Probing dynamical symmetries by bicircular high-harmonic spectroscopy beyond the Born-Oppenheimer approximation

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We explore the possibility of bicircular high-harmonic spectroscopy to probe the laser-induced dynamics of molecules in a non-Born-Oppenheimer treatment. The numerical solutions of the time-dependent Schrödinger equation for aligned H2 and its isotopologues in \(\omega-2\omega\) bicircular fields show that the intensity ratio between \(D_2\) and \(H_2\) for harmonic orders \(3q\) is lower than that for orders \(3q \pm 1\) (\(q \in \mathbb{N}\)). Based on the symmetry analysis in the strong-field approximation, we demonstrate that the vibrational wave-packet motion and the dynamical symmetry lead to the different ratio. In general, the vibrational motion causes the ratio for both \(3q\) and \(3q \pm 1\) to increase with \(q\), but a higher degree of symmetry breaking owing to the faster nuclear vibration in \(H_2\) leads to stronger harmonics of otherwise symmetry-forbidden orders \(3q\) and only slight change in orders \(3q \pm 1\), which causes the lower ratio of \(3q\) (\(D_2/H_2\)). Therefore, the nuclear dynamics is imprinted in the ratio for the orders \(3q \pm 1\), while the sensitivity of harmonic orders \(3q\) to symmetry breaking gives access to the attosecond probing of dynamical symmetries.

I. INTRODUCTION

High-order harmonic generation (HHG) from atoms and molecules driven by strong laser fields has important applications in attosecond science [1–8]. The process of HHG can be qualitatively described by the classical three-step model [9, 10] or its quantum-mechanical formulation, the Lewenstein model, also known as strong-field approximation (SFA) [11]. In the first step, an electron is removed through the potential barrier formed by the atomic or molecular potential and the laser field. In the second step, the electron is accelerated in the oscillating laser field. Finally, the electron may return to the parent ion and may recombine with the ion, emitting an extreme ultraviolet photon. Since these processes occur on the attosecond time scale and they create a mapping between electron trajectories and photon energies [12], HHG spectra are useful for probing the ultrafast dynamics of atoms and molecules [13, 14].

The fundamental challenge in attosecond science is the probing of rapidly evolving processes in atoms and molecules. The present work is related to the following two important developments in this area. One is the investigation of the vibrational motion in molecules, including isotope effects [15–24]. It offers two important schemes to detect ultrafast processes inside molecules, since the laser-driven nuclear motion introduces amplitude modulation [15, 16] and frequency modulation [22, 24, 25] in harmonic signals via the essential new degree of freedom, the intermolecular distance. The other is the use of nontrivial forms of laser pulses, such as parallel two-color fields [26], orthogonal two-color fields [27–31] and bicircular fields [32–34]. Bicircular high-harmonic spectroscopy, especially, has received attention in theory and experiment owing to its sensitivity to electronic structure [35], chirality [36–38] and atomic and molecular symmetries [39–43].

Symmetry is the origin of selection rules in HHG [44–46]. Such selection rules are important in the study of molecular structure and dynamics [14, 47]. HHG from linearly polarized laser pulses depends on inversion symmetry [44, 48]: The breaking of inversion symmetry leads to the emission of even-order harmonics that can be used as a tool to measure the molecular wave-packet dynamics [48, 49]. Recently, it has been demonstrated that the harmonic orders \(3q\), which are forbidden in threefold-symmetric systems (such as atoms plus a bicircular laser pulse), provide a probe of dynamical symmetries in atoms and molecules [42]. However, the interplay of dynamical symmetry in molecules and the vibrational motion has not been addressed.

In this article, we investigate HHG from the hydrogen molecule and its isotopologues driven by \(\omega-2\omega\) bicircular laser fields beyond the Born-Oppenheimer (BO) approximation. We observe that the intensity ratio between \(D_2\) and \(H_2\) for harmonic orders \(3q\) is similar to the results obtained with linearly polarized laser fields [15]. Interestingly, the ratio between \(D_2\) and \(H_2\) for harmonic orders \(3q\) is smaller than that for harmonic orders \(3q \pm 1\). These results can be well interpreted by invoking two factors: the vibrational wave function of nuclear motion and the dynamical symmetry. This is clearly demonstrated through a dynamical-symmetry analysis in \(\omega-2\omega\) bicircular fields within SFA. Hence, in bicircular fields, the intracycle nuclear motion can be reconstructed from the ratio between \(D_2\) and \(H_2\) for harmonic orders \(3q\) and the ratio for harmonic orders \(3q \pm 1\) is sensitive to symmetry breaking. This is a potential tool to probe time-dependent dynamical symmetries inside molecules.

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II. THEORETICAL MODEL

We describe the laser-driven correlated electronic and nuclear dynamics using a non-BO single-active electron model of H$_2$. In this model, the electron moves in two-dimensional space with a Cartesian coordinate $r$. The orientation $\theta$ of the molecule with respect to the field is held frozen, since the rotational motion can be neglected on the few-cycle time scale. The effective Hamiltonian for the interaction with a laser field $\mathbf{E}(t)$ takes the form (Hartree atomic units are used throughout)

$$H_{\text{eff}} = -\frac{\partial^2}{2M_n} - \frac{\partial^2}{2M_e} + V_{\text{eff}}(R,r) + r \cdot \mathbf{E}(t),$$

(1)

where $M_n = M_1M_2/(M_1 + M_2)$ and $M_e = (M_1 + M_2)/(M_1 + M_2 + 1)$ are the reduced masses of the nuclei and electron, respectively, with $M_{1,2}$ being the masses of the nuclei. $R$ is the internuclear distance. The effective potential is chosen as $[15]

$$V_{\text{eff}}(R,r) = V_{\text{BO}}^+(R) - \sum_{j=1,2} \frac{Z(R,|r - R_j|)}{\sqrt{|r - R_j|^2 + 0.5}},$$

(2)

where $V_{\text{BO}}^+(R)$ is the BO ground-state potential of H$_2^+$ created by the inactive electron. $R_j$ represent the positions of the two nuclei. Here, the effective nuclear charge $Z(R,r) = [1 + \exp(-r^2/a^2(R))]/2$ is introduced to describe screening, i.e. $Z(R,r) \overset{r \to \infty}{\to} 1/2$ and $Z(R,r) \overset{r \to 0}{\to} 1$. The parameter $\sigma(R)$ is adjusted such that the lowest BO potential-energy curve of the Hamiltonian matches that of real H$_2$. This model does not include electronic excitation of the molecular ion. From previous work [50] on HHG with linear polarization at parameters comparable to the present work, we judge that excitation of the ion plays a negligible role when HHG is dominated by short electron trajectories. Importantly, however, the model includes vibrational motion of the molecular ion. When the active electron is far from the core, the vibrational motion is governed by the BO potential $V_{\text{BO}}^+$. This means that ionization initiates vibrational dynamics in the ion, including also a small but unimportant fraction of dissociation. The $\omega$-2$\omega$ bicircular field composed of two counter-rotating components with equal field strengths [51, 52] reads

$$\mathbf{E}(t) = E_0 f(t) \left[ \begin{pmatrix} \cos(\omega t) \\ \sin(\omega t) \end{pmatrix} + \begin{pmatrix} \cos(2\omega t) \\ -\sin(2\omega t) \end{pmatrix} \right].$$

(3)

$E_0$ is the electric-field amplitude of each component of the bicircular field and $\omega$ is the frequency of the fundamental laser field. The bicircular field has a trapezoidal envelope $f(t)$ with a total duration of 8 optical cycles including two-cycle linear ramps.

The time-dependent Schrödinger equation (TDSE) is numerically solved by the Crank-Nicolson method [53, 54] with a time step of 0.1 a.u. The grid ranges from -170 a.u. to 170 a.u. for the electron and from 0.5 a.u. to 20 a.u. for the internuclear distance with the grid spacings $\Delta x = \Delta y = \Delta R = 0.1$ a.u. Absorbing boundaries with a $\cos^{1/8}$-shaped mask function are employed to avoid reflections of the wave function for all coordinates. The ground state of neutral molecules is prepared by imaginary-time propagation [55]. The dipole acceleration can be obtained through the Ehrenfest theorem [56]

$$\mathbf{a}(t) = \frac{1}{2M_e} \langle \psi(t)| \partial_t (V_{\text{eff}} + r \cdot \mathbf{E}(t)) | \psi(t) \rangle.$$

(4)

The total bicircular high-harmonic spectrum can be calculated from the Fourier transform of the dipole acceleration,

$$P_{\text{tot}}(\Omega) = \sum_{n=x,y} \left| \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} a_n(t) e^{i\Omega t} dt \right|^2,$$

(5)

with the harmonic frequency $\Omega$. $a_n(t)$ represent the $x$- and $y$-components of the dipole acceleration. To evaluate the harmonic intensity at harmonic order $N (N \in \mathbb{N})$, we integrate the signal over one harmonic peak at $\Omega = N\omega$.

III. RESULTS AND DISCUSSIONS

A. TDSE results

Figure 1 shows one representative HHG spectrum for aligned H$_2$ in a 912/456 nm bicircular pulse with total intensity $3.51 \times 10^{14}$ W/cm$^2$. The molecular axis is aligned along the $x$-axis. The combination of generating medium and laser field possesses $C_1$ symmetry using the notation of [46]. Therefore all integer harmonic orders are generated in Fig. 1, including orders $3g$ which are symmetry-forbidden in atoms. Moreover, the harmonic

![FIG. 1. The harmonic spectra for H$_2$ in a 912/456 nm pulse with total intensity $3.51 \times 10^{14}$ W/cm$^2$. The sketch in the lower left part illustrates the direction of the molecular axis relative to the applied electric field.](image)
spectrum exhibits a slow decrease with energy and a cut-off not far from the energy \( I_p + 3.17U_p \). Here, \( I_p \) is the vertical ionization potential and \( U_p = (2E_0)^2/4\omega^2 \) is an effective ponderomotive energy, where \( 2E_0 \) is the sum of the electric field amplitudes of the two components of the bicircular field and \( \omega = (\omega + 2\omega)/2 \) is the average frequency of the bicircular field. By transforming to a rotating frame, the bicircular field becomes linearly polarized with frequency \( \omega \), which explains the success of the simple expression for the cutoff [57–59].

We compare the harmonic spectra of \( H_2 \), \( D_2 \), and \( T_2 \), aligned parallel to the \( x \)-axis, driven by the \( \omega-2\omega \) bicircular laser field. The simulations are carried out at different fundamental wavelengths. We use 912/456 nm pulses (with amplitude \( E_0=0.05 \) a.u., total intensity \( 3.51 \times 10^{14} \) W/cm²) in Fig. 2 (a) and 1200/600 nm pulses (with amplitude \( E_0=0.04 \) a.u., total intensity \( 2.25 \times 10^{14} \) W/cm²) in Fig. 2 (b). We find that in both cases the ratios between different isotopologues for harmonic orders \( 3q \pm 1 \) are consistent with the results in [15, 16], where linearly polarized laser pulses were used. Usually, heavier isotopologues generate stronger harmonics and the ratio between the different isotopologues increases with harmonic order. This is explained by the slower nuclear motion in the heavier isotopologues together with the fact that higher harmonic orders imply longer time intervals for the vibrational wave-packet evolution [15, 16, 23], see below for further details. This concept is applicable to any molecular orientation [60]. For \( D_2 \) \((3q \pm 1)\) over \( H_2 \) \((3q \pm 1)\), the ratio reaches about 1.7 beyond the cutoff. Interestingly, however, the ratios at harmonic orders \( 3q \) are smaller than those at harmonic orders \( 3q \pm 1 \).

By considering two important factors in HHG, namely the vibrational wave-packet dynamics and the dynamical symmetry, the above TDSE results can be interpreted. Illustrations of these two aspects are shown in Fig. 3: (a) A wave-packet is launched into the lowest BO potential \( V_{BO}^+ \) of the ion when the active electron is removed from the initial state of the neutral molecule. The nuclear wave packet undergoes a time evolution during the continuum travel of the active electron. The overlap between the real initial wave function \( \chi_0 \) and the evolved wave function at the recombination time \( t_r \) influences decisively the strength of harmonic emission. Higher overlap leads to stronger harmonic generation. The figure shows the quantitative results for the initial and evolved vibrational wave packets in \( H_2 \) and \( D_2 \) in the case of harmonic order 52 for the parameters of Fig. 1. Here, we use the complex electron excursion time that arises in the SFA-based theory (see next section) as the time

![Graph showing ratios of harmonic intensities in different isotopologues](image)

**FIG. 2.** Ratios of harmonic intensities in different isotopologues (aligned along the \( x \)-axis) as a function of harmonic order for 912/456 nm (a) and 1200/600 nm (b). Results are shown for harmonic orders \( 3q \pm 1 \) and \( 3q \) as indicated. The field amplitudes are (a) \( E_0=0.05 \) a.u. and (b) \( E_0=0.04 \) a.u.

![Illustration of mechanism of molecular HHG](image)

**FIG. 3.** Illustration of the mechanism of molecular HHG for a light isotopologue on the left and a heavy isotopologue on the right. (a) Vibrational wave-packet dynamics (quantitative results for the initial and final wave packets in \( H_2 \) and \( D_2 \) as they appear in the SFA-based theory for laser parameters as in Fig. 1 and harmonic order 52). Here, the initial ground state is normalized. However, the norm of the wave packet is not conserved due to the excursion of the electron in complex time. (b) Increase of symmetry breaking by bond stretching (qualitative).
span for vibrational evolution, which leads to the non-conserved norm of the wave packet. The isotope effect is visible in the plot: the wave-function overlap is larger in the case of the heavier isotopologue due to the slower nuclear motion. (b) The ω-2ω bicircular electric field with a threefold symmetry describes a Lissajous figure, resembling a clover leaf, see Fig. 1. On the interaction of such a pulse with the aligned H2, the otherwise symmetry-forbidden harmonic orders at 3ω are emitted because the threefold symmetry is broken by the alignment [42, 46]. The change induced by symmetry breaking is only weak for harmonic orders 3q ± 1. The symmetry breaking is more pronounced for the lighter isotopologue because the faster expansion of the system after the ionization step causes a stronger deviation of the electron wave function from spherical symmetry. The figure shows a qualitative sketch of this effect.

Therefore, the ratios found in the TDSE results can be understood as follows. The small nuclear mass of H2 causes a stronger deviation of the electron wave function from its equilibrium form. The relative increase of the vibrational overlap compared to the theoretical calculations for the heavier isotopologue of H2 is a consequence of the increased nuclear mass.

Dynamical-symmetry analysis within SFA

We give a quantitative modeling on the basis of the above explanation using SFA [61] for vibrating molecules in bicircular driving fields. Previous theory [15, 60] has already extended Lewenstein model [11] to include the vibrational motion in diatomic molecules. In the extended SFA, the dependence of HHG on the electronic structure of the system is captured by the recombination transition matrix element $d_{\text{rec}}(t_i, t_r, \mathbf{R})$, which is a function of the internuclear vector $\mathbf{R}$. This implies an orientation dependence of $d_{\text{rec}}$, i.e., the spherical symmetry is broken. The degree of symmetry breaking depends on the internuclear distance $R$, which, in turn, is determined by the nuclear motion. Effectively, the harmonic vectorial amplitude is proportional to the following integral over $\mathbf{R}$ [60],

$$C(t_i, t_r) = e^{-iS(t_i, t_r) - \Omega t_r} \times \int_0^\infty d\mathbf{R} d_{\text{rec}}(t_i, t_r, \mathbf{R}) \chi_0(R) U_R^+ (t_r - t_i) \chi_0(R) ,$$

(6)

with the semiclassical action $S(t_i, t_r) = \frac{1}{2} \int_{t_i}^{t_r} dt' \left[ k(t_i, t_r) + A(t') \right]^2 + I_p(t_r - t_i)$ and the time-evolution operator for nuclear motion $U_R^+$. This time-evolution operator propagates the vibrational wave function according to the one-dimensional TDSE

$$i\hbar \frac{d\chi(R, t)}{dt} = \left[ -\frac{\partial^2}{\partial R^2} + \tilde{V}_{\text{BO}}^+(R) \right] \chi(R, t)$$

with $\tilde{V}_{\text{BO}}^+(R) = V_{\text{BO}}^+(R) - V_{\text{BO}}^+\left(\chi_0|\mathbf{R}\chi_0\right)$. Here, a constant has been added to the BO potential of H2 to be consistent with the use of the vertical ionization potential $I_p$ rather than the absolute value of the H2 ground-state energy in the SFA action. The effect of the laser field on the vibrational dynamics of H2 is neglected in this model. The times of ionization $t_i$ and recombination $t_r$ are calculated by solving the corresponding saddle-point equations for the bicircular field

$$\frac{|k(t_i, t_r) + A(t_i)|^2}{2} = -I_p,$$

(7)

$$\frac{|k(t_i, t_r) + A(t_r)|^2}{2} = \Omega - I_p.$$
cycle of the fundamental field, projected on the polarization vectors \( \mathbf{e}_\pm = (\mathbf{e}_x \pm i\mathbf{e}_y)/\sqrt{2} \) for left and right circular polarization, can thus be written as

\[
C^{\pm}(\Omega) = e^{-i\tilde{S}} \int_0^\infty dR \sum_{j=0}^2 e^{i2\pi j(\Omega \pm 1)} e_{\pm}^* \cdot \mathbf{v}(t_i, t_r) \times \cos \left( \frac{\mathbf{v}(t_i, t_r) \cdot D^{-1} \mathbf{R}}{2} \right) \chi_0(R) U_R^{\pm}(\tau) \chi_0(R)
\]

with \( \tilde{S} = S(t_i, t_r) - \Omega t_r \) and excursion time \( \tau = \tau(\Omega) = t_r(\Omega) - t_i(\Omega) \). In Eq. (14), if the recombination matrix element is independent of the direction of \( \mathbf{R} \), the frequencies \( \Omega = 3\omega q \) are symmetry-forbidden due to destructive interference of the contributions from three short trajectories, i.e. \( C^{\pm}(3\omega q) = 0 \).

The total intensity ratio between \( D_2 \) and \( H_2 \) is approximated as

\[
R_{\alpha}(\Omega) = \frac{|C_D^{\alpha}(\Omega)|^2 + |C_H^{\alpha}(\Omega)|^2}{|C_D^{\Omega}(\Omega)|^2 + |C_H^{\Omega}(\Omega)|^2},
\]

In the SFA calculations, we use the complex times \( t_i, t_r \) of the short trajectory. The short trajectory dominates the HHG, which is confirmed in our numerical results. We use the Gabor time-frequency analysis [64, 65] to isolate this trajectory in the TDSE results. The total harmonic intensity is the coherent sum over the relevant time windows at times \( t_j = (j \in \mathbb{N} | 1 \leq j \leq 12) \) that contribute to the short trajectories in the flat-top part of the trapezoidal pulse,

\[
I_G(\Omega) = I_{G_s}(\Omega) + I_{G_a}(\Omega) = \sum_{n=x,y} \sum_{j=1}^{12} \tilde{G}_n(\Omega, t_j) \left| \int_{t_j}^{t_j + \Delta t} dt \, G_n(\Omega, t) \right|^2 \]

with \( \tilde{G}_n(\Omega, t_j) = \int_{t_j}^{t_j + \Delta t} dt \, G_n(\Omega, t) \) and the Gabor transform

\[
G_n(\Omega, t) = \int dt' a_n(t') e^{-(t' - t)^2/(2\zeta^2)} e^{i\Omega t'}. \]

We choose \( \zeta = 1/(3\omega) \).

Figure 4 shows the intensity ratios between \( D_2 \) and \( H_2 \) for various orientations obtained by SFA and TDSE calculations. The laser parameters are the same as in Fig. 2(a). The harmonic orders \( 3q - 1 \) are excluded in Fig. 4, since they show the same trend as harmonic orders \( 3q + 1 \). In general, the TDSE ratios of both harmonic orders \( 3q + 1 \) and \( 3q \) are slightly reduced due to the elimination of long trajectories when compared to Fig. 2(a). This happens because the \( D_2/H_2 \) ratio for the long trajectory is higher than that for the short trajectory, which has been reported and explained previously [23, 50]. The reason is essentially that longer excursion times allow for longer vibrational motion and therefore to an increased difference between HHG in \( D_2 \) and \( H_2 \). Also, the trajectory selection leads to smoother curves. We find good agreement between SFA and TDSE results. In particular, the difference between the ratios for \( 3q + 1 \) and \( 3q \) is evident in both types of calculations. Similar results are obtained for the case of 1200/600 nm. These results are only weakly dependent on the molecular orientation as shown in Fig. 4.

Our results are significantly influenced by both vibrational dynamics and dynamical symmetry breaking. This implies that both phenomena occur on a similar time scale, namely, the attosecond time scale of electron trajectories.

IV. CONCLUSIONS

In summary, we have studied HHG in a non-BO model of aligned \( H_2, D_2 \) and \( T_2 \) interacting with \( \omega-2\omega \) bicircular...
fields. The TDSE simulations show that the harmonic intensity ratios $D_2/H_2$ and $T_2/H_2$ for harmonic orders $3q \pm 1$ and $3q$ differ. SFA results agree well with the TDSE results. Two main reasons, the vibrational wave-packet motion and the dynamical symmetry, give rise to the different ratio. On the one hand, the vibrational motion weakens harmonics of all allowed harmonic orders $(3q \pm 1$ and $3q)$ in lighter isotopologues due to the faster nuclear motion, which is familiar from previous theory and experiment [15, 16]. On the other hand, generation of harmonic orders $3q$ is allowed only if the threefold system symmetry is violated. In the lighter isotopologues, the degree of symmetry breaking induced by faster vibrational motion is higher, leading to stronger signals for $3q$ but only slightly affecting the signals for $3q \pm 1$, which finally results in the lower harmonic intensity ratio for harmonic orders $3q$. The dependence of the ratio on the electron excursion time reflects the attosecond-scale dynamics of the symmetry breaking. Observation of these effects requires HHG from an aligned sample of molecules. Although this is difficult to achieve with $H_2$ molecules, we note that partial laser-induced alignment was found in previous experiments on $H_2$ and $D_2$ when sufficiently long linearly polarized femtosecond pulses were used [17].

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