Photoionization of excited atomic states: Photoelectron anisotropy for N $2p^23p\ ^2S^\circ_{1/2}$

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The two-photon-resonant, three-photon $(2+1)$ ionization spectrum of atomic nitrogen produced by photodissociation of nitrous oxide has been determined between 2692 and 2687 Å, and shows two peaks corresponding to the N $^2S^\circ_{1/2}\leftarrow{}^2D^\circ_{3/2,5/2}$ transitions. The photoelectron spectrum for $(2+1)$ ionization via the $^2S^\circ_{1/2}$ state displays a single N^+ photoelectron peak corresponding to the production of the ^3P ground state. The photoelectron angular distribution following ionization via the $^2S^\circ_{1/2}\leftarrow{}^2D^\circ_{5/2}$ transition shows a distinct minimum along the polarization axis of the laser light $(\beta=-0.2\pm0.1)$. Implications of this anisotropy for the relative dipole amplitudes into the different εs and εd ionization channels are discussed.

I. INTRODUCTION

In the past few years laser photodissociation of molecules has proven to be a powerful technique for the generation of open-shell, first-row atoms. Pulsed lasers have been used both to photodissociate the appropriate precursor molecule and to probe the atomic system of interest. Because the first electronically excited states of the open-shell, first-row atoms generally lie in the vacuum-ultraviolet region, atoms produced in this manner are usually probed using either resonantly enhanced multiphoton ionization or multiphoton laser-induced fluorescence. Studies of this type have been performed on C,[1-3] N,[4] O,[5] and F.[6] Most of the previous studies have focused either on the mechanism of production or on the selective detection of the species of interest. However, in our earlier study of atomic carbon,[3] two-photon-resonant, three-photon $(2+1)$ ionization was used to study the photoionization dynamics of a number of excited states. In particular, we reported the photoelectron spectra and photoelectron angular distributions following ionization of individual resonant intermediate levels. The results of recent theoretical calculations by Tang[7] for the same processes are in good agreement with the experimental data.

In this paper we present new experimental results for the photoionization of an excited state of atomic nitrogen. As in a number of earlier experiments on other atoms,[1-3,5,6] a single laser is used to produce atomic nitrogen in the $^2D^\circ_{3/2,5/2}$ levels by uv multiphoton dissociation of nitrous oxide (N_2O) and then to probe the excited atoms using $(2+1)$ ionization via the N $1s^22s^22p^23p\ ^2S^\circ_{1/2}$ level. The $^2D^\circ_{3/2}$ and $^2D^\circ_{5/2}$ levels correspond to excited terms of the $1s^22s^22p^3$ configuration, and lie 19 231 and 19 223 cm^{-1} above the $^4S^\circ_{3/2}$ ground state,[8] respectively, while the $^2S^\circ_{1/2}$ level lies 93 582.3 cm^{-1} above the ground state.[8] The photoelectron spectrum and the photoelectron angular distribution have also been determined for this process. In this wavelength region the absorption of three photons from the $^2D^\circ_{3/2,5/2}$ levels can only produce the $N^+\ ^3P$ ground state, and a single N^+ peak is observed in the photoelectron spectrum. Although the N $^2D^\circ_{3/2,5/2}$ atoms may be aligned following

photodissociation of N_2O, the excited N $^2S^\circ_{1/2}$ atoms cannot be aligned or oriented if linearly polarized light is used in the two-photon excitation process. Hence, any theoretical calculation of the photoelectron angular distribution need only consider the single-photon ionizing transition from the excited $^2S^\circ_{1/2}$ level. Accordingly, the photoelectron angular distribution must have the functional form[9,10]

$$I(\theta)\propto 1+\beta P_2(\cos\theta)\ .\qquad(1)$$

Here I is the photoelectron intensity, θ is the angle between the polarization axis of the light and the detector, β is the asymmetry parameter, and P_2 is the second Legendre polynomial $P_2(\cos\theta)=\frac{1}{2}(3\cos^2\theta-1)$.

II. EXPERIMENTAL PROCEDURE

The experimental apparatus has been described in detail previously.[11] It consists of a time-of-flight mass spectrometer, an electrostatic electron energy analyzer, and an excimer-pumped dye laser. The output of the dye laser was frequency doubled and the resulting uv light was separated from the residual fundamental using dichroic beam splitters. Approximately 0.8 mJ of the uv light was focused with a 150-mm lens into an effusive beam of N_2O. The background chamber pressure was approximately 9×10^{-5} Torr with the pressure at the laser focus estimated to be a factor of 10 to 100 times higher.

The $(2+1)$ ionization spectrum of N $^2D^\circ_{3/2,5/2}$ was recorded by monitoring the N^+ ion signal with the mass spectrometer as the wavelength of the uv light was scanned. The wavelength was then fixed at the $(2+1)$ ionization feature of interest and the photoelectron spectrum was recorded. The photoelectron angular distribution was recorded by tuning the electron spectrometer to the $N^+\ ^3P$ photoelectron peak and monitoring the electron signal as the laser polarization was rotated with a double Fresnel rhomb. The data were not corrected for the finite acceptance angle ($\sim3°$) of the electron spectrometer. The $N^+\ ^3P$ ground state is split into three components with $J=0$, 1, and 2 and with $E(^3P_1)-E(^3P_0)=6.1$ meV and $E(^3P_2)-E(^3P_0)=16.3$

$meV.^{8}$ These splittings are significantly less than the electron spectrometer resolution employed (~ 80 meV), and the photoelectron angular distribution thus reflects the averaging over the N^{+} $^{3}P_{0,1,2}$ final states.

III. RESULTS AND DISCUSSION

The $(2+1)$ ionization spectrum determined between 2692 and 2687 Å of N $^{2}D^{o}_{3/2,5/2}$ via the $^{2}S^{o}_{1/2}$ state is shown in Fig. 1. The two observed peaks correspond to the transitions from the $^{2}D^{o}_{3/2}$ and $^{2}D^{o}_{5/2}$ levels to the $^{2}S^{o}_{1/2}$ level. No other two-photon transitions of either N $^{4}S^{o}_{0}$ or $^{2}D^{o}_{3/2,5/2}$ are expected in this energy region.[8]

The mechanism for the production of N $^{2}D^{o}_{3/2,5/2}$ atoms from the multiphoton dissociation of N_2O is not known. The two-photon energy used in the present experiments is well above the threshold for the single-photon photolysis of N_2O using ultraviolet light;[12] however, it is also possible that a process involving more than the two photons is responsible for the production of the N $^{2}D^{o}_{3/2,5/2}$ atoms in this case. Some evidence for this appears in Fig. 1, as the peaks corresponding to ionization via the $^{2}S^{o}_{1/2}$ level show an asymmetry characteristic of ac-Stark broadening.[13] In our experience it is usually possible to find low power conditions for which the ionization signal of the species of interest provides good signal to noise without significant ac-Stark broadening. However, in the present case this is not possible, as the peaks appear asymmetrically broadened even at the lowest powers for which there is detectable signal. This suggests that the production of N $^{2}D^{o}_{3/2,5/2}$ atoms may involve a higher-order process than the $(2+1)$ detection process.

The photoelectron spectrum obtained by pumping the two-photon $^{2}S^{o}_{1/2}\leftarrow ^{2}D^{o}_{5/2}$ transition shows an intense N^{+} ^{3}P peak at 1.67 eV, with no other structure between 1.1 and 1.9 eV. As noted above, this peak corresponds to the unresolved $^{3}P_{0}$, $^{3}P_{1}$, and $^{3}P_{2}$ multiplet. A second photo-

electron peak is observed at ~ 0.97 eV, and much weaker, broad features are observed below 0.9 eV. The features below 1.1 eV are probably due to nonresonant ionization of N_2O or NO produced by photodissociation, as both N_2O^{+} and NO^{+} are observed in the mass spectrum throughout the wavelength range of the present study. The relative intensities of the 1.67-eV atomic nitrogen peak and the 0.97-eV photoelectron peak appear to be quite sensitive to the alignment and beam quality of the uv laser light.

The photoelectron angular distribution for $(2+1)$ ionization via the $^{2}S^{o}_{1/2}\leftarrow ^{2}D^{o}_{5/2}$ transition is shown in Fig. 2, and displays a distinct minimum at $\theta=0^{\circ}$. The result of a linear least-squares fit to the functional form of Eq. (1) is also shown in Fig. 2, and corresponds to a value of $\beta=-0.2\pm 0.1$. Although no theoretical results exist for excited-state photoionization of N, Manson[14] has performed a systematic study of the β values for ionization from p subshells of all ground-state atoms. Perhaps the best comparison with the present data would be the photoionization of atomic aluminum, which has a single $3p$ electron and the configuration $1s^{2}2s^{2}2p^{6}3s^{2}3p$. The β value for the $3p$ subshell of aluminum is at a minimum of ~ 1.1 at threshold, rises to ~ 1.5 at the kinetic energy of the present study, and continues to rise to a value of 1.9 at approximately 16 eV above threshold.[14] Although the present experiments provide no information about the energy dependence of the β value of N, it is clear that the present β value is far below that calculated for Al.

Using the Cooper-Zare formula,[15] the asymmetry parameter for ionization from a $3p$ subshell can be written[14,16]

$$\beta(\varepsilon)=\frac{2[M(\varepsilon)]^{2}-4M(\varepsilon)\cos\Delta(\varepsilon)}{1+2[M(\varepsilon)]^{2}} ,\qquad (2)$$

where $M(\varepsilon)=R_{d}(\varepsilon)/R_{s}(\varepsilon)$, i.e., the ratio of radial photoionization matrix elements for d and s partial waves, and $\Delta(\varepsilon)$ is the phase difference $\theta_{\varepsilon d}-\theta_{\varepsilon s}$. The phase $\theta_{\varepsilon l}$ is the sum of a Coulomb phase and a non-Coulomb phase shift, δ_{l}, i.e.,

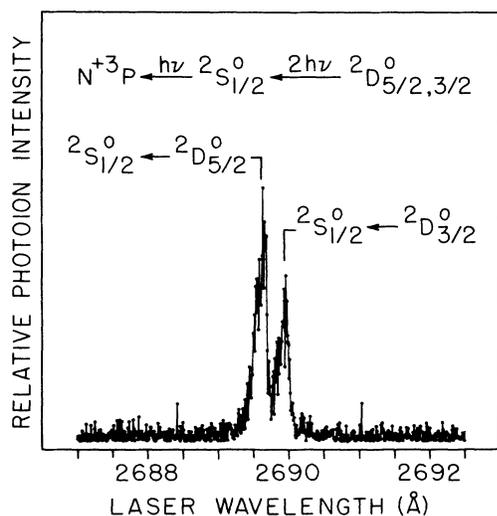$$\theta_{\varepsilon l}=\arg\Gamma(l+1-i\varepsilon^{-1/2})+\delta_{l} ,\qquad (3)$$

FIG. 1. The $(2+1)$ ionization spectrum of atomic nitrogen produced by multiphoton dissociation of N_2O between 2692 and 2687 Å.
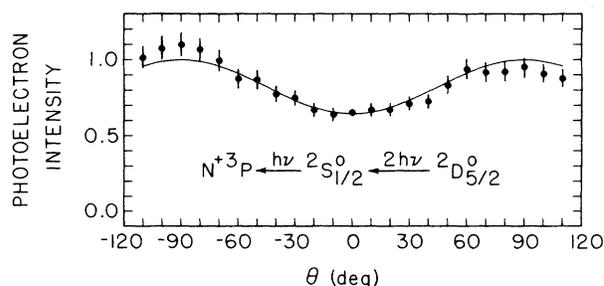

FIG. 2. The photoelectron angular distribution for $(2+1)$ ionization of atomic nitrogen obtained by pumping the $^{2}S^{o}_{1/2}\leftarrow ^{2}D^{o}_{5/2}$ transition. Data points are shown as solid circles (●). The solid line (———) is the result of a linear least-squares fit to the function form of Eq. (1). The error bars indicate statistical uncertainties only.

where ε is the photoelectron energy in rydbergs. The non-Coulomb phase shift generally varies slowly with energy and can often be obtained by extrapolating experimental data on the quantum defects of high Rydberg states. Unfortunately, the data on high Rydberg states of atomic N are quite fragmentary,[8] and no consistent quantum defects have been obtained. However, the non-Coulomb phase shifts for the s and d partial waves have been calculated by Dehmer and Saxon using a Hartree-Slater potential.[17] Substituting these non-Coulomb phase shifts, the well-known Coulomb phases,[14,18] and the experimental value of β into Eq. (2), the quadratic equation yields $M = 1.013$ and 0.104.

Although it is not possible to determine which value of M is appropriate in the present case, it is interesting that the values indicate that the $\varepsilon d \leftarrow 3p$ matrix element is either the same size as or is an order of magnitude smaller than the $\varepsilon s \leftarrow 3p$ matrix element. This is in contrast to photoionization from ground-state $3p$ orbitals, for which the $\varepsilon d \leftarrow 3p$ matrix element is usually a factor of 2 or more larger than the $\varepsilon s \leftarrow 3p$ matrix element at threshold.[17] However, in the case of ground-state atoms, one also expects a Cooper minimum in the $\varepsilon d \leftarrow 3p$ matrix element at somewhat higher kinetic energy.[14] The small values of M may indicate that the kinetic energy of the photoelectron in the present study is close to that of the Cooper minimum, and indicate that for photoionization from the N $^2S^o_{1/2}$ excited state the Cooper minimum has shifted to quite low kinetic energy. The behavior of Cooper minimum for excited atomic states has been discussed by Manson and co-workers.[19] White et al.[20] have discussed

a similar possibility in connection with photoionization studies of the $3p\pi$ Rydberg state of nitric oxide.

IV. CONCLUSIONS

The $(2 + 1)$ ionization spectrum of atomic nitrogen in the region of the $^2S^o_{1/2} \leftarrow ^2D^o_{3/2,5/2}$ two-photon transitions has been recorded following multiphoton dissociation of N_2O, and the photoelectron angular distribution for ionization via the $^2S^o_{1/2} \leftarrow ^2D^o_{5/2}$ transition has been reported. The angular distribution following ionization from the unaligned $^2S^o_{1/2}$ level displays a minimum along the laser polarization axis, corresponding to a value of $\beta = -0.2 \pm 0.1$. This implies that the radial photoionization matrix element for the $\varepsilon d \leftarrow 3p$ transition is smaller than or approximately equal to the $\varepsilon s \leftarrow 3p$ matrix element. This may suggest that the Cooper minimum observed at higher kinetic energies in the $\varepsilon d \leftarrow 3p$ matrix elements for ground-state atoms[14] has shifted to much lower energies in the photoionization of N $^2S^o_{1/2}$. Theoretical calculations of the energy dependence of the radial photoionization matrix elements and of the energy dependence of β would be extremely helpful in testing and extending these tentative conclusions.

ACKNOWLEDGMENTS

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