eous polarization of the optically pumped rubidium can substantially influence the relaxation time  $T_2$ . We measure  $T_1$ , the longitudinal relaxation time, and our system is not sensitive to field inhomogeneities, wall shifts, or alkali polarization inhomogeneities. Our measurements are also independent of the number density of Rb or Xe atoms.

Although the spin transfer efficiency  $\eta$  of (7) is much less favorable than one would infer from the numbers cited by Volk, Kwon, and Mark,<sup>2</sup> it still seems certain that large and highly polarized samples of <sup>129</sup>Xe can be prepared by spin exchange with optically pumped alkali atoms. For example, the photon current corresponding to 1 W of absorbed dye laser power and a wall-dominated relaxation rate of 1 h will allow one to polarize  $3 \times 10^{20}$  <sup>129</sup>Xe spins, according to Eqs. (5) and (7). This is 11 cm<sup>3</sup> of 100% polarized <sup>129</sup>Xe at STP. Such a sample would be of considerable interest as a target for nuclear scattering experiments. We thank Professor Keith DeConde and Professor Frank Shoemaker for many helpful suggestions. This work was supported by the U. S. Air Force Office of Scientific Research under Grant No. AFOSR-81-0104C.

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## Observation of Rydberg( $C^2\Pi$ )-valence( $B^2\Pi$ ) Interactions in NO by Multiphoton Photoelectron Spectroscopy

Michael G. White

Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973

and

Mark Seaver, William A. Chupka, and Steven D. Colson Department of Chemistry, Yale University, New Haven, Connecticut 06511

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Photoelectron spectra for the three-photon resonant, five-photon ionization of NO via the v'' = 0 level of the  $C^2 \Pi(3p\pi)$  Rydberg state show that NO<sup>+</sup>  $(X^1\Sigma^+)$  is formed primarily in v' = 0 and  $v' \ge 3$ . The relative populations of the v' = 0 to  $v' \ge 3$  levels are strongly dependent on the excited rotational level of the C state. These data are consistent with known perturbations between the nearly degenerate  $C^2\Pi$ , v'' = 0 Rydberg and  $B^2\Pi$ , v = 7 valence levels.

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Multiphoton ionization (MPI) has become an increasingly important tool in high-resolution spectroscopy because of its sensitivity and ability to detect excited states which do not fluoresce. For the most part, MPI experiments have used the total ion (or photoelectron) yield as a measure of the absorption strength. Such data have provided a great deal of spectroscopic information on the resonant, intermediate excited states.<sup>1</sup> Analysis of the ejected photoelectrons (energy and angular distribution) adds a new dimension to the MPI technique, since photoelectron spectroscopy can provide information on the finalstate (internal energy) distribution of the ion and the dynamics of the photoejection process. Several groups have recently applied multiphoton photoelectron spectroscopy (MP-PES) to the study of nonresonant and resonant ionization of

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atoms<sup>2</sup> and molecules.<sup>3,4</sup>

In this paper, we report the results of an MP-PES investigation of the  $C^2\Pi$  Rydberg state of nitric oxide. In particular, individual rotational levels of the  $C^2\Pi$ , v''=0 state were excited via a three-photon process,

NO(
$$\cdots 1\pi^4 2\pi; X^2\Pi, v=0$$
)  $\xrightarrow{3h\nu}$  NO\*( $\cdots 1\pi^4 3p\pi; C^2\Pi, v''=0, N$ )

and subsequently ionized by absorption of two additional photons,

$$NO^{*}(\cdots 1\pi^{4}3p\pi; C^{2}\Pi, v''=0, N) \xrightarrow{2h\nu} NO^{+}(\cdots 1\pi^{4}; X^{1}\Sigma^{+}, v') + e^{-}.$$
(1)

In these reactions the outermost valence electron configuration is indicated and N is the rotational quantum number.<sup>5</sup> The  $C^2\Pi$ , v''=0 state is of particular interest since it represents a near "text-book" case for the study of Rydbergvalence interactions in small molecules. From the analysis of high-resolution absorption spectra. Lagerquist and Miescher<sup>6</sup> determined that the lower rotational levels of the  $C^2\Pi$ , v''=0state are strongly perturbed by rotational levels of the nearly degenerate  $B^2\Pi$ , v=7 valence state. For high N the rotational levels of the B and Cstates are widely separated and do not interact. For N < 6, however, both the  $F_1$  and  $F_2$  rotational components of the C state undergo avoided crossings with  $F_2$  of the *B* state. Configuration interaction mixes these levels such that they actually represent rotational levels of a  $^{2}\Pi$  electronic state having varying amounts of Rydberg and valence character. As the pure  $C^2\Pi$ , v''=0 and  $B^2\Pi$ , v = 7 states would individually give rise to very different photoelectron spectra, it was expected that some qualitative measure of the Rydberg-valence interaction could be obtained from MP-PES spectra.

Photoelectrons were produced by the intersection of the focused radiation from an excimer (XeCl)-pumped dye laser (Lambda Physik) with an effusive NO gas jet. The tunable radiation from the dye laser had a bandwidth of  $\sim 0.2 \text{ cm}^{-1}$ and was focused by a 20-cm focal-length lens to a spot with an estimated cross section of  $10^{-4}$  $cm^2$  (peak power ~10<sup>9</sup> W cm<sup>-2</sup>). The gas jet was produced by expanding 15-20 Torr of NO gas through a 70- $\mu$ m-diam aperature located ~1 mm from the interaction point. A narrow cone of electrons (half-angle  $\sim 3^{\circ}$ ) ejected perpendicular to the laser beam was collected and energy analyzed by a  $160^{\circ}$  spherical-sector electrostatic analyzer (Comstock, Inc.).7 Spectra were obtained by accelerating or decelerating the incoming photoelectrons to a fixed analyzing energy (pass energy), typically 5-10 eV. The resolution ( $\Delta E/E$ ) of the electron analyzer was measured to be 1.4%; however, small shifts in

the energy scale, attributed to charging of materials near the interaction region, resulted in slightly broader peaks in those spectra which required many repetitive scans.

MP-PES spectra of rotational levels in perturbed and unperturbed regions of the *C* state are shown in Fig. 1. These spectra were taken with a 5-eV pass energy and are not corrected for the energy-dependent collection efficiency (transmission) of the electron energy analyzer. The pumped rotational lines in Figs. 1(a)-1(c) correspond to a blended line with mostly N = 3 but



FIG. 1. MP-PES spectra for the three-photon resonant, five-photon ionization via several levels in the  $C^{2}\Pi$ , v'' = 0 state rotational manifold of NO. The origin of the peak with an apparent five-photon binding energy of 10.26(1) eV [kinetic energy of 0.53(1) eV] is not known at this time.

some N = 2 character ( $\lambda = 574.50$  nm), N = 4 ( $\lambda$ = 574.62 nm), and a bandhead with  $N \sim 8$  ( $\lambda = 572.83$ nm), respectively.<sup>6,8</sup> The chosen N = 3 level was expected to have the largest non-Rydberg character.<sup>9</sup> All the MP-PES spectra exhibit several common photoelectron peaks which form a regular progression with an average energy spacing of 0.287(7) eV  $(2314 \pm 50 \text{ cm}^{-1})$ . This spacing corresponds to the average energy spacing of the lowest vibrational levels of the  $X^{1}\Sigma^{+}$  state of NO<sup>+</sup> as expected from reaction (1).<sup>10</sup> The bindingenergy  $(BE)^{11}$  scale is fixed by setting the energy of the highest kinetic energy (lowest possible BE) peak to the spectroscopically determined ionization energy (9.264 eV) of the v' = 0 level of NO<sup>+</sup>.<sup>10</sup> This assignment is reasonable since it is well known that the Rydberg states of NO have potential-wave energy curves nearly identical to that of the  $X^{1}\Sigma^{+}$  state of NO<sup>+</sup>; this simply reflects the nonbonding nature of the Rydberg orbitals. Hence, ionization from rotational levels with some  $C^2\Pi$ , v'' = 0 character should give rise to a peak corresponding to the Franck-Condon favored v' = 0 + v'' = 0 transition.

The observed Franck-Condon envelopes for these spectra can be characterized by a strong v'=0, weak v'=1, and a vanishingly small v'=2transition (all of which would be expected for ionization from the  $C^2\Pi$ , v''=0 state), followed by the relatively strong transitions leading to v'=3, 4, and 5. Furthermore, it is clear from Fig. 1, that the intensity ratio of the  $v' \ge 3$  to v'=0 and 1 vibrational states is strongly dependent on the pumped rotational level. This ratio is largest for N=3 and smallest for the bandhead spectrum. The v'=0 to v'=1 intensity ratios are approximately constant as are the intensities of the v'=3, 4, and 5 peaks relative to each other.

Qualitative interpretation of the MP-PES spectra can be made with the aid of Fig. 2 in which the relevant neutral and ionic state potential curves are shown. Since the Franck-Condon factors between the  $C^2\Pi$ , v''=0 state and the  $v' \ge 3$ levels of the  $X^1\Sigma^+$  ionic state are vanishingly small ( $<10^{-4}$ ), the observed strength of the  $v' \ge 3$ photoelectron peaks cannot be associated with direct *C* state ionization. It is clear from Fig. 2, however, that the  $B^2\Pi$ , v=7 level should have reasonably good Franck-Condon overlap with ionic vibrational states with  $v' \ge 3$ . Hence, the observed photoelectron spectra are consistent with the mixed Rydberg-valence character expected for the pumped rotational states. In addi-



FIG. 2. Potential-energy curves relevant to the photoionization of NO through the  $C^2 \Pi$  Rydberg excited state [from F. R. Gillmore, J. Quant. Spectrosc. Radiat. Transfer <u>5</u>, 369 (1965)].

tion, the relative contributions of the Rydberg (C) and valence (B) states to the different rotational levels are in qualitative agreement with the rotational analysis of Lagerquist and Miescher, i.e., the higher-N rotational levels of the C state are essentially unperturbed.

It should also be noted that Miller and Compton<sup>4</sup> have recently published an MP-PES spectrum of the *C*, v'' = 0 state following a two-photon resonant, three-photon ionization process. In their work the total three-photon excitation energy was below the ionization threshold for the v' = 2 level of the ion. Hence, they were able to observe only the v' = 0 + v'' = 0 ionization transition which reflects just the Rydberg character of the mixed *C*-*B* state.

In the Born-Oppenheimer approximation one can write the mixed Rydberg-valence (adiabatic) state wave functions as

$$\Psi({}^{2}\Pi, v'', J) = \{ a(R) \Psi_{e}{}^{0}(C^{2}\Pi) + b(R) \Psi_{e}{}^{0}(B^{2}\Pi) \} \Psi_{v''}(R) \Psi_{J},$$

where a and b are coefficients which determine the electronic character of the mixed state as a function of R,  $\Psi_{v''}(R)$  is a vibrational wave function appropriate for the double-well C-B potential shown in Fig. 2, and  $\Psi_J$  is a rotational wave function with total angular momentum J. The photoionization probability from this mixed state by a *single* photon has the form

$$P \propto |\overline{M}_{XC} \langle \Psi_{v'} | a(R) | \Psi_{v''} \rangle + \overline{M}_{XB} \langle \Psi_{v'} | b(R) | \Psi_{v''} \rangle|^2$$

where  $\overline{M}_{fi}$  represents the average electronic ionization transition moment appropriate in the Franck-Condon approximation if the B and Cstates did not interact. The coefficients a(R)and b(R) have values of nearly unity or nearly zero over most of the region of either potential well but change rapidly between these extremes in the vicinity of the avoided crossing.<sup>12</sup> Thus. the overall transition moment depends on the internuclear separation, R. That the usual form of the Franck-Condon approximation is not valid in this case is clear from Fig. 2 since there is no reason to expect  $\overline{M}_{\mathbf{X}\mathbf{C}}$  and  $\overline{M}_{\mathbf{X}\mathbf{B}}$  to be equal. In fact, in an unperturbed single-configuration description,  $\overline{M}_{XB}$  is identically zero since the dipole operator in this matrix element is a oneelectron operator while the X - B transition requires a two-electron excitation, i.e.,  $B^2\Pi$ - $(\cdots 1\pi^3 2\pi^2) \rightarrow X^1 \Sigma^+ (\cdots 1\pi^4) + e^-$ . Ionization of the C state, on the other hand, requires only removal of the Rydberg electron so that  $\overline{M}_{\textit{XC}}$  is in general nonzero in this description. Thus, the one-photon ionization probability of the mixed state would be determined only by the C-state character.

In theory, two-photon nonresonant processes, such as that used here for the ionization step, can provide allowed pathways for two-electron excitation via virtual intermediate states.<sup>13</sup> The X - B transition requires virtual intermediate states which connect to the B and X states by one-electron excitations. Since nearly all of the excited states in the energy region near that of the fourth laser photon are Rydberg states with ground ionic state cores,<sup>11</sup> it is very likely that the X - B transition remains unfavorable even for a two-photon process. Furthermore, we also note that near-resonant contributions to the twophoton ionization probability would most likely arise from these upper Rydberg states. Preliminary measurements in which a second dye laser provided the fourth photon and deliberately excited a higher-lying Rydberg state (8so) yielded an additional photoelectron peak corresponding to the v' = 0 level of the ion only.

The unusual Franck-Condon envelope for v'=3, 4, and 5 may be explained by the rapid variation of the coefficients *a* and *b* in the classically forbidden region between the two potential wells.<sup>14</sup> Since a(R) and therefore the photoionization probability decrease rapidly as *R* increases, the vibrational integral  $\langle \Psi_{v'} | a(R) | \Psi_{v''} \rangle$  will favor the region near the inner turning point of the *B* state where vibrational overlap with the v'=3 level of the ion is greatest. Thus, it is reasonable to expect a large enhancement of v'=3 over v'=4 and 5 as compared with the intensity distribution obtained simply by considering the overlap of the *B*, v=7 and the *X*,  $v' \ge 3$  vibrational states.

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<sup>11</sup>The binding energy is defined as the total five-photon energy less the observed electron kinetic energy, i.e.,  $E_B = 5h\nu - E_K$ . <sup>12</sup>A particularly good illustration of a rapid change in

<sup>12</sup>A particularly good illustration of a rapid change in electronic state character near an avoided crossing can be found in the theoretical work of Kolos and Wolniewicz [J. Chem. Phys. <u>50</u>, 3228 (1969)] on the double-minimum  $E_{,}F^{1}\Sigma_{g}^{+}$  state of H<sub>2</sub>.

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