# Photodissociation of Jet-Cooled NO<sub>2</sub> at 355 nm: Strong Alignment and Oscillations in the Rotational State Distributions of the NO(v''=1) Fragment

# Ning Changlong, Lin Hua, and Josef Pfab\*

Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh, EH14 4AS, UK Received: March 16, 1993

State-to-state photodissociation of NO<sub>2</sub> at 355 nm has been investigated by means of jet-cooling and one-photon laser-induced fluorescence probing techniques. The rotational distribution of nascent NO(v''=1) from the fast predissociation of efficiently cooled NO<sub>2</sub> shows pronounced oscillations of each spin-orbit and  $\Lambda$ -doublet component and bimodal distributions with preferred population at low and high J. Strong deviations from the statistical distributions of phase space theory are found. Alignment measurements for NO(v''=1, J>5.5) from the dissociation of slowly rotating parent molecules are reported for the first time. The well-preserved rotational alignment with a fairly constant value of  $A_0^{(2)} = -(0.35 \pm 0.05)$  confirms that photodissociation at this wavelength is initiated by a  ${}^{2}A_{1}/{}^{2}B_{2} \leftarrow {}^{2}A_{1}$  parallel electronic transition with less than 5% contribution from another possible perpendicular transition  ${}^{2}B_{1} \leftarrow {}^{2}A_{1}$ . The characteristic rotational distributions observed thus arise from this  ${}^{2}A_{1}/{}^{2}B_{2} \leftarrow {}^{2}A_{1}$  transition. Our results clearly show that the energy flow among product rotational degrees of freedom is far from complete and that dynamical effects have to be considered important in the predissociation of NO<sub>2</sub> via the ground-state surface.

# Introduction

The photodissociation dynamics of NO<sub>2</sub> in the near-UV

$$NO_2 + h\nu (250 \le \lambda \le 398 \text{ nm}) \rightarrow NO(X^2\Pi_i) + O(^3P_i)$$

are relevant in atmospheric chemistry and present one of the most intriguing test cases for models of unimolecular dissociation. They have also served for a long time as a test bed for new experimental techniques and continue to be studied intensively.<sup>1-14</sup>

The electronic absorption spectrum in this region results from the extension of the notoriously congested visible spectrum of  $NO_2$  to higher energy. It reveals coarse structure in the form of a few regular bending progressions assigned to the transition from the ground electronic state  ${}^{2}A_{1}$  to the linear excited state  $^2B_1$  and strong irregular vibronic bands associated with the transition from  ${}^{2}A_{1}$  to the  ${}^{2}B_{2}$  state. The  $\tilde{X}{}^{2}A_{1}$  and  ${}^{1}{}^{2}B_{2}$  states are heavily mixed and connected by a conical intersection. Above the dissociation threshold of  $D_0 = 25131 \pm 1 \text{ cm}^{-1}$ ,  $\frac{1,2,3,11}{2}$ photofragment angular distributions of both  $NO(X)^{4,6,7}$  and  $O(^{3}P)$ ,<sup>8</sup> the NO(v''=1) rotational alignment,<sup>4</sup> and resonance Raman studies<sup>14</sup> indicate that  $1^2A_1/{}^2B_2 \leftarrow \tilde{X}^2A_1$  is the dominant electronic transition. Since this mixed excited state is largely of ground-state character, the photodissociation mechanism can be considered a predissociation occurring mainly on the groundstate surface.<sup>1,2,15</sup> Thus, various statistical models have been proposed to predict the dissociation rate constants,<sup>2,9,10</sup> the quantum state distribution of the photofragment,<sup>1,4,5</sup> and the photofragment yield spectra.<sup>11</sup> However, in comparison with NCNO and CH<sub>2</sub>CO, for example, whose dissociation dynamics have been characterized as statistical, 16,17 NO2 represents a rather special case with a smaller level density in the region of the dissociation threshold. Predissociation rates are relatively fast, ranging from a few picoseconds at just above threshold as measured recently by Wittig and co-workers using subpicosecond photofragment spectroscopy<sup>2</sup> to less than one vibrational period well above threshold at 338 nm as suggested by Rohlfing and Valentini.<sup>14</sup> Rapid randomization of excess energy among the available degrees of freedom<sup>18</sup> and statistical behavior is certainly suspected at wavelengths shorter than 338 nm. Clearly, photo dissociation studies of  $NO_2$  in this region can provide incisive tests for the validity of statistical theories.

The internal state distributions of NO have long been recognized

as fingerprints of the dissociation dynamics of NO<sub>2</sub> and have been studied previously by a number of groups in order to complement the pioneering study of the 346-nm photofragment translational distributions by Busch and Wilson.<sup>8</sup> Zacharias, Welge, and co-workers reported the first well-resolved NO vibrational and rotational state distributions following 337-, 308-, and 351-nm photolysis using the one-photon laser-induced fluorescence (LIF) technique for probing NO directly.<sup>3</sup> Mons and Dimicoli employed time-of-flight REMPI probing of NO-(v''=1) and studied the photolysis of NO<sub>2</sub> at several wavelengths close to the NO(v''=1) threshold between 379 and 348 nm.<sup>4</sup>

All of the above studies utilized 300 K samples for which the initial quantum states of  $NO_2$  are undefined. This precludes rigorous and meaningful comparisons between experimental observation and the predictions of theoretical models. Quantum state selection in photodissociation studies requires supersonic jet expansion, optical-optical double resonance or stimulated emission pumping methods, and narrow bandwidth lasers to overcome this problem. Beam or free-jet expansion methods achieve state selection by cooling the parent sample down to a few kelvin, and hence only a few of the lowest states are populated. This approach to studies of the quantum state selective photolysis of  $NO_2$  has been adopted previously by Zacharias and Welge's<sup>3</sup> and more recently by Reisler's<sup>1</sup> group, who recorded NO fragment distributions in the vicinity of v'' = 0 and v'' = 1 thresholds, respectively.

The vibrational distributions of the NO photofragment observed so far for both 300 K and jet-cooled NO<sub>2</sub> photolysis are unambiguously nonstatistical, favoring formation of vibrationally excited NO. The rotational distributions on the other hand appear to be in better accord with statistical calculations. For 300 K samples the NO(v''=1) rotational distributions from the photodissociation of NO<sub>2</sub> near the v'' = 1 threshold are in good agreement with calculations based on statistical models such as prior<sup>4</sup> and stochastic simulations employing RRKM theory.<sup>5</sup> This apparent agreement may, however, change for photolysis at wavelengths well above the dissociation threshold. On the other hand, all NO rotational distributions from the photolysis of jetcooled samples exhibit structures which cannot be explained by conventional statistical models.<sup>1,3</sup> Reisler and co-workers concluded nevertheless that, on average, they follow the statistical distributions predicted by phase space theory (PST).<sup>1</sup> The



Figure 1. A schematic diagram of the experimental apparatus.

differences were generally attributed to Ericson fluctuations arising from the simultaneous sampling of many overlapped resonances. The resulting interferences are then thought to carry over into the product distribution. To explore this interesting phenomenon further, it is clearly necessary to perform full quantum state resolved studies over a wider wavelength range.

We present here our first results of a state-to-state study of the photodissociation of NO<sub>2</sub> at 355 nm in which we have combined LIF polarization spectroscopy of the NO fragment with supersonic jet cooling of the parent NO<sub>2</sub>. In particular, we report rotational state distributions and the first measurement of the alignment of NO(v=1). Our NO rotational population distributions reveal clear oscillations and bimodal shapes with preferential population on the low- and high-J sides that differ drastically from statistical distributions calculated by PST. The alignment measured approaches the limiting value of a pure transition with the transition dipole moment in the plane of the molecule. This implies that the mixed  ${}^{2}A_{1}/{}^{2}B_{2}$  state leads to the fluctuating rotational state population. The alignment of NO reveals the spatial distribution of product rotational angular momenta. For the photolysis of jet-cooled parent molecules, this vector attribute of the fragment provides the clearest indicator of the symmetry of the optical transition involved. At 300 K the rotation of  $NO_2$  is much faster and can significantly reduce the degree of alignment whereas the anisotropy parameter  $\beta$  depends not only on the symmetry of the transition but also on the geometry and motion of the parent molecule prior to dissociation.

#### **Experimental Section**

The experimental setup comprises a Nd:YAG laser pumped dye laser system and an in-house constructed vacuum chamber with associated pumping equipment for supersonic jet expansion as shown schematically in Figure 1. The chamber, flanges, and baffle arms are made of aluminum and anodized black to reduce scattered light. The pumping system consists of a diffusion pump with 700 L/s pumping speed (Edwards 160/700 Diffstak) backed by a two-stage rotary pump (Edwards E2M18).

The 0.5–1% purified NO<sub>2</sub> is premixed with helium to a total pressure of around 700 Torr and supersonically expanded by a pulsed solenoid valve (General Valve Corp. Series 9) into the vacuum chamber held at a background pressure of  $10^{-5}$  Torr. The valve is operated with an opening time of 0.5 ms and a circular orifice of 0.5-mm diameter. The collinearly aligned counterpropagating laser beams intersect the free-jet expansion at a distance 12 mm downstream from the nozzle orifice, where the rotational temperature of NO<sub>2</sub> is  $5 \pm 2$  K as estimated from LIF spectra of either residual NO or NO<sub>2</sub>. The K temperature of NO<sub>2</sub> is found similar to the rotational temperature.

The third harmonic of a Nd:YAG laser (Lumonics HY400) provides the vertically polarized photolysis beam and simultaneously pumps a dye laser (Lumonics HD500) operating on a coumarin dye. The polarization of the photolysis laser is improved by a vertical polarizer and a Fresnel rhomb permitting rotation of the polarization plane of the laser beam by 90° for determining the alignment. Typical pulse energies of 3 mJ with pulse duration of 5 ns are used for photolysis and monitored continuously with a photodiode in a shot-by-shot mode.

The NO photofragments are detected by LIF via excitation of the  $\gamma(0,1)$  band of the  $A^2\Sigma^+ \leftarrow X^2\Pi_i$  transition near 236 nm. A commercial frequency doubling unit (Lumonics, Hyper Trak-1000) equipped with a  $\beta$ -barium borate crystal provides tunable laser light with a bandwidth of 0.07 cm<sup>-1</sup>. The probe pulses are optically delayed by 7 ns, reduced in energy to less than 1  $\mu$ J by a telescope and beam attenuator (Newport, Model 935-3-OPT), and monitored by another photodiode. Only the central homogeneous portion of the probe laser beam is used, and its polarization is fixed horizontally by a calcite polarizer. In order to minimize the effects of beam walk-off in the alignment measurements and during long scans, the probe beam diameter (3 mm) is kept smaller than that of the photolysis beam (5 mm).

The laser-induced fluorescence is collected by a fused silica condenser and viewed in a direction perpendicular to both the laser and the molecular beams by a PMT (Thorn EMI 9635 QB). An iris in front of the multiplier acts as a spatial filter and restricts the field of view to  $3 \times 3 \text{ mm}^2$ . A reflection filter (Schott UV-R-250) and two solar blind filters (Corion) are used for the elimination of the scattered light. The PMT output and the signals from the two diodes monitoring pump and probe beams are processed by boxcar integrators (Stanford Research Systems, Model SR250), averaged, digitized, normalized, and stored in a computer (IBM PC-XT). The LIF signal intensities for nascent NO depend linearly on both intensities of dissociation and probe laser beams, and excitation spectra do not depend on the partial pressure of  $NO_2$  under the conditions employed. We are confident therefore that any contributions to the signals from the dissociation of the NO<sub>2</sub> dimer or complexes with the carrier gas as well as effects from optical saturation and multiphoton dissociation are insignificant.

For recording the state-specific photofragment yield spectra of NO, the 355-nm photolysis laser is replaced by a tunable XeCl excimer pumped dye laser (Lambda Physik, EMG101MSC/ FL3002, bandwidth 0.4 cm<sup>-1</sup>). The pump and probe lasers are synchronized with a ~50-ns delay by a digital delay generator (Stanford Research Systems, Model DG535). The detection of LIF signals was as described before.

# **Results and Discussion**

LIF Spectrum. The one-photon laser excitation spectra of NO on the  $A^2\Sigma^+ \leftarrow X^2\Pi$  transition have been assigned previously and are known in considerable detail.<sup>3,19</sup> Due to the interaction of rotation and electronic motions, each rotational level of the ground state X<sup>2</sup>II is split first into spin-orbit components  ${}^{2}\Pi_{1/2}$  (F<sub>1</sub>) and  ${}^{2}\Pi_{3/2}$  (F<sub>2</sub>) levels, following Hund's case (a) for the low and intermediate J or Hund's case (b) for high J. In addition, each level is split into two  $\Lambda$ -doublet components (e and f). The energy levels of  $A^2\Sigma^+$  are only split into F<sub>1</sub> and F<sub>2</sub> components by spinrotation coupling. The spectrum, therefore, contains eight resolved branches designated as  $\Delta J_{F'F''}$ : P<sub>12</sub>, Q<sub>22</sub> + R<sub>12</sub> and P<sub>22</sub> + Q<sub>12</sub>, R<sub>22</sub> probe e and f components of  ${}^{2}\Pi_{3/2}$  (F<sub>2</sub>); while Q<sub>11</sub> + P<sub>21</sub>, R<sub>21</sub> and P<sub>11</sub>, R<sub>11</sub> + Q<sub>22</sub> probe f and e components of  ${}^{2}\Pi_{1/2}$ (F<sub>1</sub>), respectively.

The relative intensity in the spectrum of nascent NO is found to be significantly dependent on the reservoir pressure. Figure 2 presents a part of the  $P_{12}$  branch recorded under different stagnation pressures. In the 700–400 Torr pressure region, where



**Figure 2.** P<sub>12</sub> branch of the  $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi_{3/2}(v''=1)$  LIF spectra of nascent NO from the 355-nm photolysis of NO<sub>2</sub>. The spectra were recorded with a premixed gas sample of 1% NO<sub>2</sub> in helium expanding from the different stagnation pressures indicated.

the rotational temperature of NO<sub>2</sub> is measured as  $\sim 5$  K, the intensities of J'' = 1.5 and 3.5 lines are about 2.5 times of that of J = 2.5 and 4.5. This clear intensity alternation, however, becomes smaller with decreasing pressure and vanishes at pressures lower than 100 Torr, where the rotational temperature of NO<sub>2</sub> is higher than 30 K. In addition, the large intensity ratio between low- and high-J lines (J=14.5-18.5) averages out significantly with decreasing pressure. These clear changes mirror the influence of the rotational temperature of the parent NO<sub>2</sub> on the product state distribution. In the following work the stagnation pressure is held constant at around 600 Torr.

**Determination of Alignment.** The alignment  $\mathcal{A}_0^{(2)}$  reflects the spatial distribution of the rotational angular momentum vector J of the NO photoproduct in the laboratory frame and has to be measured to extract the genuine quantum state-resolved population distributions from LIF spectra of nonisotropic fragment ensembles. Furthermore, this quantity provides important direct information on details of the dissociation dynamics.<sup>20</sup> Following the approach of Dixon the integrated line intensity of the photofragment LIF spectrum can be expressed as<sup>21</sup>

$$I = C\nu_0 q_{n'n'} SN(Q)(b_0 + b_1 \beta_0^2(0, 2))$$
(1)

where C is a proportionality constant depending on the detection efficiency,  $\nu_0$  is the central frequency of the line profile, q and S are the Franck-Condon and line strength factors, respectively, and  $b_i$  are coefficients depending on the polarization, the photolysis-detection configuration, and spectral branch. At present, we calculate them for each transition  $(J_e, J_i)$  with the sum of all possible emission lines  $(J_f, J_e)$  weighted by their line strength without final adjustment for hyperfine depolarizations. For a mixed branch S is the sum of the two transitions, and  $b_i$ are sums of components weighted by their line strength.  $\beta_0^2$ represents the bipolar moment, which is proportional to the alignment  $A_0^{(2)}$ ,  $\beta_0^2 = 5/4A_0^{(2)} = P_2(\mu \cdot \mathbf{J})$ . The  $\beta_0^2$  value of photofragments can lie between the high-J limits of -0.5 and 1.0.

To obtain the alignment parameter  $A_0^{(2)}$  of each product quantum state, one needs to measure at least two intensities with different  $b_1$  but referring to the same quantum state. In principle, this can be done either by taking data from different probe branches at a fixed geometry or by changing the geometry at a



Figure 3. Bipolar moment  $\beta_0^2(0,2)$ , for NO(v''=1) from the photolysis of jet-cooled NO<sub>2</sub>, plotted as a function of the rotational quantum number  $J_{NO}$ . The error bar stands for  $2\sigma$ . The dashed line indicates the high-J limit for a transition dipole moment  $\mu$  perpendicular to the angular momentum  $J_{NO}$ .

fixed transition. In our case, the former method is impractical because of the serious overlapping of NO lines in some branches. The second approach is used by determining the intensities of pure P/R and main Q branch lines for the two geometries  $\epsilon_p$  parallel and perpendicular to  $\epsilon_a$ . The technical difficulties with this approach are to avoid misalignment of the beams when the  $\epsilon_p$  is rotated and to ensure the absence of saturation of strong lines. Hence, special care has been taken in the experimental arrangement and conditions as outlined previously.

As a result of the rotational alignment of the NO, the change of LIF intensities with the orientation of  $\epsilon_p$  depends on the spectral branch. On rotation of  $\epsilon_p$  by 90° the configuration changes from  $\epsilon_p \perp \epsilon_a$  to  $\epsilon_p \parallel \epsilon_a$ , the intensity of P and R lines increases, and the intensity of main Q lines decreases. However, line intensities of high-J states of mixed branches, such as  $P_{22} + Q_{12}$  and  $R_{11} + Q_{21}$ , do not change due to the canceling of  $b_1$ . This criterion can be used to judge and correct the effect of misalignment. A consistent value of  $A_0^{(2)}$  from different branches probing common J" levels of NO(F<sub>1</sub>/F<sub>2</sub>) shows that the experimental approach and analysis procedures used are reliable.

Unlike the 300 K experiment with similar excess energy,<sup>4</sup> we have found that the rotational alignment of NO is very strong in the case of the 355-nm photodissociation of jet-cooled NO<sub>2</sub> as shown in Figure 3. The average value of  $A_0^{(2)}(\text{obs}) = -(0.35 \pm 0.05)$ , for 10 < N'' < 23 of both spin-orbit and A-doublet components. For N < 10 the observed value tends to decrease slightly with J probably due to the significant influence of hyperfine depolarization, except for N close to 0 where the alignment observed sharply decreases to 0.

For a strictly planar photodissociation of NO<sub>2</sub>  $A_0^{(2)}$  of the NO product can reach the high-J limiting values of -0.4 and +0.8 corresponding to  $B_2 \leftarrow A_1$  and  $B_1 \leftarrow A_1$  transitions, respectively. The former has the transition dipole moment  $\mu$  lying along the in-plane *a* axis of NO<sub>2</sub> yielding J perpendicular to  $\mu$ , while the latter has  $\mu$  directed along the out-of-plane *c* axis yielding J parallel to  $\mu$ . These limiting values for the alignment of NO may be reduced by several factors:

(1) Out-of-plane internal motion of the parent molecule. For a planar triatomic molecule such as NO<sub>2</sub>, the out-of-plane internal motions are rotation of the molecule around the *a* and *b* inertial axes. They contribute roughly 0.7kT to the perpendicular component  $E_{\perp}$  of NO rotation and yield a restricting factor  $P_2$ - $(\cos \theta) = \frac{1}{2} [3(E_{\perp}/(E_{\perp}+E_{\parallel}))-1]$ . At T = 5 K this correction is small and equals 0.99, but at 300 K the correction can be quite significant and increases with decreasing rotational energy of NO, i.e. J. A value of 0.6 is obtained for E = 400 cm<sup>-1</sup>.

(2) Out-of-plane rotation of the parent due to the finite dissociation time. The rotation of NO<sub>2</sub> around the a and b axes can cause an additional loss of alignment if the initial plane of

the parent molecule NO<sub>2</sub> is rotated by a considerable angle  $\omega t$  before the instant of bond fission. This effect increases with sample temperature, e.g., angular velocity  $\omega$  of the parent molecule, or with the lifetime t of the excited NO<sub>2</sub>. Following Hall et al.,<sup>22</sup> we calculate multiplier factors of 0.97 at 5 K and 0.46 at 300 K for NO<sub>2</sub> with an excited-state lifetime of 220 fs for the averaged effects of rotations about the a and b inertial axes. Taking into account both of the above two factors, we find limiting values, denoted as the apparent alignment  $A_0^{(2)}$  (app), reduced to -0.38 and +0.76 at 5 K and -0.12 to +0.24 at 300 K.

(3) Simultaneous excitation of the transitions  $B_2-A_1$  and  $B_1-A_1$ . In this case the alignment results from the linear combination of two values and is expected to fluctuate with NO quantum state as well as photolysis wavelength.

From the above discussion, it is apparent that the strong alignment which we observe from a jet-cooled sample directly mirrors the nature of the photoexcitation step(s) and can be used to estimate contributions of the two channels. Our alignment results for NO J > 7 indicate that the B<sub>2</sub> channel contributes more than 95% and the  $B_1$  channel less than 5%. This is not surprising since the  $B_1$  state is linear, and the bond distance changes little from the ground state. Thus, the Franck-Condon principle favors population of NO in v'' = 0 and low-J states. In fact, the nearly zero alignment observed for low-J states might be the result of a small  $B_1$  contribution. A smaller alignment at v'' =0 is also expected while the alignment from the 300 K sample cannot be strong because of the increased influence of the parent rotation and the finite lifetime of the NO<sub>2</sub>. The calculated value of -0.08 corresponding to 300 K falls within the range of Mons and Dimicoli's result.4

Another vector property, the anisotropy parameter  $\beta$  reaches its limiting values of +2 and -1 if the velocity vector is parallel and perpendicular to the transition dipole moment, respectively. However,  $\beta$  of the photofragment from the rotationally cold parent is related not only to the symmetry of the optical transitions involved but also to the bending angle of the excited complex. Taking the branching ratio determined from our alignment measurements and the equilibrium bond angles of the ground state for  ${}^{2}A_{1}/{}^{2}B_{2}$ , a  $\beta$  value of 1.5 for the dissociation of NO<sub>2</sub> at 5 K is obtained by ignoring the internal motions and the finite lifetime of the parent.<sup>23</sup> This is in good agreement with the value of 1.4 measured by Suzuki et al. for NO(v''=0) at the same photolysis wavelength.<sup>6</sup>

The Rotational and Fine Structure Distributions of NO. The quantum-state-resolved distributions of NO(v''=1) from photolysis of jet-cooled  $NO_2$  have been derived from integrated line intensities using eq 1 with the individual measured alignment values. Figure 4 displays the results for each spin-orbit and  $\Lambda$ -doublet component along with statistical distributions calculated from phase space theory (PST). The experimental data from two different branches probing the same component agree with each other and are averaged.

For the PST model the population of each quantum state  $(v,J,\Omega)$  of NO(X) is taken to be proportional to the corresponding accessible phase space of  $\{O, ^3P_J, L\}$  for a given  $J_{NO}$  and  $J_{NO_2}$  within the constraints of energy and angular momentum conservation.<sup>16,17,24</sup> Values are then averaged for  $J_{NO_2}$  with a Boltzmann weighting factor. In the case of  $T_{rot}$  of NO<sub>2</sub> below 10 K, where NO<sub>2</sub> populates mainly the N=0,2,4 and  $K_a = 0$  rotational states, the PST calculation gives a distribution showing equal population for most intermediate J states except a few of low or high J, which are limited by the conservation of angular momentum or by the available energy to surpass the effective channel potential, respectively. Details of the model are given in the Appendix.

In spite of some missing points, where data evaluation is precluded due to spectral overlap, the observed rotational



Figure 4. Rotational distributions for each NO fine-structure component from the photolysis of jet-cooled NO<sub>2</sub>. Arrows indicate the thermodynamic limits. The PST calculation is performed with T = 5 K,  $C_6 = 1.4 \times 10^{-78}$  J m<sup>6</sup>,  $b_{max} = 3$  Å.

distributions reveal pronounced structure in the form of fast oscillations on top of broader variations. The fast oscillation tends to behave in the opposite way for different  $\Lambda$ -doublets, and therefore the ratio of relative  $\Lambda$ -doublet populations fluctuates dramatically with  $J_{\rm NO}$ , and there is no distinct and consistent  $\Lambda$ -doublet preference even at high J, where Hund's case (b) is approached. In the high-J limit  $\Lambda$ -doublet levels are defined by the orientation of the singly occupied orbital lobes with respect to the plane of rotation of the nuclei with  $\Pi(A'')$  representing the out-of-plane and  $\Pi(A')$  representing the in-plane component.<sup>25</sup> The  ${}^{2}\Pi_{1/2}$  spin-orbit component is clearly favored and, on average, populated roughly twice as much as the  ${}^{2}\Pi_{3/2}$  component. Thus, our results show that the spin-orbit distribution is also nonstatistical.

Although the clear cutoff corresponding to the threshold energy is observed, the striking oscillatory pattern of the rotational distribution deviates strongly from the statistical prediction. This indicates that the initial preparation of the wavepacket on the excited level(s) of the parent molecule and its subsequent propagation under the influence of the potential energy surface are carried over to some extent into the product state distribution.

If NO<sub>2</sub> dissociation at 355 nm is initiated by few resonant transitions to single quasi-bound vibronic levels of the ground state <sup>2</sup>A<sub>1</sub>, it must be preceded by intramolecular vibrational redistribution in most cases in order to accumulate sufficient energy in the dissociation coordinate, i.e., the asymmetric stretch, to break one of the N-O bonds. The product distribution may reflect the initial preparation of the wavepacket and subsequent vibrational redistribution as in the case of dissociation of HCO- $(X^2A')$  to H + CO $(X^1\Sigma^+)$ . Dixon has recently applied threedimensional wavepacket calculations to this process, demonstrating mode selectivity in the vibrational redistribution and product state distribution.<sup>26</sup> In this case high excitation of the CO stretching mode in general results in inverted vibrational populations while the excitation of bending quanta leads to high rotational excitation of CO. The overall shape of the rotational distribution can reflect the node structure of the resonant bending wave function within the potential well, and the fast oscillation with  $J_{CO}$  stems from the interference of the outgoing wave functions which appears if the dissociation geometry is strongly bent. In the NO<sub>2</sub> case, the phase which controls the exact position of the fast oscillation varies with the initial quantum states of  $NO_2^*$ , the projection of the total parent angular momentum  $K_a$ , and the electron fine-structure states of both products  $O({}^{3}P_{j})$  and NO( $2\Pi_{\Omega}, v, \Lambda$ ), as well as the final state interaction. Thus, the



Figure 5. Channel-specific photofragment yield spectra of NO(v''=1) probed on the P<sub>12</sub> branch for transitions with J'' = 18.5 (a), 4.5 (b), 3.5 (c), 2.5 (d), and 1.5 (e).

above rapid fluctuations tend to diminish unless a specific path is followed. For the quantum state-selected photodissociation of H<sub>2</sub>O from its first absorption continuum, oscillatory rotational distributions have also been observed for each fine structure component  $OH(v''=0,F_i,\Lambda)$ . They were explained through calculations based on expanding the wave function of H<sub>2</sub>O on the product eigenfunctions including the electronic state of  $OH(^{2}\Pi)$ and spin of the H atom. Here, the fast oscillation is attributed to a phase factor in the fine-structure state population terms which changes sign for the adjacent J and is, therefore, parity related.<sup>27</sup>

In general, however, the number density of optically accessible states of NO<sub>2</sub> with  $B_2$  symmetry at 355 nm is about  $0.3/cm^{-1}$ ,<sup>2</sup> and the fwhm of an energy resonance is estimated about 30 cm<sup>-1</sup> with a lifetime of 220 fs.8 Consequently, a few vibrational levels are likely to be populated simultaneously with monochromatic photon excitation. The product state distribution is expected to be further complicated by the possible interference among these states. As a result, the nice node structure and oscillation in the product state distribution are often blurred and no longer reveal the correlation between the initial parent states and product distribution via the PES. Nevertheless, nonstatistical rotational distributions of NO(2II) fine structure components as manifested by oscillations have already been observed previously in the photodissociation of jet-cooled NO<sub>2</sub> by several other groups.<sup>1,3,19</sup> Robra et al. argued that one-photon dissociation of rotationally cold NO<sub>2</sub>, which begins predominantly with states of positive parity, leads preferentially to the population of NO product states with the same parity.3 This contrasts with the present observation where the  ${}^{2}\Pi_{3/2}$  spin-orbit components rather show a propensity for negative parity in the low-J part of the distribution. We believe that absorption and scattering processes select terms of definite parity in the exit channel coupling of NO( $^{2}\Pi$ ) and O( $^{3}P$ ) rather than the parity of NO(<sup>2</sup>II) itself.

In an attempt to clarify this further, we have recorded photofragment yield spectra by scanning the photolysis laser wavelength while monitoring NO LIF signals with the probe laser fixed to each of the first four lines in the  $P_{12}$  branch. These are the LIF NO product lines whose intensities oscillate most strongly at 355 nm. For comparison with the low-J spectra, the yield spectrum for NO(J=18.5) has also been measured. Figure 5 displays these channel-specific photofragment yield spectra in the range from 27 000 to 29 700 cm<sup>-1</sup>. Generally, for the low-J rotational states the fluctuation is more rapid when the photolysis energy is low and becomes less at higher energy. The position of the 355-nm dissociation laser in Figure 5 is indicated by an arrow. Here signals from J = 1.5 and 3.5 levels with odd nuclear rotational quantum number N of NO( ${}^{2}\Pi_{3/2}$ , e component) approach maximum intensity and are about 2 times higher than those of the J = 2.5 and 4.5 levels with even N. Thus the yield spectra are in agreement with the 355-nm measurements. This



**Figure 6.** Rotational distributions for nascent NO(v''=1) from the photolysis of room temperature NO<sub>2</sub>. The solid lines show PST calculations with T = 300 K. The calculated distribution for the  ${}^{2}\Pi_{3/2}$  spin-orbit state has been scaled with a reducing factor of 2.5, giving the best agreement with the observed distribution.

propensity pattern, however, changes with photolysis wavelength, and no distinct correlations can be drawn.

For comparison with the results obtained with jet-cooled NO<sub>2</sub>, we have also measured the rotational distribution of NO from the photolysis of room temperature NO<sub>2</sub> in a flow cell. The results are displayed in Figure 6. The population distributions reveal much less fluctuations and agree very well with PST calculations shown by the drawn-out lines.

Summarizing the information obtained so far, we propose the following photodissociation mechanism for NO2 in the near-UV via the  $\tilde{A}^2 A_1/{}^2 B_2 \leftarrow \tilde{X}^2 A_1$  electronic transition: Some eigenstates of  $NO_2^*(A)$  selected by the photoexcitation step can decay through resonant scattering, where the initial mapping of wave packets and the subsequent dynamic forces are memorized and reflect the details of the potential energy surface(s). In the jet experiment only a few of those states are excited, and the resonant effects including interference of overlapping resonances associated with these states can be retained to some extent. This is the most likely reason that we observe complex rotational population distributions for the NO product. The preference for formation of NO in states of high J can be attributed to the excitation of the  $v_2$  bending mode. At 300 K, on the other hand, the Boltzmann distribution over the quantum states of the NO<sub>2</sub> parent molecule includes many states of higher J and K, and this results in the excitation of many vibronic states of parent NO<sub>2</sub> prior to dissociation. The ensemble of states produced then becomes effectively equivalent to that produced by intramolecular energy redistribution of a single state. Alternatively, the larger ensemble of mixed eigenstates and incoherent resonances provide access to a much larger phase space. Since the molecules dissociate on the ground surface without a significant barrier, RRKM theory with a loose transition state or PST can be applied and successfully predicts the rotational product distribution.

### Conclusions

In the present work the rotational state distribution and alignment for NO(v''=1) from the photolysis of jet-cooled NO<sub>2</sub> at 355 nm have been measured in an effort to gain further insight into the photodissociation dynamics. Our alignment measurement has demonstrated the advantage of the jet-cooling technique in the determination of the symmetry of the relative long-lived excited state. The well preserved alignment, with an average value of -0.35, indicates that at this wavelength the dissociation yielding NO(v''=1) occurs predominantly via the mixed state  ${}^{2}A_{1}/{}^{2}B_{2}$ with B<sub>2</sub> symmetry.

Distinct oscillations on top of a multimodal distribution have been found to characterize the rotational populations of each spin-orbit and  $\Lambda$ -doublet component of the NO photoproduct from the photolysis of efficiently cooled parent molecules with  $T_{\rm rot} \sim 5$  K. This striking structure depends on the initial states of parent NO<sub>2</sub><sup>\*</sup> and the fine-structure electronic states of the products and has been interpreted as evidence for the existence of resonant mapping of excited state(s) into the product channel. With increasing temperature of the parent molecules, this resonant structure fades as the result of simultaneous sampling of many initial excited states of NO<sub>2</sub>. Finally, we have shown that the NO product state distribution from the photolysis of room temperature NO<sub>2</sub> approaches the other extreme—the statistical limit.

Acknowledgment. We thank Professor R. N. Dixon, F.R.S, and Professor H. Reisler for their interest, helpful advice, and the careful reading of the manuscript. We also thank the UK Science and Engineering Research Council for an equipment grant, the Commission of the European Community and the UK Ministry of Agriculture, Fisheries and Food for the partial support of this work through Contracts STEP CT 90-0071 and N677, respectively.

## Appendix

One of the aims of our study is to test the validity of a statistical theory for the description of the dynamics of the dissociation

$$NO_2 + h\nu \rightarrow NO(X^2\Pi) + O(^3P)$$

Our test consists of the comparison of predicted with observed rotational distributions of the NO photofragment. In the following section we present the formulas and parameters used in our program for the computation of these distributions.

The distribution of NO in the quantum states  $q(|q\rangle = |v,J,\Omega\rangle$  for a given photolysis energy  $E_0$  is written as

$$\bar{P}^{\text{stat}}(\text{NO},q;E_0) = \sum_p P_p(\text{NO}_2,p;E^*,J) \sum_{j \in \mathcal{N}} P_j(\text{O},{}^3\text{P}_j) \times P_{j}^{\text{stat}}(\text{NO},q;\text{O},{}^3\text{P}_j \leftarrow \text{NO}_2,p;E^*,J)$$

 $P^{\text{stat}}{}_{p,j}$  stands for the probability of forming NO(<sup>2</sup>II) in a specific quantum state q for a given fine structure state of O(<sup>3</sup>P<sub>j</sub>, j=2,1,0) and quantum number p of the parent in the excited state.  $\bar{P}^{\text{stat}}$ is the average of  $P^{\text{stat}}{}_{p,j}$  over the distribution of three possible electronic states for the O atom and the distribution of NO<sub>2</sub> parent states created by the laser excitation.

Statistical theories such as RRKM, SACM, and PST all rest on the concept of ergodicity, which assumes that the coupling between the various internal degrees of freedom of the energized complex is sufficiently strong to randomize rapidly excess energy among all active modes, and the chance of the complex sampling each accessible state or open channel is equal.  $P^{\text{stat}}_{p,j}$  is then given by

$$P^{\text{stat}}_{p,j}(\text{NO},q) = W^{\text{stat}}_{p,j}(q) / \sum W^{\text{stat}}_{p,j}(q)$$

W is the number of states of the complex which can yield NO and O in the specific quantum state q and j, respectively, for a given excess energy  $E^*$  and total angular momentum J. Clearly, the method for the evaluation of  $W^{\text{stat}}$  forms the core of statistical models and distinguish them from each other.

Phase space theory assumes that the reaction proceeds through a loose transition state. This simplifies the calculation of W to the counting of the corresponding number of L, the orbital quantum number for the relative motion of the two fragments, subject to conservation of total angular momentum and energy.

$$W^{\text{PST}}(q) = \sum_{K} \sum_{L} h$$

The conservation of angular momentum requires that

$$\mathbf{J} = \mathbf{J}_a + \mathbf{J}_i + \mathbf{I}$$

 TABLE I:
 Summary of Spectroscopic Data Used in the Program<sup>a</sup>

		Te	<i>v</i> <sub>1</sub>	<i>v</i> <sub>1</sub>	<b>v</b> 1	A <sub>0</sub>	B <sub>0</sub>	C <sub>0</sub>
NO <sub>2</sub>	Ñ	0.0	1320	750	1618	8.00	0.433	0.41
				$D_0 = 251$	31 <sup>b</sup>		•	
			- <u></u>	ωε	ພູ	c <sub>e</sub>	Be	αe
NO	<sup>2</sup> Π <sub>1/2</sub>		0.0	1904.0	14.	1	1.672	0.017
	$^{2}\Pi_{3/2}$		119.8	1904.0	14.	1	1.720	0.018
O <sup>c</sup>	$^{3}P_{2}$		0.0					
	${}^{3}P_{1}$		158.5					
	3P		226.5					

<sup>a</sup> The values listed above are in  $cm^{-1}$ . They are cited from Herzberg<sup>29</sup> except where references are indicated. <sup>b</sup> From ref 3a. <sup>c</sup> From ref 12.

or

$$JJ = J_a + J_i$$
 then  $J = JJ + L$ 

 $J_q, J_j$  denotes the total angular momentum of NO and electronic angular momentum of the O atom; JJ is the vector sum of  $J_q$  and  $J_j$ . The range of JJ is defined by

$$|J_a - J_i| < JJ < J_a + J_i$$

The total angular momentum J before dissociation is approximated by the rotational angular momentum of  $NO_2$  in the excited state,  $J_{p'}$ , neglecting its spin and electronic orbital angular momentum contributions. In this way we obtain the first set of boundary conditions for the orbital angular momentum L

$$|J_{p'} - JJ| < L < J_{p'} + JJ$$

Due to the conservation of energy the amount of excess energy of the reactive complex,  $E^* = h\nu + E_{int}(NO_2) - D_0$ , has to surpass the maximum of the effective potential along the reaction coordinate R,  $V_{eff} = V_{el}(R) + (h^2/2\mu R^2)L(L+1) + E_{products}$ , to dissociate. That is  $E^* > V_{eff}$ , which further restricts the maximum value of L by either  $\hbar^2 L_{max}(L_{max} + 1) < 6\mu C_6^{1/3}(E_{trans}/2)^{2/3}$  if  $V_{el}(R) = -C_6/R^6$  or  $\hbar^2 L_{max}(L_{max} + 1) < 2\mu E_{trans} b_{max}^2$  provided there is a maximum value for the impact parameter b.

Here,  $E_{\text{trans}}$  is the relative translational energy of the fragments

$$E_{\text{trans}} = E^* - E_{\text{vib}}(\text{NO}) - E_{\text{rot}}(\text{NO}) - E_{\text{el}}(\text{O}, {}^3\text{P}_j)$$

Since the spin-orbit splitting is substantial for NO, the rotational energy of NO is calculated using the formula for Hund's case (a) coupling.  $E_{rot}(NO,^{2}\Pi_{1/2}) = B_{v;1/2}J_{p}(J_{p}+1)$  and  $E_{rot}(NO,^{2}\Pi_{3/2})$  $= B_{v;3/2}J_{p}(J_{p}+1) + E_{so}$ .  $E_{so}$  is the spin-orbit splitting. The spectroscopic data used in the program are listed in Table I. This approximation affects the results only to a minor extent even for NO at high J.

Because photodissociation can produce  $O({}^{3}P)$  in three closely spaced fine structure levels  ${}^{3}P_{2}$ ,  ${}^{3}P_{1}$ , and  ${}^{3}P_{0}$ , the population distribution of NO needs to be summed over all those channels with their distribution function as a weighting factor. The program takes this function as input data. The main influence of this function on the rotational distribution of NO is the falling edge. We have found that the vibrational distribution and rotational distribution for v'' = 1 are quite sensitive to the  $O({}^{3}P_{j})$ distribution near the dissociation threshold for v''=1, especially at low temperature. At 355 nm, however, the distribution does not depend significantly on the choice of a statistical distribution  $(T_{\infty}: {}^{3}P_{2}:{}^{3}P_{1}:{}^{3}P_{0} = 5:3:1)$  or the experimental result of 1:0.18:  $0.04.{}^{12}$ 

Finally, we consider that a specific set of initial conditions  $(E^*, J)$  exists which corresponds to the population of NO<sub>2</sub><sup>\*</sup> in specific quantum states created by the photoexcitation step. At 300 K, in particular, this set can include quite a large number of those states. Therefore, the distribution of NO which can be tested against experimental observation is actually the average of specific  $(E^*, J)_p$  over their distribution. We assume identical



Figure 7. Simulated rotational distributions of NO( $X^2\Pi_{3/2}, v''=1$ ) from the photodissociation of NO<sub>2</sub> at room temperature, with  $h\nu - D_0 - E_{vib}$ (v''=1) = (a) 203, (b) 15, (c) 391, and (d) 1712 cm<sup>-1</sup>. Other parameters remain the same as before.

absorption cross sections for vibronic transitions because of the congestion in the absorption spectrum, and harmonic oscillator as well as symmetric top behavior for NO<sub>2</sub>, and we take the form of the distribution function to be a Boltzmann distribution of the ground-state NO<sub>2</sub> times the Hönl-London factor  $A_{Kp''Jp''}$  for the optical transitions. With this assumption, we obtain

$$P_{p}(NO_{2},p) = A_{Kp''Jp''}g_{Kp''Jp''} \times \exp[(-E_{int,p''}(NO_{2})/kT] / \sum g_{Kp''Jp''} \exp[(-E_{int,p''}(NO_{2})/kT]]$$
with

 $g_{Kp''Jp''} = 2J_p + 1$  if  $K_{p''} = 0$  and  $2(J_{p''} + 1)$  if  $K_{p''} \neq 0$ 

$$E_{\text{int},p''}(\text{NO}_2) = E_{\text{vib}} + E_{\text{rot}} \sim [(B_0 + C_0)/2]J_{p''}(J_{p''} + 1) + [A_0 - (B_0 + C_0)/2]K_{p''}^2$$

The population of NO2 in vibrationally excited states is small and therefore ignored here.  $A_{Kp''Jp''}$  factors for a parallel transition are used, and all three P, Q, R branches are included in the calculation.<sup>29</sup> The selection of the distribution functions is not important for the rotational distribution of NO at low temperature since the calculation is dominated by the results of low  $J_{p''}$ , but it can be crucial for the T = 300 K results.

Although phase space theory overestimates rate constants of unimolecular reactions, it has been applied successfully to predictions of product state distributions and serves as the favored choice of statistical models because of its simplicity. Reisler and co-workers<sup>1</sup> have compared their experimental results near the v''=1 threshold with the PST prediction. We have checked our program with their calculated rotational distributions of NO and obtained similar results. To compare the PST prediction with the stochastic calculations of Elofson and Ljungström based on RRKM theory, we have also calculated NO rotational distributions for the dissociation of  $NO_2$  at room temperature with various photolysis wavelengths used in Mons and Dimicoli's experiment. These results are presented in Figure 7 and show remarkably good agreement.

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