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Dynamics of the two-photon photodissociation of NO₂: A molecular beam multiphoton ionization study of NO photofragment internal energy distributions

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Two-photon photodissociation of NO₂ is induced by the output of a pulsed dye laser tuned over the region from 455 to 425 nm. We characterize the dynamics of this process by recording the multiphoton ionization spectrum of the product NO: intensities of spectral features associated with $\tilde{A}({}^{2}\Sigma^{+}) \leftarrow \tilde{X}({}^{2}\pi_{3/2,1/2})$ two-photon resonance enhanced, four-photon ionization of nascent NO reveal its distribution over accessible rovibronic states. A single laser pulse serves both as photodissociation source and probe. Over the wavelengths studied the dominant reaction pathway yields NO($\tilde{X}^{2}\pi$) and O(${}^{1}D$). Its dynamics in all regions of the photodissociation spectrum, save one, are comparable to those observed for the loss of O(${}^{3}P$) in one photon photolysis at comparable available excess energy. In the region of 427 nm, however, the photodissociation dynamics are dramatically different. Here we find that the photoproduct NO rotational distribution is anomalously cold, apparently limited by the rotational temperature of our supersonic molecular beam, and that a product spin-orbit state ${}^{2}\pi_{1/2}$ is missing. We argue that this result suggests a linear or near-linear dissociation geometry which imparts very little torque to the departing NO photofragment and places strict symmetry requirements on its spin-orbit state. We offer an interpretation that traces the cause of this anomalous behavior to the participation at the two-photon level of a theoretically predicted linear state of NO₂.

I. INTRODUCTION

In a previous paper we presented a survey of the visible multiphoton ionization spectrum of NO₂.¹ Our low pressure spectra obtained at wavelengths below 490 nm show that the course of ionization in this system is dominated by predissociation at the level of the second photon within the $\overline{B}^{2}B_{2}$ state. By mass analyzing the wavelength dependent ion signal, we find that by far the most prominent ion fragment generated by MPI of NO₂ at shorter wavelengths is NO⁶. Our data suggest that a high energy dissociation pathway into NO(²₁₁) + O(¹D) becomes important soon after this channel becomes energetically accessible, and that at least some of the NO so produced is born vibrationally excited.

Using a molecular beam, we have re-examined the spectrum of nascent NO from supersonically cooled NO₂, again using the same laser pulse to pump NO₂ and probe for NO. By observing NO^{*} photofragment spectra at wavelengths corresponding to the $\overline{A}(^{2}\Sigma^{*})$ + $\overline{X}(^{2}\Pi_{1/2,3/2})$ sequence band regions v' - v'' = 0, near 450 nm, and v' - v'' = 1, near 430 nm, we have been able to characterize the NO internal energy distribution.

We have found for the most part that the internal energy distribution in the nascent NO resulting from photodissociation of NO₂ at the two-photon level via the $O({}^{1}D)$ pathway qualitatively resembles that which has been observed in the one-photon dissociation of NO₂ via the $O({}^{3}P)$ pathway^{2,3} for a similar excess energy above threshold. For two-photon photolysis near 450 nm, we observe the production of both NO spin-orbit components. Vibrational and rotational excitation in the nascent NO are consistent with dissociation from the bent $\tilde{B} {}^{2}B_{2}$ upper state of NO₂.

However, in the neighborhood of 427 nm, the NO in-

ternal state distribution is dramatically different. For NO in v'' = 1, observed by means of the resonance: $\tilde{A}^2 \Sigma^* (v' = 2) - \tilde{X}^2 \Pi (v'' = 1)$, we find that the photoproduct rotational distribution is exceptionally cold, limited by the rotational temperature of our supersonic molecular beam, and that a spin-orbit component ${}^2\Pi_{1/2}$ is missing. Our data thus indicate that the dissociation dynamics are radically different in this spectral region, suggesting a linear or near-linear dissociation geometry that imparts very little torque to the departing NO photofragment, and places strict symmetry requirements on its spin-orbit state.

In this paper we present an analysis of the MPI spectrum of jet-cooled NO₂ that characterizes the anomalous behavior of the 427 nm region. We consider the source of this behavior and offer an interpretation that traces its cause to participation of the theoretically calculated but never observed $(\dots \prod_{g}^{4} 5\sigma_{g})^{2} \Sigma_{g}^{*}$ linear state of NO₂ lying above the origin of $\tilde{B}^{2}B_{2}$.

II. EXPERIMENTAL

A. General

The experimental apparatus used in our photofragment study is fully described in earlier papers.^{1,4,5} Briefly, NO₂ is introduced into our MPI source mass spectrometer system using a pulsed molecular beam value. We obtain the MPI spectrum of nascent NO from NO₂ by setting our quadrupole mass filter to m/e = 30 and scanning the dye laser over regions of the visible spectrum known to lead to state-specific resonance enhancements in NO. A diagram illustrating this detection scheme is shown in Fig. 1.

As in our previous work, two spectral regions are of particular interest. The first region from 435 to 455



FIG. 1. Multiphoton ionization scheme for the detection of nascent NO produced in the two-photon dissociation of NO_2 via the $O({}^{L}D)$ channel.

nm, covered using Coumarin 440 and spanning a twophoton photolysis energy ranging from 45 980 to 43 950 cm⁻¹, includes the NO $\tilde{A} - \tilde{X}(0, 0)$, (1, 1), (2, 2), and (3, 3) sequence bands. The second, from 422 to 422 nm and corresponding to photolysis energies from 47 400 to 46 300 cm⁻¹, includes the (1, 0), (2, 1), and (3, 2) sequence transitions.

B. Molecular beam

Our corrosion-resistant pulsed molecular beam value⁴ produces 70 μ s pulses at repetition rates up to 35 Hz. In these experiments the value is operated at 10 Hz with an orifice diameter of 800 μ m. The gas feed is a specially prepared mixture of equal proportions of NO₂ (5%) and O₂ (5%), seeded to a total pressure slightly above 1 atm with He (90%) (Air Products). We have found that the inclusion of oxygen in the reagent mixture completely suppresses the formation of NO as a contaminant. The local NO₂ pressure in the molecular beam-dye laser interaction region is the order of 60 mTorr.

We find significant rotational cooling in our supersonic expansion. Comparison of laser induced fluorescence scans of beam-cooled NO_2 in our apparatus with those published by Smalley and co-workers⁶ suggest that, under the present operating conditions, the NO_2 rotational temperature is slightly less than 30 K. As we shall find, this has important significance in our interpretation of the NO_2 photodissociation dynamics at 427 nm.

C. Laser energy

A recent study by Haas and co-workers, examining the laser energy dependence of the shapes of several MPI bands in the 400-450 nm $\overline{A} + \overline{X}$ two-photon resonance system, have revealed spectroscopic anomalies which appear at low laser power.⁷ These anomalous features substantially diminish above laser pulse energies of 1 mJ, leaving a spectrum which, for the most part, shows the proper two-photon line strength relation between lower state population and spectral intensity. All experiments in this study have been carried out with laser output energy above 1 mJ.

III. RESULTS

A. 450 nm sequence region

The NO[•] spectrum from beam-cooled NO₂ in the region from 435 to 455 nm appears in Fig. 2. From the vibrational assignment of this spectrum it is clear that an appreciable fraction of the nascent NO is formed in v'' = 1 as well as v'' = 0.

Bandheads can be clearly recognized in the (0, 0) band. It is also evident, at least in the (0, 0) band, that the NO is born with a substantial degree of rotational excitation, as evidenced by the rotational envelope, which is somewhat broader than that observed for this same resonance in room temperature NO.⁴ The rotational contour in the (1, 1) band is rather hard to discern, because the bandheads are obscured by high J lines from the (0, 0) band.



FIG. 2. Molecular beam MPI spectrum of NO^{*} from NO₂ in the 450 nm sequence region.

There are no other pronounced bands in this region of the spectrum, although there is a persistent background contribution which is not observed in the MPI spectrum of pure NO.

B. 430 nm sequence region

The spectral background seen in Fig. 2 prevails in NO^{*} spectra from NO₂ obtained at shorter wavelengths, as evidenced by Fig. 3. In this spectrum we can clearly see the (1, 0) and (2, 1) sequence transitions, with the latter dominating the former in intensity. As with the (0, 0) band, the (1, 0) feature exhibits bandheads which can be observed near the spectroscopic origins for both spin-orbit components.

This is not the case for the (2, 1) band. There, no spectral contribution whatsoever appears from rotational lines associated with the ${}^{2}\Pi_{1/2}$ spin-orbit component. This is not an artifact of a falling laser tuning curve; the laser energy is constant to within 20% over the entire duration of this scan.



FIG. 3. Molecular beam MPI spectrum of NO^{+} from NO_{2} in the 430 nm sequence region.

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Given the high intensity of this band it is also interesting to note how narrow it is when compared to either the (0, 0) or (1, 0) vibrational bands. Qualitatively, the narrow spectral width of this feature indicates that the NO produced at this wavelength has an extremely narrow rotational distribution.

Between the (2, 1) and (1, 0) bands, near 428 nm, lies a group of features which, on the basis of wavelength and intensity, cannot be readily associated with either of these bands. There is one strong feature in this group, lying furthest to the red at 428.2 nm, which we persistently observe both in leak valve and molecular beam experiments on pure NO while scanning to the blue side of the (1, 0) resonance. Under such conditions the intensity of this feature is anomalously large if it is viewed simply as a high J line belonging to the S branch of the $\tilde{A}(^{2}\Sigma^{*}) + \tilde{X}(^{2}\Pi_{1/2})$ (1, 0) band.

There is no conclusive evidence for the production of a significant amount of NO in v'' = 2 from NO₂ in this wavelength region on the basis of Fig. 3. There is a very small peak just below 423 nm which may correspond to the $\tilde{A}(^{2}\Sigma^{*}) - \tilde{X}(^{2}\Pi_{3/2})$ (3, 2) origin, the other spin-orbit component, if present, would lie off to the left of this spectrum.

IV. DISCUSSION I: SPECTROSCOPIC ANALYSIS

A. Spectral simulation

Our scans of the MPI spectrum of NO₂ yield information about the rotational and vibrational state population distributions of nascent NO produced in two-photon photodissociation of parent NO₂. In order to quantify this product-state distribution information we have developed a computer program to calculate rotational band contours for bands belonging to the $\tilde{A}({}^{2}\Sigma^{*}) - \tilde{X}({}^{2}\Pi_{1/2,3/2})$ system in NO. This program calculates the transition energies and transition amplitudes as formulated below to generate a theoretical NO spectrum.

1. Transition energies

The pattern of rotational subbands observed in the $\tilde{X}({}^{2}\Pi)$ to $\tilde{A}({}^{2}\Sigma^{*})$ MPI resonances of NO are governed by two-photon selection rules as well as by the rotational energy level structure in each of these states. Equations (1) and (2) give the energy of the rotational transition $\tilde{A}({}^{2}\Sigma^{*}, v', J' = J'' + m) \leftarrow \tilde{X}({}^{2}\Pi, v'', J'')$ for a two-photon process^{8,9}

$$E_{F'=2,F''=(1,2)}^{\Delta J=m} = 1/2 \left\{ v_0^{(1,2)} + J'' \left[B'(m+1) - B'_{(1,2)} \right] + J''^2 (B' - B'_{(1,2)}) + B'(m^2 + 2m + 3/4) \right\},$$
(1)

$$E_{F'=1,F''=(1,2)}^{\Delta J = m} = 1/2 \left[v_0^{(1,2)} + J''(2mB' - B''_{(1,2)}) + J''^2(B' - B''_{(1,2)}) + B'(m^2 - 1/4) \right].$$
(2)

In these formulas, $v_0^{(1,2)}$ are the zero point energies for the vibronic transitions $\tilde{A}(^2\Sigma^*, v') - \tilde{X}(^2\Pi_{1/2, v'})$ and $\tilde{X}(^2\Pi_{3/2, v'})$. The rotational constants B_1'' and B_2'' are different for each spin-orbit component, but are related to the quantity $B_{e'}'$ and the vibrational quantum number v'' by

$$B_{(1,2)}^{\prime\prime} = B_{v}^{\prime\prime} \left[1 \mp (B_{v}^{\prime\prime}/A) \right]$$

where

$$B_{v}'' = B_{e}'' - \alpha_{e}''(v'' + 1/2)$$
.

By setting m = -2(O), -1(P), 0(Q), +1(R), and +2(S), the transition energies for each rotational branch in the spectrum can be calculated using Eqs. (1) and (2). Each branch has four subbranches. These are traditionally classified according to the F numbers in the upper and lower states.⁹ Either Eq. (1) or (2) is then used in the calculation as the F number in the upper state is 1, or 2, respectively.

We use the spectroscopic constants tabulated by Herzberg⁹: $B'_{e} = 1.9952 \text{ cm}^{-1}$, $B''_{e} = 1.7046 \text{ cm}^{-1}$, $\alpha'_{e} = 0.0164 \text{ cm}^{-1}$, and $\alpha''_{e'} = 0.0178 \text{ cm}^{-1}$. The spin-orbit coupling constant is $A = 124.2 \text{ cm}^{-1}$ and the ${}^{2}\Sigma^{*} \rightarrow {}^{2}\Pi_{1/2}$ term difference $(T'_{e} - T'_{e'}) = 43965.7 \text{ cm}^{-1}$. Ground-state vibrational constants are $\omega'_{e} = 1904.03 \text{ cm}^{-1}$, $\omega_{e} x''_{e} = 13.97 \text{ cm}^{-1}$, while the corresponding upper state values are $\omega'_{e} = 2371.3 \text{ cm}^{-1}$ and $\omega'_{e} x''_{e} = 14.48 \text{ cm}^{-1}$.

2. Transition amplitudes

The second part of our simulation program calculates the transition amplitudes. For an absorption line the transition intensity is given by 10

$$I_{abe}(v'', j'' - v', J')$$

$$\propto f(v)q_{v',v'}, S_{J',J''}(2J''+1)^{-1}N_{v''}(J'') .$$
(3)

In this equation f(v) is a function which depends linearly on the frequency and $q_{v',v''}$ is the Franck-Condon factor for the vibrational band (v', v''). $S_{J',J''}$ is a two-photon line strength factor, and $N_{v''}(J'')$ represents the relative fraction of molecules in the state (v'', J'') with respect to the total population taken over all occupied states.

Over the narrow spectral range occupied by a group of NO sequence bands, the variation in the frequency factor f(v) is insignificant, and is omitted from the calculation. Two-photon line strengths are taken from the paper by Halpern and co-workers.¹⁰

Ideally, a characterization of the internal energy distribution of a dissociation fragment is based on the determination of $N_{\nu'}$, (J'') values for all accessible vibrational and rotational states. Our experiments, however, have insufficient resolution to yield individual state populations. Moreover, the notion of a detailed internal energy distribution is slightly distorted here by the fact that the photolysis energy steadily changes (by a small amount) over the course of a scan. As a consequence, we resort to band contour simulation to analyze our NO photofragment spectra. Although there is no basis for the a priori assumption of a Boltzmann distribution among the rotational populations in the v'' = 0and v'' = 1 levels of NO from NO₂, this distribution is computationally easy to include in the calculations and is the approach we have adopted. To the extent that a rotational temperature then determines a range of populated rotational states, we compare our observed distributions with calculated ones, without attempting to make any detailed statements about single level populations.

B. Comparison of simulation with room temperature spectrum

We have tested our simulation routine by comparison to an experimental NO MPI spectrum obtained under room temperature conditions. Although it reveals some minor differences for particular lines, this comparison shows excellent overall agreement with respect to the relative intensities of the bandheads associated with each spin-orbit component. Intensities most noticeably in disagreement are evident in the region of the Rand S branch transitions at the shorter wavelengths, where we observe a greater spectral intensity in the high J regions of the R and S branches near 450.5 nm than is predicted by calculation.

Molecular beam scans to the blue of the (0, 0) and (1, 0)bands in pure NO both show peaks which indicate that there are other, weaker MPI resonances at these wavelengths available to NO molecules starting from low rotational levels in v''=0 (see Fig. 4 of Ref. 4).^{11(a)} It appears, therefore, that the anomalous intensities seen at wavelengths corresponding to the high J rotational transitions of the R and S branches in these bands are related to the resonant participation of higher lying electronic states in the MPI process. As indicated above, the extent of this participation appears to be strongly influenced by the laser energy, although its mechanism, as well as the states involved, are not yet clear.^{7,11(b),12} In view of this slight complication we believe that the relative bandhead intensities provide the most reliable means for examining the distribution of NO photofragment rotational states produced in the twophoton dissociation of NO2.

C. Temperature dependence of NO bandhead features

Spectral calculations (assuming equal spin-orbit populations) for the NO $\tilde{A} - \tilde{X}$ (1,0) band for a series of rotational temperatures are shown on the right-hand side of Fig. 4. Legends at the top of the figure identify the prominent bandheads. At 50 K, the main spectral features are the heads due to the $P_{22} + Q_{12}$ subbranches in the ${}^{2}\Pi_{3/2}$ component and to the $P_{21} + Q_{11}$ subbranches in the ${}^{2}\Pi_{1/2}$ component. Although these heads are labeled with combined designations (e.g., $P_{21} + Q_{11}$), by far the main contribution to the spectral intensity in this region comes from rotational lines associated with the P_{21} and P_{22} subbranches whose rotational line strengths are three orders of magnitude larger than those of the Q_{11} and Q_{12} subbranches.

The reason for the prominence of these bandheads at low temperature is that they occur at low values of J. As the temperature is increased, the peak of the rotational distribution shifts to higher J and these bandheads become substantially less pronounced. Higher temperature *enhances* the appearance of other bandheads whose long wavelength limit corresponds to larger rotational quantum numbers. As a result, at 200 K and above, the $O_{21} + P_{11}$ and $O_{22} + P_{12}$ subbranches dominate the spectrum, with the O_{11} and O_{12} subbranches becoming increasingly important at still higher temperatures. in each spin-orbit component in the $\tilde{X}({}^{2}\Pi)$ state of nascent NO from NO₂, we compare the relative intensities of the $O_{21} + P_{11}$ and O_{11} bandheads corresponding to the ${}^{2}\Pi_{1/2}$ component with the analogous $O_{22} + P_{12}$ and O_{12} bandheads of the ${}^{2}\Pi_{3/2}$ component.

The rotational distribution in the ${}^{2}\Pi_{3/2}$ spin-orbit state is most easily studied in the O_{12} subbranch, which converges to a head at $J'' = 18 \frac{1}{2}$ and is not masked by any other overlapping transitions. Our calculations clearly show that the O_{12} band contour is very sensitive to the position of the maximum in the rotational distribution. It is only sharp and well defined when the rotational distribution peaks near $J'' = 18\frac{1}{2}$.

Extracting the ${}^{2}\Pi_{1/2}$ rotational distribution by a similar means is not possible because the O_{11} subbranch is overlapped by Q, R, and S transitions from the ${}^{2}\Sigma^{*} - {}^{2}\Pi_{3/2}$ subband. Comparison of the spectra calculated between 200 and 1000 K shows, however, that the ratio of apparent $O_{11}: O_{21} + P_{11}$ bandhead intensities gives a good indication as to whether the ${}^{2}\Pi_{1/2}$ spin-orbit component is present with a moderate, or substantial degree of rotational excitation. Exactly the same argument applies with respect to the relative intensities of the $O_{22} + P_{12}$ and O_{12} bandheads in the ${}^{2}\Pi_{3/2}$ spin-orbit component.

D. Analysis of the 430 nm sequence region

The calculations on the right-hand side of Fig. 4 can be compared to the experimental contour observed for the (1, 0) band of nascent NO from NO₂ shown in Fig. 3. It is clearly apparent that all bandheads predicted by the calculations in the high temperature regime at the top of Fig. 4 are present in the experimental spectrum. Based on a comparison of their relative intensities it is clear that: (a) there are approximately equal fractions of population in the two spin-orbit components; and (b) the rotational distribution is rather broad. A temperature of between 500 and 1000 K provides satisfactory agreement between calculated and experimental spectra. The low intensity of the (1, 0) band as well as the significant underlying background intensity prevent an estimation of the rotational temperature with any more certainty than this.

Behavior in the (2, 1) band is very different. Calculated spectra for this band are shown on the left-hand side of Fig. 4. Again we use a linewidth of 1.5 cm^{-1} , but in this instance we have removed the spectral contribution from the ${}^{2}\Pi_{1/2}$ component entirely. The effect of this on the overall band contour can be seen by comparing the 200 K spectra in the two halves of Fig. 4.

Several interesting features emerge as we cool the simulated spectrum at the top left of Fig. 4 to very low temperatures. As expected, the O_{12} subbranch, which is never prominent below room temperature, recedes entirely. At 200 K, the $O_{22} + P_{12}$ subbranches are stronger than the $P_{22} + Q_{12}$. The relative intensities of these features change significantly as the temperature is lowered, being approximately equal at 140 K, but with the $P_{22} + Q_{12}$ subbranches dominating at still lower temperatures. The $O_{22} + P_{12}$ subbranches have disappeared

For the purpose of estimating the relative populations



Wavelength (nm)

almost completely at 35 K. Concomitant with the falling relative intensity in this subbranch, we see that the spacing between maxima in this subbranch and the P_{22} + Q_{12} subbranch also decreases with decreasing temperature.

Wavelength (nm)

Based on the relative intensities of the $P_{22} + Q_{12}$ and $O_{22} + P_{12}$ subbranches, as well as on the overall calculated width of the (2, 1) band, we conclude that a rotational temperature of about 70 K gives a good match to our experimental data. Although the $O_{22} + P_{12}$ subbranch is a little more intense in the calculated spectrum than in the experimental one, lowering the temperature still further causes the overall calculated contour to be clearly too narrow to agree well with Fig. 3.

tral region confirm two important conclusions. First,

the relative NO spin-orbit populations as indicated by Fig. 3 are drastically different in the (1, 0) and (2, 1)bands. In the former they are approximately equal, while in the latter the lower spin-orbit component ${}^{2}\Pi_{1/2}$ is missing entirely. Second, the apparent rotational temperatures suggested in the two vibrational bands are markedly different. The width of the rotational distribution in NO (v'' = 0) is considerably greater than that at room temperature, while that in v'' = 1, as reflected by the (2, 1) band, is obviously very much narrower.

Further confirmation of this last point is to be found by examining the much higher resolution data of NO from NO₂ recorded in Fig. 5. This spectrum was obtained in the vicinity of the steeply rising region of the (2, 1)

FIG. 4. MPI band contour calculations for the NO $\widetilde{A} \leftarrow \widetilde{X}$ bands (1,0) (right), and (2, 1) (left), at a number of trial rotational temperatures. Refer to the text for details.





FIG. 5. Higher resolution scan of the region designated $\widetilde{A}(^{2}\Sigma^{*}) \leftarrow \widetilde{X}(^{2}\pi_{3/2})$ (2, 1) in Fig. 2. The unlabeled structure on the right appears in the spectrum of room temperature NO and thus cannot be associated with v'' = 1.

probe NO produced from precursor NO_2 molecules in the coldest region of the pulsed jet.

A comparison of Figs. 3 and 5 reveals some further spectral simplification in the (2, 1) band under this con-

dition, as well as a pronounced change in relative intensities, especially near the $\tilde{A}(^{2}\Sigma^{*}) - \tilde{X}(^{2}\Pi_{3/2})$ origin. Two intense peaks are observed in Fig. 5 to the blue of the $O_{22} + P_{12}$ subbranch. This behavior is precisely what we find in calculated spectra of the (2, 1) band at very low rotational temperatures, and is just beginning to become evident at a simulated temperature of 35 K in the bottom left of Fig. 4.

When the NO rotational distribution is so narrow that only a small number of rotational states are populated, we must carefully consider the low J dependence of the two-photon line strength factors, as these are of primary importance in determining the appearance of calculated spectra. The diagram in Fig. 6 shows calculated transition energies and line strengths relevant to a discussion of Fig. 5. The positions of the two bandheads $P_{22} + Q_{12}$ and $O_{22} + P_{12}$ are in the center, and toward the right edge of Fig. 5, respectively. To the blue of these features, we also find a $Q_{22} + R_{12}$ subbranch whose first member $J'' = 1\frac{1}{2}$ lies near 426.8 nm, with subsequent lines appearing at successively shorter wavelengths. The two-photon line strength formulas predict the intensities of the $Q_{12}(J'')$ and $Q_{22}(J'')$ rotational transitions to be equal, but also to decrease very rapidly as a function of increasing $J^{\prime\prime}$. The first line in each of these branches is predicted to have much greater weight than any of the other lines in this spectral region.

With the aid of Fig. 6, we now consider the expected NO MPI spectral response assuming that only a very small number of the lowest rotational levels in NO



FIG. 6. Calculated transition energies and line strengths for rotational transitions in the vicinity of the NO $\widetilde{A}(^{2}\Sigma^{*}) - \widetilde{X}(^{2}\pi_{3/2})$ (2, 1) rovibronic origin.

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(v'' = 1) are populated in the two-photon photodissociation of NO₂. For this case, we expect a strong feature near 426.9 nm, due to the pileup of rotational transitions in the $P_{22} + Q_{12}$ subbranches. If we further suppose that the distribution is confined to values of $J^{\prime\prime}$ $<5\frac{1}{2}$, we expect a sharp drop in intensity as we scan to shorter wavelengths, until we encounter the strong Q_{22} + $R_{12} J'' = 1\frac{1}{2}$ transition. Then, to still shorter wavelengths, we expect a short series of rotational transitions with a slightly increasing spacing corresponding to the low J members of the $Q_{22} + R_{12}$ subbranch. Consistent with a scheme in which only the lowest rotational levels in ${}^{2}\Pi_{3/2}(v''=1)$ are produced in the photodissociation, the $O_{22} + P_{12}$ subbranch at longer wavelengths is not expected to be pronounced, because the distribution is terminated well before the bandhead is reached at $J'' = 10\frac{1}{2}$, $11\frac{1}{2}$. The spectral assignment in Fig. 5 follows from this discussion and supports our earlier suggestion that the nascent NO in $v^{\prime\prime}$ =1 produced from photodissociation of NO₂ near 427 nm is born with very little rotational excitations. In addition our data also lends support to the predicted low J behavior of the two-photon line strength formulas.

E. Analysis of the 450 nm sequence region

The band contours presented in Sec. IV C can be compared in a similar fashion to the (0, 0) and (1, 1) bands observed in the 450 nm sequence region. Although the two-photon photolysis energy here is about 2000 cm⁻¹ less than in the 430 nm region, we find that the (0,0) band is similar to the (1,0) band. An examination of the (0,0)band in Fig. 2 suggests that slightly more NO is produced in the ${}^{2}\Pi_{1/2}$ than in the ${}^{2}\Pi_{3/2}$ spin-orbit component. However, owing to the output tuning curve of Coumarin 440, our spectrum slightly underestimates the relative contribution due to the ${}^{2}\Pi_{3/2}$ component.

The O_{12} subbranch in this band can be clearly recognized just below 455 nm. The fact that it is well defined and there is appreciable intensity extending all the way to the bandhead suggests considerable rotational excitation in the ${}^{2}\Pi_{3/2}$ spin-orbit component. An independent scan of this feature yielded a rotational temperature of 900±100 K when compared to the computer calculations. This result is verified by the observed $O_{12}: O_{22} + P_{12}$ bandhead ratio, and a similar temperature is implied for the other spin-orbit component based on the relative intensities of the O_{11} and $O_{21} + P_{11}$ subbranches.

As noted earlier, there is a considerably greater intensity in the (0, 0) band near 450.5 nm than is expected on the basis of our calculations. Unfortunately, this obscures the O_{12} subbranch belonging to the (1, 1) band, which lies in the same wavelength region. Although the spectrum in Fig. 2 does appear to show the presence of both spin-orbit components in this band, the heads are not well enough defined to permit a reliable comparison with our calculations. A quantitative analysis of the (1, 1) band is thus not possible, considering the significant degree of overlap with the high energy tail of the (0, 0) band. Also, there are clearly some anomalous intensities between 445 and 447 nm which have yet to be adequately explained. Our only remaining recourse is to examine the overall width of this feature, which suggests a rather broad rotational distribution for the NO(t' = 1) produced at this wavelength.

V. DISCUSSION II: PHOTODISSOCIATION DYNAMICS

A. Earlier studies of the $O(^{3}P)$ pathway

Conservation of energy in the photodissociation of a triatomic ABC, leading to the fragments AB and C, requires that

$$E_{avl} = E_{int}^{ABC} + h\nu - D_0(AB-C)$$
$$= E_t + E_{int}(AB, C) . \qquad (4)$$

Equation (4) expresses the partitioning of the energy in excess of the dissociation threshold E_{avl} among E_t , the center-of-mass translational energy of the fragments, and E_{int} , their internal energies.^{13,14}

The threshold energy D_0 for production of the ground state fragments $NO(^{2}\Pi)$ and $O(^{3}P)$ from NO_{2} is 25132 cm⁻¹.² If we consider photolysis energies restricted to less than $50\,000 \text{ cm}^{-1}$, then Eq. (4) constrains the total fragment internal excitation to a maximum value of 25 000 cm⁻¹. Since the lowest excited state of NO[$\tilde{a}'({}^{4}\Pi)$] lies 38 440 cm⁻¹ above the ground state $\bar{X}(^{2}\Pi)$, ¹⁵ it is energetically inaccessible. On the other hand, production of the lowest excited state of the oxygen atom $O(^{1}D)$, at 15868 cm⁻¹ above the ^{3}P state is energetically possible, with a dissociation threshold at 41 000 cm⁻¹. Electronic states of the fragments from NO_2 photodissociation at energies below 50000 cm⁻¹ are thus limited to the nitric oxide spin-orbit components ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$ (energy separation 120 cm⁻¹), and the various multiplet levels of oxygen atom ground $O(^{3}P)$ and first $O(^{1}D)$ excited states. The remaining contribution to E_{int} must include the possibility that the diatomic fragment NO may be vibrationally and rotationally excited.

Owing to the fact that there are a variety of ways of distributing E_{av1} among E_t and E_{int} , photodissociation of NO₂ results in a distribution of center-of-mass translational recoil energies E_t . If the distribution of internal energies of the original NO₂ can be ignored, so that E_{av1} is then known precisely, the fragment internal energy distribution can be inferred from a measurement of the translational energy distribution.

This approach was adopted by Busch and Wilson² in their pioneering photofragment experiments on NO₂. These workers photodissociated NO₂ in a molecular beam with doubled ruby laser radiation (347 nm) finding, by time-of-flight analysis, almost equal amounts of NO photoproduct in v'' = 0 and v'' = 1. Because of limited translational energy resolution, no information was obtained about the partitioning of the product NO between its spin-orbit states, nor with respect to the population distribution over accessible rotational levels.

Very recently, NO₂ photodissociation dynamics in the near UV has been reexamined by Welge and co-workers.³ In their experiment a nitrogen laser operating at $\lambda = 337.1$ nm (29 965 cm⁻¹) was used to photolyze NO₂ in a static cell, while a tunable UV laser monitored the production of NO in selected rovibrational states direct-

ly, through excitation of fluorescence from its $\tilde{X}({}^{2}\Pi_{1/2,3/2}) - \tilde{A}({}^{2}\Sigma^{*})$ system. Because of much improved resolution (0.6 cm⁻¹), the NO internal energy distribution was characterized in considerably greater detail in this study. The important features of this distribution were found to be (a) production of NO in vibrational levels up to, and including v'' = 2, (b) inverted vibrational population distributions, (c) broad, non-Boltzmann rotational distributions, and (d) population of both NO spin-orbit states.

On energetic grounds the dissociation pathway probed in these near UV experiments is the one leading to $NO(^{2}\Pi)$ and $O(^{3}P)$. Its dynamics can be understood in terms of a simple geometric model for energy disposition. Vibrational excitation follows from differing bond lengths in excited NO_{2} and product NO by application of intrafragment Franck-Condon arguments.^{15,16}

Broad rotational distributions are readily explained by conservation of angular momentum: The sum of the orbital angular momentum of the separating fragments land the rotational angular momentum of the NO, j, must equal the initial rotational angular momentum of the NO₂ parent. Thus, for irrotational NO₂ (a condition nearly met in our supersonic expansion) we have^{17, 18}

$$\mu g b = \hbar [j(j+1)]^{1/2} , \qquad (5)$$

where μ is the reduced mass of the separating NO and O fragments, g is their terminal relative velocity, and b is the exit impact parameter. The extensive rotational excitation of NO produced in the 337.1 nm photolysis of NO₂ suggests dissociation from a bent excited state.

B. Photodissociation dynamics of the $O(^{1}D)$ pathway

On energetic grounds, photons of wavelength longer than 397.86 nm cannot result in dissociation of NO₂ to NO+O unless more than one is absorbed. In our earlier work we established that photodissociation in the visible multiphoton ionization of NO₂ occurs above the origin of the strongly predissociated \tilde{B}^2B_2 system at the level of the second photon.¹ Soon after it becomes energetically possible the O(¹D) pathway is observed to dominate. The dynamics of this pathway as reflected in its spectroscopic signature can be summarized as follows:

In the 450 nm NO \overline{A} + $\overline{X}(0,0)$ sequence region, the nascent NO is produced only in v'' = 0 and v'' = 1 vibrational levels. As the dye laser is scanned over wavelengths at which we would expect to observe higher vibrational levels if they were populated, we see no evidence of the corresponding NO $\tilde{A} - \tilde{X}$ resonances, despite favorable Franck-Condon factors.¹⁹ Both the (0, 0)and (1, 1) sequence bands indicate that the NO₂ photodissociation results in a significant amount of rotational excitation in the NO fragment. For the former case in which our model calculations match the relative bandhead intensities in the MPI spectrum under the assumption of a Boltzmann distribution, we find a temperature of 900 K. Due to spectral overlap of the short wavelength end of the (0, 0) band with the long wavelength end of the (1, 1) band, we can only comment on the relative spin-orbit populations for nascent NO produced in v'' = 0. Here we find slightly more population in the lower spin-orbit state ${}^{2}\Pi_{1/2}$ than in the upper ${}^{2}\Pi_{3/2}$, a result which is hardly surprising considering the small ${}^{2}\Pi_{3/2} - {}^{2}\Pi_{1/2}$ energy splitting (120 cm⁻¹).

The view which emerges from an analysis of the (1, 0) band in the 430 nm sequence region is substantially the same—a broad rotational distribution with both spinorbit components populated. To shorter wavelengths, observation of the (2, 1) band again provides clear-cut evidence for the production of NO in v''=1. The remaining portion of this spectrum is devoid of any features which would definitely suggest production of NO in higher vibrational levels.

A careful examination of the (2, 1) band reveals two most intriguing facts. Besides reflecting the production of NO exclusively in its ${}^{2}\Pi_{3/2}$ spin-orbit state, the appearance of this band indicates a very narrow rotational state distribution, in both respects quite unlike any of the other bands we have studied.

With the exception of this latter feature, our results bear a marked similarity to the findings of the two earlier studies of the $O({}^{3}P)$ dissociation pathway in NO₂. In the present experiments, however, the excess energy above the $O({}^{3}P)$ dissociation threshold is at least 13 000 cm⁻¹ greater than that for nitrogen laser photolysis at 337.1 nm. This difference is almost exactly taken up by the electronic energy of $O({}^{1}D)$. Thus, for comparable, *available* excess energy we find similar dynamics at the one- and two-photon levels. Entirely consistent with the known geometry of $\tilde{B}^{2}B_{2}$ ($r_{\rm NO}$ =1.314 Å, θ = 120°), this similarity lends support to our assignment of the visible, two-photon photoexcitation and dissociation mechanism of NO₂ in all regions but that of the anomalous NO(2, 1) band.

The situation for two-photon photodissociation at 427 nm is quite different. At this wavelength the effective photolysis energy is 46840 cm⁻¹, leaving 5840 cm⁻¹ to dispose in translational and internal energy of the fragments. Recognition of the fact that we here probe photoproduct NO in v'' = 1 fixes its vibrational energy content at 1904 cm⁻¹. The extraordinarily narrow width of the observed rotational distribution establishes by energy balance that essentially all of the remaining 3940 cm⁻¹ must be released into fragment recoil. With the considerable relative velocity this implies, classical dissociation from a bent state is inadmissible on the basis of angular momentum conservation; Eq. (5), for rotationally cold reactant NO₂ and product NO, requires low orbital angular momentum, which, given the present recoil energy, can only be the case if the dissociation takes place from a linear or near linear geometry.

This conclusion is not necessarily altered when we consider the more realistic case of a quantized, nonrigid linear triatomic with finite amplitude bends associated with either the ground or excited vibrational states. Morse, Freed, and Band²⁰ have shown that under conditions where the nascent distribution of product states is well described by the corresponding distribution of bound to repulsive Franck-Condon amplitudes, the distribution of diatomic j will peak near

zero for J=0 linear triatomic parent. The precise value of the average energy of diatomic rotation will depend on the energy initially in the bend, but, interestingly, it is predicted to be smallest for molecules with largest amplitude zero-point bending motions.

On the basis of the above arguments, we thus conclude that our data can be reasonably explained if in addition to the $\tilde{B}(^{2}B_{2})$ state of NO₂, there exists a linear excited state accessible in a two-photon transition, that leads to the dissociation products $NO(^{2}\Pi)$ and $O(^{1}D)$. The missing ${}^{2}\Pi_{1/2}$ spin-orbit component in the (2, 1) band is a point of additional curiosity which we address in the next section.

C. Two-photon photodissociation at 427 nm

Ground state NO_2 is bent. Inspection of the Walsh diagram for NO_2 reveals two low-lying transitions to states that can be expected to be linear.^{21,22} The first, $6a_1 \rightarrow 2b_1$ terminates as $\bar{A}'^2 B_1$. Spectroscopic data of Douglas and Huber yield to analysis of this system as a bent to linear transition.²³⁻²⁵ Perhaps significantly, the region around 430 nm is dominated by clear progressions in this state.²⁴

The second transition to a state with potential for linearity is $6a_1 - 7a_1 (2\pi_u - 5\sigma_e)$. This configuration in the linear form of NO_2 is the dominant contributor to ${}^{2}\Sigma_{g}^{*}$. Though never observed, this state has been approximately placed by the calculations of Gillispie et al. to lie near the origin of $\tilde{B}^2 B_2$.²⁶ Thus, if we can imagine access from the bent $\tilde{X}^2 A_1$ ground state of NO₂ to low-lying vibrational levels of ${}^{2}\Sigma_{g}^{*}$, perhaps through the intermediacy of $\tilde{A}'^2 B_1$, we can rationalize the apparent linearity suggested by our spectroscopic data at 427 nm.

Explanation of the missing spin-orbit component requires that we consider the specific photodissociation pathway. We suscept on the basis of the behavior of $\bar{B}^{2}B_{2}$ that the state we are preparing at 427 nm proceeds to $O(^{1}D)$ and $NO(^{2}\Pi)$ by electronic predissociation. That is, we assume that a repulsive state, correlating to $O(^{1}D)$ and $NO(^{2}\Pi)$ crosses our optically prepared state so that internal conversion carries our system to products. To account for the data, this repulsive state must carry linear NO₂ exclusively to NO($\tilde{X}^2 \Pi_{3/2}$) and strongly connect to our optically prepared state (presumably ${}^{2}\Sigma_{g}^{*}$) by the selection rules for predissociation.

The possible choices for this repulsive state can be determined by examining the reverse problem of combining NO($^{2}\Pi$) and O(^{1}D) to form NO₂. Space quantization in the inhomogeneous electric field along the internuclear axis produces a manifold of triatomic electronic states, the identities of which are determined by coupling the projections of the fragment electronic angular momenta.

The importance of this effect for photodissociation is that, even though separate atomic orbital angular momentum projections and diatomic spin-orbit states lose their meaning in the combined triatomic, the projections: λ (combined orbital angular momentum) and Ω (total electronic angular momentum) are well defined

$$O(^{1}D) NO(^{2}\Pi) NO_{2}$$



FIG. 7. Diagram combining projected spin and orbital angular momentum components of NO($\tilde{X}^2 \pi_{1/2,3/2}$) and O(¹D) to form the correlated term manifold of NO2.

at all internuclear separations. Thus, in general, given λ and Ω values in the triatomic yield only particular magnetic quantum numbers and spin-orbit states in the separated fragment. 27

For the particular case of a diatomic molecule combining with an atom to form a linear complex, the resultant space quantized angular momentum is given by

$$\lambda = \left| M_L + M_\lambda \right| \, ,$$

where M_L refers to the orbital angular momentum projection of the atom and $M_{\lambda} = \pm \lambda$ to that of the diatomic.^{28,29} Recognizing that molecular states which differ only in their signs of M_L and M_{λ} are doubly degenerate, and that cases leading to $M_L + M_\lambda = 0$ give rise to Σ states with different energies,²⁹ the allowed list of NO₂ molecular states from $O(^{1}D)$ and $NO(^{2}\Pi)$ includes two Σ states, two II states, a Δ state, and a ϕ state.

Coupling spin to orbital angular momentum specifically connects spin-orbit states of NO($^{2}\Pi$) with M_{L} components of $O(^{1}D)$ to yield particular spin orbit components of NO2. Figure 7 diagrams each of the possible combinations.

Selection rules for predissociation recognize two types of nonradiative transitions: homogeneous and weaker heterogeneous predissociation, distinguished on the basis of whether the good electronic angular momentum

quantum number changes by 0 or by ± 1 , respectively.²⁹ Inspection of Fig. 7 reveals only one state that is both homogeneously connected to ${}^{2}\Sigma_{f}^{*}$ and exclusively correlated to NO(${}^{2}\Pi_{3/2}$). That state is NO₂(${}^{2}\Pi_{1/2}$):

 $NO_2(^2\Pi_{1/2}) \rightarrow NO(^2\Pi_{3/2}) + O(^1D, M_L = \pm 2)$.

Thus, we conclude that two-photon excitation of NO₂ at 427 nm accesses a high-lying linear state of this triatomic, probably $(\dots 1\pi_{\ell}^{4}5\sigma_{\ell})^{2}\Sigma_{\ell}^{*}$ predicted by theory. This optically prepared state appears to be efficiently predissociated by a repulsive state, probably NO₂($^{2}\Pi_{1/2}$), that correlates to NO($^{2}\Pi$) and O(^{1}D) in a process that is remarkably selective in its production of particular NO spin-orbit and oxygen atom M_{L} states.

The one-photon photodissociation dynamics of NO_2 in this energy region have not been studied. Whether or not the same states and same dynamics are realized in single-photon excitation is an intriguing question. Perhaps relaxation at the level of the first photon plays a critical role in attaining the fragmentation pathways evident here. We intend to address this question by exploring the photodissociation dynamics of NO_2 at 213 nm. We also intend to probe higher in two photons to thoroughly map what promises to be an interesting new system of electronic states for this venerable old triatomic.

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- ¹R. J. S. Morrison, B. H. Rockney, and E. R. Grant, J. Chem. Phys. **75**, 2643 (1981).
- ²G. E. Busch and K. R. Wilson, J. Chem. Phys. 56, 3626 (1972).
- ³H. Zacharias, M. Geilhaupt, K. Meier, and K. H. Welge, J. Chem. Phys. **74**, 218 (1980).
- ⁴T. E. Adams, B. H. Rockney, R. J. S. Morrison, and E. R. Grant, Rev. Sci. Instrum. 52, 1469 (1981).
- ⁵B. H. Rockney and E. R. Grant, Chem. Phys. Lett. **79**, 15 (1981).
- ⁶R. E. Smalley, L. Wharton, and D. Levy, J. Chem. Phys. **63**, 4977 (1975).

- ⁷E. Sirkin, M. Asscher, and Y. Haas, Chem. Phys. Lett. **82**, 265 (1982).
- ⁸Similar formulas were obtained in R. G. Bray and R. M. Hochstrasser, Chem. Phys. Lett. **27**, 167 (1974).
- ⁹G. Herzberg, Spectra of Diatomic Molecules (Van Nostrand, New York, 1950).
- ¹⁰J. B. Halpern, H. Zacharias, and R. Wallenstein, J. Mol. Spectrosc. **79**, 1 (1980).
- ¹¹(a) The unassigned resonances we observe in molecular beam scans are located at 450.67, 450.54, and 428.25 nm. Similar behavior is apparent in the data of Refs. 7 and 12. (b) Very recent work has assigned this structure to accidental double resonance involving the \widetilde{A} state and high-lying vibrational levels in the \widetilde{B} , \widetilde{C} , \widetilde{K} , and \widetilde{L} states. See: M. Seaver, M. White, W. A. Chupka, and S. D. Colson (to be published);
- W. Y. Cheung, Ph.D. dissertation, Yale University, 1982. ¹²L. Zandee and R. B. Bernstein, J. Chem. Phys. **71**, 1359 (1979).
- ¹³R. Bersohn, IEEE J. Quantum Electron QE-16, 1208 (1980).
- ¹⁴J. P. Simons, in Gas Kinetics and Energy Transfer (The Chemical Society, London, 1977), Vol. 2, Chap. 2.
- ¹⁵K. P. Huber and G. Herzberg, Constants of Diatomic Molecules (Van Nostrand, New York, 1979).
- ¹⁶J. P. Simons and A. J. Yarwood, Trans. Faraday Soc. 59, 90 (1963); R. C. Mitchell and J. P. Simons, Discuss. Faraday Soc. 44, 208 (1967).
- ¹⁷T. Carrington, J. Chem. Phys. **41**, 2012 (1964).
- ¹⁸J. P. Simons and P. W. Tasker, Mol. Phys. 27, 1691 (1974);
 M. N. R. Ashfold and J. P. Simons, J. Chem. Soc. Faraday Trans. 74, 280 (1978).
- 19 Franck-Condon factors for the γ bands of NO are tabulated in S. N. Suchard, Aerospace Report No. TR-0074 (4641)-6, Vol. 3, 1974.
- ²⁰M. D. Morse, K. F. Freed, and Y. B. Band, J. Chem. Phys. 70, 3604, 3620 (1979); M. D. Morse and K. F. Freed, *ibid.* 74, 4395 (1981).
- ²¹A. D. Walsh, J. Chem. Soc. 1953, 2266.
- ²²See also: D. K. Hsu, D. L. Monts, and R. N. Zare, Spectra Atlas of Nitrogen Dioxide (Academic, New York, 1978).
- ²³A. E. Douglas and K. -P. Huber, Can. J. Phys. 43, 74 (1965).
- ²⁴J. L. Hardwick and J. C. D. Brand, Chem. Phys. Lett. **21**, 458 (1973).
- ²⁵P. Robrish and H. Rosen, Chem. Phys. Lett. 37, 156 (1976).
- ²⁶G. D. Gillispie, A. U. Khan, A. C. Wahl, R. P. Hosteny, and M. Krauss, J. Chem. Phys. 63, 3425 (1975).
- ²⁷R. J. VanBrunt and R. N. Zare, J. Chem. Phys. 48, 4304 (1968).
- ²⁸K. E. Shuler, J. Chem. Phys. **21**, 624 (1953).
- ²⁹G. Herzberg, Electronic Spectra of Polyatomic Molecules (Van Nostrand, New York, 1966).