INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS B: ATOMIC, MOLECULAR AND OPTICAL PHYSICS

J. Phys. B: At. Mol. Opt. Phys. **39** (2006) S437–S444 doi:10.1088/0953-4075/39/13/S17

Influence of nuclear vibration on harmonic generation in molecules

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Received 15 December 2005, in final form 31 January 2006
Published 22 June 2006
Online at stacks.iop.org/JPhysB/39/S437

Abstract
The effect of vibrational motion on harmonic generation in molecules is studied within the strong-field approximation. Simple expressions are given for the cut-off energy and for the ratio of spectral intensities from two isotopes. The latter is based on electronic trajectories from the simple-man's model. The influence of vibration is given by a correlation function that is sensitive to the overlap between the initial vibrational wave packet and the wave packet after the evolution in the Born–Oppenheimer potential of the ionized molecule.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

When a molecule is irradiated by an intense laser field, a variety of processes can occur, e.g., ionization, dissociation and harmonic generation (HG). Phenomena induced by recollision electrons, such as HG, and fragmentation caused by inelastic scattering are of great current interest, since they allow us to determine molecular structure [1] and dynamics [2, 3] from measurable spectra.

While for atoms there are satisfactory analytical models based on *S*-matrix theory, for molecules the *S*-matrix formulation needs to include additional effects, such as the molecular orbital symmetry [4, 5], the field coupling of the low-lying electronic states [6], which can be important in the presence of charge-resonance-enhanced ionization [7, 8], and the extra degrees of freedom such as vibration and rotation.

Only a few attempts were made to include the vibrational motion in the analytical description of molecular ionization. In [9–12], the familiar Keldysh-like ionization amplitude is written for specific transitions between the vibrational ground state and vibrational states of the molecular ion. It is shown that proper treatment of the vibrational states is essential to achieve an accurate description of ionization. For H_2^+, the field-modified potential energy curves should be taken into account as well. So far, only the direct ionization has been considered. To study the recollision electrons, the evolution of the vibrational wave packet created upon ionization has to be treated accurately between the time of ionization and the time of recollision. This is important for HG in vibrating molecules [3, 13].

In this work, we analyse in detail the predictions of the strong-field approximation (SFA) including vibration [3, 13] for HG in H_2 and H_2^+. The plan is as follows: (a) in section 2, we briefly outline the method and make some comments on the computational aspects. (b) In section 3, we discuss the effect of vibration on HG spectra in H_2 and H_2^+. We calculate the ratio of HG intensities for pairs of isotopes, such as D_2/H_2, and compare with the prediction based on considering the electron trajectories [14] from the simple-man's model [15, 16] together with what we call the vibrational correlation function. The latter quantitatively describes the effect of vibration on the contribution of a single electron trajectory to the HG emission. Averaging over the molecular orientation is shown to wash out two-centre interference [17, 18] in the HG spectrum. (c) Finally, in section 4 we conclude and suggest further developments of the theoretical model.

2. Theory

The SFA for HG in atoms (also known as the Lewenstein model [19]) was recently extended to include the vibrational motion in diatomic molecules [3, 13]. For completeness, we briefly describe the derivation of the time-dependent dipole moment, given in detail in [13]. We assume that: (a) no bound states other than the Born–Oppenheimer (BO) ground state are populated, (b) the depletion of the ground state is negligible, (c) only one electron can become active and (d) while in the continuum, the active electron does not interact with the core. While the active electron is in the continuum, the remaining core evolves in the BO potential of the molecular ion created. In the following, we denote by $\mathbf{r}' \equiv (\mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_N)$ the coordinates of the remaining $N - 1$ electrons. Atomic units are use throughout this work. We expand the wavefunction as

$$\psi(\mathbf{r}, \mathbf{r}', R, t) = \mathrm{e}^{-\mathrm{i}E_0 t}\left\{\psi_0(\mathbf{r}, \mathbf{r}', R) + \int \mathrm{d}\mathbf{p}\, \phi(\mathbf{p}, R, t) \exp(\mathrm{i}\mathbf{p}\cdot\mathbf{r})\psi_R^+(\mathbf{r}')\right\}, \tag{1}$$

where $\psi_0(\mathbf{r}, \mathbf{r}', R) = \chi_0(R)\psi_R(\mathbf{r}, \mathbf{r}')$ is the ground-state wavefunction of the molecule in the BO approximation, E_0 is the ground-state energy and $\psi_R^+(\mathbf{r}')$ is the electronic ground state of the molecular ion. From the BO approximation, $\chi_0(R)$ satisfies

$$\left[-\frac{1}{M}\frac{\partial^2}{\partial R^2} + V_{\mathrm{BO}}(R)\right]\chi_0(R) = E_0\chi_0(R), \tag{2}$$

where M is the mass of one nucleus and $V_{\mathrm{BO}}(R)$ is the BO potential of the molecule, corresponding to the ground electronic state. Neglecting the non-BO couplings and the interaction with the laser field for $\psi_R^+(\mathbf{r}')$, the time-dependent Schrödinger equation leads to an equation for $\phi(\mathbf{p}, R, t)$ and the electronic dipole moment is obtained. To account for the presence of more than one valence electron, we adopt a simple estimate for the total dipole moment by multiplying the one-electron dipole by N_v, the number of equivalent valence electrons (i.e., $N_\mathrm{v} = 2$ for the H_2 molecule). This estimate follows from using antisymmetrized electronic states if they are built from the same set of single-particle orbitals in the neutral and ionized systems. Finally, the dipole moment reads

$$\begin{aligned}\mathbf{D}(t) = -\mathrm{i}N_\mathrm{v}\int_0^t \frac{\mathrm{d}t'}{(t - t' + \mathrm{i}\epsilon)^{3/2}}\int_0^\infty \mathrm{d}R\, \chi_0^*(R)x\, \mathbf{d}_{\mathrm{rec}}^*[\mathbf{p}_\mathrm{s}(t', t) + \mathbf{A}(t), R] \\ \times \exp[-\mathrm{i}S(t', t)]\hat{U}_R(t - t')d_{\mathrm{ion}}[\mathbf{p}_\mathrm{s}(t', t) + \mathbf{A}(t'), R, t']\chi_0(R) + \mathrm{c.c.}\end{aligned} \tag{3}$$

In equation (3), the saddle-point approximation was used to sum over the electron's continuum states. The saddle momentum is $\mathbf{p}_\mathrm{s}(t', t) = -\int_{t'}^{t} \mathrm{d}t''\, \mathbf{A}(t'')/(t - t')$ and ϵ is a regularization

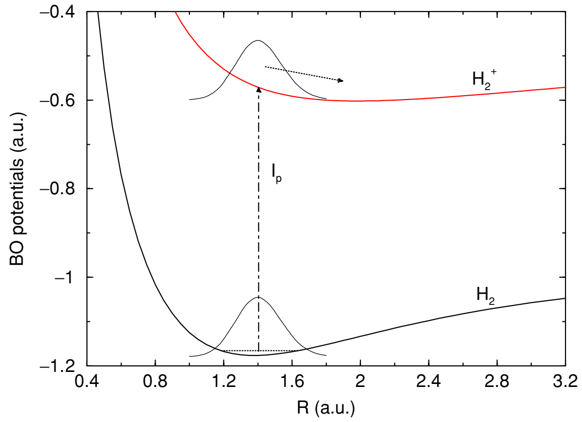

Figure 1. A schematic view of the HG process in the H_2 molecule, taking nuclear vibration into account: after the active electron tunnels in the continuum, the ground-state wave packet corresponding to the BO potential of the H_2 molecule evolves in the BO potential of the H_2^+ molecular ion.

parameter. For the semiclassical action, one has $S(t', t) = \int_{t'}^{t} \mathrm{d}t''[\mathbf{p}_s(t', t) + \mathbf{A}(t'')]^2/2 - E_0(t-t')$. For a given electric field $\mathbf{E}(t)$, the vector potential $\mathbf{A}(t)$ satisfies $\mathbf{E}(t) = -\mathrm{d}\mathbf{A}(t)/\mathrm{d}t$. The ionization and the recombination steps are described by the following matrix elements:

$$d_{\mathrm{ion}}(\mathbf{p}, R, t) = \int \frac{\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'}{(2\pi)^{3/2}} \left[\exp(\mathrm{i}\mathbf{p}\cdot\mathbf{r})\psi_R^+(\mathbf{r}')\right]^* \mathbf{E}(t)\cdot\mathbf{r}\psi_R(\mathbf{r}, \mathbf{r}'), \tag{4a}$$

$$\mathbf{d}_{\mathrm{rec}}(\mathbf{p}, R) = \int \frac{\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'}{(2\pi)^{3/2}} \left[\exp(\mathrm{i}\mathbf{p}\cdot\mathbf{r})\psi_R^+(\mathbf{r}')\right]^* \mathbf{r}\psi_R(\mathbf{r}, \mathbf{r}'). \tag{4b}$$

For the electronic ground state, the LCAO (linear combination of atomic orbitals) approximation is used. The evolution in the BO potential of the molecular ion is described by the evolution operator $\hat{U}_R(t)$, satisfying

$$\mathrm{i}\frac{\partial \hat{U}_R(t)}{\partial t} = \left[-\frac{1}{M}\frac{\partial^2}{\partial R^2} + V_{\mathrm{BO}}^+(R)\right]\hat{U}_R(t). \tag{5}$$

In the spirit of the three-step model [15, 16], the dipole moment from equation (3) can be interpreted as arising from the following sequence of events: (1) at time t' the active electron tunnels into the continuum, described by the ionization amplitude d_{ion}, (2) upon ionization, a vibrational wave packet is created and evolves in the BO potential of the molecular ion, described by the evolution operator $\hat{U}_R(t-t')$ and (3) at time t the active electron recombines with the molecular ion (described by the matrix element $\mathbf{d}_{\mathrm{rec}}$) and harmonic radiation is emitted. A schematic view of the process is given in figure 1. We define the 'vertical' ionization potential for the active electron as $I_p = V_{\mathrm{BO}}^+(R_p) - E_0$. Here, R_p is the internuclear distance at which the modulus of the initial vibrational wave packet $|\chi_0(R)|$ peaks. In analogy to atoms, a simple expression for the HG cut-off in a monochromatic field is

$$\Omega_c = I_p + 3.17U_p \equiv V_{\mathrm{BO}}^+(R_p) - E_0 + 3.17U_p, \tag{6}$$

where U_p is the ponderomotive potential of the electron in the external field. This estimate is in good agreement with the numerical calculations.

We study an H_2 molecule with its axis in the plane xz, oriented at an angle θ relative to the electric field. The electric field is linearly polarized along the x axis. The spectral intensity of the harmonics is calculated as the modulus squared of the Fourier transform $a_x(\Omega)$ of the dipole acceleration along x:

$$a_x(\Omega) = \frac{1}{(2\pi)^{3/2}} \int_0^{T_\mathrm{p}} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}\Omega t} \ddot{D}_x(t), \tag{7}$$

with T_p being the laser pulse duration. Another way to calculate the dipole acceleration makes use of the Ehrenfest theorem: one calculates the expectation value of the dipole velocity P_x and the dipole acceleration reads

$$a_x(\Omega) = \frac{1}{(2\pi)^{3/2}} \int_0^{T_\mathrm{p}} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}\Omega t} \dot{P}_x(t). \tag{8}$$

Due to the approximations made in the SFA, the two expressions (7) and (8) (to which we refer hereafter as the dipole and the velocity formulations, respectively) are not equivalent. We found the velocity formulation given in equation (8) to be more suitable for reproducing the two-centre interference effect [17, 18] in the HG spectra. Hereafter, we use the velocity formulation in the numerical calculations. The required modification in equation (3) is to replace $\mathbf{d}_\mathrm{rec}$ given in equation (4*b*) by

$$\mathbf{v}_\mathrm{rec}(\mathbf{p}, R) = \frac{\mathbf{p}}{(2\pi)^{3/2}} \int \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}' \left[\exp(\mathrm{i}\mathbf{p}\cdot\mathbf{r})\psi_R^{+}(\mathbf{r}')\right]^{*} \psi_R(\mathbf{r}, \mathbf{r}'). \tag{9}$$

Using the LCAO approximation for the electronic ground states of H_2 and H_2^+, it follows from equation (9) that $v_{\mathrm{rec},x}(\mathbf{p}, R) \propto \cos(\mathbf{p}\cdot\mathbf{R}/2)$. This describes the two-centre interference effect within the plane-wave approximation for the electronic continuum states.

In the last part of section 2, we discuss some features of the integrand in equation (3) which are useful for computational purposes. Due to the presence of the evolution operator $\hat{U}_R(\tau)$, the evaluation of the dipole moment becomes prohibitive for large propagation times τ (i.e., for long laser pulses). The contributions of different times τ can be roughly assessed using the autocorrelation function [3],

$$C(\tau) = \int_0^{\infty} \mathrm{d}R\, \chi_0^{*}(R)\hat{U}_R(\tau)\chi_0(R), \tag{10}$$

shown in figure 2 for several molecules. From the behaviour of $C(\tau)$, it turns out that one can safely restrict the integration over t' in equation (3) such that $\tau = t - t' < 120$ au. For larger time intervals, the decay of $C(\tau)$ renders the contribution of the integrand in equation (3) negligible. This procedure greatly reduces the computational time. This holds without doubt for HG with H_2^+, where $C(\tau)$ monotonically decreases with τ, describing the repulsion of two bare protons. For HG with H_2, the vibrational wave packet returns after one vibrational period, but this is irrelevant for the ultrashort pulses used in this work. To corroborate this assertion, we carried out the full numerical integration and found no differences in the HG spectra on the scale of the graphs when compared with those obtained from the restricted time integration. In order to perform the propagation prescribed by the evolution operator $\hat{U}_R(\tau)$ from equation (5), we project on the bound vibrational states $\chi_v^{+}(R)$ ($v = 0, 1, \ldots$) of the molecular ion: $\chi_0 d_{\mathrm{rec},x} = \sum_v c_{\mathrm{rec},x}(v)\chi_v^{+}(R)$, $d_\mathrm{ion}\chi_0 = \sum_v c_\mathrm{ion}(v)\chi_v^{+}(R)$. Then, the propagation can be easily done for arbitrary time intervals τ: $\langle\chi_0 d_{\mathrm{rec},x}|\hat{U}_R(\tau)|d_\mathrm{ion}\chi_0\rangle \equiv \sum_v c_{\mathrm{rec},x}^{*}(v)c_\mathrm{ion}(v)\exp(-\mathrm{i}E_v\tau)$, with E_v being the energy of the eigenstate $\chi_v^{+}(R)$. In practice, the first 15 bound vibrational states were enough for converged propagation.

To study the ratio of HG spectral intensities from different isotopes, we give a simple estimate for the contribution of one-electron trajectory to the emission of a harmonic with frequency Ω:

$$a_x(\Omega) \propto \tilde{C}(\mathbf{k}_\mathrm{ret}, \tau) \exp\left[-\frac{1}{3}\frac{(2I_\mathrm{p})^{1/3}}{|E(t_\mathrm{s}')|}\right], \tag{11}$$

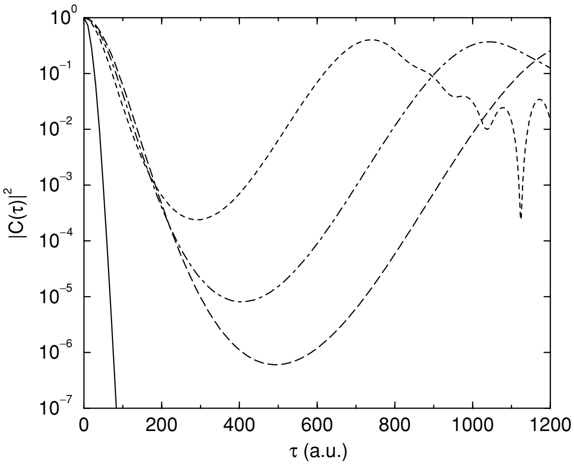

Figure 2. The modulus squared of the autocorrelation function characterizing the nuclear motion after ionization of H_2^+ (——) , H_2 (- - - -) and its isotopes, D_2 (— · —) and T_2 (— — —).

with t_s' and $t_s = t_s' + \tau$ being the time of ionization and the time of recombination in the simple-man's model, and $\mathbf{k}_{\text{ret}} = \hat{\mathbf{x}}\sqrt{2(\Omega - I_p)}$ is the momentum of the returning electron.

The presence of the exponential term in equation (11) is due to the instantaneous ionization rate. The rate emerges straightforwardly [20, 21] from the analysis of the SFA expression for the electronic dipole moment in terms of electron trajectories. The correlation function

$$\tilde{C}(\mathbf{k}, \tau) = \int_0^\infty \mathrm{d}R\, d^*_{\text{rec},x}(\mathbf{k}, R)\chi_0^*(R)\hat{U}_R(\tau)\chi_0(R) \tag{12}$$

describes recombination and incorporates the nuclear motion. By explicitly including the electronic matrix element $d_{\text{rec},x}$, interference effects are taken into account. The R-dependence of the ionization matrix element is neglected in this estimate.

3. Results and discussion

We consider molecules irradiated by a trapezoidal laser pulse, with three optical cycles turn-on and turn-off and a plateau of four optical cycles with constant amplitude. (This description of the envelope refers to the vector potential $\mathbf{A}(t)$.) The laser intensity is $I = 5 \times 10^{14}$ W cm^{-2} and the wavelength is 800 nm.

In the region of low photon energies, there are many electron trajectories that contribute to the emission of a certain harmonic. With vibration affecting each of these contributions, the interference between different trajectories can change significantly when compared to the same calculation done with the internuclear distance fixed to the equilibrium value. In contrast, for high-order harmonics where the number of corresponding electron trajectories is smaller, the effect of vibration is mainly a decrease of the overall harmonic amplitude. This effect can be clearly seen in figure 3, where we compare the HG spectra calculated with the nuclei fixed at the equilibrium position (1.4 au for H_2 and 2.0 au for H_2^+) to the spectra calculated with vibration taken into account, for both H_2 and H_2^+.

The vibration also attenuates the signature of the two-centre interference effect. Based on our analysis of the recombination matrix element in the momentum formulation, from

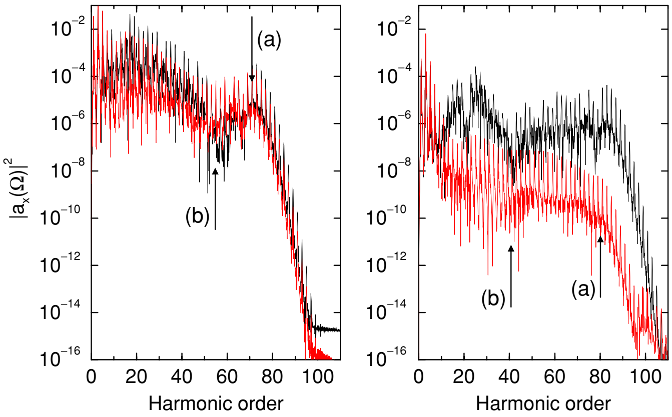

Figure 3. Harmonic spectra for an H_2 molecule (left panel) and an H_2^+ molecular ion (right panel), aligned along the field. The HG spectra are calculated without vibration (black) and with vibration taken into account (red). Arrows (a) show the cut-off estimate for the vibrational case (see equation (6)). Arrows (b) show the predicted position of the two-centre interference minimum (see the text).

equation (9), and on the description of harmonic generation in terms of electronic trajectories, the predicted interference minima occur at frequencies

$$\Omega_m = [(2m+1)\pi/(R\cos\theta)]^2/2 + I_\mathrm{p}, \tag{13}$$

with m an integer number. The predicted minima for aligned molecules are shown in figure 3 by the arrows (b). They agree well with the interference minima in the calculated spectrum. Note that in numerical TDSE calculations, the interference minima are slightly shifted [18, 22] due to Coulomb effects and can be reproduced by ignoring I_p in equation (13).

Specific to HG with the H_2^+ molecular ion, the effect of vibration is to strongly suppress the long trajectories due to rapidly decaying behaviour of the autocorrelation function (see figure 2). Thus, the HG spectrum is more affected than in the case of the H_2 molecule (see the right panel in figure 3).

The effect of vibration can also be studied by considering different molecular isotopes. Figure 4 shows the ratio of the harmonic intensities in D_2 and H_2. The spectral intensities are integrated over each odd-order harmonic peak. The strong oscillations are probably due to interference between different types of trajectories. Also shown is the same calculation done by using the simple estimate from equation (11). For the estimate, we use short trajectories during the plateau part of the pulse envelope. The sudden decrease in the estimated ratios visible in the graphs at low photon energies is caused by the fact that the semiclassical model for HG can only describe the generation of harmonics with photon energies above the ionization threshold. The decrease is positioned at the harmonic order $I_\mathrm{p}/\omega_\mathrm{laser}$. The minimum in the ratio for $\theta = 0°$ and $\theta = 30°$ corresponds to the interference minimum in the spectrum of the heavier isotope D_2. The survival of this structure indicates that the two-centre interference can resolve the different vibrational dynamics in H_2 and D_2.

Averaging over the molecular orientation leads to the harmonic spectra shown in figure 5. One can see that the spectrum is relatively flat. The reason is that the main contribution to the averaged result comes from angles close to $\theta = 90°$, where the two-centre interference effects are absent.

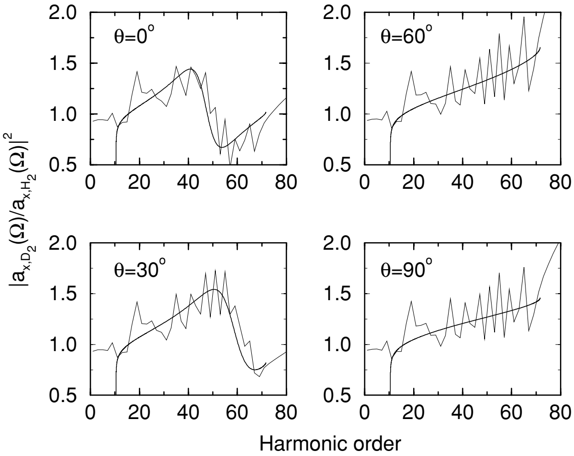

Figure 4. The ratio of the harmonic intensity between D_2 and H_2, compared to the ratio calculated using the estimate from equation (11).

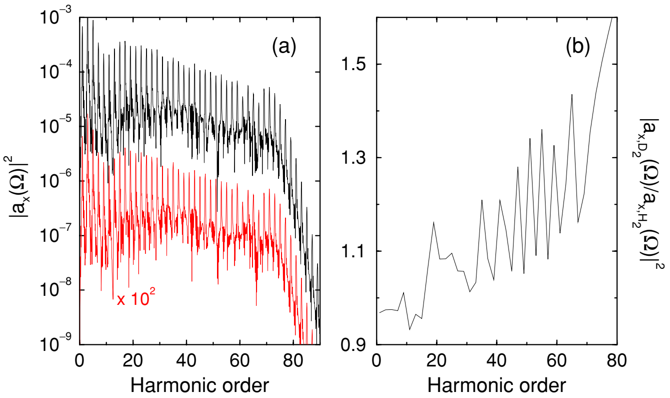

Figure 5. (a) Orientation-averaged harmonic intensities for H_2 (black) and D_2 (red). For clarity, the D_2 curve has been divided by 100. (b) Ratio of harmonic intensities in D_2/H_2 from (a).

4. Conclusions

We have studied the effects of nuclear vibration on HG in molecules and have given a simple estimate for the photon-energy cut-off. Based on electron trajectories from the simple-man's model, the ratio of HG intensities from two isotopes (e.g., H_2 and D_2) can be approximated in a simple way that captures the main features of the physical process. This approximation is found to be in good agreement with the full SFA calculation. We show that the two-centre interference minimum becomes less pronounced when compared to the calculation made with frozen nuclei. In addition, the average over the molecular orientation eliminates any obvious sign of two-centre interference. On the other hand, we have seen a clear signature of the two-centre interference in the ratio between isotopes at fixed orientation. This indicates that interference is sensitive to the small changes of the molecular geometry during the HG process. For HG in H_2^+, the vibration strongly suppresses the long electronic trajectories and the HG spectrum shows less interference features in contrast to the case of frozen nuclei.

Further improvement of the model will be to take into account the coupling of the low-lying electronic states in the molecular ion due to the external field. This is subject of future work. The described effects of vibration will only be visible for nuclei light enough to undergo significant nuclear motion on the few fs time scale, so that there will be only very small effects in heavier molecules such as N_2.

Acknowledgment

We acknowledge discussions within the NSERC SRO network.

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