Strong-field ionization and high-order-harmonic generation during polyatomic molecular dynamics of N_2O_4

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We present state-of-the-art ab initio–type computations of strong-field ionization (SFI) and the single-molecule response contribution to high-order-harmonic generation (HHG) in the polyatomic molecule N_2O_4. The numerical method uses a mixed orbital- and grid-based approach to model the multielectron bound states and single-electron continuum. The effects of ionic-core attraction and Coulomb-mediated interchannel coupling are rigorously included. We show that full-dimensionality time-dependent multielectron computations of SFI and HHG in polyatomic molecules are now feasible. The computational results indicate that (a) SFI yields in N_2O_4 are dominated by a single ionic state (the A_g state), and are strongly modulated by the N-N stretch coordinate; and (b) the HHG radiating dipole as a function of the N_2O_4 N-N stretch is dominated by the same, single state. The molecular-beam coincidence measurements presented here support the computational results. Due to the differences in the estimated vibrational amplitude, however, the computations are not in full agreement with previous HHG data.

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I. INTRODUCTION

Attosecond science [1], driven by the underlying processes of strong-field ionization (SFI) and high-order-harmonic generation (HHG) [2], offers the promise of measuring electronic motion with angstrom and subfemtosecond resolution. In the process of HHG, an atom or molecule is first ionized by a strong laser field. The liberated electron is then accelerated in the laser field to tens of eV and recombines with the parent ion, emitting its energy as a burst of XUV radiation. Although much work in this field has focused on the atomic and small-molecule limits where existing semianalytical strong-field-ionization theories remain applicable, experiments on polyatomic systems have begun to appear [3–7]. The electronic and structural properties of these polyatomic systems lie far from the expected range of validity of the simple theories. Even more challenging to theory is the use of HHG in time-resolved probing of polyatomic molecular dynamics [4]. In such situations, both vibrational and electronic structures generally evolve as a function of time [8]. In order to model the results of such measurements, we will require theories of SFI and HHG which extend to real polyatomic systems.

Here, we apply a recently developed ab initio–type method [9], potentially capable of handling SFI and HHG in gas phase molecules of arbitrary size. We use the previously studied N_2O_4 system [4] as the target for the theoretical method. In past work [4], a vibrational wave packet on the electronic-ground-state surface of neutral N_2O_4 was prepared via impulsive stimulated Raman scattering. The wave packet exhibited large-amplitude motion along the symmetric N-N stretch coordinate. The wave-packet dynamics were probed using a time-delayed intense probe pulse which generated the HHG signal, with all observed harmonic orders maximizing at the outer turning point. Using traditional tunneling theories for the SFI and HHG processes, the time-resolved HHG spectra were interpreted in terms of switching between two active ionic continua, with the B_{2g} state dominating at the inner turning point and the A_g ground state dominating at the outer turning point.

The method employed here [9] uses a full-dimensionality multielectron time-dependent mixed orbital- and grid-based approach to model the multielectron bound states and the single-electron continuum. The effects of ionic-core attraction and Coulomb-mediated interchannel coupling are rigorously included. To mimic a full nuclear wave-packet dynamics calculation, we apply this approach to model single-molecule response in HHG and SFI in N_2O_4 as a function of the N-N bond length. The A_g-state ionization dynamics dominates over the whole range of internuclear distances considered. The B_{2g} excited state does play a minor role, but mostly beyond the outer turning point where it affects the total HHG signal through destructive interference with the dominant A_g channel. The results show a strong bond-length dependence of the angle-resolved ionization yields for the B_{2g} excited-state channel but little bond-length dependence for the A_g ground-state channel. We note that, while our calculations do predict modulations of the HHG yield as a function of the vibrational coordinate, they do not fully reproduce the modulations seen in the HHG data of Ref. [4]. However, they do clearly demonstrate that a two-state tunneling-type calculation, as given in Ref. [4], is insufficient. Specifically, for the comparison of the A_g and B_{2g} ionization rates, the authors of Ref. [4] used the Keldysh rate \( a_K = \exp[-(2/3)(2I_p)^{3/2}/E_0] \) which incorporates only the ionization potential \( I_p \) and the peak field strength \( E_0 \), but not the details of the electronic structure or the ion potential. The present ab-initio–type calculations are a significant improvement over the approximate methods used in Ref. [4] and suggest a necessary departure from traditional tunneling theories developed for atomiclike systems, as high-order-harmonic probing and attosecond methods extend into the regime of polyatomic molecules. As applications of ab
\textit{initio}-type methods are expanded to include even more electronic continua, laser-driven interchannel coupling, coherent vibrational wave-packet effects, focal volume averaging, and propagation effects, we anticipate the ability to compare directly with time-resolved HHG studies of dynamics in polyatomic molecules.

\section{II. SFI Simulations}

We focus primarily on the independent-ionic-channel version of the method \cite{9}. That is, we consider ionization to multiple final ionic states (the $A_g$ and $B_{2g}$ states) but calculate ionization to each state individually, neglecting ionic interchannel couplings. The independent-channel version of Ref. \cite{9} can be used as the starting point from which all formulas used in the theoretical analysis of Ref. \cite{4} can be derived by making further approximations. In particular, the present method allows for the rigorous inclusion of the ionic electrostatic binding potential during ionization, recollision, and recombination, all of which were either neglected or included only semiclassically in the previous model \cite{4}. In order to facilitate the comparison, the present model uses the same quantum chemistry calculations used in Ref. \cite{4} to obtain the required potential energy surfaces, ionic potentials, and Dyson orbitals. We have also performed coupled-channel calculations that include coupling terms between the ionic states, arising from the Coulomb interaction between the continuum electron and the ionic cores. Since laser-driven coupling \cite{11} between the $A_g$ and $B_{2g}$ ionic states is forbidden by symmetry due to the vanishing transition dipole, the Coulomb interaction is the only coupling mechanism present. For these states we find negligible qualitative differences between the coupled and uncoupled results, further justifying the use of the uncoupled-channel calculations. Other states not included here could potentially be coupled.

We use a laser pulse at $\lambda = 800$ nm, with a $\sin^2$ envelope, full width at half maximum of 4.8 fs, and $1.5 \times 10^{14}$ W/cm$^2$ peak intensity. The calculations employ three-dimensional Cartesian grids extending to $\pm 25$ a.u. in all directions. Absorbing boundaries \cite{11} with width of 4.3 a.u. are used at the grid edges. For this grid size and intensity, the long trajectories are mostly absorbed at the grid edges before they recollide, and therefore the calculated HHG spectra effectively included the short trajectories alone. Ionization and single-molecule HHG yields are calculated for different angles between the molecular frame and the polarization direction of the laser. The conventional wisdom derived from angle-resolved ionization rates for diatomics and electron \cite{9}. In the Koopmans approximation they become the highest occupied molecular orbital (HOMO) and the next lower orbital (HOMO-1). For diatomics, it has been shown \cite{13} that orbitals with nodes along dominant axes of symmetry have suppressed ionization rates. Strong-field ionization picks out the low-momentum components of the ionizing orbitals on the order of $k \approx 2/\sqrt{\omega}$ \cite{13}. Orbitals with nodes along the dominant axes of symmetry, such as the $B_{2g}$ state, have suppressed amplitude of the low-momentum components and consequently show a suppression of ionization. In contrast, orbitals without nodes along the dominant axes of symmetry, such as the $A_g$ state, have no expected suppression of the low-momentum components and show no suppression in ionization.

Of further interest to the ionization dynamics are the angle-resolved ionization yields, shown in Fig. 2, where the angle is between the molecular frame and the electric field polarization direction of the laser. The conventional wisdom derived from angle-resolved ionization rates for diatomics and...
FIG. 3. (Color online) Bond-length-dependent HHG signal: HHG from the $A_g$ channel ($\times$), HHG from the $B_{2g}$ channel ($\circ$), and the coherent sum of the two channel contributions ($+$). Also see Fig. 1 caption.

FIG. 4. (Color online) HHG spectra calculated with (dashed curves) and without (solid curves) Coulomb interchannel coupling for a N-N distance of 2.6 Å. Shown are the HHG yields for the $A_g$ channel ($\times$), the $B_{2g}$ channel ($\circ$), and the coherent sum of the two channel contributions ($+$).

three-step decomposition of the HHG process. Thus, the ionization yields discussed above and the HHG yields presented in Fig. 3 all come from the same time-dependent calculation, and there is no ambiguity in either assigning an instantaneous ionization rate or assigning the harmonic photon energy to a particular recollision energy. From the calculated HHG intensities, it can be seen that the $A_g$ state dominates over the whole range of N-N bond lengths considered, whereas HHG from the $B_{2g}$ state remains about an order of magnitude lower for all bond lengths. When the HHG signal from both states is added coherently, as is the case in experiment, the $B_{2g}$ state does have an effect on the total HHG yield. It lowers the yield at large N-N bond lengths through destructive interference with the $A_g$ channel. The predictions of Fig. 3, over the 1.6–2.2 Å bond-length range, differ from the experimental results [4], which saw all measured HHG orders peak in phase at the outer turning point. The differences could be due to a number of factors, including ionic states not included here, phase-matching effects, pulse shape, and focal volume averaging, etc.

In Fig. 4, we present coupled-channel simulations of the HHG signal for an N-N bond length of 2.6 Å. These more elaborate calculations include the Coulomb interaction between the continuum electron and the ionic cores. Coulomb coupling of the ionic states can occur during the ionization [15] and recollision [16] steps. As can be seen in Fig. 4, these Coulomb couplings between $A_g$ and $B_{2g}$ cause only small quantitative changes in the HHG yields, thus justifying the use of the uncoupled simulations.

III. HHG SIMULATIONS

We now turn to the calculation of HHG signals. The single-molecule HHG yield was calculated using the length form of the dipole operator. The HHG signal as a function of N-N bond length for harmonic orders 17 to 27 is shown in Fig. 3. The figure plots the HHG yield from the two ionic states independently, as well as their coherent sum. These HHG yields include the coherent sum of emission coming from all angles of the molecular axes relative to the electric field polarization direction. We emphasize that the method of Ref. [9] is a realization of the time-dependent Schrödinger equation and does not assume any type of

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coherent vibrational wave-packet effects, higher-lying ionic states, laser-driven interchannel coupling to these additional states, and phase-matching and propagation effects. In order to test the present theoretical results under different conditions that allow measurements of isolated molecular ionization, we developed molecular-beam photoelectron-photoion coincidence SFI yield measurements of vibrational wave-packet dynamics of N$_2$O$_4$. Briefly, a vibrational wave packet in the N-N stretch coordinate is prepared by impulsive stimulated Raman scattering (SRS) using an ultrashort laser pulse (35 fs) at $\lambda = 2100$ nm. We measure the SFI yield as a function of time delay with respect to the SRS pump using a probe laser pulse at $\lambda = 800$ nm. In order to minimize focal volume averaging, the 800 nm SFI probe pulse interrogated a small volume within that of the $\lambda = 2100$ nm SRS pump pulse. Furthermore, the molecular beam was tightly skimmed to intersect with only the central third of the Rayleigh range of the laser foci. Spherical reflective focusing optics were implemented so as to minimize chromatic effects. The pump-probe time delay was scanned by a computer-controlled delay stage. The temporal width (full width at half maximum (FWHM)) of the probe pulse was around 35 fs; the multiphoton-ionization cross correlation between pump and probe pulses was around 50 fs. Zero time delay was set by the cross-correlation measurements performed before the scans. Temporal stability was ensured by confirming zero time delay after all scans were complete. The peak intensity of both laser pulses was $I_0 = 0.9 \times 10^{14}$ W/cm$^2$, higher than the SRS pump pulse ($0.2 \times 10^{14}$), but lower than the HHG probe ($2 \times 10^{14}$) in Ref. [4]. N$_2$O$_4$ is supplied at an estimated interaction-region number density of around 90% at the low target density required for the N-N stretching motion, we calculated the polarizability of the N-N bond. The oscillation period matches the gas-phase N-N symmetric stretch for the stretched N-N bond. The oscillation period matches that SFI should occur mainly at the outer turning point of the potential energy curve of Ref. [4].

For the SRS wave-packet dynamics alone resulted in a constant background of around 2.4 electrons and 1.4 ions per laser shot, which was subtracted. (Ion and electron yields differ due to collection and detection efficiencies.) We observed strongly pronounced oscillations in the SFI yield, with the initial modulation depth exceeding 30%. The oscillation period as determined from the data in Fig. 5 (and three similar data sets) is $T = 131.25 (0.40)$ fs. The positions of the maxima occur at $nT + T/4 (n \in \mathbb{N}^+)$, consistent with an initial outward stretch of the N-N bond. For comparison, linear interpolation of the calculated ionization yields (Fig. 1) obtains an $\approx 40\%$ modulation depth, with the yield maximizing for the stretched N-N bond.

The pump laser wavelength here is longer than that of Ref. [4] and therefore the amplitude of the wave-packet motion could be different. To estimate the amplitude of the N-N stretching motion, we calculated the polarizability derivative of N$_2$O$_4$ with respect to the N-N bond length using numerical differentiation of the unrelaxed static polarizabilities in coupled-cluster theory with single, double, and connected triple excitations [CCSD(T)] using augmented correlation-consistent valence triple-zeta (aug-cc-pVTZ) basis set [17–19]. The N-N bond length was fixed at $R_{NN} = 1.786$ and 1.686 Å, with the remaining structural parameters optimized at the CCSD(T)/aug-cc-pVTZ level. The resulting isotropic polarizability derivative $\partial \alpha / \partial r$ is 12.2 bohr$^2$. For a 2.1 µm pump wavelength, the differences between the static and frequency-dependent polarizabilities are expected to be negligible. For a pump pulse much shorter than the vibrational period, the overall momentum transfer to the vibrational mode is [20] $p = \frac{1}{2m} F_0 \int f(t)^2 dt$, where $F_0$ is the peak amplitude of the electric field, and $f(t)$ is the carrier envelope. [For a Gaussian pulse with FWHM of $\tau$, the envelope integral is $\tau (\pi / \ln 16)^{1/2}$.] The amplitude of the vibration can be estimated from the classical turning points at the energy $p^2 / 2 \mu$, where $\mu$ is the reduced mass of the oscillator. For the SRS conditions in our experiment ($I_0 = 0.9 \times 10^{14}$ W/cm$^2$; $\tau = 35$ fs), the resulting vibrational amplitude is $-0.14 / +0.18$ Å, based on the anharmonic potential energy curve of Ref. [4].

In Fig. 5 we present the total (i.e., energy- and angle-integrated) photoelectron and photoion yield per laser shot as a function of the pump-probe time delay. The polarizations of pump and probe pulse were parallel. The data were averaged over $9.5 \times 10^4$ laser shots at each time delay, accumulated over 19 time-delay scans. Ionization by the SRS pump laser pulse alone resulted in a constant background of around 2.4 electrons and 1.4 ions per laser shot, which was subtracted. (Ion and electron yields differ due to collection and detection efficiencies.) We observed strongly pronounced oscillations in the SFI yield, with the initial modulation depth exceeding 30%. The oscillation period as determined from the data in Fig. 5 (and three similar data sets) is $T = 131.25 (0.40)$ fs. The positions of the maxima occur at $nT + T/4 (n \in \mathbb{N}^+)$, consistent with an initial outward stretch of the N-N bond. For comparison, linear interpolation of the calculated ionization yields (Fig. 1) obtains an $\approx 40\%$ modulation depth, with the yield maximizing for the stretched N-N bond. The oscillation period matches the gas-phase N-N symmetric stretch $\nu_3$ Raman-active mode located at $254 \pm 2$ cm$^{-1}$ [21], which corresponds to a period of $131.3 \pm 1.0$ fs. For these SRS wave-packet dynamics experiments (at $\lambda = 2100$ nm), the SFI yield is modulated in phase with the previously reported HHG modulations [4], both periodically maximizing at $nT + T/4$. These experimental results support the present theoretical model, which suggests that SFI should occur mainly at the outer turning point of the N-N stretch due to the dominance of the $A_g$ ground-state channel.

V. CONCLUSIONS

Our calculations represent one of the most complete simulations of SFI and single-molecule HHG response in a polyatomic molecule to date. It is now feasible to rigorously include in SFI simulations effects of orbital symmetry, structured binding potentials, and Coulomb-driven interchannel couplings. The present example of HHG in N$_2$O$_4$ as a function of N-N bond length highlights the importance of effects often neglected in traditional strong-field approximation (SFA).
based approximate methods. The dynamics of polyatomic systems generally involves the motions of the atoms, the rearrangements of the valence electrons, and, importantly, the coupling between these [8]. In such a situation, the simple SFA-based methods are unlikely to apply. As the field of attosecond science evolves toward dynamics in polyatomic molecules, there is a need for high-level ab initio computations of both SFI and HHG. Emerging theoretical methods, such as the one presented here, will play an increasingly important role in this development.

[17] J. F. Stanton, J. Gauss et al., computer code CFOUR (University of Texas at Austin, USA and Universität Mainz, Germany). For the current version, see [http://www.cfour.de].