PHYSICAL REVIEW A **71**, 043407 (2005)

Phase-sensitive x-ray absorption driven by strong infrared fields

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(Received 24 November 2004; published 21 April 2005)

In this paper it is demonstrated that electron vibrational absorption of molecules driven by strong IR field provides rich physical interpretations of dynamical processes on a short time scale. The phase of an infrared field influences strongly the trajectory of the nuclear wave packet and the probing spectrum. It is shown that the probe spectrum keeps memory of the infrared phase even after that the pump field left the system. The phase effect takes maximum value when the duration of the probe pulse is of the order of the infrared field period, and can be enhanced by a proper control of the duration and intensity of the pump pulse. The phase effect is different for oriented and disordered molecules and depends strongly on the intensity of pump radiation. It can be an effective tool to study charge transfer processes like proton transfer in hydrogen bonded networks.

DOI: 10.1103/PhysRevA.71.043407 PACS number(s): 32.80.Qk, 33.80.Eh, 33.70.Ca, 34.50.Gb

Manipulation and control of the motion of electrons and nuclei at the quantum level is of fundamental as well as applied importance. The determination, or resolution, of a molecular state prepared by a strong external field provides a step towards quantum control. Various superpositions of molecular states or wave packets can be created in strong fields of an infrared laser or a laser in the visible region. In such a case one can expect a transfer of the coherence of the light to the system, which means that the evolution of the wave packet must be sensitive to the phase of the pump radiation. The phase of the pump radiation gives new opportunity to map out the vibronic motion of molecules. The main notion of this paper is that the phase sensitive dynamics of molecular wave packets can be probed with the help of optical, UV or x-ray radiation, thereby manifesting the following effect—phase sensitive photoabsorption.

Light pulses with the duration 1–100 fs are needed to trace the wave packet (WP) propagation in a potential well. Ultrashort optical pulses are available directly now [1]. Only very recently, extreme ultraviolet subfemtosecond pulses have become available [2]. The current development of femtosecond light sources constitutes a central endeavor in the x-ray community: The x-ray free-electron laser will be able to produce pulses with the duration around 100 fs. A wakefield-induced energy chirp in the electron bunches allows us to get strong bunch compression up to 15 fs in a linear accelerator [3]. Approaches based on slicing technology produce 50 fs x-ray pulses [4–6]. In a recent experiment, Drescher *et al.* applied ultrashort x-ray pulses of ≈0.9 fs in a time-resolved pump-probe experiment [7].

The pump radiation affects the absorption of probe pulse in two qualitatively different ways. The first refers to the incoherent population ρ_ν of vibrational levels ν which takes place when the IR radiation is incoherent. In this case the photoabsorption spectrum constitutes an incoherent sum of electron-vibrational transitions from different initial vibrational states: $P(\omega_X)=\Sigma_\nu \rho_\nu P^{(\nu)}(\omega_X)$. Here $P^{(\nu)}(\omega_X)$ is the ordinary probability of electron-vibrational transitions from the stationary vibrational level ν of the ground electronic state and ω_X is the frequency of the probe photons. Our simulations demonstrate that different initial vibrational states lead to very different absorption spectra (Fig. 1). This dependence can be traced to the Franck-Condon distributions for the various vibrational states ν. Apparently, the phase effect is absent for an incoherent IR field.

A coherent pump pulse with the strength $\mathbf{E}_L(t)$ and phase φ_L changes the scenario drastically because it creates a coherent superposition of vibrational states in the ground electronic state

$$i\frac{\partial}{\partial t}\phi(t)=\{H_0-[\mathbf{d}\cdot\mathbf{E}_L(t)]\cos(\omega_L t+\varphi_L)\}\phi(t), \qquad (1)$$

where H_0 is the nuclear Hamiltonian of the ground electronic state. To be specific we assume that the IR frequency ω_L is

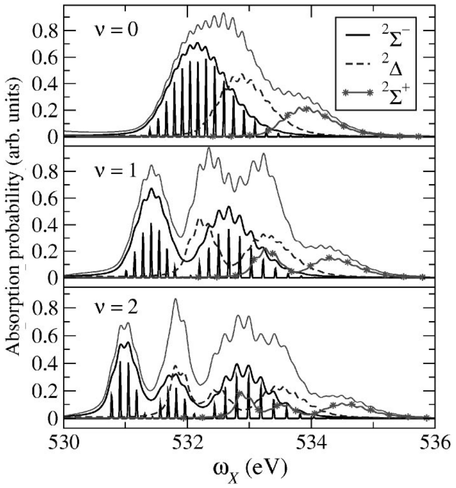

FIG. 1. Partial OK x-ray absorption profiles $P^{(\nu)}(\omega_X)$ of NO excited incoherently in ground state vibrational levels $\nu=0,1,2$ for different core-excited states: $^2\Sigma^-$, $^2\Delta$, and $^2\Sigma^+$. The total spectral profiles are shown by the thin solid lines. Narrow resonances display the spectral distribution of Franck-Condon factors for the $^2\Sigma^-$ core-excited state.

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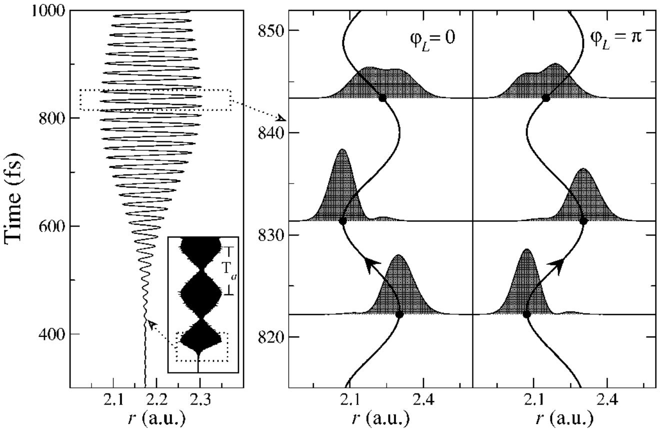

FIG. 2. Trajectory of the WP $\overline{r(t)}$ (3) versus phase of the pump field. Solid lines show the trajectories of the WP. The shaded areas at the right-hand side panel represent WP. $T_a \approx 1210$ fs.

tuned in resonance with the first vibrational transition: $\omega_L = \omega_{10}$. The interaction with the coherent IR field makes the dynamics of the nuclear WP phase sensitive. It is seen from the perturbative solution of the Schrödinger equation (1)

$$|\phi(t)\rangle \approx \sum_{\nu=0}^{\infty} |\nu\rangle c_\nu(t) e^{-i(\nu\varphi_L+\epsilon_\nu t)}, \tag{2}$$

where the coefficients $c_\nu(t)$ do not depend on φ_L in the rotating wave approximation. The numerical simulations show that the trajectory of the center of gravity of the WP,

$$\overline{r(t)} = \langle\phi(t)|r|\phi(t)\rangle, \tag{3}$$

is very sensitive to the phase of the IR light (see Fig. 2). This effect has nothing to do with the role of the phase in few-cycle experiments [1,8,9]; in the present case the duration of the IR pulse is longer than the inverse frequencies of the IR field. Such a dependence is also seen directly from Ehrenfest's expression for the force that affects the center of gravity of the WP, $\langle F\rangle = \langle\phi(t)|(d/dr)(\mathbf{E}_L(t)\cdot\mathbf{d})\cos(\omega_L t+\varphi_L)|\phi(t)\rangle$. For instance, this force changes sign when $\varphi_L \rightarrow \varphi_L + \pi$. The trajectory of the WP (Fig. 2) experiences oscillations in the potential well with two qualitatively different frequencies. The WP performs fast back and forth oscillations with the vibrational frequency. These oscillations are modulated due the anharmonicity of the ground state potential with a period, $T_a = \pi/\omega_e x_e$ (see the inset in Fig. 2). The measurement of the time interval between the adjacent nodes of the trajectory gives directly the revival time T_a. This allows to measure the anharmonicity constant $\omega_e x_e$.

The simulations of the nuclear WPs are here based on numerical solutions of the Schrödinger equation (1) applied to the NO molecule. To be specific we consider here electron-vibrational transition in x-ray region. Apparently the same effect takes place in electronic transitions in optical and UV regions. The absorption of x-ray probe radiation by the laser excited molecules is defined as the expectation value of the interaction of the x-ray field with the system

$$\begin{aligned} P(\Omega) &= -\,\mathrm{Im}\int_{-\infty}^{\infty} \mathrm{Tr}[\rho(t_1)(\mathbf{E}_X(t_1)\cdot\mathbf{D})]dt_1 \\ &= \langle\phi_c(-\Omega)|\phi_c(-\Omega)\rangle, \end{aligned} \tag{4}$$

where $\rho_{ij}(t,\Omega) = a_i(t)a_j^*(t)$ is the density matrix of the molecule, and

$$|\phi_c(-\Omega)\rangle = \int_{-\infty}^{\infty} dt\, e^{-i\Omega t} E_X(t)|\phi_c(t)\rangle, \tag{5}$$

$|\phi_c(t)\rangle = e^{iH_c t}\zeta|\phi(t)\rangle$ is the nuclear WP in the potential surface of the core excited state. $\zeta = (\mathbf{E}_X\cdot\mathbf{D})/2E_X$, $\mathbf{E}_X(t)$ is the strength of the x-ray field, $\mathbf{D}$ is the dipole moment of x-ray transition, $\Omega = \omega_X - \omega_{c0}$ is the detuning of the frequency for x-ray photon from the adiabatic excitation energy ω_{c0}. Morse potentials with parameters from Ref. [10] are used to model the ground and exited electronic states. The physics of the process is highlighted by studying the x-ray absorption band related to the lowest final state ${}^2\Sigma^-$. The x-ray band profiles were computed with the eSPec wave packet propagation program [11] assuming a Gaussian shape of the IR and x-ray pulses with the durations $\tau_L = 100$ fs and τ_X, respectively. The delay time of the x-ray pulse $\Delta t = t_X - t_L$ is defined relative to the peak position of the IR pulse, $t_L = 700$ fs. In the simulations we use the IR pulse intensity of $\mathrm{I}_L = 2.3\times10^{12}$ W/cm^2, except Figs. 3 and 4. Our simulations are performed for oriented molecules, $\mathbf{E}_L \uparrow\uparrow \mathbf{d}$, except Fig. 4 where we also presented calculations for randomly oriented molecules. The r-dependence of the dipole moment $\mathbf{d}$ was calculated by the CASSCF method using the DALTON program [12].

When the x-ray pulse is short ($\tau_X = 3$ fs) a proper choice of the delay time, $\Delta t = t_X - t_L$, (or IR phase) allows to obtain a snapshot of X-ray spectra for WPs localized near the left (B) or right (C) turning points. The spectra B and C (Fig. 3) differ qualitatively because their vertical transitions have different energies. The x-ray spectrum is approximately the sum of spectra B and C if the duration of the x-ray pulse is longer or comparable with the period of oscillations of the wave packet: $\tau_X \gtrsim 2\pi/\omega_{10} \approx 17$ fs (see spectrum D in Fig. 3). This is because the WP then has time to move from left to right turning points during the interaction with the x-ray pulse.

The phase of the IR field strongly influences the shape of x-ray absorption spectra of oriented molecules. This is clearly seen from Fig. 4, where the x-ray absorption probabilities are shown for four different phases $\varphi_L = 0$, $\pi/2$, π, and $3\pi/2$. It is important to note that in this case the x-ray pulse probes the system after the pump pulse left the system, which is an evidence of the phase memory effect. The long lifetime of vibrational levels of the ground state (it is assumed to be infinite in simulations) allows such a long memory of the phase.

The interference of absorption channels and, hence, the phase effect depends strongly on the duration of the x-ray pulse, τ_X (see Fig. 5). The interference takes maximum value when τ_X is one fourth of the infrared field period, $\pi/2\omega_L \approx 4$ fs. The phase dependence is suppressed both for shorter and longer x-ray pulses. A short pulse diminishes the spectral resolution and, hence, the phase sensitivity of the x-ray spec-

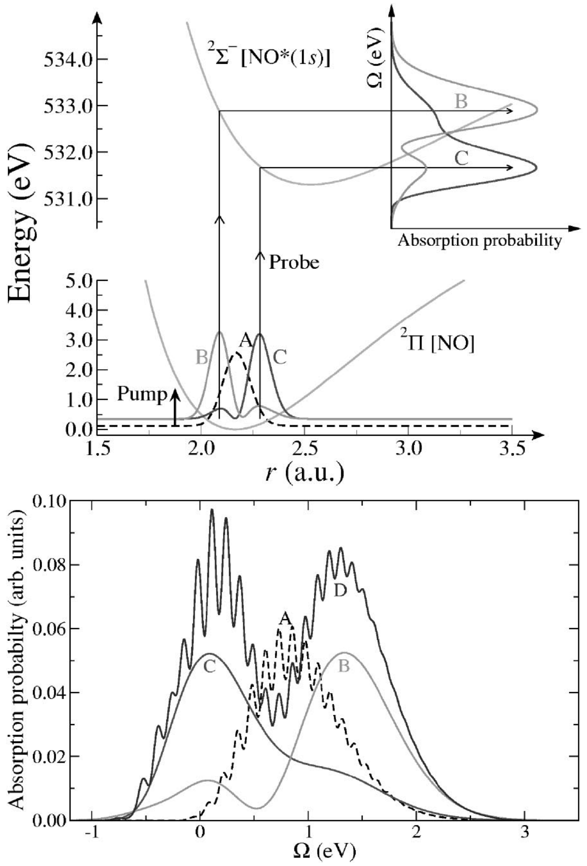

FIG. 3. Main features of x-ray absorption spectra of NO in a strong IR field. $\varphi_L=0$. WPs and corresponding x-ray spectra are marked by labels A, B, C, and D. (A) $I_L=0$; $\tau_X=15$ fs. (B) $I_L=2.3\times10^{12}$ W/cm^2; $\tau_X=3$ fs; $\Delta t=1035$ fs. (C) $I_L=2.3\times10^{12}$ W/cm^2; $\tau_X=3$ fs; $\Delta t=1025$ fs. (D) $I_L=2.3\times10^{12}$ W/cm^2; $\tau_X=15$ fs; $\Delta t>2(\tau_L+\tau_X)$.

trum. The phase sensitivity is suppressed also for a long pulse $\tau_X \gg 2\pi/\omega_L$ because the x-ray pulse probes the molecule at different sites of the potential well (Fig. 3).

Until now we considered the interaction of radiation with oriented molecules, while usually molecules are randomly oriented. However, x-ray spectra of oriented (or fixed-in-space) molecules can be detected even for disordered molecules in many experimental setups, e.g., when measuring x-ray absorption in the ion-yield mode [13,14]. The core excited states experience Auger decay to many final states most of which are dissociative and the detection of the ionic fragment of dissociation selects a certain orientation of the molecule. This technique, widely used in studies of x-ray spectra of fixed-in-space molecules, is thus nicely adapted for observation of the discussed phase effect.

In conventional x-ray measurements the x-ray absorption of randomly oriented molecules is detected. To understand the role of orientational disorder it is useful to recall that the phase sensitivity arises from interference terms like $c_\nu^*(t)c_0(t)$ in $\langle\phi(t)|\phi(t)\rangle$, see Eq. (2). Such an interference in the probe signal means interference between one- $[1\times(\text{x-ray pulse})]$ and many- $[1\times(\text{x-ray pulse})+\nu\times(\text{IR pulse})]$ photon absorption channels. We consider first the case of a weak pump

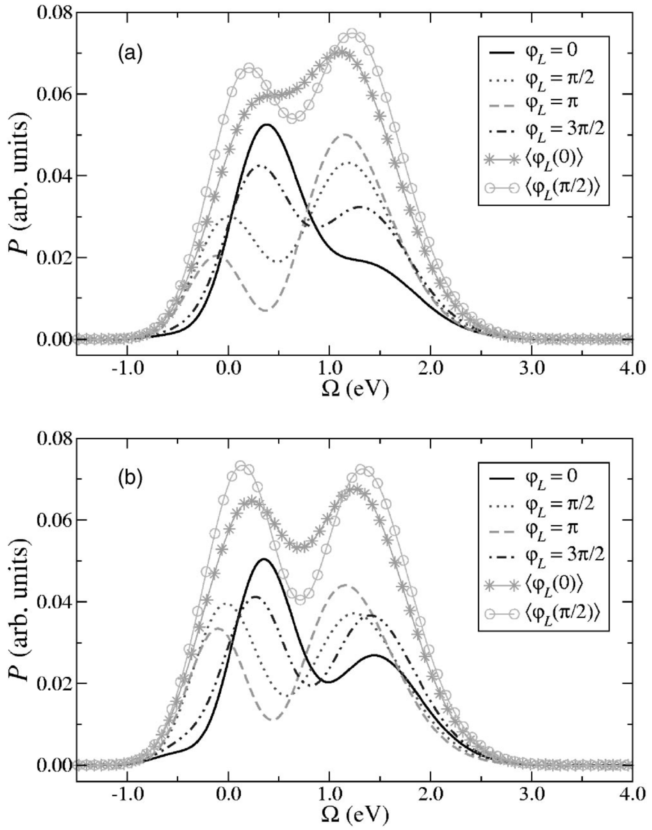

FIG. 4. Phase dependence of the probability of OK x-ray absorption of NO (4). The spectra averaged over molecular orientations are marked by $\langle\varphi_L\rangle$ with $\varphi_L=0$ and $\pi/2$. $\tau_X=3$ fs. $\Delta t=610$ fs. (a) $I_L=1.5\times10^{12}$ W/cm^2. (b) $I_L=2.3\times10^{12}$ W/cm^2.

radiation which populates only the first vibrational level. The phase effect origins in this case from the interference between one- and two-photon channels: $\overline{(\mathbf{d}_{10}\cdot\mathbf{E}_L)|\mathbf{D}\cdot\mathbf{E}_x|^2}=0$. We see that the orientational averaging deletes almost completely the phase sensitivity if the IR intensity is weak. The picture changes qualitatively for stronger IR pulses which are able to populate the second vibrational level $|0\rangle\to|1\rangle\to|2\rangle$. In this case the interference of one- and three-photon

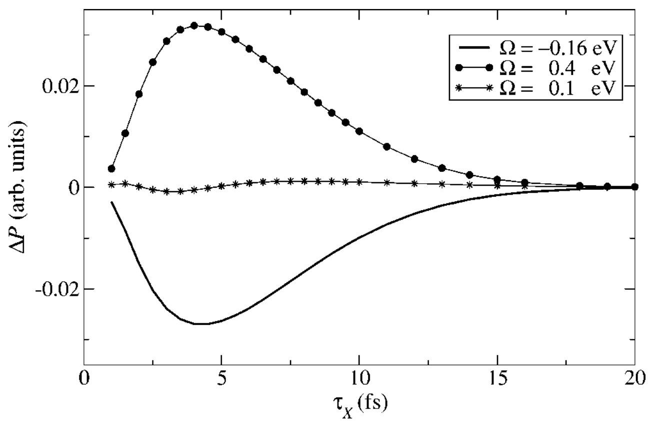

FIG. 5. Difference between probabilities of x-ray absorption (O $1s\to2\pi$) of NO, $\Delta P=P(\varphi_L=0)-P(\varphi_L=\pi/2)$ versus duration of x-ray pulse, τ_X. $\Delta t=610$ fs.

channels averaged over orientations is not equal to zero: $\overline{|\mathbf{d}_{10}\cdot\mathbf{e}_L|^2|\mathbf{D}\cdot\mathbf{e}_x|^2}\neq 0$. Thus conventional x-ray measurements for randomly oriented molecules can be used to measure the phase effect if the intensity of the IR light is sufficiently large to populate even vibrational levels. Our simulations confirm this finding: The orientationally averaged x-ray spectra display an increase of the phase effect with the increase of IR intensity (compare spectra A and B marked by labels $\langle\varphi_L\rangle$ in Fig. 4).

In conclusion, with the present paper we have demonstrated that phase sensitive pump-probe spectroscopy provides rich physical interpretations of dynamical processes on a short time scale. We have found a strong sensitivity of probe spectra on the phase of a pump IR pulse. The origin of this effect is traced to the phase dependence of the trajectory of the nuclear wave packet. The phase effect is found to be sensitive to the duration of the probe pulse and takes maximum value when the pulse duration is comparable with the period of oscillations of the IR field. We have demonstrated the occurrence of a phase memory effect: The probe signal is affected by the phase even after the time when the IR pulse left the system. We believe that the phase effect can be an effective tool to study the dynamics of chemical reactions and charge transfer, for instance proton transfer in hydrogen bonded networks [15].

This work was supported by the Swedish Research Council (VR) and by the STINT foundation. V.C.F. and F.F.G. acknowledge financial support from Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) (Brazil).

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