High-order harmonic generation in vibrating two-electron molecules

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Abstract

By solving the time-dependent Schrödinger equation numerically, we simulate high-order harmonic generation from one-dimensional hydrogen molecules driven by intense laser pulses of different wavelengths. The electron-electron interaction and the vibrational degree of freedom are treated fully quantum mechanically. We show that the ratio of harmonic signals from D_2 and H_2 can be understood as a consequence of two-center interference in the presence of nuclear motion. For 800 nm laser wavelength, high-order harmonic generation is essentially a one-electron process. For 1500 nm the interaction of both electrons with the laser field should be taken into account in the numerical calculation. Nevertheless, a simple model based on the shortest possible trajectories of a single active electron in the laser field predicts the ratio D_2/H_2 reasonably well.

Key words: one-dimensional H_2 molecule, time-dependent Schrödinger equation, high-harmonic generation
PACS: 33.80.Rv, 42.65.Ky

Atoms or molecules irradiated by an intense linearly polarized laser field can undergo a multiphoton process that converts laser photons into high-frequency photons, leading to the emission of coherent radiation that is typically in the extreme ultraviolet (XUV) range. This process is known as high-order harmonic generation (HHG) and has been studied in great detail in the last two decades [1, 2, 3, 5, 4]. The intuitive three-step model [4] explains HHG as a sequence of laser-induced ionization, acceleration of the free electron by the laser field, and return of the electron to the parent ion. Recombination of the electron with the ion gives rise to the emission of a XUV photon. Using Newton's equation of motion for an electron, the maximum kinetic energy of the returning electron is $3.17\,U_\mathrm{p}$ where $U_\mathrm{p} = E_0^2/(4\omega^2)$ is the ponderomotive potential for a laser field

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with electric field amplitude E_0 and frequency ω. The maximum harmonic photon energy is therefore $3.17\,U_\mathrm{p} + I_\mathrm{p}$ where I_p is the ionization potential of the atom or molecule. The entire three-step procedure takes place on a time scale below the optical cycle of the laser field. The periodic repetition of the generating process in every cycle thus leads to the emission of an attosecond XUV pulse train [6, 7]. An isolated attosecond pulse can be generated if the driving laser pulse is sufficiently short [8].

HHG from molecules is of special interest because of the sensitivity to the molecular structure [9, 10, 11, 12, 13, 14]. In the simplest possible case, which is realized for example in the molecules H_2^+ or CO_2, the highest occupied molecular orbital (HOMO) is reasonably well approximated by a single linear combination of two atomic orbitals. In this case, if HHG is assumed to be caused only by ionization from the HOMO, the harmonic emission spectrum shows the signature of two-center interference. It appears as a pronounced minimum in the harmonic spectrum for suitable molecular alignment [9, 15, 16, 11, 12].

The effect of the nuclear motion has been investigated in a number of early theoretical studies [17, 18, 19, 20]. Differences between the isotopes H_2 and D_2 were predicted [21] by solving the time-dependent Schrödinger equation (TDSE) for a single-active-electron (SAE) model. The isotope effect can be understood as follows. In general, the first step of the three-step model creates not only a free electron but also a vibrational wave packet in the molecular ion. As the evolving wave packet loses its overlap with the initial wave packet, HHG is suppressed. The different speeds of the vibrational wave packets in D_2 and H_2 lead to different degrees of suppression. Therefore measuring the ratio of harmonics in different isotopes gives information about the nuclear motion in the molecular ion. The isotope effect has been confirmed experimentally and has been exploited to perform the fastest ever measurement of vibrational dynamics [22]. A recent study on a variety of molecules has shown that nuclear motion is important also in heavier molecules [23].

The motion of the nuclei also changes the conditions for two-center interference which depends crucially on the internuclear separation. Therefore, for a detailed understanding of HHG in H_2 and D_2, both nuclear motion and interference have to be taken into account [24].

We have recently developed [25] an extended version of the Lewenstein model [5] in order to assess the relevance of the interaction between the molecular ion and the laser field (*dressing*). For H_2, it was found that the effect of dressing is negligible for the commonly used laser wavelength of 800 nm. Yet, it becomes important at longer wavelengths, for which the molecular ion has more time to stretch towards increased internuclear separation during the time between ionization and recombination. In this case laser-induced excitation of the H_2^+ ion to the first excited electronic state is possible. The main consequences are a reduction of the harmonic signal and strong suppression of the long trajectories.

It has been argued recently that a proper theoretical treatment of HHG should take the multielectron nature of atoms and molecules into account. In particular, the frequently used assumption that HHG is a one-electron process starting and ending in the HOMO, has been questioned [26, 27, 28, 29, 30]. It

is therefore natural to ask whether the above-mentioned isotope and dressing effects are reproduced in fully numerical calculations for systems with more than one electron.

The purpose of the present work is to confirm the existence of two-center interference and isotope effects in a fully numerical solution of the TDSE for a two-electron molecule. We restrict ourselves to the case of moderate laser intensities such that the contribution of HHG from dissociating H_2^+ [31, 32] is small. We study a one-dimensional H_2 model molecule similar to the one used in [33]: the direction of the molecular axis is fixed along the laser polarization axis, and also both electrons are allowed to move along this direction only. We follow here the strategy of Saugout *et al.* [34, 35] who adjusted the electron-nuclear and electron-electron interaction potential in this model such that the ground-state Born-Oppenheimer potentials of H_2 and H_2^+ are reproduced. Neglecting mass-polarization terms, the Hamiltonian for the laser-driven molecule with internuclear distance R and electron coordinates x_1, x_2 then reads (atomic units are used throughout)

$$\begin{aligned} H &= T_{\rm n} + T_{\rm e} + \frac{1}{R} + W_{\rm en}(R,x_1) + W_{\rm en}(R,x_2) \\ &\quad + W_{\rm ee}(x_1 - x_2) + (x_1 + x_2)E(t), \end{aligned} \tag{1}$$

where $E(t) = E_0(t)\sin(\omega t)$ is the electric field of a linearly polarized laser pulse. The kinetic-energy operators for the nuclear and electronic degrees of freedom are

$$T_{\rm n} = -\frac{1}{M}\frac{\partial^2}{\partial R^2} \tag{2}$$

and

$$T_{\rm e} = -\frac{1}{2\mu_{\rm e}}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_1^2}\right) \tag{3}$$

with M being the mass of one nucleus and $\mu_{\rm e} = 2M/(2M+1)$ the reduced mass of the electron. The particle-particle interaction terms are soft-core potentials

$$W_{\rm en}(R,x_j) = -\sum_{s=\pm 1}\frac{1}{\sqrt{(x_j + \frac{sR}{2})^2 + \beta^2(R)}} \tag{4}$$

and

$$W_{\rm ee}(x) = \frac{1}{\sqrt{x^2 + \alpha^2(R)}}. \tag{5}$$

The R-dependence of the softening parameters α and β is shown in Ref. [35]. For the laser field envelope $E_0(t)$ we use a trapezoidal function with 2 optical cycles turn-on and turn-off times and a middle plateau of 3 optical cycles. The TDSE $i\partial_t\Psi(R,x_1,x_2,t) = H\Psi(R,x_1,x_2,t)$ is solved numerically using the split-operator method with about 1500 time steps per optical cycle. This means that the time step is longer but still sufficiently small for the longer wavelength studied below. The wave function is represented on a three-dimensional grid

with $N_R \times N_{x_1} \times N_{x_2} = 80 \times 768 \times 768$ points. The spatial step sizes are 0.1 a.u. for the R coordinate and 0.36 a.u. for the electron coordinates.

The harmonic emission spectrum is obtained as the power spectrum of the time-dependent dipole acceleration expectation value [36, 37]

$$a(t) = \frac{1}{\mu_e} \left\langle \Psi \left| \frac{\partial H}{\partial x_1} + \frac{\partial H}{\partial x_2} \right| \Psi \right\rangle . \tag{6}$$

Figure 1 shows the spectra obtained for D_2 and H_2 driven by an 800 nm pulse with an intensity of $3{\times}10^{14}\,\mathrm{W/cm^2}$. On the scale of the graph, the two spectra are very similar to each other. The dashed vertical line indicates the position where the two-center interference minimum is expected for the equilibrium internuclear distance $R = 1.4$ a.u., using the condition $R = \pi/k$ for destructive interference with k being the wave vector of the returning electron. We relate k to the harmonic frequency Ω by the heuristic relation $k(\Omega) = \sqrt{2\Omega}$, which has proven to agree well with TDSE results for fixed nuclei [15, 16]. For the parameters of Fig. 1, the minimum is expected at harmonic order 44. The calculated spectra exhibit a broad dip in this region, but it appears to be shifted to harmonic orders slightly lower than 44. This is a clear signature of the dynamic interference effect described in [24]: due to the laser-triggered nuclear motion, the internuclear distances are slightly larger than the equilibrium distance.

Our main quantity of interest is the ratio between harmonics in the isotopes D_2 and H_2. To this end, we calculate for each odd harmonic order n the integrated harmonic yield in the range between $n-1$ and $n+1$ before taking the ratio. To assess the importance of two-electron effects, we have also carried out calculations in which the laser field interacts with only one of the two electrons, i.e. the interaction term in the Hamiltonian is $x_1 E(t)$ instead of $(x_1 + x_2)E(t)$. In the following, we denote this type of calculation as 1e-calculation. However, we emphasize that both electrons are still treated fully quantum mechanically and they are allowed to interact with each other via the interaction W_{ee}. The characteristic feature of the 1e-calculation is that only one of the two electrons can be laser excited, so that HHG will be mainly due to this electron. Laser dressing of the molecular ion takes place in the full 2e-calculation, but not in the 1e-calculation.

For physical interpretation of the numerical results, we compare with the simple model introduced in [38]. The idea is that ionization initiates vibrational wave-packet motion in the molecular ion, with the initial wave packet being the vibrational ground-state $\chi_0(R)$ of H_2 (or D_2) in the spirit of the Franck-Condon principle. For the molecule aligned parallel to the laser field, the signal for harmonic frequency Ω depends on the factor

$$c(\Omega) = \int \chi_0(R)\chi\big(R, \tau(\Omega)\big) \cos\big(k(\Omega)R/2\big) dR, \tag{7}$$

where $\chi(R,t)$ is the time-dependent vibrational wave packet evolving in the ground-state Born-Oppenheimer potential of the ion, $\tau(\Omega)$ is the electron travel time between ionization and recombination in the three-step model, see Eq. (12)

of Ref. [21]. For given Ω, only the shortest possible electron trajectory is considered, since it usually makes the most dominant contribution. The cosine function in Eq. (7) describes the two-center interference. The harmonic ratio between D_2 and H_2 is then modeled as

$$r(\Omega) = \left| c^{D_2}(\Omega)/c^{H_2}(\Omega) \right|^2 . \tag{8}$$

In the following, we denote this approach as simple man's (SM) model. We deliberately resort here to the simplest possible model that can explain the main features of the numerical results. We have also calculated the ratios using an extended SM model along the lines of [25], taking the dressing of the ion into account by propagating vibrational wave packets in two coupled potential surfaces instead of only the ground-state potential. The results are not shown, since for the short trajectories, there is almost no difference compared to the results presented here.

Figure 2 shows the calculated ratio of harmonics in D_2/H_2 for 800 nm pulses of different laser intensities. The numerical results from the 2e- and 1e-calculations are compared with the SM ratios. Since the SM ratios rely on classical electron trajectories, they can be calculated only for the interval of classically allowed harmonic frequencies between I_p and $3.17\,U_p + I_p$.

The agreement is generally good. The similarity between the 2e- and 1e-results tells us that HHG can be understood as a one-electron process and that the dressing of the ion plays a minor role for 800 nm. Furthermore, the ratios are reasonably well predicted by the SM model, Eq. (8). The small deviations may be due to various reasons, e.g. non-applicability of classical trajectories for low-order harmonics, generation of harmonics at the lower instantaneous intensities on the rising and falling edge of the laser pulse, or failure of the Franck-Condon principle for the ionization step [39].

Figure 3 shows results for 1500 nm laser pulses with two different intensities. For the lower intensity $10^{14}\,\mathrm{W/cm^2}$ we find a similar picture as before. The SM ratio is in reasonable agreement with the numerical ratio apart from the fact that the SM curve appears to be shifted to slightly lower harmonic orders. This may be seen as a limitation of the simple heuristic Coulomb correction $k(\Omega) = \sqrt{2\Omega}$. For the higher intensity $2\times10^{14}\,\mathrm{W/cm^2}$, the agreement of the 2e-calculation and the SM model is still good although the depth of the modulation in the ratio is slightly larger in the numerical ratio. The 1e-calculation, however, yields an unexpected, very sharp and strong modulation in the ratio. Since the SM ratios still agrees reasonably well with the full 2e-ratios, we must conclude that the 1e-calculation introduces in this case some type of non-physical behaviour and should be used with care. Nevertheless, the conclusions are consistent with our previous results [25] based on the Lewenstein model: the two-electron calculation yields results that are well reproduced by the simple-man's model when only the short trajectories are used.

To summarize, we have confirmed the existence of two-center interference in HHG from H_2 molecules by integrating the TDSE for a one-dimensional model system that fully incorporates the motion of two interacting electrons in the

presence of the vibrational motion. The ratio between harmonics generated by the isotopes D_2 and H_2 is well predicted by an intuitive model based on classical trajectories and the vibrational wave-packet motion in the molecular ion. For 800 nm laser wavelength, switching off in the TDSE the laser-electron interaction for one of the two electrons leads to very small changes of the harmonic ratio D_2/H_2. This indicates that laser dressing of the ion plays a minor role. For 1500 nm we cannot switch off the interaction for one electron without creating artifacts. Nevertheless the full two-electron results again agree reasonably well with the simple short-trajectory model.

This work was supported by the Deutsche Forschungsgemeinschaft.

References

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

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

[3] K.C. Kulander, K.J. Schafer, J.L. Krause, in Proceedings of the Workshop, Super Intense Laser Atom Physics (SILAP) III, edited by B. Piraux, A. L'Huillier, and J. Rzążewski, Plenum Press, New York, 1993.

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

[5] M. Lewenstein, P. Balcou, M.Y. Ivanov, A. L'Huillier, P.B. Corkum, Phys. Rev. A 49 (1994) 2117.

[6] P.M. Paul, E.S. Toma, P. Breger, G. Mullot, F. Augé, P. Balcou, H.G. Muller, P. Agostini, Science 292 (2001) 1689.

[7] A. Scrinzi, M.Y. Ivanov, R. Kienberger, D.M. Villeneuve, J. Phys. B 39 (2006) R1.

[8] M. Hentschel *et al.*, Nature 414 (2001) 509.

[9] M. Lein, N. Hay, R. Velotta, J.P. Marangos, P.L. Knight, Phys. Rev. Lett. 88 (2002) 183903.

[10] J. Itatani *et al.*, Nature 432 (2004) 867.

[11] T. Kanai, S. Minemoto, H. Sakai, Nature 435 (2005) 470.

[12] C. Vozzi *et al.*, Phys. Rev. Lett. 95 (2005) 153902.

[13] M. Lein, J. Phys. B 40 (2007) R135.

[14] M. Lein, C.C. Chirilă, in Advances in Multi-photon Processes and Spectroscopy 18, edited by S.H. Lin, A.A. Villaeys, Y. Fujimura, World Scientific, Singapore, 2008.

[15] M. Lein, N. Hay, R. Velotta, J.P. Marangos, P.L. Knight, Phys. Rev. A 66 (2002) 023805.

[16] G. Lagmago Kamta and A.D. Bandrauk, Phys. Rev. A 71 (2005) 053407.

[17] S. Chelkowski, T. Zuo, O. Atabek, A.D. Bandrauk, Phys. Rev. A 52 (1995) 2977.

[18] K.C. Kulander, F.H. Mies, K.J. Schafer, Phys. Rev. A 53 (1996) 2562.

[19] W. Qu, Z. Chen, Z. Xu, C.H. Keitel, Phys. Rev. A 65 (2001) 013402.

[20] B. Feuerstein, U. Thumm, Phys. Rev. A 67 (2003) 063408.

[21] M. Lein, Phys. Rev. Lett. 94 (2005) 053004.

[22] S. Baker *et al.*, Science 312 (2006) 424.

[23] S. Patchkovskii, Phys. Rev. Lett. 102 (2009) 253602.

[24] S. Baker *et al.*, Phys. Rev. Lett. 101 (2008) 053901.

[25] C.C. Chirilă, M. Lein, Phys. Rev. A 77 (2008) 043403.

[26] R. Santra, A. Gordon, Phys. Rev. Lett. 96 (2006) 073906.

[27] A. Gordon, F.X. Kärtner, N. Rohringer, R. Santra, Phys. Rev. Lett. 96 (2006) 223902.

[28] S. Patchkovskii, Z. Zhao, T. Brabec, D.M. Villeneuve, Phys. Rev. Lett. 97 (2006) 123003.

[29] S. Patchkovskii, Z. Zhao, T. Brabec, D.M. Villeneuve, J. Chem. Phys. 126 (2007) 114306.

[30] O. Smirnova *et al.*, Phys. Rev. Lett. 102 (2009) 063601.

[31] A.D. Bandrauk *et al.*, Phys. Rev. Lett. 101 (2008) 153901.

[32] A.D. Bandrauk *et al.*, J. Phys. B 42 (2009) 075602.

[33] T. Kreibich, M. Lein, V. Engel, E.K.U. Gross, Phys. Rev. Lett. 87 (2001) 103901.

[34] S. Saugout, C. Cornaggia, A. Suzor-Weiner, E. Charron, Phys. Rev. Lett. 98 (2007) 253003.

[35] S. Saugout, E. Charron, C. Cornaggia, Phys. Rev. A 77 (2008) 023404.

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

[37] K. Burnett, V.C. Reed, J. Cooper, P.L. Knight, Phys. Rev. A 45 (1992) 3347.

[38] Supporting online material, S. Baker *et al.*, Science 312 (2006) 424.

[39] X. Urbain *et al.*, Phys. Rev. Lett. 92 (2004) 163004.

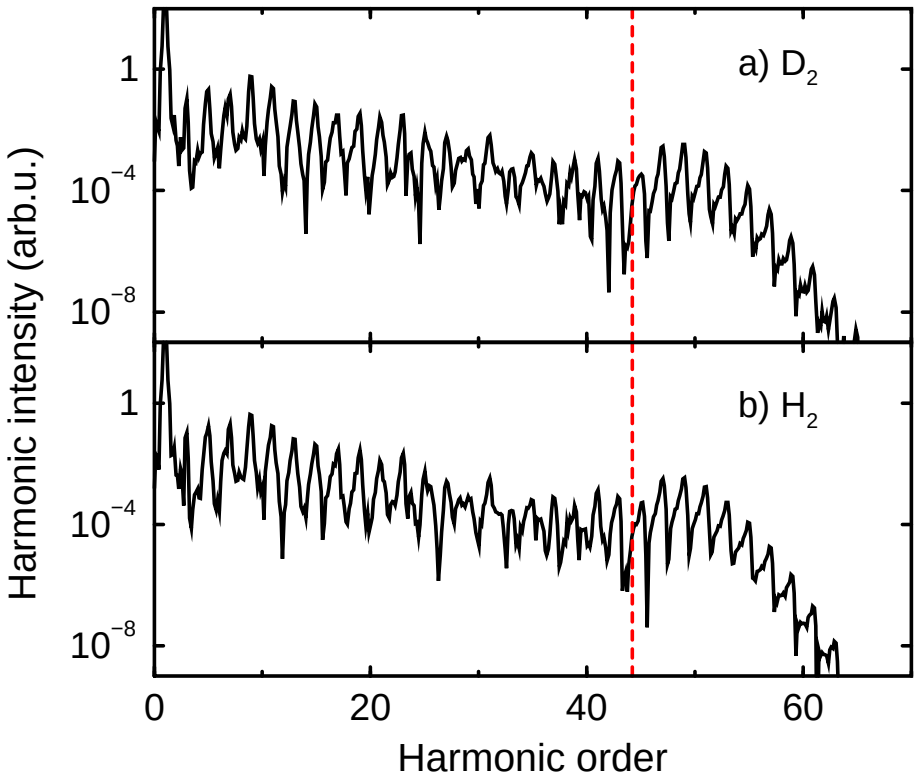

Figure 1: Harmonic spectra generated by D_2 (a) and H_2 (b) in an 800 nm laser pulse with intensity 3×10^{14} W/cm^2. The dashed vertical line indicates the position where the two-center interference minimum is expected for $R = 1.4$ a.u.

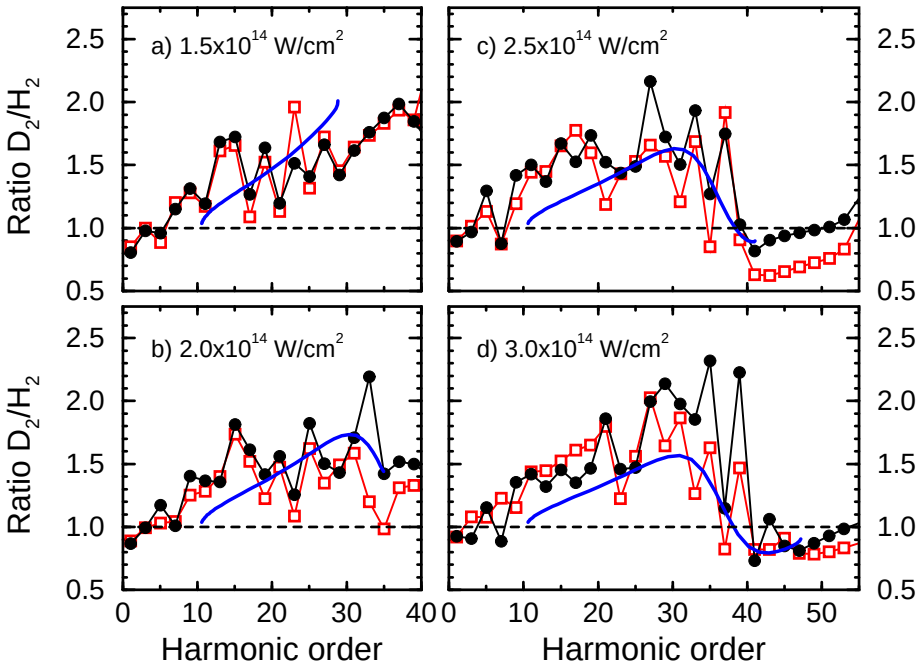

Figure 2: Ratios of harmonics in D_2 and H_2 for 800 nm laser pulses with various laser intensities as indicated. Filled circles, TDSE 2e-calculations. Empty squares, TDSE 1e-calculations. Smooth blue lines, ratios from the SM model in Eq. (8).

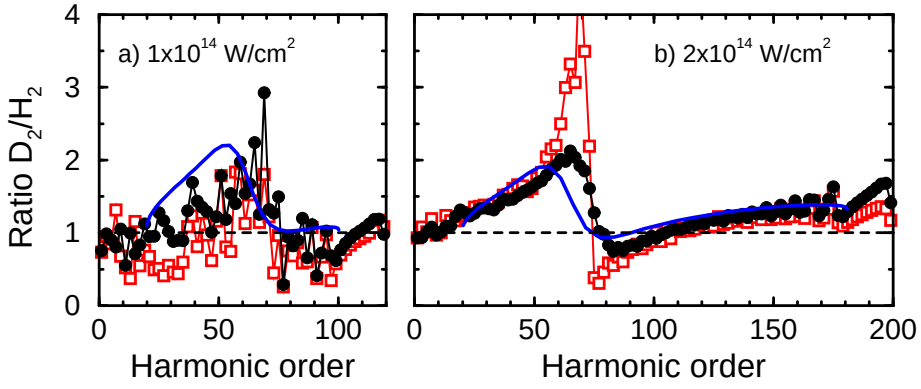

Figure 3: Same as Fig. 2 for 1500 nm laser pulses with two different laser intensities as indicated.