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# Photoexcitation of NO at 1576 Å

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An accidental resonance between the 1576.299 Å line of the  $F_2$  laser and the  $Q_{11}$  (7.5) line in the  $B'^2 \Delta - X^2 \Pi$  3-0 band of NO provides a means of generating intense emission in three NO transitions— $B'^2 \Delta - X^2 \Pi$ , and  $B'^2 \Delta - B^2 \Pi$ , and  $B^2 \Pi - X^2 \Pi$ . By accessing a particular  $B'^2 \Delta$  level in this manner, state-to-state kinetics involving a variety of high electronic states of NO can be easily studied. These include the H' E, D, C, B, and A states. The specific nature of the process makes it possible to use the emission as an unambiguous measure of laser power and also as a technique for detecting small amounts of NO. Observations can be made at wavelengths from the vacuum UV to the visible, and intercalibration between UV and visible bands result in a branching ratio of 155 for emission from NO( $B'^2 \Delta$ ) to the  $X^2 \Pi$  and  $B^2 \Pi$  states.

### INTRODUCTION

A variety of techniques exist for generating the electronically excited states of NO by direct photoexcitation. Many of these involve finding accidental resonances between NO levels and fixed-frequency radiation sources, examples being the excitation of the  $A^2\Sigma^+$  state by the Se I 1961 Å line<sup>1</sup> and the  $B^2\Pi$  state by the Hg 1849 Å line.<sup>2</sup> More recently, multiphoton processes using dye lasers have been employed,<sup>3.4</sup> so that specific rotational levels could be accessed, but in general it has been only the  $A^2\Sigma^+$  and  $B^2\Pi$  states that have been generated in this manner. A notable exception has been the work of Banić *et al.*,<sup>5</sup> in which a range of  $B'^2\Delta$  vibrational levels has been pumped by three-photon absorption.

In the present experiment, where the  $B'^2 \Delta$  state is produced by 7.88 eV photoexcitation, there are ten excited states of NO that lie below it, and thus state-to-state kinetics to these lower states can in principle be investigated. The  $^2\Delta$  states of NO that lie above the dissociation limit do not predissociate,<sup>7</sup> so that losses are either radiative or collisional. The  $B'^2\Delta$  state radiates only to the two valence doublet states lying below it,  $X^2\Pi$  and  $B^2\Pi$ . However, there have been few studies of these transitions, and no determinations of the branching ratio.

#### EXPERIMENTAL

The laser used in these studies was a Lumonics model 861T-3, operating on a mixture of  $F_2$  and helium. Lasing occurs on two  $F_2$  lines in the VUV region, at 1576.299 and 1575.233 Å, with weaker lasing transitions occuring from atomic fluorine in the red spectral region. By using a VUV filter (Acton Research Corp.) in the laser path, we were able to reduce scattered light from these visible transitions by a large factor. The laser light was coupled to the experimental cell by a purge chamber flushed with N<sub>2</sub>.

Several spectrometers were used to take the spectra. The visible emission was photographed with a high-speed transmission grating image tube system, and higher resolution measurements utilized a McPherson 0.5 m scanning instrument, both in the visible and down to 2000 Å. The VUV measurements were made with a 0.3 m MacPherson 218 monochromator, fitted with a solar-blind phototube. The responses of the monochromators and photomultipliers were checked against a standard deuterium lamp ( $\lambda = 2000-4000$  Å) and a halogen-tungsten lamp ( $\lambda = 3000-8000$  Å).

The absorption cell was constructed of brass, and the radiation was viewed at 90° to the laser axis. The residence time of gas in the cell was about 200 ms. NO and He supplied by Matheson were used in the experiments, with no further purification.

#### **RESULTS AND DISCUSSION**

The fluorescence of NO came to our attention when NO<sub>2</sub> was irradiated with the  $F_2$  laser and an intense yellow glow was observed. We were soon able to show that it was due to the NO produced in the photodissociation, and that a stronger spectrum could be produced from NO itself. This is an observation very similar to that made earlier on the 2485 Å photodissociation of NO<sub>2</sub>,<sup>7</sup> in which it was demonstrated that emissions in the UV were a result of laser induced fluorescence (LIF) involving vibrationally excited NO product molecules. In the present case, however, it is the ground vibrational level of NO that is pumped, and therefore NO<sub>2</sub> is not needed to study the phenomenon.

In Fig. 1 is shown a spectrum in the visible region of the observed emission. From the absorption spectrum of Lagerqvist and Miescher<sup>8</sup> it is evident that absorption, if any, will be to the v = 3 level of the  $B'^2 \Delta$  state, and the 3-v''progression in the  $B'^2 \Delta - B^2 \Pi$  system is clearly present in Fig. 1. The two additional features are the  $E^{2}\Sigma^{+}-A^{2}\Sigma^{+}$ 1-1 band, and the  $H'^2\Pi - A^2\Sigma^+$  0-0 band, both of which have been previously reported in connection with 1470 Å photoexcitation of NO.<sup>9</sup> The E-A and H-A bands in the spectrum are due to the presence of He; in pure NO, only the B'B bands appear. A very similar spectrum can be generated when an  $H_2$  laser is used to photoexcite NO<sup>10</sup>; the same bands appear as in Fig. 1, in addition to the dominant radiation, the 2-v'' progression in the B'-X system. This is generated by photoexcitation at the wavelength where the multiline  $H_2$  laser emission is most intense, 1605–1610 Å.

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FIG. 1. NO fluorescence spectrum 5200-6900 Å, 1576.299 Å excitation, [NO] = 500 mTorr.

Although not evident in Fig. 1, there are weak NO( $B^2\Pi - X^2\Pi$ ) bands in the region below 5000 Å. They are a cascade emission from the B'-B 3-v'' bands, and as such are expected to reflect the B'-B Franck-Condon factors. Since, as is apparent from Fig. 1, there is very little B'-B 3-2 emission, there should be little B-X 2-v'' emission, and this is borne out by the spectra; emissions from  $B^2\Pi$  (v = 0, 1, 3) are dominant.

In Fig. 2 are shown spectra of the emission in the UV above 1900 Å, in the presence and absence of He. The pairs of triplets in the unrelaxed emission demonstrate that single rotational levels are excited by the laser, as three lines to each of the ground state spin components are expected in a  ${}^{2}\Delta - {}^{2}\Pi$ transition. The addition of helium has a large effect on the spectrum; since the radiative lifetime of the  $B' {}^{2}\Delta$  state is only 118 ns,<sup>6</sup> helium is obviously very effective in moving the



FIG. 2. NO fluorescence spectrum 1900-2700 Å, 1576.299 Å excitation, [NO] = 100 mTorr. (a) 20 Torr He; (b) without He.

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FIG. 3. NO fluorescence spectrum 1550–1800 Å, 1576.299 Å excitation. (a) [NO] = 100 mTorr, [He] = 10 Torr; (b) [NO] = 60 mTorr, [He] = 0.

population to nearby states. However, there is no evidence that there is any vibrational relaxation, as no  $B'^2 \Delta (v = 2)$  is detected.

Figure 3 shows the emission in the vacuum UV, and it may be seen that the only change upon He addition is that the  $D^2 \Sigma^+(v=4)$  level is generated. Thus, it would seem that transfer to D(4) is the first step in the pathway to bring the population to other states. This can be understood by considering the energy gaps and the Franck-Condon overlaps to nearby states, as has been discussed by Katayama *et al.*<sup>11</sup> in conjunction with  $CN(A^2\Pi)$  relaxation. Within 1500 cm<sup>-1</sup> of  $B'^2 \Delta$  (v = 3) are found the  $F^2 \Delta$  (0),  $E^2 \Sigma^+(1)$ ,  $H'^2 \Pi$  (0), and  $D^2 \Sigma^+(4)$  levels, as well as  $B'^2 \Delta$  (v = 2). In Table I are shown the rotationless energy gaps and the Franck-Condon factors for transitions from  $B'^2 \Delta$  (3) to these other states, and it is evident that the  $B'^2 \Delta$  (3)- $D^2 \Sigma^+(4)$  transition is favored if the FC overlap is important, whereas the transition requir-

TABLE I. Franck-Condon factors between  $B'^{2}\Delta(v=3)$  and other states.

State	FC factor	$\Delta E (\mathrm{cm}^{-1})$
$\overline{E^2 \Sigma^+ (v=1)}$	1.4×10 <sup>-2</sup>	281
$H'^{2}\Pi(v=1)$	$1.4 \times 10^{-3}$	780
$B'^2 \Delta (v=2)$	3.2×10 <sup>-31</sup>	1119
$D^2\Sigma^+(v=4)$	$6.8 \times 10^{-2}$	1379
$F^2 \Delta (v=0)$	$2.1 \times 10^{-3}$	1435



FIG. 4. Resolved NO(B'-B) bands [NO] = 100 mTorr.

ing the smallest energy change is  $B'^{2}\Delta(3)-E^{2}\Sigma^{+}(1)$ . The experimental conclusion is that the B'-D transfer occurs efficiently, but there is no indication of any other transition in the VUV spectrum. On the other hand, helium does induce some production of both  $E^{2}\Sigma^{+}$  and  $H'^{2}\Pi$ , as seen in the visible spectrum. The most obvious explanation for this apparent ambiguity is that the branching ratios I(E-A)/I(E-X)and I(H'-A)/I(H'-X) are likely to be considerably larger than the ratio I(B'-B)/I(B'-X), discussed below. This is because of the large matrix elements connecting Rydberg-Rydberg transitions, exemplified by the fact that the IR  $C^{2}\Pi - A^{2}\Sigma^{+}$  transition is so strong that the branching ratio I(C-A)/I(C-X) is 0.61.<sup>12</sup> Thus, the appearance of E-A and H'-A emission in Fig. 1 should be taken as an indication of the large oscillator strengths of these bands, not that the Eand H' states are produced efficiently by B'  $^{2}\Delta$  (3)-He collisions. The most likely origin of the  $C^2 \Pi$  and  $A^2 \Sigma^+$  bands in Fig. 2 is IR radiative cascading from higher levels. It should also be borne in mind that some of the states produced by collisional relaxation of  $B'^2 \Delta$  (3) will predissociate and will thus appear to be inefficiently produced.

In order to understand the spectroscopy of the system, it is necessary to identify the rotational level produced in the initial absorption. There is no tabulation of B'-X 3–0 band absorption lines, but the 2–0 band has been tabulated by Miescher.<sup>13</sup> To make the identification, we found it most convenient to use the observation demonstrated in Fig. 4, that is the visible region there is a coincidence of line posi-

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tions such that in the B'-B 3-1 band only five lines appear, rather than the expected six. In the 3-3 band the rotational constants change enough to resolve the central line. Since there is obviously a coincidence of an R and a P line in the spectrum of the 3-1 band, it is a simple matter to express this in spectroscopic terms, in order to calculate the transition. The expression

 $B_{\nu(1/2)} (J'' + 2) (J'' + 3) = A + B_{\nu(3/2)} J'' (J'' + 1) - \delta$  (1) includes the  $B'^2 \Delta$  and  $B^2 \Pi$  rotational constants and the  $B^2\Pi$  spin splitting A, obtainable from the literature,<sup>14</sup> and a term  $\delta$  for the splitting between the coincidental R and P lines for the spectral resolution used. This is zero for the 3-1 band and  $-4 \text{ cm}^{-1}$  for the 3-3 band. When Eq. (1) is solved for both bands, a value close to J = 6.5 is obtained in each case, which is the rotational level in the  $B^2\Pi$  state of the coincidental R line. Thus, the rotational level in the upper state is J = 7.5, from which it follows that the F<sub>2</sub> laser line is coincident with an R (6.5), a Q (7.5), or a P(8.5) line in the  $B'^{2}\Delta - X^{2}\Pi$  3-0 band. With this information, it is then possible to use the spectroscopic constants and the rotationless spacing between the v = 2 and 3 levels in the  $B'^2 \Delta$  state to calculate the transition energies in the 3-0 B'-X band. The result is that the best match to the 1576.299 Å laser line is the  $Q_{11}$  (7.5) line, 0.25 cm<sup>-1</sup> to shorter wavelength. This somewhat roundabout method was used to identify the transition because of the redundancy that it provides.

Although the relevant energy level has certainly been identified by this determination, the energy mismatch can also be calculated from a measure of the absorption cross section. Using a power meter to measure light transmission, we find that NO absorbs the laser radiation with a cross section of  $3.7 \times 10^{-19}$  cm<sup>2</sup>, which becomes  $4.8 \times 10^{-18}$  cm<sup>2</sup> when the population in J = 7.5 at 300 K is considered. From the radiative lifetime of  $B'^2 \Delta (v=3)$ , given by Brzozowski et al.<sup>6</sup> as 118 ns, one may calculate that the peak absorption cross section is  $5.5 \times 10^{-15}$  cm<sup>2</sup>, some three orders of magnitude larger than the measured value. To determine the mismatch requires assumptions about the absorption and emission line shapes. For NO, we assume a 300 K Gaussian profile, i.e.,  $\sigma \alpha \exp(-0.693x^2)$ , where x is in units of 1/2 the Doppler width, 0.065 cm<sup>-1</sup>. For the  $F_2$  line we have no information; the width may well be much less. Taking this assumption to the limit, we then need only calculate where the parameter  $exp(-0.693x^2)$  falls from unity to  $9 \times 10^{-4}$ , the observed cross section decrease. This occurs at x = 3.2, and thus the mismatch is 0.21 cm<sup>-1</sup>, in good agreement with the calculated value of  $0.25 \text{ cm}^{-1}$ . Assuming a finite width for the laser line further improves this agreement. It follows that the NO absorption cross section should be very temperature dependent, and that the NO fluorescence intensity should be much greater at higher temperatures.

The 3-v" B'-X progression, observed from 1576 to 2400 Å, exhibits an interesting distortion in the 3-6 band at 1900 Å, shown as an inset in Fig. 2. All other bands show the expected six lines, with the long wavelength triplet stronger than the short wavelength. However, for the 3-6 band the short wavelength triplet is distinct, whereas the long wavelength triplet is unclear and weakened by an order of magni-

tude. This effect is almost certainly due to absorption of the lines by trapping in the C-X 0-0 band, which has heads at 1910 and 1914 Å, degraded towards shorter wavelengths. As the C-X system is strongly predissociated above  $J = 4.5^{6}$ the light is not remitted. This coincidence provides in principle very accurate rotational energy level positions for  $B'^{2}\Delta (v = 3)$ , as the spectroscopy of the C-X 0-0 band is well known. That the weakened subband is still B'-X 3-6 and not C-X 0-0, is demonstrated by the fact that the potentially stronger C = X = 0 band at 1985 Å is not present.

As there are no literature values for oscillator strengths of the B'-B transition, the ratio of B'-X to B'-B system intensities is not known. We have compared the emission intensities of the B'-X 3-12 and the B'-B 3-1 bands, using standard deuterium and tungsten lamps for spectral calibration. On the assumption of a constant transition moment in the two systems, band intensities are proportional to the product of the Franck-Condon factor and the cube of the transition frequency. With the aid of FC factors calculated by Nicholls,<sup>15</sup> we have determined that the branching ratio between the two systems I(B'-B)/I(B'-X) is 1/155. Thus, the relatively intense visual fluorescence is in fact much weaker than the UV fluorescence.

As the F<sub>2</sub> laser is the shortest wavelength laser commercially available at the present time, it can be expected that its use will increase, and we have found that the photoexcitation process in NO is a very useful method for monitoring the laser output, which falls relatively rapidly with time  $(3 \times 10^4)$ shots to half-power). The advantage of observing NO fluorescence, rather than using a power meter to measure intensity, is that the NO response is unique to the stronger of the two laser lines  $(I_{1576.3}/I_{1575.2} \sim 5)$ , whereas the power meter is completely unspecific, and will even respond to the F red lines. Thus, a monitoring fluorescence cell, containing 1 Torr NO, could be interposed between the laser and a reaction cell, giving strong UV and visible fluorescence, linear in laser power, with very little absorption.

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