Theory of wave packet dynamics: resonant Auger spectrum of HF

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Abstract

The time-dependent theory of wave packet dynamics accompanying the excitation and decay in the molecular Auger process is reviewed and applied to the resonant Auger spectrum of HF. When the core-excitation is performed by an energetically non-selective source ('broad-band' excitation), many intermediate states are populated during the excitation process and their decay gives many interplaying contributions within the same energy region. To interpret the spectrum we have carried out a detailed theoretical study of all the decaying and final electronic states involved. In order to restrict the number of participating decaying states, narrow-band excitation has to be performed, so that only one intermediate decaying state is populated. We have studied in detail one particular transition between purely repulsive potential curves, where we show the effects introduced by the energetically selective excitation. By detuning the excitation energy off the resonance, very prominent interference patterns can be found. These explain the quenching of the so-called 'atomic lines' and the surprising new features which appear in the case of small detuning towards higher excitation energies. The effects discussed are shown to be of a general nature. The description in the time-dependent picture allows for a novel and deeper understanding of the underlying mechanisms of these effects since the physically relevant quantities can be traced on the real time scale of the process. © 1998 Elsevier Science B.V. All rights reserved

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1. Introduction

Molecular decay spectroscopies, like e.g. Auger electron or X-ray emission spectroscopy, have become important tools for studying the electronic structure and the nuclear dynamics of electronically highly excited states. Nuclear dynamics affects the observed spectra because the lifetime of the excited states lies in the same range as typical times of internal vibrations in these states. Since vibrations or fragmentation dynamics may occur in both the decaying and the final states, one observes interference effects which influence strongly the shape of the spectra [1,2].

In this contribution, we shall concentrate on the so-called resonant decay spectroscopy, which investi-
gates core-excited states, in contrast to non-resonant techniques which study the decay of core-ionized states. In comparison with non-resonant decay spectra, the resonant analogues reveal some additional features which may complicate the interpretation of the observed spectra: in general, there exist a number of energetically close-lying electronic states of the core-excited molecule. Thus, if the excitation is performed by an energetically non-selective source, as it happens by ‘broad-band excitation’ with photons, or excitation by electron impact, various intermediate states are populated. The decay of these states into the manifold of final states leads to a large number of different contributions which can all be found within the same energy region of the spectrum. Additionally, the different core-excited states may vary strongly in character, in contrast to the generally bound character of core-ionized states. Depending on whether the core-electron is excited into an anti-bonding molecular orbital or into a Rydberg-like orbital, the corresponding potential curves may exhibit dissociative or bound character, respectively. In the case of strongly repulsive curves, the time of dissociation of the molecule can be of the same order of magnitude as the decay time, leading to a competition between the direct molecular decay and the decay of the atomic fragments after dissociation of the molecule. Such an interplay between ‘molecular’ and ‘atomic’ contributions has widely been observed, starting with the first observation of ‘atomic’ lines in the resonant Auger spectrum of HBr [3]. For these reasons, a detailed theoretical study of all potential curves involved and of the nuclear dynamics of them is, in general, indispensable for the interpretation of the observed spectra.

Even if the excitation is performed selectively (‘narrow-band excitation’) and only one intermediate state is populated, as has been achieved in many experiments (e.g. [4,5,3,6,7]), an intuitive interpretation of the observed spectra may fail. The reason for this is that an energetically selective excitation implies a prolongation of the excitation pulse, as opposed to the ‘sudden’ broad-band excitation, whereby the excitation time may become of the same order of magnitude as both the decay time and the typical times for internal vibrations. In this case, the usually assumed separability of excitation and decay is not possible [8], and new interference effects in the intermediate state may appear and influence strongly the spectra. As we shall show, by detuning the excitation energy away from the resonance energy, these effects may be strongly enhanced.

In this paper, we shall first give a brief outline of the theory of wave packet dynamics [1,9,8] (Section 2). In Section 3 we shall turn to a realistic case, the resonant Auger electron spectrum of HF. This example has been chosen because it was possible to compute all the potential curves involved for this molecule with ab initio quantum chemical methods (Section 3.1). However, the phenomena studied are quite general and only depend on the bound vs. dissociative character of the potential curves involved. Discussing this example, we shall first show the interplay between the vast number of contributions which occur after broad-band excitation of the molecule (Section 3.2). Our results will be compared with an experiment [10] where core-excitation has been performed by energetically non-selective electron impact. In the subsequent Section 3.3, we shall then study the interference effects which are introduced upon narrow-band excitation, by focusing on one particular transition where both the intermediate as well as the final state are dissociative. By varying the excitation energy one finds a resonance energy which is characterized by a maximum in the total integrated intensity of the resulting spectra. The spectrum taken on-resonance resembles closely the corresponding broad-band spectrum, whereas by detuning away from this resonance dramatic changes are exhibited. Special attention will be paid to the influence of detuning on the atomic contributions and to the case of small detuning towards higher excitation energies, where very pronounced interferences are found. The theory of wave packet dynamics is shown to provide a very useful tool for understanding these phenomena. By virtue of the time-resolution accessible by propagating the nuclear wave packets, the formation of the spectrum can be traced on the real time scale for the process and thus more insight is gained.

2. Theory

The theory of wave packet dynamics to describe the nuclear dynamics accompanying the decay of an electronically highly excited state has been developed in recent years starting with its first
formulation for the case of non-resonant decay spectroscopy involving individual electronic states [1]. Subsequently, the theoretical description has been extended to cover also cases where non-adiabatic interactions among several electronic states take place either in the intermediate or in the final state manifolds [9,11]. Finally, the theory has been augmented by including the excitation process into the description. This is indispensable for resonant decay spectroscopy, where the whole process cannot be divided into two successive steps of excitation and decay [8].

Here, we shall only give a brief outline of the theory used to compute the Auger spectrum of HF upon core-excitation of the molecule. The total intensity of the emitted Auger electrons $\sigma(E)$ as a function of their energy $E$ is the quantity which is measured in the experiment. We shall now show how this quantity can be extracted from the propagated nuclear wave packets and then present the differential equations which enable us to propagate the wave packets in time.

We start with the following ansatz for the total wavefunction of the system $\Psi_{\text{tot}}$ as a sum over all the molecular states involved in the process. These are the initial state $\psi_i$ in which the molecule is found at the beginning, all the intermediate, decaying states $\psi_d$ populated during the excitation, and all the different decay channels described by the final molecular states $\psi_f(E)$ (containing the emitted Auger electron of energy $E$):

$$\psi_{\text{tot}}(R, r, t) = \psi_i(R, r, t) + \sum_d \psi_d(R, r, t) + \sum_f \int dE \psi_f(E, R, r, t)$$

(1)

The total wave function $\psi_{\text{tot}}$ depends on the set of electronic coordinates $r$, nuclear coordinates $R$, and on the time $t$.

In a Born–Oppenheimer picture, all the molecular states are given as a product of the electronic states $\Phi_i$, $\Phi_d$ and $\Phi_f(E)$ and the corresponding nuclear wave functions $\Psi_i$, $\Psi_d$ and $\Psi_f(E)$ of the initial, decaying and final states, respectively. $\Phi_f(E)$ denotes the electronic wave function of the final electronic state of the ionized molecule and the emitted electron of energy $E$:

$\psi_i(R, r, t) = \Psi_i(R, r, t) \cdot \Phi_i(x)$

$\psi_d(R, r, t) = \Psi_d(R, r, t) \cdot \Phi_d(x)$

$\psi_f(E, R, r, t) = \Psi_f(E, R, r, t) \cdot \Phi_f(E, x)$

The nuclear wave functions $\Psi$ contain all the dependence on the nuclear coordinates $R$ and on the time $t$. The nuclear wave functions of the final states depend additionally on the energy $E$ of the emitted Auger electron as a parameter, because for each energy a different final electronic state $\Phi_f(E)$ is populated and the corresponding wave packets evolve in a different manner. Because the emitted electron can adopt any energy within some range, a continuum corresponding to each ionized final state exists.

The ansatz (Eq. (1)) can now alternatively be seen as a weighted sum of the electronic states involved in the process. The weights are just given by the nuclear wave functions! From this point of view, it becomes clear that the intensity of the emitted Auger electron $\sigma(E)$, which is proportional to a sum of the populations of the final electronic states $\Phi_f(E)$, is simply given by the long-time limit of the sum over the norms of the final state wave packets $\Psi_f(E, t)$:

$$\sigma(E) = \lim_{t \to \infty} \sum_f \int dR |\Psi_f(E, R, t)|^2$$

(2)

The intensity can thus be extracted by propagating the nuclear wave packet $\Psi_f(E, t)$ in time. Since the propagation time $t$ represents the real time of the process, the formation of the spectrum in time $\sigma(E, t)$ can be monitored. This time resolution gives a very useful insight into the process, and the interpretation of the spectra is facilitated. It should be emphasized that the quantity $\sigma(E, t)$ can—at least in principle—be investigated experimentally: after some delay time the decay process has to be interrupted, e.g. by a 'probe' light pulse, with depopulation of the decaying state. Although the required time resolution is not available today, it could be in the near future.

For the propagation of the nuclear wave packets of the intermediate and final states $\Psi_d(t)$ and $\Psi_f(E, t)$, respectively, differential equations have been derived.
for the case where interaction with a time-dependent external field is present [8]. In the derivation one makes use of the local approximation, which then allows for the derivation of a simple, effective, non-hermitian Hamiltonian of the intermediate state. The imaginary part of this Hamiltonian accounts for the irreversible decay of the intermediate electronic state into the continuum of final electronic states. Here we show the differential equations obtained within the weak-field approximation, in which the recoupling of the intermediate state to the initial state is neglected:

\[
i\dot{\Psi}_d(t) = g(t)\hat{V}\Psi_j(t) + (\hat{H}_d - \frac{i}{2}\hat{\Gamma})\Psi_d(t)
\]

\[
i\dot{\Psi}_j(t) = \hat{W}\Psi_d(t) + (\hat{H}_j + E)\Psi_j(t)
\]

For the sake of a simple notation we have omitted the dependence of the wave functions on the nuclear coordinates \( \mathbf{R} \), and we restrict ourselves to the description of a single transition between one intermediate and one final state. As long as there is no vibronic coupling between the electronic states either in the intermediate or in the final states’ manifold, all contributions resulting from different transitions between intermediate and final states can be computed separately and the intensity of the emitted Auger electrons \( \sigma(E) \) is essentially given by a sum of all these contributions. Our calculations of the potential curves showed that in the present case HF vibronic coupling can indeed be neglected.

In the differential equations (Eq. (3)) the Hamiltonians \( \hat{H}_d \) and \( \hat{H}_j \) describe the nuclear motion of the wave packets on the corresponding intermediate and final state potential curves. The decay of the intermediate state is accomplished by the imaginary part \( \frac{i}{2}\hat{\Gamma} \) where \( \hat{\Gamma} \) denotes the decay width of the intermediate state in the local approximation. The decay width is inversely proportional to the lifetime of this state. New contributions to the wave packets are introduced by the inhomogeneities \( g(t)\hat{V}\Psi_j(t) \) and \( \hat{W}\Psi_d(t) \). \( \hat{V} \) and \( \hat{W} \) are matrix elements over the electronic wave functions and describe the transitions between the initial electronic state and the intermediate state and between the intermediate and the final electronic states, respectively. The excitation function \( g(t) \) describes the interaction with the time-dependent external field.

In the case of broad-band excitation this function may be approximated by a \( \delta \)-function \( g(t) = \delta(t) \) and the differential equation for the intermediate state wave packet is replaced by

\[
i\dot{\Psi}_d(t) = (\hat{H}_d - \frac{i}{2}\hat{\Gamma})\Psi_d(t)
\]

with the initial condition \( \Psi_d(0) = \hat{V}\Psi_j(t) \). This means that the initial state wave packet is directly transferred to the intermediate electronic state in the first step of the process and in a subsequent step the nuclear dynamics and the decay begin (two-step model).

3. Resonant Auger spectrum of HF

In this section we shall show the effects which can be introduced by the interplay between excitation, nuclear dynamics and decay, by studying the resonant Auger spectrum of HF. We shall first discuss the manifold of transitions which can occur upon broad-band excitation of this molecule. A comparison with an experiment [10] is drawn where the core-excitation has been performed by energetically non-selective electron impact. Subsequently, we shall concentrate on the Auger spectrum obtained for one single transition in order to discuss different effects which can be introduced by narrow-band excitation. Special attention will be paid to the case of small detuning towards higher excitation energies, where very pronounced interference effects are found.

3.1. Potential curves of HF involved in the Auger process

For an exact treatment of the nuclear dynamics, the knowledge of all the potential curves involved is necessary. We have therefore computed the ground state, all the intermediate electronic states that can be populated by electron impact, as well as the lowest lying ionic final states by accurate ab initio methods. Details of the computation will be described elsewhere [12]. The potential curves obtained are depicted in Fig. 1.

At the beginning of the process, the molecule is found in its electronic and vibrational ground state; the initial wave function is therefore of Gaussian
shape and centered at the equilibrium distance of HF at 0.92 Å. The equilibrium distance is indicated by the dashed line in Fig. 1. The lowest lying intermediate state, resulting upon excitation of the F1s electron into the anti-bonding 4σ(σ*) molecular orbital, is a strongly repulsive state dissociating into \( \text{H}^2(\Sigma^+) \) and core-excited fluorine \( \text{F}^+(1s \rightarrow 2p) \). Above this state, a series of bound Rydberg states is found, corresponding to the excitation of the F1s electron into atomic-like Rydberg orbitals of 3p, 4s, or 4p character. Except for the two lowest-lying final states which exhibit bound character, all the other final states are strongly repulsive dissociating into \( \text{H}(2\Sigma^+) \) and \( \text{F}^+(1\Sigma^+, 1\Pi, 2\Sigma^+) \).

For a check of the potential curves and in order to find out which states are populated through electron impact excitation, we first computed the electron energy loss spectrum and compared it with the experimental one of Hitchcock and Brion [13], which could be reproduced very well [12]. The calculations reveal that all the intermediate states depicted in Fig. 1 are significantly populated during the excitation and can thus all contribute to the Auger spectrum.

In Fig. 1 only the intermediate singlet states are shown but, of course, the corresponding triplet states can also be populated through electron impact and have therefore been computed as well. The computation revealed that the triplet curves are essentially parallel to the corresponding singlets, i.e. they appear with the same shape at approximately the same energy, and thus yield contributions of similar shape as the singlet states to the excitation spectrum and to the Auger spectrum. The relative intensities of the contributions of the triplet transitions can, of course, vary compared to the corresponding singlet ones.

3.2. Broad-band excitation

Starting from the computed potential curves it is now possible to study the interplay between the different types of Auger transitions occurring upon core-excitation of HF. In the experiment [10] the excitation of the molecule has been accomplished by energetically non-selective electron impact. Due to the broad-band excitation both core-ionization and core-excitation of the molecule was possible. The normal, non-resonant Auger spectrum is found at energies below 650 eV whereas the resonant Auger spectrum appears at higher energies, at about 656.5 eV. One relatively intense peak at 656.7 eV as well as three weak ‘peaks’ at about 653.8 eV, 657.9 eV and 659.4 eV have been identified above a noisy background (see Fig. 2(a)). The most intense peak as well as the lowest and highest peaks have been assigned to atomic contributions originating from the decay of the atomic fragments of the dissociative \( ^1 \Sigma^+ \) state into final states which dissociate into \( \text{H}(2\Sigma^+) \) and \( \text{F}^+(1\Sigma^+, 1\Pi, 2\Sigma^+) \) and \( \text{F}^+(1\Pi, 2\Sigma^+) \), respectively. For the peak at 657.9 eV no explanation has been found [10].

In Fig. 2(c) all the contributions resulting from the decay of the dissociative \( ^1 \Sigma^+ \) state are displayed; in Fig. 2(d) the same for the decay of the lowest lying Rydberg state is shown as an example for the possible contributions originating from the Rydberg states. A
large number of transitions are thus found which may all contribute to the Auger spectrum within the same energy region. For a detailed assignment of the peaks in the spectrum, the knowledge of the Auger rates for all of these transitions would be necessary. An exact computation of these rates would imply a large numerical effort which does not seem to be sensible at the present stage of experiment. For a rough estimate of the Auger rates for the transitions originating from the decay of the dissociative $^1\Sigma^+$ state the corresponding Auger rates of Ne [14] can be used instead. At least for the intense atomic transitions of the core-excited F*(1s → 2p) these rates should provide a very good estimate. By using these rates to weight the different contributions of the $^1\Sigma^+$ state the spectrum shown in Fig. 2(b) is obtained.

Now we are able to give the following interpretation: our calculations confirm that the most intense peak in the spectrum at 656.7 eV originates from atomic transitions between the first $^1\Sigma^+$ state and the final states that dissociate into $\text{H}^*(^2\Sigma)$ and $\text{F}^+(^1\Delta)$. The high intensity of this peak is in agreement with the high Auger rate for the corresponding transition in the Ne Auger spectrum, as can be seen in Fig. 2(b). As a consequence of the preference of these transitions, the corresponding weaker molecular contributions are also visible in the spectrum. They form the (probably dominant) part of the energetically lowest peak in the spectrum at 653.8 eV, which also contains atomic contributions due to transitions between the $^1\Sigma^+$ state and the final state which dissociates into $\text{H}^*(^2\Sigma)$ and $\text{F}^+(^1\Sigma)$. Of course, because we do not know the exact Auger rates we cannot analyse precisely the relative importance of the atomic with respect to the molecular contributions to this peak.

Turning to the remaining two peaks at 657.9 and 659.4 eV, we found that they cannot originate from the decay of the $^1\Sigma^+$ intermediate state. The peak at 659.4 eV was assigned [10] to atomic transition from the $^1\Sigma^+$ state into the final states dissociating into $\text{H}^*(^2\Sigma)$ and $\text{F}^+(^3\Pi)$. The Ne Auger rates, however, indicate that these transitions are strongly suppressed, whereas transitions to the two lowest final states appear at higher energies and do not contribute in the energy region of interest. The peak at 659.4 eV may instead result from the atomic transition of the dissociative $^3\Sigma^+$ state to the final state dissociating into $\text{H}^*(^2\Sigma)$ and $\text{F}^+(^3\Pi)$. As discussed above the triplet states are of similar shape to the singlet states and thus give rise to similar contributions in the spectra. The probability of this special transition could be strongly enhanced in comparison with the corresponding singlet transition because both the intermediate and the final states are triplets. Another possible explanation for this peak, as well as for the still unexplained peak at 657.9 eV, are the contributions originating from the decay of the Rydberg states. These contributions also provide an explanation for the strong background in this energy regime of the spectrum.

Concluding, we have seen in this section that a vast number of transitions can be found if the core-excitation is performed in an energetically unselective manner. To restrict the number of transitions, and thus facilitate the interpretation, it is sensible to use energetically sharp
pulses, so that only one intermediate state is populated during the excitation. In the next section we shall therefore concentrate on resonant Auger spectra obtained upon narrow-band excitation.

3.3. Narrow-band excitation

In order to achieve a selective excitation, the duration of the excitation has to become longer, which can lead to comparable time scales of the excitation process and the nuclear dynamics in the intermediate state. Interferences in the intermediate state necessarily occur to ensure energy selection. Therefore new and unexpected effects appear as will be seen in the following.

To investigate these phenomena we have chosen the transition between the dissociative $^1\Sigma^+$ intermediate state and one of the dissociative final states, $\text{HF}^+(^{3}\Pi: \ldots 3\sigma^11\pi^34\sigma^1)$. This particular transition contributes to the most intense atomic peak in the broad-band resonant Auger spectrum discussed above. In Fig. 3 its broad-band contribution is shown again; the corresponding potential curves are depicted in Fig. 4. One finds the typical two peak structure formed by the intense and sharp atomic peak at 656.7 eV and a weaker broader part at about 652 eV originating from the molecular contributions.

The energy position and shape of molecular type transitions are influenced by the overlaps between the intermediate state wave packet and the eigenvectors of the final state. This argument is similar to the well-known Franck–Condon principle where the overlaps of corresponding eigenstates enter. Due to the dissociative character of the final state its ‘eigenvectors’ are to a large part localized close to the potential wall. Therefore, transitions occurring at an internuclear distance $R'$ lead to a contribution to the Auger spectrum at an energy $E'$ which is just given by the difference between the excitation energy and the value of the final state potential $V_f(R')$. The dissociative character of the final state potential ensures that

![Fig. 3. Contribution to the broad-band Auger spectrum corresponding to the transition between the intermediate $^1\Sigma^+$ state dissociating into $\text{H}(^3\text{S})+\text{F}(^3\text{S})$, and the $^3\Pi$ final state which dissociates into $\text{H}+\text{F}^+(^1\text{D})$. Evident is the typical two peak structure formed by an intense and sharp atomic peak at 656.7 eV and a broad molecular part at about 652 eV.](image1)

![Fig. 4. Potential curves of the intermediate $^1\Sigma^+$ state dissociating into $\text{H}(^3\text{S})+\text{F}(^3\text{S})$, and the $^3\Pi$ final state which dissociates into $\text{H}+\text{F}^+(^1\text{D})$. The spectral contribution of the transition between these curves is in Fig. 3. Shown in the insert are the Franck–Condon overlaps between the initial state wave function $\Psi_i$ and the eigenvectors of the intermediate state $|n_i\rangle$. In the case of narrow-band excitation a resonance $E_{\text{res}}$ is found characterized by a maximum in total integrated intensity (see text). This resonance is related to the maximum of the Franck–Condon overlaps. 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.](image2)
transitions occurring at smaller internuclear distances contribute to the spectrum at lower energies than transitions occurring at larger distances. This leads to a mapping of the spatial distribution of the intermediate state wave packet onto the Auger spectrum, as long as the transition takes place in the molecular region (see Fig. 7). The atomic peak, however, corresponds to transitions in the 'atomic' region of the potential curves, i.e. for larger internuclear distances where the potential curves are already flat or even constant. In this region the corresponding 'eigenfunctions' look like plane waves and transitions between intermediate and final electronic states have to obey momentum conservation for the atomic fragments. Thus the energy of the atomic lines is given by the energy difference of the asymptotes of the corresponding potential curves. The relative position of the atomic and molecular contributions to the spectrum is thus governed by the particular shape and relative position of the potential curves involved. A steeper increase of the final state potential \( V_f(R) \) for small \( R \) compared to the intermediate state potential \( V_i(R) \) causes the atomic peak to appear at the high energy side of the spectrum (see Fig. 4).

When turning now to narrow-band excitation, we first notice that by varying the excitation energy a resonance is found, characterized by a maximum in the total integrated intensity of the resulting spectrum. The appearance of such a resonance in the case of a dissociative intermediate state potential curve can be explained by the Franck-Condon overlaps between the initial state wave function \( \Psi_i \) and the eigenvectors of the intermediate state. The magnitude of absorption of the incoming radiation, and thus also the total integrated intensity \( \Omega \) in the spectra, depends strongly on these overlaps. The Franck-Condon overlaps in the case considered here are shown in the insert of Fig. 4. The resonance energy coincides approximately with the maximum of the overlaps at about 687 eV. By detuning away from the resonance, the total integrated intensity is reduced according to the decrease of the Franck-Condon overlaps.

At the top of Fig. 5 the spectrum taken on-resonance is shown. Below on the left-hand side are the spectra obtained by detuning towards lower excitation energies, and on the right-hand side those resulting from detuning towards higher excitation energies. We can see that the on-resonance spectrum closely resembles the broad-band spectrum of Fig. 3, whereas by varying the excitation energies towards lower and higher excitation energies the spectra exhibit dramatic changes. Besides the expected decrease in the total integrated intensity \( \Omega \), we observe first of all that the atomic peak is quenched upon detuning in either direction. The spectrum is therefore more and more

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Fig. 5. Computed resonant Auger spectra for the \(^1\Sigma^+ \rightarrow \Pi\) transition obtained by narrow-band excitation at different excitation energies \( E_{exc} \). The FWHM of the excitation pulse is chosen to be 0.2 eV. At the top is the spectrum taken on-resonance (\( E_{exc} = 687 \) eV), which closely resembles the broad-band spectrum of Fig. 3. Below, on the left-hand side, are the spectra at lower excitation energies (from top to bottom: \( E_{exc} = 685 \) eV, 684 eV, and 682 eV). On the right-hand side are the spectra at higher excitation energies (from top to bottom: \( E_{exc} = 689 \) eV, 690 eV, and 691 eV). Note that the total integrated intensity \( \Omega \) decreases strongly by detuning. Having set \( \Omega = 1 \) for the broad-band spectrum of Fig. 3, we find \( \Omega = 0.357 \) on-resonance. For the detuned spectra on the left, from top to bottom: \( \Omega = 0.04, 0.005, \) and 0.001. For the detuned spectra on the right, from top to bottom: \( \Omega = 0.016, 0.03, \) and 0.002.
dominated by the molecular contributions until, at excitation energies of 682 eV and 691 eV, only the broad molecular peak remains. For large detuning, the molecular part shifts linearly with the excitation energy. The most striking effect is found for small detuning towards higher excitation energies. Here, an additional, very pronounced structure is encountered!

The excitation width of the incoming radiation is chosen to be 0.2 eV. The appearance of the described effects does not depend strongly on this excitation width, as long as it is of the same order of magnitude as the decay width of the intermediate state (0.202 eV). The effects studied 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. We shall now analyse the observed effects in some detail.

3.3.1. Quenching of the atomic peak by detuning

The first effect which requires a more detailed discussion is the appearance of the atomic peak and its suppression in the off-resonance spectra. This effect has already been observed and discussed in detail [8], where the appearance and disappearance of atomic lines in a model for the decay of core-excited O2 has been studied. The origins of the atomic peak are contributions due to transitions which occur after dissociation of the molecule into atomic fragments. The sharpness of the peak is caused by the required momentum conservation in the atomic fragments. Whereas the molecular contributions develop after a short propagation time, the atomic peak is formed later, after the dissociation of the molecule. When the excitation energy is increased, the core-excited molecule gains nuclear kinetic energy and the dissociation occurs more rapidly. One thus might expect a growing relative intensity of the atomic peak with respect to the molecular part.

But as we can see in the spectra of Fig. 5 computed above resonance, the opposite actually takes place: the atomic peak is more and more suppressed with increasing excitation energy. A first explanation of this phenomenon is provided by an analysis of the intermediate state wave packet $\Psi_{\alpha}(t)$. In Fig. 6 the time evolution of the norm of $\Psi_{\alpha}(t)$ is displayed on a logarithmic scale for different excitation energies.

Exciting on-resonance, the norm of the intermediate state wave packet increases until the exponential decay takes over. In the logarithmic plot the exponential decay can be recognized as a straight line. Upon detuning, we notice that the norm of $\Psi_{\alpha}(t)$ follows more and more directly the intensity changes of the incoming radiation. The maximum of the norm is therefore shifted to $t = 0$, corresponding to the intensity maximum of the excitation pulse. The initial creation of the intermediate wave packet is followed by a strong decrease by destructive interference until the Auger decay becomes the dominant destruction channel, as signalled by the curve turning into a straight line.

The origin of the described behaviour resides in the selectivity of the excitation pulse. The energy selection is achieved by interferences between earlier created parts of the intermediate wave packet and the parts added later. In dependence of the Franck–Condon overlaps between the initial state $\Psi_i$ and the eigenvectors of the intermediate state in the selected energy region (see insert of Fig. 4), these interferences are mainly constructive (on-resonance) or of increasingly destructive character (with larger detuning). Thus for stronger detuning a smaller part of the intermediate wave packet survives the excitation process and leaves the region of the molecular decay. The spectrum is dominated by the molecular contributions occurring after short propagation times.

![Fig. 6. Time evolution of the norm of the intermediate state wave packet $\Psi_{\alpha}(t)$ computed at different excitation energies $E_{\text{exc}}$. Displayed is the logarithm of the norm $\log_10|\Psi_{\alpha}(t)|^2$, whereby the onset of exponential decay can be detected as a straight line.](https://example.com/f6.png)
and the atomic peak is increasingly suppressed. The short-time behaviour now governs the spectrum. This can be seen as a decrease of the ‘effective lifetime’ of the intermediate state induced by detuning [8,15].

3.3.2. Behaviour for large detuning

The behaviour of the molecular contributions for large detuning is well explained by the reduction of the effective lifetime. The spectrum is now exclusively formed by the short-time molecular contributions. The energies corresponding to these contributions become independent of the intermediate state and depend only on the difference between the excitation energy and the final state energies. The linear dispersion of the molecular parts originates from energy conservation. The width of the molecular peak is determined by the width of the Franck-Condon overlaps between the initial wave packet and the eigenvectors of the dissociative final state (in the present case the FWHM of these overlaps is about 6 eV) and not by the width of the (energetically much narrower) excitation pulse. This explains the broad shape of the molecular contributions and the fact that no noticeable change of the peak width is found by varying the width of the excitation pulse [12].

3.3.3. Behaviour for small detuning

For small detuning towards higher excitation energies the spectrum exhibits a very pronounced structure, as described above (see Fig. 5, right-hand side). For an excitation energy of 689 eV (which lies 2 eV above resonance) we can distinguish three well defined peaks in the molecular region below the persisting atomic peak. The appearance of such a prominent structure would commonly be expected only when bound potential curves are involved. In the present case, however, we are concerned with the transition between purely dissociative potential curves! A detailed study of this effect will be presented [12], but we outline here the main ideas.

The explanation is again connected with the selectivity of the excitation. For an excitation energy of 689 eV, the Franck-Condon overlaps are already smaller than on-resonance, but still large enough that the selection can work and significant parts of the intermediate state wave packets with the ‘correct’ energy can survive the excitation process (see Fig. 6).

By inference, not only the energy selection is achieved, but also the nodal structure of the ‘eigenvectors’ of the selected energy region can be transferred to the intermediate state wave packet \( \Psi_d(t) \). The formation of this structure in \( \Psi_d(t) \) is shown in Fig. 9 and will be discussed below. The structure is directly mapped onto the Auger spectrum because of the dissociative character of the final state potential curve. In particular, transitions occurring at larger internuclear distances lead to higher energy contributions in the spectrum, as explained above (see also Fig. 7).

These considerations lead to the following question: why does this structure appear only for small detuning towards higher excitation energies and not on-resonance or for detuning towards lower excitation energies? The answer is that in the latter cases no structure develops in the intermediate state wave packet that can be transferred to the Auger spectrum.

In order to understand how the structure in the

Fig. 7. Schematic illustration of the ‘mapping’ of the intermediate state wave packet \( \Psi_d(t) \) onto the Auger spectrum. The spatial structure of \( \Psi_d(t) \) is energetically resolved due to the dissociative character of the final state potential curve \( V_f(R) \) and the fact that the ‘eigenvectors’ \( |n_f_1> \) (sketched by the dashed lines) are mainly localized about the potential wall. Transitions occurring at larger internuclear distances contribute to the spectrum at higher Auger energies \( E_1 < E_2 < E_3 \).
intermediate state wave packet is formed, it helps to recall the conditions that are necessary for interference. Interference takes place between parts of a wave function which are created earlier in time and parts added later. Thus interference in the intermediate state is observed when the time scales of excitation and nuclear dynamics in the intermediate state are comparable, whereas final state interference requires comparable time scale of nuclear dynamics and decay. Another necessary condition for interference is, of course, that the earlier created parts of the wave functions can still be found at the same internuclear distances where new parts are created later in time. Realizing this condition, it becomes clear that, in general, interferences should be more pronounced for bound than for repulsive potentials. In the case of bound curves the wave packet describes the vibration of the molecule and remains within the potential well. Interference is thus important and gives rise to the prominent ‘vibrational structure’ observed in the resulting spectra. For repulsive potentials, however, the parts of the wave function that describe the dissociation can move out of the interaction zone after being created, leading to suppression of interference.

Returning to our problem we can now summarize it as follows: when the excitation is performed off-resonance, the intermediate state wave packet experiences the repulsive forces of the potential curve on which it is transferred. It directly begins to dissociate and moves out of the region of its creation. Thus there is no possibility for interference to shape the spatial structure of the intermediate state wave packet and, consequently, there is no structure in the spectrum. Going to higher excitation energies, the wave packet now possesses enough kinetic energy to ‘move up the potential wall’ before being reflected. Hence, a part of the wave packet stays longer in the molecular region and interference can affect its spatial structure and lead to nodes in the wave packet. A schematical picture illustrating these phenomena is shown in Fig. 8.

In order to consolidate the explanation given above, we finally wish to demonstrate the formation of the structure in the intermediate state wave packet and the time evolution of the corresponding spectrum $\sigma(E,t)$ recorded for an excitation energy of 689 eV (see Fig. 9 and Fig. 10). At the very beginning of the process the intermediate state wave packet 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 $\Psi_d(t)$ onto the Auger spectrum described above. After some time delay the structure in the intermediate state wave packet 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 arise in accordance with a large outgoing part of the intermediate state wave packet.

It should be mentioned that the formation of the spectra in time is a process that can in principle be measured. In order to trace the time-evolution, the decay process must be interrupted by depopulating the intermediate state after some time-delay from the excitation. This could be realized, for example, with the help of a ‘probe’ light pulse or by offering some competing decay channel such as electron transfer. Fast electron transfer processes are known to
occur for molecules absorbed on surfaces or between parts of large molecules.

4. Conclusions

Using a time-dependent formalism, we have given an overview of the phenomena which can be observed in the resonant Auger spectra of diatomic molecules obtained upon broad-band and narrow-band excitation. A specific example, the resonant Auger spectrum of HF, has been studied and satisfactorily interpreted.

In the case of broad-band excitation a complex interplay of many contributions to the Auger spectrum is generally found. The numerous transitions originate from the decay of the variety of energetically close-lying core-excited states which are populated. In addition, the shape of the contributions of the individual transitions varies according to the dissociative or bound character of the intermediate and final state potential curves involved. In the particular case of a dissociative decaying state, one finds atomic lines in the spectrum in addition to the molecular transitions. For an interpretation of this ensemble of different contributions a detailed theoretical study is necessary, which we could carry out for the resonant Auger spectrum of HF. It was possible to improve the assignment of the peaks and to clarify the origin of a so far

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Fig. 9. Time evolution of the norm of the intermediate state wave packet $\Psi(t)$ for the case of small detuning above resonance ($E_{exc} = 689$ eV). The FWHM of the excitation pulse is chosen to be 0.2 eV. The maximum of the excitation pulse defines the zero of the time scale. Note that the ordinate scale changes. On the left-hand side the behaviour for short propagation times in the molecular region is shown. For $t = 0$ an additional magnified frame is shown in the center. On the right-hand side the long-time behaviour of $\Psi(t)$ is depicted on an extended scale of internuclear distances. It can be seen that the dissociation of the decaying state happens on a slower time scale than the establishing of the nodal structure which can be connected with the excitation process.
unexplained part of the experimental spectrum obtained after broad-band excitation by electron impact [10].

In order to restrict the number of participating intermediate states, narrow-band excitation has to be performed. The duration of the excitation pulse is related to the inverse of its energy width. Therefore a new time scale is introduced by energetically selective excitation. If this time scale becomes of the same order of magnitude as the typical times for the nuclear dynamics in the intermediate state, significant interference effects can occur. We have shown how these interferences depend strongly on the excitation energy.

By varying the excitation energy a resonance characterized by a maximum in the total integrated intensity is found. This resonance coincides approximately with the maximal Franck–Condon overlap between the initial state wave function and the eigenvectors of the intermediate state. This is to be expected because the amount of absorption of the incoming radiation depends on these overlaps. By detuning away from this resonance, dramatic changes in the spectra are observed and can be explained by interference mechanisms which shape the intermediate state wave packet.

In order to investigate these new effects in some detail we have focused upon one transition between purely dissociative intermediate and final states. Various regimes of excitation energy have been studied. The two limiting cases are represented by on-resonance excitation, where the spectrum is similar to the broad-band spectrum, and far off-resonance excitation, which leads to a true short-time behaviour. In between these limits, i.e. upon detuning the excitation energy away from the resonance, two striking

![Graph of kinetic energy vs. time](image)

**Fig. 10.** 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 chosen to be 0.2 eV. The zero of the time scale is defined by the maximum of the excitation pulse. It can be seen that the ‘atomic peak’ develops after the ‘three peak structure’ has been established. Note that the intensity scale changes between the different plots.
effects have been found to take place: a general quenching of the atomic lines and, for small detuning towards higher excitation energies, the formation of a strong interference structure in the spectra. Both effects are connected with the energy selectivity of the excitation. Upon detuning, narrow-band excitation selects a ‘wrong’ energy region characterized by poorer Franck–Condon overlaps, leading to a decrease of the effective life-time of the intermediate state. This explains the suppression of the atomic lines, whose appearance is a long-time effect because the dissociation of the molecule has to take place before decay. When selecting an energy region not too far away from the resonance, parts of the intermediate state wave packet with the ‘correct’ energy survive the excitation pulse. Therefore, whereas off-resonance the intermediate-state wave packet $\Psi_d(t)$ describes a direct dissociation and leaves the zone of its creation very quickly, higher excitation energies allow parts of $\Psi_d(t)$ to remain longer in the molecular region because there is now enough kinetic energy opposing direct dissociation. Depending on how long the created parts of $\Psi_d(t)$ remain in the initial region, the nodal structure of the eigenvectors of the selected energy region may be forced by interference upon $\Psi_d(t)$. This structure is directly transferred to the Auger spectrum by a simple ‘mapping effect’: owing to the dissociative character of the final state, transitions at larger internuclear distances contribute at higher Auger energies.

The time-dependent approach used here offers great advantages for the understanding of these effects compared with the conventional time-independent picture. By enabling the time resolution of all the physically relevant quantities, novel insights into the process and thus a deeper understanding of the underlying mechanisms can be achieved. In particular, by looking at the time evolution of the intermediate state wave packet, it was possible to identify the exact nature of the interference effects induced by selective excitation. The time-dependent theory also permits us to trace observable processes such as the formation in time of the Auger spectrum. This can indeed, at least in principle, be investigated experimentally by a time delayed depopulation of the intermediate decaying state.

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