to a second laser with a frequency near the resonant frequency of the $3 \rightarrow 4$ vibrational transition, this absorption stranglehold will be loosened. Much lower intensities can be used in the two-laser situation because each laser will only be required for pumping a limited number of nearresonant transitions. These transitions will initially be between adjacent vibrational energy levels; as the energy of the molecule increases these lasers will be nearly resonant with overtone transitions.

B. Overtone Absorption. In the second part of this study we simulated continuous wave overtone excitation of HF using classical trajectories. In particular we sought to determine the relative importance of mechanical and electrical anharmonicity in promoting overtone absorption in our model HF molecule in a subpicosecond time scale. We considered only the first and strongest vibrational overtone transition, n = 0 to n = 2. Twenty-four trajectories were run for each of two forms of the dipole moment, μ_1 , a linear form, and μ_2 , a linear plus quadratic form. The driving frequency used was the field-free resonant frequency of the n = 0 to n = 2 transition, 7757.8 cm⁻¹. Trajectories were followed for 1 ps.

We obtained the time-dependent transition probability for the n = 0 to n = 2 transition as follows. First, the vibrational energy of the diatomic molecule was recorded every 25 time steps during the course of the integrations. A quantum number was assigned to each of these energies by a standard histogram method.²⁵ If $\Delta E(n,n+1) = E(n+1) - E(n)$ is the quantum mechanical energy difference between vibrational states $|n + 1\rangle$ and $|n\rangle$ and if $E_{\rm cl}$ is a recorded classical energy, we assign the quantum number n if $E(n) - 1/2\Delta E(n-1, n) \leq E_{\rm cl} < E(n) + 1/2\Delta E(n, n+1)$. In particular we are interested in n = 2. Second, if we denote by $N_2(t)$ the number of trajectories assigned the quantum number 2 at time t, then the transition probability is given by

$$P_{n=2}(t) = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int_{t}^{t+\Delta t} \mathrm{d}t' N_2(t') / N \tag{8}$$

where N is the total number of trajectories, presently 24. A histogram approximation to $P_{n=2}(t)$ is obtained by considering finite values of Δt .

(25) J. M. Bowman and A. Kuppermann, Chem. Phys. Lett., 12, 1 (1971).



Figure 5. Histogram representation of $P_{n=2}(t)$ for overtone excitation when μ_2 (shown in Figure 1) is used as the dipole moment.

We found that $P_{n=1}(t)$ and $P_{n=2}(t)$ were zero for all times considered (up to 1 ps) for the *linear* approximation to the dipole moment. For the quadratic approximation to the dipole moment $P_{n=2}(t)$ is shown in Figure 5 as a histogram where Δt of eq 8 is 25 integration steps. After an initial short time transient peak absorption, the absorption probability attains a fairly steady value of 0.12 ± 0.04 . From these results we can conclude that overtone excitation of an oscillator can occur in a subpicosecond time scale and that nonlinearity of the dipole moment function is critical for this to happen. To understand the second conclusion we note that $\mu \cdot \mathbf{E}$ contains a term proportional to $R_{\rm HF}^2(t)E(t)$. If $R_{\rm HF}(t)$ is given approximately by $R_{\rm HF}^0$ $\cos(\omega t + \phi)$, where ω is the natural harmonic frequency, then $R_{\rm HF}^2(t)$ is $(R_{\rm HF}^0)^2[1 + \cos(2\omega t + 2\phi)]/2$. The $\cos 2\omega t$ term is evidently the source of a "resonant" absorption under the influence of a driving field, E(t), of frequency 2ω

An immediate speculation based on these limited results is the following. Overtone transitions of local mode bonds which have substantial ionic character can be pumped on a picosecond time scale. The basis for this, of course, is that bonds with strong covalent/ionic character (or more generally, a multiconfiguration ground electronic state) will have nonlinear dipole moment functions.

Acknowledgment. This work was supported in part by the National Science Foundation.

Rate Constants for the Reaction of N₂($A^{3}\Sigma_{u}^{+}$, v = 0, 1, and 2) with O₂

M. P. Iannuzzi and F. Kaufman*

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260 (Received: April 30, 1981)

The title reaction was studied at 298 K in a fast flow system by use of laser-induced fluorescence (LIF) detection of $N_2(A)$ at band heads of the first positive system to monitor the v = 0, 1, and 2 states. From a decrease of LIF intensity with increasing $[O_2]$ for fixed reaction times, applying an experimentally measured correction factor for the development of laminar flow, we obtained rate constants of $(2.5 \pm 0.4) \times 10^{-12}$, $(3.9 \pm 0.6) \times 10^{-12}$, and $(4.3 \pm 0.7) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. These results are compared with published data and the reaction mechanism is discussed.

The lowest electronically excited state of nitrogen, N_2 -($A^3\Sigma_u^+$), has a long radiative lifetime¹ (Vegard-Kaplan

emission, $\tau \sim 2$ s), but is highly reactive. It plays an important role in the normal and perturbed upper atmo-



Figure 1. Diagram of apparatus.

sphere² as well as in laboratory studies of "active nitrogen". Although its quenching and/or reaction processes with O_2 have been investigated many times,³⁻¹³ several questions remain: (i) the range of reported rate constants is large, i.e., 1.9×10^{-12} to 7.6×10^{-12} cm³ molecule⁻¹ s⁻¹; (ii) many studies have used indirect methods of detection such as energy transfer to NO or Hg and therefore do not provide information on the rate constants for specific vibrational states of N₂(A); and (iii) the identity of the product channels has been examined quantitatively only recently¹² for the first time.

Even in its ground vibrational state $N_2(A)$ carries 6.2 eV of excitation energy and is thus able to dissociate O_2 into $O(^{3}P) + O(^{3}P)$. It may also react with O_2 to produce N_2O + $O(^{3}P \text{ or } {}^{1}D)$ for which Zipf¹² has reported a yield of 0.6 ± 0.2 per $N_2(A)$ removal, or it may be quenched without reaction.

The present work was carried out in a rapidly pumped discharge-flow system in which $N_2(A)$ is produced by reaction of Ar* with N_2 and detected by laser-induced fluorescence (LIF) of $N_2(B\rightarrow A)$ while atomic species such as $O(^{3}P)$ and $N(^{2}D,^{2}P)$ are detected by resonance fluorescence.¹⁴ This paper presents the results of rate

(1) D. E. Shemansky and N. P. Carleton, J. Chem. Phys., 51, 682 (1969); D. E. Shemansky, *ibid.*, 51, 689 (1969).

(2) D. C. Cartwright, J. Geophys. Res., 83, 517 (1978).

(3) R. A. Young, G. Black, and T. G. Slanger, J. Chem. Phys., 50, 303 (1969).

(4) J. A. Meyer, D. W. Setser, and D. H. Stedman, J. Phys. Chem., 74, 2238 (1970).

(5) J. A. Meyer, D. H. Klosterboer, and D. W. Setser, J. Chem. Phys., 55, 2084 (1971).

- (6) A. B. Callear and P. M. Wood, Trans. Faraday Soc., 67, 272 (1971).
 (7) J. A. Meyer, D. W. Setser, and W. G. Clark, J. Phys. Chem., 76, 1 (1972).
- (8) T. G. Slanger, P. M. Wood, and G. Black, J. Photochem., 2, 63 (1974).
- (9) J. W. Dreyer, D. Perner, and C. R. Roy, J. Chem. Phys., 61, 3164 (1974).
 - (10) O. J. Dunn and R. A. Young, Int. J. Chem. Kinet., 8, 161 (1976).
 (11) W. G. Clark and D. W. Setser, J. Phys. Chem., 84, 2225 (1980).

- (13) L. G. Piper, G. E. Caledonia, and J. P. Kennealy, J. Chem. Phys., 74, 2888 (1981).
- (14) M P. Iannuzzi and F. Kaufman, J. Chem. Phys., 73, 4701 (1980).

measurements for $N_2(A, v = 0, 1, \text{ and } 2) + O_2$ and their comparison with earlier work.

Experimental Section

Figure 1 shows a diagram of the flow system which is pumped by a Roots blower (Heraeus, Model RG-350) to produce average flow velocities of up to $40-50 \text{ m s}^{-1}$ in the 2.54-cm i.d. flow tube. Ar metastables are generated in the upstream dc discharge between Ta electrodes at 200 V, ~ 1 mA. Ar (Matheson, UHP) is purified by passage over Cu mesh at 900 K and over molecular sieve (5X) at 1 atm pressure, and through a liquid N_2 trap packed with glass wool at flow tube pressure. $N_2(O_2 \text{ free})$ added downstream of the discharge produces excited states that rapidly decay to the A state. The N_2 flow constitutes about 20% of the total flow. The reactant O_2 diluted with about 5% of the total Ar flow is added through the movable glass loop injector attached to a 3-mm o.d. glass tube placed along the surface of the flow tube. Mixing of the injector flow was checked by examining the onset of the O + NOchemiluninescence upon adding NO to an O-atom flow and found to be complete within about 2 cm axial distance. Typical flow conditions were as follows: 40 standard cm³ s⁻¹ of Ar, 10 standard cm³ s⁻¹ of N₂, $p \sim 1.8$ torr, $\bar{v} \sim 40$ $m s^{-1}$.

The fluorescence cell consists of the LIF port for $N_2(A)$ detection and a vacuum UV resonance fluorescence port, 5 cm downstream, for atom detection. The Nd:YAG dye laser (Chromatix Models 1000E and 1050) excites the first positive system of $N_2(B^3\Pi \leftarrow A^3\Sigma)$ at the P_1 band heads of the $\Delta v = 4$ bands at 618.7 nm (4, 0), 612.7 nm (5, 1), and 606.9 nm (6, 2) using rhodamine-B dye, with 3 or 0.3 cm^{-1} line width. The laser is operated in the burst mode, i.e., with about five laser flashes each at the 80-Hz flashlamp repetition rate. The LIF signal, $I_{\rm F}$, was measured at longer wavelengths by using a Corning CS2-58 filter (cutoff at 637 nm) and was mainly due to the $\Delta v = 3$ bands at 677.2 nm (4, 1), 668.9 nm (5, 2), and 660.8 nm (6, 3). Quenching of $N_2(B)$ by the added O_2 was negligible. The cooled, redsensitive photomultiplier (RCA 31034) was operated in pulse-counting mode and gated for about $60-\mu s$ collection time per laser burst that consisted of about five flashes 15 μ s apart. Fluoresence signal was collected for 10 s. The laser intensity, $I_{\rm L}$, was also continuously monitored, and $I_{\rm F}$ and $I_{\rm L}$ were either ratioed or recorded separately.

 $[O(^{3}P)]$ could be measured 5 cm downstream from the LIF cell by resonance fluorescence near 130 nm with a microwave discharge lamp at 1.5 torr of He containing a trace of added O₂ and a vacuum UV monochromator (Jarrell Ash, 0.5 m, Model 84-110) and solar blind photomultipler (EMR, 541GX).

In a separate experiment in the same flow tube and under identical pressure and flow conditions the radial and axial velocity profile was measured by using a dynamic Pitot tube^{15,16} consisting of two side-by-side 3.2 mm o.d. stainless steel tubes movable both radially and axially to map the flow, one pointing into the flow (10° concave nozzle) and the other pointing perpendicular to the flow. The measured pressure differences (MKS Baratron, Type 77) were corrected for compressibility¹⁵ and viscosity¹⁷ and converted to flow velocities. Under our conditions of pressure, gas composition, tube radius, tube length, and total flow, Langhaar's¹⁸ calculated transition from a flat

- (16) R. M. Olson, "Essentials of Engineering Fluid Mechanics", Inernational Textbook, Scranton, 1961.
- ternational Textbook, Scranton, 1961. (17) F. S. Sherman, N.A.C.A. Technical Note 2995, 1953.
 - (18) H. L. Langhaar, Am. Soc. Mech. Eng. Trans., E64, A55 (1942).

⁽¹²⁾ E. C. Zipf, Nature (London), 287, 523 (1980).

⁽¹⁵⁾ S. Eskinazi, "Principles of Fluid Mechanics", Allyn Bacon, Boston, 1962.

Letters



Figure 2. Typical plots of I_F vs. $[O_2]$: (**A**) v = 0, t = 7.19 ms; (**B**) v = 1, t = 6.44 ms; (O) v = 2, t = 6.83 ms.

to a parabolic velocity profile would give a correction factor, α , of 1.43 whereas the averaged measured factor was found to be $\alpha = 1.34$.

Results and Discussion

The corrected rate constant, k^v , for the removal of N₂(A)^v is given by $k^v = -\alpha t^{-1} \operatorname{d} \ln I_{\rm F}/\operatorname{d}[{\rm O}_2]$, where t is the average flow time from O₂ injector to LIF detector, and $t = d/\bar{v}$, normally 6–7 ms. Figure 2 shows typical $\ln I_{\rm F}$ vs. [O₂] plots for different vibrational levels. Seven, six, and six experiments for $v = 0, 1, \operatorname{and} 2$ gave $(2.5 \pm 0.2 \times 10^{-12}, (3.9 \pm 0.4) \times 10^{-12}$, and $(4.2 \pm 0.5) \times 10^{-12} \operatorname{cm}^3$ molecule⁻¹ s⁻¹, where the stated uncertainty is the random error at 1 σ . When systematic errors due to pressure, flow rates, α , and d $\ln I_{\rm F}/\operatorname{d}[{\rm O}_2]$ slopes are included, the accuracy is estimated to be $\pm 15\%$.

The question whether the faster removal of the v = 1and 2 levels is due, in part, to vibrational relaxation to lower vibrational levels cannot be completely resolved, but for the v = 1 level a large contribution due to $1 \rightarrow 0$ relaxation can be ruled out. Semiquantitative estimates of the relative concentrations of N₂(A) based on the observed $I_{\rm L}$ and $I_{\rm F}$, transition probabilities of the $\Delta v = 4$ and 3 bands of the N₂ first positive system, and the line spacings near the P₁ band heads indicate ratios of 1:0.5:0.1 for the v =0, 1, and 2 populations of N₂(A). If one assumed that the difference between $k^{v=1}$ and $k^{v=0}$ is due entirely to v = 1to 0 relaxation the resultant replenishment of v = 0 by cascade leads to curved ln $I_{\rm F}$ vs. [O₂] for small [O₂]. Since such curvature was not observed, an approximate upper limit of about 5 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹ can be assigned to the 1 to 0 vibrational relaxation of N₂(A) by O₂.

For v = 0 and 1, our rate constants are in good agreement with recent measurements by Zipf¹² and Piper et al.,¹³ i.e., $k^{v=0} = 1.9$, $\times 10^{-12}$, 2.3×10^{-12} , and 2.5×10^{-12} in the sequence ref 12, 13, this work; and $k^{v=1} = 4.0 \times 10^{-12}$, 4.1×10^{-12} , and 3.9×10^{-12} . For v = 2, only Dreyer et al.⁹ have reported a measurement, but even though their value of 5.0 is in good agreement with our 4.3×10^{-12} , their $k^{v=1} = 7.4 \times 10^{-12}$ is far out of line with the above well established value of 3.9×10^{-12} to 4.1×10^{-12} cm³ molecule ⁻¹ s⁻¹. The present results are the first based on the technique of laser-induced fluorescence.

The product channels of this process are still uncertain. $Zipf^{12}$ has reported a 60% vield of N₂O formation, but since the reaction was carried out in an active, pulsed discharge, a contribution due to ion reactions cannot be ruled out. If the four-center reaction to form NO + NO is discounted, the three sets of available exothermic product channels are $N_2(X) + O_2^*$, $N_2(X) + O + O$, and $N_2O + O(^{3}P \text{ or } {}^{1}D)$. Under our experimental conditions $O(^{1}D)$ would be very rapidly quenched, so that the experimental problem reduces to the measurement of the $O(^{3}P)$ and $N_{2}O$ yields. A substantial production of $O(^{3}P)$ was measured in several of our experiments, but the initial $N_2(A)$ concentration was not known sufficiently accurately to provide a reliable O-atom yield. Experiments that will measure N₂O by electron capture gas chromatography are under preparation. Preliminary experiments in which the O-atom yield was measured both when the Ar metastables were reacted directly with O_2 and when N_2 was interposed indicate a smaller yield for $N_2(A)$. Although this is qualitatively consistent with N₂O formation as a major reaction channel, a direct proof awaits N₂O measurements in the afterglow. Further $N_2(A)$ quenching studies and O-atom yield measurements in its reactions with other oxygen-containing molecules are also under way.

Acknowledgment. This work was supported by the Air Force Geophysics Laboratory and Defense Nuclear Agency under Task S99QAXHD.