conditions in the reaction cell, and the same dye and doubling crystal in the laser exciting LIF. Variations in the intensity of the dye laser were monitored and appropriate corrections made to the observed spectrum. Relative vibrational populations were then estimated by comparing the observed spectra with simulated spectra, allowance being made for the different strengths of the bands giving rise to LIF.

As indicated in Table I, a number of spectral regions were examined to obtain information about all the NO vibrational levels populated in reaction (1). However, the information gained in each spectral region can be related to that from other regions and hence the full distribution of NO over all vibrational levels from $v=0$ to $v=9$ could be estimated. In particular it should be noted that bands from $v=4$ could be observed in each group of spectra. The results deduced from several spectra recorded in each region have been averaged and then consolidated. This procedure leads to the final estimate of the NO product vibrational distribution from reaction (1) which is shown in Fig. 4. The average vibrational yield is $\Sigma P_v E_v$, where P_v is the probability that NO is formed in level v ($\Sigma P_v = 1$) and E_v is the energy of the level v. Dividing this energy yield by the average energy available $\langle E_{\text{avl}}\rangle = -\Delta H_0^0 + (5/2)RT + E_{\text{el,OH}}$, where $(5/2)RT$ allows for the average relative translational and rotational energies of the reagents and $E_{\text{el,OH}}$ for the average electronic energy of OH in its $X\,^2\Pi_i$
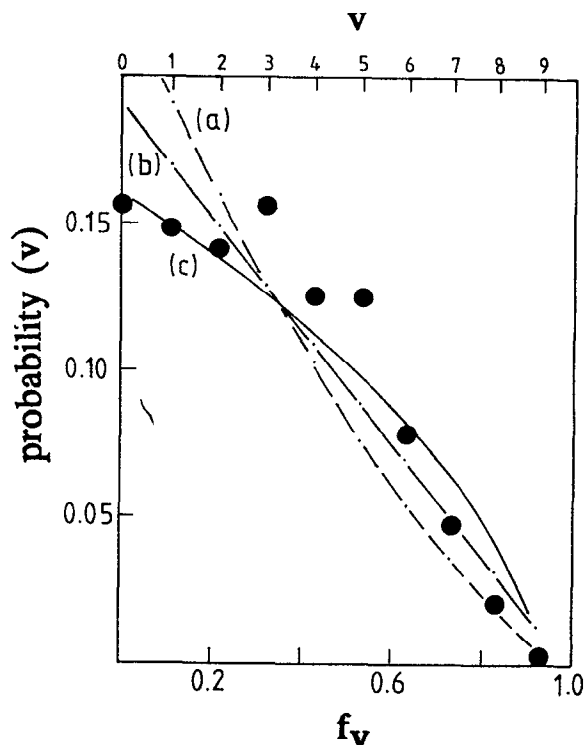
ground state, yields the fractional vibrational energy yield $\langle f_{\text{vib}}\rangle = 0.31 \pm 0.03$.

IV. DISCUSSION

Combination of the electronic ground states of N atoms and OH radicals (^4S_u and $^2\Pi_i$) gives rise to 16 electronic states in all ($^3A' + ^3A'' + ^5A' + ^5A''$). Of these only the $^3A''$ surface is attractive and correlates with the electronic ground states of the products of reaction (1), NO($^2\Pi_i$) + H(^2S_g). In view of its rapidity, it seems likely that reaction (1) occurs adiabatically over this surface.

The most recent theoretical calculations of the *ab initio* surfaces for the HNO/NOH system are those by Walch and Rohlfing.[19] Their results show that the $^3A''$ surface has a potential well corresponding to the NOH species, which must presumably be involved in the reaction of N+OH yielding NO+H. The energy at this minimum is ca. 90 kJ mol^{-1} below that associated with separated NO($^2\Pi_i$) + H(^2S). There seems little doubt that many, if not all, reactive collisions between N atoms and OH radicals will proceed through this deep energy minimum, but given the exothermicity of reaction (1) and the small number of atoms involved, it is not obvious that trajectories will be "trapped" long enough even to execute a few traversals of the well, never mind long enough for complete energy randomization.

To serve as "benchmarks" with which to compare our experimentally determined distribution of NO over vibrational states, we have calculated "statistical" *prior* distributions according to two models. In the first set of calculations, a *prior* vibrational distribution, $P^0(v)$, was calculated according to the formula given by Levine and Bernstein:[1(c)] $P^0(v) \propto (1 - f_v)^{3/2}$, where f_v is the energy of the vth vibrational level of the diatomic product of a three-atom reaction, divided by the average energy available to the products. This formula is based on the supposition that the product state distribution is the one which, for a constant total energy, maximizes the entropy of the system. However, no account is taken of the need to conserve total angular momentum. Quack and Troe[32] have argued convincingly that the *prior* should and can take account of the requirement to conserve total angular momentum. The *prior* for a given rovibrational level then is simply proportional to its degeneracy. Summing over all rotational levels which are energetically accessible in a given vibrational level leads to a vibrational *prior* distribution in which $P^0(v) \propto (1 - f_v)$.

The requirement to conserve angular momentum is also included in phase space theory (PST).[33] In addition, in phase space theory one limits the angular momentum states which are accessible by recognizing that the *total* angular momentum quantum number (J) must lie between the sum and difference of the individual quantum numbers associated with orbital and rotational angular momentum in both reagents and products. The values of the orbital quantum numbers are constrained by the need for the system to surmount the centrifugal barriers on the long-range potentials in the entrance and exit channels. Phase space theory was also used to generate a vibrational distribution for comparison with experiment. In carrying out these calculations, the small spin–orbital contributions to the total angular momentum was ignored. We further assumed that the crucial parts of the intermolecular potentials between the N+OH reagents and between the NO+H products were due to dispersion forces varying as $(-C_6/r^6)$. The C_6 constants were estimated[34] from the ionization potentials of the individual species. Preliminary calculations were carried out for a specified collision energy (ca. $3/2\ kT$) and for individual rotational (j) states of OH. The results were found to be virtually independent of j through the range of states containing significant populations at 298 K, so the main calculations were carried out for a specified j, but were properly averaged over the thermal spread of collision energies.

The calculated *prior* and PST distributions are compared with the experimental distribution in Fig. 4. Phase space theory and the Quack and Troe model both predict greater populations in high vibrational levels than the Levine and Bernstein model, because the requirement to conserve total angular momentum reduces the probability of populating the high rotational states of product formed in low vibrational levels and consequently lowers the overall probability of populating low v states.

The experimental distribution is quite close to that predicted by phase space theory. However, this does *not* mean

that reaction necessarily proceeds via a long-lived collision complex which allows full energy randomization; indeed, as stated earlier, this seems unlikely. It does, however, seem possible that the constraints of angular momentum are particularly severe in the N+OH reaction. Since it is an example of a *heavy+heavy–light → heavy–heavy+light* system,[35] and as reaction can apparently occur out to quite high impact parameters, the initial orbital angular momentum will generally be appreciably larger than the initial rotational angular momentum. As a result, the majority of reactive collisions must proceed through states of appreciable angular momentum which must be distributed among the products' rotational and orbital momenta. However, the small reduced mass associated with the reaction products means that high centrifugal barriers are associated with appreciable values of the final orbital angular momentum, and this will lead to significant yields of relative translational energy associated both with the orbital motion and with that along the NO+H separation coordinate. Put another way, in the *heavy+heavy–light* N+OH reaction, the dynamical constraint imposed by the need to conserve angular momentum may be predominant, whether or not the reaction proceeds via true collision complexes. If this is so, then one would expect the product state distribution to be similar to that predicted by phase space theory.

The questions raised and the speculations made in the previous paragraph point to the importance of further work on reaction (1), and we hope to measure the nascent rotational state distributions of the NO product. This experiment will clearly provide important dynamical information, but the experiments will be demanding because of the difficulty of creating more than ca. 1% of atomic nitrogen in N_2 molecules, and because N_2 will rapidly relax the nascent NO rotational distributions.

As mentioned in the Introduction, the experiments reported here constitute the third dynamical study of a system containing N, O, and H atoms. The three systems have similar overall energetics but may occur over different potential energy surfaces, or probe different regions of the same surface. Leone and co-workers[15] investigated the vibronic distribution of NO excited in inelastic collisions with translationally hot H atoms at collision energies corresponding to 91.6 and 212.2 kJ mol^{-1}. Both infrared fluorescence[15(a)] and laser-induced fluorescence[15(b)] measurements of the vibrationally excited NO molecules indicated a vibrational distribution which falls monotonically with quantum number and which, as far as the distribution between $v=1$ and $v=2$ is concerned, is similar for the two collision energies studied. Colton and Schatz[20] have carried out a detailed quasiclassical trajectory calculation on this system including adiabatic collisions on four different potential energy surfaces, three of which included minima associated with both HNO and HON structures. They obtained good agreement with experimental results. At the higher collision energy (212.2 kJ mol^{-1}), Colton and Schatz found that the vibrationally inelastic cross sections contained a 20% contribution from trajectories which were not direct, in that they included *more than one inner turn-*

ing point at which the rate of change of the distance between H and the center of mass of NO changed sign. In view of the short lifetimes of these complexes and the minor, if significant, contribution of these trajectories to vibrational energy transfer, Coltrin and Schatz concluded that the agreement between the NO vibrational distributions calculated via trajectory and statistical methods was "partly accidental."

The reaction between $O(^3P)$ atoms and $NH(^3\Sigma^-)$ yielding $NO+H$ is 299 kJ mol^{-1} exothermic. Kinematically it is very similar to the $N+OH$ reaction studied in the present work, although it can occur over $^1A'$ and $^1A''$ surfaces,[19] as well as the $^3A''$ surface implicated in the reaction between N atoms and OH. Furthermore, the $O+NH$ reaction presumably proceeds via transient HNO, rather than HON, structures. Huang and Dagdigian[16] concluded that the NO vibrational distribution from the $O+NH$ reaction is appreciably colder than is predicted by phase space theory, and corresponds to only ca. 8% of the total energy available to the reaction products, in contrast to our finding of a vibrational energy yield from the $N+OH$ reaction of ca. 31% of the energy available. Huang and Dagdigian[16] invoked a Franck–Condon model to explain the surprisingly cold vibrational distribution which they observed. For such a proposition to be correct, it would seem to be necessary for the HNO complex, from which an H atom departs to yield products, to have undergone internal relaxation so that the NO vibration is unexcited and the NO internuclear distance as the H atom departs is that associated with unexcited HNO.

There is no doubt that thorough quasiclassical trajectory studies of the dynamics of the $N+OH$ and $O+NH$ reactions would be very worthwhile, especially as the information is available to construct realistic potential energy surfaces.[17–19] Such trajectory calculations should be able, inter alia, to clarify the roles of angular momentum conservation and complex formation in these two reactions, as well as testing the hypothesis of Huang and Dagdigian concerning the low yield of NO vibrational energy from the $O+NH$ reaction.

Finally, we note that the observation that the rate of the reaction between $N+NO(v)$ is, at most, only slightly enhanced by vibrational excitation of the NO is unsurprising. Assuming that reaction occurs adiabatically on a single triplet surface connecting reagents to products, the room temperature rate constant corresponds to a thermal averaged cross section for reaction on that surface of ca. 16 Å^2. This suggests that the transition state region is at a large N–NO distance where motion orthogonal to the reaction coordinate is the NO vibration at a frequency scarcely perturbed from its value in the isolated NO molecule. Consequently, vibrationally adiabatic surfaces for $N+NO(v)$ will be parallel up to this transition state region and the rate constants, $k(v)$, will be essentially the same.[3]

ACKNOWLEDGMENTS

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