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Nuclear Dynamics in Polyatomic Molecules and High-Order Harmonic Generation

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High-order harmonic generation in molecular gases is accompanied by short-time evolution of the nuclear vibrational wave function. Using normal coordinate representation, I derive a simple analytical theory of short-time autocorrelation functions and apply it to a test set of 15 small molecules. The results explain large isotope effects observed in CH₂. At the harmonic cutoff in 800 nm driving field, nuclear dynamics reduces the emission intensity from NO and NO₂ molecules by more than 50%. Autocorrelation functions are sensitive to the initial vibrational state, with the nodal structure of the initial vibrational wave packet reflected in the frequency spectrum of the harmonics.

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Atomic and molecular gases subjected to intense near-infrared laser fields emit trains of attosecond pulses of high-order harmonic (HHG) radiation. Its spectrum contains information on the electronic and nuclear structure and dynamics [1–3]. Potentially, HHG experiments enable measurements with simultaneous attosecond temporal and subangstrom spatial resolution [4–6].

In the standard model [7,8] of high-harmonic generation, an electron is liberated near the peak of the intense laser field. It is then accelerated by the field, and recombines with the parent ion emitting a photon. The intermediate ion exists for a fraction of the laser cycle, with the most intense laser field. It is then accelerated by the field, and recombines with the parent ion emitting a photon. The intermediate ion exists for a fraction of the laser cycle, with the most energetic photons emitted ~0.65τc after ionization (τc = 2π/ω is the laser period). At the 800 nm wavelength, cutoff harmonics correspond to the cation existing for only ~1.7 fs—a fleeting time for nuclear dynamics. Only the lightest nuclei are able to move appreciably in this time. The femtosecond-scale nuclear motion has been predicted [9] and observed [10,11] in the lightest molecules—H₂ and D₂, as well as in methane and CD₄. It is widely assumed [2] that molecular HHG could only be affected by the nuclear motion of hydrogen isotopes.

Although the higher mass of other nuclei does decrease the displacements on the HHG time scale, the intensity of harmonic radiation is modulated by the square modulus of the nuclear autocorrelation function [9]:

\[ I \propto I_N(t_c) = |\langle \Psi_n(t_c) | \Psi_c(t_c) \rangle|^2 \]  

rather than by the displacements per se. In Eq. (1), \( \Psi_n(t) \) is the vibrational wave packet evolving on the potential energy surface of the neutral species. Wave packet \( \Psi_c(t) \) evolves on the cationic surface. Evolution starts at the time of electron’s birth (\( t = 0 \)), at which time the two wave packets are assumed to coincide: \( \Psi_c(0) = \Psi_n(0) \).

The width of the “probe” wave packet \( \Psi_n \) scales as \( m^{-0.5} \), where \( m \) is the effective mass of the oscillator. Because at short times the displacement of \( \Psi_c \) decreases as \( m^{-1} \), the two effects partially compensate, and significant modulation of the HHG spectra may occur.

Equation (1) is already an approximation. It assumes that the ionization and recombination amplitudes do not depend on the molecular geometry, no depletion of the ground-state occurs, and that the Born-Oppenheimer potential energy surfaces of both species are not affected by the laser field. Although approximate, Eq. (1) is a useful starting point for studies of polyatomic molecules, where the exact treatment is at present prohibitively expensive.

In the harmonic approximation, vibrational Hamiltonian of the neutral species is given by [12]

\[ \hat{H}_n = \sum_i \left\{ -\hbar^2 \frac{\partial^2}{\partial q_i^2} + \frac{\omega_i^2}{2} q_i^2 \right\} \]  

where the mass-weighted normal coordinates \( q_i \) are linear combinations of the Cartesian coordinates \( r_a \):

\[ q_i = \sum_a Q_{ai} m_a^{1/2} (r_a - r_0^a) \]  

and \( Q_{ai} \) and \( \omega_i^2 \) are, respectively, the eigenvectors and eigenvalues of the mass-weighted Hessian matrix at the equilibrium coordinates \( r_0^a \):

\[ H_{ab} = m_a^{-1/2} m_b^{-1/2} \frac{\partial^2 U}{\partial r_a \partial r_b} \]  

The eigenfunctions of \( \hat{H}_n \) are given by

\[ \varphi_i(q) = \prod_i \left( \frac{\omega_i}{\pi \hbar} \right)^{1/4} e^{-q_i^2/2} \left( \frac{2 \omega_i \hbar}{\pi} \right)^{1/4} H_{ab}(z_i) \]  

where \( H_b \) are Hermite polynomials and \( z_i = (q_i / \hbar)^{1/2} \).

The cationic vibrational Hamiltonian in the region accessed by short-time dynamics is

\[ \hat{H}_c = \hat{H}_n + \hat{H}_1 + \frac{1}{2} \hat{H}_2 \]  

where the gradient (\( \hat{H}_1 \)) and the Hessian (\( \hat{H}_2 \)) coupling terms are evaluated at \( \vec{r} = \vec{r}_0 \):

\[ \hat{H}_1 = \sum_i g_i H_1(z_i) \]  

\[ \hat{H}_2 = \sum_{i \neq j} h_{ij} H_1(z_i) H_1(z_j) + \sum_i h_i [H_2(z_i) + 2] \]
Additionally, it assumes that the initial state is an eigenstate of the Hamiltonian. The nuclear autocorrela-
tion factor [Eq. (1)] becomes

\[ I_{\nu,\mu}(t) = 1 + \sum_{s=1}^{\infty} \frac{1}{(2s)!) B_{\mu}^{(2s)} f_{2s}^{(s)}. \]  

Equation (17) is subject to all the limitations of Eq. (1). Additionally, it assumes that the initial state is an eigenfunction of the Hamiltonian. The wave packets do not leave the region of space where quadratic expansion of the cationic potential energy surface is valid. Its accuracy is expected to improve for shorter times, heavier nuclei, and spatially constrained nuclear motion. 

At high expansion orders (s), many of the intermediate amplitudes in Eq. (16) appear repeatedly. Formally, the total number of distinct intermediates grows as \( O(s^{d+1}) \), where \( d \) is the number of vibrational degrees of freedom in the system. The number of numerically significant amplitudes is much smaller. These amplitudes can be stored efficiently as a sparse binary tree [13,14].

Although for practical calculations one would use Eq. (16) directly, qualitative insight is also valuable. For most molecules considered here, the gradient term \( \hat{H}_g \) [Eq. (7)] dominates. Neglecting change in the curvature \( \hat{H}_g \), Eq. (8), the lowest-order term in Eq. (18) for the ground vibrational state is

\[ B_{(g)}^{(2)} = -\frac{1}{2\hbar} \sum_{i} \frac{1}{\omega_i} \left( \sum_{a} \frac{Q_{ai}}{m_a^{1/2}} \frac{\partial U_a}{\partial r_a} \right)^2. \]  

Thus, nuclear dynamics is significant whenever the intermediate cationic surface possesses a large gradient along a soft degree of freedom in the neutral species.

Electronic structure calculations on selected molecules use correlation-consistent polarized triple-zeta basis set (cc-pVTZ) [15] and GAMESS-US [16] package. Basis functions with the highest angular momenta (f on C, d on H) are omitted for CH\(_4\). Structures are optimized for the neutral species. Hydrogen molecule calculations use five-orbital complete active space (CAS) wave functions. Diatomic molecules (CO, Cl\(_2\), N\(_2\), F\(_2\), O\(_2\), and NO) use eight-orbital CAS, with the valence ns and np shells included. Triatomic CO\(_2\) and NO\(_2\) use ten-orbital CAS wave functions, while C\(_3\)H\(_4\) calculations employ a nine-orbital CAS. Methane’s electronic structure is treated with an eight-orbital CAS. In either case, 1s core orbitals are not correlated. The heavier C\(_4\)H\(_6\) and PF\(_3\) molecules are treated with spin-unrestricted frozen-core second-order Moller-Plesset (MP2) approach. Active spaces and state weights are chosen such as not to lift electronic degeneracies artificially.

Treatment of the electronic structure of methane cation C\(_{1}^{+}\) requires separate discussion. Ionization of the \( T_d\)-symmetric CH\(_4\) leads to the intersection point of the three branches of the Jahn-Teller distorted \( 2F_{2} \) state. The initial vibrational wave packet spans all three branches. Its composition depends on the relative orientation of the molecule and the ionizing field, as well as on the subcycle field evolution. A fully satisfactory treatment of the problem requires a coupled simulation of the electronic and nuclear degrees of freedom. For the very short times considered presently, I choose to ignore the nonadiabatic coupling of the electronic surfaces, and treat each branch of the \( 2F_{2} \) surface independently. In order to separate the branches, I apply static electric field of 0.05 atomic units along a \( C_2 \) axis of symmetry. The field splits the components of the \( 2F_{2} \) state by \( \approx \pm 16 \) mH from the barycenter, completely lifting the degeneracy. The results below are for the lowest component of the multiplet. Autocorrelation functions for the remaining two components are numeri-
cally similar. As a consistency test, I also vary splitting fields between 0.04 and 0.08 a.u.

Nuclear factors $I_N$ calculated for the ground-state initial vibrational wave packet are shown in Fig. 1. The fastest dynamics occurs in $D_2$, $H_2$, $CD_2$, and $CH_4$. Nuclear motion is important for other molecules as well. Thus, for the NO radical nuclear dynamics decreases HHG radiation intensity by a factor of $0.44 \times$ at the 800 nm cutoff. A smaller, but still substantial, effect ($0.65 \times$) is found for $O_2$. The modulation is due to the change in equilibrium geometry upon ionization. In both molecules, the chemical bond contracts by $\Delta r = -0.17$ bohr upon ionizing, producing large forces on the atoms: $=0.19$ a.u. in $NO^+$, $=0.13$ a.u. in $O_2^+$. These forces are comparable to the initial gradient in $H_2^+$ ($=0.14$ a.u., $\Delta r = +0.59$ bohr).

Less expected is the rapid evolution in $NO_2$ and $PF_3$. In the bent $NO_2$ radical, the ground-state cation is linear. Removal of an electron creates a large force ($g = 6.0 \times 10^{-3}$ hartree) along the 815 cm$^{-1}$ (harmonic) bending mode. The $1470$ cm$^{-1}$ symmetric stretch mode is also strongly affected ($g = 6.5 \times 10^{-3}$ H), reflecting the $=0.10$ bohr decrease in the N–O bond length. In $PF_3$, removal of the lone-pair electron reduces pyramidalization, with the F–P–F angle increasing by $\approx 10^\circ$ and the P–F bond shortening by $= 0.14$ bohr. Large forces arise along the inversion mode ($\nu = 480$ cm$^{-1}$, $g = 3.2 \times 10^{-3}$ H) and the symmetric stretch mode ($\nu = 900$ cm$^{-1}$, $g = 5.9 \times 10^{-3}$ H).

One experimental consequence of the short-time nuclear dynamics is the isotope effects in harmonic intensity [9,10]. Deuterium isotope effects as large as $3 \times$ were demonstrated in methane. In hydrogen, the calculated ratio of harmonic autocorrelation functions [Fig. 2(a)] shows the same trend, but underestimates the magnitude of the experimental isotope effect. The calculated harmonic ratios are smaller than in the previous anharmonic treatment [9]: 1.16 vs $=1.3$ at 0.8 fs, increasing to 1.35 vs $=1.5$ at 1.7 fs. The discrepancy is likely due to the very large displacements ($=0.5$ bohr at 1.7 fs [9]) reached in the $H_2^+$ cation, which make harmonic approximation inappropriate. Smaller displacements (and therefore better accuracy) are expected for molecules where hydrogen motion is not involved. The remaining deviation from experiment is likely due to the neglect of the electronic contributions, which are particularly important for $H_2$ [17,18]. In particular, tunneling ionization in $H_2$ is biased towards longer bond lengths [19], so that the initial wave packet deviates from the pure $\nu = 0$ vibrational ground state of the neutral [20,21]. The difference in recombination dipoles between $H_2$ and $D_2$ is also significant for HHG [10].

Despite severe approximations, a reasonable agreement with experiment is found in methane [Fig. 2(b)]. Here, the calculated isotopic ratios are sensitive to the artificial splitting field imposed on the system. The fields I use are comparable to the electric fields present in the experiment (estimated intensity of $\approx 2 \times 10^{14}$ W cm$^{-2}$ [10], $E_{max} = 0.08$ a.u.). As a result, the cationic energy surface is strongly affected by the subcycle evolution of the laser field, making a more rigorous simulation of this system highly desirable.

Remarkably, nuclear autocorrelation function in methane decays faster than in lighter hydrogen (Fig. 1), even though a concerted motion is involved in $CH_4$. The effect arises due to the extreme change in the potential energy surface upon ionization. Both the gradient [Eq. (7) and

![FIG. 1 (color online). Nuclear vibrational factors $I_N$ [Eq. (17)]. Dotted vertical lines correspond to evolution times of the cutoff harmonics for $\lambda = 800$ nm ($t_{cut} = 1.73$ fs) and 1600 nm (3.47 fs). The curves continue to the time $t$ where the order-$(N - 2)$ expansion deviates from the order-$N$ result. $N$ is 80 for $H_2$, $D_2$, NO, CH$_4$, and CD$_4$; 32 for CO, F$_2$, N$_2$, O$_2$, and NO$_2$; 16 for Cl$_2$ and CO$_2$; 12 for C$_2$H$_4$ and C$_4$H$_6$; 10 for PF$_3$.](image)

![FIG. 2 (color online). Autocorrelation contribution to isotope effects in HHG. Top: $D_2$ vs $H_2$. Bottom: $CD_2$ vs $CH_4$. For methane, magnitudes of the splitting field (see text) are between 0.04 a.u. (maximum field at laser intensity of $\approx 6 \times 10^{13}$ W cm$^{-2}$) and 0.08 a.u. ($\approx 2 \times 10^{14}$ W cm$^{-2}$). Experimental values are from Ref. [10].](image)
curvature [Eq. (8)] terms are large in methane cation, with 
the change in curvature accounting for about half of 
the decay rate. Large change in curvature is characteristic 
of Jahn-Teller cations. Comparable isotope effects may be 
expected in other spatially degenerate cases.

The final question I would like to address is the de-
pendence of HHG intensities on the nodal structure of the 
initial vibrational wave function. I consider pure vibra-
tional states of NO. The nuclear factor for the \( \nu = 0 \)
ground vibrational state shows featureless, nearly 
Gaussian decay pattern (Fig. 3). Excited vibrational states 
yield faster decay up to \( \approx 1.5 \) fs, as could be expected from 
the increase in coupling strength with the quantum number \( \nu \) 
[Eq. (13)]. However, at slightly longer times, the \( \nu = 1 \) 
\( I_N \) factor goes to zero at \( \approx 1.9 \) fs, then exhibits a maximum 
at \( \approx 3.1 \) fs. The \( \nu = 2 \) autocorrelation function passes 
through zero at \( t = 1.4 \) and 3.5 fs, and develops local 
maxima at 2.3 and 4.9 fs, before finally decaying. At a 
sufficiently long laser wavelength, the nodes of the vibra-
tional wave packet map directly onto the high-harmonic 
spectrum of vibrationally excited NO. A similar mapping 
is expected in other systems where the short-time dynamics 
is dominated by the linear term \( [\hat{H}_1, \text{Eq. (7)}] \) and a single 
normal mode is excited.

Even in molecules where nuclear autocorrelation factors 
are not significant for HHG at \( \lambda = 800 \) nm, they will 
become more important at longer wavelengths. Indeed, 
the short-time \( I_N \) factors for ground-state initial vibrational 
wave packets behave as \( \approx \exp(-B_0^{(2)} t^2/2) \) with increasing 
wave packet evolution time.

Nuclear dynamics is a universal and essential feature of 
high-harmonic generation in molecules, especially at lon-
ger wavelengths. It presents both a challenge and an op-
portunity for the attosecond molecular science. Nuclear 
dynamics reduces the HHG efficiency in molecules. It may 
interfere with electronic structure reconstruction tech-
niques [22], otherwise expected to benefit from longer 
driving field wavelengths. At the same time, nuclear dy-
namics creates a possibility of a direct observation of both 
amplitudes and phases of vibrational wave packets through 
the HHG spectra. In principle, the technique could be 
applicable to small polyatomic molecules as well, provided 
that ionization does not cause excessive mixing of the 
normal modes of the neutral species.

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