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High-order harmonic cutoff extension of the O_2 molecule due to ionization suppression

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High-order harmonic generation has been observed experimentally from O_2 molecules at the saturation ionization intensity. The harmonic cutoff extends far beyond the cutoff of Xe despite both have nearly equal ionization potentials. In contrast, the harmonic spectra for N_2 and Ar, which have almost the same ionization potentials, are essentially close to each other. We show the extension of harmonic cutoff in O_2 is a consequence of ionization suppression. Using a simple modified tunneling ionization model for molecules, we predict both the harmonic cutoff extension and the ionization suppression semiquantitatively.

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The study of high-order harmonic generation (HHG) has attracted a great deal of attention because of its possible applications as a coherent desktop x-ray source in the femtosecond or even attosecond regimes [1], which can be used to probe the dynamic processes involving electronic transitions. Since the early discovery of HHG [2], most of the studies have been concentrated on rare-gas atoms. There have been a number of experimental studies of HHG from molecules [3–5], but a general picture for molecules in a laser field still has not emerged. In an earlier experiment [4], it was found that the HHG spectra of O_2 are close to that of Xe. Compared to the preliminary study of HHG from molecules, the ionization of molecules has been studied more extensively. Recently, it was found that the ionization of O_2 is suppressed by about one order of magnitude when comparing with Xe [6–8]. However, there is no ionization suppression for N_2 when comparing with Ar, which has nearly the same ionization potential as N_2. As is known, HHG is closely related to ionization in an intense laser field. Generally speaking, the HHG cutoff energy is decided from $E_{cutoff}=I_p+3.17U_p$, with I_p the ionization potential and U_p the quiver energy. Thus, we should observe a higher cutoff energy in a higher laser intensity. Meanwhile, the valence electron will be totally ionized when the laser intensity is above the saturation intensity. Therefore, we can only obtain the highest cutoff energy with an optimized laser intensity. The suppressed ionization of O_2 should lead to a significant extension of harmonic spectra, which was not observed in the previous HHG measurements [3,4]. Stimulated by such a controversy and the desire to further explore the relation between the HHG and ionization, we studied the HHG cutoff behavior for molecules and their companion atoms, for cases with a strong ionization suppression (O_2, Xe), and for cases with no ionization suppression (N_2, Ar).

The experiment was carried out with the newly established Ti:Sapphire laser system, Kansas Light Source, at Kansas State University. The laser system has an output of 1.5 mJ at 800 nm center wavelength, and a duration of 25 fs with a repetition rate of 1 kHz. The laser is focused by a 250 mm lens into the gas jet formed by a nozzle. The focal spot size (W_0) is 25 μm full width at half maximum (FWHM). The gas nozzle [9] provides a 200 μm interaction region with a gas density of 10^{17} molecules/cm^3. To get a good phase matching, the nozzle is placed 4 mm after the focal spot. The generated HHG signal is imaged by a focusing mirror at grazing incidence, then dispersed by a 2000 lines/mm transmission grating and recorded by a multichannel plates (MCP)/charge-coupled device system. In the experiment of O_2, Ar, and N_2 gases, a 0.2 μm perelyne (C_8H_8) filter was used. The transmission rate of this filter increases from 10% to 80% when the photon energy changes from 50 eV to 150 eV. We use it here to suppress the signal intensity of lower-order harmonics so that a better signal/noise ratio in the cutoff region (80–100 eV) can be obtained. For Xe, a 0.2 μm Al filter was used, which has a good transmission ($>70\%$) in the range from 20 eV to 70 eV.

In the experiment, we tuned the laser intensity to reach the highest cutoff, which is defined as the distinguishable HHG peak with the highest photon energy. The optimized laser intensity for Xe is 4×10^{14} W/cm^2; for O_2 it is 9×10^{14} W/cm^2. Under these intensities, the cutoff position for O_2 ($q_c=53$) is nearly twice to that for Xe ($q_c=29$). For Ar and N_2, the optimized laser intensity is $\approx 9\times10^{14}$ W/cm^2, the same as in the O_2 case. The cutoff positions for Ar and N_2 are $q_c=63$ and $q_c=57$, respectively. For comparison, we also measured HHG of Xe with the same intensity used for O_2 (9×10^{14} W/cm^2). This laser intensity is already far beyond the saturation intensity of Xe. At this intensity we did not get higher cutoff photon energy, compared with the measurement at 4×10^{14} W/cm^2. The measured HHG spectrum is originated from the unsaturated part of the laser profile, both temporal and spatial. The measured HHG signals for the four different gases near the harmonic cutoff region are shown in Fig. 1.

In comparing the atomic and molecular species, we note that Ar and N_2 have nearly the same ionization potentials, at 15.76 eV and 15.58 eV, respectively, and they have nearly identical harmonic cutoff. On the other hand, while Xe and O_2 have nearly the same ionization potentials, at 12.13 eV and 12.06 eV, respectively, the harmonic cutoff for O_2 is much higher than for Xe. We attributed this to the fact that O_2 molecule is much harder to ionize than Xe although they have the same ionization potential. This is known as ionization suppression, and it has been investigated extensively

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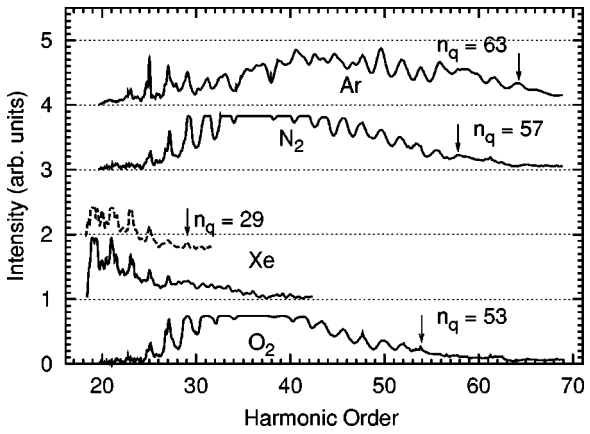

FIG. 1. Measured high-order harmonic signals from Xe, O_2, Ar, and N_2 gases with a Ti:Sapphire laser (800 nm, 25 fs) at a laser intensity of 9×10^{14} W/cm^2. The Xe signal is measured with a 0.2 μm Al filter and the O_2, Ar, and N_2 measurements are measured with a 0.2 μm perelyne (C_8H_8) filter. The dashed curve is the high-order harmonic signals of Xe recorded at an optimized laser intensity of 4×10^{14} W/cm^2.

[6–8] at different laser intensities and pulse lengths. Therefore, the harmonic cutoff extension and the ionization suppression are strongly correlated.

To explore the relation between HHG and ionization, we simulate the HHG spectra by using the Lewenstein model [10], which has been modified to take into account the ground-state depletion by the laser pulse. The depletion of the ground state was calculated by using the Ammosov Delone Krainov (ADK) model [11]. The Lewenstein model is valid in the tunneling ionization regime for calculating harmonics when the photon energy is much larger than the ionization potential. This model should work well here since we are interested in calculating only the harmonic cutoff at the saturation intensities.

The key issue is how to calculate the ionization rate for molecules in the framework of the ADK model. For a complex atom, the ADK ionization rate is [11]

$$w(l,m,E)=C^2_{n^*l^*}I_p\frac{(2l+1)(l+|m|)!}{2^{|m|}|m|!(l-|m|)!}\left(\frac{3E}{\pi F_0}\right)^{1/2}\times\left(\frac{2F_0}{E}\right)^{2n^*-|m|-1}e^{-2F_0/3E} \quad (1)$$

with $F_0=(2I_p)^{3/2}$, where I_p is the ionization potential, and E is the laser field strength. Information on the initial state is given by the angular momentum l and its projection m along the polarization axis of the laser field, while n^* is the effective principal quantum number and depends only on the ionization potential; $l^*=0$ for the present systems. For Ar and Xe, the l and m in Eq. (1) are well defined. To extend the ADK model to diatomic molecules, what l and m should we use? As we know, the most important ingredient in the ADK model is the wave function of the electron in the tunneling region, i.e., the asymptotic region. In the asymptotic region, the molecular orbital can be expressed as a superposition of

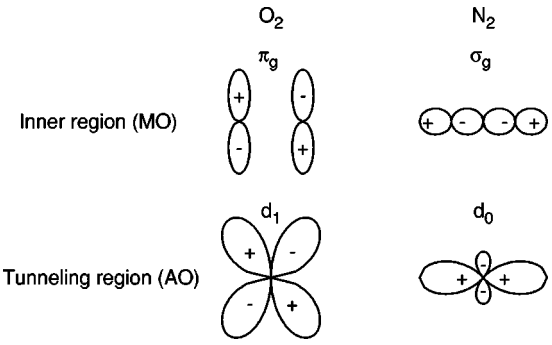

FIG. 2. Approximate two-centered molecular orbitals of the valence electrons of O_2 (π_g) and N_2 (σ_g) and their closest one-centered atomic orbitals. Only the outer region of the electronic wave function is of interest.

atomic orbitals at the two centers. To apply the ADK model to diatomic molecules, we need to extract the dominant atomic orbital or partial waves centered at the charge center of the molecule. Figure 2 shows the two-centered molecular orbitals and their closest atomic orbitals centered at the midpoint of the internuclear line. The O_2 valence orbital (π_g) wave function in the outer region is constructed mainly by the two $2p_1$ orbitals located at the two nuclei. In terms of atomic orbitals centered at the midpoint of the molecules it is best approximated by d_1 partial wave, or $l=2$, $m=1$. For the N_2 valence orbital (σ_g), we choose $l=2$, $m=0$, as shown in Fig. 2. The above parameters are for molecules aligned along the laser field direction. We list all the parameters we used in the ADK model in Table I.

To check the validity of our theoretical model, we first study the ionization of O_2 comparing with Xe. To compare with experiment, we calculate ionization probability at a given position from the ADK rate as

$$P_{lm}(r,z)=1-\exp\{-\int w[l,m,E(t,r,z)]dt\}, \quad (2)$$

and an ionization signal as

$$S_{lm}\propto\int P_{lm}(r,z)2\pi r dr dz. \quad (3)$$

TABLE I. Harmonic cutoff and parameters in the ADK model for molecules and their companion atoms.

	O_2	Xe	N_2	Ar
I_p (eV)	12.56	12.13	15.58	15.76
MO	π_g		σ_g	
AO	d_1	p_0	d_0	p_0
l	2	1	2	1
m	1	0	0	0
I_s (10^{14} W/cm^2)	3.01	1.75	3.71	4.40
q_c (calculated)	45	29	55	65
q_c (measured)	53	29	57	63

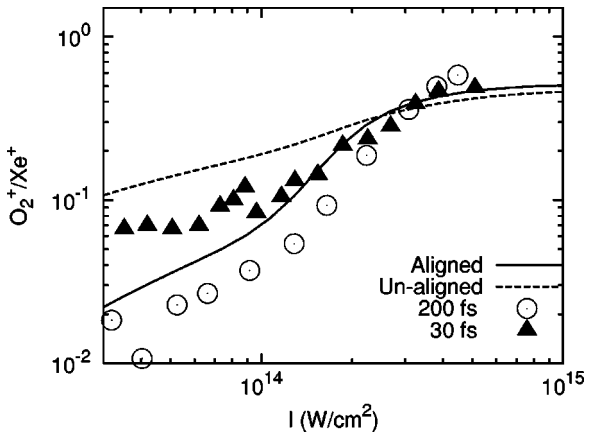

FIG. 3. The ratio of single-ionization signals between O_2 and Xe vs the peak intensity of the laser field. The open circles are from Ref. [6] and the filled triangles are from Ref. [7].

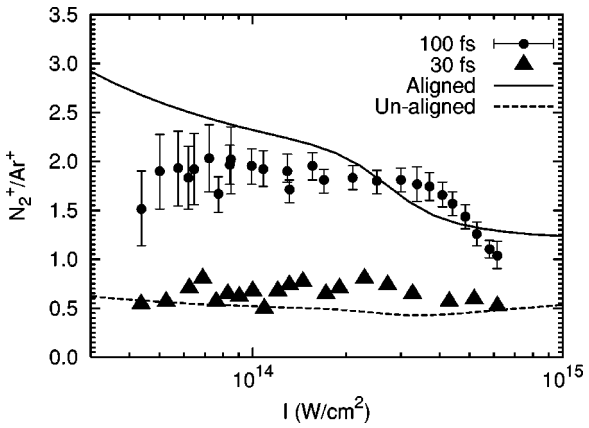

FIG. 4. The ratio of single-ionization signals between N_2 and Ar vs the peak intensity of the laser field. The filled circles are from Ref. [8] and the filled triangles are from Ref. [7].

The laser field's temporal and spatial distribution $E(t,r,z)$ is taken to be

$$E(t,r,z)=\frac{E_0 W_0}{W(z)}e^{-2ln2\, r^2/W^2(z)}e^{-2ln2\, t^2/\tau^2},$$

with $W(z)=W_0\sqrt{1+z^2/z_R^2}$, where W_0 is the size of the focal spot, $z_R=\pi W_0^2/\lambda$ is the Rayleigh range, and λ is the laser wavelength. τ is the pulse length at FWHM and E_0 is the laser field peak strength. S_{lm}, the ionization signal, is the quantity directly proportional to the measured ion signal. If the molecules are randomly distributed, we calculate the ionization signal as

$$S_{av}=\sum_m \frac{S_{lm}}{2l+1}. \tag{4}$$

Although the calculated ionization signal depends on the pulse length, the ratio of the ionization signals is not sensitive to the pulse length. The saturation intensity moves slightly to the lower intensity in a long pulse. Here, we calculate the ionization signal by using a 25 fs laser pulse to be consistent with our present experimental conditions. In Fig. 3, we present the ratios of single ionization signals of O_2:Xe measured at 200 fs by 800-nm pulsed laser by Talebpour *et al.* [6] (open circles), at 30 fs by 800-nm pulsed laser by Guo *et al.* [7] (filled triangles) and with our predicted ones. Here, we plot two curves, one for molecules aligned on the laser field direction (solid line, calculated from Eq. (3) with $l=2$, $m=1$) and another for molecules randomly distributed (dashed line, calculated from Eq. (4) with $l=2$). Overall this simple modified tunneling ionization model does predict the O_2 ionization suppression comparing with Xe, and the predicted suppression strengths are in reasonable agreement with the experiment. We emphasize that in the ADK model, the ionization rate depends on the ionization potential and the quantum numbers l and m. We attributed the lower ionization signal of O_2 vs Xe to the geometry effect, or to the different values of l, m as listed in Table I. This is different from the model of Guo [12] who used a larger effective ionization potential ($I_p=16.9$ eV) for O_2 in the ADK model. So far, the proposed larger ionization potential lacks direct experimental proof or direct theoretical support. The ionization suppression of O_2 also has been explained by the interference model [13], i.e., interference from the two atomic centers. Our present model does not contradict with this model, but it is much simpler, and attributes the suppression to the nature of the molecular orbitals instead of quantum interference. Within the ADK model, the suppression in O_2 is due to ($l=2,m=1$) as compared to ($l=1,m=0$) for Xe.

A similar comparison of ionization signals of N_2 vs Ar is shown in Fig. 4. The solid line is the ratio for the aligned N_2 molecule on the laser field direction and the dashed line is for the unaligned one. The experimental data were measured at 100 fs and 800 nm by DeWitt *et al.* [8] (filled circles with errorbars) and at 30 fs and 800 nm by Guo *et al.* [7] (filled triangles). Indeed, we do not see a significant suppression in N_2 vs Ar. Within the ADK model, ($l=1,m=0$) for Ar, ($l=2,m=0$) for N_2, thus, there is no suppression.

In the present experiment, we have no knowledge if the molecules are aligned or not. At intensities near 10^{14} W/cm^2, simple estimate based on the static polarizabilities of the molecules indicates that these molecules are not aligned for a short 25 fs pulse. However, ionization suppression does occur whether the molecules are aligned or not. For simplicity, in calculating the HHG spectra using the modified Lewenstein model [10], the molecules were assumed to be aligned and the parameters used in the ADK model are those listed in Table I. Note that, we only calculated the single atom or molecule HHG spectra and did not consider phase matching due to the laser temporal and spatial distribution. The resulting HHG spectra are shown in Fig. 5. The calculated harmonic cutoff order for Xe and Ar are 29 and 65, respectively, which are in good agreement with the measured values of 29 and 63, respectively. The calculated harmonic cutoff for O_2 is at $q_c=45$, to be compared to the measured value at 53. For N_2, the calculated cutoff is at $q_c=55$, as compared to the experimental value at 57. More importantly, the theoretical results clearly show that there are little differences between the HHG for Ar and N_2, but there are drastic differences in the high-order HHG between Xe and O_2. The agreement

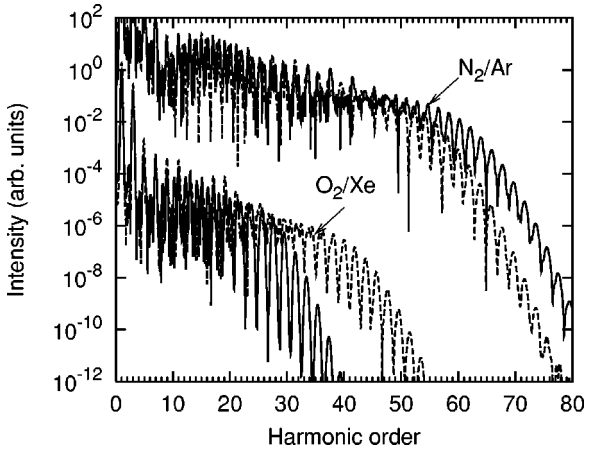

FIG. 5. Theoretical simulated HHG power spectra from Xe, O_2, Ar, and N_2 in an 800 nm, 25 fs intense laser field at the saturation intensities listed in Table I. Solid lines are for atoms and dashed lines are for molecules. Note that the results of N_2 and Ar have been shifted by a factor of 10^7.

between the calculated and the measured HHG cutoff is not so good for O_2 molecules comparing with rare-gas atoms Xe and Ar. The discrepancies between the calculation and the experiment for molecules are understandable since we approximate each two-center molecular orbital by a single one-center atomic orbital within the framework of the ADK model. Note that the cutoff order in the calculation is defined as the intercept of the plateau and the sharp dropoff of the spectrum.

In summary, we have observed a significant extension of the harmonic cutoff for O_2 molecules, as compared to Xe atoms, when both are exposed to an intense laser field, even though both have nearly identical ionization potentials. No such extension has been observed for the other pairs, N_2 vs Ar, which also have nearly identical ionization potentials. The origin of the harmonic cutoff extension is traced to the well-known ionization suppression of the O_2 molecules. By replacing the two-center molecular orbital with the closest one-center atomic orbital in the ADK model to account for the symmetry and the geometry of the molecular orbitals, we have shown that the ADK model can be used to interpret the ionization rates of diatomic molecules. The present simple ADK model offers possible new directions for studying molecules in an intense laser field. The cutoff extension caused by the ionization suppression provides another avenue for obtaining higher-energy x-ray photons, complementary to the schemes demonstrated previously [14].

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[1] M. Hentschel, R. Kienberger, C. Spielmann, G.A. Reider, N. Milosevic, T. Brabec, P. Corkum, U. Heinzmann, M. Drescher, and F. Krausz, Nature (London) **414**, 509 (2001).

[2] X. Li, A. L'Huillier, M. Ferray, L. Lompre, and G. Mainfray, Phys. Rev. A **39**, 5751 (1989).

[3] Y. Liang, S. Augst, S.L. Chin, Y. Beaudoin, and M. Chaker, J. Phys. B **27**, 5119 (1994).

[4] C. Lynga, A. L'Huiller, and C.G. Wahlstrom, J. Phys. B **29**, 3293 (1996).

[5] R. Velotta, N. Hay, M.B. Mason, M. Castillejo, and J.P. Marangos, Phys. Rev. Lett. **87**, 183901 (2001).

[6] A. Talebpour, C.Y. Chien, and S.L. Chin, J. Phys. B **29**, L677 (1996).

[7] C. Guo, M. Li, J.P. Nibarger, and G.N. Gibson, Phys. Rev. A **58**, R4271 (1998).

[8] M.J. DeWitt, E. Wells, and R.R. Jones, Phys. Rev. Lett. **87**, 153001 (2001).

[9] B. Shan, A. Cavalieri, and Z. Chang, Appl. Phys. B: Lasers Opt. **74**, s23 (2002).

[10] M. Lewenstein, P. Balcou, M.Y. Ivanov, A. L'Huillier, and P.B. Corkum, Phys. Rev. A **49**, 2117 (1994).

[11] M.V. Ammosov, N.B. Delone, and V.P. Krainov, Zh. Éksp. Teor. Fiz. **91**, 2008 (1986) [Sov. Phys. JETP **64**, 1191 (1986)].

[12] C. Guo, Phys. Rev. Lett. **85**, 2276 (2000).

[13] J. Muth-Bohm, A. Becker, and F.H.M. Faisal, Phys. Rev. Lett. **85**, 2280 (2000).

[14] B. Shan and Z. Chang, Phys. Rev. A **65**, 011804(R) (2002).