

Controlled Interplay between Decay and Fragmentation in Resonant Auger Processes

E. Pahl, L. S. Cederbaum, and H.-D. Meyer

Theoretische Chemie, Physikalisch-Chemisches Institut, INF 253, D-69120 Heidelberg, Germany

F. Tarantelli

Dipartimento di Chimica, Università di Perugia, I-06123 Perugia, Italy

(Received 2 September 1997)

Wave packet dynamics applied to the resonant Auger spectrum of HF bring to light novel interference effects introduced by selective excitation. By detuning the excitation energy off the resonance these effects are shown to be strongly enhanced. Besides the quenching of the so-called “atomic lines” by detuning, an unexpected prominent structure dominates the spectrum in the case of small detuning towards higher excitation energies. The underlying interference mechanisms are identified by tracing the physically relevant quantities on the real time scale of the process. [S0031-9007(97)05272-1]

PACS numbers: 33.80.Eh, 33.20.-t, 33.70.-w

The study of electronically highly excited, short-lived molecular states by means of decay spectroscopy (e.g., Auger or x-ray emission spectroscopy) is a field of current vivid interest. New impetus was given in the last years by experimental progress in measuring high-resolution vibrationally resolved spectra (see, e.g., [1]) on one hand, and, on the other hand, by the development of the time-dependent theory of wave packet dynamics [2–4], which allows for a *time-resolved* description of the processes under study as a complement to the longer known time-independent approach [5,6].

In the following, we shall concentrate on the so-called *resonant Auger spectroscopy* which investigates the decay of core-excited molecules. In general there exists a manifold of energetically close-lying core-excited states. For a selective population of only one core-excited state it is therefore necessary to perform the excitation in an energetically selective manner. This “*narrow-band excitation*” implies a prolongation of the excitation pulse duration, and hence the excitation time may become of the same order of magnitude as the decay time and the typical times of internal vibrations or of fragmentation of the molecule. Interferences in the decaying state can thus appear and strongly influence the observed spectra [3]. Additional complexity for the interpretation of the resonant spectra is introduced if the populated core-excited state is of purely repulsive nature, due to excitation of the core electron into an antibonding molecular orbital. In this case the time of dissociation of the molecule can become comparable to the decay time, leading to a competition between the direct molecular decay and the decay within the atomic fragments after dissociation of the molecule. Such an interplay between “molecular” and “atomic” contributions has widely been observed (see, e.g., [7]) starting with the first observation of atomic lines in the resonant Auger spectrum of HBr [8].

In this Letter we shall report astonishing effects which occur in narrow-band resonant Auger spectra in the case where the decaying as well as the final electronic states

exhibit dissociative character. In particular, by detuning away from the resonance energy, interferences in the decaying state can be strongly enhanced owing to the energetically selective excitation. Besides the quenching of the atomic lines by detuning [3,9], very pronounced interference patterns are shown to dominate the spectrum for small detuning towards higher excitation energies. All these effects will be demonstrated on the basis of a realistic example, the narrow-band resonant Auger spectrum of HF.

For the interpretation of these effects the time-dependent description provides a very useful tool because it allows for a deep insight in the underlying interference mechanisms. By virtue of the accessible time resolution, the formation of the Auger spectrum can be traced on the real time scale of the process. It should be emphasized that this time evolution of the Auger spectrum may also be investigated experimentally when the process can be interrupted after some time delay. This could be realized by a sudden depopulation of the decaying state, in, e.g., “pump-probe” like experiments, or, more indirectly, by opening a competitive decay channel like, e.g., electron transfer (see, e.g., [10]).

The core of the theory of wave packet dynamics is the derivation of differential equations for the nuclear wave functions of the decaying and the final states, $\Psi_d(R, t)$ and $\Psi_f(E, R, t)$, respectively, which describe their propagation in time. The wave functions depend on the nuclear coordinates R and the time t . Note that $\Psi_f(E, R, t)$ depends additionally on the energy E of the ejected Auger electron as a parameter because for each energy a different final electronic state is populated and the corresponding wave packet evolves differently. The following differential equations have been derived [3] in the weak-field case, i.e., when the recoupling of the decaying to the initial state is neglected,

$$\begin{aligned} i\dot{\Psi}_d(R, t) &= g(t)V\Psi_i(R, t) + (\hat{H}_d - i\Gamma/2)\Psi_d(R, t), \\ i\dot{\Psi}_f(E, R, t) &= W\Psi_d(R, t) + (\hat{H}_f + E)\Psi_f(E, R, t). \end{aligned} \quad (1)$$

Here the Hamiltonians \hat{H}_d and \hat{H}_f describe the nuclear motion of the wave packets on the corresponding potential curves. The decay of the core-excited state is accomplished by the imaginary part $i\Gamma/2$ where Γ denotes the decay width of the core-excited state. The decay width is inversely proportional to the lifetime of this state. V and W describe the transitions between the initial electronic state and the intermediate state, and between the intermediate and the final electronic states, respectively. Here they are assumed to be independent of the nuclear coordinates. The excitation function $g(t)$ describes the interaction with the time-dependent external field.

The time evolution of the wave packets is of interest because information about the Auger spectrum $\sigma(E)$ as a function of the kinetic energy E of the emitted Auger electrons and its time evolution $\sigma(E, t)$ is contained in the final state nuclear wave packets [11],

$$\sigma(E, t) = \int dR |\Psi_f(E, R, t)|^2, \quad (2)$$

$$\sigma(E) = \lim_{t \rightarrow \infty} \sigma(E, t). \quad (3)$$

We now turn to the study of the resonant Auger decay of HF occurring upon narrow-band excitation. For this example we have computed the lowest-lying potential curves of the core-excited states and of the final cationic states by *ab initio* correlated quantum chemical methods [12]. With the help of these curves, we were able to reproduce the experimental electron energy loss spectrum [13] and the broad-band resonant Auger spectrum [14] very well [12]. In order to study the effects of detuning in the case of narrow-band excitation, we concentrate in this Letter on the particular transition between the lowest-lying core-excited $^1\Sigma^+$ state and the $^4\Pi$ final state, which yields one of the main contributions to the broad-band spectrum. The HF molecule is particularly well suited for this study because the core-excited $^1\Sigma^+$ state is energetically very well separated from the above-lying Rydberg states. In Fig. 1 the computed potential curves of the $^1\Sigma^+$ and the $^4\Pi$ final states are depicted. As one can see, both states exhibit strongly repulsive character. We have chosen an excitation width [full width at half maximum (FWHM)] of the incoming radiation of 0.2 eV. The appearance of the described effects do not depend strongly on this width as long as it lies in the same range as the decay width of the core-excited state of 0.202 eV taken from [15] (the corresponding lifetime is 9 fs). The effects are also general in the sense that they only depend on the dissociative nature of the potential curves involved and not on the particular transition or molecule under consideration.

Performing narrow-band excitation one first notices a resonance at an excitation energy of 687 eV characterized by a maximum in the total integrated intensity. This resonance coincides approximately with the maximum in the Franck-Condon overlaps between the initial wave function Ψ_i (the vibrational ground state of the electronic ground

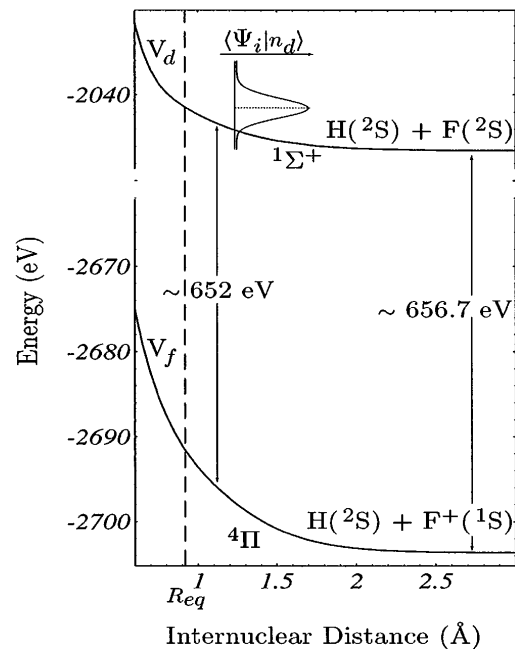


FIG. 1. Potential curves of the core-excited $^1\Sigma^+$ state dissociating into $H(^2S) + F(^2S)$ and the $^4\Pi$ final state which dissociates into $H + F(^1D)$. Shown in the inset are the Franck-Condon overlaps between the initial state wave function Ψ_i and the eigenvectors of the intermediate state $|n_d\rangle$. The arrows indicate the region of the molecular transitions contributing at about 652 eV to the spectrum and the zone of atomic transitions leading to the atomic peak at 656.7 eV.

state of HF) and the eigenfunctions of the core-excited state $|n_d\rangle$, shown as the inset of Fig. 1. The magnitude of absorption of the incoming radiation depends crucially on these overlaps. By detuning away from the resonance the total integrated intensity is reduced according to the decrease in these Franck-Condon overlaps.

In Fig. 2 the Auger spectrum recorded on resonance is shown at the top while the spectra resulting from detuning towards lower and higher excitation energies are depicted below. The on-resonance spectrum shows a two-peak structure formed by an intense and sharp atomic peak at 656.7 eV and a broader molecular tail at about 652 eV, closely resembling the corresponding broad-band spectrum. Upon detuning, the spectrum exhibits dramatic changes: the relative intensity of the atomic peak compared to the molecular contributions is reduced drastically by detuning either towards lower or towards higher excitation energies. For large detuning a Raman-like behavior is found: only the broad molecular part remains, showing a linear dispersion with the excitation energy. For small detuning towards higher excitation energies a prominent three-peak structure is found in the molecular part of the spectrum. Here, the appearance of this interference structure may be surprising because we are concerned with transitions between purely dissociative curves.

The quenching of atomic peaks by detuning has been predicted before [3]. It is connected with the selectivity of the excitation in combination with detuning. During

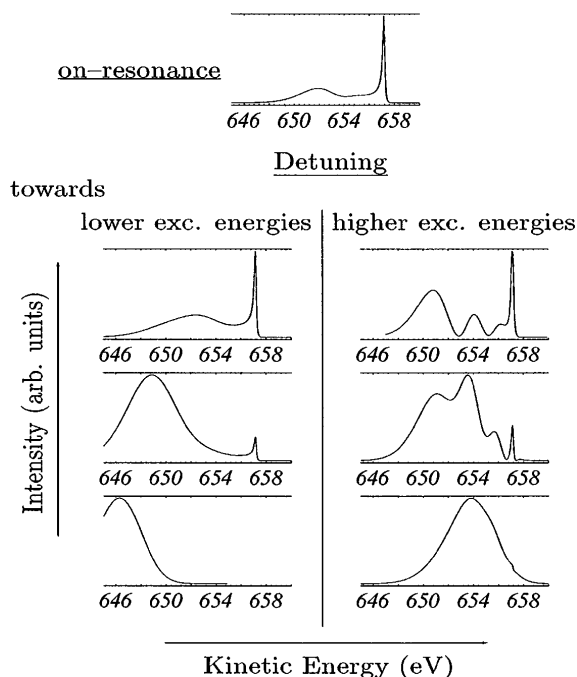


FIG. 2. Resonant Auger spectra for the ${}^1\Sigma^+ \rightarrow {}^4\Pi$ transition obtained by narrow-band excitation at different excitation energies E_{exc} . The FWHM of the excitation pulse is 0.2 eV. At the top is the spectrum taken on resonance ($E_{\text{exc}} = 687$ eV). Below, on the left-hand side are the spectra at lower excitation energies (from top to bottom: $E_{\text{exc}} = 685, 684,$ and 682 eV). On the right-hand side are the spectra at higher excitation energies (from top to bottom: $E_{\text{exc}} = 689, 690,$ and 691 eV).

the excitation process the intermediate state wave packet $\Psi_d(R, t)$ is continuously created by transfer from the initial state. At each time step new parts are superposed to the old parts of $\Psi_d(R, t)$ which propagate according to the force they experience on the potential energy curve. This superposition of earlier and later created parts causes interferences by which the energy selection is achieved. Depending on the Franck-Condon overlaps $\langle \Psi_i | n_d \rangle$ in the energetically selected region (see inset of Fig. 1), one finds mainly constructive interferences on resonance and increasingly destructive interferences for increasing detuning. Thus, by detuning smaller and smaller parts of $\Psi_d(R, t)$ survive the selection process which takes place on the time scale of the excitation pulse. This can be seen as a decrease of the “effective lifetime” of the decaying state [3]. Consequently, the spectrum is more and more dominated by the direct molecular contributions, and the atomic peak is correspondingly suppressed. The reduction of the effective lifetime also explains the Raman-like behavior found for large detuning. The spectra are now formed exclusively by the short-time molecular contributions corresponding to almost direct transitions between the initial and the final states, independent of the intermediate state. The linear dispersion with the excitation energy is a consequence of energy conservation.

Also the explanation of the interference structure found for small detuning towards higher excitation energies

is connected with the selectivity of the excitation. For an excitation energy of 689 eV (2 eV above resonance), an energy region is selected where the Franck-Condon overlaps are already small but still large enough that parts of the intermediate state wave packet $\Psi_d(R, t)$ with the “correct energy” can survive the excitation. Looking at the time evolution of $\Psi_d(R, t)$ in Fig. 3 one can see that, as a consequence of the selection of a small energy region, the nodal structure of the corresponding eigenvectors is forced onto $\Psi_d(R, t)$. Provided that this structure exists long enough (which is the case owing to the dissociative character of the core-excited state), it can now be mapped onto the Auger spectrum. The mapping is particularly simple as a consequence of the dissociative character of the final state potential curve [16]: transitions which occur at larger internuclear distances lead to higher energy contributions in the spectrum.

The central question now concerns the conditions for the appearance of a structure in $\Psi_d(R, t)$. In particular, the question arises why this structure is formed only for small detuning towards higher excitation energies and not at the resonance or below it. In order to understand this it is helpful to realize the conditions for the appearance of interference in general. As mentioned above, interference takes place between parts of a wave packet created earlier in time and parts added later. Therefore, the time scales of excitation and nuclear dynamics in the excited state have to be comparable for interference to occur in the

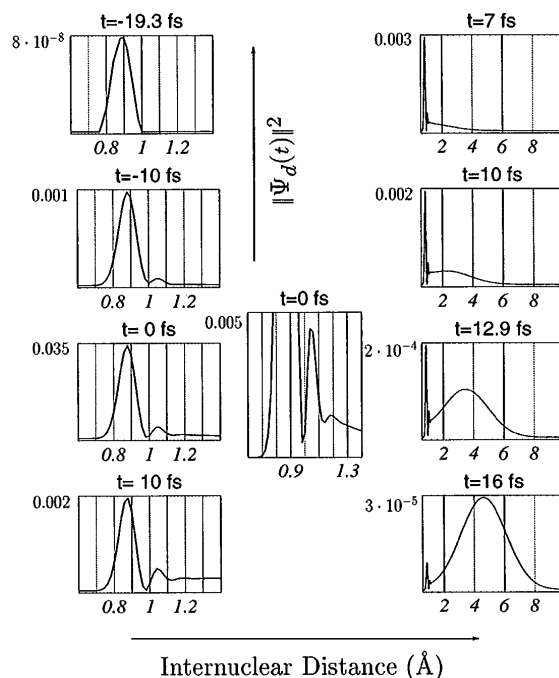


FIG. 3. Time evolution of the norm of the intermediate state wave packet $\Psi_d(R, t)$ for the case of small detuning above resonance ($E_{\text{exc}} = 689$ eV). The FWHM of the excitation pulse is 0.2 eV. Since the pulse is a Gaussian this corresponds to a duration of 13 fs. For $t = 0$ fs (at the maximum of the excitation pulse) an additional magnified frame is shown in the center in order to demonstrate the three-peak structure.

decaying state. This condition is fulfilled as long as the excitation width, which is related to the inverse of the pulse duration, is small enough. Another condition is that parts of the wave packet created earlier remain localized in the zone of interaction where new parts are created later in time. In the case of bound potential curves the nuclear wave packet remains within the potential well. Interference can thus lead to very prominent “vibrational structure.” For repulsive potentials, however, the parts of $\Psi_d(R, t)$ describing the dissociation of the molecule move directly out of the interaction zone, leading to a suppression of interference.

When the excitation is performed at the resonance or below it, the created wave packet $\Psi_d(R, t)$ experiences immediately the repulsive forces of the potential to which it was transferred. Consequently, there is no possibility to form the spatial structure in $\Psi_d(R, t)$ by interference, and thus no structure is found in the spectrum. Going to higher excitation energies, parts of $\Psi_d(R, t)$ now can propagate also in the direction of smaller internuclear distances and thus can resist immediate dissociation. Additionally, the region where interferences can occur becomes larger because shorter internuclear distances are accessible by excitation above the resonance. In conclusion, parts of $\Psi_d(R, t)$ can stay longer in the (enlarged) interaction zone, and thus interferences become more pronounced leading to the nodal structure of $\Psi_d(R, t)$.

In order to consolidate this explanation, the formation of the norm of $\Psi_d(R, t)$ and the evolution of the spectrum $\sigma(E, t)$ are shown for an excitation energy of 689 eV in Figs. 3 and 4, respectively. At the very beginning of the process, $\Psi_d(R, t)$ reflects the shape of the initial state wave function. The spectrum exhibits the same shape too, due to the “mapping” of the spatial distribution of $\Psi_d(R, t)$ onto the Auger spectrum. After some time delay the structure in $\Psi_d(R, t)$ develops and, accordingly, the three-peak structure in the spectrum is formed. After the molecular part of the spectrum is almost completely formed, the atomic peak begins to appear, arising from decay of the large outgoing part of the intermediate state wave packet.

To summarize, we have seen that a variation of the excitation energy allows for a *controlled mapping* of the nodal structure of a zone of eigenvectors selected by the excitation. Only in the limiting ideal case of monochromatic excitation, $\Psi_d(R, t)$ would show the “perfect” structure of the eigenvector which is filtered out by the excitation. A monochromatic excitation is, of course, only achieved when the excitation time tends to infinity. In all realistic cases the finite excitation time implies a finite energy width of the excitation pulse and can suppress the formation of the nodal structure, especially in the on-resonance case. In general, the interferences forming the structure can be enhanced by small detuning towards higher excitation energies.

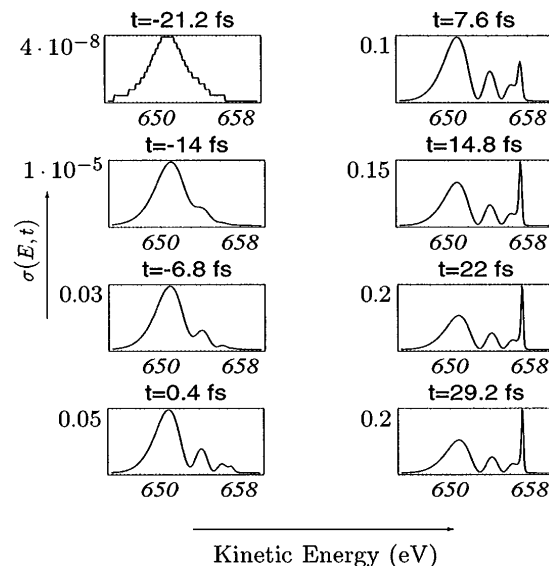


FIG. 4. Formation of the Auger spectrum $\sigma(E, t)$ as a function of time t taken at an excitation energy of $E_{\text{exc}} = 689$ eV, i.e., for small detuning above resonance. The FWHM of the excitation is 0.2 eV.

Enlightening and fruitful discussions with Joachim Brand are gratefully acknowledged. This work has been supported financially by the DFG and by traveling funds of the “Vigoni” programme.

- [1] M. N. Piancastelli *et al.*, Phys. Rev. Lett. **77**, 4302 (1996), and references therein.
- [2] L. S. Cederbaum and F. Tarantelli, J. Chem. Phys. **98**, 9691 (1993); **99**, 5871 (1993).
- [3] E. Pahl, H.-D. Meyer, and L. S. Cederbaum, Z. Phys. D **38**, 215 (1996).
- [4] E. Pahl *et al.*, J. Chem. Phys. **105**, 9175 (1996).
- [5] F. Gel'mukhanov, L. Mazalov, and A. Kondratenko, Chem. Phys. Lett. **46**, 133 (1977).
- [6] F. Kaspar, W. Domcke, and L. S. Cederbaum, Chem. Phys. **44**, 33 (1979).
- [7] A. Menzel *et al.*, Chem. Phys. Lett. **258**, 265 (1996), and references therein.
- [8] P. Morin and I. Nenner, Phys. Rev. Lett. **56**, 1913 (1986).
- [9] O. Björneholm *et al.*, Phys. Rev. Lett. **79**, 3150 (1997).
- [10] D. Menzel, J. Electron. Spectrosc. Relat. Phenom. **72**, 19 (1995).
- [11] L. S. Cederbaum and F. Tarantelli, J. Chem. Phys. **98**, 9691 (1993).
- [12] E. Pahl *et al.* (to be published).
- [13] A. P. Hitchcock and C. Brion, J. Phys. B **14**, 4399 (1981).
- [14] S. Svensson *et al.*, J. Electron. Spectrosc. Relat. Phenom. **50**, c1 (1990).
- [15] K. Zähringer, H.-D. Meyer, and L. S. Cederbaum, Phys. Rev. A **45**, 318 (1992).
- [16] F. Gel'mukhanov and H. Ågren, Phys. Rev. A **54**, 379 (1996).