Anomalous intensity-dependent vibrational distributions of oxygen molecules in a nonresonant laser field: A molecular perspective

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We report on the results of nonlinear ionization and dissociation of gas-phase oxygen molecules in an intense ($10^{11-13}$ W/cm$^2$) laser field. The investigations were performed with the second- and third-harmonic wavelengths of two different laser systems; a 50-ps Nd:YLF (where YLF denotes yttrium lithium fluoride) and a 10-ns Nd:YAG (where YAG represents yttrium aluminum garnet). Measurements include energy resolved photoelectron and mass spectroscopy. We report on an interesting observation made with excitation of the neutral with green ($\sim$2.3 eV) photons, in which the vibrational distribution of the molecular ion shows a strong intensity dependence. We have analyzed this intensity-dependent behavior to be a result of a complex interplay between different resonant and nonresonant electronic channels, which to first approximation does not require dynamical Stark shifting of states. A model is presented that describes this behavior and results in the determination of the molecular constants for the intermediate states.

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I. INTRODUCTION

Interest in the behavior of isolated atoms in intense radiation fields has resulted in a cumulative literature rich in new phenomena [1], unresolved issues, and exciting predictions for future studies. Recently, systematic theoretical [2] and experimental [3,4] investigations have begun to examine similar questions concerning the high-field behavior of molecules. The additional challenge associated with studying molecules in strong fields results from the difficulty of sorting out the general behavior of field-induced effects from the details or specifics of the molecular structure. This becomes inherently more cumbersome due to the many internal degrees of freedom of molecules compared to atomic systems. However, these strong-field studies raise some interesting and unique questions concerning the role and interplay of ionization and dissociation. Furthermore, the attraction for studying molecules derives its fundamental interest from the ability to control molecular dynamics by external variation of a laser field. Although premature in realization, an understanding of the influence of both intensity and pulse duration in concert with frequency may ultimately lead to our ability or inability to control chemical dynamics.

We have begun a systematic investigation of homonuclear and heteronuclear diatomics in an intense field. In this paper, we focus on the results obtained from the multiphoton ionization of oxygen which exhibits a final-state ionic vibrational distribution that is strongly intensity dependent. A model developed by Smith [5] and later applied by Eland [6] to describe the photoelectron spectrum resulting from single-photon ionization of oxygen is adopted to simulate our multiphoton results. Although there exists an extensive amount of spectroscopic studies [7–12] on oxygen dating back to 1930, many aspects of the spectrum near threshold remain unexplained. The goal of this study is to understand the high-field behavior of diatomic molecules, but as a result we have acquired an insight into the bound-state structure of this molecule. This is not surprising since "nonresonant" multiphoton excitation should lose its definition in molecules, suggesting a greater need for intermediate or bound-state structure than atoms. However, the results presented here for oxygen demonstrate this fact in a very dramatic nature.

II. RESULTS AND DISCUSSION

Briefly, the experimental apparatus consists of an ultrahigh vacuum system equipped with a time-of-flight electron and mass spectrometer. The electron spectrometer provides both angular and energy (50 meV at 1 eV total energy) resolution, while the mass spectrometer provides mass/charge and fragment kinetic energy information. The data presented in this paper were taken with the linearly polarized laser field parallel to the detector axis. The electron spectrometer has an acceptance angle of $1 \times 10^{-3}$ sr with respect to the source. The vacuum system has a base pressure of $1 \times 10^{-9}$ Torr. Oxygen densities of $10^9-11$ molecules/cm$^3$ were introduced via an effusive source. Various grades of dry-ice-trapped oxygen were used to systematically eliminate the possibilities of impurities. The number of ions formed in the interaction volume was kept fixed at 50–100 ions/shot, in order to minimize space-charge effects. Harmonics from well characterized Nd:YAG (where YAG denotes yttrium aluminum garnet) ($1.06 \mu$m) and Nd:YLF (where YLF denotes yttrium lithium fluoride) ($1.05 \mu$m) lasers were used in this study, the details of each are described elsewhere [13].

Figure 1 shows a partial potential-energy diagram for
neutral oxygen and its ion. The adiabatic ionization potential is 12.071 eV, which corresponds to four- and six-photon ionization processes for 0.355 and 0.532 μm excitation, respectively. The neutral and ionic ground states have dissociation energies D0 of 5.1 and 6.7 eV, respectively. An inspection of the potential curves in Fig. 1 shows a large dissimilarity between the ground state and excited states, as well as the ionic states. The decrease in bond distance from the neutral to the ionic ground state is a consequence of the removal of an electron from the 2p, πg antibonding orbital. The variance between potential curves results in large Franck-Condon spreading in oscillator strength throughout the spectral region. In fact, the well-known Schumann-Runge [14] system (B3Σu−−−X 3Σg−) is the strongest absorption band which absorbs over an extensive region from visible to ultraviolet (UV). Figure 2(a) shows the oxygen photoelectron spectrum resulting from 0.355 μm, four-photon ionization. The ionic vibrational structure is well resolved and assignable to the first seven vibrations, v* = 0-6, of the O2+ 2Πg ground state. Weak five-photon above threshold ionization (ATI) structure is observed which mimics the low-order four-photon vibrational distribution. Furthermore, the photoelectron intensity and energy distribution is unaltered with varying laser power over the range of 1-10 MW per pulse. The 0.355-μm radiation was focused by a 10-cm focal length lens with an f number of 4. Analysis of the intensity dependence for both the total O2+ yield curves and the individual electron peaks gives a slope consistent with four-photon nonresonant ionization. Likewise, analysis of the experimental photoelectron vibrational peak distributions in Fig. 2(a) is in excellent agreement with Franck-Condon factors calculated assuming a direct nonresonant O2 X → O2+ X transition. This calculation predicts a 0.5:1:0.8:0.4:0.1:0.01 final-state distribution for v* = 0-5, respectively, and is shown in Fig. 2(b) for comparison. The only anomalous feature in the photoelectron spectrum is for the v* = 5 peak, but this could be understood by considering the near resonance at the three-photon level with the v' = 5 vibration of the D or ß 3Σg− Rydberg state. This near resonance (~1 cm−1) transition is observed as a weak peak in the single-photon absorption spectrum [11]. The ß 3Σg− series converges to the ionic ground state and consequently has poor overlap with the neutral ground state, but diagonal transitions to the ionic ground state. This could result in a slight enhancement in the v* = 5 final ionic state amplitude, but an overall distribution that is best characterized by a direct nonresonant X → X transition. The amount of total fragmentation detected as O* is approximately 7%. The kinetic energy of the O* fragments are characterized by two distinct velocity groups of approximately equal amplitude. The distribution has a slow component with a kinetic energy of 0.15 eV and a 1-eV fast component. No detectable atomic oxygen peaks are observed in the photoelectron spectrum, suggesting that the origin of these fragments could be molecular ion dissociation. However, in general the amount of atomic ion formation is observed to decrease with longer wavelengths.

Excitation with 0.532-μm radiation requires a min-

![FIG. 1. Partial potential-energy diagram of neutral and ionic oxygen molecules. Note that the lowest-order photoionization at both 0.355 and 0.532 μm are even photon absorptions and energetically degenerate.](image1)

![FIG. 2. Photoelectron spectrum of oxygen molecules via 0.355-μm ionization. The tick mark indicate the energies of the unperturbed vibrational levels of the O2+ ground state. The bar diagram (b) is the Franck-Condon factors resulting from a nonresonant O2 X 3Σg− → O2+ X 2Πg transition.](image2)
FIG. 3. Intensity-dependent photoelectron spectra of oxygen molecules via 0.532-μm excitation taken at (b) $9 \times 10^{11}$ W/cm², (c) $2 \times 10^{12}$ W/cm², and (d) $4 \times 10^{12}$ W/cm². The bar diagrams (a) and (c) are model simulations for $9 \times 10^{11}$ and $4 \times 10^{12}$ W/cm² intensities, respectively.

imum absorption of six photons to ionize oxygen, similar to xenon atoms. Figure 3 shows the photoelectron spectrum recorded at various intensities ranging from $0.9-4 \times 10^{12}$ W/cm². All the major features in these spectra are assignable to vibrations of the O$_2^+$, X$^2\Sigma_g^+$ ground state. However, a dramatic effect evident in Fig. 3 is a strong dependence of the amplitudes of the photoelectron distribution with varying laser intensity. This implies an energy-dependent change in the ion’s vibrational content. The photoelectron spectrum in Fig. 3(b) taken at an intensity of $9 \times 10^{11}$ W/cm² shows a strong peak at 1.91 eV energy which is assignable to the $v^+=0$ vibration of the O$_2^+$ ground state. The weaker peaks fit to the vibrational progression of the ground state from $v^+=1-4$. As the intensity is increased in Figs. 3(c) and 3(d) the peak at 1.68 eV (tentatively assigned as $v^+=1$) increases in intensity and at saturation dominates over the $v^+=0$ by a factor of 2. Likewise, the weaker structure assigned to $v^+=2-4$ becomes less pronounced. Also noticeable is the absence of appreciable ATI structure, electrons with kinetic energy in excess of a photon energy, at the highest intensities. An atomic xenon spectrum recorded under the same unsaturated intensities shows approximately 20% of the electrons ejected into the ATI channels. Closer examination of the intensity behavior of the electron spectrum reveals two important features. First, the electron peaks labeled $v^+=0$ and 1 have an intensity dependence that scale as I$^5$ and I$^7$, respectively, as shown in Fig. 4(a). Furthermore, the fits show very little deviation from these power laws except at saturation. This result is verified by the total ion yield curves which yield a slope consistent with an average I$^5$ dependence. L’Huillier, Mainfray, and Johnson [15] have measured the same I$^5$ total ion power dependence using 30-ps, 0.532-μm excitation. However, such an averaged result is obviously misleading since it would suggest an ionization process that is nonresonant. Second, the 1.91- and 1.68-eV electron peaks show differing degrees of variation in linewidth as a function of laser intensity, as shown in Fig. 4(b). The 1.91-eV ($v^+=0$) peak linewidth shows no

FIG. 4. Plots of (a) counts and (b) linewidth for both the 1.68- and 1.91-eV photoelectron peaks as a function of 0.532-μm intensity. The straight lines in (a) are the result of a nonlinear fit to the data, while the curves in (b) are drawn for visual aid.
intensity dependence within our spectrometer’s resolution, but 1.68-eV ($\nu^+=1$) peak changes by a factor of 2 in linewidth in the intensity regime where the rates of the two peaks become comparable. At higher intensities where the system starts to saturate the linewidth of the $\nu^+=1$ peak decreases to a limiting value which is about 50% larger than the $\nu^+=0$ peak. The amount of atomic oxygen ions detected at these intensities is $\sim$0.3% and no detectable atomic peaks are present in the electron spectrum.

A similar series of experiments were performed using the second-harmonic output of a 40-ps Nd:YLF laser system at 0.527 $\mu$m. Beside the difference in pulse duration, the frequency change between the two laser systems is $\sim$200 cm$^{-1}$/photon. This translates into a total change of 1200 cm$^{-1}$, less than half a vibrational spacing, in the final-state energy. Both the photoelectron and the mass spectra at 0.527 $\mu$m show similar behavior to the 0.532- $\mu$m results, although the details differ. The amount of dissociation is less than 1% and the photoelectron spectrum exhibits a similar strong intensity dependence of the ions vibrational distribution. Thus this intensity-dependent distribution is not a fortuitous result of a specific wavelength, but instead occurs over a frequency range.

The data resulting from third-harmonic excitation are well described by a calculation using static Franck-Condon factors. Both the second- and third-harmonic excitations share the same final continuum state gerade symmetry (even number photon absorption) and total energy. Consequently, the strong vibrational intensity dependence observed with green excitation is not a final-state effect but instead an intermediate-state effect. The simplest intermediate state effect that could result in such an intensity dependence would involve dynamical Stark shifting of two successive vibrational levels (i.e., $\nu^-=0$ and 1) belonging to the same ungerade Rydberg series. Here we have assumed that the measured power dependence implies that the resonances are occurring at the five-photon level ($\sim$0.42 eV below threshold) and the Rydberg series is converging to the $2^3\Pi_g$ ground state of O$_2^+$. At low intensity, the unperturbed $\nu^+=0$ Rydberg level is resonant with five-photons resulting in mostly $\nu^+=0$, O$_2^+$ as a consequence of the $\Delta v=0$ propensity rule. Assuming that most of the Stark shift comes from the ponderomotive energy of photons, we calculate that an intensity of $\sim 9 \times 10^{12}$ W/cm$^2$ is needed to shift the Rydberg level by one vibrational quanta ($\Delta v \sim 1900$ cm$^{-1}$). However, this scenario is inconsistent with the experiment for a number of reasons. First, the intensities used in our experiment are an order of magnitude lower than the calculated intensities needed. Second, the predicted sign of the Stark shifts are opposite to those necessary to describe our results. Each Rydberg level is blue shifted similar to the ionization potential and thus the $\nu^+=1$ level never shifts into resonance. Third, the slopes of the vibrational peaks shown in Fig. 4(a) fit well with an $I^2$ scaling law. A dynamical Stark shift will give rise to intensity dependence more complex than this simple scaling, as demonstrated in cesium [16, 17]. Even if one assumes that the Stark shifting occurs between two consecutive vibrations of Rydberg series with differing principal quantum numbers (using known quantum defect [9]), one finds similar inconsistencies with the data.

We propose a mechanism that is conceptually based on a model developed by Smith [5] and applied to describe the photoelectron spectra resulting from single-photon ionization of oxygen [6]. Eland uses two continuum paths in Eq. (6) of Ref. [6] to describe the photoelectron data at various excitation wavelengths. Our model relies on three paths as illustrated in Fig. 5, (1) excitation through the $3^3\Sigma_g^+$ Rydberg level (dotted arrow), (2) excitation through $2^3\Pi_u$ adiabatic state (dark shaded arrows), and (3) direct $X \rightarrow X$ six-photon nonresonant ionization (not shown). The final-state vibrational distribution results from an incoherent sum of these various channels determined by their Franck-Condon overlap with the O$_2^+$ ground state. The $\nu'=0, 6\nu$ Rydberg series is estimated to be near resonant at the five-photon level based on measured quantum defects [11]. The $2^3\Pi_u$, $3^3\Pi_u$, and $2^3\Sigma_u^-$ are adiabatic neutral potential curves calculated by Buenker and co-workers [18]. The adiabatic potentials result from avoided crossings of Rydberg states with low-lying valence states producing curves that are strongly mixed. Moreover, interaction among these states will be sensitive to internuclear distance since the balance between the valence-Rydberg character of these adiabatic potentials is strongly R dependent. These calculated potentials have resulted in assignments of three previously unidentified absorption bands [19] and have

![FIG. 5.](image-url) An expanded view of the potential curves near the ionization potential. Five 0.532- $\mu$m photon absorption occurs adiabatically at $r_e$ of the O$_2$ ground state, while the one-photon ionization proceeds via the two paths illustrated by the dotted and dark shaded arrows. The corresponding dotted and dark shaded horizontal lines represent significant vibrational population transfer via favorable Franck-Condon factors for each path. The $2^3\Pi_u$, $3^3\Pi_u$, and $2^3\Sigma_u^-$ adiabatic neutral potential curves are calculated by Buenker and co-workers (Ref. [18]).
been ascribed to as perturbers to the \(v''=1\) and \(2\) levels of the \(\text{H}_2\Pi_u(3\sigma_g)\) state [12]. The calculations do not explicitly include interaction with \((\pi, \pi^*)\) species, which are expected to undergo significant mixing with the \(2\Pi_u\) and \(2\Pi_u\) adiabatic states.

Our model assumes that a five-photon absorption occurs vertically from the oxygen vibrationless ground state at an internuclear distance of 1.2075 Å. Furthermore, this transition leads to near resonances at the five-photon energy for both the \(v'=0\), \(6\) Rydberg level and the \(v'=3\), \(2\Pi_u\) adiabatic state. These strongly mixed states are assumed to be long lived compared to the ionization step. The transition to the continuum can then be visualized as separate paths occurring from the various near-resonant states and at very different internuclear distances. The analysis relies upon the Franck-Condon projection of the individual zero-order excited vibrational wave functions onto the ionic ground state. The final-state distribution can then be described as an incoherent sum of the individual Franck-Condon factors with intensity-dependent electronic amplitudes. The essence of the model then relies upon absorption of an additional 0.532-μm photon to occur via two resonant paths (1) \(6\) Rydberg and (2) \(2\Pi_u\) state. The direct ionization path (3) is also included in this formalism but with much less weight.

The amount of excess energy above the ionization potential resulting from six-photon ionization can reach up to \(v''=8\) of the ionic ground state. The Franck-Condon factors via path (2) give poor overlap with the \(v''=0\) levels of the ionic ground state while path (1) proceeds via a \(\Delta v=0\) propensity rule. Consequently, at low intensity the photoelectron spectrum will be characterized by a strong \(v''=0\) peak \((\varepsilon_0=1.91 \text{ eV})\) plus weaker higher vibrational peaks corresponding to contributions from paths (2) and (3) illustrated as dotted horizontal lines in Fig. 5. As the intensity is increased the transition rate favors absorption of an additional photon(s) in the continuum (AT), i.e., seven photons. Path (1) results in an electron peak that is characteristic of atomic ATI, that is with a total energy given by \((\varepsilon_0 + \varepsilon_1 = 4.24 \text{ eV})\). However, due to favorable Franck-Condon factors path (2) results in a significant population in the \(v''=11\) and \(12\) levels of the \(X^2\Pi_g\) ionic ground state (see dark shaded lines in Fig. 5). The electron energies via seven-photon ionization for \(v''=11\) and \(12\) are \(\varepsilon_{11} = 1.91 \text{ eV}\) and \(\varepsilon_{12} = 1.72 \text{ eV}\), respectively. These electrons are near degenerate in energy with the \(v''=0\) and \(1\) electrons resulting from six-photon ionization; in fact, the differences are \(\Delta \varepsilon_{10}=0\) and \(\Delta \varepsilon_{11}=40 \text{ meV}\) and are not resolvable with our electron spectrometer. However, \(\Delta \varepsilon_{11}=40 \text{ meV}\) is discernible as an intensity-dependent broadening and shifting in the peak center at 1.68 eV, as shown in Figs. 3 and 4(b). Referring to Fig. 4(b), the electron peak at 1.91 eV shows a constant 60-meV linewidth, while the 1.68-eV peak undergoes a significant change in width with intensity. In both the low- and high-intensity extremes the linewidth is constant representing a peak characterized by low and high \(v''\), respectively, while the intermediate-intensity regime, where the linewidth is a maximum, represents a blended \(v''=1\) and \(12\) peak with comparable amplitudes.

Figure 3 shows a direct comparison at the two extreme laser intensities between the experimental photoelectron spectrum and a bar diagram simulation incorporating our model. The agreement is excellent and reproduces all the major features of the experiment at all intensities. The molecular constants for the adiabatic states are varied to give the best fit to a photoelectron spectrum at one intensity. All other molecular constants are taken from the literature [19]. Once the adiabatic constants are determined they are kept fixed in all subsequent simulations. Thus the data are fit with three parameters corresponding to the electronic amplitudes for each path. The determined molecular constants for the \(2\Pi_u\) adiabatic state that give consistent fits for our data are \(\varepsilon_0=2500 \text{ cm}^{-1}\), \(\varepsilon_0\varepsilon_1=36 \text{ cm}^{-1}\), and \(R_e=1.32 \text{ Å}\). The vibrational frequency and anharmonicity agree with those determined by Tonky, Winniczek, and White [12] and differ from the calculated [18] values by 1.5%. Our internuclear distance is 0.04 Å longer than that calculated by Buenker and co-workers [18], but this difference is well within the numerical accuracy. Our determination of the electronic energy \(T_e\) is 0.3% higher than previously reported [12,18] with a value of \(\sim 87,000 \text{ cm}^{-1}\). However, considering the inaccuracy associated with deriving a meaningful \(T_e\) in our nonresonant experiment our result should be viewed as consistent with the previous reports.

III. CONCLUSIONS

In conclusion, we have studied the multiphoton ionization of oxygen molecules in an intense nonresonant laser field. We have described the intermediate resonances involved in the production of ionic final-state vibrational distributions and present a model that simulates the complex intensity dependence of these distributions with green (\(\sim 2.3 \text{ eV}\)) excitation. An interesting physical implication of our model is that the oxygen molecular ion is being formed in a strongly polarized bimodal vibrational distribution. Besides gaining some insight into the nature of multiphoton ionization in molecules, we have inadvertently learned about the bound-state molecular structure. Our results provide experimental evidence for these calculated adiabatic potentials [18] and the model allows for refinements in the predicted molecular constants. The complex behavior exemplified in this study implies that the study of high-field molecular multiphoton ionization requires detailed investigations into the "true" nature of resonant contributions.

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See, for example, Atomic and Molecular Processes with Short Intense Laser Pulses, edited by A.D. Bandrauk (Plenum, New York, 1988).


