Laser-induced coherence in ultrafast multiphoton excitation of individual molecules

C. Mainos

Laboratoire de Physique des Lasers, Université Paris-Nord, Avenue Jean-Baptiste Clément, 93430 Villetaneuse, France

The transfer of the intrinsic coherence of short pulses to molecular systems is investigated and an explicit derivation of the excitation probability of the ultrafast multiphoton process is presented. We show that for ultrafast excitation the angular cross section splits into two distinct factors: the ''frozen orientation weight,'' which involves the space configuration and nonlinear dependence, and the ''laser-induced coherence,'' which reflects the coherent superposition of the ground- and excited-state orientations. Quantum interferences give rise to a ''coherent polarizability'' and provide evidence for a sharp confinement of the excited electron motion. The confinement is inversely proportional to the number of coherently excited rotational states.

PACS number(s): 42.50.Hz, 32.80.Wz, 42.65.−k

I. INTRODUCTION

Over the last decade, important progress has been made with the advent of Fourier-limited laser pulses ($\Delta\omega\Delta t \simeq 1$). These pulses provided evidence for novel effects in physics and chemistry [1–3] and are already used as a powerful tool in the study of the quantum behavior of atomic and molecular systems [4–6]. Their increased intrinsic coherence can be transferred to a molecular system by simultaneously exciting a large number of degenerate states, thus making the system undergo quantum interferences during a dephasing time characteristic of the energy relaxation. A representative case reflecting this quantum behavior is the case of a ''rotationally frozen individual molecule.'' In the absence of significant molecular rotation, the rotational states cease to be spectrally observed and the deposited energy is associated with a high number of rotational states.

Here we report on the coupling scheme for multiphoton ultrafast laser-molecule interaction for symmetric-top, linear, or diatomic molecules and optical polarized incident radiation assumed in n-photon resonance with an electronic transition. With the ultrashort-pulse intense laser fields available nowadays, multiple photons may interact coherently with the molecule while the pulse duration does not allow significant rotation of the molecule. Such coherent interaction with atoms and molecules is of increasing interest, both for ultrafast dynamics and multiphoton spectroscopy. The key aspect of the ultrafast excitation of an individual molecule is the high-coherence regime that is established in the excited electronic state through the degeneracy of the rotational structure. The description of the interaction is built, rather, in terms of the number N of coherently excited rotational states. The coherence is thus quantified with the number of excited rotational states, and induces in the molecule an interference regime. Here we intend to define the number N that is intrinsically related to the time duration of the coherent pulse. A further purpose of this work is to find the dependence of the angular cross section on the number n of interacting photons. In particular, by exciting an individual molecule with optical frequencies, the intrinsic coherence of the laser pulse is experienced by the excited electron. Under these conditions, the spatial distribution of the excited electron reflects characteristics of the laser pulse, the order of the nonlinear process,

and the spectral extent of the induced coherence within the rotational structure. By establishing such a large molecular coherence, the polarizability of the individual molecule exhibits a dramatic dependence on its spatial configuration: the anisotropy of the ultrafast multiphoton excitation process is first limited by a broad envelope characteristic of the number of interacting photons, which is spectrally observed in the excited state of an isotropic molecular gas. For the rotationally frozen individual molecule, however, this anisotropy is singular, and for optical frequencies it shows a sharp space confinement for the excited-electron motion.

II. LASER-INDUCED ROTATIONAL COHERENCE

The theory of multiphoton excitation has been established for more than four decades [7] and, with the advent of the laser, has become a powerful spectroscopic tool for the study of atomic and molecular structure. The n-photon excitation probability for the molecular transition $|g\rangle \rightarrow |e\rangle$ is $S_{eg}^{(n)} = [1/(2J_g+1)]\Sigma_{M_e M_g}|A_{eg}^{(n)}|^2$: the amplitude probability

$$A_{eg}^{(n)} = \sum_{i_1 \ldots i_{n-1}} \langle e|\mu_p|i_{n-1}\rangle \ldots \langle i_1|\mu_p|g\rangle / [\omega_{g,i_{n-1}} - (n-1)\omega]\ldots[\omega_{g,i_1} - \omega]$$

is the n-photon transition amplitude and μ_p the laboratory-fixed component ($p=0,\pm1$) of the induced electric-dipole operator. ω stands for the angular frequency and, in the absence of external fields, we sum incoherently over the Zeeman levels M_g and M_e. This quantum expression has been used repeatedly in the past with matrix elements assuming orientation averaging for the freely rotating molecules. Nevertheless, the presence of orientation averaging during the interaction process washes out space-distribution properties inherent in an excited electron moving in a space-fixed molecular frame and experiencing the electric field of a polarized coherent pulse.

If we use the Born-Oppenheimer approximation and keep in mind that for short pulses there is no significant molecular rotation [8], we find

$$S_{eg}^{(n)} = \frac{1}{4} \int_0^\pi \int_0^\pi \sin\beta' \, d\beta' \sin\beta \, d\beta S_{P,\Delta K}^{(n)}(J_e\beta';J_g\beta).$$

The angular dependence of the individual molecule is written as

$$S_{P,\Delta K}^{(n)}(J_e\beta';J_g\beta) = q_{v_e v_g} \sum_{k'=T_0}^{n} \sum_{k=T_0}^{n}$$
$$\times \Theta_{P,\Delta K}^{k'k}(J_e\beta';J_g\beta) M_{P,\Delta K}^{k'*} M_{P,\Delta K}^{k}.$$
$$(1)$$

This is the excitation probability for the coupling of the ground-state orientation $|J_g,\beta\rangle$ and the excited state $|J_e,\beta'\rangle$; $q_{v_e v_g}$ is the Franck-Condon factor, and the tensor $M_{P,\Delta K}^{k}$ contains the frequency and electronic-vibrational dependence (this tensor is considered in the Appendix). $P = np(=0 \text{ or } \pm n)$ stands for the polarization state of the n identical photons, and ΔK is the electronic resonance. Since P and ΔK are the projections of the n-photon angular momentum k (or k'), we have $T_0 = |\Delta K|$ or n whether the polarization is linear or circular, respectively. The angles β and β' describe the orientation of the molecular axis in the laboratory frame [9] for the ground- and excited-electronic state, respectively, and J is the total angular momentum of the molecule. Finally, the tensor $\Theta_{P,\Delta K}^{k'k}(J_e\beta';J_g\beta)$ is the individual molecule rotational factor that has been presented previously [10]. Here we need to determine the number of coherently excited rotational states and, for purposes that will become clear in the following, we write

$$\Theta_{P,\Delta K}^{k'k}(J_e\beta';J_g\beta) = \sum_{\tau=T_0}^{N+T_0'-1} \sum_{l'=0}^{N-1} \sum_{l=0}^{N-1}$$
$$\times (2l'+1)(2\tau+1)(2l+1)$$
$$\times \begin{pmatrix} k' & l & \tau \\ -P & 0 & P \end{pmatrix} \begin{pmatrix} \tau & l' & k \\ -P & 0 & P \end{pmatrix}$$
$$\times \xi_{\Delta K} \begin{pmatrix} J_e & l' & * \\ l & \tau & k' \\ * & k & J_g \end{pmatrix}$$
$$\times P_{l'}(\cos\beta') P_l(\cos\beta). \quad (2)$$

The ξ tensor is a scalar product of five Racah coefficients [10], the asterisks indicating a summation over all adjacent rotational states J and J' that interfere with J_e through the integer angular momenta l and l'. This tensor possesses the closure relation

$$\xi_{\Delta K} \begin{pmatrix} * & l & * \\ l & * & k \\ * & k & J_g \end{pmatrix} = 1.$$

We observe that l and l' couple the rotational structure with the molecular orientation through the Legendre polynomials.

The integer N involved in the summations is the number of excited rotational states and the $3j$ symbols show that $T_0' = k'$ if $k' \le k$ or $T_0' = k$ if $k \le k'$. In particular, for $N=1$ we have an absence of interferences ($l = l' = 0$) and only one τ angular momentum is present in the laser-molecule interaction: observation of a single rotational state demands $\tau = T_0 = T_0' = k = k'$ while the rotational factor reduces to

$$\Theta_{P,\Delta K}^{k'k}(J_e\beta';J_g\beta)_{N=1} = \left(\frac{\delta_{k'k}}{2k+1} \right)(2J_e+1)$$
$$\times \begin{pmatrix} J_e & k & J_g \\ -K_e & \Delta K & K_g \end{pmatrix}^2.$$

This is the incoherent rotational line factor that provides the allowed rotational branches $|\Delta J| \le k \le n$. We also obtain the same results, if instead of setting $N=1$, we average Eq. (2) over all β and β'. In contrast, if we consider the case where multiple rotational states are excited coherently, the rotational branches lose their usual meaning; i.e., $|\Delta J| \le \tau \le N + n - 1$. One has to sum coherently over all rotational states overlapped by the broad spectral bandwidth of the short pulse. It can be seen that, when summing Eq. (2) over all interference-allowed rotational states J_e, the excitation process becomes independent of the ground rotational state [10]: the coupling of the ground- and excited-state molecular orientations is then described by

$$\Theta_{P,\Delta K}^{k'k}(\beta';\beta) = \sum_{\tau=T_0}^{N+T_0'-1} (2\tau+1) \zeta_{P,\Delta K}^{\tau k}(\beta') \zeta_{P,\Delta K}^{k'\tau}(\beta),$$
$$(3)$$

with

$$\zeta_{P,\Delta K}^{\tau k}(\beta') = \sum_{l'=0}^{N-1} (2l'+1) \begin{pmatrix} \tau & l' & k \\ -P & 0 & P \end{pmatrix}$$
$$\times \begin{pmatrix} \tau & l' & k \\ -\Delta K & 0 & \Delta K \end{pmatrix} P_{l'}(\cos\beta').$$

Here we focus on the case of a rotationally frozen molecule [11] where N is significant compared to the number of photons. Under these conditions, the ζ tensor can be replaced by the product of two reduced rotation matrix elements [12], and Eq. (3) simplifies to

$$\Theta_{P,\delta K}^{k'k}(\beta';\beta)_{N \gg 1} = Q_{P,\Delta K}^{N}(\beta';\beta) \, d_{P,\Delta K}^{k}(\beta') \, d_{P,\Delta K}^{k'}(\beta).$$
$$(4)$$

The quantity $Q_{P,\Delta K}^{N}(\beta';\beta) = \sum_{\tau=T_0}^{N+T_0-1}(2\tau+1)d_{P,\Delta K}^{\tau}(\beta')d_{P,\Delta K}^{\tau}(\beta)$ is the molecular orientation overlap factor (MOOF); the sum is truncated at $T = N + T_0 - 1 (\simeq N + T_0' - 1)$ and involves the number of excited rotational states. This means that the integer T must be determined by the full width at half-maximum (FWHM) of the laser pulse that overlaps N rotational states. It has been shown [10] that the integer T is related to the peak power of the laser pulse. Important values for N are then intrinsically related to the

short-pulse high-peak powers, and the large rotational coherence in the excited electronic state demands the condition $\hbar\Delta t \ll I_B$. I_B is the moment of inertia of the molecule about an axis perpendicular to the molecular axis; i.e., this stands for a rotationally frozen molecule where the induced rotational coherence becomes independent of the initial rotational state. The MOOF cannot exceed the value $Q_{T_0,T_0}^N(0;0) = N(N+2T_0)$ (where the molecule and laboratory quantization axes have a common orientation in space), and it contains the intrinsic coherence of the short pulse; i.e., only this factor depends on the number of excited rotational states. Nevertheless, the coherent nature of the excitation process does not allow us to regard the orientation of the molecular axis in the ground and excited state separately but rather requires consideration of these two orientations in a coherent superposition. Furthermore, β' is not well defined and we must take contributions from all β' values. In such circumstances, we must introduce two new variables:

$$\beta^{\sim} = \beta' - \beta, \tag{5a}$$

$$\beta^* = (\beta' + \beta)/2. \tag{5b}$$

$\beta^{\sim}$ is the angular spread, which can be seen as the separation of two coherent-state wave packets in phase space, and β^* is the coherence center, which is a mean orientation for the molecular axis during the interaction time interval. k or k' cannot exceed n and $N \gg 1$; the MOOF is a sharp distribution (it is important only if β' is close to β), whereas the part associated with the order of the nonlinear process (the summation is limited by n) is only a broadband distribution. We have a slowly varying envelope where the amplitude and phase do not vary significantly over the wavelength of the coherent wave packet. Summing Eq. (1) over all β' contributions, the excitation probability splits into two distinct factors: the coherence factor, $Q_{P,\Delta K}^N(\beta^{\sim})$ $= \frac{1}{2}\int_0^\pi \sin\beta' \, d\beta' \, Q_{P,\Delta K}^N(\beta';\beta'-\beta^{\sim})$, whose FWHM reflects the uncertainty in the molecular orientation during excitation; and a molecular orientation weight factor, $\sigma_{P,\Delta K}^{(n)}(\beta^*)$. We further observe that $Q_{P,\Delta K}^N(\beta^{\sim})$ is a superposition of N convolution products taken over the sphere of the unit radius: since $q_{P,\Delta K}^N(\beta^{\sim}) = Q_{P,\Delta K}^N(\beta^{\sim})/Q_{P,\Delta K}^N(0)$ cannot exceed unity, we write

$$S_{P,\Delta K}^{(n)}(\beta^*;\beta^{\sim}) \simeq \sigma_{P,\Delta K}^{(n)}(\beta^*)q_{P,\Delta K}^N(\beta^{\sim}) \tag{6}$$

with

$$q_{P,\Delta K}^N(\beta^{\sim}) = \frac{1}{N}\sum_{\tau=T_0}^{N+T_0-1} (2\tau+1)d_{P,\Delta K}^\tau(\beta^{\sim})*d_{P,\Delta K}^\tau(-\beta^{\sim}), \tag{7a}$$

$$d_{P,\Delta K}^\tau(\beta^{\sim})*d_{P,\Delta K}^\tau(-\beta^{\sim})$$
$$= \frac{1}{2}\int_0^\pi \sin\beta' \, d\beta' \, d_{P,\Delta K}^\tau(\beta') \, d_{P,\Delta K}^\tau(\beta'-\beta^{\sim}). \tag{7b}$$

The factor $q_{P,\Delta K}^N(\beta^{\sim})$ is the laser-induced rotational coherence (LIRC). The dependence on the order of the nonlinear process is found in $\sigma_{P,\Delta K}^{(n)}(\beta^*)$ $= q_{v_e v_g}|\Sigma_k M_{P,\Delta K}^k d_{P,\Delta K}^k(\beta^*)|^2$. This numerical coefficient depends on the frozen orientation β^* and the number of interacting photons n: due to the absence of intermediate resonances with real states, the orbitals associated with the $n-1$ intermediate virtual states are diffuse and the shape of the nuclear frame can be disregarded in the determination of the tensor $M_{P,\Delta K}^k$; i.e., for the ultrashort-pulse intense laser fields involved in multiphoton processes, the molecule behaves in many aspects as an atom [13]. We will consider the tensor $M_{P,\Delta K}^k$ with an excited electron moving in a central field; we will treat the excited electron as a Rydberg electron and subsequently average over all allowed orbital states. With the aid of the Appendix, we obtain

$$\sigma_{P,\Delta K}^{(n)}(\beta^*) = \sum_{k=T_0}^n \frac{2n+1}{2k+1}|c_k^{(n)}(P)|^2|d_{P,\Delta K}^k(\beta^*)|^2. \tag{8a}$$

For simplicity, the global factor $q_{v_e v_g}|M_{fg}^c|^2/(2n+1)$ has been dropped. The geometrical coefficient $\sigma_{P,\Delta K}^{(n)}(\beta^*)$ is the frozen orientation weight (FROW). In circular polarization, we have

$$\sigma_{\pm n,\Delta K}^{(n)}(\beta^*) = [n!/(2n-1)!!]|d_{\pm n,\Delta K}^n(\beta^*)|^2. \tag{8b}$$

For linear polarization and one-photon excitation, $\sigma_{0,\Delta K}^{(1)}(\beta^*) = |d_{0,\Delta K}^1(\beta^*)|^2$, whereas for $n=2$ and $n=3$ we obtain, respectively, $\sigma_{0,\Delta K}^{(2)}(\beta^*) = \frac{5}{9}\delta_{0,\Delta K} + \frac{4}{9}|d_{0,\Delta K}^2(\beta^*)|^2$ and $\sigma_{0,\Delta K}^{(3)}(\beta^*) = \frac{21}{25}|d_{0,\Delta K}^1(\beta^*)|^2 + \frac{4}{25}|d_{0,\Delta K}^3(\beta^*)|^2$. In general, the FROW coefficient cannot exceed unity and contains the properties $\sigma_{0,0}^{(n)}(0) = 1$ and $\sigma_{\pm n,\pm n}^{(n)}(0) = n!/(2n-1)!!$; i.e., the amplitude of the angular cross section is maximum (unity) for a molecule aligned along the linearly polarized vector and an electronic resonance $\Delta K = 0$. We also observe that the excitation probability of a molecule aligned with the linearly polarized vector or a molecule oriented in the direction of the laser beam for circularly polarized light [14] differs by the factor $n!/(2n-1)!!$. This is the polarization intensity ratio. Therefore the numerical value of $\sigma_{P,\Delta K}^{(n)}(\beta^*)$ gives the polarizability amplitude with respect to the most favorable space configuration ($P = \Delta K = 0$), while $q_{P,\Delta K}^N(\beta^{\sim})$ provides the uncertainty in the molecular orientation about the coherence center β^*. The coherent excitation probability $S_{P,\Delta K}^{(n)}(\beta^*;\beta^{\sim}) = \sigma_{P,\Delta K}^{(n)}(\beta^*)q_{P,\Delta K}^N(\beta^{\sim})$ constitutes the angular cross section of the ultrafast multiphoton excitation of the rotationally frozen molecule. Furthermore, it is important to remark that after having separated the angular dependence in the multiphoton process, the frequency-dependent multiphoton electronic-vibrational constants involved in $\sigma_{P,\Delta K}^{(n)}(\beta^*)$ can be determined by a simple analytic expression if we assume a spherically symmetric ion core for the excited electron.

III. DISCUSSION AND CONCLUDING REMARKS

The key result of this work is the explicit derivation of the angular cross section for ultrafast multiphoton excitation and the separation of the coherence and the nonlinear dependence: we can give direct evidence for the coherent behavior of $q_{P,\Delta K}^N(\tilde{\beta})$ by considering linear polarization ($P=0$) and electronic states of the same symmetry ($\Delta K=0$); we obtain

$$q_{00}^N(\tilde{\beta}) = \frac{1}{N}\sum_{\tau=0}^{N-1}\cos(\tau\tilde{\beta}) = \mathrm{Re}\left[\frac{1}{N}\sum_{\tau=0}^{N-1}e^{i\tau\beta'}e^{-i\tau\beta}\right],$$

which shows that the LIRC is a superposition over the harmonics of the angular spread $\tilde{\beta}$, and the coherent-state wave packets of the ground and excited electronic states initially show a common phase: we find an additive accumulation of amplitudes when $|\tau\tilde{\beta}|$ remains smaller than $\pi/2$ for all τ. This takes place, for instance, when $|2\tilde{\beta}| < \pi/T$ and, for $T_0=0$, the FWHM obeys $\Delta\tilde{\beta} = \pi/(T+1) = \pi/N$. Then if one considers $q_{P,\Delta K}^N(\tilde{\beta})$, one will find

$$\Delta\tilde{\beta} = \pi/\sqrt{N(N+2T_0)}. \tag{9}$$

Therefore the FWHM of the angular spread decreases with an increasing number of coherently excited rotational states: it is easy to obtain N as a function of the pulse duration. The LIRC is a wave packet formed by the coherent superposition of the τ-harmonic waves, $C_{P,\Delta K}^\tau(\tilde{\beta}) = (2\tau+1)d_{P,\Delta K}^\tau(\tilde{\beta})*d_{P,\Delta K}^\tau(-\tilde{\beta})$: we have N harmonic waves and the frequency (cm^{-1}) associated with the τ-harmonic wave is $\nu_\tau = 2B\sqrt{\tau(\tau+1)} \simeq B(2\tau+1)$, with $B(\mathrm{cm}^{-1})$ the rotational constant. Provided that the uncertainty in energy ΔE is associated with N degenerate rotational states, we may assume that $N=\Delta E/\langle E\rangle = \Delta\nu/\langle\nu\rangle$ with $\Delta\nu$ the spread in frequency intrinsic to the short pulse. Then, for the average frequency we have $\langle\nu\rangle = (1/N)\Sigma_{\tau=T_0}^T\nu_\tau = B(T+T_0+1)$ and obtain $T = Int\sqrt{\Delta\nu/B+T_0^2}$. Thus for Fourier-limited pulses the number of coherently excited rotational states is

$$N = (1-T_0) + Int\sqrt{\frac{1}{\gamma\Delta t}+T_0^2}, \tag{10}$$

with $\gamma = 2\pi cB = \hbar/2I_B$ a typical rotational frequency and Δt the pulse duration. If either $\gamma\Delta t$ is close to or larger than unity, we have $N=1$; the condition $\Delta\nu\leqslant B$ indeed implies orientation averaging. Furthermore, the normalization constant $N(N+2T_0)$ of the MOOF equals the dimensionless parameter $\Delta\nu/B = (2I_B/\hbar^2)\Delta E$; i.e., ΔE is the uncertainty in the energy of the laser pulse and thus N varies with the square root of ΔE.

For the ultrafast excitation we have $\Delta\nu\gg B$ and may write $N \simeq T \simeq \sqrt{\Delta\nu/B} \simeq 1/\sqrt{\gamma\Delta t}$; the number of events increases as $1/\sqrt{\gamma\Delta t}$. This is characteristic of diffusion. For the CO or NO molecule and a pulse duration longer than $\gamma^{-1} \simeq 2.7\,\mathrm{ps}$, we excite only one state. In contrast with $\Delta t \simeq 2.7\,\mathrm{fs}$, we excite 31 degenerate states while each state possesses the energy $\langle E\rangle = \Delta E/N = [|M|]\hbar/N\Delta t \simeq 10^{-21}\,\mathrm{J}$. For $\Delta t \simeq 1.7\,\mathrm{fs}$, the number of coherently excited rotational states
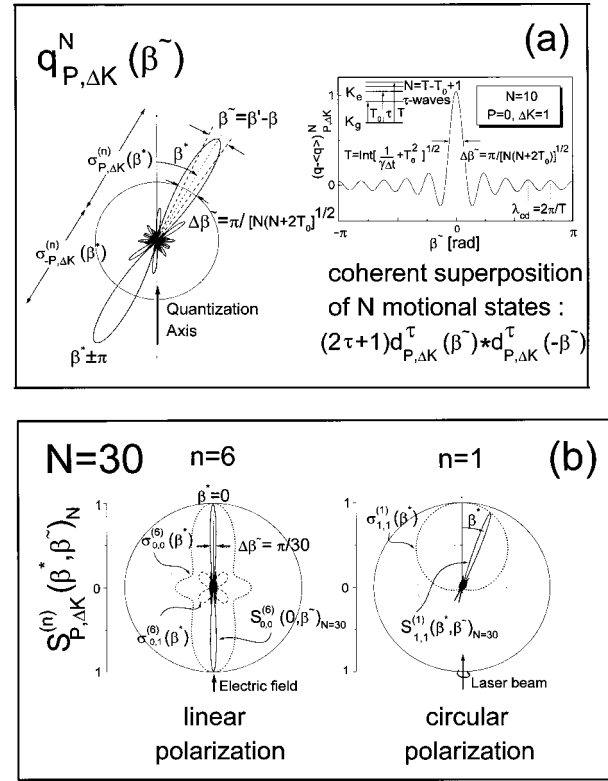

FIG. 1. (a) With the ultrafast excitation the ground- and excited-state molecular orientations β and β' are found in a coherent superposition. The ground electronic state K_g is coupled coherently with N rotational states of the excited electronic state K_e. We have the simultaneous presence of N waves (see text), which interfere around the coherence center $\beta^* = (\beta'+\beta)/2$. For optical frequencies, the coherent superposition $q_{P,\Delta K}^N(\tilde{\beta})$ is experienced by the excited electron and a ''coherent transition dipole'' is induced in the molecule. The angular confinement $\Delta\tilde{\beta}$ of this dipole reflects the number of excited rotational states. (b) The coherent polarizability $S_{P,\Delta K}^{(n)}(\beta^*;\tilde{\beta})_N = \sigma_{P,\Delta K}^{(n)}(\beta^*)q_{P,\Delta K}^N(\tilde{\beta})$: the electron motion is confined dramatically in space and can display either an oscillating motion along the molecular axis or a transverse confinement with a net helicity. The amplitude of the coherent polarizability (dimensionless) depends on the frozen orientation β^* and the number of photons n. It is limited by the slowly varying envelope $\sigma_{P,\Delta K}^{(n)}(\beta^*)$, which is unity (maximum) for the most favorable space configuration where the excited molecule is aligned with the electric field of linearly polarized light.

is $N \simeq 40$, whereas for a heavier molecule such as C_6H_6, we obtain $N \simeq 128$. The number of excited states for lighter molecules such as HCl or H_2 and for the same pulse duration is found to be $N \simeq 17$ and 7, respectively. With the coherent pulse we have created a quantum superposition of distinct motional states $C_{P,\Delta K}^\tau(\tilde{\beta})$, and the coherent motional state $q_{P,\Delta K}^N(\tilde{\beta})$ induced in the excited molecule is found to be expanded into the basis of the harmonics of the angular spread. We see in Fig. 1(a) that mutual interferences between the motional states become rapidly destructive with increasing $\tilde{\beta}$, whereas for $\tilde{\beta} < \pi/2N$ it exhibits an additive accumulation of amplitudes. For optical frequencies, the coherent superposition of the ground- and excited-state molecular ori-

entations is experienced by the excited electron, and the superposition of the motional states results in a spatial confinement providing evidence for a ''coherent transition dipole'': each τ wave (motional state) is associated with a transition dipole since it couples the ground rotational state with some degenerate rotational state of the excited electronic state. Nevertheless, each transition dipole is readily related to the molecule's symmetry and to the symmetry of the electronic transition; i.e., from symmetry considerations, the dipole moment must lie along the molecular axis (parallel type) or in a plane perpendicular to the molecular axis (perpendicular type). Furthermore, the motional state $C_{P,\Delta K}^{\tau}(\tilde{\beta})$ is the autocorrelation function of $\sqrt{2\tau+1}\,d_{P,\Delta K}^{\tau}(\tilde{\beta})$; this is the probability amplitude for the orientation of the angular momentum τ when the angular spread is $\tilde{\beta}$ and can be seen as the angular part of a one-electron orbital. From the coherent superposition of a large number of such states we have indeed an angular momentum aligned with the molecular axis and thus a transition-dipole moment of parallel or perpendicular type depending on the light polarization [14]. In Fig. 1(b), we see that the longitudinal component of the ''coherent transition dipole'' is oscillating along the molecular axis if the polarization is linear, whereas for circular polarization the electron motion is confined in a plane transverse to the molecular axis with a net helicity. The angular confinement is given by $\Delta\tilde{\beta}=\pi\sqrt{B/\Delta\nu}=\sqrt{\mathcal{D}\Delta t}$, the FWHM of the angular spread of the molecular axis. The constant $\mathcal{D}=\pi^{2}\gamma$ (rad^{2}/sec) is the phase-diffusion coefficient. The damped oscillations of $[q(\tilde{\beta})-\langle q\rangle]_{P,\Delta K}^{N}$ drawn in Fig. 1(a) elucidate how the coherent superposition of the motional states dephases with molecular rotation and the coherent polarizability collapses with the increased relative phase rotation of the ground- and excited-coherent-state wave packets. The corresponding angular wavelength is $\lambda_{cd}=2\Delta\tilde{\beta}=\sqrt{4\mathcal{D}\Delta t}$ $=2\pi\sqrt{\gamma\Delta t}$, and the enhancement remains important roughly within a single λ_{cd}. This wavelength can thus be seen as a ''coherence-angular length,'' and the integer $T(=2\pi/\lambda_{cd})$ can be characterized as the wave number of the LIRC. The number of complete cycles during an angular spread of 2π is T. For the rotationally frozen individual molecule where $N\gg1$ and $\Delta\tilde{\beta}\simeq\pi/N$, the number of coherently excited rotational states is then reflected directly on the spatial confinement of the excited electron motion. Finally, we can give an estimate for the time constant τ_{cd} of the energy relaxation if we assume that the relaxation is characterized by the collapse of the coherent polarizability: provided that γ stands for a typical rotational frequency and the coherence angular length is λ_{cd}, we may write $\tau_{cd}/\gamma^{-1}=\lambda_{cd}/2\pi=1/T$. This leads, for instance to $\tau_{cd}\simeq1/\gamma N\simeq\sqrt{\Delta t/\gamma}\simeq\sqrt{2I_{B}/\Delta E}$; for the C$_{6}H_{6}$ molecule and $\Delta t\simeq1.7$ fs, we find $\tau_{cd}\simeq2\times10^{-13}$ s, whereas for HCl we obtain $\tau_{cd}\simeq3\times10^{-14}$ s. This time scale is characteristic of vibration. If the deposited energy of the short pulse is not absorbed by some vibrational mode, subsequent laser-induced reorientation takes place with the coherent polarizability and it may be as fast as a simple molecular vibration. Instead, for $\Delta t>\gamma^{-1}$ we find $\tau_{cd}>\gamma^{-1}$ as well and thus energy relaxation is taking place with molecular rotation while $\lambda_{cd}>2\pi$.

In conclusion, the angular cross section for the ultrafast multiphoton excitation has been investigated. Coherence effects are dominant in the interaction. The space distribution of the excited electron in the frozen molecular frame can be deduced from the number of coherently excited rotational states and the number of interacting photons. This space localization for the electron motion is found to be inherent in a ''laser-induced quantum superposition''; due to the factorization of the coherence and the nonlinear dependence, the rotationally frozen individual molecule can be used as a quantum device for inducing a quantum superposition of distinct motional states in the excited electron. This quantum superposition is characterized by the amplitude $\sigma_{P,\Delta K}^{(n)}(\beta^{*})$ and the angular confinement $\Delta\beta^{\sim}$.

APPENDIX

The high intrinsic uncertainty in energy and the absence of intermediate resonances with real states allow one to assume diffuse orbitals for the $n-1$ intermediate virtual states. For the ultrashort-pulse intense laser fields involved in multiphoton processes, the molecule behaves in many aspects as an atom and, in order to have at hand an analytic expression for the tensor $M_{P,\Delta K}^{k}$, we will assume that the excited electron is a Rydberg electron. The tensor $M_{P,\Delta K}^{k}$ involved in Eq. (1) is written as

$$M_{P,\Delta K}^{k}=(-1)^{\Delta K}\beta_{k}(P)\sum_{q_{1}\ldots q_{n}}B_{k,\Delta K}^{(n)}(q_{n}\ldots q_{1})\sum_{\eta_{1}\ldots\eta_{n-1}}$$
$$\times\langle\eta_{f}|\mu_{\tilde{q}_{n}}|\eta_{n-1}\rangle\ldots\langle\eta_{1}|\mu_{\tilde{q}_{1}}|\eta_{g}\rangle/[\omega_{g,\eta_{n-1}}$$
$$-(n-1)\omega]\ldots[\omega_{g,\eta_{1}}-\omega]. \tag{A1}$$

The tensors $\beta_{k}(P)$ and $B_{k,\Delta K}^{(n)}(q_{n}\ldots q_{1})$ have been defined elsewhere [15]. Although the electron cannot be localized for a stationary state, for the intermediate states that are not stationary states but states dressed by the incident field, the moving electron can be roughly localized along the induced electric-dipole vector. We then write $\mu_{\tilde{q}}\simeq D_{0q}^{(1)}(0\,\vartheta\phi)\mu$ for each molecule-fixed dipole component. The angles ϑ and ϕ are assigned to the orientation of the electric-dipole vector in the molecular frame and μ is the modulus of the induced electric dipole. For the wave functions of the orbital states of the excited electron and the ion core we write $|\eta\rangle=|\eta_{0};l\lambda\rangle$. We neglect the l dependence in the energy denominator and we use the closure relation for all intermediate states. We further contract the product of the n-rotation matrices and split the sum $\Sigma_{q_{1}\ldots q_{n}}$ into $\Sigma_{Q}\Sigma_{a(Q)}\Sigma_{p(a)}$: within the first summation only the term $Q=q_{1}+\cdots q_{n}=\Delta K$ is nonvanishing. The second summation is performed over the transitional paths $a(\Delta K)$ and the third one over all distinguishable permutations of the q elements inside each transitional path. We then obtain

$$M_{P,\Delta K}^{k}=\left\{\sum_{m}\beta_m(0)\beta_k(P)\left(\sum_{a(\Delta K)}p(a)B_{m,\Delta K}^{(n)}(a)B_{k,\Delta K}^{(n)}(a)\right)\right.$$

$$\left.\times\langle l_f\lambda_f|D_{0,\Delta K}^{(m)}|l_g\lambda_g\rangle\right\}M_{fg}^{c} \tag{A2}$$

with

$$M_{fg}^{c}=\sum_{\eta_1^c\cdots\eta_{n-1}^c}\langle\eta_f^c|\mu|\eta_{n-1}^c\rangle\ldots\langle\eta_1^c|\mu|\eta_g^c\rangle/[\omega_{g,\eta_{n-1}^c}$$

$$-(n-1)\omega]\ldots[\omega_{g\cdot\eta_1^c}-\omega].$$

The quantity between parentheses vanishes whenever $m\neq k$. Furthermore, it becomes independent of ΔK if $m=k$. The above arguments lead to

$$M_{P,\Delta K}^{k}=(-1)^{\lambda_f}[l_f,l_g]\begin{pmatrix}l_f & k & l_g\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_f & k & l_g\\ -\lambda_f & \Delta K & \lambda_g\end{pmatrix}$$

$$\times c_k^{(n)}(P)M_{fg}^{c}, \tag{A3}$$

with

$$c_k^{(n)}(P)=\beta_k(0)\beta_k(P)\sum_{a(\Delta K)}p(a)|B_{k,\Delta K}^{(n)}(a)|^2.$$

For brevity, we have set $[l_f,l_g]=\sqrt{(2l_f+1)(2l_g+1)}$. Finally, Eq. (A3) allows one to obtain the closure relation

$$[l_g]^{-2}\sum_{\lambda_g}\sum_{l_f\lambda_f}M_{P,\Delta K}^{k'*}M_{P,\Delta K}^{k}=(\delta_{k',k}|c_k^{(n)}(P)|^2/[k]^2)|M_{fg}^{c}|^2. \tag{A4}$$

This closure relation provides an average value for the electronic-vibrational constants involved in the tensor $\sigma_{P,\Delta K}^{(n)}(\beta^*)=q_{v_ev_g}|\Sigma_k M_{P,\Delta K}^{k}d_{P,\Delta K}^{k}(\beta^*)|^2$ and leads to Eq. (8a). Numerical values for $c_k^{(n)}(0)$ are already available [16] and we are thus able to perform numerical simulations for Eqs. (6) and (8a). Note that for circular polarization we find $c_k^{(n)}(\pm n)=\delta_{k,n}\sqrt{n!/(2n-1)!!}$ and the tensor $c_k^{(n)}(0)$ possesses the closure relations $\Sigma_{k=n,n-2,\ldots}([n]^2/[k]^2)|c_k^{(n)}(0)|^2=1$ and $\Sigma_{k=n,n-2,\ldots}c_k^{(n)}(0)=1$.

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