Evidence of Nuclear Motion in H₂-like Molecules by Means of High Harmonic Generation

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Abstract—The dynamics of hydrogen-like molecules is investigated beyond the usual fixed nuclei approximation. The nuclear motion introduces in the familiar spectrum of emitted radiation additional regular lines whose separation is essentially given by the vibrational frequency of nuclear motion. A wavelet analysis of the emitted spectrum shows that the intensity of the harmonic lines is modulated with the same period of the nuclear motion; this suggests the possibility of the real-time control of the nuclear dynamics.

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1. INTRODUCTION

High-harmonic generation (HHG) is a process that stems from the nonlinear response of the electron wave function to intense laser fields: an electron is driven nonperturbatively by a strong laser field away from its parent atom or molecule, propagates in the field, and returns to the parent ion with the emission of high-energy photons [1]. The emitted radiation can be used in the production of UV or XUV pulses and to probe the electron dynamics; it carries information on the emitting source allowing a tomographic image of atoms and molecules [2]. The atomic spectra present features largely independent of the atomic species, while the large number of molecular degrees of freedom makes the radiation scattered from molecules strongly dependent on the molecular species. The molecular harmonic spectra thus also carry information about the molecular structure, and, in particular, about the dynamics of the electrons and nuclei [3]. The motion of the electrons in laser-driven atoms and molecules has been extensively investigated. In this paper, we show the possibility of monitoring the nuclear vibration of a molecule. In particular, we are interested in the response of a diatomic molecule to a monochromatic field, whose intensity is low enough to prevent a high rate of ionization and dissociation of the molecule, but strong enough to leave the nuclei in a slow oscillatory motion. The influence of the nuclear vibration on the harmonic generation in molecules has been recently investigated [4–6] and, now, we show that we can obtain information about the frequency of the nuclear vibration by means of a Fourier and a wavelet analysis.

2. MODEL AND RESULTS

In order to investigate the dynamics of a H₂-like molecule in the presence of an external laser field, we start by considering a simple 1D model for the molecule, treated beyond the fixed nuclei approximation. Since the nuclear mass M of the nuclei is much larger than the mass m of the electron, the nuclei will be considered as classical particles whose dynamics can be described by means of the Newton laws [7–9]. The 1D model is justified by assuming that the molecule has been previously aligned to the linearly polarized field [10, 11].

The one dimensional time-dependent Schrödinger equation (TDSE) for the electrons wave function ψ is

$$i\hbar \frac{\partial}{\partial t} \psi(X_1(t), X_2(t); x_1, x_2, t) = H_e \psi(X_1(t), X_2(t); x_1, x_2, t), \quad (1)$$

where x_1 and x_2 identify the positions of the electrons, $X_1(t)$ and $X_2(t)$ are the nuclear coordinates treated as the external parameters and the electron Hamiltonian is

$$H_e(t) = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} \right) + U(X_1(t), X_2(t); x_1, x_2) + e(x_1 + x_2)\mathcal{E}(t). \quad (2)$$

The laser electric field $\mathcal{E}(t)$ is given by

$$\mathcal{E}(t) = \mathcal{E}_0 f(t) \sin(\omega_L t), \quad (3)$$

where $\mathcal{E}_0$ is the laser field amplitude, ω_L is the laser angular frequency, and $f(t)$ is the pulse shape. We use a

soft-core potential for the interaction potential U :

$$U(X_1(t), X_2(t); x_1, x_2) = \frac{e^2}{\sqrt{A_{12} + [x_1 - x_2]^2}} - \sum_{j, \mu=1}^2 \frac{e^2}{\sqrt{A + [x_j - X_\mu(t)]^2}}, \quad (4)$$

with A and A_{12} being appropriate screening parameters. where

The nuclei dynamics is given by two coupled Newton equations

$$M \frac{d^2}{dt^2} X_\mu(t) = F_{\mu e}(t) + F_{\mu v}(t) + F_{\mu L}(t), \quad (5)$$

$$\mu \neq v = 1, 2,$$

$$F_{\mu e}(t) = - \sum_{j=1}^2 \iint_B \frac{e^2 [x_j - X_\mu(t)] |\psi(X_1(t), X_2(t); x_1, x_2, t)|^2}{\{A + [x_j - X_\mu(t)]^2\}^{3/2}} dx_1 dx_2, \quad (6)$$

$$\mu = 1, 2$$

is the force exerted by the electron-cloud upon the μ -th nucleus,

$$F_{\mu v}(t) = \frac{e^2 [X_\mu(t) - X_v(t)]}{\{A_N + [X_\mu(t) - X_v(t)]^2\}^{3/2}}, \quad (7)$$

$$\mu, v = 1, 2, \quad \mu \neq v$$

is the nucleus–nucleus interaction force, and

$$F_{\mu L}(t) = e X_\mu \mathcal{E}(t) \quad (8)$$

represents the force acted upon the nuclei by the laser. In (6), B indicates the width of the spatial propagation box for the electrons.

The laser field induces a strong acceleration on the electrons, which are stimulated to emit electromagnetic radiation; the radiated power is given by the Larmor formula

$$P(t) = \frac{4e^2}{3c^3} |a_1(t) + a_2(t)|^2, \quad (9)$$

where $a_i(t)$ is the quantum-averaged acceleration of the i -th electron and can be obtained by using the Ehrenfest theorem. The spectrum of the emitted radiation is

$$P(\omega) = \frac{4e^2}{3c^3} |\tilde{a}_1(\omega) + \tilde{a}_2(\omega)|^2, \quad (10)$$

with $\tilde{a}_i(\omega)$ as the Fourier transform of $a_i(t)$. The equilibrium internuclear distance in the absence of the laser is given by the value of R , which minimizes the ground state energy of the molecule $E_0 + e^2/\sqrt{A_N + R^2}$. The generic eigenenergy value $E_n(R)$ is obtained by solving the time-independent Schrödinger equation

$$\left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} \right) + U\left(-\frac{R}{2}, \frac{R}{2}; x_1, x_2\right) \right] \varphi_n\left(-\frac{R}{2}, \frac{R}{2}; x_1, x_2\right) = E_n(R) \varphi_n\left(-\frac{R}{2}, \frac{R}{2}; x_1, x_2\right), \quad (11)$$

in which R is assumed to be fixed, $E_n(R)$ and $\varphi_n(-R/2, R/2; x_1, x_2)$ ($n = 0, 1, \dots$) indicate, respectively, the eigenenergies and eigenstates. For the screening parameters $A = A_{12} = 0.5$ and $A_N = 0.03$, the equilibrium internuclear distance is calculated as $R_0 \approx 1.57a_0$. The initial wave function is chosen to be the ground state of the molecule at the equilibrium distance $\psi(-R_0/2, R_0/2; x_1, x_2, 0) = \varphi_0(-R_0/2, R_0/2; x_1, x_2)$; in ([12]), the interested reader can find an exhaustive discussion on the parity properties of $\varphi_0(-R_0/2, R_0/2; x_1, x_2)$ and on its numerical evaluation. The dynamics of the system is obtained by numerically solving coupled Eqs. (1) and (5).

In what follows, we present the results concerning the dynamics of a H₂-like molecule embedded in a laser field of peak intensity $I_0 = 10^{14} \text{ W cm}^{-2}$ and wavelength

$\lambda = 600 \text{ nm}$ (corresponding to $\hbar\omega_L = 2.065 \text{ eV}$); the laser pulse has a trapezoidal shape with 8 optical cycles (oc) of turn-on and turn-off and a constant intensity for 240 oc. The intensity of the laser used in our calculation does not induce dissociations of the molecule, but excites nuclear oscillations around the equilibrium position. The TDSE is numerically solved by means of a split-operator technique. The extension of the spatial box is $B = 256a_0$ (a_0 being the Bohr radius) and the spatial grid step is $\Delta x = 0.25a_0$; in order to prevent reflections, an absorbing mask is inserted at the boundary.

The spectra emitted by H₂ ($M = M_0 = 1836.27m$) and by two artificial molecules ($M = 4M_0$ and $M = 16M_0$) are shown in the main plots of Figs. 1a–1c; the molecular spectra present the usual comb of odd harmonics, but an increasing resolution provides evidence of the presence of satellite lines around the odd harmonics, as the

Fig. 1. The main plots show the total HHG spectra emitted by the molecule under the influence of the laser field. The insets show the details of the spectra. (a) $M = M_0 = 1836.27m$; (b) $M = 4M_0$; and (c) $M = 16M_0$. The laser parameters are $\lambda = 600$ nm, $I_0 = 10^{14}$ W cm $^{-2}$.

Fig. 2. Plot of the internuclear distance as a function of time for different nuclear masses. Dotted line, $M = M_0$; dashed line, $M = 4M_0$; and continuous line, $M = 16M_0$. Laser parameters as in Fig. 1.

Fig. 3. Plot of the details of the HHG spectra of Fig. 1. Dotted line, $M = M_0$; dashed line, $M = 4M_0$; and continuous line, $M = 16M_0$. Increasing the mass of the molecule by a factor of 4, the satellite peak-spacing halves as expected.

insets show. The presence of sidebands has been previously demonstrated in the spectra emitted by molecular ions [6] and attributed to the nuclear motion. Similar to the results obtained for molecular ions, in every molecular spectrum, the satellite lines are evenly spaced by a particular $\Delta\omega_n$ given by the nuclear vibrational frequency. This is evident by inspecting Fig. 2, where we

plot the time evolution of the internuclear distance: the field forces the nuclei to vibrate around the equilibrium internuclear distance with regular oscillations at frequency ω_M , different for molecules of different masses. We have numerically checked that these values of ω_M coincide with the spacing $\Delta\omega_n$ observed in the satellite peaks of the emitted radiation, as shown in Fig. 3. It is,

Fig. 4. Temporal evolution of the intensity of the Morlet transform of the 9-th harmonic (continuous line) and the internuclear distance (dashed line) for (a) $M = 4M_0$ and (b) $M = 16M_0$. Laser parameters as in Fig. 1.

thus, evident that the presence of the side peaks in the HHG spectra for different isotopes is strongly related to the nuclear oscillations, since the ionization and dissociation of the molecule is small, this means that it is possible to physically investigate the nuclear motion by means of a nondisruptive technique.

We also note that increasing the mass of the molecule, the spacing between the satellite peaks scales as $1/\sqrt{M}$: this behavior can be understood by considering that, in our numerical results, the nuclei displacement from the equilibrium position is relatively small and regular, so that we can approximate the nuclear motion with a harmonic motion whose oscillation frequency is proportional to the inverse square root of the mass of the vibrating particles as already shown in [6] for molecular ions.

Since from the Fourier transform we cannot gain information about the emission time of the harmonics, we resort to a wavelet transform in order to collect information on the temporal evolution of the spectrum. We use the Morlet power spectrum [13]

$$P_W(\omega, t) = \frac{4e^2}{3c} |\mathbf{a}_W(\omega, t)|^2, \quad (12)$$

where $\mathbf{a}_W(\omega, t)$ is the wavelet transform of the electron acceleration

$$\mathbf{a}_W(\omega, t) = \int_{-\infty}^{\infty} w(\omega; t, \tau) \mathbf{a}(\tau) d\tau, \quad (13)$$

and $w(\omega; t, \tau)$ is the kernel of the transform given by

$$w(\omega; t, \tau) = \sqrt{\omega} [e^{-i\omega(\tau-t)} - e^{-\sigma_0^2/2}] e^{-\omega^2(\tau-t)^2/2\sigma_0^2}, \quad (14)$$

where σ_0 is a constant parameter. Therefore, the Morlet transform gives the Fourier transform of the signal multiplied by a Gaussian centered at τ , apart from the term proportional to $\exp\{-\sigma_0^2/2\}$, which usually is dropped from the calculations as negligible.

Figure 4 shows the temporal evolution of the 9-th harmonic for (a) $M = 4M_0$ and (b) $M = 16M_0$ and of the corresponding internuclear distances. It is evident that a strong correlation between the temporal evolution of the intensity of the harmonic and the vibrational dynamics: the intensity modulation of the emitted radiation has the same periodicity as the nuclear motion. This means that the direct observation of the intensity modulation of the emitted radiation can be used to obtain real-time information about nuclear vibrations in molecules. The wavelet analysis, already successfully employed to investigate the electron dynamics in atoms and molecules [12, 14–18], is thus also a powerful tool to gain information on the nuclear motion in molecules.

3. CONCLUSIONS

Numerical simulations show that the motion of the nuclei of a laser-driven homonuclear diatomic molecule introduces in the HHG spectrum satellite peaks of usual odd harmonics. Since such sidebands are absent in the fixed nuclei spectra, they provide direct evidence of the nuclear vibrational motion. Furthermore, their

spacing is given by the oscillation frequency of the nuclei, thus allowing the direct measurement of the nuclear oscillation frequency simply by inspection of the HHG spectra. The wavelet analysis indicates that the intensity variation of the emitted radiation has the same modulation as the internuclear distance: this suggests that the nuclear oscillation frequency can be measured in real-time without destroying the molecule, simply by monitoring the intensity modulation of the emitted radiation.

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