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Even-Harmonic Generation due to Beyond-Born-Oppenheimer Dynamics

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We calculate the harmonic spectrum generated by a model HD molecule in a strong laser pulse. The unequal nuclear masses lead to the emission of even harmonics, i.e., photon frequencies which are even multiples of the laser frequency. The effect does not occur within the Born-Oppenheimer approximation. In the high-frequency region, the even harmonics are almost of the same order of magnitude as the odd ones.

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Atoms and molecules driven by intense laser pulses radiate at frequencies that are integer multiples of the laser frequency. This so-called harmonic generation [1–4] has been the subject of numerous experimental and theoretical studies, mainly because the emission of high-order harmonics is a promising method to produce coherent x rays and attosecond pulses: Experimentally, orders up to about 300 have been reported [5,6].

Frequencies other than the usual integer multiples may be emitted by a single atom or molecule as a consequence of resonances. However, if a large number of atoms or molecules is involved in the process, then the coherent part of the resulting spectrum consists of pure integer multiples of the fundamental frequency since only these can survive the propagation through the medium [7], while the others undergo destructive interference. Additionally, an incoherent fluorescence background may be present [2]. Typically, only odd harmonics are observed in experiment. One routinely invokes the concept of inversion symmetry to explain the absence of even harmonics. Intuitively speaking, when an electron in a symmetric potential is driven by a laser it performs a "symmetric" oscillation consisting of odd frequency components only [8]. More precisely, parity is a good quantum number in a system with inversion symmetry; i.e., the eigenstates of the system have a defined parity, $+1$ or -1. In the picture of perturbation theory, the generation of the nth harmonic proceeds by first absorbing n laser photons of frequency ω and then emitting one photon of frequency $n\omega$. The latter process must be a transition between two states of different parity. Therefore, the initial absorption cannot involve an even number of photons. This leads to the fact that in general neither atoms nor molecules produce even harmonics. One could try to break the symmetry by choosing heteropolar molecules: the potential seen by the electrons in such a molecule is not inversion symmetric if we think of the nuclei as fixed. However, the full field-free molecular Hamiltonian (including all nuclear and electronic coordinates) is always inversion symmetric so that even-harmonic generation is still forbidden.

Violations of the above selection rule have been found in numerical calculations [9]; they are caused by accidental degeneracies of Floquet states. It is demonstrated in Ref. [9] that the even harmonics generated in this way are a special case of radiation which generally occurs at noninteger multiples of the fundamental frequency. (As mentioned above, such noninteger harmonics can be produced at the single-molecule level but are not phase matched in a gas of molecules.)

In an ensemble of oriented diatomic molecules, the inversion symmetry is broken except in the case of homonuclear molecules. In this Letter, we consider an interesting kind of symmetry breaking which is realized in the HD molecule: the nuclear masses M_1, M_2 are different while the nuclear charges are equal. The HD molecule possesses a permanent electric dipole moment which has been calculated previously [10]. As we will show below, the asymmetry also results in the generation of even harmonics. In the high-frequency range, their magnitude is comparable to that of the odd harmonics. Note that the potential seen by the electrons is still symmetric if we use the Born-Oppenheimer approximation. That is, we are dealing with even-harmonic generation by non-Born-Oppenheimer dynamics. The important implication of this finding is obvious: *Nonadiabatic effects play an important role in high-harmonic generation and can change the emission spectrum drastically.*

For our numerical calculations we use a model of the HD molecule where the motion of nuclei and electrons is restricted to the polarization direction of the linearly polarized laser. The coupling to the laser field $E(t)$ is treated within the dipole approximation. As a result, the center-of-mass motion does not couple to the laser field and can be separated off. We are then left with the internal degrees of freedom. Placing the origin for the electronic coordinates z_1 and z_2 at the nuclear center of mass and neglecting mass-polarization terms (which, in the chosen coordinates, occur merely due to the fact that we have more than one electron), the Hamiltonian reads (atomic units are used throughout)

$$
\begin{aligned}
H = &-\frac{1}{2\mu_{\mathrm{n}}}\frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_{\mathrm{e}}}\left(\frac{\partial^2}{\partial z_1^2} + \frac{\partial^2}{\partial z_2^2}\right) \\
&+ \frac{1}{R} + w(z_1, z_2) - \sum_{j=1}^{2} w\left(z_j, \frac{M_2}{M_{\mathrm{n}}} R\right) \\
&- \sum_{j=1}^{2} w\left(z_j, -\frac{M_1}{M_{\mathrm{n}}} R\right) - E(t)D, \qquad (1)
\end{aligned}
$$

with the dipole operator

$$D = -(z_1 + z_2) + \lambda R\,. \qquad (2)$$

For the interactions, we choose the soft Coulomb potential [11]

$$w(x,y) = \frac{1}{\sqrt{(x-y)^2 + 1}}\,. \qquad (3)$$

R is the internuclear distance, $M_{\mathrm{n}} = M_1 + M_2$ is the total nuclear mass, $\mu_{\mathrm{n}} = M_1 M_2 / M_{\mathrm{n}}$ and $\mu_{\mathrm{e}} = M_{\mathrm{n}}/(M_{\mathrm{n}} + 1)$ are the reduced masses, and $\lambda = (M_2 - M_1)/M_{\mathrm{n}}$ is the mass-asymmetry parameter. The laser field has the form $E(t) = E_0 f(t) \sin\omega t$ with peak amplitude E_0, envelope function $f(t)$, and frequency ω. The wave function $\Psi(R, z_1, z_2, t)$ is numerically represented on a three-dimensional grid. After the ground state has been obtained by propagation in imaginary time, the evolution under the influence of the laser is calculated by numerical solution of the time-dependent Schrödinger equation. For the propagation, we use the split-operator method [12]. To our knowledge, this is the first non-Born-Oppenheimer integration of the Schrödinger equation for a laser-driven molecular system with more than one electron.

For an ensemble of molecules, the spectrum of emitted radiation is approximately (i.e., neglecting incoherent processes) proportional to the squared modulus of the Fourier transform of the dipole acceleration expectation value [13],

$$S(\omega) \sim \left| \int e^{i\omega t} \frac{d^2}{dt^2} \langle \Psi(t) | D | \Psi(t) \rangle \, dt \right|^2 . \qquad (4)$$

The dipole acceleration expectation value is calculated via the Ehrenfest theorem:

$$
\begin{aligned}
\frac{d^2}{dt^2} \langle \Psi(t) | D | \Psi(t) \rangle = &\frac{1}{\mu_{\mathrm{e}}} \left\langle \Psi(t) \left| \frac{\partial H}{\partial z_1} + \frac{\partial H}{\partial z_2} \right| \Psi(t) \right\rangle \\
&- \frac{\lambda}{\mu_{\mathrm{n}}} \left\langle \Psi(t) \left| \frac{\partial H}{\partial R} \right| \Psi(t) \right\rangle . \qquad (5)
\end{aligned}
$$

In our numerical work we employ a laser with peak intensity 10^{14} W/cm^2 and wavelength 770 nm. The envelope function $f(t)$ is a linear ramp from zero to one during the first 10 optical cycles. Afterwards, the field amplitude is held constant. The total time of propagation is 30 optical cycles.

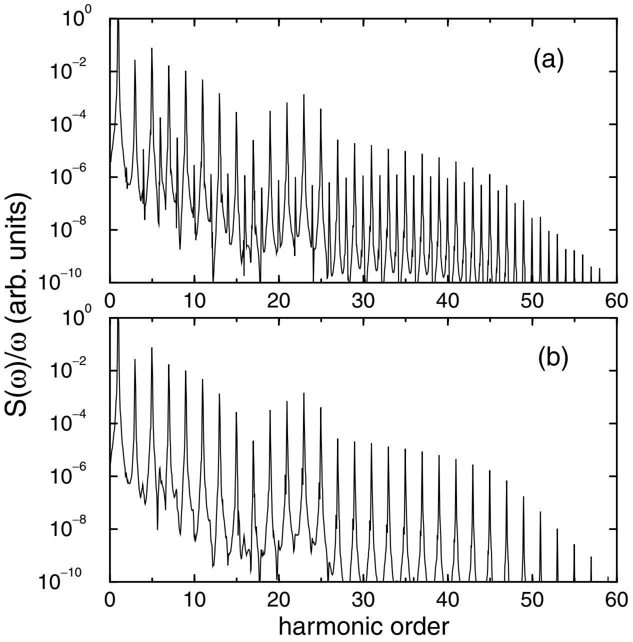

FIG. 1. (a) Harmonic spectrum generated from the model HD molecule driven by a laser with peak intensity 10^{14} W/cm^2 and wavelength 770 nm. The plotted quantity is proportional to the number of emitted photons. (b) Same as panel (a) for the model H_2 molecule.

The harmonic spectrum generated by the model HD molecule is shown in the upper panel of Fig. 1. The lower panel contains the spectrum for the H_2 model under exactly the same conditions. In both cases, we observe the familiar rapid decrease of magnitude in the low-frequency range (harmonic order lower than 17). Between the 19th and the 25th orders, the envelope exhibits a local maximum. It is followed by a plateau extending up to the 45th order. H_2 generates only odd harmonics as expected, whereas HD produces a series of even harmonics throughout the entire range of observed frequencies. Low even orders are much weaker than low odd orders, but the difference becomes less pronounced at very high frequencies. The shapes of the two envelopes are similar at low frequencies, but on the whole the envelope of the even-harmonic spectrum is less frequency dependent than the odd-harmonic envelope. This is in contrast to other mechanisms of symmetry breaking, where even and odd harmonics usually exhibit similar envelope shapes throughout the spectrum. See, e.g., Ref. [14] for static magnetic fields or Ref. [15] for static electric fields.

We have found numerically that the HT (hydrogen-tritium) molecule generates more intense even harmonics than HD as a consequence of the greater mass asymmetry. However, the difference is barely visible on the logarithmic scale of Fig. 1.

To show that the effect occurs only beyond the Born-Oppenheimer approximation, we expand the wave function in Born-Oppenheimer states, $\Psi(R, z_1, z_2, t) = \sum_j \psi_{\mathrm{n}}^j(R,t)\psi_{\mathrm{e}}^j(R, z_1, z_2)$, where $\{\psi_{\mathrm{e}}^j(R, z_1, z_2)\}$ is an orthonormal set of stationary electronic eigenfunctions. We insert into the time-dependent Schrödinger equation $i\frac{\partial}{\partial t}\Psi = H\Psi$, multiply with $\psi_{\mathrm{e}}^k(R, z_1, z_2)^*$, and integrate over the electronic coordinates to obtain

$$i\frac{\partial}{\partial t}\psi_{\mathrm{n}}^{k}(R,t)=\left[-\frac{1}{2\mu_{\mathrm{n}}}\frac{\partial^2}{\partial R^2}+V^k(R)\right]\psi_{\mathrm{n}}^{k}(R,t)-E(t)\sum_j D^{kj}(R)\psi_{\mathrm{n}}^{j}(R,t)+\sum_j\left[A^{kj}(R)+2B^{kj}(R)\frac{\partial}{\partial R}\right]\psi_{\mathrm{n}}^{j}(R,t), \tag{6}$$

where V^k are the Born-Oppenheimer potentials and $D^{kj}(R)=\langle\psi_{\mathrm{e}}^{k}|D|\psi_{\mathrm{e}}^{j}\rangle_{\mathrm{e}}$ are the dipole matrix elements. (The subscript "e" indicates that the integration is over the electronic coordinates only.) A^{kj} and B^{kj} are the nonadiabatic couplings,

$$A^{kj}(R)=-\frac{1}{2\mu_{\mathrm{n}}}\int\psi_{\mathrm{e}}^{k}(R,z_1,z_2)^*\frac{\partial^2}{\partial R^2}\psi_{\mathrm{e}}^{j}(R,z_1,z_2)\,dz_1\,dz_2 \tag{7}$$

and

$$B^{kj}(R)=-\frac{1}{2\mu_{\mathrm{n}}}\int\psi_{\mathrm{e}}^{k}(R,z_1,z_2)^*\frac{\partial}{\partial R}\psi_{\mathrm{e}}^{j}(R,z_1,z_2)\,dz_1\,dz_2\,. \tag{8}$$

For HD, the origin of the electronic coordinate system is not at the geometric center between the nuclei. Therefore, the electronic states ψ_{e}^{j} are not eigenstates of the electronic inversion operator P_{e} which acts as $\{z_1\rightarrow -z_1, z_2\rightarrow -z_2\}$. We can, however, shift the origin to the geometric center, i.e., replace $\psi_{\mathrm{e}}^{j}(R,z_1,z_2)=\tilde{\psi}_{\mathrm{e}}^{j}(R,z_1-\frac{\lambda}{2}R,z_2-\frac{\lambda}{2}R)$ where the shifted states $\tilde{\psi}_{\mathrm{e}}^{j}$ are eigenstates of P_{e}: They have gerade or ungerade symmetry because they are the eigenstates of an electronic Hamiltonian with a symmetric potential. (The $\tilde{\psi}_{\mathrm{e}}^{j}$ would be identical with the electronic Born-Oppenheimer states of the H_2 system, if the reduced electronic mass was not slightly different.) We immediately find that

$$D^{kj}(R)=\tilde{D}^{kj}(R)=\langle\tilde{\psi}_{\mathrm{e}}^{k}|\tilde{D}|\tilde{\psi}_{\mathrm{e}}^{j}\rangle_{\mathrm{e}}\,, \tag{9}$$

where $\tilde{D}$ is the shifted dipole operator $\tilde{D}=-(z_1+z_2)$. Since the $\tilde{\psi}_{\mathrm{e}}^{j}$ are eigenstates of P_{e}, the dipole operator couples only states with different eigenvalues of P_{e}. Adopting the Born-Oppenheimer approximation means that the nonadiabatic couplings in Eq. (6) are neglected. Then, as a consequence of Eq. (9), HD obeys the same selection rules as H_2. Beyond the Born-Oppenheimer approximation, the situation is different: In the case of H_2, the nonadiabatic couplings A^{kj} and B^{kj} are zero if the states k and j have different symmetry, leaving the selection rules unchanged. In the case of HD, the nonadiabatic couplings mix all states. [The replacement $\psi_{\mathrm{e}}^{j}\rightarrow\tilde{\psi}_{\mathrm{e}}^{j}$ in Eqs. (7) and (8) would lead to additional terms because the derivative $\partial/\partial R$ acts on the R dependence of the coordinate shift $\frac{\lambda}{2}R$.] Therefore, the selection rules that prevent even-harmonic generation are violated in the case of oriented HD.

We have thus found that nonadiabatic effects give rise to a qualitative difference between H_2 and HD, namely the generation of even harmonics by HD. H_2 and HD obey different selection rules, whereas in the Born-Oppenheimer approximation, both molecules would obey identical selection rules and none of them would generate even harmonics. In the H_2 molecule, nonadiabaticity does not alter the selection rules so that even-harmonic generation remains forbidden.

The numerical results show that the magnitude of the even harmonics relative to the odd harmonics is largest at high harmonic frequencies. We conclude that nonadiabatic effects are particularly important in the high-order range. The explanation of this behavior lies in the mechanism of high-harmonic generation [16]: The laser field first ionizes the molecule. The released electron is accelerated by the field and can return to the core where recombination leads to the emission of a photon. The electron motion between ionization and recombination can be understood as the motion of an electron wave packet consisting of continuum states. The Born-Oppenheimer approximation then breaks down since the vibrational energy differences are not small compared to the energy differences between the electronic states. Roughly speaking, while the electron travels away and back to the core it does not instantaneously adjust to the potential created by nuclei.

To summarize, we have shown that nonadiabatic effects in an oriented and isotopically asymmetric diatomic molecule lead to the emission of even harmonics. They are particularly intense at high-harmonic frequencies. The strong influence of nonadiabatic effects is important in the light of the current efforts to optimize the efficiency of high-harmonic output. Our results are relevant not only from a fundamental point of view, but also have the practical implication that one cannot generally expect to obtain reliable harmonic spectra from fixed-nuclei calculations.

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[1] A. McPherson *et al.,* J. Opt. Soc. Am. B **4**, 595 (1987).

[2] A. L'Huillier, K. J. Schafer, and K. C. Kulander, J. Phys. B **24**, 3315 (1991).

[3] M. Protopapas, C. H. Keitel, and P. L. Knight, Rep. Prog. Phys. **60**, 389 (1997).

[4] P. Salières, A. L'Huillier, P. Antoine, and M. Lewenstein, Adv. At. Mol. Opt. Phys. **41**, 83 (1999).

[5] Z. Chang *et al.,* Phys. Rev. Lett. **79**, 2967 (1997).

[6] M. Schnürer *et al.,* Phys. Rev. Lett. **80**, 3236 (1998).

[7] P. Salières, P. Antoine, A. de Bohan, and M. Lewenstein, Phys. Rev. Lett. **81**, 5544 (1998).

[8] We call the electron oscillation symmetric if it has the form $z(t)=-z(t+T/2)$ where T is the duration of one optical cycle.

[9] R. Bavli and H. Metiu, Phys. Rev. A **47**, 3299 (1993).

[10] W. R. Thorson, J. H. Choi, and S. K. Knudson, Phys. Rev. A **31**, 22 (1985).

[11] R. Grobe and J. H. Eberly, Phys. Rev. A **48**, 4664 (1993).

[12] M. D. Feit, J. A. Fleck, Jr., and A. Steiger, J. Comput. Phys. **47**, 412 (1982).

[13] B. Sundaram and P. W. Milonni, Phys. Rev. A **41**, 6571 (1990).

[14] J.-P. Connerade and C. H. Keitel, Phys. Rev. A **53**, 2748 (1996).

[15] M.-Q. Bao and A. F. Starace, Phys. Rev. A **53**, R3723 (1996).

[16] P. B. Corkum, Phys. Rev. Lett. **71**, 1994 (1993).