



Nonlocal thermodynamic equilibrium effects of vibrationally excited NO

C. Moralejo, R. J. Cody, and J. E. Allen Jr.

Citation: The Journal of Chemical Physics **98**, 4707 (1993); doi: 10.1063/1.464974 View online: http://dx.doi.org/10.1063/1.464974 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/98/6?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

Non-local thermodynamic equilibrium effects on isentropic coefficient in argon and helium thermal plasmas Phys. Plasmas **21**, 033502 (2014); 10.1063/1.4867367

Reactive and internal contributions to the thermal conductivity of local thermodynamic equilibrium nitrogen plasma: The effect of electronically excited states Phys. Plasmas **19**, 122309 (2012); 10.1063/1.4771689

Mechanisms of nonlocal effect on the vibration of nanoplates Appl. Phys. Lett. **98**, 153101 (2011); 10.1063/1.3579249

Nonlocal effects in nonisothermal hydrodynamics from the perspective of beyond-equilibrium thermodynamics J. Chem. Phys. **130**, 214908 (2009); 10.1063/1.3148891

Effective superconfiguration temperature and the radiative properties of nonlocal thermodynamical equilibrium hot dense plasma Phys. Plasmas **12**, 063302 (2005); 10.1063/1.1931109



This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 130.239.20.174 On: Mon, 24 Nov 2014 12:59:28

Nonlocal thermodynamic equilibrium effects of vibrationally excited NO

C. Moralejo,^{a)} R. J. Cody,^{b)} and J. E. Allen, Jr.^{b)} Astrochemistry Branch, NASA/Goddard Space Flight Center, Greenbelt, Maryland 20771

(Received 10 September 1992; accepted 8 December 1992)

The vibrational distribution of NO($X^2\pi$) from the reaction O(^{3}P)

 $+NO_2(X^2A_1) \rightarrow NO(X^2\pi,v'') + O_2$ was studied at room temperature in a fast-flow system. Oxygen atoms were produced via the microwave-discharge dissociation of molecular oxygen with argon as the carrier gas. The reaction time between the NO₂ molecules and the oxygen atoms was kept at \sim 3 ms to minimize vibrational energy quenching. NO(X) radicals were detected via laser-induced fluorescence of the $A^{2}\Sigma^{+} \leftarrow X^{2}\pi$ electronic transition. The relative vibrational population ratio of NO in the ground electronic state was determined to be 87.4 $\pm 2.6\%$ and $12.6 \pm 2.7\%$ in the v''=0 and v''=1 levels, respectively. No higher vibrational states were observed. The NO vibrational population ratio measured in this study correlates well with the earlier observation of high vibrational excitation in O_2 .

I. INTRODUCTION

The reaction between O and $NO_2(1)$ is an important source of NO in the stratosphere and is a principal part of the catalytic cycle which interconverts NO and NO₂ during the daytime,

$$O(^{3}P) + NO_{2}(X^{2}A_{1}) \rightarrow NO + O_{2}.$$
 (1)

Kinetic studies have shown that the reaction proceeds with a rate constant of 9.7×10^{-12} cm³ molecule⁻¹ s⁻¹ at 298 K.¹ Although controversy exists over how the reaction proceeds,²⁻⁵ there is sufficient experimental evidence to suggest that a significant portion of the reaction energy is released as vibrational excitation of the $O_2(X^{3}\Sigma_{\sigma}^{-})$. Lipscomb et al.⁶ observed vibrationally excited O₂ molecules upon photolysis of NO₂ in a flash photolysis system and concluded, based on the reaction kinetics, that the excited molecules were produced as a result of reaction (1). The vibrational excitation of O2 was confirmed by Basco and Norrish,⁷ who may have also observed the first and second vibrational levels of NO. While no experimental studies of the vibrational distribution of the NO formed in this reaction have been reported, studies of the analogous $H+NO_2 \rightarrow OH+NO$ reaction have shown that ~72% of the energy is released as vibrational, translational, and rotational (25%, 25%, and 22%, respectively) excitation of $OH(X^2\pi)$ (Ref. 8) and the remaining 28% as excitation of the NO($X^{2}\pi$).^{9,10} Of the energy distributed into vibrational excitation of the NO(X), approximately 75%, 19%, 5%, and 1% reside in the v=0,1,2,3 levels, respectively, with minor amounts found in v=4 and 5.9

Based in part upon the results of Lipscomb et al.,⁶ who observed that oxygen molecules were produced with up to eight quanta of vibrational energy in reaction (1), and the results of Norrish and McGrath, 11-13 who observed excited O2, ClO, and BrO molecules from reactions between O and O₂, Cl and O₂, and Br and O₂, respectively, it has been

concluded that in an exothermic reaction between an atom and a triatomic molecule the newly formed bond will accumulate most of the energy.^{7,11} In the case of reaction (1)it can be assumed that if $\sim 75\%$ of the energy is released as vibrational excitation of the $O_2(X)$ molecule, the remaining energy would be sufficient only to excite the NO vibrationally up to v=1 of its electronic ground state. We have, therefore, undertaken the study of the vibrational distribution of NO(X) from reaction (1) in order to verify this assumption.

In addition to the contribution that this information makes to the general body of knowledge concerning the products of the reaction, the information is of practical value with respect to the measurement of the concentration of NO produced in the upper atmosphere. Nitric oxide is one of the stratospheric molecules whose concentration is being measured by infrared (IR) spectrometers on board the Upper Atmosphere Research Satellite. The retrieval algorithm must take into account any nonlocal thermodynamic equilibrium (LTE) effects of vibrationally excited molecules in order to infer their concentrations correctly. Laboratory studies indicate that non-LTE effects are possible for NO from reaction (1),⁶ and non-LTE NO emission has been observed in the thermosphere.¹⁴ Model calculations¹⁵ indicate that the population of NO (X, v=1)could be 30% above that expected for LTE at 30 km with smaller enhancements above and below this altitude. Non-LTE effects for NO (X, v=1,2) are possible for the stratosphere based on calculations derived for the mesosphere and lower thermosphere.^{16,17} This paper, therefore, reports the results of our recent laboratory studies on the vibrational distribution of NO from reaction (1). The experiments were performed in a fast-flow system to minimize vibrational quenching. The NO(X, v'') molecules were monitored with laser-induced fluorescence (LIF).

II. EXPERIMENT

A. Fast-flow system

The experimental apparatus is illustrated in Fig. 1. The fast-flow system consisted of a Pyrex flow tube which was

a)NAS/NRC Research Associate. Presently at Wastewater Technology Centre, Burlington, Ontario, Canada.

^{b)}Authors to whom correspondence should be addressed.



FIG. 1. Schematic representation of the experimental apparatus. A, argon, O_2 in; B, argon in; C, NO_2 in; 1, microwave discharge; 2, nitrogen laser; 3, dye laser; 4, lens; 5, BBO crystal; 6, 7, 11, mirrors; 8, 10, MgF₂ windows; 9, photomultiplier tube; 12, photodiode; 13, pulse generator; 14, computer; 15, boxcar integrator.

60 cm in length and coated with halocarbon wax. The flow tube terminated in a stainless steel, 7 cm cubic photolysis cell equipped on four faces with 2.5 cm o.d. MgF₂ windows. A microwave discharge produced oxygen atoms from the dissociation of O_2 (Matheson, 99.999% purity), and NO₂ was added through a movable injector. Argon (Air Products, 99.999%) was used as the carrier gas. The flow speed was ~ 1000 cm/s, and the total pressure was varied between 300 and 1300 mTorr. An MKS baratron pressure measurement system and mass flow controllers (model No. 1259B) were used to monitor the pressures and introduce the gases into the system. NO2 was obtained from Matheson (research grade) and purified by mixing with equal pressures of O_2 for 12 h followed by three freeze-pump-thaw cycles to obtain the pure white solid. The NO $(A^{2}\Sigma^{+}-X^{2}\pi, v=0,0)$ transition was used to verify that no NO impurity was present in the NO₂ prior to use. The pure NO_2 was kept in a darkened bulb at all times.

B. Irradiation and detection procedures

Detection of the ground-state NO product was achieved by LIF of the A-X electronic transition. The output from a Molectron nitrogen laser (model UV-22)pumped dye laser (model DL-14) was doubled with a β -barium borate crystal to produce the required excitation wavelengths. The NO emission was isolated with an Oriel 200-320 nm bandwidth interference filter and the radiation detected with a Hamamatsu R928 photomultiplier tube. The NO fluorescence signal and the signal from a photodiode used to monitor the relative energy of the doubled dye laser wavelength were processed by an EG&G model No. 4420 boxcar averager and recorded with an EG&G model No. 4402 signal processor for storage and subsequent analysis. A Hewlett-Packard model No. 214A pulse generator provided the timing pulses to trigger the nitrogen laser and the boxcar integrator.





C. NO emission spectra

The maximum NO fluorescence intensity for the v (0,0) or v (0,1) transitions was obtained by scanning the emission of various lines of the NO produced in reaction (1) between 226.16 and 226.50 nm for the (0,0) transition and between 236.62 and 236.72 nm for the (0,1) transition. In these experiments, the laser was most often tuned to 226.22 ± 0.01 or 236.65 ± 0.01 nm for the (0,0) or (0,1) transition, respectively.

III. RESULTS AND DISCUSSION

In experiments where initial energy state distributions are measured, quenching of these states by collisions is a major concern. To minimize collisional quenching in the experiments reported here, several types of measurements were taken. Some of these measurements (see Sec. III B) set the physical conditions for the experiments. In addition, the NO laser fluorescence signals were corrected for several factors.

A. NO fluorescence measurements

Collisional quenching of the NO fluorescence would have decreased the emission lifetime from that for radiation alone. Therefore, the time decay of the NO fluorescence was measured with the boxcar integrator in the scanning mode. Figure 2 shows a typical example of the decay of the NO emission for the (0,0) transition produced from reaction (1). The total intensity containing both the NO fluorescence and the scattered dye laser emission background is superimposed on the background emission. The decay time is calculated from the corrected NO emission and measures 225 ns. Nitric oxide emission lifetimes for the $A \rightarrow X$ transitions have been reported to be on the order of 200 ns.¹⁸ The comparison of our lifetimes with the radiative lifetimes indicates collisional quenching was not a problem in these experiments.

For the NO fluorescence measurements which yielded the vibrational population ratio, the boxcar averager was used in the static-gate mode so that the intensities were monitored at a fixed time rather than over the entire decay time interval. The fixed gate time was usually selected to maximize the difference between the NO and scattered la-



FIG. 3. Fluorescence intensity measurements for the v(0,1) (A) and the v(0,0) (B) transitions at 200 ns corrected for background, variation in dye laser energy, and Einstein A coefficients. T is the total number of samples since the initiation of the scan.

ser emission intensities. A typical example of the fluorescence intensities of the v(0,0) and v(0,1) transitions with the boxcar averager set in the static-gate mode is given in Fig. 3. The fluorescence data for both transitions were taken under the same experimental conditions and then corrected for background, dye laser energy, and Einstein A coefficients.

B. Pressure measurements

Oxygen atoms were produced by the microwavedischarge dissociation of high purity O₂, and the carrier gas argon was introduced through the bypass inlet. Purified NO₂ was added to the main gas stream through the movable injector at a point \sim 3 cm from the area irradiated by the nitrogen-pumped dye laser. The injector was maintained at this distance to minimize quenching of the NO fluorescence by argon. In one set of experiments the pressure of O_2 and the total pressure were kept constant at 120 and 800 mTorr, respectively. Varying pressures of NO₂ were then added to the main gas flow, and changes in the relative populations of the v=0 and 1 vibrational levels of NO(X) were monitored. Figure 4 demonstrates that the maximum population of v=1 occurred when the pressure of NO₂ reached a critical concentration. This concentration of NO₂ was generally the amount required to extinguish the green emission which was observed and which was attributed to reaction (2),¹⁹

$$O + NO \rightarrow NO_2^*$$
 (2)



FIG. 4. Variation in the relative vibrational populations of NO(X) v=0 (A) and v=1 (B) levels with the pressure of NO₂.



FIG. 5. Variation in the relative vibrational populations of NO(X) v=0 (A) and v=1 (B) levels with the total pressure.

It was observed over several trials that the average population of NO in the v=1 level appeared to slowly decrease upon further addition of NO₂; therefore, the critical concentration of NO₂ was used in the vibrational distribution measurements to eliminate quenching by NO2. This was attributed to the quenching of the NO (v=1) by excess NO₂.²⁰ The excess oxygen atoms not consumed in the reaction with NO2 were likely responsible for the quenching of the NO prior to addition of the critical concentration of NO_2 .²¹ At this NO_2 concentration, the O atoms were titrated to the endpoint and were, therefore, unavailable to quench NO (v=1). Since atomic oxygen had the fastest quenching rate constant $(k=6.5\times10^{-11} \text{ cm}^3 \text{ molec}^{-1})$ s^{-1}),²¹ of the gas constituents, this titration was important to the measurement of the nascent vibrational distribution of NO.

In a second set of experiments, the pressures of O_2 and NO_2 were kept constant, the total pressure of the system was varied, and the populations of NO in the v=0 and 1 levels monitored. Argon was again used as the carrier gas. The pressure of O_2 was kept at 120 mTorr, the NO_2 added was just enough to extinguish the green glow, and the argon was added in varying pressures to increase the total pressure from 300 to 1300 mTorr. The results of these experiments are shown in Fig. 5. As can be observed from this figure, once the total pressure reaches ~700 mTorr, the populations of NO in the v=0 and 1 levels remain steady. Reduction of the NO fluorescence at pressures < 600 mTorr is attributed to the slower gas flow and, consequently, longer flow times.

C. Calculations

Having determined the optimum conditions that gave the highest concentration of NO in the v=1 level, we derived the vibrational state population ratio from the NO fluorescence signals. These signals were corrected for the background, the scattered dye laser emission, and the variation of dye laser power with wavelength. The NO(0,0) intensity was then corrected for the variation in the Einstein A coefficients between the (0,0) and the (0,1) transitions as shown in Eq. (3). The values for these Einstein coefficients were taken from the work of Piper and Cowles.²² The vibrational population ratio was then calculated from these corrected fluorescence intensities as shown in Eqs. (4) and (5),

TABLE I. Prior distribution calculations.

v(NO)	<i>P</i> ⁰ (NO) ^a	<i>P</i> (NO) ^b		
		(8,9,10)	(9,10)	(10)
0	0.381	0.797	0.892	0.990
1	0.255	0.188	0.108	0.010
2	0.163	0.015		
3	0.099			
4	0.056			
5	0.028			
6	0.012			
7	0.004			
8	0.001			
9	0.0001			-

^aThe prior distribution.

^bThe distribution when O_2 vibrational levels are constrained.

$$I_{\rm NO}^{0} = I_{\rm NO}(0,0) \times \frac{A_{\rm NO}(0,1)}{A_{\rm NO}(0,0)},$$
(3)

 $\% \text{NO}(v=0) = [I_{\text{NO}}^0 / (I_{\text{NO}}^0 + I_{\text{NO}}^1)] \times 100,$ (4)

$$\text{%NO}(v=1) = 100 - \text{%NO}(v=0),$$
 (5)

where I_{NO}^0 and I_{NO}^1 are the corrected NO intensities, and A(0,0) and A(0,1) are the Einstein coefficients in s⁻¹ for the (0,0) and (0,1) transitions, respectively. We observed that, on average, $87.4\pm2.6\%$ and $12.6\pm2.7\%$ of NO resided in the v=0 and 1 levels, respectively.

D. Prior distribution

Early observations by Lipscomb *et al.*,⁶ and Basco and Norrish⁷ of the vibrationally excited O_2 molecules produced from the reaction between O and NO₂ indicate that little of the energy from this reaction is distributed as vibrationally excited NO. Our experimental results confirm that only 13% of energy from this reaction is distributed as vibrationally excited NO. This, in turn, suggests that the remaining energy could be distributed as vibrationally excited O₂. We have used some simple calculations²³ to demonstrate the feasibility of this assumption. The prior distribution for the NO vibrational levels was calculated using Eq. (6) from the work of Kelley,²⁴

$$P^{0}(f_{v},f_{v'}) = (1 - f_{v} - f_{v'})^{5/2} / \Sigma_{v} \Sigma_{v'} (1 - f_{v} - f_{v'})^{5/2}.$$
(6)

In this equation, f_v is E_v/E_{av} from the reaction; E_v is the energy of the vibrational level v above the energy of the v=0 level; E_{av} is the sum of the reaction enthalphy, the activation energy, and the thermal energy of the reactants (=3RT). When the vibrational excitation of O_2 is not constrained, then NO vibrational levels can be populated to v=9 as shown in Table I. Under these conditions, NO vibrational levels up to v=5 would have been observed in our experiments. Only v=0 and 1 levels were detected. When the population of the O_2 vibrational levels is restricted to the v=8, 9, and 10 levels, only the lower levels in NO are excited. These results are given in Table I. Since the NO population ratio measured in the work reported here is (v=0):(v=1)=0.874:0.126, the prior distribution suggests that the O₂ is formed in the v=8,9,10 or v=9,10levels.

IV. CONCLUSIONS

The early work by Lipscomb *et al.*⁶ as well as Basco and Norrish⁷ on the reaction $O+NO_2 \rightarrow NO+O_2$ demonstrated that O_2 is formed vibrationally excited up to v=8 of the ground electronic state. Basco and Norrish observed excitation up to v=11 levels. Excitation up to the v=8level can account for up to 34 kcal/mol of the energy released by the reaction. The remaining energy would, therefore, be sufficient to excite NO vibrationally only up to v=2 of the ground electronic state. In our experiments, vibrational levels higher than v=1 were not observed. This information complements well the observations of Lipscomb *et al.*⁶ What remains to be verified for this reaction is how the distribution of the energy into NO and O_2 as observed is achieved.

ACKNOWLEDGMENTS

We thank Dr. D. J. Bogan for calculating the prior distribution for the NO vibrational levels. This research was supported by the Planetary Atmospheres Program and the Upper Atmosphere Research Program of the National Aeronautics and Space Administration and the Director's Discretionary Fund of NASA/Goddard Space Flight Center.

- ¹W. B. DeMore et al., JPL Publication 90-1, 20 (1990).
- ²M. A. A. Clyne and B. A. Thrush, Trans. Faraday Soc. 58, 511 (1962).
- ³S. W. Benson, J. Chem. Phys. 38, 1251 (1963).
- ⁴M. A. A. Clyne and B. A. Thrush, J. Chem. Phys. 38, 1252 (1963).
- ⁵F. S. Klein and J. T. Herron, J. Chem. Phys. 41, 1285 (1964).
- ⁶F. J. Lipscomb, R. G. W. Norrish, and B. A. Thrush, Proc. R. Soc. London, Ser. A 233, 455 (1956).
- ⁷N. Basco and R. G. W. Norrish, Can. J. Chem. 38, 1769 (1960).
- ⁸A. M. L. Irvine, I. W. M. Smith, R. P. Tuckett, and X. F. Yang, J. Chem. Phys. **93**, 3177 (1990).
- ⁹A. M. L. Irvine, I. W. M. Smith, and R. P. Tuckett, J. Chem. Phys. 93, 3187 (1990).
- ¹⁰D. G. Sauder and P. J. Dagdigian, J. Chem. Phys. 92, 2389 (1990).
- ¹¹W. D. McGrath and R. G. W. Norrish, Z. Phys. Chem. 15, 245 (1958).
 ¹²W. D. McGrath and R. G. W. Norrish, Proc. R. Soc. London, Ser. A
- ²⁴², 265 (1957).
 ¹³W. D. McGrath and R. G. W. Norrish, Proc. R. Soc. London, Ser. A
- 254, 317 (1960).
- ¹⁴ A. T. Stair, Jr., R. D. Sharma, R. M. Nadile, D. J. Baker, and W. F. Grieder, J. Geophys. Res. **90**, 9763 (1985).
- ¹⁵J. A. Kaye and J. B. Kumer, Appl. Opt. 26, 4747 (1987).
- ¹⁶T. C. Degges, Appl. Opt. 10, 1856 (1971).
- ¹⁷G. E. Caledonia and J. P. Kennealy, Planet. Space Sci. 30, 1043 (1982).
- ¹⁸J. F. Burris, T. J. McGee, and J. Barnes, Chem. Phys. Lett. **121**, 371 (1985).
- ¹⁹ M. A. A. Clyne and B. A. Thrush, Proc. R. Soc. London, Ser. A 269, 404 (1962).
- ²⁰ R. P. Fernando and I. W. M. Smith, J. Chem. Soc. Faraday Trans. 2 77, 459 (1981).
- ²¹R. P. Fernando and I. W. M. Smith, Chem. Phys. Lett. 66, 218 (1979).
- ²²L. G. Piper and L. M. Cowles, J. Chem. Phys. 85, 2419 (1986).
- ²³Dr. D. J. Bogan kindly performed the prior distribution calculations.
- ²⁴J. D. Kelley, Chem. Phys. Lett. **41**, 7 (1976).