# Photodissociation of NO<sub>2</sub> Adsorbed on LIF(001)

## St. J. Dixon-Warren,<sup>†</sup> R. C. Jackson, J. C. Polanyi,<sup>\*</sup> H. Rieley,<sup>‡</sup> J. G. Shapter,<sup>§</sup> and H. Weiss<sup>⊥</sup>

Department of Chemistry, University of Toronto, 80 St. George St., Toronto, Ontario, Canada M5S 1A1 (Received: March 18, 1992; In Final Form: May 21, 1992)

The photochemistry of NO<sub>2</sub> physisorbed on single-crystal LiF(001) at 100 K has been studied at  $\lambda_1 = 248$  nm. The adsorbate was examined by polarized FTIR in both the presence and absence of  $\lambda_1$  radiation. In the absence of UV irradiation the adlayer is composed of dimeric  $(NO_2)_2$ . In the presence of UV, FTIR shows that some  $N_2O_3$  is formed. Photodissociations (PDIS) giving both NO(g) and molecular NO<sub>2</sub>(g) were the predominant mechanisms as determined by time-of-flight mass spectrometry (TOF-MS) and resonantly enhanced multiphoton ionization (REMPI). The main objective of this work was the characterization of the photoproduct, NO, internal state distribution by 1 + 1 REMPI. Vibrational levels from v'' =0 to 9 were probed with rotational resolution using a tunable laser,  $\lambda_2$ . The rotational distributions for each vibrational level could be described by one Boltzmann temperature. The spin-orbit states of NO(g) were equally populated in all vibrational levels. The lambda doublet states,  $\Pi(A')$  and  $\Pi(A'')$ , were equally populated. The principal observation was that the vibrational distribution in NO(g) was inverted and bimodal with a peak in v'' = 0 and a second substantial peak in v'' = 3-4, qualitatively resembling but quantitatively different from that for photolysis of  $NO_2(g)$ . Time delays between the two lasers were used to probe the translational energy of the NO(g) photofragment in specified states of internal excitation. The translational energy distributions were invariant over all vibrational levels, except v'' = 0 for which much slower fragments were observed. This complete determination of the energy distribution in the degrees of freedom of the NO(g) from photodissociation of adsorbate has implications for the identity of the photolyzing species and the dynamics of photodissociation. Two mechanisms for photoformation of NO<sub>2</sub>(g) were found: one at low coverages and one at higher coverages, the former giving peak translational energies  $\sim 1.2$  kcal/mol and the latter 0.4 kcal/mol.

### I. Introduction

The photochemistry of adsorbates is a rapidly expanding field which includes studies of photodissociation and photoreaction within the adsorbed layer as well as desorption of intact molecules.<sup>1</sup>

The specific goal of the present experiments was to determine the energy distribution-translational, vibrational, and rotational-for a photofragment molecule leaving the surface as a result of photodissociation in the adsorbed state. The fact that the photodissociation has taken place in the adsorbed state should be evident in the energy distribution of the photofragments. Ultimately, these energy distributions can be expected to yield information as to the dynamics (the molecular motions and hence the forces) governing the photodissociative event, as has been the case in gases.

Though very few studies have been made up to the present time of photofragment internal energies following photodissociation of adsorbates, there is substantial information concerning the inelastic scattering of NO from surfaces<sup>2-7</sup> and limited data regarding the thermal dissociation of NO<sub>2</sub>(ad) on Ge to give NO(g).<sup>8</sup> As regards photodesorption, the ultraviolet irradiation of multilayer NO films on  $MgF_2$  has been shown to give rise to parent molecules with as much as 1 eV of energy.<sup>9</sup> These experiments probed the internal states of the NO, which were found to be very rotationally cold. The desorption was attributed to energy transfer in the film. Explanations of the low rotational energies centered on postdesorption collisional cooling in the gas phase. Other experiments irradiating NO films on Ag(111) also used UV excitation to desorb NO.10 Two types of molecules were observed. "Slow" desorption was attributed to thermal processes while the "fast" desorption with peak translational energy of 0.22 eV was attributed to direct excitation of the film. Resonantly-enhanced multiphoton ionization (REMPI) was used to probe the internal energy distributions for the "fast" NO. A photodesorption study with probing of internal state excitation has also been performed on oxygen-covered nickel

as well as on Pt. On the Ni surface, a fast peak exhibited a large preference for one lambda doublet state at low K's.<sup>11</sup> The experiments on Pt gave non-Boltzmann rotational distributions and inverted spin state populations.<sup>12</sup> Yield as a function of wavelength and polarization indicated that the desorption on Pt was driven by the interaction of the adsorbate with hot carriers produced in the near-surface region.

Two reports have appeared of measurements of the internal energy of photofragments from photodissociation (PDIS) of adsorbates. In one case, a REMPI technique coupled with a time-of-flight mass spectrometry was used to investigate PDIS of multilayers of CH<sub>3</sub>I at 266 nm.<sup>13</sup> The experiments allowed vibrational resolution of the CH<sub>3</sub>. Ground-state CH<sub>3</sub>I as well as  $I^*({}^2P_{1/2})$  was also detected by REMPI. Two types of CH<sub>3</sub> photofragments were observed with differing velocity distributions, indicating two dissociation channels. These channels were attributed to the formation of  $I({}^{2}P_{3/2})$  and  $I^{*}({}^{2}P_{1/2})$  as the atomic product. Methyl radicals were observed in vibrational levels up to v'' = 3 in the umbrella mode.

Resonantly-enhanced MPI experiments giving not only vibrational but also rotational resolution, as in the present work, have been performed for the first time recently for photofragment NO(g) from adsorbed  $NO_2$ . The dissociation of  $NO_2$  on  $NO_2$ saturated Pd(111) was studied at wavelengths from 351 to 193 nm.<sup>14</sup> Two categories of NO were identified in these state-specific time-of-flight experiments. A fast channel could be characterized by a single Boltzmann temperature, much higher than that of the surface. Laser polarization and wavelength-dependence experiments were used to assign these fast-moving photofragments to a charge-transfer mechanism leading to dissociative electron attachment at  $NO_2(ad)$ . The second slow channel was not investigated in detail. It was characterized by two rotational Boltzmann temperatures,  $T_{\rm R}$ . One had a rotational temperature approximately equal to the surface temperature, while the second had  $T_{\rm R} > T_{\rm S}$ .

In the present experiments we independently paralleled the above work using a different substrate, NO<sub>2</sub> on LiF(001).<sup>15</sup> The internal energy distribution of the photoproduct NO was probed using REMPI. In contrast to the group in Berlin<sup>14</sup> who monitored only v'' = 0 and 1, we studied the full range of NO vibrational levels from v'' = 0 to 9. The experiment was performed using the classic pump-probe method in which the first laser,  $L_1$ , at 248

<sup>&</sup>lt;sup>†</sup>Present address: Department of Chemistry, Lensfield Road, University of Cambridge, Cambridge CB2 1EW, England. <sup>‡</sup>Present address: Department of Chemistry, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, England.

<sup>&</sup>lt;sup>1</sup> Present address: Department of Chemistry, University of Western On-tario, London, Ontario N6A 5B7, Canada.

<sup>+</sup> Present address: Institut für Physikalische Chemie und Electrochemie der Universität Hannover, Callinstr., 3-3a, D-3000 Hannover 1, Germany.

nm dissociated the adsorbed molecules and the second "probe" laser, L<sub>2</sub>, at a variable time later, detected the photoproducts and identified their vibrational and rotational distribution  $\sim 3$  cm above the crystal. Owing to the use of an insulator as substrate, the present study relates only to direct dissociation of adsorbate, in contrast to the substrate-mediated mechanism observed in the Pd work. Since the majority of NO from direct dissociation is found to be in v'' > 1, it would have escaped observation (if present) in the experiments reported in ref 14.

Nitrogen dioxide was chosen as the molecule for photolysis for a variety of reasons. In recent years the gas-phase dynamics of this molecule at the wavelength of interest have been examined in detail in our laboratory.<sup>16</sup> In addition, the environmental importance of this molecule has made it the subject of numerous studies.<sup>17</sup> The photochemistry of NO<sub>2</sub> is characterized by a complex manifold of electronic states in NO2. The electronic band excited at the same wavelength of 248 nm used here has been investigated by detailed rotational analysis.<sup>18</sup> The experiments determined the geometry of the excited  ${}^{2}B_{2}$  state as well as a predissociation lifetime of 42 ps from the spectral line widths.<sup>18-20</sup> Experiments in which NO<sub>2</sub> has been adsorbed on various metal surfaces have been concerned with the adsorption properties and geometries along with the decomposition pathways and kinetics.<sup>21</sup> State-specific detection of thermal decomposition products has also been performed.8

The first experiment to use a laser to dissociate gaseous NO<sub>2</sub> used the doubled output of a ruby laser at 347.1 nm.<sup>22</sup> Photodissociation studies of NO<sub>2</sub>(g) at ultraviolet wavelengths are numerous. These include work at 382,<sup>23</sup> 351,<sup>24</sup> 337,<sup>25</sup> 308,<sup>23,26</sup> and 157 nm.<sup>27</sup> In all these cases, with the exception of 382 nm, the internal energies of the NO fragments have been measured by laser-induced fluorescence (LIF). Without exception, the photolysis product was highly vibrationally and rotationally excited with a nonstatistical distribution of energy in both vibration and rotation. At both 351 and 337 nm, the highest accessible vibrational level was the most populated, while for 308 nm v'' =3 was the most populated (the thermodynamic limit being v'' =4). At 157 nm, vibrational levels from 4 to 20 were observed. Levels even higher than this may have been populated, but they were not probed.

Gas-phase photolysis experiments at still longer wavelengths have been performed using a flashlamp-excited dye laser as the photolytic source.<sup>28</sup> The wavelengths ranged from 295 to 365 nm, and the emission observed was ascribed to photoproduct NO<sub>2</sub>. The excitation spectrum obtained was very much like the absorption spectrum of N<sub>2</sub>O<sub>4</sub>. This led to the conclusion that photolysis of a NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> mixture involved dissociation of the dimer to give electronically excited NO<sub>2</sub>.

More pertinent to the present work, photodissociation of gasphase NO<sub>2</sub> has also been investigated at 248 nm.<sup>29</sup> Two separate experiments using LIF detection of the NO both reported high vibrational excitation in the product of NO<sub>2</sub> photolysis. The first experiment saw evidence for population in v'' = 6.<sup>29a</sup> The partial vibrational distribution obtained by the second group showed a peak in v'' = 7 with population observed up to v'' = 8 which is the thermodynamic limit.<sup>29b</sup> Despite the overlapping of the rotational lines, there was evidence that the rotational populations were excited.

A more extensive study of NO<sub>2</sub> photolysis has (as noted above) recently been completed in this laboratory.<sup>16</sup> The entire vibrational distribution was obtained along with the rotational populations in each vibrational level. The vibrational distribution was found to be bimodal peaking in both v'' = 0 and 5. The rotational distributions were also anomalous, showing increasing excitation with increasing vibrational level. These rotational distributions were nonstatistical, with the greatest populations occurring as high as K = 30. Attempts were made to model the dissociation; it was found that a Franck-Condon model could account adequately for the vibrational distribution.

The main goal in this work has been once again to map out the rotational and vibrational distributions of NO arising from the photolysis of NO<sub>2</sub> at 248 nm, but in this instance using as the



Figure 1. Schematic view of the uhv apparatus. The LiF(001) crystal is mounted on a manipulator in the center of the machine and can rotated through  $360^{\circ}$ . On the right side on the diagram is a differentially-pumped mass spectrometer that is used for TOF experiments. The ion detection system used for the REMPI experiments is shown on the left side of the figure. The probe laser passes 3 cm above the crystal (at the  $\times$ ) traveling into the page.

parent molecule NO<sub>2</sub> adsorbed on a LiF(001) surface at 100 K. The NO molecules were probed after they had left the surface, using a 1 + 1 MPI scheme. Wavelength scans with rotational resolution were performed to probe vibrational levels from v'' =0 to 9. These experiments resulted in the determination of the vibrational energy distribution of the fragments along with the relative populations in the spin-orbit and in the lambda doublet states.

#### II. Experimental Section

The photochemistry of  $NO_2$  in the adsorbed state was investigated in this work using a number of techniques. By temperature-programmed desorption (TPD), evidence was obtained concerning the adsorption conditions. Time-of-flight (TOF) experiments in conjunction with mass spectrometry (MS) were used to measure yields and translational energies of  $NO_2(g)$  and NO(g)formed in the 248-nm laser irradiation of  $NO_2(ad)/LiF(001)$ .

The main thrust of these experiments was, however, to determine the distribution of energy, especially in the vibrational and rotational degrees of freedom of the NO(g) photoproduct after adsorbate irradiation at 248 nm. This was done by turning the crystal through 180° and then using a two-laser pump-probe experiment in which the photolysis product was detected using REMPI (see Figure 1). Vibrational levels from 0 to 9 were probed. In addition, variation of yield with delay time gave a measure of the translational energy for state-specific photoproduct NO(v'',K'').

The ultrahigh-vacuum (uhv) equipment for the MS and MPI experiments has been described in detail previously,<sup>30</sup> and only the modifications necessary to perform the present MPI work will be described in this paper. The adsorbate was examined in a separate (very similar) apparatus using Fourier transform infrared spectroscopy (FTIR) in both the presence and absence of UV irradiation.

1. Gas Handling. A glass gas-handling manifold with Teflon stopcocks was used to introduce NO<sub>2</sub> into the uhv apparatus. The manifold could reach a base pressure of  $\sim 5 \times 10^{-6}$  Torr. A glass vacuum line was used to prevent degradation of the NO<sub>2</sub> due to reactions with metals. Silicon grease was used on the glass joints for the same reason.

The NO<sub>2</sub> gas used in this experiment was purchased from Matheson Gas Products and certified 99.9% pure in the liquid state. The gas delivered from the cylinder was purified before every experiment. The NO<sub>2</sub> was frozen at around -50 °C (freezing point of NO<sub>2</sub>: -11 °C), and the solid was then pumped to remove low-boiling gases such as NO or CO<sub>2</sub>.

An excess of  $O_2$  was added to the solid  $NO_2$ , and the mixture was isolated and allowed to warm up. The  $O_2$  reacted with any remaining NO to form  $NO_2$ .<sup>31</sup> After an hour or more, the sample was frozen again and the excess  $O_2$  was pumped away. The procedure was repeated until the  $NO_2$  solid was pure white. A blue tinge to the solid indicated the presence of impurity NO in the form of  $N_2O_3$  (also written  $NO_2$ ·NO).

A mass spectrum of purified NO<sub>2</sub> shows no contaminant peaks. A large peak at mass 30 (NO) is due to cracking of NO<sub>2</sub> in the mass spectrometer's ionizer.<sup>32</sup> Confirmation of the purity of the NO<sub>2</sub> was obtained from infrared absorption studies of the gas adsorbed on the substrate, as reported below.

The surface was continuously dosed with adsorbate molecules by one of two methods. The chamber could be back-filled to a static pressure, measured by a nude ionization gauge. The second method used a crystal doser mounted  $\sim 1$  cm away from the target which provided a directed spray of gas toward the surface, permitting experiments at higher coverages to be performed with reduced background pressures. The background chamber pressures were monitored as a indication of the dosing rate. The dosing rate was controlled by Varian leak valves mounted directly on the chamber (background dosing) or on the crystal doser line (direct dosing). At the end of the purification procedure, there was a pressure of between 5 and 10 Torr behind the leak valves.

2. Infrared Apparatus. The uhv apparatus used to record polarized infrared spectra was quite similar in design to others in this group. The crystal geometry with respect to a mass spectrometer and a photolysis laser was the same. This apparatus is described in greater detail elsewhere.<sup>33</sup>

The infrared spectrometer was a Nicolet 740 Fourier transform infrared (FTIR) spectrometer. The collimated external beam was focused onto the sample surface, recollimated, and focused onto a liquid nitrogen cooled MCT (mercury cadmium telluride) detector. The spectrometer and the whole beam path were purged with air processed by an air dryer/CO<sub>2</sub> remover unit. The geometry of the apparatus allowed both reflection spectroscopy at a fixed angle of incidence of 57.5° or transmission spectroscopy at angles between 0 and 70°. All the experiments in this work were done in the transmission mode at an angle of incidence of 50° using a resolution of 2 cm<sup>-1</sup>.

Spectra were taken under a variety of experimental conditions. Both s- and p-polarized light were used. A wire-grid polarizer (Specac, Orpington, England) on a BaF<sub>2</sub> substrate, with a specified polarization ratio of 98% at 3  $\mu$ m, was used to obtain the polarized light. Spectra were recorded by averaging 1000 scans. Baseline spectra (stable to less than 0.05%) were also recorded. Every effort was made to ensure that the absorbing contaminants of the purge gas, namely CO<sub>2</sub>, N<sub>2</sub>O, and NO, were held at a low and stable concentration. Following a series of experiments, an air background was taken to allow subtraction of the residual absorptions, especially that due to water. Spectra could not be recorded below 1300 cm<sup>-1</sup> due to the LiF cutoff in the infrared.

The IR absorption experiments were performed in three different ways. (a) In some cases, a coverage was adsorbed on the surface and a spectrum was obtained immediately. Alternately, (b) a coverage was dosed onto the surface and followed by laser irradiation during which IR spectra were taken. In a variant on this, (c) the laser was turned on before the dosing started and then was left on while IR spectra were recorded. Scans were recorded over an extended period of time with the laser firing in the (b) or (c) modes, in an attempt to determine the influence of the laser on the adsorbate structure and composition as a function of time.

It should be noted that the laser did not irradiate the entire surface of the crystal, but the IR beam interrogated the entire crystal; this made determination of laser effects on the IR spectrum more difficult. Background dosing was used in all these experiments, but other than this, conditions were very similar to those used in the MPI experiments. Both s- and p-polarized light were used to examine the adsorbate. This allowed determination of geometries of adsorption.

3. **REMPI Apparatus.** The photolysis event that produced NO(g) using laser  $L_1$  took place on the LiF crystal where  $NO_2$  was adsorbed at 100 K. The photolytic NO(g) escaped from the surface and drifted into the path of the probe laser,  $L_2$ , above the crystal. Laser  $L_1$  and  $L_2$  and their synchronization are described

below. Following this we give an account of the REMPI procedure and also the measurement of TOF.

The photolysis laser was a Lumonics TE861-4 operating at 248 nm (KrF) on stable optics which provided  $\sim 10-15$ -ns pulses of unpolarized UV radiation. The excimer was operated at 10 Hz. It delivered pulses of cross section 2 cm  $\times$  3 cm and energy ranging from 2 to 20 mJ/pulse. The beam was directed by three dielectric-coated mirrors, following which the central uniform region of  $\sim 1$ -cm diameter was selected by a pair of irises. The radiation was focused with a 75-cm Suprasil lens and steered onto the LiF crystal by a Suprasil turning prism through a uhv Suprasil laser port.

The photolysis laser beam was brought down vertically, collinear with the crystal rotation axis. The mass spectrometer viewed the center of the crystal along a perpendicular (horizontal) axis. The crystal normal was at  $\sim 7^{\circ}$  to this detection axis (i.e., the laser impinged on the crystal at 83° incidence relative to the normal—glancing incidence). The laser pulse power was measured with a pyroelectric joulemeter which sampled at  $\sim 10\%$  reflection from a quartz plate beam splitter. The output of the joulemeter was recorded by a computer-monitored sample and hold.

The probe laser system, a YAG-pumped dye, provided continuously tunable UV pulses of 10-ns duration from 225 to 285 nm. The fundamental, second, and third (when present) harmonics of the YAG (Quanta-Ray DCR-1A) were separated using high-power dielectric mirrors coated for the appropriate wavelength. The unwanted wavelengths passed through these mirrors and were dumped into beam blocks. Since the YAG laser fired at 10 Hz the two-laser MPI experiments were done at this repetition rate.

Both the 532- and 355-nm YAG radiation pumped a Quanta-Ray PDL-1 dye laser. The dye laser was used without the preamplifier cell in order to lower the amplified spontaneous emission (ASE) which constituted about 5% of the power of the dye laser output. Measurement with a 0.25-cm<sup>-1</sup> Fabry-Perot etalon gave a 0.8-cm<sup>-1</sup> bandwidth for the dye laser, in agreement with the line widths measured from the isolated lines of the spectra. The YAG power was varied depending on the dye efficiency in order to ensure that the final doubled output was low enough to avoid severe saturation problems in the NO transitions.

The wavelengths from the dye lasers were checked by passing the radiation through a 0.5-m scanning monochromator.

The vertically-polarized visible output of the dye laser went directly into an Inrad Autotracker which contained one of two  $\beta$ -BaB<sub>2</sub>O<sub>3</sub> (BBO) crystals that covered the range of wavelengths 222-285 nm needed to probe the NO transitions. The visible fundamental and doubled ultraviolet were separated using four identical quartz pellin brocas. The mirror-image arrangement of the prisms allowed separation of the two wavelengths of light without introducing any possibility of beam walk. The UV power ranged from 25 to 200  $\mu$ J/pulse, as measured by placing a pyroelectric joulemeter directly in the beam.

The UV probe radiation was directed horizontally through the machine. Before entering the machine through a UV grade Suprasil window, the beam was mildly focused with a 50-cm lens placed such that the focal point was directly above the crystal at  $0^{\circ}$  to the surface normal passing 3 cm away from the crystal. Subsequently, the beam was absorbed by a Pyrex viewpoint at the far end of the machine. The beam's position was obvious from the fluorescence of this viewpoint. The power of the probe was measured by taking a small reflection from a quartz flat onto a joulemeter.

The time delay between the lasers was under computer control and could be varied with a resolution of 5 ns. The computer (Macintosh SE) was interfaced to a LeCroy 4222 programmable delay generator which had four ports from which pulses of variable time delay could be obtained. Three of these ports were programmed with the appropriate time delays, and their output went to a home-built interface which shaped the pulses both temporally and in voltage so they could be used to trigger the excimer and YAG lasers. The delay between the two lasers was determined by the difference in time between the pulse to the excimer and the pulse to the YAG Q-switch. This time delay was checked periodically using the excimer trigger pulse and the output from the probe (L<sub>2</sub>) joulemeter. All spectra were recorded with a time delay of 30-40  $\mu$ s except one set of spectra for v'' = 0 which was taken with  $\Delta t = 80 \ \mu$ s.

In the state-resolved TOF studies, the delay between the two lasers was varied, usually in  $10-\mu s$  intervals, using a computer program. At each time delay (as in power studies) 100 shots were taken to obtain the average laser powers, and ion signals were recorded. These time studies amounted to state-specific timeof-flight spectra.

In the multiphoton ionization experiments the NO(g) photofragments were detected 3 cm above the crystal by 1 + 1 resonantly enhanced multiphoton ionization (REMPI). Vibrational levels from v'' = 0 to 9 were probed by exciting various ro-vibrational bands of the  $A^2\Sigma^+ - X^2\Pi$  system ( $\gamma$ -bands). The NO<sup>+</sup> was extracted toward the Galileo FTD 2003 microchannel plate (MCP) by a negatively charged front plate which was part of a time-of-flight drift tube (Figure 1). The field where the ions were born was estimated to be 25 V/cm as the drift tube was held at -250 V. Both 2-in. apertures of the drift tube were covered with a fine nickel mesh for field homogeneity. Upon exiting the drift tube, the ions were turned 90° toward the MCP by a combination of a repeller plate held at +280 V and the MCP itself, which generally had a voltage of -1.9 kV. This was done to place the detector out of the line of sight of the crystal since otherwise the scattered photolysis light from the crystal saturated the MCP causing severe "ringing".

The drift tube and the repeller plate were mounted on 1/4-in. rods from an 8-in. flange such that they were electrically isolated from the machine. This flange also had a small CaF<sub>2</sub> window which faced the crystal directly and was very useful in aligning the photolysis laser in the MPI experiments.

The MCP was supported by an assembly constructed of Kimball Physics eV parts and  $1/_{32}$ -in.-thick sheet stainless steel. The detector was mounted on a translation table which was in turn mounted on linear bearings that rolled along a rod. Hence, it was possible to move the MCP with respect to the repeller plate by manipulation of a Vacuum Generators linear feedthrough attached to the support table. This entire apparatus was mounted on an 8-in. flange which faced the repeller plate (see Figure 1). The MCP itself consisted of two plates typically set at a voltage of -1.9 kV. The impact of the ions on the microchannels started an avalanche of electrons toward the grounded anode. Each plate provided a gain of about 10<sup>3</sup> and had an impedance of over 100 M $\Omega$ . A bakable 1-M $\Omega$  resistor was placed between the second plate and ground to ensure that the 50- $\Omega$  anode was at a negative potential with respect to the detector.

The current produced by the ions at the microchannel plate was amplified by an Ortec 9302 amplifier/discriminator and then input to a SRS 250 gated integrator and boxcar averager. The boxcar was triggered by a photodiode which detected scattered 532-nm light from the probe laser.

The last sample from the boxcar (ion signal) and the outputs from the two joulemeter sample and holds were input into the ADC channels of the SRS 245 computer interface. This scheme allowed for shot-to-shot measurement of all the laser powers and the ion signal. After storing the data for a particular wavelength in a scan, the computer stepped the dye laser one half step, corresponding to about 0.4 cm<sup>-1</sup>, and began recording a new series of data for the next wavelength.

Two complete sets of experiments were done in this work. The first set simply recorded the two-laser signal for each dye laser step. A second series of spectra embodied a procedure designed to subtract out any probe-only background signal. This was done by using a fast 04-IES-001 Melles Griot electronic shutter in the photolysis beam. These experiments were performed by first recording the two-laser signal for 10 shots and then closing the shutter by sending a pulse to a home-built shutter interface so that the LiF crystal was not irradiated, and recording the one-laser signal for 10 shots. For all 20 laser shots, laser powers and ion signals were recorded on a shot-to-shot basis so that both signals The data analysis methods for both the one- and two-laser experiments have been described in detail previously.<sup>15,16,30</sup> The velocity distributions in the one-laser experiments are described by a "shifted" Maxwell-Boltzmann distribution. These distributions are obtained from the data using nonlinear least-squares fitting routines.<sup>34</sup> From the velocity distribution, it is also possible to obtain flux and energy distributions.

The rotational spectra were analyzed using known spectroscopic constants<sup>35,36</sup> as well as literature formulas for the Hönl-London rotational line strength.<sup>37</sup> Each ro-vibronic band was analyzed using peaks with <10% overlap with its neighbors. The extracted populations could be described by Boltzmann distributions. Ratios of peaks heights were used to determine the relative vibrational populations along with the relative populations in the lambda doublet and spin-orbit states in each vibrational level. This analysis was tested on a 300 K sample of NO. The average energy deposited in each degree of freedom during the photodissociation was also calculated using these population distributions.

Finally, we note that two types of TOF measurement were made. With the sample facing the differentially-pumped MS, TOF spectra were recorded using a current-to-voltage amplifier with a gain of 10<sup>5</sup> and a bandwidth of  $\sim 2$  MHz. This amplified MS signal was read using a LeCroy 8837F transient recorder. The laser power of L<sub>1</sub> was recorded on a shot-to-shot basis using a Stanford Research Systems SRS 245 computer interface. Both the transient recorder and the interface module were triggered by the photolysis (L<sub>1</sub>) laser. The second approach to TOF with the crystal turned the other way involved measurement of the MPI signal from L<sub>2</sub> at various times after L<sub>1</sub>. This procedure for generating time delays has been summarized above. The data in this case constitute state-resolved TOF.

#### III. Results and Discussion

1. Adsorbate Characterization. Two approaches were used for the characterization of the adsorbate: temperature-programmed desorption (TPD) and Fourier transform infrared spectroscopy (FTIR).

Temperature-programmed desorption experiments were performed at a variety of coverages. It was found that the desorption energy was almost constant over the exposure range 0.1-10 langmuirs. An average value of ~0.37 eV was obtained for the heat of desorption, 0.1 eV higher than previous values of desorption energies obtained for CH<sub>3</sub>Br, OCS, and HBr on LiF.<sup>1,30</sup> The increased heat of desorption may be connected with the presence of dimers or large clusters on the surface. Though TPD experiments were performed in which the mass spectrometer was tuned to detect dimers and higher order clusters, no evidence was found for any of these species. (It should be noted that N<sub>2</sub>O<sub>4</sub><sup>+</sup> is unstable; however, daughter ion N<sub>2</sub>O<sub>3</sub><sup>+</sup> is stable and none was found.)

Since NO was found not to adsorb on LiF at 100 K (the same has also been reported for NO on NaCl at temperatures >60  $K^{38}$ ), we do not expect NO(ad) from gas impurities or photolysis to contribute to the NO(g) observed.

The only direct evidence concerning the identity of the species undergoing photodissociation at the surface comes from infrared absorption spectroscopy. These FTIR experiments showed the presence of a large concentration of NO<sub>2</sub> dimers as indicated (in Figure 2) by the characteristic twin peaks centered at 1745 cm<sup>-1</sup> (peaks A and B in Figure 2). These peaks were present at the lowest coverages examined.

The presence of dimers was not surprising as the bond energy for the dimer is 0.5 eV.<sup>39</sup> This is higher than the desorption energy, and so it seems reasonable that even at low coverages the NO<sub>2</sub> on the surface will form dimers. On the basis of the gas-phase equilibrium constant for dimer formation, one expects only N<sub>2</sub>O<sub>4</sub> at 100 K.<sup>39,40</sup> Less than 5% of the dosing gas was composed of dimers; therefore, dimer formation must occur at the surface.



Figure 2. Infrared spectrum of  $NO_2$  on LiF at about 5-langmuir coverage with concurrent laser irradiation. The top panel is the entire recorded spectrum while the lower panel is the same spectrum expanded on both the x and y axes. This scan was done in the transmission mode with an incidence angle of 50°, using p-polarized light. Lower wavenumbers cannot be probed due to the LiF cutoff.

Other peaks at 1853 cm<sup>-1</sup> (C) and a small sharp peak at 1960 cm<sup>-1</sup> (D) may be due to  $N_2O_3$  or one of the D-isomers of the  $NO_2$  dimer.<sup>41</sup> Neither of these peaks was present upon initial dosing; they appeared only after UV laser irradiation. Peaks due to monomeric  $NO_2$  at 1610 cm<sup>-1</sup> were in the same region as water absorption (due to trace water vapor in the spectrometer purge gas), making detection of  $NO_2$  difficult. No evidence was found for impurity NO.

Any of the observed species— $N_2O_3$ ,  $N_2O_4$ , and the D-isomer of the dimer  $N_2O_4$ —could be photolyzed to contribute to the observed NO rotational and vibrational distribution. This will be discussed in the following section.

Measurement of the sticking probability of NO<sub>2</sub> proved difficult. These experiments involve determination of the coverage as a function of dose. For most systems the coverage increases linearly until a certain dose is reached, following which the coverage levels off.<sup>42</sup> The sticking coefficient can be determined from the slope of the linear part of the curve. However, for NO<sub>2</sub> the coverage did not plateau (to exposures of 250 langmuirs) so the sticking coefficient could not be measured. This type of behavior has been previously observed in studies with NO<sub>2</sub> on W(110).<sup>21b</sup> Work in other laboratories,<sup>8,14,21-es</sup> together with the fact that the vapor pressure of N<sub>2</sub>O<sub>4</sub> at 100 K is of the order of 10<sup>-10</sup> Torr, suggests that the sticking probability at ~10<sup>-7</sup> Torr should be unity. This is the value that was assumed in surface coverage calculations.

2. Multiphoton Ionization. Experiments were performed in which the ion signal at the MCP was monitored as a function of time, with the photolysis laser,  $L_1$ , defining t = 0. Ion peaks were observed at two characteristic times. The earlier peak was due to photolysis of  $NO_2(ad)$  by  $L_1$  with subsequent ionization of NO(g) by the same laser, while the later peak required that both lasers  $L_1$  and  $L_2$  be fired. The latter was from initial photolysis of  $NO_2(ad)$  by the excimer and subsequent ionization of NO(g)by the probe laser, 3 cm above the crystal. These conclusions were supported by the fact that if the crystal was "warm", i.e., at room temperature so there could be no adsorbed  $NO_2$ , no L<sub>1</sub>-only signal and no two-laser signal were observed. For a "warm" crystal, a small L<sub>2</sub>-only (probe-only) signal was observed. Based on observations in the gas-phase experiments,<sup>16</sup> the small probe-only,  $L_2$ , signal (like the pump-only,  $L_1$ , signal) is believed to be due to photolysis of  $NO_2(g)$  by a single laser followed by 1 + 1



Figure 3. Translational energy distributions derived from time delay curves. The vertical lines represent the expected translational energy for a gas-phase photolysis given that the internal degrees of freedom have been determined. These calculated translational energies assume a statistical distribution of translational energy between the O atom and NO molecule.

resonantly-enhanced MPI of the NO(g) photofragment by the same laser. The arrival of the photolytic  $(L_1 + L_2)$  NO(g) at approximately 40–90  $\mu$ s was used to set the gate for monitoring of the ion signals during wavelength scans.

The possibility that the observed NO(g) is due to photodesorption of NO(ad) impurity in the NO<sub>2</sub> was disproved by the fact that NO(g) in v'' = 1-7 was seen. Desorbing impurity NO would only be present in low v'' levels. In addition, NO in the adsorbed state is not seen in the TPD or the infrared spectra. Moreover, work in this and other laboratories has shown that NO will not adsorb on alkali halide crystals until well below 100 K, which was the temperature of the crystal in this work.<sup>38</sup>

Detailed time delay studies for each vibrational level were performed in which the  $L_1$  and  $L_2$  ion signal was monitored as a function of the time between the two laser pulses. Specimen results of these experiments are shown in Figure 3. These experiments explored the distribution in time of the photolytic products as they reached a point 3 cm from the surface. The known separation of the probe laser from the crystal made possible determination of state-resolved photoproduct velocities. The time delay curves and hence the translational energy distributions (Figure 3) for all vibrational levels, except NO(v''=0), were found to be the same. At least two delay curves were recorded for different rotational transitions within each vibrational level above NO(v''=0). In all cases, for v' > 0 the peak in the time delay occurred at  $35 \pm 5 \ \mu s$ . This peak corresponded to  $0.11-0.15 \ eV$ (920-1250 cm<sup>-1</sup>).

The reasons for the slow speed of NO(v''=0) in Figure 3, which appeared at a time delay of  $80 \pm 5 \mu s$ , is believed to be that it originates in the adsorbed NO<sub>2</sub> dimer (N<sub>2</sub>O<sub>4</sub>) via a dissociation pathway that has been observed in the gas phase and that only has enough excess energy at 248 nm to populate NO(v''=0) in the NO(g) photoproduct.<sup>43</sup> This low-energy NO(v''=0) pathway will be discussed in more detail later (section III.4).

The most important feature in Figure 3 is that the observed translational energy distributions are not the same as the distributions expected from gas-phase photolysis. The gas-phase distributions are delta functions since the energies in all the other degrees of freedom have been determined. The broad distributions observed in this work must therefore be due to a process other than gas-phase photolysis; i.e., the observed NO(g) must arise from *adsorbed-state* photolysis.

Further evidence of the difference between the gas-phase photolysis and the process observed here is that, as shown in Figure 3 for v'' = 3, 5, and 7, a substantial fraction of the NO(g) has translational energies greater than that expected from a gas-phase dissociation. If we were observing a gas-phase process in which the photolytic products were relaxed after their formation, the gas-phase translational energy would constitute the maximum allowable. The presence of NO(g) translational energies ~0.3 eV greater than this limit rules out photolysis of NO<sub>2</sub>(g) as the source of this NO(g). The fact that the NO(g) in v'' = 7 has a peak translational energy greater than that in the gas (Figure 3) whereas for v'' = 3 it has a peak  $E_T$  less than that in the gaseous photolysis argues strongly against gas-phase photolysis followed by collisional relaxation.

A comparison of the average translational energy of the NO photofragment from gas-phase experiments and that observed here confirms that the two processes are different. The translational energy of the NO photofragment from the gas-phase photolysis was determined using conservation of energy.<sup>16</sup> Since the energy in all the other degrees of freedom was measured in the gas-phase study, the average translational energy (over all vibrational levels) could be obtained; it was 0.33 eV (2680 cm<sup>-1</sup>). The average translational energy observed in this study is 0.16 eV, approximately half that for the gas-phase which again indicates that we are studying adsorbed-state photolysis.

Measurement of the translational energy of the NO(g) photoproduct by one-laser TOF spectra using the mass spectrometer as detector was complicated by the cracking of the parent  $NO_2$ in the mass spectrometer ionizer. The NO<sup>+</sup> signal was predominantly from cracking of NO<sub>2</sub> in the ionizer. In many of the low-coverage spectra, there seemed to be a peak on the short-time side of the large NO<sup>+</sup> peak, i.e., faster NO. Softer ionizing conditions (i.e., lower electron impact energy) did not afford any better resolution of these photolytic NO<sup>+</sup> peaks. Nonetheless, calculation of the velocity of this poorly-resolved fast peak showed agreement in translational energy with that determined in the two-laser experiments.

All wavelength scans were recorded at a time delay between the two lasers that corresponded to the translational energy of the maximum in the NO<sup>+</sup> signal, i.e., the most probable  $E_{\rm T}$ . The exception was NO(v''=0) where two sets of experiments were performed: one at the peak of the NO(v''=0) time delay curve (approximately 80  $\mu$ s) and the second at the peak of the time delay curves for v'' > 0 (approximately 40  $\mu$ s). These are referred to as v'' = 0 experiments at "long" and "short" time delay, respectively.

The populations in the ro-vibrational states (v'',K'') of NO were obtained from wavelength scans of the  $\gamma$ -bands (222-285 nm). All spectra were obtained from adsorbate coverages of about 5 monolayers (ML). Signal was observed for vibrational levels from v''=0 to 7. Although NO(v''=8) is thermodynamically accessible, no evidence for population in this level was found. Scans were also performed for NO(v''=9). No signal above the noise was observed, as expected since this level is energetically higher than the total available energy.

Rotational populations were obtained from the scans. Each complete band was scanned 4-10 times, and the rotational populations in each vibrational level of interest were determined the equivalent number of times. An example of a spectrum from v'' = 3 is presented in Figure 4. Some bands were not scanned in their entirety; instead, selected nonoverlapped rotational peaks



Figure 4. Rotational spectrum obtained for v'' = 3. The upper half of the figure shows the entire spectrum while the lower half is a expansion of a portion of the spectrum to give a clearer picture of the actual signal recorded. The lines above each spectrum are the peak position assignments used to obtain populations.

were used to determine the population in a vibrational level.

The spectra as a whole were characterized by uniformly good signal-to-noise ratio, since bands with low populations had the largest Franck-Condon factors (v'' = 2, for example). Assignment of the spectra was not difficult, as prominent bandheads were evident in all the vibrational levels. Peaks were assigned to transitions through comparison with calculated spectrum.

Laser power studies were made for about three different rotational states in each vibrational level. Signal strength as a function of laser intensity was measured for both lasers  $L_1$  and  $L_2$ . Figure 5 shows that the signal increased linearly with excimer power,  $L_1$ , consistent with the expected one-photon absorption of NO<sub>2</sub> to give NO. No evidence of saturation was observed.

The  $L_2$  power dependence showed slopes that ranged from 1.3 to 1.8 depending on the absolute laser power and the particular rotational transition. This is indicative of a partially saturated 1 + 1 MPI process; it was observed in every vibrational level probed. The ionization cross section for NO<sup>+</sup>  $\rightarrow$  NO<sup>+</sup> is quite high, and this partial saturation suggests that ionization of NO<sup>\*</sup> was  $\sim 100\%$  as expected. The analysis of the data took the measured degree of saturation into account.

The rotational populations within each NO vibrational level were obtained from each of the eight energetically different rotational branches observed. Since the relative population distributions were quite similar for all the branches, the populations from the different branches were averaged to give one mean distribution. The spread in populations between branches may be due to the assumption that all the branches have the same probe laser,  $L_2$ , power dependence. This is an approximation since certain transitions (the satellite branches for example) have lower



Figure 5. Photolysis laser (i.e., excimer,  $L_1$ ) power dependence of the MPI signal recorded using a nonoverlapped line in v'' = 6. Other photolysis laser,  $L_1$ , power studies for other vibrational levels showed the same one-photon power dependence. Errors shown are 10% of the value.

 
 TABLE I: Boltzmann Temperatures for Each Vibrational Level (Errors Shown Are One Standard Deviation)

ground vibrational level	Boltzmann temp of rotational distributions, K
0ª	252 🖿 15
0 <sup>b</sup>	$341 \pm 42$
1	765 ± 178
2	$900 \pm 264$
3	910 ± 158
4	$983 \pm 152$
5	$833 \pm 58$
6	~1200
7	~1200
8	

<sup>a</sup> Long delay times. <sup>b</sup> Short delay times.

line strength factors and hence should be less saturated.<sup>37,44</sup> If Boltzmann plots were made to obtain "temperatures" for each branch and these "temperatures" were averaged, the final temperature was very close to that derived by averaging the populations first and then using the Boltzmann fit.

Figure 6 gives one example of the rotational population distribution obtained for each vibrational level. These populations were averages of those obtained from all the branches of the NO spectrum.

A specimen Boltzmann plot, for v'' = 3, is shown in Figure 7. Linear fits of the Boltzmann plots are used to obtain "rotational temperatures". A list of the average "rotational temperatures" obtained in each vibrational level is given in Table I.

In contrast, two-component Boltzmann plots have been observed previously in the decomposition of adsorbed NO<sub>2</sub> by either thermal processes<sup>8</sup> or laser irradiation.<sup>14</sup> The rotationally "hot" and "cold" populations are thought to be due to photolytic events in which the NO is born and either escapes directly into the gas phase ("hot") or is trapped on the surface briefly and then escapes ("cold"). The trapped molecules undergo several encounters with the substrate or, for multilayers, other adsorbed molecules. The lack of a two-component Boltzmann plot in this work does not mean that the substrate plays a passive role in this photodissociation. The rotational distributions must also be affected by the surface since the average rotational energy does not increase

**ROTATIONAL DISTRIBUTIONS** 



Figure 6. Relative rotational populations obtained for each vibrational level detected. Each plot shows a comparison with gas-phase results obtained in this laboratory. The gas-phase results are represented by open squares while the surface results use closed diamonds.

substantially with vibrational quantum number from v'' = 2 to 6 as it does in the gas phase (see Figure 8). This difference is another indication of altered photodissociation dynamics in the adsorbed state.

Comparison of the intensity of ro-vibrational bands covering overlapping spectral regions permitted determination of the relative vibrational populations. The adsorbed-state distribution is shown in Figure 9 along with the gas-phase result. The vibrational distribution was determined using the results obtained at short time delays (40  $\mu$ s) in all the vibrational levels. Two populations are presented for v'' = 0 corresponding to the two different sets of experiments performed in v'' = 0 at "short" and "long" time delays (the latter being only observed for v'' = 0). The scatter in the vibrational populations was an accumulated error from the ratios used to determine the distribution.

The vibrational distribution obtained was in part an inverted one, with peaks at v'' = 0 and 3-4. Qualitatively, it resembled that for the gas phase but with significantly less vibrational excitation, the mean v'' excitation in the range v'' = 2-9 falling at v'' = 5.1 for the gaseous NO<sub>2</sub> parent and v'' = 4.0 for the adsorbed nitrogen dioxide, the corresponding mean vibrational energies being



Figure 7. Boltzmann plot obtained for v'' = 3. The plot is characteristic of the Boltzmann curves in each vibrational level as determined from the rotational populations of Figure 6.



Figure 8. Average rotational energy obtained from the rotational distribution in each vibrational level. A comparison of the adsorbate results (black diamonds) with those of the gas-phase work (open squares) is also given. The average rotational energy shown for the adsorbed state assumes that the entire rotational population can be described by the Boltzmann temperature. Errors shown are one standard deviation.

 $\langle E_{\rm VIB} \rangle = 1.27 \, {\rm eV}$  (gaseous) and 1.03 eV (adsorbed) relative to v'' = 0. In addition, the fraction of the NO(g) product that is formed in the high-v'' part of this bimodal distribution is less than half as great as it is for photolysis of NO<sub>2</sub>(g).

The vibrational distribution for both the adsorbate and gasphase photolysis were marked by the presence of a bimodal product vibrational excitation suggestive of two dynamical pathways for the photodissociation. In the case of the gas-phase photolysis it was suggested that the two pathways might correspond to different



Figure 9. Vibrational populations obtained from both the gas-phase and surface experiments. Squares are used to represent the gas-phase result. Two populations in v'' = 0 from the surface work are given corresponding to the two sets of experiments done for v'' = 0 at different time delays between the two lasers (open diamonds represent long time delay (low  $E_T$ ); dark diamonds represent short time delay (higher  $E_T$ )). Errors reported are from a propagation of errors in the ratios. The populations are normalized to 1 in v'' = 3.

vibrational modes in the electronically-excited parent molecule.<sup>16</sup> If this is correct, the mode leading to the more highly vibrationally excited products accounts for markedly less of the total photodissociation in the adsorbed state than in the gas.

Rotational energy distributions for the NO(g) product of photolysis were determined. The overall average rotational energy, undifferentiated as to the vibrational state, was determined to be  $610 \text{ cm}^{-1}$  while the average vibrational energy was 5000 cm<sup>-1</sup>. The translational energy was given by the time delay between the two lasers and was 0.16 eV (1250 cm<sup>-1</sup>) for all vibrational levels except v'' = 0 at long time delays for which the translational energy was 0.025 eV (200 cm<sup>-1</sup>). The electronic excitation energy was 60.6 cm<sup>-1</sup> due to equal population of the spin–orbit states split by 121.2 cm<sup>-1</sup>. Thus, on average a total of 6920 cm<sup>-1</sup>, i.e., 45.2% of the available energy (defined as the photon energy plus the internal energy of the NO<sub>2</sub> minus the bond dissociation energy), was accounted for in the various degrees of freedom of the NO(g).

The photolysis of NO<sub>2</sub> produces two species, namely NO and O. Observation of the atomic fragment proved impossible. Multiphoton ionization of atomic oxygen in this wavelength region is known to be difficult due to efficient fluorescence from the excited electronic state.<sup>16,45</sup> Very high laser densities are needed to obtain any signal. For this reason, detection of O atoms in a two-laser experiment was not attempted. Efforts were made to detect the O atom photofragments using TOF-MS, but the background at m/e = 16 in the mass spectrometer chamber was quite high and prevented detection of O.

A complete description of the deposition of the excess energy in the adsorbate photodissociation is not possible since the photoproduct O atoms could not be detected. Energy balancing due to conservation of momentum could not be applied to molecules in the adsorbed state due to the unknown momentum transfer to the surface. As a result, it was impossible to estimate how much energy had been lost in the adlayer. The maximum energy that can be transferred to the adlayer was 1.08 eV ( $8682 \text{ cm}^{-1}$ ). This is obtained using the excess energy for the photodissociation (1.90 eV,  $15298 \text{ cm}^{-1}$ ) and the energy that is already accounted for in the degrees of freedom of the NO photoproduct. Even though

#### Photodissociation of NO<sub>2</sub> Adsorbed on LiF(001)

the energy in all degrees of freedom could be determined for the NO photoproduct, it was not possible to determine the fate of all the energy released in photolysis.

3. Spin-Orbit and Lambda Doublet Populations. The spectroscopy of NO is quite complex. While this leads to difficulty in analysis of the spectra, it also means that detailed information is obtainable. The wavelength scans probe the populations in the two electronic spin-orbit states as well as the populations in the lambda doublet states within each of these spin-orbit states.

All the spin-orbit states of the ground  $X^2\Pi$  state of NO(g) were found to be equally populated. The spin-orbit states are separated by 121.2 cm<sup>-1</sup>. At the temperatures observed in these experiments, the two states should be equally populated. A large number of photolysis experiments that produce either or both NO<sup>46</sup> and OH<sup>47</sup> (which has the same spectroscopy as NO) have been performed. There were no clear examples of nonstatistical populations in the spin-orbit states.

Highly state-specific behavior in photodissociation is not unprecedented.<sup>48,49</sup> For example, in the photolysis of NOCl, it was found that for D-band excitation at 499.4 nm the ratios of the lambda doublet populations for the two spin-orbit states were different by a factor of  $4.^{49}$  A scheme involving coupling of electronic states of spin in a  $M_s$ -specific manner was proposed to explain this observation. Within the same spin-orbit state, the  $\Lambda$  doublets have been shown to yield two different Boltzmann temperatures in the photolysis of single rotational states of water.<sup>47d</sup>

The average ratio of populations of the  $\Pi(A'')$  states to the populations of the  $\Pi(A')$  states over all vibrational levels for the adsorbed state process was  $0.90 \pm 0.15$ . This compares to a value of  $0.7 \pm 0.1$  for the analogous gas-phase dissociation.<sup>16</sup> It should be noted that the lambda doublets are only truly resolved in Hund's case b which, in the case of NO, occurs at quite high K's on the order of 35 or 40. The population in these rotational levels was not large enough to allow a precise analysis, but transitions above K = 15 were used to determine the population ratios in the present work, as in the gas-phase work.

The  $\Pi(A'')$  state has the unpaired electron occupying a p  $\Pi$  orbital perpendicular to the plane of rotation of the NO, and the  $\Pi(A')$  state has the electron in a p  $\Pi$  orbital in the plane of molecular rotation.<sup>50</sup> For the photolysis of NO<sub>2</sub>(g), the preference is for the electron to be in p  $\Pi$  orbital in the plane of NO rotation. It appears that this preference either vanishes in the adsorbed state or (more likely) is lost in the process of desorption of the NO(g).

There is another form of alignment to consider, namely, that between the J vector of NO(g) and the surface normal. The infrared studies using polarized light were not analyzed in detail, but the ratios of the absorption intensities for the two polarizations of light used (s and p) indicated that the molecules in the multilayer were adsorbed in random geometries on the surface. This was true with or without the photolysis laser  $(L_1)$  irradiating the surface. Therefore, NO ejected *directly* into the gas phase following photodissociation, without subsequent interaction with the surface, should not have exhibited alignment. Since the P and R rotational branches give the same population ratios as the Q branch, we again conclude that there is no alignment of NO(g). Alignment would mean preferential detection of the P and R or the Q branch, which would lead to different rotational population ratios from different branches.

4. Source of Vibrationally Excited NO(g). The fact that the NO(g) photoproduct was only obtained from a cold crystal was not conclusive evidence that  $NO_2(ad)$  was being photolyzed. The molecule could be desorbed first and subsequently dissociated in the gas phase above the crystal. This process would, however, have a two-photon power dependence whereas it appears (section III.2) that the MPI signal is due to a single-photon process. We therefore reject a photodesorption mechanism followed by photodissociation as the source of NO.

Further evidence is available to show that the NO<sub>2</sub> is dissociated in the *adsorbed* state. As noted in section III.2, we observed a cooler vibration and rotation in NO(g) than is reported for NO<sub>2</sub>(g)  $\rightarrow$  NO(g).<sup>16</sup> We can ascribe this to photolysis of NO<sub>2</sub>(ad) rather than vibrational and rotational deactivation of NO(g) in view of the observed translational energy distributions,  $E_{\rm T}$ , as described below. Time delay curves were obtained for several rotational levels in each vibrational level (see examples in Figure 3). As anticipated, the NO photoproduct with low K has reduced  $E_{\rm T}$ relative to NO(g) from gas-phase photolysis, since partial accommodation with the surface cools both rotation and translation. What is striking is the fact that the rotationally "hot" NO(g) is translationally cold as compared with photodissociation of NO<sub>2</sub>(g). This is strong evidence against rotational and vibrational relaxation in the gas phase, since such cooling would transfer appreciable energy into translation.

The concurrent observation of high K with low  $E_T$  in newly-born NO from gas-phase photolysis would be accounted for in terms of a high-torque repulsive energy release in bent O-NO (the dot being the locus of repulsion). Since in the gas-phase photolysis the high-K product exists along with higher  $E_T$  than is observed here, we must postulate a more complex process for the release of NO(g) from NO<sub>2</sub>(ad). The NO<sub>2</sub>(ad) of this study is likely to be bound in some manner to adjacent NO<sub>2</sub>(ad). Under these circumstances the NO(g) leaving the surface can, it appears, partially equilibrate with coadsorbate and surface resulting in translational cooling.

In further experiments, a change of  $\sim 2$  times was made in the NO<sub>2</sub> gas density over the crystal by altering the laser (L<sub>1</sub>) intensity and thereby the amount of photodesorption. There was no detectable change in the rotational populations of NO(g), confirming that gas-gas collisions are not responsible for rotational relaxation and, hence, a fortiori, that they do not cause vibrational relaxation.

It was to be expected that gas-gas collisions above the crystal would be of negligible importance. We have found that such collisions are of negligible importance even in systems where the photodesorption efficiency, and hence gas density above the crystal, is  $\gtrsim 10$  times that in the present case.<sup>1,30</sup>

The vibrational distribution for NO(g) formed photolytically from the adsorbed state is qualitatively similar to that in the gas phase though it is unmistakably shifted to lower v'' (Figure 9); the dynamics make  $v'' \approx 4$  the most populated vibrational level rather than v'' = 5 as in the gas. The high vibrational levels v''= 6-8 which were substantially populated in the photolysis of NO<sub>2</sub>(g) were only slightly populated in the photolysis of NO<sub>2</sub>(ad).

One possible reason for this apparent difference in dynamics is collisional deactivation. However, collisional relaxation of vibrational energy is inefficient both for collisions between two gaseous molecules<sup>51</sup> and for collisions between molecules and solid surfaces.<sup>5</sup> (It has been shown that vibrationally excited NO(v=1) recoiling from LiF has a 90% probability of retaining its vibrational energy.<sup>5</sup>) In addition, neither the observed translational nor rotational distributions can be accounted for by collisions in the gas or with the surface, nor therefore can the shift in vibrational distribution be due to these causes. The diminished vibrational excitation in the photoproduct is ascribed instead to altered dynamics for photolysis of NO<sub>2</sub>(ad) as compared with NO<sub>2</sub>(g).

There is a further reason for ascribing the observed bimodal vibrational distribution to the photodissociative dynamics rather than to relaxation of a unimodal vibrational distribution. Much effort was spent in the early days of reaction dynamics in modeling vibrational relaxation.<sup>52</sup> It was found that an initially excited Boltzmann distribution relaxed to a final Boltzmann distribution through a series of intermediate Boltzmann distributions without at any time giving rise to a bimodal distribution. The bimodal vibrational distribution observed in these experiments gives this further evidence of being due to the dynamics of the photodissociation process rather than to collisional relaxation.

Photolysis of dimer in the adsorbed state is thought to be important in yielding the slow component of NO(v''=0). Dimer[(NO<sub>2</sub>)<sub>2</sub>] photolysis in the gas phase by Kawasaki et al.<sup>43</sup> yielded NO(g) only in v'' = 0 due to the fact that at least one of the NO<sub>2</sub> molecules was produced in an electronically excited state. Since the lowest excited state is 1.18 eV above the ground state, the excess energy for the photolysis of the dimer can be calculated and was 1609 cm<sup>-1</sup> (0.20 eV), which was only enough energy to populate v'' = 0,  $K \le 30$ . This calculation was an upper

limit for the rotational energy since it assumed that neither molecule was given any translational energy. This source of NO(g)is likely to be the explanation for the very slow photolysis product which is part of that observed in v'' = 0. The lack of excess energy in the dimer photolysis is consistent with the low translational energy in v'' = 0 as well as with the fact that there is less rotational excitation in the NO(g) (v'' = 0) at lowest  $E_T$  which is attributed to  $N_2O_4(ad)$  photolysis. The  $N_2O_4(ad)$  is known to have a 50-100 times higher absorption cross section ( $\sim 9.3 \times 10^{-19} \text{ cm}^2$ ;  $\sim 0.093$ A<sup>2</sup>, the actual numbers are still the subject of some controversy)<sup>53</sup> than the monomer at 248 nm. To summarize, it appears that the experiments for v'' = 0 at the "long" time delays (section III.2), i.e., low translational energy, probe the dimer photoproduct distribution, while those at "short" delays minimize this contribution, giving the rotational distribution for another pathway that yields the higher vibrational levels.

For this second pathway we observe NO(g) in states up to v'' = 7, K = 40. In this highest vibrotational state NO(g) has 1.87 eV of energy in excess of the ground state. The photodissociation of the dimer to give NO<sub>2</sub> which subsequently falls apart to give NO has an excess energy of 1.43 eV even if one assumes that there is no electronic excitation of the NO<sub>2</sub>. The highest state that can be populated in this case reaction is v'' = 5, K = 30. The population in the levels above this must come from another source.

Photodissociation of  $N_2O_4$  directly to NO and NO<sub>3</sub> would allow population up to NO(v''=16). We did not scan levels above v''= 9 in view of the diminishing population in v'' = 8 and 9. Moreover, no evidence for higher vibrational levels was seen during the scans of the lower levels. The exothermic pathway to NO + NO<sub>3</sub> is unlikely since it involves a complex rearrangement of the atoms prior to product separation. In addition, there was no evidence for the existence of NO<sub>3</sub> in the infrared spectra even after long periods of laser irradiation.

However, during laser irradiation new species such N<sub>2</sub>O<sub>3</sub> or the D-geometric isomer are observed.<sup>39,54</sup> The N<sub>2</sub>O<sub>3</sub> or the Disomers of the NO<sub>2</sub> dimers (in which the bonding is between the N atom of one NO<sub>2</sub> to one of the O atoms of the second NO<sub>2</sub>) present under laser irradiation may be the source of the vibrationally excited photoproduct. No data regarding the infrared absorption cross sections of N<sub>2</sub>O<sub>3</sub> or the D-isomers of the NO<sub>2</sub> dimers are available, and hence the exact concentration of these species on the surface is not clear. The photolysis of these molecules has not been studied elsewhere. We discuss below whether it is possible that these species could be responsible for the photoproduct NO(g)( $v'' \geq 0$ ).

It is somewhat surprising that the D-isomer is observed on the LiF crystal at 100 K. Most observations of this species have been made in very cold ( $\sim 20$  K) matrices.<sup>55,56</sup> This molecule is very unstable and easily converts to the  $D_{2h}$  form of the dimer. For this reason we believe that the concentration of the D-isomer is low and plays no significant part in producing the observed NO(g) photoproduct.

The other molecule which is present is  $N_2O_3$ . Its structure has been determined.<sup>57</sup> Studies have shown that dinitrogen trioxide does absorb at 248 nm. In fact, this wavelength is near a peak in the absorbency curve.<sup>58</sup> The dimer N-N bond lengths in the  $D_{2h}$  dimer and  $N_2O_3$  are very similar. The strength for the N-N bond in  $N_2O_3$  is 0.4 eV.<sup>59</sup> In the rupturing of the N-N bond in  $N_2O_3$ , NO is produced directly. There is an excess of energy of 4.6 eV at 248 nm which is enough to populate NO in v'' = 22. As noted above, no evidence for population above v'' = 7 was observed in the present experiments. Consequently, we have no reason to suppose that photolysis of  $N_2O_3(ad)$  is responsible for the observed vibrationally excited NO(g).

This seems to leave one plausible pathway. Photolysis of the stable dimer to give two  $NO_2$  molecules still trapped in the adsorbate layer followed by dissociation to give NO in two single-photon process.

The vibrational distribution obtained for the surface work is strikingly similar to that obtained in the gas phase where conditions ensured that only monomers were photodissociated (Figure 9).<sup>16</sup> Water absorption as well as the mismatch between continuous IR detection and pulsed photolysis makes IR observation of the NO<sub>2</sub>(ad) monomer absorption peak difficult. We believe that NO<sub>2</sub>(ad), present as a transitory species, might be the source of the observed NO(g) in v'' > 0. This accords with the range of v'' levels and the qualitative resemblance to the distribution obtained from NO<sub>2</sub>(g) photolysis.

A possible scenario would be if the monomer produced by dissociation of the dimer were then photodissociated by a second photon. The dissociation lifetime of the dimer in the gas phase is quite short, 0.8 ps, and hence, the light pulse is still present when the monomers are created.<sup>43</sup> As already noted, the extent of photodissociation is linear in photolysis laser power rather than quadratic as this mechanism might imply. However, the gas-phase absorption cross section of the gaseous dimer is very high ( $\sim 9.3$  $\times 10^{-19}$  cm<sup>2</sup>;  $\sim 0.093$  Å<sup>2</sup>)<sup>53</sup> and has been shown to be 2 times higher in the adsorbed state.<sup>60</sup> It is possible therefore in the range of laser powers used here the first step in the proposed mechanism dissociates  $\sim 100\%$  of the N<sub>2</sub>O<sub>4</sub>. In a caged environment electronic excitation of one NO<sub>2</sub> in  $N_2O_4$  could result in 0.5-eV intramolecular energy flow to break the N-N bond, contributing to the efficiency of photodissociation. In the case of complete dissociation variation of laser power would not change the yield of NO<sub>2</sub>(ad), and a one-photon power dependence would be observed. This mechanism is speculative.

In the other photolysis experiments involving adsorbed NO<sub>2</sub> on NO-saturated Pd(111), performed concurrently with the present work, two distinct photodissociative mechanisms for the production of NO were observed.<sup>14</sup> The first of these pathways led to NO(g) with higher  $E_{T}$  (0.070 eV) and the second to NO(g) with low  $E_{T}$  (0.011 eV). As noted earlier, one mechanism for forming the faster NO(g) was thought to involve charge transfer from the surface leading to dissociative electron attachment in  $NO_2(ad)$ . The second pathway leading to slower NO(g) was not examined in detail. Nonetheless, certain characteristics resembled those observed in these experiments. For example, the mean translational energy of the low- $E_{\rm T}$  channel was found to be invariant with rotational level in v'' = 0. (Vibrational levels higher than v'' = 1 were not examined.) On the basis of the experiments performed in the present work on LiF(001) where charge transfer is not possible, we believe that the low- $E_{T}$  channel in ref 14 is likely to be due to photon absorption in  $NO_2(ad)$  rather than the substrate absorption leading to charge transfer proposed by the authors for the "fast" channel.

5. Formation of NO<sub>2</sub>(g). The photodesorption at 248 nm of  $NO_2(g)$  coming from LiF(001) has been examined in this work. Temperature-programmed desorption (TPD) and IR absorption spectroscopy were both used to measure the photodesorption efficiency. The initial coverage in the TPD experiments was 1 langmuir. The experiments were performed at a laser fluence of 8 mJ/cm<sup>2</sup>. The desorption efficiency was measured to be only 0.8% per incident laser pulse. Results from the IR experiments cannot be compared directly as they were performed at a far greater initial coverage. However, the photodesorption efficiency as measured by decrease in IR absorption was found to be extremely low (see below). Previous photodesorption efficiencies obtained varied from roughly 90% for CH<sub>3</sub>Br or OCS on LiF(001) to 10% for HBr on the same substrate;<sup>1,30</sup> these efficiencies vary significantly from one LiF crystal to another. In the HBr case photodesorption efficiency was thought to be reduced as a result of hydrogen bonding to the surface. The still lower value found for  $NO_2(g)$  desorption is likely to be related to the high heat of adsorption and desorption which we ascribe to the presence of dimers.

Single-laser experiments were used to characterize the translational energy of intact parent molecules,  $NO_2(g)$ , leaving the surface. A surprising observation of these experiments was the lack of a photodesorption signal for the adsorbed species,  $N_2O_4$ . This is the first case of an adsorbate studied in this laboratory that has shown no photodesorption yield at any coverage. Moreover, clusters have been observed from previous TOF experiments in which adsorbate was irradiated in the UV.<sup>61</sup> In this case the expected dimers and higher order clusters were not ob-



Figure 10. Series of TOF recorded consecutively showing the effect of increasing coverage with time. The top scan was recorded first and each following scan was recorded at 5-min intervals, with the lowest spectrum being the final one. The NO<sub>2</sub> pressure was  $1 \times 10^{-7}$  Torr. m/e = 46. All spectra are plotted to the same scale.

served even at very high coverages. Neither  $N_2O_4$  nor  $N_2O_3$ , a stable cracking product of  $N_2O_4$  in the mass spectrometer ionizer, was found. It appears that no  $N_2O_4(g)$  leaves the surface, only  $NO_2(g)$ .

Time-of-flight spectra for mass 46 (NO<sub>2</sub>) were obtained using a variety of experimental conditions. For lower coverages, the peak energy was 0.049 eV. At higher coverages, the peak energy shifted to lower values,  $\sim 0.015$  eV. This is barely above the thermal energy of the crystal at 100 K.

Figure 10 shows a series of TOF recorded at 5-min intervals as a high steady-state coverage was on the way to being established. The slower peak remained approximately constant with increasing time, while the faster peak decreased. Photodesorption efficiency has been found in the other cases using LiF substrate to decrease with increasing coverage. In the case of adsorbed CH<sub>3</sub>Br the efficiency dropped to zero above 1 ML.<sup>30</sup> A decrease in the coupling between the uppermost layers of the adsorbate and the substrate as the adlayer thickens is likely to be responsible for this loss in desorption efficiency. Evidence for the decrease in desorption efficiency has also been obtained in the present system; at 1 ML coverage, the efficiency was ~1% while IR experiments at 250 ML gave an efficiency of ~10<sup>-3</sup>%.

The time-of-flight spectra presented in Figure 10 indicate a progressively increasing coverage over the 30 min required for recording the spectra. The low initial desorption efficiency meant that coverage would be expected to increase for  $\sim 100$  laser shots before reaching a steady-state value. However, the decrease in desorption efficiency with increasing coverage led to ever increasing coverage that reached steady state much later—30 min in this case. The signature of this increasing coverage was the loss of the high- $E_T$  signal.

We believe the high- $E_{\rm T}$  peak of Figure 10 is due to photodesorption of the photolytically created NO<sub>2</sub>(ad). The peak energy of this NO<sub>2</sub>(g) (~0.05 eV) is the same as has been observed for photodesorption in other systems.<sup>30</sup> This substrate-mediated photodesorption decreases with increasing coverage as the uppermost layers of the adsorbate move further from the surface.

The source of the second 46 amu peak (that at low  $E_T$ ; see Figure 10) is uncertain. This low- $E_T$  peak may be due to laser heating of the adsorbate layer subsequent to electronic excitation and quenching of N<sub>2</sub>O<sub>4</sub>\*(ad). The high UV absorption cross

section of  $N_2O_4(ad)$  followed by E-V (electronic-to-vibrational) transfer could channel a sufficient fraction of the incident photon energy into heating of the adsorbate, resulting in small temperature rise leading to desorption of the photolytically created  $NO_2(g)$ .

#### **IV.** Conclusions

The dynamics of the UV photochemistry of  $NO_2$  adsorbed at approximately 5 ML coverage on LiF(001) were examined by both time-of-flight mass spectrometry (TOF) and resonantly enhanced multiphoton ionization (REMPI).

These experiments have led, for the first time, to a full characterization of the energy in the NO(g) photofragment from the UV (248 nm) photolysis of nitrogen dioxide in the adsorbed state. One photodissociative pathway yielding v'' = 0 resembled that for N<sub>2</sub>O<sub>4</sub>(g). A separate pathway gave rise to a bimodal vibrational energy distribution over v'' = 0-7, which was ascribed to a mechanism for dissociation of N<sub>2</sub>O<sub>4</sub>(ad) characteristic of the adsorbed state.

Time-selected state-specific multiphoton ionization experiments permitted determination of the energy distribution in all the degrees of freedom of the NO photofragment: translation, vibration, and rotation.

(i) The translational energy distribution,  $P(E_T)$ , was identical in all vibrational levels with the notable exception of v'' = 0 for which much slower photoproduct (~0.025 eV) was observed in addition to that at 0.16 eV, which was the  $E_T$  characteristic of all v'' > 0. This slow v'' = 0 component was believed to be due to the photolysis of the dimer via a mechanism which only produced v'' = 0. Two sets of experiments were performed on this vibrational level in order to characterize the rotational energy distribution for v'' = 0 with and without contributions from the slow-product pathway. The average rotational energy was found to be lower for the slow component (average rotational energy, 175 cm<sup>-1</sup>) than for the fast component (rotation, 238 cm<sup>-1</sup>).

(ii) A bimodal vibrational distribution was obtained for the NO photoproduct which was qualitatively similar but quantitatively different from that observed in the gas phase. The distribution had two peaks, one at v'' = 0 and one at v'' = 3-4, with a marked minimum at v'' = 2. The adsorbed-state distribution differed from that for photodissociation of gaseous  $NO_2$  in that the vibrationally excited NO(g) from the adlayer peaked at a vibrational level 1-2 quantum levels lower. This was attributed to perturbed dynamics in the adsorbed state. The low  $E_{\rm T}$  component of v'' = 0 was ascribed to the direct photolysis of  $N_2O_4(ad)$ , whereas the high- $E_T$ component of v'' = 0 together with v'' = 1-7 was tentatively attributed to  $N_2O_4(ad) \xrightarrow{h\nu} 2NO_2(ad) \xrightarrow{h\nu} NO + O$ . Simultaneous IR absorption spectroscopy and photolysis experiments were performed. The postulated transient NO<sub>2</sub>(ad) was not evident in the IR spectrum; it would be obscured by H<sub>2</sub>O and would be difficult to see since the IR spectrum was recorded continuously and not in the  $10^{-8}$  photolysis periods. The NO<sub>2</sub> concentration even during the  $10^{-8}$  UV illumination periods will moreover be low since  $NO_2$  is concurrently formed and photodissociated.

(iii) The rotational energy distributions were determined for every vibrational level observed (v'' = 0-7). The distributions could be described by linear Boltzmann plots with "temperatures" ranging from 250 to 1200 K. The average rotational energy gives direct evidence that the substrate plays a significant role in the photodissociation.

(iv) The *spin-orbit* states of the NO were found to be equally populated in all vibrational levels.

(v) The populations in the *lambda doublet* states were measured using high-K levels. There was no preference for the  $\Pi(A')$  state over the  $\Pi(A'')$  state.

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