Supplemental Material for
"Theory of high harmonic generation for probing time-resolved large-amplitude molecular vibrations with ultrashort intense lasers"

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I. COLLINEAR MODEL OF H_2^+

We consider a collinear model of H_2^+ with the Hamiltonian [1, 2] (in atomic units)

$$H_0(z,R) = -\frac{1}{2}\frac{\partial^2}{\partial z^2} - \frac{1}{2\mu}\frac{\partial}{\partial R^2} + V(z,R), \tag{1}$$

where z is the distance from the electron to the center of mass of the two nuclei, R is the internuclear separation, and μ is the reduced mass of the two nuclei. We use a soft core potential for the Coulomb interaction

$$V(z,R) = \frac{1}{\sqrt{R^2+\epsilon_n}} - \frac{1}{\sqrt{(z-0.5R)^2+\epsilon_e}} - \frac{1}{\sqrt{(z+0.5R)^2+\epsilon_e}}, \tag{2}$$

where $\epsilon = 0.03$ and $\epsilon_e = 1.0$ are softening parameters. Here we have neglected the terms related to the small ratio of the electron mass to that of the nuclei. For cases of mass-scaled H_2^+ with mass of hydrogen of $M_p = 1836$ and heavier, considered in this paper, this approximation leads to unnoticeable differences in the calculated HHG spectra. The interaction between the molecule and a laser field is written as

$$H_I(z,t) = zE(t). \tag{3}$$

We approximate the initial total wavefunction as a product of the nuclear and the electronic wavefunctions in the spirit of the Born-Oppenheimer (BO) approach as

$$\Psi(z,R,t=0) = \chi(R)\Phi(z;R). \tag{4}$$

We have checked that this approximation leads to unnoticeable differences in the calculated HHG spectra. In this paper we limit ourselves with the case when the initial state is in the ground electronic potential curve. We numerically solve this time-dependent Schrödinger equation (TDSE) using the split-operator method with sine functions [3]. It can be carried out efficiently with the Fast-Fourier Transformation (FFT). The total wavefunction at any moment in time can be calculated numerically by repeatedly applying the split-operator on the initial wavefunction. Once the total wavefunction is obtained for any moment in time, the induced dipole and HHG spectrum can be calculated using the standard procedures [4]. Typically we use an electron spatial box of $L_z = 400$ a.u. and a nuclear box of $L_R = 20$ a.u. with up to 1024 and 512 grid points, respectively. To avoid artificial reflection due to the finite box size, we use absorbing mask functions [4] for both electronic and nuclear coordinates. The TDSE for the case of frozen nuclei is solved in a similar manner.

We show in Fig. S1 a comparison of the HHG spectra from the exact TDSE and the model [by using Eqs. (1) and (2) of the main paper] for the case of $v = 1$ and $v = 2$ vibrational states. Here the mass of "hydrogen" is chosen to be $4M_p$, with M_p being the mass of a proton. An 6-cycle, sine-squared envelope laser pulse of 800-nm wavelength with an intensity of 2.5×10^{14} W/cm^2 is used in our calculations. This comparison indeed show good agreements between the two methods. We comment that the approximation in which the nuclei are fixed at the equilibrium geometry, does not agree with the "exact" TDSE solution. This fact has be noticed earlier [2].

A similar comparison is shown in Fig. S2 for the case of a vibrational wave packet at two different time delays of $\tau_D = 0.125T$ and $0.75T$ between the preparation and beginning of the probe laser pulse. Here T is the vibrational period of the mass-scaled H_2^+. The initial wave packet is prepared at $t = 0$ as a linear combination of $v = 0, 1$, and 2 vibrational states with the coefficients of 0.8, 0.5, and 0.332, respectively, and propagates freely afterward until the probe laser is turned on. Again the results from the two methods are nearly indistinguishable.

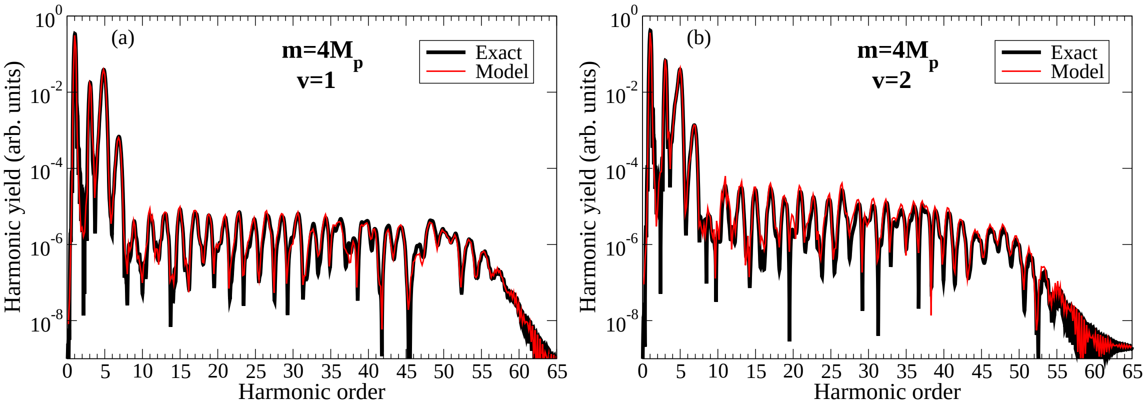

FIG. S1: (Color online) Comparison of the HHG spectra from the TDSE and the model using Eqs. (1) and (2) of the main paper for a $v = 1$ (a) and $v = 2$ (b) vibrational states. The "hydrogen" atom mass is $4M_p$.

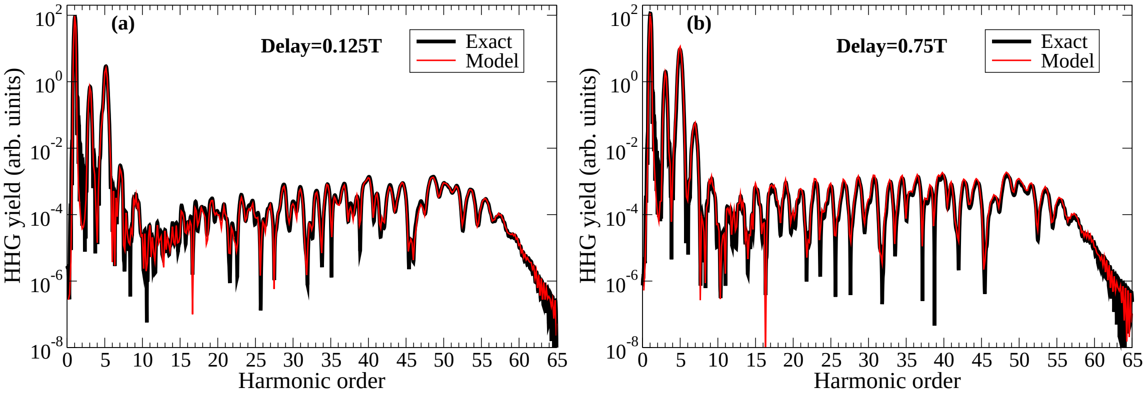

FIG. S2: (Color online) Comparison of the HHG spectra from the TDSE and the model for a time delay of $0.125T$ (a) and $0.75T$ (b). The "hydrogen" atom mass is $16M_p$.

II. EVOLUTION OF THE N_2O_4 NUCLEAR WAVE PACKET

In our simulation the dipole polarizability was calculated by using *Gaussian* package [5], within the density functional theory with the B3LYP exchange-correlation functional and the aug-cc-pVTZ basis set. For the equilibrium geometry, the calculated polarizabilities are 21.8, 48.7 and 56.6 (in atomic units) for α_{xx}, α_{yy}, and α_{zz}, respectively, which agree quite well with an earlier theoretical calculation by Goebel *et al.* [6]. The potential energy curves as a function of N-N internuclear distance R_{NN} are calculated using *Molpro* package [7]. We assume relaxation of all structural parameters other than R_{NN}. For the N_2O_4 cation the structural parameters are assumed to be the same as for the neutral. Our potential energy curves are in reasonably good agreement with that of Li *et al.* [8]. To simulate the influence of the pump and probe laser pulses on the vibrational wave packet, we solve Eq. (2) of the main paper, in which N_2O_4 is treated as an effective diatomic molecule with an effective mass scaled by a factor of 0.7. We note that the same scaling factor was also used by Li *et al.* [8] in order to match the experimental vibrational frequency of the symmetric stretch mode. In our calculation a laser intensity of 2×10^{13} W/cm^2 (1.5×10^{14} W/cm^2) and a duration of 30 fs (20 fs) are used for the pump (probe) pulse. Both pump and probe are of 800-nm wavelength.

We show in Fig. S3(a) and S3(b) the temporal evolution of the N_2O_4 nuclear wave packet during the pump and probe pulses, respectively. In Fig. S3(b) the probe pulse is delayed by 70 fs with respect to the pump pulse. These results were obtained from the numerical solution of the Eq. (2) of the main paper. As can be seen from the figure, the probe pulse (which is much more intense than the pump pulse) has much stronger effect on the nuclear dynamics, especially near the end of the probe pulse. Equivalently, we found that vibrational states up to $v = 2$ are populated (for more that about 5%) after the pump pulse. However, states up to $v = 15$ are populated near the peak of the probe pulse. In order to understand the behavior in Fig. 4(a) of the main paper, one needs to analyze the nuclear distribution near the peak of probe pulse, when the HHG production is most efficient. We show in Fig. S3(c) the

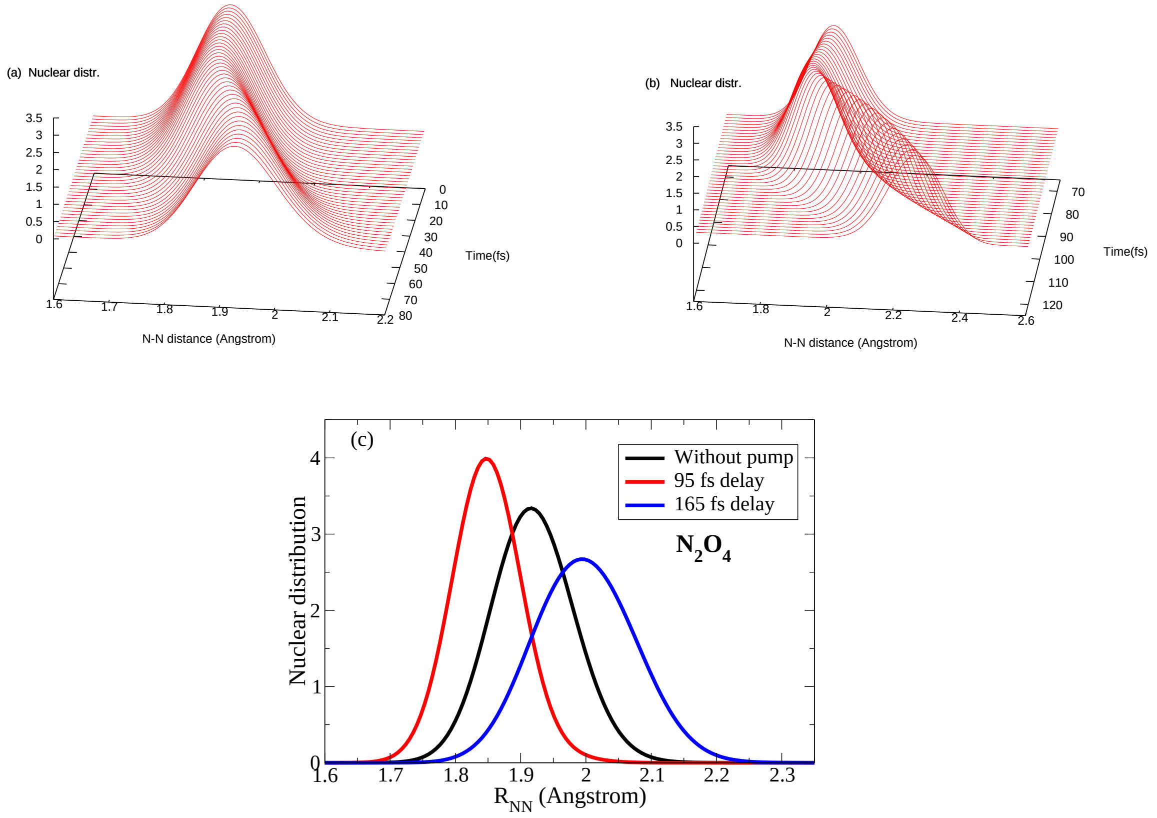

FIG. S3: (Color online) Temporal evolution of N_2O_4 nuclear wave packet during the pump (a) and probe (b). The probe is delayed by 70 fs with respect to the pump. (c) Nuclear distribution at the peak of the probe pulse for different pump-probe time delays of 95 fs and 165 fs. For a reference, the distribution at the peak of the probe pulse from the initial $v = 0$ state (i.e., without the pump) is also shown. See text for other laser parameters.

nuclear distribution at the peak of the probe pulse for different time delays of 95 fs and 165 fs, when the HHG yields are close to the first minimum and the first maximum, respectively [see Fig. 4(a) of the main paper]. For a reference we also plot the distribution for the case when no pump is used. Clearly, the minimum (maximum) in HHG yield is associated with a nuclear distribution at smaller (larger) R_{NN}.

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