# The photodissociation dynamics of NO<sub>2</sub> at 308 nm and of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> at 226 nm

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(Received 10 October 2005; accepted 21 December 2005; published online 10 February 2006)

Velocity-map ion imaging has been applied to the photodissociation of NO<sub>2</sub> via the first absorption band at 308 nm using (2+1) resonantly enhanced multiphoton ionization detection of the atomic  $O(^{3}P_{I})$  products. The resulting ion images have been analyzed to provide information about the speed distribution of the  $O({}^{3}P_{J})$  products, the translational anisotropy, and the electronic angular momentum alignment. The atomic speed distributions were used to provide information about the internal quantum-state distribution in the NO coproducts. The data were found to be consistent with an inverted NO vibrational quantum-state distribution, and thereby point to a dynamical, as opposed to a statistical dissociation mechanism subsequent to photodissociation at 308 nm. Surprisingly, at this wavelength the O-atom electronic angular momentum alignment was found to be small. Probe-only ion images obtained under a variety of molecular-beam backing-pressure conditions, and corresponding to O atoms generated in the photodissociation of either the monomer, NO<sub>2</sub>, or the dimer, N2O4, at 226 nm, are also reported. For the monomer, where 226 nm corresponds to excitation into the second absorption band, the kinetic-energy release distributions are also found to indicate a strong population inversion in the NO cofragment, and are shown to be remarkably similar to those previously observed in the wavelength range of 193-248 nm. Mechanistic implications of this result are discussed. At 226 nm it has also been possible to observe directly O atoms from the photodissociation of the dimer. The O-atom velocity distribution has been analyzed to provide information about its production mechanism. © 2006 American Institute of Physics. [DOI: 10.1063/1.2166631]

## **I. INTRODUCTION**

Photodissociation of the nitrogen dioxide molecule has been the source of considerable interest for many years. The reason is essentially twofold, the photochemistry of the nitrogen oxide family  $(NO_x)$  being of great importance in atmospheric and combustion chemistry, and the photolysis of  $NO_2$  itself having become a key benchmark system in the study of fundamental photodissociation dynamics.

A number of factors have contributed to the popularity of the photolysis process,

$$NO_2 + h\nu \to NO(^2\Pi_{\Omega}; \nu, J_{NO}, \Lambda) + O(^3P_J),$$

$$\Delta H_{\circ}^{\ominus} = 300.6 \text{ kJ mol}^{-1}.$$
(1)

as a focus for dynamical studies. The NO<sub>2</sub> molecule is a rare example of a stable yet simple open-shell molecule, possessing a number of low-lying electronic states and an energetic threshold to dissociation at a wavelength (around 398 nm) that has allowed the photolysis to be studied over a broad range of excitation energies (and consequently product excess energies). Much attention has focused on the precise nature of the dissociation pathway, particularly subsequent to excitation into the first absorption band. What electronic states are accessed in the photon absorption step, and during the subsequent evolution of these excited molecular states into products? Can the dissociation be described by statistical methods (which assume a randomization of energy throughout the internal modes at some critical point along the reaction pathway), or do state-to-state, dynamical effects make an important contribution to experimentally observed results? How must one's picture of the dissociation be modified as the photolysis energy is changed?

Since the seminal photofragment studies of Busch and Wilson,<sup>1,2</sup> a vast body of data, collected over a wide range of photodissociation energies, has been amassed. The UV dissociation of NO2 at wavelengths longer than about 250 nm occurs via excitation of the parent molecule from its  $\tilde{X}^2 A_1$ ground state to a surface of mixed  $\tilde{A}^2 B_2 / \tilde{X}^2 A_1$  electronic character.<sup>3-11</sup> A rapid nonadiabatic transition<sup>12</sup> through a conical intersection then transfers the excited-state population back onto the ground state, where decay into products occurs. Product state distributions suggest that at low excess energies (down to wavelengths around 350 nm), this unimolecular decay can be described, at least on average, using statistical theories.<sup>13–26</sup> However, as evidenced, for example, through highly inverted NO photofragment vibrational distributions,<sup>27–32</sup> at higher energies, where the dissociation becomes more rapid, such models cease to be valid. In particular, population of the product vibrational degree of freedom appears to be determined somewhat earlier along the

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reaction coordinate than the rotational (and electronic) degrees of freedom.<sup>17,19,21</sup> A visualization has emerged whereby each product vibrational level is treated in isolation, with the transition state used to determine the product rotational distributions corresponding to each such channel tightening as the excess energy is increased.<sup>17,19,21,24</sup> This picture is further supported through complementary time-resolved studies of the dissociation rates.<sup>7,24,33–39</sup>

Excitation of NO<sub>2</sub> at wavelengths between 200 and 250 nm takes place via a second absorption band,  $^{29,31,32,40-52}$ thought to involve an electronic state of  ${}^{2}B_{2}$ symmetry,  ${}^{41,45-48,51}$  usually termed the  $\widetilde{D} \, {}^2B_2$  or  $2 \, {}^2B_2$  state. At wavelengths close to 249 nm fluorescence is observed  $^{40,41,43,51}$  with a lifetime of around 42 ps,  $^{40}$  but this decreases rapidly with vibronic level,<sup>51</sup> due to homogeneous predissociation possibly by the lower  $\tilde{A}^2 B_2$  state.<sup>51</sup> Below 244 nm O(<sup>1</sup>D) production becomes energetically allowed, and is produced with a near constant quantum yield of around 50% between 244 and 193 nm.<sup>41,48,52</sup> Although the photodissociation dynamics in this region of the NO<sub>2</sub> absorption spectrum are less well characterized than for the first absorption band, there is clear evidence for the production of vibrationally highly excited NO at wavelengths between 248 and 193 nm.  $^{32,46,47,52}$  Both the O-atom velocity distribution obtained at 212.8 nm (Ref. 46) and the vibrational population distribution observed at 193 nm (Ref. 52) show evidence of bimodality. Excitation at the latter wavelength may involve a higher electronic state than the  $2^{2}B_{2}$  state, but the similarities between the NO photofragment vibrational population distribution at 193 nm (Ref. 52) and the corresponding  $O({}^{3}P_{I})$  velocity distribution at 212.8 nm (Ref. 46) are striking.

Studies of vector correlations in this system focus principally on the first absorption band, and are generally consistent with the dissociation mechanism outlined above, <sup>2,13,15,16,25,26,53–60</sup> with some studies providing additional information about excited-state lifetimes, <sup>15,25,56,59</sup> and possible fluctuations in state-to-state rate coefficients. <sup>24,61–63</sup> The alignment of the atomic O(<sup>3</sup>*P<sub>J</sub>*) ( $J \neq 0$ ) product has been specifically investigated only once previously<sup>46</sup> at a photolysis wavelength of 212.8 nm. Evidence of atomic angular momentum polarization at longer wavelengths is mixed, with one study suggesting alignment is present,<sup>54</sup> and another finding it to be absent.<sup>55</sup>

In the present work we describe a new investigation of the photofragmentation dynamics of  $NO_2$  at 308 and 226 nm using velocity-map ion imaging. The following section describes the experimental and data analysis techniques employed. Section III presents the results from the study, while in Sec. IV they are discussed in the light of previous experimental and theoretical works. With Sec. V the paper concludes with a brief summary of our principal findings.

#### **II. METHOD**

## A. Experimental procedures

The experiments were carried out using a standard velocity-map<sup>64</sup> ion imaging<sup>65</sup> apparatus, which has been described in detail previously.<sup>57,66–69</sup> Briefly, the majority of

the experiments employed a mixture of 5% NO<sub>2</sub> seeded in He at a backing pressure of  $\sim 2$  bars, which was expanded through a pulsed nozzle (General valve) with a 0.8 mm-diam orifice, and collimated by a 1-mm-diam skimmer. Additional experiments were also performed with up to 5%  $O_2$  in the gas mixture, to reduce residual levels of NO in the molecular beam. The rotational temperature of the beam was determined to be  $\sim 50$  K. Further downstream, the molecular beam was passed through a 2 mm hole in the repeller plate of the velocity mapping ion optics assembly and crossed 5 cm away from the nozzle exit by two counterpropagating laser beams. The photolysis radiation was provided by a Lambda Physik EMG103 excimer laser operating at 193 nm, while the probe radiation was obtained by frequency doubling the output of an excimer-pumped dye laser (Lambda Physik LPD series). The time delay between the two laser pulses was  $\sim 10$  ns. Two planoconvex lenses of 30 cm focal length were used to focus the radiation onto the molecular beam. The  $O({}^{3}P_{I})$  photofragments were probed by (2+1) resonantly enhanced multiphoton ionization (REMPI) via the  $3p {}^{3}P \leftarrow {}^{3}P_{J}$  transitions near 225 nm. The probe laser energy was typically around 500  $\mu$ J pulse<sup>-1</sup>. During image acquisition, the probe laser wavelength was scanned over the Doppler profile of the  $O({}^{3}P_{J})$  transitions in order to ensure an equal detection sensitivity for all the product velocities. The oxygen ions were velocity mapped onto an imaging detector consisting of a pair of 40 mm chevron double microchannel plates (MCPs) coupled to a P47 phosphor screen (DelMar Ventures). The image on the phosphor was captured by an intensified charge-coupled device (CCD) camera (Photonic Science), electronically gated to the flight time of the detected ions, and sent to a personal computer (PC) for signal processing (thresholding, event counting,<sup>70</sup> and accumulation). Images were averaged over 20 000 laser shots. Velocity calibration of the final images was achieved using images of  $O({}^{3}P_{I})$  from the photodissociation of  $O_{2}$ , the energetics for which are well characterized.

In order to extract information on  $O({}^{3}P_{I})$  alignment, images were obtained in four geometries, labeled HH, HV, VH, and VV according to the polarization of the pump and probe lasers lying parallel (H) or perpendicular (V) to the image plane. Pairs of images were collected simultaneously by using a photoelastic modulator to switch the polarization of the probe laser on alternate laser shot. This procedure not only reduced the errors due to experimental drift during the measurements but also enabled the measurement of the total angular momentum alignment,  $\langle A_{20} \rangle$ , from the measured intensity ratios.<sup>71</sup> This alignment parameter is required to normalize the image intensity prior to data analysis. In addition to this procedure, images were recorded on alternate pairs of shots with and without firing the photolysis laser. This procedure thus generated "pump-probe" and "probeonly" ion images to be accumulated concurrently, and subsequently subtracted if necessary to remove background probe-only signal from the pump-probe images.

Attempts were made to obtain separate REMPI spectra to determine the relative spin-orbit populations arising from the photolysis. For this purpose, the total signal output of the phosphor screen was sent to a boxcar averager, gated at the appropriate arrival time. In principle the integrated signal corresponding to each spin-orbit state could be used to determine the ratio of the photofragment populations. However, as discussed in Sec. III, these measurements were compromised by the weak pump-probe signal for  $O({}^{3}P_{1})$  and  $O({}^{3}P_{0})$ , compared with the probe-only signal, and by an overlap between the REMPI transitions used for  $O({}^{3}P_{1})$  detection, and (1+1) REMPI transitions in NO. The pump-probe signal for  $O({}^{3}P_{0})$  was so weak compared to the probe-only signal that satisfactory ion images for this fragment could not be obtained.

#### B. Data analysis

The method used to extract dynamical information from the velocity-map images is identical to that described in previous papers on the photodissociation of N<sub>2</sub>O (Ref. 67) and SO<sub>2</sub>.<sup>69</sup> Briefly, the laboratory frame scattering distribution  $P(v, \Omega_v, \Omega_j)$  of the O(<sup>3</sup>P<sub>J</sub>) product following polarized laser photolysis of NO<sub>2</sub> may be expanded semiclassically in spherical harmonics,

$$P(\nu, \Omega_{\nu}, \Omega_j) = \sum_{k,q} \rho_q^k(\nu, \Omega_{\nu}) C_{kq}^*(\Omega_j), \qquad (2)$$

where v is the product speed and  $\Omega_v = (\theta_v, \phi_v)$  and  $\Omega_i$  $=(\theta_i, \phi_i)$  are the laboratory frame polar coordinates of the product velocity vector (i.e., the scattering angle) and total angular momentum vector, respectively. The expansion coefficients (or *rotational moments*)  $\rho_a^k(v, \Omega_v)$  are functions of both velocity and scattering angle, and the spherical harmonic components depend only on the angular momentum polar coordinates  $\Omega_i$ . The laboratory frame is defined such that the z axis lies along the polarization vector and the x axis along the propagation vector of the photolysis light. The first step in obtaining the rotational moments of a velocity-map image is to express the distribution in Eq. (2) in terms of coordinates in a new reference frame, known as the time-offlight (TOF) frame, in which z lies along the time-of-flight axis. (x is still defined to lie along the photolysis laser propagation direction.) The image rotational moments are then obtained simply by integrating the distribution along the timeof-flight axis, mirroring the compression of the ion cloud along this axis during the experiment. A second rotation, to a detection frame, is often required to allow use of expressions in the literature for the rotational line strengths (see, for example, Ref. 72). The final expression for the rotational moments of the images may then be written as

$$\rho_{q''}^{k}(v_{p},\phi_{T})_{\text{DET}} = \frac{1}{4\pi} \sum_{q'} e^{iq'\phi_{T}} \sum_{K=0,2} \sum_{k_{1}} \left[ 1 + (-1)^{k_{1}+q'} \right] \\ \times f_{0}^{K}(k_{1},k,q',q'',R,R') F_{0}^{K}(k_{1},k,q';v_{p}),$$
(3)

in which  $v_p$  and  $\phi_T$  are the radial and angular coordinates of the image, and  $\theta_T$  is the angle that the product velocity vector makes with the time-of-flight axis.  $R = (\alpha, \beta, \gamma)$  and  $R' = (\alpha', \beta', \gamma')$  are Euler angles for the frame transformations, defined in Table I of Ref. 57. The indices  $k_1$ , q' and k, q''denote the spherical harmonic components of the velocity and angular momentum distributions of the product in the final or "detection" reference frame.

Equation (3) takes the form of a Fourier cosine series, in which the coefficient of each term is a sum over products of "geometrical factors"  $f_0^K$  and "dynamical factors"  $F_0^K$ . The geometrical factors depend only on experimental geometry and are easily calculated, while the dynamical factors are functions of a set of alignment parameters which define the scattering dynamics. Analytical expressions for the  $f_0^K$  and  $F_0^K$ factors have been given in previous publications.<sup>57,66,67</sup> Note that simple relationships exist between each of the commonly used sets of alignment parameters (e.g., the bipolar moments  $b_0^K(k_1,k;v)$  introduced in the semiclassical treatment by Dixon,<sup>73</sup> the polarization parameters  $a_q^k(p)$  used by Rakitzis *et al.*,<sup>74,75</sup> and the alignment anisotropy parameters of Bracker et al.<sup>71</sup>). Here we use the alignment anisotropy parameters  $\beta$ ,  $s_2$ ,  $\alpha_2$ ,  $\gamma_2$ , and  $\eta_2$  since these are appropriate for a full photodissociation.<sup>71</sup> quantum-mechanical treatment of

The Hertel-Stoll scheme<sup>76</sup> is used to convert the (potentially) complex quantities  $\rho_{q''}^k$  into the real quantities  $\rho_{q''\pm}^k$ ,

$$\rho_{q''+}^{k}(\nu_{p},\phi_{T}) = \frac{1}{\sqrt{2}} [(-1^{q''})\rho_{+q''}^{k}(\nu_{p},\phi_{T}) + \rho_{-q''}^{k}(\nu_{p},\phi_{T})], \quad 1$$
$$\leq q'' \leq k \tag{4}$$

and

$$\rho_{0+}^{k}(\nu_{p},\phi_{T}) = \rho_{0}^{k}(\nu_{p},\phi_{T}).$$
(5)

Using linearly polarized pump and probe radiation, and probing the O( ${}^{3}P_{J}$ ) photofragments via (2+1) REMPI, the analytical form of the images obtained depends only on the  $\rho_{0}^{0}$ ,  $\rho_{0}^{2}$ , and  $\rho_{2+}^{2}$  rotational moments. For the four experimental geometries used the appropriate expressions for the images are<sup>66,71</sup>

$$\begin{split} \mathcal{I}_{\rm HV}(\upsilon_p,\phi_T) &= \mathcal{I}_{\rm VV}(\upsilon_p,\phi_T) = \rho_0^0(\upsilon_p,\phi_T) + \sqrt{5}\frac{P_2}{P_0}\rho_0^2(\upsilon_p,\phi_T),\\ \mathcal{I}_{\rm VH}(\upsilon_p,\phi_T) &= \mathcal{I}_{\rm HH}(\upsilon_p,\phi_T) = \rho_0^0(\upsilon_p,\phi_T) - \frac{\sqrt{5}}{2}\frac{P_2}{P_0}[\rho_0^2(\upsilon_p,\phi_T)] \end{split}$$

$$+\sqrt{3}\rho_{2+}^{2}(v_{p},\phi_{T})],$$
(6)

where  $P_2/P_0$  are line strength factors for the probe (2+1) REMPI transition, taking the values 0,  $\sqrt{1/2}$ , and  $-\sqrt{7/10}$  for the *J*=0, 1, and 2 spin-orbit components of O( ${}^{3}P_{J}$ ).<sup>77,78</sup> Explicit expressions for the  $\rho_q^k(v_p, \phi_T)$  appearing in these equations have been given by Bracker *et al.*<sup>71</sup>

These expressions may be used in conjunction with Eqs. (3) and (4) to obtain analytical expressions for the Fourier moments of the measured images. As described previously,<sup>67</sup> here we have used a basis set made up of a sum of Gaussian functions to describe the speed dependence of the various angular momentum polarization parameters. These may be fit to the Fourier moments extracted from the experimental data in order to obtain the (velocity-dependent) alignment parameters characterizing the scattering distribution, using the

methodology described in Ref. 67. The experimental Fourier moments,  $c_n(v_p)$ , of the ion images,  $\mathcal{I}(v_x, v_y)v_p = \mathcal{I}(v_p, \phi_T)$ , are defined

$$c_n(v_p) = N \int_0^{2\pi} \mathcal{I}(v_x, v_y) \cos(n\phi_T) v_p d\phi_T, \tag{7}$$

where the normalization constant N is equal to 1 when n = 0 and 2 when n > 0. With linearly polarized pump and probe radiation, n is restricted to even terms.

Four sets of pump-probe and probe-only images were collected for each experimental geometry and spin-orbit state of  $O({}^{3}P_{J})$  and used to determine the alignment parameters. Some data for individual pump-probe geometries (identified in the text to follow) were also analyzed using Abel inversion methods described fully elsewhere.<sup>79</sup> Error estimates for the speed distributions and alignment parameters are given as the standard deviation in the parameters returned from fits, and were determined using a Monte Carlo procedure described previously.<sup>57</sup>

## **III. RESULTS**

# A. NO<sub>2</sub>+ $h\nu$ (308 nm) $\rightarrow$ NO+O(<sup>3</sup> $P_2$ )

The summed and background-subtracted velocity-map ion images for the J=2 products obtained in these experiments are shown in Fig. 1. Also presented are the Fourier moments extracted from the images, and the fits to these data obtained using the analysis procedure described in Sec. II B. Both the zeroth-order (large and positive in sign) and the second-order (small and negative in sign) moments are extremely similar in shape and magnitude for the two experimental geometry pairs HH/HV and VH/VV. This invariance in the profile of the images to the probe laser polarization provides a visual indication that the angular momentum alignment of  $O({}^{3}P_{2})$  in this system is very small. The fourthorder moment in the HH geometry, which in principle can arise only from terms describing angular momentum polarization, is also very close to zero. Note that the second-order moment in the VV geometry, and the fourth-order moments in the HV, VH, and VV geometries, must be zero for the pump-probe process of interest.<sup>57</sup>

The speed distribution extracted from the analysis is shown as the dashed line in Fig. 2. As expected, the oxygenatom products are generated with a broad spread of speeds, peaking around 1900 m s<sup>-1</sup>, and extending out towards the energetic limit at around 2700 m s<sup>-1</sup>. The speed-dependent spatial anisotropy is also shown in Fig. 2.  $\beta(v)$  exhibits small oscillations around a mean value of  $1.0\pm0.2$  (obtained by averaging over the speed distribution). As expected from the appearance of the images and their corresponding Fourier moments, the terms parametrizing the angular momentum polarization are very small. The speed-averaged polarization moments, alongside their limiting values, are presented in Table I. It is immediately obvious that within the experimental error, almost no angular momentum polarization is observed.

The absence of angular momentum polarization renders the three-dimensional (3D) distribution of oxygen products cylindrically symmetric, and the Abel inversion method



FIG. 1. (Color online) Background-subtracted images (left panels) and Fourier moments (right panels) for  $O({}^{3}P_{2})$  products following NO<sub>2</sub> photolysis at 308 nm. The experimental geometries are, from top to bottom, HH, HV, VH, and VV. Experimental Fourier moments are in bold (—) and the fitted moments dashed (----). Only those moments which are nonzero by symmetry are shown. The fourth-order moment,  $c_4(u_p)$ , is only nonzero for the HH geometry, and the second-order moment,  $c_2(u_p)$ , is zero for the VV geometry. Note that the second-order moments are negative in the HH and HV geometries, and all the zeroth-order moments,  $c_0(u_p)$ , are positive. The straight horizontal lines mark zero on the y axis.

should provide confirmation of the results obtained from the Fourier moment analysis method. It may be seen from Fig. 2 (dashed line) that these data are generally in excellent agreement with the parameters extracted from the full Fourier mo-



FIG. 2. Comparison between the speed (left) and anisotropy (right) distributions returned for the  $O({}^{3}P_{2})$  products of the 308 nm photodissociation of NO<sub>2</sub>, obtained using a full Fourier moment analysis (—), and a simpler Abel inversion of ion images collected in the HH geometry (----), which ignores rotational alignment effects.

TABLE I. Speed-averaged angular momentum alignment parameters for  $O({}^{3}P_{2})$  products of NO<sub>2</sub> photodissociation at 308 nm. Numbers in parentheses give the experimental error in the final decimal place. The right column gives the limiting values of the alignment parameters (Ref. 71).

Alignment parameter	This study	Limiting values	
<i>s</i> <sub>2</sub>	-0.003(2)	-0.20 to +0.10	
$\alpha_2$	-0.008(6)	-0.10 to +0.15	
$\eta_2$	-0.004(6)	-0.21 to +0.21	
$\gamma_2$	0.006(7)	-0.20 to +0.20	

ment analysis. A slightly larger average value of 1.2 is obtained for the translational anisotropy using an Abel inversion of the data collected in the HH experimental geometry (shown as the smooth line on the right of Fig. 2), compared with that obtained using the Fourier inversion method. The small discrepancy between these values may arise from several factors, but most likely reflects the fact that the latter method uses information from only one experimental geometry (i.e., one quarter of the total data collected).

# B. NO<sub>2</sub>+ $h\nu$ (308 nm) $\rightarrow$ NO+O(<sup>3</sup> $P_1$ )

The summed and background-subtracted velocity-map ion images for the J=1 products are shown in Fig. 3. Alongside are the extracted Fourier moments for these images and the fits returned to the data by the Fourier moment analysis procedure. It is clear, both from the images themselves and from their corresponding moments, that the data in this case possess a pronounced bimodality. This bimodality was found



FIG. 3. (Color online) Background-subtracted images (left) and Fourier moments (right) for  $O({}^{3}P_{1})$  products subsequent to NO<sub>2</sub> photodissociation at 308 nm. Experimental geometries are, from top to bottom, HH, HV, VH, and VV. Experimental Fourier moments are in bold (—) and the fitted moments dashed (----). See also the caption to Fig. 1.



FIG. 4. (a) Speed distribution returned by Fourier moment analysis of the  $O({}^{3}P_{1})$  images arising from NO<sub>2</sub> photolysis at 308 nm. (b) Speed distributions returned by Abel inversion of the  $O({}^{3}P_{1})$  images in the HH (—) and HV (----) geometries.

to persist even in the presence of added O2 to the gas mixture, suggesting that the outer ring of the images did not arise solely from NO contamination in the NO<sub>2</sub> gas sample. The speed distribution extracted from Fourier moment analysis of the images confirms this bimodality, and is shown in Fig. 4(a). The lower-velocity component is similar to that extracted for the  $O({}^{3}P_{2})$  products. It begins at around 500 m s<sup>-1</sup>, but is somewhat broadened compared to that for  $O({}^{3}P_{2})$ , apparently peaking at ~2300 m s<sup>-1</sup>, and possibly extending slightly beyond the energetic limit for single photon dissociation, which corresponds to a maximum velocity of around 2680 m s<sup>-1</sup>. The oscillations in the data probably result from the increased experimental noise in this detection channel [the signal being much reduced as compared to the  $O({}^{3}P_{2})$  channel due to a lower population in this state]. The component in the high-velocity region of the distribution cannot arise from a single photon dissociation of NO2 at 308 nm, since it lies well beyond the aforementioned energetic cutoff.

The presence of the high-velocity (multiphoton) peak complicates the analysis, and the HH and HV images were Abel inverted in order to extract an alternative, approximate measure of the speed and anisotropy distributions. The speed



FIG. 5. Speed-dependent spatial anisotropy parameters  $\beta(v)$  returned by Fourier moment analysis (—) and Abel inversion (----) of the O( ${}^{3}P_{1}$ ) images arising from NO<sub>2</sub> photolysis at 308 nm. Note that the analysis assumes a single photon dissociation mechanism, whereas energetically O-atom products possessing velocities greater than ~3000 m s<sup>-1</sup> must originate from a multiphoton process, and are therefore not shown. See text for details.

distribution is shown in Fig. 4(b). While the overall nature of the distribution closely resembles that in Fig. 4(a), the high-velocity component is somewhat less intense than when the Fourier moment analysis is used. Again, the distribution for the low-velocity component peaks at higher speed than was found for the  $O({}^{3}P_{2})$  products.

The spatial anisotropy parameters obtained via the two analysis methods are shown in Fig. 5. Agreement between the two distributions is excellent in the low-velocity (one photon) regime (that lying between 1000 and 2700 m s<sup>-1</sup>, as displayed in the figure), indicating that for the 308 nm photolysis component leading to  $O({}^{3}P_{1})$ , angular momentum polarization is extremely small. Averaging over the speed range of this peak, an anisotropy of  $\beta = 1.3 \pm 0.2$  is obtained from the Fourier moment fit, which is slightly higher than was measured for the  $O({}^{3}P_{2})$  product channel. The apparent spatial distribution of the products in the high-velocity region (not shown in Fig. 5) is more complicated. The apparent  $\beta(v)$ parameter at these high speeds is strongly dependent on the analysis method employed, the Fourier moment method returning an effectively velocity-independent spatial anisotropy of around 0.9 in this region, and the Abel-inverted image exhibiting a distribution characterized by a  $\beta(v)$  parameter of greater than 2. The latter value is nonphysical for a single photon dissociation in which product angular momentum alignment is assumed to be zero (see further discussion in Sec. IV).

The angular momentum alignment parameters returned by the Fourier moment fit are shown in Fig. 6. In the lowvelocity (one photon) region displayed in the figure, the alignment parameters oscillate around zero and suggest that angular momentum polarization is very small [although their residual values are somewhat higher than for the  $O({}^{3}P_{2})$ case]. In the high-velocity region, not shown in the figure, the returned, apparent values for the alignment parameters  $s_{2}(v)$  and  $\eta_{2}(v)$  become relatively large, a fact that explains the discrepancy between the effective  $\beta(v)$  parameters ob-



FIG. 6. Speed-dependent alignment anisotropy parameters  $s_2(v)$  (—),  $\alpha_2(v)$  (----),  $\gamma_2(v)$  (·---),  $\alpha_2(v)$  (·---) returned by Fourier moment analysis of the O( ${}^{3}P_1$ ) images shown in Fig. 3. Note that, as with Fig. 5, the analysis assumes a single photon dissociation process throughout, and therefore is not appropriate for O-atom velocities greater than 3000 m s<sup>-1</sup> (not shown).

tained at high velocities, discussed above. It should be stressed that the Fourier moment analysis method in the form described in Sec. II B does *not* explicitly account for the existence of multiphoton dissociation processes. As will be discussed further in Sec. IV, it seems likely that a multiphoton process is responsible for the high-velocity component of the distribution, and involves at least one photon from the probe laser. Thus, the ion images and the derived spatial anisotropy of the  $O({}^{3}P_{1})$  atoms are influenced by the polarization vector of the probe laser radiation, and both the Abel inversion and Fourier moment analyses are likely to break down in this case.

# C. NO<sub>2</sub>+ $h\nu$ (226 nm) $\rightarrow$ NO+O(<sup>3</sup> $P_J$ )

The primary function of the images collected with only the probe laser in operation was to allow for a background subtraction of the contribution made to the total photolysis signal by photodissociation at the REMPI detection wavelengths. However, this procedure also generates an additional data set that is amenable to analysis. Representative images collected on the probe-only transitions for  $O({}^{3}P_{2})$ ,  $O({}^{3}P_{1})$ , and  $O({}^{3}P_{0})$  are presented in Fig. 7. These data were collected with  $O_{2}$  added to the gas mixture, which in this case helped to suppress background signals from NO contaminants. A relatively isotropic central feature is evident for all the spin-



FIG. 7. Probe-only velocity-map ion images of  $O({}^{3}P_{0})$  (left),  $O({}^{3}P_{1})$  (middle), and  $O({}^{3}P_{2})$  (right), generated subsequent to photolysis of NO<sub>2</sub> at 226 nm. The data were obtained with a mixture of 10% NO<sub>2</sub> in He.

orbit products, but this component is dominant in the case of  $O({}^{3}P_{2})$ . The  $O({}^{3}P_{0})$  and  $O({}^{3}P_{1})$  products show a particularly pronounced bimodal structure, with the fast component showing clear evidence of spatial anisotropy.

The probe-only images for the  $O({}^{3}P_{1})$  and  $O({}^{3}P_{2})$  products provide insufficient data to extract angular momentum alignment information, and this must be assumed to be zero (unlike in the pump-probe data above, where a full data analysis concluded this to be the case). Ahmed et al.<sup>46</sup> found evidence for angular momentum alignment in the  $O({}^{3}P_{1})$ products of the 212.8 nm photodissociation of NO2. If similar angular momentum polarization effects were to occur at 226 nm, this would result in some error in the Abel-inverted speed distributions and translational anisotropies for  $O({}^{3}P_{1})$ and  $O({}^{3}P_{2})$ . However, it is reassuring to note that the returned speed distribution for the  $O({}^{3}P_{1})$  photofragment (see below) is very similar to that for the  $O({}^{3}P_{0})$  products, which necessarily cannot possess angular momentum alignment, suggesting that the effects of any alignment on the returned velocity distributions for  $O({}^{3}P_{1})$  and  $O({}^{3}P_{2})$  are not that large in the present case.

The speed distributions returned from an Abel inversion of the  $O({}^{3}P_{0})$ ,  $O({}^{3}P_{1})$ , and  $O({}^{3}P_{2})$  images are presented in Fig. 8. Bimodal structure is present for all three spin-orbit products, with the ratio of the fast component to the slow component much greater for the  $O({}^{3}P_{0})$  and  $O({}^{3}P_{1})$  channels than for  $O({}^{3}P_{2})$  (as can be seen from the raw images). Close inspection of the probe-only data revealed day-to-day variations in the ratio of the fast to slow components of the speed distributions. Variations in laser power over the range of 0.5-1.5 mJ were found to have no marked effect on the image profiles. However, the relative concentration of NO<sub>2</sub> in the NO<sub>2</sub>/He gas mixture was found to influence strongly the resulting images. Shown in Fig. 8 are the speed distributions returned for the  $O({}^{3}P_{0})$ ,  $O({}^{3}P_{1})$ , and  $O({}^{3}P_{2})$  photolysis products as the NO<sub>2</sub> concentration was successively reduced, from 10% (by partial pressure), to 1%, and then to a nominally trace quantity (obtained by evacuating the gas line several times and refilling with He only). It should be stressed that the true variation in reagent partial pressure will not be close to as dramatic as indicated, since a significant quantity of NO<sub>2</sub> is likely to remain within the gas system adsorbed onto surfaces even under evacuation. Nonetheless, it is immediately evident that the relative intensity of the slow component in the overall  $O({}^{3}P_{1})$  speed distributions, in particular, increases as the concentration of NO2 in the gas line becomes greater.

The strong partial pressure dependence observed appears to indicate a product channel arising from the dissociation of a higher-order cluster of NO<sub>2</sub>. NO<sub>2</sub> is well known to exist in equilibrium with its dimer, and the dissociation of N<sub>2</sub>O<sub>4</sub> itself has been the subject of a number of dynamical studies.<sup>32,80–85</sup> In the region of the probe laser wavelength, the absorption cross section of this species is between one and two orders of magnitude greater than that of the monomer.<sup>86,87</sup> Consequently, even small N<sub>2</sub>O<sub>4</sub> concentrations may contribute significantly to the observed results in the probe-only channel if a dissociation pathway forming O(<sup>3</sup>P<sub>1</sub>) fragments existed. Note that this is unlikely to be the



FIG. 8. Speed distributions extracted from probe-only velocity-map ion images of  $O({}^{3}P_{0})$  (top),  $O({}^{3}P_{1})$  (middle), and  $O({}^{3}P_{2})$  (bottom) obtained at 226 nm, and at various NO<sub>2</sub> partial backing pressures: (—) high pressure; (----) medium pressure; (·····) low pressure. See text for further details.

case in the pump-probe dissociation channel at 308 nm, since the absorption cross sections are comparable in magnitude at this wavelength. Estimates of the contribution of  $N_2O_4$  to the probe-only signal can be made based on the known equilibrium constant between NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub>, their relative absorption cross sections at the probe wavelength,<sup>86,87</sup> and the approximate partial pressures of NO<sub>2</sub> employed, and these are in broad agreement with the observations shown in Fig. 8. Interestingly, the contribution of the dimer to the total probe-only signal is very dependent on O(<sup>3</sup>P<sub>J</sub>) spin-orbit state, a point that will be returned to in Sec. IV C.

Abel inversion of the images suggests that the low speed component, associated with photodissociation of  $N_2O_4$ , is characterized by a low value of  $\beta$  around 0.1. By contrast, as is clearly visible from the raw  $O({}^{3}P_{0})$  ion images, the fast component is much more anisotropic, and is characterized by a  $\beta$  parameter close to unity.

## **IV. DISCUSSION**

# A. NO<sub>2</sub>+ $h\nu$ (308 nm) $\rightarrow$ NO+O(<sup>3</sup> $P_2$ )

# 1. Speed distribution

The distribution of  $O({}^{3}P_{2})$  product speeds presented in Fig. 2 reflects the manifold of populated rovibronic levels within the undetected NO coproducts. The  $O({}^{3}P_{2})$  and  $O({}^{3}P_{0})$  recoil energy distributions obtained by Demyanenko et al.<sup>55</sup> are the closest in photolysis wavelength (338.9 nm) to compare with the present work, and it is striking how different the longer wavelength distributions are from those obtained here at 308 nm. Literature reports of the NO internal energy disposal at 308 nm, which can be thought of as bridging the high and low excess energy regimes under which the dissociation has been studied, are currently somewhat contradictory.<sup>19,20,28</sup> In particular, there is some disagreement as to whether the NO vibrational distribution at this (relatively high) excess energy can be described by statistical methods,<sup>19</sup> or rather is best thought of as being under dynamical control.<sup>20,28</sup> NO rotational populations within the various energetically accessible  $(0 \le v \le 3)$  vibrational levels are, on the other hand, relatively well characterized at this wavelength.<sup>19,28</sup> Due to the difficulties associated with determining vibrational populations by laser-induced fluorescence (LIF), it seems reasonable to suppose that the rotational distributions reported in these studies are likely to be more robust than the corresponding vibrational populations. In order to investigate the deposition of vibrational energy in the NO products implied by the current data, we have therefore chosen to assume that one or other of the rotational distributions previously reported at this wavelength<sup>19,28</sup> represent a reasonable approximation to the true NO rotational populations in the present data. A series of "vibrational envelopes"whose individual rotational distributions are taken directly either from Refs. 28 or 19-were constructed to model the internal energy deposition in the NO coproduct, and therefore reproduce the speed distribution generated in the present experiment. The vibrational populations were used as adjustable parameters in a fit of the vibrational envelopes to the experimental speed distribution. The resulting fit assuming the rotational distributions of Knepp *et al.*<sup>19</sup> is shown as the dashed line in Fig. 9. The "vibrational envelopes" used as basis functions in the fitting are shown as dotted lines towards the bottom of the figure. The magnitudes of the basis functions are obtained by a simple genetic algorithm fit of the overall product speed distribution to that measured in the current study.

The best fit to the extracted speed distribution was obtained when the rotational populations used to construct the basis functions were taken from the experimental results of Knepp *et al.* (which, as in the current study, made of use of a jet-cooled reactant beam).<sup>19</sup> The returned relative NO vibrational populations for this fit, and for the best fit achieved when the results of the room-temperature study of Zacharias



FIG. 9. Fit (----) to the  $O({}^{3}P_{2})$  speed distribution following 308 nm photolysis (---), using vibrational basis functions (.....) constructed from the data of Knepp *et al.* (Ref. 19) (see text for further details). From right to left (high product speed, low internal excitation to low product speed, high internal excitation), these functions correspond to the v=0, v=1, v=2, and v=3 NO products, respectively.

*et al.* was used to generate the vibrational envelopes,<sup>28</sup> are shown in Fig. 10 and Table II. Note that the two alternative vibrational distributions are in reasonable agreement, although the preferred population distribution, that obtained using the data of Knepp *et al.*,<sup>19</sup> is somewhat hotter than that obtained using the rotational populations of Zacharias *et al.*<sup>28</sup> Also shown in the figure for comparison are the previously reported vibrational populations from these two LIF studies,<sup>19,28</sup> and from the Fourier transform infrared (FTIR) experiment of Doughty *et al.*<sup>20</sup> In contrast to the vibrational populations reported in Refs. 28 and 19, the present data show an inverted population distribution, with very little NO borne in its lowest v=0 vibrational level. Broadly speaking, the relative populations in v>0 are in reasonable agreement with the results of Knepp *et al.*<sup>19</sup> One problem reported in



FIG. 10. Comparison between NO vibrational distributions obtained in this work (—) subsequent to NO<sub>2</sub> photodissociation at 308 nm, with those extracted in previous studies (----). Labeling is as follows:  $-\Delta$ -, current work, rotational populations taken from Zacharias *et al.* (Ref. 28);  $-\nabla$ -, current work, rotational populations taken from Knepp *et al.* (Ref. 19); -- $\blacksquare$ -- Zacharias *et al.* (Ref. 28); -- $\blacklozenge$ -- Knepp *et al.* (Ref. 19); -- $\blacksquare$ -- Hancock *et al.* (Ref. 20).

TABLE II. The first two columns show estimated vibrational population distributions determined from fits to the experimentally determined  $O({}^{3}P_{2})$  velocity distribution shown in Fig. 2 assuming the rotational distributions measured previously either by Knepp *et al.* (Ref. 19) or Zacharias *et al.* (Ref. 28). The three columns on the right show the vibrational distributions obtained by Knepp *et al.* (Ref. 19), Zacharias *et al.* (Ref. 28), and Doughty *et al.* (Ref. 20).

Vibrational level	Fit (Knepp)	Fit (Zacharias)	Knepp <sup>a</sup>	Zacharias <sup>b</sup>	Hancock <sup>c</sup>
0	0.07	0.07	0.55	0.29	•••
1	0.40	0.51	0.22	0.28	0.28
2	0.40	0.35	0.13	0.19	0.38
3	0.13	0.07	0.10	0.22	0.34

<sup>a</sup>Reference 19.

<sup>b</sup>Reference 28.

<sup>c</sup>Reference 20.

both the earlier LIF experiments was the presence of cold NO as a contaminant in the NO<sub>2</sub> source—the vast majority of this would be in its lowest vibrational state and could therefore lead to artificially high levels of v=0 NO "products." The present results are in reasonable agreement with the results of Doughty et al. (who were unable to extract the population in v=0,<sup>20</sup> although the latter work reported a higher proportion of NO( $\nu$ =3) products than observed here. It is possible that the present estimate for the yield of v=3 is particularly sensitive to the assumed rotational distribution in lower vibrational levels. Qualitative inspection of Fig. 9 suggests that the population in v=3 might be as much as double the present estimate if the v=2 rotational distribution employed to generate the fitting functions was somewhat colder than the one reported by Knepp *et al.*<sup>19</sup> Such an enhancement in v=3 population would bring the current vibrational distribution into much better agreement with those of Doughty *et al.*<sup>20</sup>

It should also be noted that in each of the aforementioned previous studies of the 308 nm photodissociation of NO<sub>2</sub>, the NO species was measured directly, and therefore provided a weighted average over each of the three  $O({}^{3}P_{J})$ spin-orbit levels populated. If the three oxygen spin-orbit states were to be correlated with rather different ensembles of rovibrational quanta in the corresponding NO coproducts, the current results would no longer merit direct comparison with these studies. We return to this point in Sec. IV B.

#### 2. Spatial anisotropy

The spatial anisotropy parameters obtained in the photodissociation at 308 nm have been explored in previous studies by Brouard *et al.*<sup>56</sup> and Bass *et al.*<sup>57</sup> The values reported for the  $\beta$  parameter were  $1.4\pm0.1$  (under jet-cooled conditions) and  $1.22\pm0.04$  (at room temperature). At first glance, the current results seem to be rather low, but it is important to note that the previous results reported the spatial anisotropy for a single NO quantum state (v=0, N=30).<sup>56,57</sup> In fact, the present data show that at the O( ${}^{3}P_{2}$ ) speed correlating with these products (around 2500 m s<sup>-1</sup>), the anisotropy reported here agrees well with the previously determined NO quantum-state resolved values.

The  $\beta(v)$  parameter observed at any given velocity represents a weighted average over the various overlapping

 $O({}^{3}P_{2})$ +NO( $v, J_{NO}$ ) product channels, and as such any discussion of its functional form is necessarily complicated. In fact, even at 2500 m s<sup>-1</sup>, the present results are not directly comparable with those detecting the NO(v=0, N=30) species.<sup>56,57</sup> As may be seen from Fig. 9, low rotational levels of the first vibrationally excited state of NO already overlap the v=0 products at this speed. Only at the far extremities of the product speed range do single NO vibrational levels contribute to the distribution, and may the NO rotational level dependence of the anisotropy properly assessed. Unfortunately, it is just at these extremes of the distribution where the intensity is small, and extraction of reliable translational anisotropy parameters most problematic.

#### 3. Angular momentum alignment

The present results indicate that the  $O({}^{3}P_{2})$  fragments of NO<sub>2</sub> photodissociation at 308 nm do not show angular momentum alignment. Although there are no studies with which these results bear direct comparison, the conclusions drawn here are similar to those of Demyanenko *et al.*, who suggested that atomic polarization was not present in dissociation between 372 and 388 nm.<sup>55</sup> These results are somewhat surprising, given that the spin-orbit states of  $O({}^{3}P_{J})$ , particularly at longer wavelengths, are produced with nonstatistical populations,<sup>44</sup> and that polarized oxygen atoms have been observed subsequent to photodissociation via the second absorption band.<sup>46</sup>

Although we have no quantitative explanation for the absence of O-atom polarization in the photodissociation of NO<sub>2</sub> via the first absorption band, consideration of the orbital correlation diagram provides some clues as to the origin of the behavior. At linearity, the  $O({}^{3}P) + NO({}^{2}\Pi)$  products correlate with doublet and quartet states of the NO<sub>2</sub> molecule with  $\Sigma^+$ ,  $\Sigma^-$ ,  $\Pi$ , and  $\Delta$  symmetries.<sup>6,8</sup> The  $\Pi$  state is formed by bringing the filled *p*-orbital on the oxygen atom up to the NO molecule at linearity, and this state is therefore the most repulsive. The  $\Sigma^+$ ,  $\Sigma^-$ , and  $\Delta$  states are formed by bringing a half-filled p-orbital on the oxygen atom up to the NO molecule. On bending, the symmetries of these states are reduced to A', A'', and A' + A'', respectively. In the asymptotic region, the  $\Sigma^+$  state is the lowest in energy, and at nonlinear configurations this state correlates adiabatically with the ground 1<sup>2</sup>A' state of NO<sub>2</sub>.<sup>6,8</sup> It is worthwhile comparing

these state correlations with those for other systems that dissociate via states of  $\Sigma$  symmetry, and for which O-atom polarization has been observed, for example, SO<sub>2</sub> (Ref. 69) and  $N_2O.^{67}$  Unlike these other systems, for NO<sub>2</sub> the  $\Pi$  character of the NO coproduct means that twice as many A' and A" states are generated when the half-filled O-atom orbital is directed towards the diatomic molecule (these states being the aforementioned  $\Sigma^+$ ,  $\Sigma^-$ , and  $\Delta$  at linearity) compared with the case in  $SO_2$  and  $N_2O$ . Thus, on bending, a more dense manifold of crossings and avoided crossings will be present for NO<sub>2</sub> than for SO<sub>2</sub> or N<sub>2</sub>O, possibly leading to scrambling of the O-atom alignment. Why the alignment should be seen subsequent to absorption via the second adsorption band remains a mystery, although it is perhaps significant that, in that case, dissociation may not proceed ultimately on the ground-state potential-energy surface.

# B. NO<sub>2</sub>+ $h\nu$ (308 nm) $\rightarrow$ NO+O(<sup>3</sup> $P_1$ )

## 1. Speed distribution

The speed distribution for the  $O({}^{3}P_{1})$  products shown in Fig. 4 raises several questions. The lower-velocity peak represents the pump-probe signal from dissociation at 308 nm, but while it is generally in reasonable accord with the  $O({}^{3}P_{2})$  data, the distribution is somewhat broader, and clearly peaks at higher velocity, than that of the  $O({}^{3}P_{2})$  products. Meanwhile, the feature at high velocity, which is absent entirely in the  $O({}^{3}P_{2})$  images, cannot energetically arise from photolysis at 308 nm.

The differences between the speed distributions for the two detected oxygen spin-orbit states in the low speed (308 nm photolysis) region may reflect a number of factors. First, as noted above, it is possible that the dynamics of the dissociation do genuinely lead to atomic products that, depending on their spin-orbit level, correlate to different quantum states of the NO cofragments. In fact, in the coresampling experiments of Hsieh et al.,54 which used REMPI detection to establish the speed distributions of each of the  $O({}^{3}P_{I})$  spin-orbit states following dissociation at 355 nm, such variations were indeed observed. Their study revealed all three  $O({}^{3}P_{I})$  spin-orbit states to be correlated with differratios of NO(v=0):NO(v=1)ent and NO(v=1,low  $J_{\rm NO}$ ):NO(v=1,high  $J_{\rm NO}$ ) coproducts. Similar spinorbit state specific behavior has also been observed by Demyanenko et al.55 at selected wavelengths as short as 338.9 nm. In the current experiments, the consequence would be that a larger quantity of NO( $\nu=0$ ) would be formed in conjunction with  $O({}^{3}P_{1})$  products than with  $O({}^{3}P_{2})$  products. A fit to the low speed component of the  $O({}^{3}P_{1})$  velocity distribution, along the same lines as that shown in Fig. 9 for  $O({}^{3}P_{2})$  and assuming the rotational population distributions determined by Knepp et al., yields a vibration population P(v=0:1:2:3)=0.40:0.35:0.15:0.09. We may use these NO coproduct vibrational populations, together with those for the  $O({}^{3}P_{2})$  products, to estimate the spin-orbit averaged NO vibrational populations. In making this estimate, we have assumed an average of the O-atom spin-orbit populations of Miyawaki et al.<sup>88</sup> at 266 nm, (P(J=2:1:0)=1.00:0.17:0.03), (P(J=2:1:0))and 337 nm

=1.00:0.23:0.04), and that the  $O({}^{3}P_{0})$  products are partnered exclusively by NO in v'=0. The latter assumption ensures that our estimate for the average vibrational population distribution is the coldest that is compatible with the  $O({}^{3}P_{1})$ and  $O({}^{3}P_{2})$  data [the population in  $O({}^{3}P_{0})$  is so small that in any event it has little influence on the averaged distribution]. The resulting spin-orbit averaged NO coproduct populations are then predicted to be P(v=0:1:2:3)=0.15:0.38:0.35:0.12. These estimated vibrational populations are closer to the previous results from the LIF studies.19,28 Nevertheless, in spite of the uncertainties involved in averaging the present results over O-atom spinorbit state, it is important to stress that a clear conclusion from the present work is that the NO coproducts must be produced with a vibrational population inversion. This result suggests a dynamical, as opposed to a statistical, interpretation of the dissociation mechanism. The vibrational population inversion is likely to reflect changes in bond length and/or vibrational frequency during excitation and dissociation, with the latter occurring on a time scale that is prompt relative to that for the statistical redistribution of internal energy in the excited NO<sub>2</sub> molecule. At the excess energies supplied in the present work, it should also be borne in mind that dissociation may not only occur exclusively via the ground electronic state potential-energy surface but may also take place directly on the excited  $\tilde{A}^2 B_2(2^2 A')$  electronic state.

While the scenario in which different spin-orbit states of the O atom correlate with different NO coproduct vibrational populations is an appealing one, this interpretation of the  $O({}^{3}P_{1})$  results should be treated with some caution. The differences in the spin-orbit state-resolved velocity distributions observed here seem quite large compared with the data obtained by Hsieh et al. at 355 nm,<sup>54</sup> and the data of Demyanenko *et al.* at 338.9 nm.<sup>55</sup> At the higher recoil velocities accessed in the present work, one might expect smaller differences in the speed distributions for the three spin-orbit states compared with those observed at 338.9 and 355 nm.<sup>67,69<sup>1</sup></sup> It is possible that another phenomenon is responsible for the broadening of the  $O({}^{3}P_{1})$  nascent product velocity distribution. One additional source of such broadening is the space charging effect. It should be noted that a large ion signal was detected at the mass corresponding to NO<sup>+</sup> at the REMPI wavelength for detection of the O( ${}^{3}P_{1}$ ) [and  $O({}^{3}P_{0})$ ] products. This could have resulted in the large ion density in the interaction region necessary to cause this effect.

A consideration of the potential sources of the highvelocity products observed in these experiments provides some evidence that space charging may be responsible, at least in part, for the broadening of the  $O({}^{3}P_{1})$  speed distribution with respect to that for the  $O({}^{3}P_{2})$  products. As has been indicated already, this component cannot arise from a single photon dissociation process, lying beyond the physical limit for photolysis at 308 nm. The probe-only dissociative contribution at 226 nm, which could give rise to products with these velocities, has already been subtracted from the total signal. A further requirement for the high-velocity component is that it must involve resonant detection of O<sup>+</sup> ions. One is therefore left to consider what combination of photons from the 308 nm laser and the 226 nm laser could lead to further generation of oxygen products. The NO  $A(^{2}\Sigma^{+})$  $\leftarrow X(^{2}\Pi)$  electronic transition, its 0-0 band lying at around the wavelength of the probe laser wavelength of 226 nm, is known to be a highly efficient process.<sup>89</sup> It therefore seems likely that a large quantity of electronically excited NO would be generated if the probe laser wavelength were to coincide with a resonant transition in this band. Indeed, the wavelengths of the  $O({}^{3}P_{1})$  and  $O({}^{3}P_{0})$  REMPI transitions are near resonant with a number of  $A \leftarrow X$  transitions in the 0-0 band originating from low rotational levels in NO.<sup>90,91</sup> These levels would be populated significantly by photodissociation of  $NO_2$  at 308 nm. It is also possible that a very small NO residual impurity remains in the molecular-beam expansion, even when  $O_2$  is added to the gas mixture. The electronically excited NO species thereby produced may then absorb a further photon that will cause either dissociation or ionization,

NO(<sup>2</sup>Π) + 
$$h\nu$$
(226 nm) → NO(<sup>2</sup>Σ<sup>+</sup>)  
+  $h\nu$ (308 or 226 nm)  
→ N(<sup>4</sup>S) + O(<sup>3</sup>P), (8)

NO(<sup>2</sup>Π) + 
$$h\nu$$
(226 nm) → NO(<sup>2</sup>Σ<sup>+</sup>)  
+  $h\nu$ (308 or 226 nm)  
→ N(<sup>2</sup>D) + O(<sup>2</sup>P), (9)

NO(<sup>2</sup>Π) + 
$$h\nu$$
(226 nm) → NO(<sup>2</sup>Σ<sup>+</sup>)  
+  $h\nu$ (308 or 226 nm) → NO<sup>+</sup>.  
(10)

The two-photon dissociation process shown in Eq. (8) has been observed by Bakker et al.<sup>89</sup> In their experiments, the photolysis laser was tuned to the 226.19 nm, which lies in the center of the  $Q_{11}+P_{11}$  bandhead. Although the focus of the study was on subsequent dissociation of the excited  $A(^{2}\Sigma^{+})$  state at 339 nm, an intense ring was also observed in their velocity-map imaging study that corresponded to dissociation at the probe laser wavelength [in this case the wavelength of the  $O({}^{3}P_{2})(2+1)$  REMPI transition at 225.7 nm]. A leakage signal that corresponded to the production of large quantities of NO<sup>+</sup> was also present and was assigned to the process indicated in Eq. (10). Interestingly, the same authors noted that at the  $O({}^{3}P_{1})(2+1)$  REMPI detection wavelength, an accidental resonance (or near resonance) in the NO  $A(^{2}\Sigma^{+})-X(^{2}\Pi)$  transition generated large quantities of residual  $NO^+$  through (1+1) REMPI, with resulting space charge effects that precluded the collection of images for this spin-orbit product.

In the light of this information, it seems probable that a multiphoton process, possibly incorporating first the dissociation of  $NO_2$  by the photolysis laser at 308 nm followed by resonant excitation of NO to the *A* state, and then photodissociation or photoionization at either 308 or 226 nm, is responsible for the high-velocity peak observed in these experiments. Formation of the product ions incident on the

detector would then result either from (2+1) REMPI of the atomic oxygen products formed in Eq. (8) or alternatively via photodissociation of the  $NO^+$  ions produced in Eq. (10). (A further two-probe laser photons would be required to dissociate  $NO^+$  into  $N+O^+$ .) Processes (8) and (9) generate O-atom products with velocities of 4120 and 1886 m s<sup>-1</sup>, and the former is quite close to the observed secondary peak in the velocity distribution, allowing for the effects of spacecharge broadening. The sign and approximate magnitude of the anisotropy parameter for process (8) (Ref. 89) is also consistent with present observations. The space charging effect which precluded the collection of images at this probe laser wavelength in the experiments of Bakker et al.,<sup>89</sup> might also cause deviations between the low-velocity features for the  $O({}^{3}P_{1})$  images, as opposed to the  $O({}^{3}P_{2})$  data, and could potentially blur the nascent product distribution significantly.

In summary, the energetics of the components in the speed distribution, their energy broadening, and the observations of previous work are consistent with the operation of a second, multiphoton dissociative channel described above. It is also conceivable that this process might be the cause of some of the discrepancies we have observed at 308 nm between the two spin-orbit states detected in this study. However, irrespective of these potential complications, it is worth reiterating that a firm conclusion from the present work is that subsequent to the photodissociation of NO<sub>2</sub> at 308 nm NO is produced with a vibrational population inversion.

## 2. Spatial anisotropy and alignment parameters

As mentioned in Sec. III B, the presence of multiphoton processes in the high-velocity region of the  $O({}^{3}P_{1})$  velocity distribution complicates the analysis of the angular distributions and angular momentum alignment. Nevertheless, at the low speeds characterizing the component arising from single photon photolysis at 308 nm, the alignment is again found to be extremely small—in accord with the data from the  $O({}^{3}P_{2})$ products presented in Sec. III A. The spatial anisotropy obtained from the Fourier moment analysis for these products is well reproduced by a simple Abel inversion procedure, and is also of similar magnitude to that for the  $O({}^{3}P_{2})$  channel.

The interpretation of the translational anisotropy of the high speed component of  $O({}^{3}P_{1})$  has already been touched on in the preceding section. At second photon wavelengths around 339 nm, process (8), generating  $O({}^{3}P_{2})$ , is known to possess a positive  $\beta$  parameter of around unity.<sup>89</sup> The angular distribution in the outer high-velocity ring observed here for  $O({}^{3}P_{1})$  at second photon wavelengths around 308 nm is consistent with this finding, though the distribution is severely broadened by space-charge effects. In light of this broadening, more detailed analysis is probably unwarranted.

# C. NO<sub>2</sub>+ $h\nu$ (226 nm) $\rightarrow$ NO+O(<sup>3</sup> $P_J$ )

## 1. Photodissociation at high NO<sub>2</sub> partial pressures

As noted in Sec. III, analysis of the probe-only images at 226 nm is complicated by photodissociation of  $N_2O_4$ , particularly under conditions of high partial backing pressures of  $NO_2$ . A number of studies of  $N_2O_4$  photolysis have been conducted at a dissociation wavelength of 193 nm.<sup>80–82</sup> The

experiments of Kawasaki et al.<sup>80</sup> and of Sisk et al.<sup>81</sup> detected emission from electronically excited NO2 that was assigned by the latter researchers to a dissociation channel that yielded electronically excited NO<sub>2</sub>(1  ${}^{2}B_{2}$ )+NO<sub>2</sub>(1  ${}^{2}B_{2}$ ) products. A more recent study at 193 nm by Mueller et al.<sup>82</sup> used photofragment translational spectroscopy to observe two-product dissociation channels, which were tentatively assigned  $NO_2(\tilde{X}^2A_1) + NO_2(1 {}^4B_2/1 {}^4A_2)$ and to  $NO_2(\tilde{X}^2A_1)$  $+NO_2(2^2B_2)$  products, respectively. In this experiment, a slight broadening of peaks in the NO<sup>+</sup> and O<sup>+</sup> TOF spectra relative to the corresponding peak in the  $NO_2^+$  spectrum was concluded to arise from secondary dissociation of some of the NO<sub>2</sub> products into O+NO fragments. (No evidence of NO formation had previously been observed in the earlier study of Kawasaki et al.<sup>80</sup>) The observations of Mueller et al. are consistent with the current results, which suggest that  $O({}^{3}P_{I})$  products are generated via the process,

$$N_2O_4 + h\nu(226 \text{ nm}) \rightarrow NO_2 + NO + O({}^3P_J),$$
 (11)

on the time scales of the present experiments. Once scaled for the different photon energies employed, the O-atom velocity distribution observed in the present work at 226 nm is similar to the fast component of the NO<sub>2</sub>, NO, and O velocity distributions observed in the work of Mueller *et al.*,<sup>82</sup> and assigned to production of NO<sub>2</sub>( $\tilde{X}^2A_1$ )+NO<sub>2</sub>( $1^4B_2/1^4A_2$ ). Note that the slow velocity component observed by Mueller *et al.*<sup>82</sup> assigned to the channel leading to NO<sub>2</sub>( $\tilde{X}^2A_1$ ) +NO<sub>2</sub>( $2^2B_2$ ), is energetically inaccessible at the present wavelength of 226 nm.

In their FTIR studies of emission from NO and NO<sub>2</sub> following the photodissociation of NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> at 248 nm, Morrell *et al.* have drawn similar conclusions about the possible involvement of process (11).<sup>32</sup> In these experiments, the authors observed an emission band thought to be from NO that became markedly more intense as the ambient conditions were altered to increase the concentration of N<sub>2</sub>O<sub>4</sub> (while keeping the NO<sub>2</sub> concentration approximately constant). Although other processes could not be ruled out, it was concluded that this emission band most likely arose from direct dissociation of N<sub>2</sub>O<sub>4</sub> as indicated in Eq. (11). If this were indeed the case, the quantum yield for the formation of NO in low vibrational levels by this mechanism appeared to be significant.

Evidence of direct NO formation from  $N_2O_4$  has also been seen at various wavelengths around 200 nm by Parsons *et al.*<sup>83</sup> In these experiments, fluorescence was observed from NO( $A^2\Sigma^+$ ), which was suggested to be formed either by a secondary photon absorption and subsequent dissociation of the NO<sub>2</sub> products of N<sub>2</sub>O<sub>4</sub> photolysis, or by absorption and consequent emission of the NO product formed in Eq. (11). A much earlier study of N<sub>2</sub>O<sub>4</sub> photolysis at 265 nm was also seen to yield a large quantity of NO,<sup>85</sup> with a quantum yield of around 0.2 being suggested for the photolytic contribution of Eq. (11) (the remainder of the NO being formed by secondary reaction of atomic oxygen fragments with NO<sub>2</sub>).<sup>84</sup>

It will be apparent from the above discussion that, although previous studies of  $N_2O_4$  photodissociation do not provide a universally consistent picture, the weight of



FIG. 11. (a) The velocity distribution for  $O({}^{3}P_{2})$  photofragments obtained using high partial backing pressures of NO<sub>2</sub>, and associated here with the production of O atoms in the photodissociation of N<sub>2</sub>O<sub>4</sub>.  $v_{12}$  and  $v_{13}$  are the recoil velocities of the NO<sub>2</sub> fragments generated in step (12) and  $O({}^{3}P)$  in step (13), respectively. (b) (——) The kinetic-energy release distribution for  $O({}^{3}P_{0})$  fragments obtained at a photolysis wavelength of 226 nm using a low partial backing pressure of NO<sub>2</sub>, and associated here with the photodissociation of the NO<sub>2</sub> monomer. Note that the data are plotted as a function of NO internal energy. For comparison, the NO vibrational populations obtained by Hancock and co-workers at 248 nm (···••···) (Ref. 32) and 193 nm (··•••··) (Ref. 52), and the O({}^{3}P\_{1}) velocity obtained by Ahmed *et al.* (----) (Ref. 46) at 212.8 nm are also shown. See text for details.

evidence<sup>32,82–84</sup> seems to suggest that oxygen-atom products may be formed either by direct photodissociation of the dimer, or, more likely, by the secondary unimolecular dissociation of internally excited primary NO<sub>2</sub> photofragments. In the light of this, together with the backing-pressuredependent data present here, it would appear that photolysis of N<sub>2</sub>O<sub>4</sub> accounts for the low-velocity component seen in the present probe-only images. The O( ${}^{3}P_{J}$ ) speed distributions arising from photolysis of the NO<sub>2</sub> *monomer* would thus contain a single component that peaks at around 3000 m s<sup>-1</sup> (see further discussion below).

Supporting evidence for the role of process (11) is provided by a more detailed consideration of the  $O({}^{3}P_{2})$  velocity distribution obtained at high NO<sub>2</sub> backing-pressure conditions, shown in Fig. 11(a). This distribution can be crudely characterized as a square-shaped distribution, centered at

1300 m s<sup>-1</sup> with a maximum width of  $\pm$ 700 m s<sup>-1</sup>. The 193 nm data of Parsons *et al.* suggest that the production of O(<sup>3</sup>*P*) follows a two-step mechanism:

$$N_2O_4 + h\nu(226 \text{ nm}) \to NO'_2 + NO''_2,$$
 (12)

$$\mathrm{NO}_{2}^{\prime\prime} \to \mathrm{NO} + \mathrm{O}({}^{3}P_{J}). \tag{13}$$

Little kinetic energy is released in step (13), such that the velocity distributions of the O and NO secondary fragments essentially mirror those of the nascent NO<sub>2</sub> photofragments born in step (12). If the same were true at 226 nm, the interpretation of the present O-atom data would be that the central velocity of  $\sim 1300 \text{ m s}^{-1}$  must be associated with the recoil velocity of the nascent NO2 products formed in step (12), while the  $\pm 700 \text{ m s}^{-1}$  width must be associated with the maximum kinetic-energy release in step (13). The latter assignment, together with the conclusions of Doughty et al. that at 248 nm the NO fragments in step (13) are produced in low vibrational states, between v=1 and 3, implies that the dissociating NO<sub>2</sub>" molecule must possess an internal energy of at most 335 kJ mol<sup>-1</sup> (the sum of the dissociation energy of NO<sub>2</sub>, an estimate of the vibrational energy of NO of  $\sim$ 25 kJ mol<sup>-1</sup>, and the maximum total kinetic-energy release associated with an O-atom velocity of  $\sim$ 700 m s<sup>-1</sup>). This internal energy could reside in electronic or rovibrational degrees of freedom, or a combination of the two, and would be consistent with production of NO<sub>2</sub>" in either of the  $\tilde{X}$ , the 1  $B_2$ , or the 1  ${}^2B_1$  electronic states [recall that production of  $NO_2(2^2B_2)$  at 226 nm can be excluded on energetic grounds]. The  $1 {}^{4}B_{2}/1 {}^{4}A_{2}$  electronic states, favored by Mueller et al.,<sup>82</sup> might also be involved, but the electronic excitation energy from the ground to these excited states  $(T_0)$ , which is at present unknown, would have to be less than about 3 eV. With the above interpretation of the O-atom velocity distribution, a central velocity of  $\sim 1300 \text{ m s}^{-1}$  corresponds a total kinetic-energy release in step (12) of about 80 kJ mol<sup>-1</sup>. This leaves only 60 kJ mol<sup>-1</sup> of internal energy in the  $NO'_2$  cofragment of the dissociating  $NO''_2$  species, insufficient either for the former to also undergo secondary dissociation or for it to be produced in an electronically excited state. Our conclusion, therefore, is that step (12) can be refined as leading to  $NO_2(\tilde{X}) + NO_2''$ , with  $NO_2''$  borne in either the  $\tilde{X}$ , the 1  ${}^{2}B_{2}$ , the 1  ${}^{2}B_{1}$ , or (possibly) the 1  ${}^{4}B_{2}/1 {}^{4}A_{2}$ states, with a total internal energy of around  $335 \text{ kJ mol}^{-1}$ .

A particularly interesting feature of the current probeonly data is the variation in fast and slow O-atom velocity components with spin-orbit state. The current data consistently show a greater intensity of the low speed versus the high speed component for the  $O({}^{3}P_{2})$  products (this is clearly evident in Fig. 8). The conclusion must be that the process described by Eq. (11) generates very different O-atom spin-orbit populations compared with the direct NO<sub>2</sub> monomer photodissociation at 226 nm. The latter process is known to generate O atoms with a near-statistical spin-orbit population distribution<sup>44</sup> (in the ratio 1.00:0.50:0.17 for J=2, 1 and 0). Analysis of the data shown in Fig. 8 suggests that the spin-orbit populations arising from process (11) must therefore be close to 1.00:0.03:0.02 for J=2, 1, and 0. Such a preferential population of the lowest  $O({}^{3}P_{2})$  spin-orbit orbit channel is reminiscent of the near-adiabatic dissociation observed for NO<sub>2</sub> photodissociation via the  $1^{2}B_{2}$  state at wavelengths around 355 nm,<sup>44</sup> which, as discussed in Sec. I, proceeds via internal conversion to the ground electronic state. The spin-orbit populations observed here therefore provide some additional support for the notion that O-atom production from N<sub>2</sub>O<sub>4</sub> follows the two-step mechanism described above. By analogy with the long-wavelength photodissociation of NO<sub>2</sub>, it is suggested that the second step in the dissociation of N2O4 involves near threshold dissociation of a low-lying electronic state of NO<sub>2</sub><sup>"</sup>, perhaps the 1  $^{2}B_{2}$ state, subsequent to internal conversion to the ground electronic state. Secondary dissociation of NO<sub>2</sub>" borne in the  $1 {}^{4}B_{2}/1 {}^{4}A_{2}$  seems a somewhat less likely candidate, as dissociation involving an excited quartet might be expected to generate rather different spin-orbit propensities than for the ground doublet state of NO<sub>2</sub>.

## 2. Photodissociation at low NO<sub>2</sub> partial pressures

As noted in the previous subsection, at low partial backing pressures of NO<sub>2</sub> the velocity distributions for  $O({}^{3}P_{1})$ and  $O({}^{3}P_{0})$  can be assigned as arising from photodissociation of NO<sub>2</sub> monomers at the probe-only wavelength. The kinetic-energy release distribution for  $O({}^{3}P_{0})$  under these conditions is shown in Fig. 11(b). The implicit distribution of cofragment NO vibrational states at this wavelength, peaking around v=5, is clearly highly nonstatistical in nature, as expected from the previous results at a variety of photon energies above and below 226 nm.<sup>29–32,46,47,52</sup>

Velocity-map ion images of the  $O({}^{3}P_{0})$  products of NO<sub>2</sub> monomer photodissociation at 226 nm have been reported previously by Ahmed et al.<sup>47</sup> The resulting speed distribution and translational anisotropy are in excellent accord with the present low partial pressure data, although the speed distribution reported here is somewhat sharper than that obtained previously. [Note, however, that the energy scale on Fig. 2(a) of Ref. 47 is incorrect.] Interestingly, both the present work and that of Ahmed et al. at 226 nm (Ref. 47) indicate that the O-atom velocity distribution arising from photolysis of monomer NO<sub>2</sub> is unimodal. This behavior should be contrasted with the shorter-wavelength studies of Ahmed et al.<sup>46</sup> at 212.8 nm and Hancock and Morrison<sup>52</sup> at 193 nm, both of which showed evidence for a bimodal NO vibrational state distribution arising from photofragmentation of the NO<sub>2</sub> monomer (see Sec. IV C). The data reveal the opening of a new dissociation pathway at wavelengths between 226 and 212.8 nm, although inspection of the absorption spectrum in this region suggests that this new mechanism must be ascribed to exit channel dynamics, rather than to excitation into a different electronic state.

The  $O({}^{3}P_{0})$  kinetic-energy release distribution arising from NO<sub>2</sub> photolysis at 226 nm deserves special comment. Two aspects of this distribution are of interest. First, as shown in Fig. 11(b), it is a very sharply peaked distribution, suggesting that the NO cofragments are born in a narrow range of rovibrational states centered around  $\nu'=4-6$ . Second, as demonstrated by the comparison with previous work at other wavelengths shown in Fig. 11(b), apart from the bimodal feature that appears at shorter wavelengths, the position of the main peak in the associated vibrational distribution appears remarkably insensitive to photolysis wavelength. The sharp, inverted NO internal state distribution is indicative of population through a Franck-Condon-type mechanism, associated either with the excitation to the  $2^{2}B_{2}(D^{2}B_{2})$  state, or with the homogeneous predissociation of the 2  ${}^{2}B_{2}$  state, possibly by the 1  ${}^{2}B_{2}(\tilde{A} {}^{2}B_{2})$  state.<sup>51</sup> The  $2 {}^{2}B_{2}$  state has a similar bond angle to the ground state, but a considerably extended N–O bond length,<sup>40</sup> which would favor initial excitation to vibrationally excited stretching levels of the 2  ${}^{2}B_{2}$  state. Indeed, the  $\widetilde{D} \rightarrow \widetilde{X}$  dispersed fluorescence spectrum from the (0, 0, 0) level of the  $\tilde{D}$  state shows a pronounced progression in the  $\nu_1$  symmetric stretching mode, which peaks in intensity at  $v_1'=5$ ,<sup>92</sup> in remarkable agreement with the peak in the NO vibrational populations inferred here for the photodissociation of NO<sub>2</sub> via the same electronically excited state. One puzzling feature is that, if the NO vibrational populations were established in the excitation step, one might expect from simple Franck-Condon grounds that the position of the peak in the vibrational distribution might shift with photodissociation wavelength, which it clearly does not. The alternative explanation for the sharply peaked, inverted NO vibrational distribution is that it is associated with the homogeneous coupling between the  $\tilde{D}^2 B_2$  and probably the  $\tilde{A}^2 B_2$  states.<sup>51</sup> If the avoided crossing between these two surfaces occurred at extended N-O bond lengths, homogeneous predissociation would be expected to occur over a relatively narrow range of configuration space, that would be insensitive to the photolysis wavelength.

## **V. CONCLUSIONS**

The photodissociation of NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> mixtures has been studied at 308 and 226 nm using REMPI detection of the  $O({}^{3}P_{I})$  photofragments, coupled with velocity-map ion imaging. At the longer photolysis wavelength, where only NO<sub>2</sub> photofragmentation is involved, the velocity distributions of  $O({}^{3}P_{2})$  and  $O({}^{3}P_{1})$  products suggested a nonstatistical population distribution over the internal rovibrational quantum states of the NO cofragments. The atomic fragments were produced with very little electronic angular momentum polarization. Probe-only O-atom ion images were also recorded at wavelengths around 226 nm. At this wavelength, the O-atom velocity distributions were found to be bimodal, with the relative intensities of the two components depending sensitively on the NO<sub>2</sub> partial backing pressure used in the molecular-beam expansion, consistent with the competitive production of O atoms from both photolysis of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub>. The fast O-atom component, arising from the photolysis of the monomer, possessed a velocity distribution corresponding to an inverted, and sharply peaked NO cofragment vibrational distribution, consistent with previous work on the dissociation of  $NO_2$  via the second absorption band. The slow O-atom products, generated in the photolysis of the dimer, were found to be produced with a highly nonstatistical spin-orbit state population distribution, consistent with a two-step dissociation mechanism involving initial production of  $NO_2(\tilde{X}) + NO_2^*$ , followed by subsequent unimolecular dissociation of internally excited  $NO_2^*$ , possibly via the ground  $\tilde{X}$ .

## ACKNOWLEDGMENTS

We gratefully acknowledge the Royal Society for the award of a Royal Society Fellowship to one of the authors (C.V.), and the EPSRC for a research grant.

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