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Duration of x-ray Raman scattering

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There has recently been much interest in using the notion of a duration time to analyze resonant x-ray Raman scattering (RXS) of atoms, molecules, and solids. This notion implies a selection of processes with different time scales responsible for the formation x-ray Raman spectra, and has been useful for actual predictions of various phenomena associated with RXS and that subsequently have been experimentally verified. However, the notion of a duration time for the x-ray scattering event can also have some paradoxical consequences, as when comparing the RXS duration with the relaxation time of the wave packet evolution in the case when the inverse detuning of the excitation energy is shorter than the time of flight or the lifetime of the core excited state. We present here a solution of this contradiction and give a detailed analysis of the notion of the duration time for RXS. It is shown that this time is complex and consists of two qualitatively different contributions. The first originates in the irreversible decay of the core excited state, while the imaginary part is caused by a reversible dephasing in the time domain. We investigate also the evolution of the wave packets of bound and dissociative states to stationary distributions. The theoretical analysis is accompanied by numerical examples of the time evolution of the wave packet in bound and dissociative core excited states of the N_2 and HCl molecules. [S1050-2947(99)06101-6]

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I. INTRODUCTION

The continuous development of resonant x-ray Raman scattering (RXS) spectroscopy has led to a revelation of many new phenomena [1–9]. Despite the fact that the studies of RXS at the present time have involved only stationary experiments, time-dependent treatments have gained an increased popularity on the theoretical side owing to their inherent interpretability and our inclination to relate spectral features to processes rather than to states. One of the important characteristics of the dynamics of a resonant x-ray Raman scattering process is the ''duration time'' [10–14]. It presents a pure quantum notion based on the interference, or dephasing, suppression of large time contributions to a scattering amplitude.

The concept of the RXS duration time has provided deeper insight into the formation of the RXS spectral profile [11,4,13–15]. With the variation of the duration time through detuning the energy, one can control—or manipulate—different microscopic dynamical processes responsible for the spectral shape of RXS. The notion has lead to the prediction of several new—and experimentally verified—features, such as ''symmetry restoration'' [11], ''vibrational collapse'' [13], and ''control of dissociation'' [14]. A principal aspect of this notion, yet to be understood, is the contradiction between the time of the evolution of the wave packet at the core excited state and the duration time T of the RXS process. Contrary to the relaxation time of the wave packet, the effective duration of RXS strongly depends on the detuning Ω of the frequency of incident radiation from the photoabsorption band. Moreover, T tends to zero for large $|\Omega|$. The relaxation of the wave packet is characterized by the time of flight and the lifetime of the core excited state, Γ^{-1}, both of which can considerably exceed the RXS duration. This leads to the following paradox: To reach the fast limit for the RXS amplitude (short duration of RXS), the time of the wave-packet evolution must exceed the lifetime Γ^{-1} by several times.

A goal of this paper is to find an explanation for the contradiction formulated above and to make a detailed analysis of the notion of RXS duration together with the characteristic times of the wave-packet evolution on the core excited state. After a short theoretical introduction (Sec. II) we introduce the ordinary time-dependent representation for the RXS amplitude and three definitions of the RXS duration time (Sec. III). We show that the real and imaginary parts of the complex duration time are responsible for the irreversible decay and reversible dephasing processes, respectively. The conceptually new time-dependent representation for the scattering amplitude presented in Sec. III C allows us to make a direct connection between the RXS amplitude (or the wave packet) and the RXS duration. In Sec. IV we apply the general theory to RXS of molecules with nuclear degrees of freedom, and present an explanation of the above-formulated paradox. A detailed analysis of the relaxation times versus core excitation below or above dissociation threshold is given in Sec. IV. RXS and wave-packet evolution for core excitation below the dissociation threshold are investigated in Sec. IV A, while the qualitatively different picture for the evolution of the wave packet and the RXS profile taking place when the molecule is core excited above the dissociation threshold is explained in Sec. IV B. An important point here is the time evolution of the space distribution of the wave packet of the core excited state. The final section, Sec. V, summarizes our findings. Atomic units are used throughout the paper.

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II. THEORETICAL BACKGROUND

The spectral properties of RXS are guided by the double differential cross section

$$\sigma(E,\omega)=\int d\omega_1\sigma_o(E,\omega_1)\Phi(\omega_1-\omega,\gamma) \tag{1}$$

which is the convolution of the spectral distribution $\Phi(\omega_1-\omega,\gamma)$ of the incident radiation with the RXS cross section $\sigma_o(E,\omega_1)$ for a monochromatic incident light beam. To be specific, let us assume that the spectral function $\Phi(\omega_1-\omega,\gamma)$ with width γ is centered at frequency ω. According to the Fermi golden rule, the cross section $\sigma_o(E,\omega)$ reads

$$\sigma_o(E,\omega)\propto\sum_f |F|^2\Delta(\omega-E-\omega_{fo},\Gamma_f), \tag{2}$$

where $\Delta(\omega,\Gamma)=\Gamma/\pi(\omega^2+\Gamma^2)$. We will consider the following process: By absorbing an incoming x-ray photon with the frequency ω, the molecule in the ground state $|o\rangle$ is core excited to the state $|c\rangle$. Due to the Coulomb interaction and vacuum fluctuations this intermediate core excited state decays to the final state $|f\rangle$ by emitting an x-ray photon or an Auger electron with the energy E.

Close to the resonant region the radiative and nonradiative RXS amplitudes have the same structures [1]. Physically, it is convenient to consider the Kramers-Heisenberg scattering amplitude as a projection of the stationary wave packet $\Psi_T(\infty)$ on the final state:

$$F=-\imath\langle f|\Psi_T(\infty)\rangle,\quad \Psi_T(\infty)=\imath\sum_c\frac{Q|c\rangle\langle c|\mathcal{D}|o\rangle}{\omega-\omega_{co}+\imath\Gamma}. \tag{3}$$

Here $\omega_{cf}=E_c-E_f$, E_c is the energy of the cth state, and Γ and Γ_f are the lifetime broadenings of the core excited and final states, respectively. In order to make the formal manipulations more transparent, we drop the index f for the scattering amplitude: $F_f\rightarrow F$. The operator $\mathcal{D}$ describes the interaction of the target with the incident x-ray photon. In the case of nonradiative RXS, Q is the Coulomb operator and $Q=\mathcal{D}'^*$ when the emitted particle is the final x-ray photon [1]. The wave packet $\Psi_T(\infty)$ reflects one of the important peculiarities of RXS, namely that the incident photon creates a coherent superposition of the core excited states.

We would like to note that the Kramers-Heisenberg amplitude (3) is based on an isolated-pole approximation. This single-pole approximation leads to an exponential law for the decay of the core excited state (5). As is well known [16], the scattering amplitude can in the general case have double- or multiple-pole contributions. These contributions change the law for the decay of the excited state. However, the analysis shows that these multiple-pole contributions are very exotic [16,17], and we have therefore restricted our analysis to the traditional single-pole expression (3) for the scattering amplitude.

III. COMPLEX DURATION TIME

The half-Fourier transform of the denominator at the right-hand side of Eq. (3) yields the time-dependent representation for the scattering amplitude

$$F=F(\infty),\quad F(\tau)=-\imath\langle f|\Psi_T(\tau)\rangle. \tag{4}$$

Here

$$\Psi_T(\tau)=\int_0^\tau dt\, e^{-t/T}Q\psi(t),\quad \psi(t)=e^{-\imath\mathcal{H}t}\mathcal{D}|o\rangle,$$

$$\mathcal{H}=H-\overline{E}, \tag{5}$$

H is the molecular Hamiltonian, and $\overline{E}$ is the average energy of a core excited state (see below).

A. Decay and dephasing times

One can directly see from Eq. (5) that the complex time

$$T=T_\Gamma+\imath T_\Omega=\frac{1}{\Gamma-\imath\Omega}=\frac{e^{\imath\varphi}}{\sqrt{\Omega^2+\Gamma^2}},\quad \tan\varphi=\frac{\Omega}{\Gamma} \tag{6}$$

characterizes the time scale of the RXS process. Following [11–14] we refer to this time as the duration of RXS. $\Omega=\omega-\overline{\omega}$ is defined here as the detuning of ω relative to the characteristic frequency $\overline{\omega}=\overline{E}-E_o$ of the x-ray-absorption band. A more precise definition of this characteristic frequency depends on the problem of interest; $\overline{\omega}$ can be the position of the strongest peak or edge in the x-ray-absorption spectrum. When the electron-vibrational band is analyzed, it is convenient to choose $\overline{\omega}$ as the position of the center of gravity of the electronic peak (see below).

Wave packets $\psi(t)$ and $\Psi_T(\tau)$ (5) have the following physical meaning. At time $t=0$ a molecule is core excited and arrives there as the wave packet $\psi(0)=\mathcal{D}|o\rangle$. This initial wave packet propagates on the core excited state surface. At some time t the wave packet $\exp(-t/T)\psi(t)$ decays with decay amplitude Q to any of the final states; $\exp(-\imath E_f t)|f\rangle$. Since the time of the decay transition is not known, we need to integrate over the time domain beginning from the moment of the photoabsorption, $t=0$. The integration results in a coherent sum $\Psi_T(\tau)$ (5) of all photoabsorption-decay paths up to the time τ. The amplitude $F(\tau)$ of all decay events up to this time is the projection of $\Psi_T(\tau)$ on the particular final state (5). Clearly, the RXS cross section collects all the decay up to $\tau=\infty$.

It is worth mentioning that $\psi(t)$, $\Psi_T(\tau)$, and $F(\tau)$ cannot be measured in current stationary RXS experiments due to the small intensity of the x-ray beam and the insufficient time resolution. Here we clarify the meaning of the introduced time-dependent wave packets appealing also to a gedanken experiment. We consider the core excitation by a short x-ray pulse with duration time ($\propto 1/\gamma$) shorter than Γ^{-1} or by a long x-ray pulse with a fast swith-off. The fast measurements at moments t allow us in principle to find the squared wave packet $|\psi(t)|^2$. One can measure this squared wave packet $|\Psi_T(\tau)|^2$ [and $|F(\tau)|^2$] if the signals in the time domain $0\leqslant t\leqslant\tau$ are collected. The wave packet $\Psi_T(\infty)$ and stationary RXS amplitude $F=F(\infty)$ correspond to measurements for a long duration time ($\tau\gg\Gamma^{-1}$) or to the ordinary stationary RXS experiments.

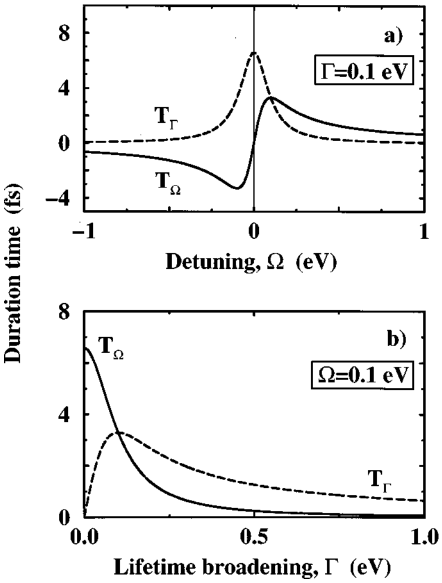

FIG. 1. The dependence of the real and imaginary parts of the duration time (6) and (7) on the detuning and lifetime broadening.

Going back to the main subject of our interest, we consider the fact that the duration time (6) is complex and that it consists of two qualitatively different contributions,

$$T_\Gamma=\frac{\Gamma}{\Omega^2+\Gamma^2},\quad T_\Omega=\frac{\Omega}{\Omega^2+\Gamma^2}. \tag{7}$$

The real part T_Γ of T coincides with the lifetime of the core excited state Γ^{-1} if $\Omega=0$. It is interesting to note that T_Γ is equal to the delay time [16,20] $T_d=d\delta/d\omega$ for scattering in the vicinity of a Breit-Wigner resonance: $F\propto 1/(\Omega+\imath\Gamma)$. Here $\delta=-\arctan(\Gamma/\Omega)$ is the phase shift under scattering. The imaginary contribution T_Ω vanishes when $\Omega=0$ and $T_\Omega=1/\Omega$ if the lifetime broadening is small. Thus T_Ω originates mainly from detuning. This time can be called the ''dephasing time'' for to the following reason. The contributions to F (4) from different times t_1 and t_2 interfere destructively owing to the phase difference $\Omega(t_2-t_1)$. This destructive interference suppresses the long-time contribution to the scattering amplitude F if $|\Omega|$ is large and if a damping Γ (even infinitesimal) exists. We shall see below that only decay transitions in the time domain $0<t<|T|$ contribute significantly to F. Real, T_Γ, and imaginary, T_Ω, parts of the RXS duration time depend differently on the detuning and the lifetime broadening, see Fig. 1.

One important feature of T deserves a comment, namely that the duration time (6) is complex. This is not ''accidental'' but has a deeper physical reason. We can refer to the real (T_Γ) and imaginary (T_Ω) parts of T as the irreversible and reversible contributions, respectively. Indeed, the dephasing is a reversible process contrary to the decay which is irreversible.

B. RXS duration as a mean time of scattering

The duration of RXS can be introduced also as the mean time $\bar{T}$ over all RXS events with decay of the core excited state at moment t:

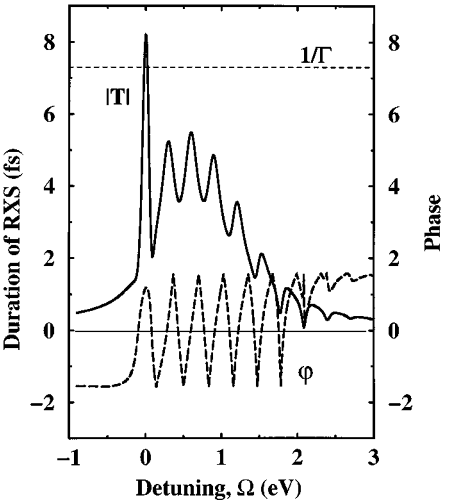

FIG. 2. The dependence of the absolute value $|\bar{T}|$ and phase $\varphi=\arcsin(\mathrm{Im}\,\bar{T}/|\bar{T}|)$ of the mean duration time (9) on the detuning. The RXS duration decreases when the excitation energy is tuned far from the photoabsorption band. $\omega_o=0.3$ eV, $\Gamma=0.1$ eV, $\beta=1.5$.

$$\bar{T}=\frac{1}{F}\int_0^\infty dt\, t\mathcal{F}(t),\quad \mathcal{F}(t)=\langle f|\mathcal{F}(t,R)\rangle$$

$$|\mathcal{F}(t,R)\rangle=-\imath Q|\psi(t)\rangle e^{-t/T}. \tag{8}$$

Here $\mathcal{F}(t)$ is the amplitude of x-ray scattering with decay at time t, and $F=\int_0^\infty dt\mathcal{F}(t)$. The use of $\mathcal{F}(t)$ in the averaging procedure (8) instead of as the real distribution $|\mathcal{F}(t)|^2$ can be motivated by the fact that in the latter case the coherent properties of the RXS amplitude—which play a crucial role in the notion of the RXS duration—are lost.

Making use of the resolution of the identity $\underline{1}=\Sigma_c|c\rangle\langle c|$, one receives the stationary representation for $\bar{T}$,

$$\bar{T}=-\imath\frac{\partial}{\partial\omega}\ln F=\frac{\imath}{F}\sum_c\frac{\langle f|Q|c\rangle\langle c|D|o\rangle}{(\omega-\omega_{co}+\imath\Gamma)^2}. \tag{9}$$

This representation shows immediately that $\bar{T}$ coincides with the duration time T (6) for large detuning or lifetime broadening ($\bar{T}\rightarrow T$). The absolute value $|\bar{T}|$ and phase $\varphi=\arcsin(\mathrm{Im}\,\bar{T}/|\bar{T}|)$ of this complex duration time are depicted in Fig. 2 assuming the harmonic approximation for the nuclear degrees of freedom (see Sec. IV A). The duration of RXS increases up to the lifetime of the core excited state for an exact photoabsorption resonance. One notes a nonmonotonous behavior of the duration time in the region of the strong photoabsorption, see Fig. 2.

One can also use an alternative definition of the RXS duration based on the averaging procedure

$$\tilde{T}=\langle t(R)|t(R)\rangle^{1/2},\quad |t(R)\rangle=\int_0^\infty dt\, t\frac{|\mathcal{F}(t,R)\rangle}{\langle F(R)|F(R)\rangle^{1/2}}, \tag{10}$$

where $|F(R)\rangle=\int_0^\infty dt|\mathcal{F}(t,R)\rangle$. Contrary to Eqs. (6) and (8), the mean duration time (10) is real and gives a correct as-

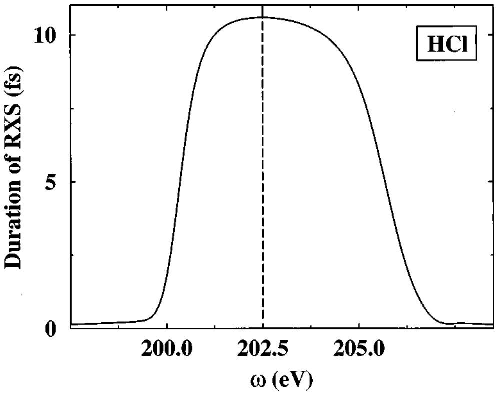

FIG. 3. The dependence of the mean duration $\tilde{T}$ (10) on the detuning. The resonant scattering through the Cl $L(2p^{-1}\sigma^*)$ dissociative core excited state in the HCl molecule [21]. $\Gamma=0.065$ eV. The resonant frequency of the vertical transition, $\omega_{\rm ver}=U_c(R_o)-U_o(R_o)-\omega_o/2$, is equal to 202.5 eV. The mean duration time $\tilde{T}$ depends asymmetrically on the detuning $\omega-\omega_{\rm ver}$.

ymptote $\tilde{T}\simeq(\Omega^2+\Gamma^2)^{-1/2}$ for large Ω or Γ. Such a definition for the RXS duration is convenient for the analysis of the decay transitions to the continuum final states (Fig. 3) due to the independence of $\tilde{T}$ on the final state.

Figures 2 and 3 show a strong asymmetry of $\overline{T}$ and $\tilde{T}$ as a function of the detuning. One can see that the RXS duration decreases faster for core excitation below the frequency of the vertical transition $U_c(R_o)-U_o(R_o)-\omega_o/2$ than above this crossing point.

C. RXS amplitude and wave packet versus the RXS duration time

1. Dynamical representation

We now consider an entirely different time-dependent representation for the RXS amplitude, one which is based on the time-dependent representation (4) and an integration of the right-hand side of Eq. (5),

$$F(\tau)=\left\langle f\left|Q\frac{1}{\Omega+\imath\Gamma-\mathcal{H}}\left(1-e^{\imath(\Omega+\imath\Gamma-\mathcal{H})\tau}\right)\mathcal{D}\right|o\right\rangle. \qquad (11)$$

A comparison of this equation with Eq. (4) and the identity

$$\frac{1}{\Omega+\imath\Gamma-\mathcal{H}}=-\imath T\lim_{t\to 0}\left(1-T\frac{\partial}{\partial t}\right)^{-1}e^{-\imath\mathcal{H}t} \qquad (12)$$

yields the following general dynamical representation for $\Psi_T(\tau)$, which is valid for all values of the complex time T:

$$\Psi_T(\tau)=\lim_{t\to 0}QT\left(1-T\frac{\partial}{\partial t}\right)^{-1}\left[\psi(t)-e^{-\tau/T}\psi(\tau+t)\right],$$

$$\Psi_T(\tau)=QT[\psi(0)+T\psi'(0)+\cdots-e^{-\tau/T}$$
$$\times\{\psi(\tau)+T\psi'(\tau)+\cdots\}]. \qquad (13)$$

Such a time-dependent representation differs conceptually from the representation (5) and allows us to predict directly which time domain gives the main contribution to the stationary RXS amplitude $F=F(\infty)$ (4) with the stationary wave packet

$$\Psi_T(\infty)=\lim_{t\to 0}QT\left(1-T\frac{\partial}{\partial t}\right)^{-1}\psi(t). \qquad (14)$$

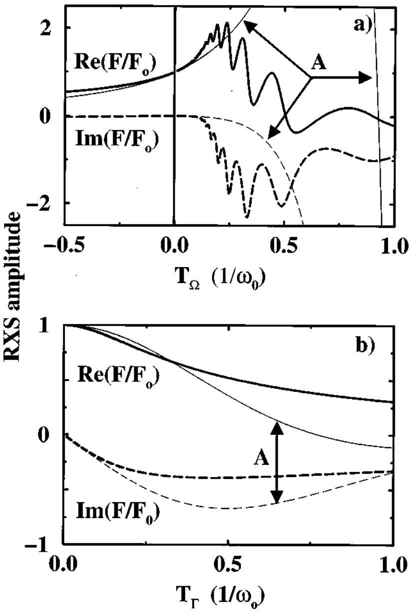

FIG. 4. The dependence of the relative RXS amplitude F/F_o (16) on the complex duration time $T=T_\Gamma+\imath T_\Omega$ (6) and (7) for the bound core excited state (see Sec. IV A). $F_o=-\imath T$ (27). The potentials of the ground and final states have the same shape. The RXS scattering from the lowest ground-state vibrational level to the lowest final-state vibrational level (0-0 scattering). $\beta=1.5$. (a) $\Gamma/\omega_o=0.3$. (b) $\Omega=0$. The curves (A) show the limit of the fast RXS (21) with the strict $\langle o|\psi(T)\rangle$ (25).

This is most easily understood by considering the important special case of short RXS duration, see Sec. III C 3. It should be pointed out that the expression (14) is equivalent to the following differential equation:

$$\frac{\partial}{\partial t}\phi(t)=\frac{1}{T}\phi(t)-Q\psi(t), \qquad \Psi_T(\infty)=\phi(0) \qquad (15)$$

with the solution (5). The right-hand side of this equation consists of a decay-dephasing part, $(\Gamma-\imath\Omega)\phi(t)$, and a source, $-Q\psi(t)$.

2. The exact dependence of the scattering amplitude on the RXS duration

An exact formula for the scattering amplitude versus the RXS duration follows directly from Eq. (3),

$$F=-\imath T\sum_c\frac{\langle f|Q|c\rangle\langle c|\mathcal{D}|o\rangle}{1+\imath T\Delta E_c}=F_o\sum_{n=0}^{\infty}(-\imath T)^n\Delta E^{(n)},$$

$$\Delta E_c=E_c-\overline{E}. \qquad (16)$$

This dependence is depicted in Fig. 4 for electrovibronic transitions (see Sec. IV A). We introduced here the scattering amplitude

$$F_o=-\imath T\langle f|Q\psi(0)\rangle=-\imath T\langle f|Q\mathcal{D}|o\rangle \tag{17}$$

corresponding to the sudden RXS [10]. The coefficients in the expansion (16) are the moments of the RXS amplitude

$$\Delta E^{(n)}=\frac{\sum_c \langle f|Q|c\rangle\langle c|\mathcal{D}|o\rangle(\Delta E_c)^n}{\langle f|Q\mathcal{D}|o\rangle}. \tag{18}$$

The expansion (16) shows that the dependence of the stationary scattering amplitude and the wave packet, $\Psi_T(\infty)=\Sigma_c Q|c\rangle\langle c|\mathcal{D}|o\rangle T/(1+\imath T\Delta E_c)$, on the RXS duration T is defined by the moments $\Delta E^{(n)}$. One can see immediately that this expansion over T is valid if the RXS duration is shorter than the inverse width $\Delta\omega$ of the photoabsorption band close to $\bar{\omega}$,

$$\tau_o=\frac{1}{\Delta\omega}. \tag{19}$$

This time scale characterizes the quantum beats of the wave packets $\psi(t)$ and $\Psi_T(\tau)$ and is the main time scale in the problem concerning the RXS duration. As is well known, $\Delta\omega\lesssim 1$ eV in problems connected with the nuclear dynamics. This spectral width has an order of magnitude 1–10 eV or more for the dynamics of the relaxation of the electronic shells due to creation of the core hole.

To conclude this section, let us note that the observable quantity in the RXS experiment is the real squared scattering amplitude $|F|^2$ which depends on the real times T_Γ and T_Ω [see Eq. (6)] but not on the complex time T (6). This means that the RXS experiment is characterized by real irreversible (T_Γ) and reversible (T_Ω) times. A similar problem with complex time appears in the discussion of traversal time in quantum tunneling [18,19].

3. Fast RXS

If the excitation energy is tuned to the wing of the photoabsorption band, the duration of the scattering (6) can be shorter than τ_o (19),

$$|T|\ll\tau_o. \tag{20}$$

Let us keep the first two terms in the expansion over T in Eq. (13). This yields immediately the following remarkable result:

$$F\simeq-\imath T\langle f|Q\psi(T)\rangle,\quad \Psi_T(\infty)\simeq QT\,\psi(T),\quad |T|\ll\tau_o. \tag{21}$$

We see that the spectral shape of fast RXS is given by a simple projection of the wave packet $Q\psi(T)$ at the complex time T (6) onto the final state $|f\rangle$. Equations (21) generalize the corresponding results from Ref. [10]. Figure 4 shows that the exact RXS amplitude (16) coincides with the fast limit (21) only for small $|T|$.

It is worthwhile to compare $\Psi_T(\infty)$ (21) and $\Psi_T(\tau)$ (13),

$$\Psi_T(\tau)\simeq QT[\psi(T)-e^{-\tau/T}\psi(\tau+T)],\quad |T|\ll\tau_o. \tag{22}$$

One sees, contrary to intuition, that the wave packets $\Psi_T(\infty)$ [(14) and (21)] and $\Psi_T(\tau)$ [(13) and (22)] do not coincide even when τ essentially exceeds the RXS duration time $|T|$. A coincidence takes place only if the time of the wave-packet evolution τ is larger than the lifetime Γ^{-1}. One can say that the fast limit (21) for the RXS amplitude is obtained only when the wave packet (21) must go through the long time evolution (longer than the lifetime, $\tau\gg\Gamma^{-1}$). This somewhat paradoxical statement shows the qualitative distinction between the RXS duration time T and the characteristic time Γ^{-1} of the wave-packet evolution.

It should be pointed out that the interference of the intermediate core excited states serves as the key point in the representation (13) and for the formulated contradiction. This, together with the results of Sec. III concerning the destructive interference in the time domain, stresses the quantum nature of the notion of the RXS duration.

IV. CHARACTERISTIC TIMES OF THE WAVE-PACKET EVOLUTION AND THE DURATION OF RXS

The finite time representation (4) for the RXS amplitude deserves further comments due to the contradiction between the RXS duration and the characteristic time of the wave-packet evolution. Let us select from $F(\tau)$ (4) the stationary RXS amplitude $F=F(\infty)$ and the time-dependent extra term

$$F(\tau)=F+\Delta F(\tau),$$
$$\Delta F(\tau)=-e^{-\Gamma\tau}\sum_c\frac{\langle f|Q|c\rangle\langle c|\mathcal{D}|o\rangle}{\omega-\omega_{co}+\imath\Gamma}e^{-\imath(\omega-\omega_{co})\tau}. \tag{23}$$

This time-dependent term $\Delta F(\tau)$ accounts for the evolution in the region $\tau<t<\infty$. As one can see directly from Eq. (4) or Eq. (23), this term does not contribute to the stationary RXS amplitude $F=F(\infty)$ (4) since

$$\Delta F(\tau)\rightarrow 0,\quad \text{if}\quad \tau\gg\frac{1}{\Gamma}. \tag{24}$$

According to Eqs. (23) and (24) [compare also Eqs. (21) and (22)], all times from $t=0$ up to Γ^{-1} are important for the scattering amplitude $F(\tau)$. So it is apparent that the RXS duration time and the relaxation time of the wave packet do not coincide, and one can ask what times characterizes the relaxation of the wave packet to the stationary value?

A. Bound core excited state

We consider first a bound core excited state and a simple model based on the harmonic approximation of the potentials. For more transparency we select only one final state with the lowest vibrational level, $f=o$, and assume identical vibrational frequencies ω_o for the ground, core excited, and final states, and identical potentials for the ground and final states, $Q\rightarrow 1$, $\mathcal{D}\rightarrow 1$. $\bar{E}=U_c(R_o^{(c)})+\omega_o/2$ and $\Omega=\omega-[U_c(R_o^{(c)})-U_o(R_o)]$. Here $U_c(R_o^c)$ and $U_o(R_o)$ are internuclear potentials for the equilibrium distances for the core excited and ground states, respectively. The RXS spectral profile is defined by the Franck-Condon (FC) factor $\langle c|o\rangle$

$=\beta^c\exp(-\beta^2/2)/\sqrt{c!}$ with $\beta=(R_o-R_o^{(c)})/(a_o\sqrt{2})$, $a_o=1/\sqrt{\mu\omega_o}$, $c=0,1,2,\ldots$, and μ is the reduced mass of the molecule.

1. Time of relaxation

Insertion of the resolution of the indentity $1=\Sigma_c|c\rangle\langle c|$ and the FC factors $\langle c|o\rangle$ into Eq. (5) yields

$$\langle o|\psi(t)\rangle=e^{-\beta^2}\exp(\beta^2 e^{-\imath\omega_o t}). \tag{25}$$

We emphasize the periodicity of this function. The origin of this is the well-known Schrödinger result for the wave packet of the harmonic oscillator,

$$\psi(t)=\left(\frac{1}{\pi a_o^2}\right)^{1/4}\exp\left(-\frac{x^2(t)}{2a_o^2}\right)e^{\imath\eta}, \tag{26}$$

where $\psi(0)=|o\rangle$, $x(t)=x-x_o\cos\omega_o t$, $x=R-R_o^{(c)}$, $x_o=R_o-R_o^{(c)}$, and the phase $\eta=-(x_o/a_o^2)\sin(\omega_o t)\{x-(x_o/2)\cos\omega_o t\}$. This periodic wave packet does not spread during the motion since it is confined by the potential walls. The center of gravity, $x_o\cos\omega_o t$, performs a harmonic oscillation, following the same path as a classical particle. Obviously, the back and forth periodic motion is present only for a bound potential.

One can see clearly that the amplitude (4) and (16) of the bound-bound-bound RXS

$$F(\tau)\simeq F_o\{1-e^{-\tau/T}\exp[\beta^2(e^{-\imath\tau\omega_o}-1)]\},$$
$$F_o=-\imath T,\quad |T|\omega_o\ll 1 \tag{27}$$

does not coincide with the stationary value $F\simeq F_o$ even for very large τ if the lifetime broadening Γ is negligibly small. Both $F(\tau)$ and $\Psi_T(\tau)$ (22) perform nondamped oscillations and never reach F and $\Psi_T(\infty)$ if $\Gamma=0$, see Figs. 5 and 6. Apparently, $F(\tau)\rightarrow F$ only when $\tau\gg\Gamma^{-1}$.

So one can conclude that the time of relaxation τ_r of $F(\tau)$ and $\Psi_T(\tau)$ to the asymptots $F(\infty)$ and $\Psi_T(\infty)$ is equal to the lifetime

$$\tau_r=\Gamma^{-1} \tag{28}$$

when the wave packet propagates the bound potential of the core excited state (more precisely, for core excitation below the dissociation threshold of a bound potential). This behavior stands in contrast to the qualitatively different picture obtained in the case of core excitation above the dissociation threshold.

2. Revival time

Simulations (Fig. 5) for bound core excited and final states show that the scattering amplitude $F(\tau)$ nearly recovers its fast Ω oscillations with the period $T(\Omega)=2\pi/\Omega$. Such a ‘‘revival’’ occurs because of the discreteness of the spectrum and the constant value of the excitation frequency ω. The revival time depends on the both Ω and ω_o and is—according to our simulations—equal to

$$n\ \max\{T(\Omega),T(\omega_o)\}, \tag{29}$$

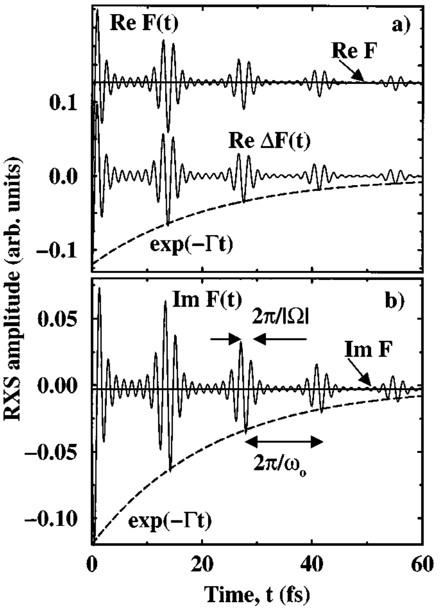

FIG. 5. The dependence of the RXS amplitude $F(t)$ (3) and (23) on the real time t for the bound core excited state shows damped revival oscillations. The potentials of the ground and final states have the same shape. The RXS scattering from the lowest ground-state vibrational level to the lowest final-state vibrational level (0-0 scattering). $\omega_o=0.3$ eV, $\Gamma=0.03$ eV, $\Omega=3$ eV, $\beta=1.5$. $T\simeq\imath 0.2$ fs.

where the integer n also depends on Ω and ω_o. In the special case of Fig. 5, the revival time is equal to the vibrational period $T(\omega_o)=2\pi/\omega_o$. Due to the finite lifetime of the core excited state these ‘‘revival’’ oscillations become damped $[\propto\exp(-\Gamma\tau)]$ and are totally suppressed when $\tau\gg\Gamma^{-1}$. It is relevant here also to look at the time dependence of the space distribution of $\Psi_T(\tau)$ neglecting lifetime broadening, $\Gamma=0$. Figure 6 shows nondamping oscillations with the revival time $29T(\omega_o)$ for N_2. As we see, the character of these oscillations depends strongly on the internuclear distance R.

Equation (23) and Figs. 5 and 6 demonstrate that the quenching of $F(\tau)$ has nothing to do with the RXS duration T (6). One can see that $F(\tau)$ tends to the fast limit (17) and (21) only if $\tau\gg\Gamma^{-1}$ (24) (but not $\Gamma^{-1}>\tau\gg|T|$). It is interesting to note that the RXS duration T can be estimated approximately as the smallest complex root τ of the equation $F(\tau)=F(\infty)$ ($\tau\approx 0$ according to Fig. 5, where the case of large Ω is presented).

Since the term $\Delta F(\tau)$ is absent (24) in the strict stationary RXS amplitude F, we cannot use time scales of $\Delta F(\tau)$ in the time analysis of F. On can then ask which time domain gives a main contribution to $F=F(\infty)$? According to Eqs. (13) and (21), it is the region restricted by the RXS duration $0\leqslant t\lesssim|T|$ (but not Γ^{-1}). The contribution to F from the long time region ($|T|<t<\infty$) is strongly suppressed due to the destructive interference or the dephasing in the time domain [see the discussion following Eq. (7)]. This interference leads also to the suppression of the large distance contribution to $\Psi_T(\infty)$ if the RXS duration is short (large detuning), see Fig. 7. The wave packet $\Psi_T(\infty)$ copies the space distribution of the ground-state wave function $|o\rangle$ in the limit of the fast RXS (20), Fig. 7(c).

At this point it should be noted that the role of this de-

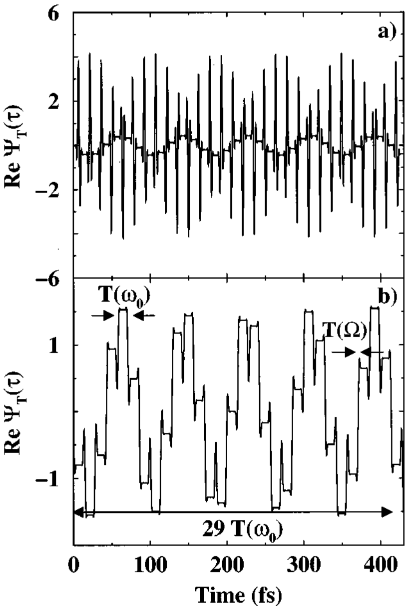

FIG. 6. The nondamping time oscillations of the space distribution of $\mathrm{Re}\Psi_T(\infty)$ for the bound core excited state $^1\Pi_u$ of N_2 ($\Gamma=0$). (a) $R-R_o=0.32$ a.u., (b) $R-R_o=-0.18$ a.u. The parameters for N_2 are taken from [22]. The details of the corresponding time-dependent calculations are described in Ref. [21]. $\omega_o=0.29$ eV, $R_o^{(c)}-R_o=0.12$ a.u. The resonant energy of the photoabsorption transition, $U_c(R_o)-U_o(R_o)-\omega_o/2$, is equal to 400.95 eV. $\omega=402.5$ eV. $T(\omega_o)=2\pi/\omega_o\simeq14.3$ fs, $T(\Omega)=2\pi/\Omega\simeq2.7$ fs. Here and in Figs. 7, 9, 10, and 11, a different definition of the detuning is used: $\Omega=\omega-[U_c(R_o)-U_o(R_o)-\omega_o/2]$.

structive interference in $F(\tau)$ for $\tau<1/\Gamma$ is strongly reduced due to the extra term $\Delta F(\tau)$ (23). The interference quenches the contribution to $F(\tau)$ of the long time evolution ($|T|<t<\tau$) only if $\tau>\Gamma^{-1}$, see Figs. 5 and 6 (the physical picture for a dissociative core excited state is more complex, see Sec. IV B). Indeed, one can see that $F(\tau)$ tends to $F(0)$ of the fast RXS ($\Omega=3$ eV) only for large times, $\tau\gg\Gamma^{-1}$.

Figures 5 and 6 show also the crucial role played by the damping Γ in the destructive interference or dephasing. One can see that $F(\tau)$ (4), as well as the space distribution of $\Psi_T(\tau)$ (Fig. 6), oscillates in time due to $\Delta F(\tau)$ (23) during the infinite time if $\Gamma=0$. The dephasing and the destructive interference are again strong only when $\tau\gg\Gamma^{-1}$. One can conclude that the idea to connect the RXS duration T (6) with the characteristic evolution time of $F(\tau)$ fails.

We can now select one of the main results of the discussed problem: The time-dependent amplitude $F(\tau)$ (4) consists of two terms. The first one $F=F(\infty)$ is characterized by the frequency depending duration time T (6). However, the deviation $\Delta F(\tau)$ of the time-dependent RXS amplitude $F(\tau)$ has a different time scale; $F(\tau)$ tends to the stationary value F exponentially with a characteristic time equal to the lifetime Γ^{-1}.

One can say that to receive the sudden limit, the time of the ''measurement'' must be equal to infinity, $\tau\to\infty$, when Γ is small. Only in this case does the destructive interference suppress the contribution to $F(\infty)$ for times larger than the RXS duration, $|T|$. Such an experiment with $\tau=\infty$ corresponds to the ordinary stationary RXS measurements (4).

Another property of $F(t)$ should be emphasized (Fig. 5): Our simulations show that the maximum value of $F(t)$ can exceed several times the stationary RXS amplitude $F=F(\infty)$. This leads to the important conclusion that in time-resolved measurements one can obtain signals $|F(t)|^2$ that are stronger in comparison with the stationary value $|F(\infty)|^2$. The destructive interference in the entire time domain is the reason behind this.

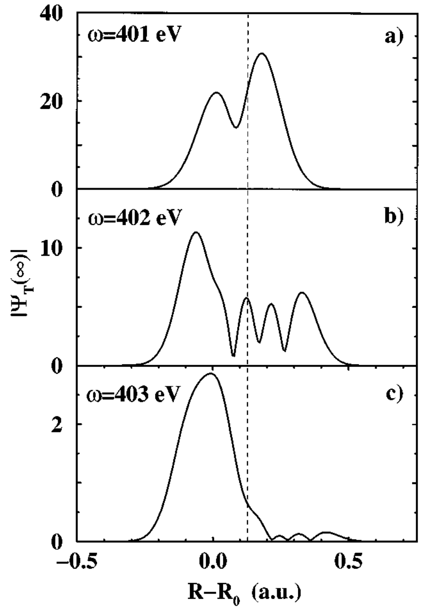

FIG. 7. The space distribution of $|\Psi_T(\infty)|$ versus the RXS duration (detuning) for the bound core excited state $^1\Pi_u$ of N_2. The contribution of the region outside of the ground-state vibrational wave function is suppressed when Ω is large. Input data are the same as for Fig. 6 except $\Gamma=0.065$ eV and ω. The RXS durations are $|T|\simeq5.6$ fs, 0.73 fs, and 0.35 fs for the excitation frequencies $\omega=401$ eV, 402 eV, and 403 eV, respectively.

B. Space distribution of wave packets in the dissociative core excited state versus RXS duration and time evolution

To emphasize the principal distinction between wave-packet evolution for core excitation below and above the dissociation threshold, we consider a core excited state with a repulsive potential. To be specific, let us consider RXS by the HCl molecule close to the Cl L edge. The excitation energy is tuned in the vicinity of the $2p^{-1}\sigma^*$ dissociative core excited state (details of the time-dependent calculations for this example can be found in Ref. [21]). The repulsive force $\mathcal{F}(R)=-U_c'(R)>0$ moves the atoms in opposite directions. Instead of the back and forth periodic motion in a bound potential (Fig. 6), the initial Gaussian wave packet $\psi(0)=|o\rangle$ now spreads in the forward direction only, see Fig. 8. It is necessary to mention that contrary to the absolute value $|\psi(t)|$ (Fig. 8), the wave packet $\psi(t)$ has strong space oscillations in the dissociative region [21]. The amplitude of $\psi(t)$ decreases due to this spread and the finite lifetime. The reason for the spread can be found in the different phase velocities of the Fourier components of the wave packet.

1. Time evolution behind and close to the wave front

A propagation of $\psi(t)$ only in the forward direction leads to the qualitatively different scenario for the formation of the

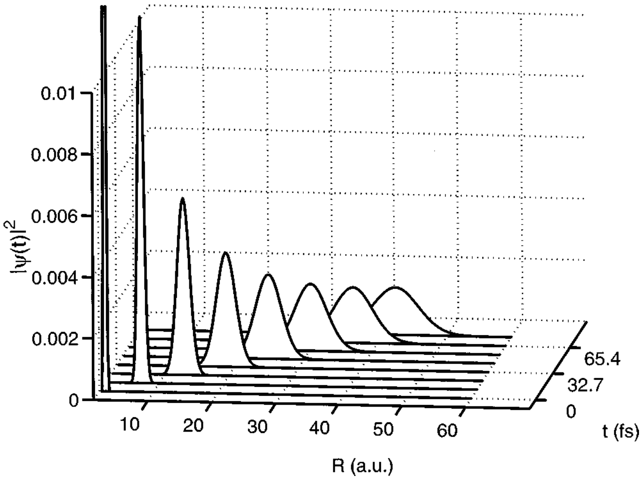

FIG. 8. Time evolution of $|\psi(t)|^2$ (5). Cl L $(2p^{-1}\sigma^*)$ dissociative core excited state in the HCl molecule. Maximal value of $|\psi(0)|^2$ is equal to 0.039.

wave packet $\Psi_T(\tau)$ (5). Recall that $\Psi_T(\tau)$ (5) is the sum of $\psi(t)\exp((\imath\Omega-\Gamma)t)$ over all times t. Due to the forward propagation, the wave packets $\psi(t)$ will never reach the point R of departure. This results in the fact that the part of the wave packet $\Psi_T(\tau)$ which is behind the wave front, $R-R_o<v\tau$, does not change for the later times $\tau'>\tau$. Clearly, $\Psi_T(\tau)=0$ for $R-R_o>v\tau$ since the wave packets $\psi(t)$ with $t<\tau$ have no time to reach this region ahead of the wave front of $\Psi_T(\tau)$ (here v is some average speed of the wave-packet propagation). One can summarize the results given above as follows:

$$\Psi_T(\tau)\simeq\begin{cases}\tau|o\rangle & \text{if } \tau<\tau_o,\\ \Psi_T(\infty) & \text{if } t_f(R)<\tau,\\ 0 & \text{if } t_f(R)>\tau,\end{cases} \tag{30}$$

where

$$t_f(R)=\int_{R_o}^{R}\frac{dR}{v(R)}\sim\frac{R-R_o}{v},$$

$$v(R)\simeq\left(\frac{2}{\mu}[U(R_o)-U(R)]\right)^{1/2} \tag{31}$$

is the time of flight from the crossing point R_o to R and $\tau_o=\sqrt{2\mu a_o/\mathcal{F}(R_o)}$ is the time of flight through the width a_o of the initial wave packet $|o\rangle$. This equation describes the three-step formation of the wave packet $\Psi_T(\tau)$ (5): (i) the beginning of the formation of the ''molecular'' part; (ii) the termination of the formation of the ''molecular'' part and formation of the long distance or dissociative contribution; and (iii) the formation in the region near the wave front. The results of numerical simulations (Figs. 9 and 10) confirm Eqs. (30) and (31) except for some transitions in the region close to the oscillatory front $(R-R_o=v\tau)$ of the wave packet $\Psi_T(\tau)$. We see the ''molecular'' peak close to $R_o=2.4$ a.u., a flat dissociative contribution which decreases as $e^{-\Gamma t_f(R)}$, and an oscillatory front. The finite lifetime blurs these oscillations and reduces the amplitude of the front (Figs. 9 and 10). The molecular contribution increases when the RXS duration T (6) decreases [10,12,14], and one finds indeed a quenching of the amplitude of the dissociative contribution when Γ or detuning $|\Omega|$ increases, see Figs. 9 and 10. We stress only that the length of the dissociative contribution to $\Psi_T(\tau)$ increases as $v(\infty)\tau$ up to $v(\infty)\Gamma^{-1.}$ Figures 9 and 10 show clearly the role of the RXS duration and relaxation times of the wave packet $\Psi_T(\tau)$ for the formation of this wave packet.

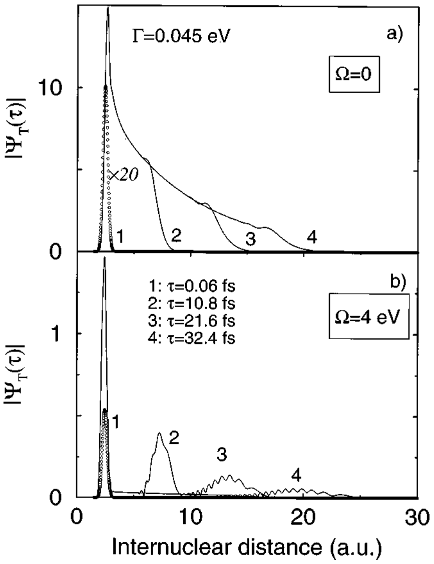

FIG. 9. Time evolution of the absolute value of the wave packet $\Psi_T(\tau)$ (5) for different excitation energies. The shape of the wave packet behind the wave front does not change. Cl $L(2p^{-1}\sigma^*)$ dissociative core excited state in the HCl molecule. $\Gamma=0.045$ eV. (a) $\Omega=0$ eV, $|T|\simeq14.6$ fs. (b) $\Omega=4$ eV, $|T|\simeq0.16$ fs.

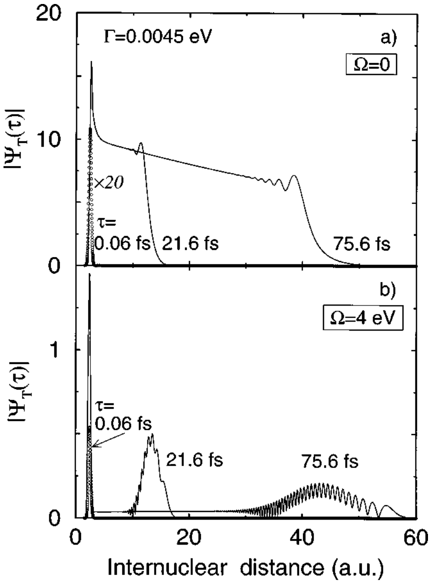

FIG. 10. Same as Fig. 9 but $\Gamma=0.0045$ eV. (a) $\Omega=0$ eV, $|T|\simeq146$ fs. (b) $\Omega=4$ eV, $|T|\simeq0.16$ fs.

2. Role of the RXS duration time

Figures 9 and 10 demonstrate another principal distinction between wave-packet evolutions in bound (Figs. 5, 6, and 7) and unbound potentials. The forward propagation in the dissociative potential changes drastically the role of the RXS duration in the formation of $\Psi_T(\tau)$. One can see in Figs. 9 and 10 a strong suppression of the flat dissociative contribution when the RXS duration is small. We emphasize that this suppression takes place even for $\Gamma \rightarrow 0$ (an effect which is absent for discrete vibrational states, Fig. 6). Moreover, contrary to the dissociative state, the space distribution $\Psi_T(\tau)$ oscillates without damping in the case of the bound core excited state and infinite lifetime Γ^{-1} (compare Fig. 6 and Figs. 9 and 10). It is necessary to mention that the suppression of the long distance contribution to $\Psi_T(\tau)$ for bound core excited state takes place only if $\tau \gtrsim \Gamma^{-1}$, Fig. 7.

One obtains here an important conclusion: The space shape of the wave packet $\Psi_T(\tau)$ (30) behind its front (Figs. 9 and 10) does not depend on time (except for very small τ); the amplitude of the flat dissociative contribution to $\Psi_T(\tau)$ is suppressed when the RXS duration decreases. This means that when the wave front has left the molecular region, the role of τ is only to change the intensity of the atomic-like peak. This peak is formed due to a flat long-distance contribution to $\Psi_T(\tau)$ (Figs. 9 and 10) which damps as $\exp(-(R-R_o)\Gamma/v(\infty))$ (as does the molecular contribution). The front of this contribution $\Delta R = v(\infty)\tau$ propagates with the velocity $v(\infty)$.

So we have the following times characterizing the relaxation of the wave packet $\Psi_T(\tau)$. The molecular contribution to $\Psi_T(\tau)$ is formed during the time of propagation, $\tau_m = (R_d - R_o)/v$, into the dissociative region R_d. After this time, the dissociative contribution begins to shape during the lifetime Γ^{-1}. An important subsequent question refers to the role of the RXS duration T in the formation of $\Psi_T(\infty)$ and in the time evolution of $\Psi_T(\tau)$. The effect of T is seen directly from the dependence of the space distribution of $\Psi_T(\tau)$ on the excitation energy. Both wave packets $\Psi_T(\tau)$ (Figs. 9 and 10) and $\Psi_T(\infty)$ (Fig. 11) show the suppression of the amplitude of the long distance contribution (for the dissociative core excited state) when the RXS duration decreases.

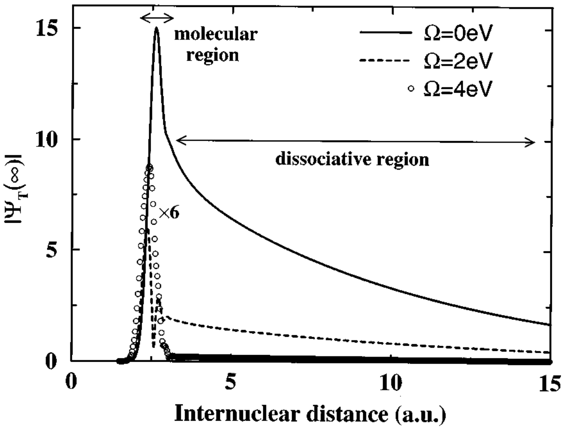

FIG. 11. The absolute value of the stationary wave packet $\Psi_T(\infty)$ (5) for different excitation energies. The dissociative part of $\Psi_T(\infty)$ decreases faster than the molecular contribution when the RXS duration decreases. Cl $L(2p^{-1}\sigma^*)$ dissociative core excited state in the HCl molecule. $\Gamma = 0.045$ eV. The RXS durations are $|T| \simeq 14.6$ fs, 0.3 fs, and 0.16 fs for the detunings $\Omega = 0$ eV, 2 eV, and 4 eV, respectively. The wave packet for $\Omega = 0$ eV is increased six times.

V. SUMMARY

With this paper we have shown that the notion of a duration time for the x-ray Raman scattering is far from trivial. It contradicts the naive picture of connecting the time lapse of the scattering process with the temporal evolution of the wave packet of the core excited state. The RXS duration provides a well defined notion for the stationary RXS amplitude and for the corresponding stationary wave packet. The time-dependent representation for the scattering amplitude leads to a complex duration time consisting of two qualitatively different contributions, the decay and dephasing parts, which are irreversible and reversible, respectively. The mean times $\overline{T}$ and $\tilde{T}$ of the RXS process provide stricter definitions of the RXS duration. We found a strong asymmetry of these mean times as a function of the detuning.

The evolution and relaxation of the wave packet confined to a bound potential differ qualitatively from a propagation above the dissociative threshold. The relaxation time of the wave packet in a bound potential is given by the lifetime of the core excited state, which can be large compared with the RXS duration. This relaxation time has nothing to do with the frequency depending RXS duration if the detuning is large. An explanation of this paradox can be found in the destructive interference or dephasing in the entire time domain. It is shown here that the concept of the RXS duration can be applied only to the stationary RXS amplitude, but not to the amplitude referring to the finite time of ''measurement.''

The dephasing caused by the phase Ωt is strong when the absolute value of the detuning exceeds the effective width of the photoabsorption band. A second necessary attribute of this dephasing in the case of a bound core excited state was here emphasized, namely the lifetime damping of the wave packet. This damping plays a crucial role for the problem since without it the time-dependent scattering amplitude oscillates for an infinitely long time if the core excited state is bound. A suppression due to dephasing is absent in this case, while the introduction of even an infinitesimal damping changes the picture drastically. The dephasing and the destructive interference will again be strong for a sufficiently large time of measurement: $\tau > \Gamma^{-1}$. The final result of this dephasing in a bound core excited state is a strong suppression of the dynamical contributions to the scattering amplitude $F = F(\infty)$ from the time domain beyond the RXS duration, $\tau > |T|$.

The wave packet evolves in one direction in a dissociative potential, in contrast to a bound potential where it moves back and forth periodically. As a result, two relaxation times characterize the evolution of the wave packet in the continuum: the time of flight and the lifetime. We found that the space distribution of the wave packet behind the wave front ceases to depend on time when this front leaves the molecular region. Even without damping, the amplitude of the dissociative contribution to the wave packet decreases if the RXS duration decreases, something that agrees with the naive picture. Without damping, the wave front propagates for an infinitely long time, which results in a continuous increase of the intensity for the atomiclike peak. We have also shown that time-resolved RXS measurements make it possible to obtain stronger signals than in the stationary RXS experiment.

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