Photoionization of an autoionizing level of atomic oxygen

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Direct evidence for the photoionization of an autoionizing level of atomic oxygen is presented. Atomic oxygen is produced in the $1s^2 2s^2 2p^4\,{}^1D_2$ level by photodissociation of NO_2 or N_2O and excited to the $(^2D^\circ)3p\,{}^1P_1$ and ${}^1F_3$ levels by two-photon absorption. These levels lie above the $O^+\,{}^4S^\circ_{3/2}$ ionization threshold but are forbidden to autoionize in LS coupling. Although the autoionization rates are thus very small, photoelectron spectra demonstrate that both levels do autoionize into the ${}^4S^\circ_{3/2}$ continuum. At laser intensities of $\sim 3\times 10^9$ W/cm^2, photoionization of the ${}^1F_3$ level competes effectively with autoionization. The implications of this work for high-intensity multiphoton ionization studies of above-threshold ionization and multiple ionization are discussed.

I. INTRODUCTION

The multiple ionization of atoms by intense laser pulses is generally discussed in terms of two distinct mechanisms corresponding to "sequential" and "direct" processes.[1–4] The sequential process consists of a series of events in which first the neutral atom and then the increasingly charged ions undergo simple multiphoton ionization. This process is fairly well understood in terms of the standard descriptions of multiphoton ionization. The direct process involves the simultaneous multiphoton excitation and subsequent ionization of two or more electrons, and it may involve transitions between quasibound or autoionizing levels of the atom. In general, the sequential mechanism overwhelmingly dominates the direct mechanism.[1–4] For the direct process to become important, the photoabsorption rate of the atom above the ionization threshold must become comparable to the ionization rate. Resonant transitions between autoionizing levels will greatly enhance this photoabsorption rate, and they are therefore important in determining the relative contributions of the direct and sequential mechanisms.[1–4] Unfortunately, few unambiguous experimental results exist for transitions between autoionizing levels.[5] The related phenomenon of above-threshold ionization (ATI), in which more photons than are energetically necessary to ionize the atom are absorbed with the additional energy deposited in the kinetic energy of the ejected electron, has also been the subject of intense study,[1–4] but, again, the role of autoionizing levels in ATI has not been examined in detail.

In this work we used low-intensity multiphoton ionization of atomic oxygen to demonstrate that an autoionizing level can be produced and then photoionized before it decays into the underlying continuum. A schematic diagram of the energy levels[6–8] involved is shown in Fig. 1. The $O^+\,{}^2D^\circ_{5/2,3/2}$ ion states occur at 136 645.1 and 136 666.1 cm^{-1}, respectively; $^2D^\circ$ will be used to denote this pair of levels when they are unresolved. The $O^+\,{}^2P^\circ_{3/2,1/2}$ levels occur at 150 306.6 and 150 308.1 cm^{-1}, respectively, but they are not shown in Fig. 1. Atomic oxygen is produced in the ${}^1D_2$ level by photodissociation of a suitable precursor molecule,[9] and two-photon transitions are then excited from the ${}^1D_2$ level to the $(^2D^\circ)3p\,{}^1P_1$ and ${}^1F_3$ levels that lie above the $O^+\,{}^4S^\circ_{3/2}$ ionization threshold. Although these levels may decay into the $O^+\,{}^4S^\circ_{3/2}$ continuum, their autoionization rates are very small.[8] In the present experiments, we demonstrate that the photon absorption rate from the ${}^1F_3$ level can be increased to the point at which photoionization into the $O^+\,{}^2D^\circ_{5/2,3/2}$ continua competes with autoionization. Although the present study was performed at low to moderate laser intensities, what is important for gaining insight into the high-intensity studies is that the relative magnitudes for direct ionization, autoionization, and photoionization of the superexcited levels can be made comparable. Thus, in the present system the coupling between the quasidiscrete state and the ionization continuum can be made

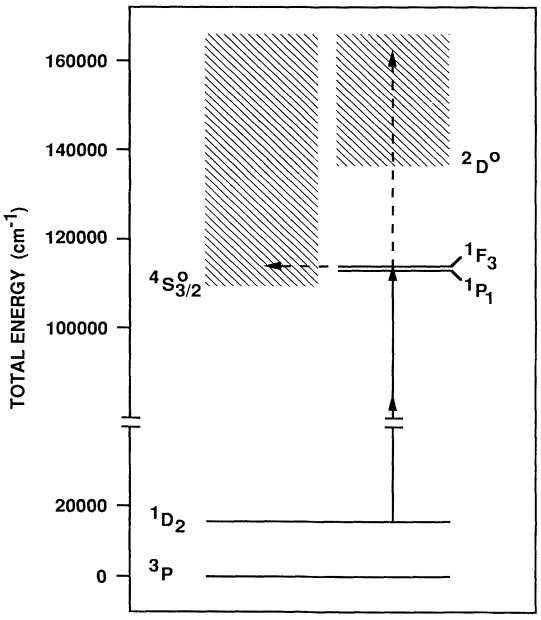

FIG. 1. Schematic energy-level diagram of the states of interest in atomic oxygen.

the same magnitude as the coupling between the quasi-discrete state and the photon field at moderate laser intensities. While we believe this capability will lead to the study of resonant transitions between autoionizing states in this system, the present study focuses on the competition between photoionization and autoionization.

II. EXPERIMENT

The time-of-flight mass spectrometer and the hemispherical electron-energy analyzer used in this work were described in earlier papers.[10,11] A single laser was used to produce O $^1D_2$ by photodissociation of a suitable precursor gas and to excite the two-photon transitions from the $^1D_2$ level to the $(^2D^\circ)3p\ ^1P_1$ and $^1F_3$ levels. Several possible precursor gases have significant photodissociation branching ratios for the production of O $^1D_2$ in the wavelength region 2036–2056 Å,[9] but other factors determine their suitability in the present experiments. We have used both NO_2 and N_2O. While NO_2 produces a much stronger signal for the O $^1D_2$ transitions, the other photoproduct is NO, which is efficiently ionized by near-resonant, two-photon ionization throughout this region. This ionization is not a factor in the experiments with the mass spectrometer, but it does produce problems in the experiments with the photoelectron spectrometer because of space charge and stray electrons. Although O $^1D_2$ production is much less efficient from N_2O,[9] the other photoproduct is N_2, which is not readily ionized under the present conditions. Thus N_2O is a more suitable source for the photoelectron measurements. In the present wavelength region, the O $^1D_2$ production from O_2 is not sufficient to detect the transitions of interest.

As in earlier studies,[11] light between 2036 and 2056 Å was generated by frequency tripling the output of a Nd:YAG pumped dye laser (where YAG is yttrium aluminum garnet) operating between 6108 and 6168 Å with pulse durations of approximately 8 nsec. Typically, 10–30 μJ of the third-harmonic light was separated from the lower harmonics with a series of prisms and was focused into the ionization region by using a 150-mm focal-length lens. The precursor gas was introduced into the ionization region via an effusive jet, producing a chamber pressure of approximately 5×10^{-5} Torr, with an estimated 10–100 times higher pressure in the interaction volume.

The experiments were performed in two parts. First, the O^+ ion signal was determined as a function of the laser wavelength by using the mass spectrometer. The energy levels of atomic oxygen[6–8] accessed in the present study were used to calibrate the laser wavelength. Second, the laser was tuned to the transition of interest, and the photoelectron spectrum was recorded. The transmission function of the electron-energy analyzer was calibrated from the He I photoelectron spectrum of O_2 by using the method described in an earlier publication.[10]

III. RESULTS AND DISCUSSION

Within the approximations of *LS* coupling, a Rydberg or continuum electron coupled to the $O^+\ ^4S^\circ_{3/2}$ ion core can produce only triplet and quintet Rydberg series and ionization continua.[12,13] The unusual result is that, within *LS* coupling, direct photoionization from the $^1D_2$ level is forbidden between the $O^+\ ^4S^\circ_{3/2}$ ionization threshold and the $O^+\ ^2D^\circ_{5/2}$ limit, as no singlet continua exist in this energy region. Thus the direct two-photon ionization cross section from the $^1D_2$ level into the $O^+\ ^4S^\circ_{3/2}$ continuum is expected to be very small, and it will gain intensity only as a result of spin-orbit, spin-spin, or other, presumably weaker, interactions that couples states with different spins.[12–15] Autoionization of singlet levels converging to the $O^+\ ^2D^\circ_{5/2,3/2}$ and $^2P_{3/2,1/2}$ thresholds will also be forbidden below the $O^+\ ^2D^\circ_{5/2}$ threshold and will occur again only through the influence of a magnetic interaction.[14,15]

The $(^2D)3p\ ^1P_1$ and $^1F_3$ levels are therefore predicted to have long lifetimes with respect to autoionization. In fact, the $(^2D^\circ)3p\ ^1P_1$ and $^1F_3$ levels were first observed in emission studies by Edlén[7] and by Eriksson and Isberg,[8] and transitions were observed both to these levels from higher-lying levels and from these levels to lower-lying levels. The transitions involving the $^1P_1$ level were broadened by approximately 0.20 cm^{-1}, and in addition, transitions from the $^1P_1$ level were significantly weaker than expected.[8] Eriksson and Isberg[8] attributed these observations to autoionization into the $^4S^\circ_{3/2}$ continuum, with a lifetime of 3×10^{-11} sec. All transitions involving the $^1F_3$ level were sharp, and no abnormalities were noted in the intensities. Thus, while the branching ratio for autoionization of the $^1P_1$ level is expected to be large, the branching ratio for autoionization of the $^1F_3$ level may be significantly smaller.

The higher autoionization rate for the $^1P_1$ level can be understood in terms of the selection rules for autoionization induced by spin interactions.[14] For spin-orbit and spin-other-orbit interactions, the selection rules are $\Delta L=0,\pm1$; $\Delta S=0,\pm1$; and $\Delta J=0$. For spin-spin interactions, the selection rules are $\Delta L=0,\pm1,\pm2$; $\Delta S=0,\pm1,\pm2$; and $\Delta J=0$. The $^1P_1$ level can decay into the $(^4S^\circ_{3/2}+\epsilon p)\ ^3P_1$ continuum by either the spin-orbit or spin-spin interaction and into the $(^4S^\circ_{3/2}+\epsilon p)\ ^5P_1$ continuum by the spin-spin interaction. In contrast, the $^1F_3$ level can autoionize into the $(^4S^\circ_{3/2}+\epsilon p)\ ^5P_3$ continuum only by the spin-spin interaction, although additional continua become available with the consideration of higher (e.g., ϵf) partial waves.

Similar instances of forbidden autoionization in atomic oxygen have been discussed by Huffman, Larrabee, and Tanaka[16] and Dehmer and co-workers[17–19] for Rydberg states of odd parity excited from the $^3P_{2,1,0}$, $^1D_2$, and $^1S_0$ states that result from the $1s^22s^22p^4$ ground-state configuration. Huffman, Larrabee, and Tanaka[16] observed the single-photon absorption spectrum from the $^1D_2$ and $^1S_0$ levels to singlet Rydberg series in the region above the $^4S^\circ_{3/2}$ ionization threshold. Between the $^4S^\circ_{3/2}$ and $^2D^\circ_{5/2,3/2}$ thresholds, the singlet series converging to the $^2D^\circ$ and $^2P^\circ$ thresholds are generally sharp, although some levels show broadening that is due to interactions with neighboring triplet levels that are more rapidly autoionized.[16] Dehmer and co-workers[17–19] observed the

single-photon ionization spectrum from the ^3P ground state to triplet Rydberg series. The discussion above indicates that the $^3P^\circ$ Rydberg series are forbidden to autoionize into the $^4S^\circ_{3/2}+\epsilon s$ or ϵd continua in LS coupling because there is no $^3P^\circ$ continuum; below the $^2D^\circ_{5/2}$ threshold, these levels can autoionize only by spin-orbit or spin-spin interactions. Dehmer and co-workers[17–19] observed these levels in the single-photon ionization spectrum and performed detailed studies of the competition between fluorescence and autoionization.

Figure 2 shows the two-photon ionization spectrum of the O $^1D_2$ state obtained by using NO_2 as the source gas and by monitoring the O^+ ion signal as the third-harmonic wavelength of the laser was scanned between 2036 and 2056 Å. The spectrum shows two intense, sharp features that can be assigned to two-photon transitions from the $^1D_2$ level to the $(^2D^\circ)3p\ ^1P_1$ and $^1F_3$ levels,[6–8] and the energy axis is labeled accordingly [i.e., $E=E(^1D_2)+2h\nu$, where $E(^1D_2)=15\,867.862\ \text{cm}^{-1}$].[6] The transitions to the $^1P_1$ and $^1F_3$ levels are the only ones observed in Fig. 2. Ionization from any of the ground-state $^3P_{2,1,0}$ levels requires three photons, and no two-photon resonant, three-photon ionization processes from these levels are expected in this region.[6] Figure 2 shows that little ionization is observed between the $^1P_1$ and $^1F_3$ resonances, in agreement with the prediction that the two-photon ionization cross section from the $^1D_2$ state into the $O^+\ ^4S^\circ_{3/2}$ continuum is extremely small. Thus the spectrum is essentially as expected for two-photon transitions from the $^1D_2$ level alone.

Because the photodissociation and excitation steps in these experiments were performed with a single laser, the relative intensities of the $^1P_1$ and $^1F_3$ transitions are not particularly meaningful, as the wavelength dependences of the photodissociation cross section and the $^1D_2$ branching ratio have not been determined. The two peaks are somewhat saturated in Fig. 2, and their widths do not reflect the natural lifetimes. At low laser intensities the widths of the peaks are comparable and equal to about 0.8 cm^{-1}. This is significantly larger than the width of the $^1P_1$ transitions reported by Eriksson and Isberg[8] and is a result of the laser bandwidth (the two-photon transition involves six photons at the fundamental wavelength) and the Doppler width.[20] The threshold for O $^1D_2$ formation is 2439 Å from NO_2 and 3407 Å from N_2O, approximately 1.0 and 2.4 eV below this photon energy range, respectively.[9] In both cases, the Doppler widths may be significant and depend on the fraction of available energy deposited in translational degrees of freedom.

Figure 3 shows the photoelectron spectrum obtained by pumping the two-photon $(^2D^\circ)3p\ ^1P_1\leftarrow{}^1D_2$ transition at a laser pulse energy of approximately 15 μJ. The photoelectron peak disappears when the laser is tuned off resonance, and no changes in the spectrum are observed for pulse energies between 10 and 30 μJ. From the energies of the process,[6] the peak is assigned to the autoionization of the $(^2D^\circ)3p\ ^1P_1$ state into the $^4S^\circ_{3/2}$ continuum. Figure 4 shows the photoelectron spectrum obtained by pumping the two-photon $(^2D^\circ)3p\ ^1F_3\leftarrow{}^1D_2$ transition at laser pulse energies of approximately 10 and 25 μJ. Both photoelectron peaks disappear when the laser is tuned off resonance, and the higher energy peak increases in intensity with increasing pulse energy. The lower energy peak is assigned to autoionization of the $(^2D^\circ)3p\ ^1F_3$ level into the $^4S^\circ_{3/2}$ continuum, and the higher energy peak is assigned to an overall three-photon process corresponding to the excitation of the two-photon transition $(^2D^\circ)3p\ ^1F_3\leftarrow{}^1D_2$ followed by photoionization of the $(^2D^\circ)3p\ ^1F_3$ level into the $O^+\ ^2D^\circ_{5/2,3/2}$ continuum. This latter process is expected to be the dominant pathway for the $^1F_3$ level because it requires no change in the ion core of the Rydberg state; no photoelectron peaks are observed at the energies expected for photoionization of the $^1F_3$ level into the $^4S^\circ_{3/2}$ or $^2P^\circ_{3/2,1/2}$ continua. For the spectra of Figs. 3 and 4, N_2O was used as the source gas, and the polarization axis laser was parallel to the entrance axis of the electron spectrometer ($\theta=0°$). Since the $^1D_2$ state may be aligned following the photodissociation step, no attempt was made to record photoelectron

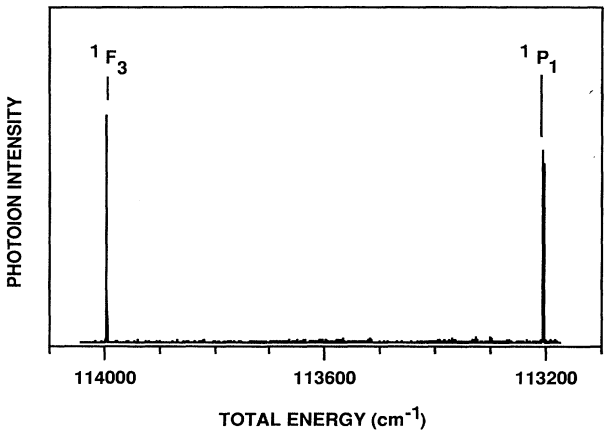

FIG. 2. Two-photon ionization spectrum of O $^1D_2$ produced by the photodissociation of NO_2. The total energy corresponds to $E=2h\nu+E(^1D_2)$, where $E(^1D_2)$ is 15 867.862 cm^{-1} (Ref. 6).

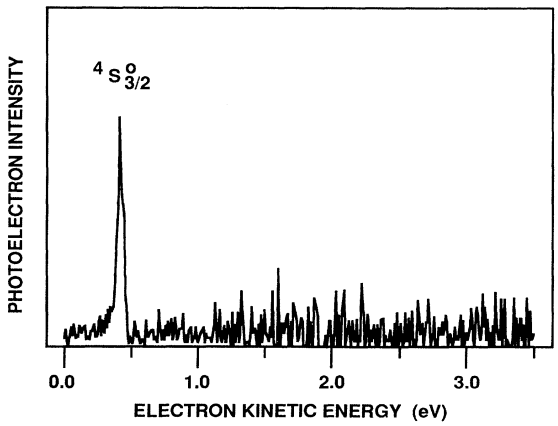

FIG. 3. Photoelectron spectrum obtained by pumping the two-photon $(^2D^\circ)3p\ ^1P_1\leftarrow{}^1D_2$ transition.

angular distributions. The observation of the photoionization of an autoionizing level at such low intensities is made possible by the extremely slow decay rate of the $^1F_3$ level. Although the natural lifetime of the $^1F_3$ level is not known, it is possible to make some estimates based on the present results. First, no O^+ $^2D^\circ$ photoelectron peak is observed for the $^1P_1$ resonance of Fig. 3. For a $^1P_1$ decay rate[8] of 3.3×10^{10} sec^{-1} and an assumed signal-to-noise ratio of 10 to 1 for the photoelectron spectrum, the photoionization rate of the $^1P_1$ level must be less than 3.3×10^9 sec^{-1}, even at the highest laser intensities used in this study. If we assume that the $^1P_1$ and $^1F_3$ levels have similar photoionization cross sections, the natural decay rate of the $^1F_3$ level must be smaller than 3.3×10^9 sec^{-1}, since photoionization of the $^1F_3$ level is observed.

A second estimate of the decay can be obtained from some of the laser beam parameters. For an 8-nsec, 25-μJ pulse and an assumed spot size of approximately 100 μm^2, the laser intensity (I) is 3.1×10^9 W/cm^2 (3.25×10^{27} photons/cm^2 sec). Although no experimental or theoretical determinations of the photoionization cross sections σ_{pi} for the $(^2D^\circ)3p$ $^1F_3$ and $^1P_1$ levels have been made, it is not unreasonable to assume that they will have approximately the same value as those of the $(^2S^\circ_{3/2})3p$ $^3P_{0,1,2}$ levels, and for the sake of argument we use the value 5.3×10^{-19} cm^2 determined by Bamford, Jusinski, and Bischel.[21] These assumptions yield an ionization rate $\sigma_{pi}I$ of 1.7×10^9 sec^{-1}. This rate is consistent with the natural decay rate of the $^1P_1$ level and the absence of the O^+ $^2D^\circ$ peak in the spectrum of Fig. 3. It also suggests that, because the O^+ $^4S^\circ_{3/2}$ autoionization peak and the O^+ $^2D^\circ$ photoionization peak have similar intensities, the natural decay rate of the $^1F_3$ level is also approximately 1.7×10^9 sec^{-1}, corresponding to a lifetime of 5.8×10^{-10} sec. It should be remembered, however, that the integrated photoelectron branching ratios are not necessarily equal to the $\theta=0^\circ$ branching ratios from Fig. 4 and that the rates and lifetimes derived here are only meant to provide order-of-magnitude estimates of their true values. Furthermore, the photoionization of the $^1F_3$ level will decrease the lifetime of this level and should produce in a broadening of the $(^2D^\circ)3p$ $^1F_3\leftarrow{}^1D_2$ transition linewidth. Unfortunately, our present resolution is insufficient to allow the observation of this increase in the width.

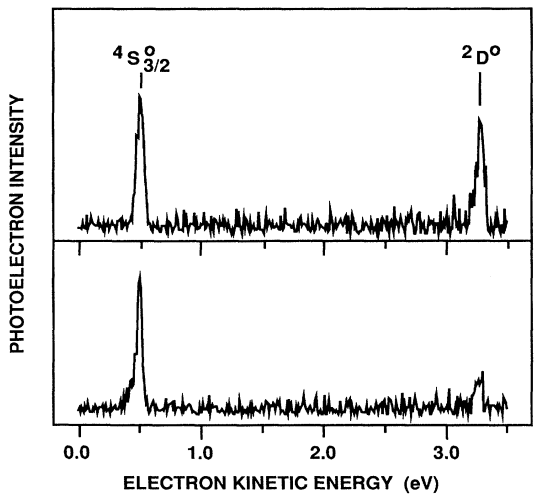

FIG. 4. Photoelectron spectra obtained by pumping the two-photon $(^2D^\circ)3p$ $^1F_3\leftarrow{}^1D_2$ transition. Upper frame: 25 μJ pulse energy. Lower frame: 10 μJ pulse energy.

IV. CONCLUSIONS

The principal result of this work is the unambiguous observation of the photoionization of an autoionizing level in atomic oxygen. This observation was readily made because direct two-photon ionization is forbidden by spin-selection rules.[12–14] In addition, because the autoionizing level has a long natural lifetime,[7,8] photoionization of the quasibound level competes with autoionization at very low laser intensities. While the present results demonstrate photoionization of an autoionizing level, future experiments will focus on the observation of transitions between autoionizing levels. This observation will be accomplished by using a second laser to probe transitions from the $(^2D^\circ)3p$ $^1F_3$ level to $(^2D^\circ)ns$ and nd Rydberg series and to series converging to the $^2P^\circ$ ionic state. Although fluorescence from the $^1F_3$ level has been observed,[7,8] the branching ratio for autoionization is presumably large. Thus it is not surprising that initial two-color studies[22] in which the $^1F_3$ level is pumped show no enhancement in the ion yield when the second laser is introduced. However, transitions induced by the second laser will produce photoelectrons with kinetic energies different from those produced by the first laser alone. Thus transitions between autoionizing levels may be observable when the photoelectron signal is monitored at the appropriate kinetic energy. In a similar experiment, Van Woerkom, Story, and Cooke[5] have observed transitions from a long-lived autoionizing level of atomic barium to higher-lying autoionizing levels. If such experiments are successful for atomic oxygen, they will provide a convenient system in which to study transitions between autoionizing levels and laser-induced structures in the continuum.

The present results provide an example in which photons are absorbed by a system that is energetically above the first ionization threshold and suggest that a suitable choice of experimental systems may allow the enhancement of the direct process for double ionization over the sequential process. For example, Feldman and Novick[14] have used electron-impact excitation to produce autoionizing levels of the alkali-metal atoms with microsecond lifetimes. These states are assigned as quartet states that are forbidden to autoionize into the continuum of the $^1S_0$ ground ionic state. Spong *et al.*[23] have excited analogous quartet levels of rubidium that decay predominantly by fluorescence, and have studied transitions from these levels to higher excited states by depletion of the fluorescence from the initial state. Although spin-orbit interactions in most of the upper levels lead to rapid decay by autoionization, the first allowed photoionization continu-

um for quartet states produces alkali-metal ions in excited electronic states that are energetically relatively close to the double ionization threshold.[6] Thus, with the suitable choice of laser frequency and intensity, these metastable atoms might provide a system in which the direct and sequential double ionization pathways are equally important.

Finally, the present experiments suggest a sensitive detection scheme for $^1D_2$ atoms. For low laser intensities, excitation of the $(^2D^\circ)3p\ ^1P_1$ level is more favorable, because its ionization branching ratio is expected to be higher than that of the $^1F_3$ level. At higher laser intensities, photoionization of the $^1P_1$ and the $^1F_3$ levels will dominate other decay paths, and either transition would be suitable.

ACKNOWLEDGMENTS

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