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Core-level spectroscopy and dynamics of free molecules

R. Feifel^{1,*} and M.N. Piancastelli¹

¹*Department of Physics and Astronomy, Uppsala University, Box 516, SE-751 20 Uppsala, Sweden*

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A review of recent results on spectroscopy and dynamics of free molecules is presented. The experimental research reported here is mainly concerned with processes of core excitation and decay of isolated molecules, primarily investigated by resonant Auger spectroscopy. Several examples are shown concerning the interplay of the timescales of electron decay with nuclear motion involving dissociation processes, the occurrence of interference phenomena and recoil. The capability of such studies to reveal subtle details of the light-matter interaction, of the electronic structure and of the evolution of the short-lived states thus created is enlightened.

INTRODUCTION

The investigation of structure and dynamics of core-excited and core-ionized molecules with experimental techniques based on synchrotron radiation as ionizing source has been established as a very powerful tool during the last two decades. Here we review some of the most recent developments, focusing on the decay dynamics of core-excited species.

The simultaneous implementation of narrow-bandwidth synchrotron radiation sources and high-resolution electron energy analyzers in recent years has given a tremendous impulse to the development of new research trends in the field of atomic and molecular resonant excitation and subsequent radiative and non-radiative decay.

In resonant photoemission studies of gas-phase molecules, the exciting photon energy is tuned to one of the core-excited states (unoccupied molecular orbitals or Rydberg states) which exist below an ionization threshold. The neutral intermediate state prepared in this way has a relatively short lifetime and subsequently decays by emitting electrons or photons (non-radiative or radiative decay). In non-radiative decay processes, the core hole is filled, and a valence electron is emitted. Electron decay spectra include features related to valence single-hole states (due to so-called participator decay), or valence two-hole/one-particle states (due to so-called spectator decay). This phenomenon is known as resonant Auger decay.

Several comprehensive review papers have been published in recent years dealing with core excitation-deexcitation processes in isolated molecules (see e.g. Refs. [1–6]). In the present review we will be mostly concerned with new developments which have taken place in the last few years, but we will also refer to some material already included in Refs. [1–6] when we consider a topic being of particular importance.

We will concentrate on works concerning core-to-bound excitations in isolated molecules and subsequent electron decay investigated under the so-called Auger resonant Raman (ARR) conditions [7]. The analogous

research line where radiative decay is investigated will not be reviewed here, although comparably interesting results have been obtained in narrow-bandwidth resonant X-ray emission studies. Furthermore, we will mainly focus on the experimental findings, and shall discuss theoretical aspects, which were often developed hand-in-hand with the experiments, only briefly where necessary.

The main topics treated in the following sections are:

Nuclear Motion in Core-Excited Systems: We will describe how the nuclear motion in the core-excited state is reflected in the vibrational distribution of the final states reached after resonant Auger decay. In particular, we will provide examples of cases where the geometry of the intermediate state is different from that one of the ground state, i.e. cases where the molecule deforms upon core excitation. Another important category of nuclear motion affecting the resonant Auger decay concerns linear triatomic molecules which in the intermediate state relax via Renner-Teller splitting into two states, a bent and a linear one, slightly separated in energy. Some examples of this behaviour will be described.

Interference Phenomena: One of the basic interference mechanism known to show up in resonant Auger electron spectra, lifetime vibrational interference, is briefly recapitulated. Subsequently, we will discuss some of the most recent findings which comprise an interference quenching of a vibrational line upon photon energy detuning and bond distance dependent Auger transition rates. Furthermore, examples where the resonant and direct scattering channels interfere are discussed.

Ultrafast Dissociation and Doppler Effect: We will describe several new cases where dissociation processes occur on the low femtosecond time scale, leading either to sharp atomic or vibrationally excited molecular fragment species. We shall come across a novel interference mechanism, which involves non-fragmented and fragmented Auger decay channels. As another new phenomenon which is found in ultrafast dissociating systems, we will discuss the resonant Auger electron

Doppler effect, and we will elucidate, for several systems, dynamic information obtainable from the analysis of this effect.

Resonant Auger Decay Near Threshold: A comparison between resonant Auger decay spectra recorded for excitations to neutral Rydberg states close to the ionization threshold and a normal Auger spectrum will be presented, and their interconnection will be discussed. The complexity of below threshold, near-edge X-ray absorption fine structure resonances will be exemplified.

Above Threshold Resonances: The above-threshold region is characterized by the presence of an ionization continuum. However, resonant features are still possible, superimposed to this continuum. In particular, a gross subdivision can be made between one-electron processes, namely shape resonances, and multi-electron processes such as neutral states created by the simultaneous excitation of one core and one valence electron. We will present one example of the shape resonance affecting the vibrational distribution of states reached after normal Auger decay, together with some examples of decay of multiply-excited neutral states embedded in ionization continua.

Recoil Effects: For this category of phenomena, we deal with direct (as opposed to resonant) photoemission. Very interesting results have been reported in the last four years concerning recoil phenomena, and in particular inelastic momentum transfer from the outgoing photoelectron to the nucleus where the electron vacancy is created, with consequent non-Franck-Condon effects in the vibrational structure of the photoline. We will describe the few known examples of recoil in both core and valence ionization.

NUCLEAR MOTION IN CORE-EXCITED SYSTEMS

When a core electron in a molecule is excited, the core hole can relax by non-radiative decay, i.e. by resonant Auger electron emission. The core-hole decay takes place on a typical time scale of few or few tens of femtoseconds. This time scale is in the same order of magnitude as the period of molecular vibrations and thus a signature of nuclear motion is likely to be detected in the decay spectra. Within a semiclassical picture, as soon as a wave packet is created on the potential energy surface of the neutral core-excited state by photoabsorption, this wave packet starts to propagate, exploring details of this intermediate state potential energy surface and, at the same time, decaying to various final ionic states. Due to this so-called dynamical Auger emission [8–10], the resonant Auger line profile measured will directly reflect the nuclear motion taking place in the core-excited state modulated by its relative shape and position with respect to the poten-

tial energy surface of the final state reached by Auger decay.

If the lifetime of the core-excited state is longer than one period of molecular vibrations, the natural linewidth is smaller than the vibrational spacing, and the excitation to a specific vibrational level will occur for a sharp bandwidth of the incident photon. In this situation, the deexcitation spectrum can be approximately described by a Franck-Condon factor between the core-excited state and final states of the decay. On the other hand, if the lifetime is shorter than the vibrational period, one can no longer say which vibrational level is excited, and a coherent nuclear motion will be induced as a result of interference between excited vibrational levels; this type of interference and others will be discussed in more detail in the subsequent section. When the lifetime is not much shorter than the vibrational period, this nuclear motion will be reflected in the Auger electron spectral shape.

Such phenomenon may affect the electronic decay and also the fragmentation dynamics in case of dissociative core-excited states. While the so-called ultrafast dissociation will be treated in another section of this paper, here we concentrate on cases where the geometry of the intermediate state is different from the one of the ground state. As an example, core-excited states of linear molecules can be bent and those of planar molecules can be pyramidal. In such a case, the molecule begins to deform just after the core excitation. In more complex cases, a core-excited linear molecule can undergo Renner-Teller splitting to stabilize the intermediate state, and this Renner-Teller effect has visible consequences in the vibrational distribution of the final states reached after resonant Auger decay. We will provide some examples in what follows.

The first example is the observation of nuclear motion effects in core-excited boron trifluoride. Following B1s core excitation of BF_3 , it was shown that the nuclear motion for the molecular deformation can be observed by resonant Auger spectroscopy [8].

The BF_3 molecule is a planar molecule with D_{3h} symmetry. The B1s excitation (absorption) spectrum shows a strong resonance $\text{B1s} \rightarrow 2a_2''$ below the B1s ionization threshold [8]. Extensive studies on this resonance and its decay dynamics revealed that the molecule deforms to the C_{3v} pyramidal structure following the $\text{B1s} \rightarrow 2a_2''$ excitation in competition with the electronic decay.

The electronic decay following the $\text{B1s} \rightarrow 2a_2''$ excitation consists of the spectator Auger decay and the participator Auger decay. The dynamical aspect of the molecular deformation in the core-excited state is directly reflected in the spectrum because the Auger decay occurs while the nuclear motion proceeds.

In Fig. 1 taken from Ref. [8], resonant Auger spectra following the $\text{B1s} \rightarrow 2a_2''$ excitation of BF_3 are shown.

The resonance enhancement is significant for the $1a''$, $2e'$, and $2a_1'$ final ionic states. The participator Auger spectrum has a long tail toward the low kinetic energy side, though such a tail does not appear in the corresponding non-resonant photoemission peak [8]. A linear dispersion of kinetic energy of the participator Auger electrons, as well as a non-dispersion of kinetic energy of the spectator Auger electrons as a function of photon energy is evident in Fig. 1. The non-dispersion of the spectator Auger kinetic energy with the photon energy implies that the potential surfaces of the spectator Auger final states are nearly parallel to the potential surface of the intermediate core-excited state and therefore unstable along the coordinate corresponding to the out-of-plane vibration, in the vicinity of the equilibrium geometry of the ground state where the excitation takes place. In such a case the decay leading to the spectator Auger peak occurs perpendicularly downward in the configuration coordinate space because of the orthogonality of the vibrational states. Thus, the kinetic energy of the ejected electron, which corresponds to the energy difference between the initial and final states of the decay, is constant irrespective of the excitation photon energy. In case of participator Auger decay, the final state adiabatic potential is stable at the origin along the out-of-plane vibration coordinate. The prominent peak of the participator Auger spectral region, which shows the linear dependence on the photon energy, corresponds to the prompt decay near the origin where the excitation takes place, and thus to a decay process where the coherence is maintained throughout the whole process in the resonant Auger emission.

A long tail is also observed in the participator Auger lines towards the higher binding energy (i.e. lower kinetic energy). This tail is a consequence of the nuclear motion in the $B1s \rightarrow 2a_2''$ excited state. If the B atom begins to move to the out-of-plane direction immediately after the core excitation, the kinetic energy of the Auger electron would be decreased by the energy conversion to the nuclear motion in the core-excited state.

Such long tail was investigated in more detail in a subsequent study [9], where it was shown that the excitation of the out-of-plane bending mode in the intermediate state, related to a dramatic geometry change, induces an exceptional excitation of this mode in the final ionic states. A local intensity enhancement at the outer classical turning point of the intermediate state potential energy curve is responsible for the observed broad structures within the tail. Moreover, their photon-energy dependence allows mapping the potential energy curves of these states over a wide energy range along the out-of-plane bending coordinate.

Similar effects have been reported for the analogous system BCl_3 [10]. In this system, Auger emission following the $B1s$ excitation to the unoccupied $4e'$ orbital enhances the shoulder structure in the low kinetic en-

FIG. 1. Observed (a) and calculated (b) resonant Auger spectra in BF_3 . The participator and spectator Auger spectra are shown in the left hand and right hand panels, respectively. The results for the excitation at the $B1s \rightarrow 2a_2''$ resonance and for 200 meV lower and higher photon energy with respect to the resonance peak are shown. See Ref. [8] for details. Reproduced with permission.

ergy side of the photoemission from the $2e'$ final state. This shoulder structure is interpreted as the dynamical Auger emission which reflects the B-Cl stretching nuclear motion and appears as a result of the purely multi-state vibronic coupling effect among the Jahn-Teller split $B1s^{-1} 4e' E'$ states and the closely lying $B1s^{-1} 3a_1' A_1'$ state.

Another example of nuclear motion being reflected in the vibrational distribution of Auger decay spectra is the core excitation-decay in water. It has been shown that the two-dimensional nuclear motion of the Auger final state can be probed by resonant Auger spectroscopy, and furthermore that it can be mediated by sampling a different portion of the potential curve and changing the nuclear motion in the core-excited state [11].

Fig. 2 taken from Ref. [11] shows the electron emission spectra of H_2O recorded at four different photon energies across the $O1s \rightarrow 2b_2$ resonance together with calculated vibrational progressions. The spectra cover the binding energy region 17.0 - 20.0 eV, where the B band corresponding to electron emission from the $1b_2$ orbital is present. The bottom spectrum (a) was recorded at the foot of the $O1s \rightarrow 2b_2$ resonance and thus can be considered close to the direct photoemission. Vibrational frequencies of 375 and 203 meV for symmetric stretching (ν_1) and bending (ν_2) modes, respectively, are present for the B band. In the case of direct photoemission, both modes are highly excited, exhibiting a very broad band structure (spectrum (a))

FIG. 2. Continuous and dashed curves: measured and calculated resonant Auger spectra of H_2O for decay to the $1b_2^{-1}$ Auger final state at various excitation energies across the $\text{O}1s \rightarrow 2b_2$ band. Photon energies and corresponding vibrational components in the core-excited state are also displayed. The vertical bars represent the calculated vibrational components. See Ref. [11] for details.

in Fig. 2). The other three spectra in Fig. 2(b) - (d) were recorded at approximately the photon energies of the (0,0), (1,0) and (2,0) components, respectively, of the $\text{O}1s \rightarrow 2b_2$ band, where (0,0) is the vibrational ground state and (1,0) and (2,0) refer to one and two quanta of vibrational excitation in the stretching mode.

In the work of De Fanis et al. [11], the observed vibrational structure is attributed mostly to the ν_2 mode. The vibrational structure becomes less resolved at the $\text{O}1s \rightarrow 2b_2$ (1,0) excitation (cf. spectrum (c)) and at the (2,0) excitation (cf. spectrum (d)). The band peak appears at higher binding energy when the excitation energy is increased, indicating that higher vibrational components are excited in the Auger final state.

With the aid of *ab initio* calculations, the following picture was developed: Both the experimental and theoretical data clearly show that the intensities of the final state vibrational components change dramatically, depending on the excitation energy. The most interesting finding is that this mode selectivity decreases when the excitation energy is increased. At the $h\nu = 535.95$

eV excitation, in addition to the $(1, \nu_2)$ main progression, also the $(0, \nu_2)$ and $(2, \nu_2)$ progressions were identified [11]. At the $h\nu = 536.12$ eV excitation, the intensity of the $(2, \nu_2)$ components is comparable to those of the other components.

As a result, many more vibrational components pile up to form the unresolved band that can be seen in Fig. 2(d). The calculations show that symmetric stretching and bending motions are not completely separated where the wavefunctions overlap with those of the core-excited state. In such a case, the ν_1 and ν_2 modes have both symmetric stretching and bending characters. The ν_1 and ν_2 modes in the core-excited state also have both symmetric stretching and bending characters as pointed out previously. These two modes are however significantly different in the core-excited state and in the Auger final state. As a result, the ν_1 mode caused in the core-excited state can be transferred not only to the ν_1 mode but also to the ν_2 mode in the Auger final state. In this way, complex two-dimensional nuclear motion is stimulated in the Auger final state by the Auger resonant process via the $(\nu_1, 0)$ components in the core-excited state. In the work of De Fanis et al. [11] it was confirmed that indeed the two-dimensional nuclear motion of the Auger final state is mediated by tuning the incident energy to different portions of the core-excited state.

Another series of examples will be given concerning linear molecules whose core-excited states can be split by Renner-Teller effect, and in which such splitting is reflected in the resonant Auger decay.

In the linear molecule N_2O , the role played by the Renner-Teller effect on the electronic decay spectra of the core-excited $\text{N}_t 1s \rightarrow \pi^*$ was emphasized, together with the contribution of the nuclear motion in the core-excited state to the vibrational energy distribution of the $\text{X}^2\Pi$ electronic ground state of the N_2O^+ ion created through resonant Auger decay [12]. The investigation was made by combining high resolution resonant Auger spectroscopy and *ab initio* quantum chemical calculations for the three-dimensional potential energy surfaces of the ground, core-excited and final states, as well as for the Auger transition rates.

The participating Auger decay mainly populates the $\text{X}^2\Pi$ ground state of N_2O^+ . The vibrational intensity distribution in the $\text{X}^2\Pi$ electronic state shows some significant evolution when the photon energy is scanned through the $\text{N}_t 1s \rightarrow \pi^*$ resonance profile. N_2O is known to undergo a conformational change from linear ($\text{C}_{\infty v}$ point group) to bent (C_s point group) which takes place when a $\text{N}1s$ or $\text{O}1s$ core electron is promoted into the unoccupied π^* molecular orbital. Upon bending, the degeneracy of the π^* orbitals is lifted, giving rise to a' (in-plane) and a'' (out-of-plane) orbitals in the C_s symmetry. The $\text{N}_t 1s \rightarrow a'^*$ and $\text{N}_t 1s \rightarrow a''^*$ core-excited states were shown to correspond to bent and

FIG. 3. Resonant Auger decay spectra of the $N_t 1s \rightarrow \pi^*$ core-excited state in N_2O to the $X^2\Pi$ electronic ground state. The spectra were recorded for photon energies lower than the resonance maximum ($\Omega < 0$): $h\nu = 400.1, 400.5, 400.7, 400.9, 401.0, 401.1, 401.2$, and 401.3 eV (resonance maximum), respectively. See Ref. [12] for details.

linear structures, respectively, the $N_t 1s \rightarrow a'^*$ state being lowered in energy by bending of the molecule. This behavior can be rationalized by the Renner-Teller effect [12].

Due to linear conformation of the molecule in the ground state, and using the Franck-Condon principle for the $N_t 1s \rightarrow \pi^*$ transition, the bending mode will be strongly excited when the photon energy is tuned below the resonance maximum (negative detuning), while only stretching modes can be effectively excited when the photon energy is tuned above the resonance maximum (positive detuning).

Figs. 3 and 4 taken from Ref. [12] illustrate the resonant Auger decay spectra of the $N_t 1s \rightarrow \pi^*$ core-excited state to the $X^2\Pi$ electronic ground state of N_2O^+ measured for various excitation energies along the π^* resonance profile for negative (cf. Fig. 3) and positive (cf. Fig. 4) photon energy detunings. The energy distribution between the normal modes is fundamentally different in the two cases: while for positive detuning the N-N stretching mode is the most active ($\nu_3 = 0.22$ eV), for negative detuning no stretching vibrational progression can be observed, suggesting that the unresolved ($\nu_2 = 0.051$ eV) bending mode is mostly active. Moreover, when increasing the photon energy from 400.1 to 402.5 eV, one can observe a continuous transition from the situation where the bending mode is mainly populated to the one where the N-N stretching mode is populated, exactly as one would expect by considering the continuous transition discussed above from a bent to a linear core-excited state configuration.

In the case of another linear molecule, CO_2 , the core-excited $C 1s \rightarrow \pi^*$ state is separated by Renner-Teller

FIG. 4. Resonant Auger decay spectra of the $N_t 1s \rightarrow \pi^*$ core-excited state N_2O to the $X^2\Pi$ electronic ground state. The spectra were recorded for photon energies higher than the resonance maximum ($\Omega > 0$): $h\nu = 401.3$ (resonance maximum), 401.4, 401.5, 401.6, 401.7, 401.9, 402.1, and 402.5 eV, respectively. See Ref. [12] for details.

splitting into two states. The lower energy state has a bent equilibrium geometry and is reached by excitations to the π^* orbitals that lay in the bending plane of the molecule. The higher-energy linear state is formed by excitations to the out-of-plane π^* orbitals. The two Renner-Teller split components merge into one broad peak in the photoabsorption spectrum.

The Auger electron spectra, measured at a number of photon energies across the absorption peak [13, 14], are shown in Fig. 5 taken from Ref. [14]. Strong resonant enhancement is evident only for the $A^2\Pi_u$ state, which also shows dramatic changes of the vibrational envelope. The spectra in Fig. 5, taken from Ref. [14], can be divided into two groups with different behavior: in the spectra recorded below 290.7 eV photon energy (spectra A-C in Fig. 5) the shape of the vibrational envelope of the $A^2\Pi_u$ state changes little, only its absolute intensity increases towards the resonance maximum; in the spectra above 290.7 eV (spectra E-G in Fig. 5), strong redistribution of the vibrational intensity takes place.

The behavior of the vibrational structure in the Auger spectra can be related to the decay of the bent or linear core-excited intermediate states. The bent state is expected to be populated at the lower photon energy side of the absorption peak, while the linear state becomes accessible only at higher photon energies.

The vibrational structure of the Auger electron spectra is sensitive to the excitation energy. In particular, the decay of the bent and linear Renner-Teller split components of the $C 1s \rightarrow \pi^*$ state produces clearly different vibrational patterns. The numerical simulations in Ref. [14] explain the characteristic features in the Auger electron spectra excited at the lower part of

FIG. 5. Resonant Auger electron spectra in CO_2 . Labels refer to the photon energies across the $\text{C}1s \rightarrow \pi^*$ resonance where spectra were taken (see Ref. [14]). Also shown is a non-resonant valence photoelectron spectrum (V), taken at 280 eV photon energy. See Ref. [14] for details. Reproduced with permission.

the absorption peak. Here, mainly the bent Renner-Teller component is populated by photoabsorption. It is clear that the Auger electron spectrum originates from several closely spaced bending mode vibrational levels of the bent intermediate state. That is indeed the case in Fig. 5 (spectra A-C) taken from Ref. [14]. The above-described features are related to the bending mode vibrations of the bent core-excited state. Strong excitations of the symmetric stretch mode in the photoabsorption to the bent state is not expected, based on the $Z+1$ model.

In the excitation and decay of the linear state, (spectra E-G in Fig. 5 taken from Ref. [14]) the bending vibrations do not play a major role. The vibrational structure observed in the Auger spectra is mainly due to the symmetric stretch excitations. A strong photon energy dependence appears, since higher vibrational levels of the linear state are excited as the photon energy increases and they have completely different overlap with the final state vibrational wavefunctions.

It was concluded from the analysis of the Auger electron spectra that high levels of the bending vibrations

of the bent state are excited in photoabsorption and the symmetric stretching excitations play only a minor role. In contrast, higher levels of symmetric stretch vibrations can be excited in the photoabsorption to the linear component, for which the bending mode excitations are much less important. The photon energy-dependent features in the resonant Auger spectra were explained using these main characteristics of the core excitations [14].

INTERFERENCE PHENOMENA

In the previous section, we discussed some cases where the nuclear motion in the core-excited state is reflected in the vibrational intensity distribution of the final electronic states reached by resonant Auger decay. This was possible since the time scale for the core-hole decay via Auger emission is similar to the nuclear motion. If the natural lifetime width of the core-excited state is in the same order of magnitude as the vibrational spacing of the intermediate state potential energy surface, the vibrational levels in the core-excited state overlap, as schematically shown in Fig. 6, and hence get coherently excited. In analogy to light diffraction by a grating, the intermediate electronic state (denoted as (c) in Fig. 6) decays via a manifold of possible pathways to one of the possible final states (denoted as (f) in Fig. 6), giving rise to constructive or destructive interference pattern observable in the resulting resonant Auger electron spectrum. This is referred to as Lifetime Vibrational Interference (LVI), which has been predicted and theoretically described by Gel'mukhanov and co-workers in the 1970's using the so-called Kramers-Heisenberg formalism [15]. Since then, it was experimentally identified in several experiments like e.g. the first $\text{C}1s \rightarrow \pi^*$ resonant Auger spectrum for CO, excited by narrow monochromator bandwidth synchrotron radiation, where it gave rise to modulations of the final state vibrational intensity distributions which could not be explained by a simple Franck-Condon two-step excitation-deexcitation picture [16]. A more recent study of LVI can be found, for instance, in Ref. [17].

Generally, with resonant Auger electron spectroscopy, one probes different parts of the final state potential curves compared to conventional valence photoelectron spectroscopy, as has been demonstrated in several works (see e.g. Ref. [18] and references therein). Furthermore, the vibrational intensity distribution in the final state may vary strongly upon tuning of the excitation energy across the intermediate resonance state [16, 19].

Fig. 7 taken from Ref. [20] shows, as a first example, experimental and numerically calculated resonant Auger spectra for the decay into the singly-ionized

FIG. 6. A schematic figure illustrating Lifetime Vibrational Interference (LVI). Due to the core-hole lifetime width Γ being in the same order of magnitude as the vibrational spacing, the vibrational sublevels in the core-excited state overlap and hence get coherently excited. Several decay paths are possible, giving rise to interference in analogy to light diffraction by a grating. Also indicated is the direct pathway from the neutral ground state to the final ionic state, which can interfere with the resonant channel.

$X^2\Sigma_g^+$ (right panel) and the $B^2\Sigma_u^+$ (left panel) final states of N_2 for different photon energy detunings Ω relative to the adiabatic (0-0) transition of the $N1s \rightarrow \pi^*$ resonance at 400.88 eV (for the absorption spectrum, see e.g. Ref. [21]). Off-resonance spectra recorded at a photon energy of 95 eV are also included for comparison. In the spectra marked with a star, an artificial line contribution due to Stokes doubling (see e.g. Ref. [22] and references therein) was removed.

As one can see from this figure, for both final states presented, the vibrational intensity distribution measured on top of the resonance ($\Omega = 0$) is very different from the one in the corresponding valence band photoelectron spectrum measured at 95 eV, and the relative vibrational intensity distribution within each final state varies as a function of photon energy detuning. In particular, the vibrational fine structure resembles the intensity distribution of the direct photoionization spectrum after a comparatively small detuning value Ω (X-state: $\Omega = -150$ meV; B-state: $\Omega = -500$ meV). This observation is also known as the collapse of vibrational fine structure in the Auger resonant Raman spectrum upon photon energy detuning of the exciting radiation [20, 23, 24]. It was first observed by Sundin et al. [23, 24] for negative sub-eV energy detuning relative to the $\nu' = 0$ component of the $C1s \rightarrow \pi^*$ resonance in CO for the decay into the singly-ionized $X^2\Sigma^+$ final state of this system. The basis of this effect can

FIG. 7. Experimental and numerically calculated resonant Auger spectra for the decay into the singly-ionized $X^2\Sigma_g^+$ (right panel) and the $B^2\Sigma_u^+$ (left panel) final states of N_2 for different photon energy detunings Ω relative to the adiabatic (0-0) transition of the $N1s \rightarrow \pi^*$ resonance. All spectra are normalized to the same area of the final state vibrational line $\nu'' = 0$. See Ref. [20] for details.

be traced to the duration time of the scattering process [25] and to the relative positions of the potential energy curves of the neutral ground, core-excited, and final ionized states. In particular, the collapse effect is observable if the ground and the final state potential curves have very similar equilibrium bond distances. In this case, when the excitation energy is detuned from the nominal resonant energy, the scattering duration time will be drastically reduced compared to the core-hole lifetime. The nuclear wave packet does not have time to develop in the core-excited state, but the molecule will almost instantaneously decay into the final state [23, 24]. The vibrational intensity distribution in the Auger spectrum collapses into that of the direct photoionization spectrum for a detuning Ω for which the resonant cross section is still much larger than the direct cross section. As discussed in the original work of Sundin et al. [23], the relative intensity follows a smooth, monotonous function of detuning Ω . It should be noted that this is a pure resonant effect.

In comparing the numerical simulations shown in Fig. 7 taken from Ref. [20], which take only the resonant pathway into account, one can see that the quantitative agreement for the $B^2\Sigma_u^+$ is not very good, even though the breakdown of the very long resonant progression is also mimicked numerically. In particular, discrepancies are encountered in some of the spectra for the two lowest vibrational components ($\nu'' = 0$ and $\nu'' = 1$) of this final state, due to the fact that the direct channel cannot be neglected for this final state as we will discuss further below. However, for the X-state, the simulated spectra reproduce the experimental data to a very high degree of accuracy.

FIG. 8. The ratio $\nu'' = 1/\nu'' = 0$ of the integrated intensities for the singly-ionized $X^2\Sigma_g^+$ final state of N_2 as a function of photon energy detuning Ω . Both experimental and theoretical values are presented. Values derived from spectra showing a Stokes line in the binding energy of region of interest are marked in this figure by the shaded region labeled "Stokes doubling". See Ref. [20] for details.

By looking more closely into the evolution of the X-state progression, one can see that for increasingly negative detuning, the $\nu'' = 1$ component decreases in intensity compared to $\nu'' = 0$ until it has almost completely vanished at $\Omega = -500$ meV, and then it grows again. In order to illustrate this behaviour, the ratio of $\nu'' = 1$ and $\nu'' = 0$ integrated intensities as a function of detuning Ω is plotted in Fig. 8 taken from Ref. [20], both for the experimental and numerical X-state spectra. As one can see, both the experimental and numerical curves show a non-monotonous form with a minimum for a photon energy detuning of $\Omega = -500$ meV, which is qualitatively different from e.g. the CO case of Sundin et al. [23].

This 'interference quenching' of the $\nu'' = 1$ vibrational line of the $X^2\Sigma_g^+$ in N_2 has been analysed in Refs. [20, 26] in details using the Kramers-Heisenberg formalism, and models were developed which show a direct relation between the detuning value at which this minimum is observed and the equilibrium bond

FIG. 9. Left: experimental resonant Auger decay spectra of $N1s \rightarrow \pi^*$ excited N_2 to the singly-ionized $B^2\Sigma_u^+$ final state measured at photon energies (bottom to top): 400.88, 401.10, 401.32, 401.54, 401.76, 401.98 and 402.20 eV, corresponding to excitation to the $\nu' = 0 - 6$ vibrational components of the core-excited state. For the sake of comparison, the spectra are scaled such that the intensity of the lowest binding energy peak is always the same. Right: $N1s \rightarrow \pi^*$ absorption curve plotted to show the one-to-one connection between the decay spectra and the vibrational peaks in the intermediate state. See Ref. [27] for details.

distance R_c^0 of the core-excited state. I.e. a new way was established of determining the equilibrium bond distance for the core-excited state.

Also positive photon energy detuning can result in peculiar behaviour of the vibrational intensity distribution in the final electronic state. A very interesting case was found for the $B^2\Sigma_u^+$ final state of N_2^+ which is shown in Fig. 9 taken from Ref. [27]. The spectra were measured at photon energies corresponding to the maxima of the $\nu' = 0 - 6$ vibrational components of the intermediate state. When the lowest vibrational state of the core-excited N_2 is selected, one notes only one group of vibrational peaks in the decay spectrum. When higher vibrational excitations are selected, one notes that the vibrational peaks become divided into two groups, one at a lower and one at a higher binding energy. Furthermore, in between the two groups of lines the spectra show less and less structure, eventually becoming totally flat at the excitation energy corresponding to $\nu' = 5$.

The simplest qualitative explanation which accounts for the gross features of the spectra relies on the reflection principle and the possibility of mapping the in-

intermediate state vibrational wavefunctions. Classically speaking, the vibrational kinetic energy tends to zero at the inner and outer turning points of the intermediate state potential curve, where the system resides for a longer time. If the potential curve of the final state is sufficiently different from that of the intermediate state, as is the case for the B-state [27], the resonant Auger decay will sample two different subregions of the vibrational envelope of the final state, with a region in between where the transition amplitude is lower. This is, of course, a very simplified picture but it is important to note that the position of the maxima of the two groups gives direct information about the classical turning points, thus a simple procedure to map the potential curve could be devised.

In order to obtain a deeper understanding of the observations made, in particular of the essentially flat part in between the two groups of vibrational structure, various sets of numerical simulations were carried out in the work of Piancastelli et al. [27], and in extension to that, in the work of Salek et al. [28]. These theoretical calculations showed that the interference between direct and resonant photoemission, as schematically indicated in Fig. 6 above, is important in the case of the singly-ionized B-final state of N_2 , and a strong geometry dependence of the decay probability on the bond distance is present. The latter implies that the first electronic state of $2\Sigma_u^+$ symmetry needs to be described adequately as a superposition of at least two electronic configurations, one one-hole and one two-hole/one-particle states, which means that the otherwise useful distinction between participator and spectator decay breaks down completely in this particular case. Due to an avoided crossing, the CI coefficients depend substantially on the bond distance which, in turn, implies that the deexcitation transition probabilities are not independent of the bond distance as assumed in the Franck-Condon approximation.

Another case of a significant bond distance dependence of the Auger transitions rates has been reported by Sorensen et al. [29] for the decay of $O1s \rightarrow 1\pi_g^*$ excited molecular oxygen to the singly-ionized $X^2\Pi_g$ state. The interested reader is referred to Ref. [29] for a detailed discussion.

Furthermore, prominent cases where the interference between the direct and resonant channels turns out to be significant were found more recently in $O1s \rightarrow 2\pi^*$ excited CO, both for positive photon energy detuning (see the work of Tanaka et al. [30]) and for negative photon energy detuning (see the work of Feifel et al. [31]). In particular, in the work of Feifel et al. [31] the quenching and restoring of the entire $A^2\Pi$ final state of CO^+ is reported for photon energy detuning below the adiabatic 0-0 transition of the $O1s \rightarrow 2\pi^*$ resonance. This finding is explained in terms of a Fano interference between the direct and resonant photoionization channels

FIG. 10. Experimental and numerical resonant Auger spectra of N_2 for the three outermost singly-ionized final states $X^2\Sigma_g^+$, $A^2\Pi_u$ and $B^2\Sigma_u^+$, for positive photon energy detuning. The numerical spectra are based only on the resonant pathway. Resonant excitation to certain core-excited vibrational levels is considered. The highest panels show the valence photoelectron spectra measured at 95 eV. So-called resonant and vertical bands are marked by labels R and V, respectively. See Ref. [32] for details.

in the presence of strong lifetime vibrational interference.

In the next section, where we discuss ultrafast dissociation of core-excited molecules, we will meet another, novel type of interference effect, which involves so-called molecular (early) and fragment (late) Auger decay channels. This interference effect can, in a certain sense, be regarded as the counterpart to lifetime vibrational interference for a repulsive intermediate state.

Before concluding this section, we would like to make a general remark. Fig. 10 taken from Ref. [32] shows experimental and numerical resonant Auger spectra of N_2 for the three outermost singly-ionized final states $X^2\Sigma_g^+$, $A^2\Pi_u$ and $B^2\Sigma_u^+$, for positive photon energy detuning. The numerical spectra are based only on the resonant pathway, which is fine for the $X^2\Sigma_g^+$ and $A^2\Pi_u$ states, but which is somewhat shortcoming for the $B^2\Sigma_u^+$ final state as discussed above; the latter is, however, not crucial in the present context. As one can see from this figure, upon positive photon energy detuning, the vibrational fine structure breaks up into two groups, not only for the $B^2\Sigma_u^+$ as already discussed above, but also for the $X^2\Sigma_g^+$ and $A^2\Pi_u$ states.

As discussed in Ref. [32] this spectral behaviour can be understood in terms of fast "vertical" (labeled as V in Fig. 10) and slow "resonant" (labeled as R in Fig. 10) scattering channels which compete with each other. The fast and slow or early and late Auger decay channels are central for the next section.

FIG. 11. A schematic and simplified representation of the ultrafast dissociation process in water. Shown is a cut through the three-dimensional H_2O^+ potential energy surface along the HO^+-H bond direction. See Ref. [38] for details.

ULTRAFAST DISSOCIATION

Ultrafast dissociation is the terminology used for dissociation processes taking place on a time scale comparable to that of the Auger decay, which is typically in the low femtosecond time regime. It has pioneeringly been observed for core-excited HBr [33], and has since then been found for other systems such as HCl [34, 35], H_2S [36, 37], and many more, some of which we shall enlighten in this section and in the subsequent one.

Since the early 1990's, there has been a long-standing discussion on the possible occurrence of ultrafast dissociation in core-excited water, leading to fragmentation into an excited OH species (which will be denoted as O^*H in what follows) and H (see e.g. Ref. [38] and references therein) as illustrated schematically in Fig. 11 taken from Ref. [38]. The first direct experimental evidence for ultrafast dissociation of molecular water came finally in 2001 from high resolution resonant Auger measurements made by Hjelte et al. [38] in the excitation energy region of the $\text{O}1s \rightarrow 4a_1^*$ resonance. It is based on qualitatively different behaviours of spectral features when the excitation energy is varied. As one can see from Fig. 12(a) taken from Ref. [38], there are two different types of behaviour encountered in the spectra; one set of spectral features exhibits a linear

kinetic energy dispersion as a function of photon energy detuning, whereas another set of features remains at constant kinetic energy. The dispersive features are identified in this work by Hjelte et al. [38] as participator or spectator transitions in the non-fragmented H_2O molecule and belong to the so-called early Auger decay events (cf. Fig. 11). The non-dispersive structures are identified as originating from so-called late Auger decays (cf. Fig. 11) in the O^*H fragment. The identification of the latter ones is strongly supported by *ab initio* calculations of the Auger decay of a $\text{O}1s \rightarrow 1\pi^*$ excited OH molecule, which is the intermediate electronic state reached by the O^*H fragment in the ultrafast dissociation process of H_2O [38]. In two of the fragment peaks (see Fig. 12(b) taken from Ref. [38]), there are transitions resolved which agree well with those calculated for the Auger decay of the vibrationally excited OH molecule. Furthermore, the intensity of this 'hot-band' like structure decreases with decreasing excitation energy, and its dynamics thus follows qualitatively the change in excess energy [38].

In a subsequent study, Hjelte et al. [39] investigated the resonant Auger decay of $\text{N}1s \rightarrow 4a_1^*$ core-excited ammonia, which is isoelectronic to the water molecule. Also for this hydride system, evidence for ultrafast dissociation has been found on the grounds of non-dispersive behaviour of spectral lines related to fragments. As the most likely dissociation pathway, the fragmentation into $\text{NH}_2^* + \text{H}$ was identified, based on both quantum chemical calculations and comparison with electron-ion coincidence measurements [39].

In a simplified picture, ultrafast dissociation of molecules can be thought as a two-step process: the first step is the excitation of a core electron from the neutral ground state to the dissociative intermediate state, where the molecule breaks apart, and the second step is autoionization in one of the fragments via late (cf. Fig. 11) Auger decay. Statistically, it is also possible that the Auger decay occurs before the molecule dissociates. As we have seen above, indeed both possibilities are experimentally observed and can be distinguished due to different dispersive behaviours upon photon energy detuning. In the case of diatomic systems, the late Auger decay gives rise to sharp atomic-like lines, whereas the early Auger decay leads to smooth molecular-like background caused mainly by electronic transitions near the equilibrium distance of the molecule (see e.g. Ref. [35] and references therein).

The two-step description, however, can be far too simple. It neglects, e.g., the interplay between two time scales, the photon energy-dependent duration time of the resonant X-ray Raman scattering (RXS) process [25] and the dissociation time, which are both in the range of a few femtoseconds. It also neglects possible interference between various scattering channels as

FIG. 12. Auger electron decay spectra of molecular water following $O1s \rightarrow 4a_1^*$ core excitation. The photon energy detuning is measured relative to the center of the $O1s \rightarrow 4a_1^*$ absorption band. (a) The dashed lines in the figure underline different dispersive behaviours of spectral features as the photon energy is varied. (b) An enlarged view of the vibrationally resolved fragment lines around 510 eV kinetic energy including OH final state assignments. See Ref. [38] for details.

schematically illustrated in Fig. 13 taken from Ref. [40].

The first experimental observation of such an interference between molecular and fragment contributions to the resonant Auger decay has been made by Feifel et al. [40] for Cl 2p core-excited HCl. As can be seen in the left panel of Fig. 14 taken from Ref. [40], an atomic spectral line develops into a negative spectral contribution, a "hole", when detuning the excitation energy from the maximum of the Cl $2p^{-1} \sigma^*$ resonance. Resonant X-ray scattering (RXS) theory quantitatively explains this observation as due to a novel destructive continuum-continuum interference between the molecular and atomic Auger decay channels. In contrast, the spectral hole is not present for DCl, as can be seen in the right panel of Fig. 14 taken from Ref. [40]. With the higher reduced mass for DCl, the dissociation time is

FIG. 13. Schematic illustration of possible interference channels of atomic-resonant, molecular-resonant, and molecular-direct contributions to the total RXS cross section. See Ref. [40] for details.

prolonged for this system. This influences both the relative weight and the relative phase between the atomic and molecular portions of the wave packet and thus the interference pattern. The observations are compatible only with a unified one-step description of the RXS process.

Often, the below core-threshold resonances are quite complex. One prominent example is the σ^* resonance region in $O1s$ core-excited O_2 , where both exchange splitting and molecular orbital-Rydberg character come into play. Furthermore, this resonance is known to be ultrafast dissociative [41]. By applying a filter-technique like e.g. constant-atomic-final-state yield spectroscopy, one can single out intermediate states of ultrafast dissociative character for such a complex resonance region. This has been demonstrated in a recent work of Hjelte et al. [42] for $O1s \rightarrow \sigma^*$ core-excited O_2 . In limiting the kinetic energy range of the photoelectron spectrometer to atomic fragment lines as indicated in Fig. 15 taken from Ref. [42], and in measuring the relative intensities of these lines as a function of photon energy, which is shown in Fig. 16 taken from Ref. [42], one can get a signature of the relative weight of the ultrafast dissociative character of such a resonance.

As this work of Hjelte et al. [42] shows, ultrafast dissociation occurs mainly within the Auger decays of intermediate resonance states contained within the low-energy part of the $O1s \rightarrow \sigma^*$ resonance of O_2 (cf. Fig. 16 taken from Ref. [42]). We shall come back to this resonance region further below (see section on Resonant Auger Decay Near Threshold).

DOPPLER EFFECT

The $O1s \rightarrow \sigma^*$ core excitation induced ultrafast dissociation of O_2 revealed historically an intriguing ef-

FIG. 14. Magnified $4\sigma^{-1}$ molecular part and the A atomic peak of resonant Auger decay spectra of HCl and DCl measured for various photon energies in the excitation region of the Cl $2p^{-1} \sigma^*$ resonance. The spectral hole, which is clearly visible for HCl at the photon energy detuning $\Omega = +1.9$ eV, has completely disappeared for DCl for the same detuning value. See Ref. [40] for details.

fect, a Doppler energy splitting of the atomic Auger emission lines [43] as e.g. discernable in some of the spectral lines of Fig. 15 taken from Ref. [42] or, in greater detail, in Fig. 17 taken from the original experimental work on this subject of Björneholm et al. [43]. Such a Doppler effect had been predicted prior to Ref. [43] by Gel'mukhanov and co-workers for other systems [25, 44].

A key point for the understanding of this effect is the partial alignment of the molecules during the resonant photoabsorption process. As discussed in the work of Björneholm et al. [43], the absorption cross section for the $O1s \rightarrow \sigma^*$ excitation is proportional to $\cos^2\Theta$, where Θ is the angle between the molecular axis and the polarization vector of the ionizing radiation. Molecules lying parallel to the polarization vector will be preferentially excited, resulting in the creation of a partially aligned ensemble of core-excited molecules within the

FIG. 15. Atomic Auger lines (with Doppler splitting; see next section) connected to different final ionic states produced by ultrafast dissociation in the $O1s \rightarrow \sigma^*$ resonance region of O_2 . See Ref. [42] for details.

FIG. 16. Relative intensities of atomic Auger lines of O_2 (see Fig. 15 for line assignment) as a function of photon energy in comparison to the near-edge X-ray absorption profile of O_2 . See Ref. [42] for details.

otherwise randomly distributed collection of molecules (cf. Ref. [43] and references therein). The partial alignment persists sufficiently long, since the Auger decay and dissociation processes occur typically on a time scale approximately 100 x shorter than the period of rotation around the molecular axis.

FIG. 17. Upper panel: resonant Auger spectrum of O_2 measured on top of the $O1s \rightarrow \sigma^*$ resonance of O_2 . Lower panel: Auger lines resulting from atomic oxygen subsequent to ultrafast dissociation of O_2 measured parallel (0°) and perpendicular (90°) to the polarization direction of the exciting radiation. See Ref. [43] for details.

It is important to note that in the excitation step, the two oxygen atoms are completely equivalent due to inversion symmetry. I.e. the core hole may be created on either of them with equal probability, and hence the core-excited state has to be treated as a coherent superposition of the O^*O and OO^* states.

The spectral features shown in the lower panel of Fig. 17 taken from Ref. [43] were measured with the electron-energy analyzer parallel (0°) and perpendicular (90°) to the polarization direction of the exciting radiation. Apparently, the 0° spectrum reveals two peaks, separated by 0.75 eV, whereas the 90° spectrum consists of a single peak, situated in between the two 0° peaks.

As discussed in the work of Björneholm et al. [43], the observed behaviour can be understood only by assuming localization of the core holes. In the 90° case, the two dissociation directions are symmetric with respect to the direction of the measurement which is the reason why only a single line is observed. In contrast, in the 0° case, the two fragmented oxygen atoms take off in line of the direction of the polarization vector. Such a dissociation gives the atom containing the core hole a velocity either in direction toward the analyzer or away from it (cf. Fig. 17 taken from Ref. [43]), resulting in a Doppler shift of the observed electron kinetic energy.

We would like to emphasize that by the observation of the Doppler-split electron kinetic energies, as revealed in the asymmetric 0° measurement, the electron

emission site becomes localized and, as a consequence of that, one "labels" the apart-moving oxygen atoms which are otherwise indistinguishable in a normal photoemission experiment by a "which way" information. With respect to quantum mechanics, this is a nice illustration of how the measurement operator can select coherently superposed or incoherent states, depending on the information gained by the experiment.

A similar Doppler splitting of atomic oxygen lines was also found in the work of Rosenqvist et al. [45] for $O_T 1s \rightarrow \sigma^*$ ($7a_1$) core-excited ozone. The interested reader is referred to Ref. [45] for a detailed discussion on this second case.

In a subsequent work by Wiesner et al. [46] the Auger-Doppler effect was investigated both experimentally and numerically for $F1s \rightarrow 4\sigma^*$ excited HF and DF molecules. Special attention was paid to the dynamical behaviour of ultrafast dissociation in the core-excited state as a function of excitation energy detuning and its influence on the Doppler splitting of the fragment lines.

Fig. 18 taken from Ref. [46] shows resonant Auger spectra of DF measured for photon energy detunings of -1, 0 and +1 eV relative to the $F1s \rightarrow 4\sigma^*$ resonance energy of 687.4 eV. The spectra were recorded at an angle of 0° with respect to the polarization vector of the ionizing radiation. Also included in this figure are numerical results based on a Born-Haber cycle type model developed by Wiesner et al. [46] which mimics the dependence of the Doppler splitting on the kinetic energy release of the fragments [44, 47]. DF was chosen as the showcase, since the higher reduced mass leads to a higher velocity of the F-fragment and thus a larger Auger-Doppler splitting in comparison to HF.

As can be seen from Fig. 18 taken from Ref. [46], both the experimental and numerical results show clearly that a change in the excitation energy from -1 eV below the resonance to +1 eV above the resonance is transferred into the kinetic energy of the fragments, leading to a change of the Doppler splitting of the order of 80 meV. I.e. according to the model by Wiesner et al. [46], the photon energy detuning Ω changes the kinetic energy release of the dissociation by the amount of Ω , which affects the momentum of the emitted Auger electron and hence the Doppler splitting. This is the concept of the so-called dynamic Auger-Doppler effect [46].

As discussed in one of the previous sections above, in polyatomic molecules the geometry of the core-excited state is often different from that of the ground state, and thus core excitation effectively initiates nuclear motion. This nuclear motion may break the symmetry of the molecule, affecting subsequent electronic decay and ionic fragmentation processes. In particular, highly symmetric spherical top molecules such as CF_4 or SF_6 are very interesting cases in this respect.

In anisotropic angular distribution studies of F^+ frag-

FIG. 18. Resonant Auger spectra of DF (circled) measured for photon energy detunings of -1, 0 and +1 eV relative to the $F1s \rightarrow 4\sigma^*$ resonance energy of 687.4 eV and at an angle of 0° with respect to the polarization vector of the ionizing radiation. Theoretical simulations based on a model developed in Ref. [46] are displayed with solid lines. The spectra are aligned to the right peak maximum of the simulations. Additional lines are drawn through the peak maximum of the upper and the lower spectrum as a guide for the eye. See Ref. [46] for details. Reproduced with permission.

ment ions (see e.g. Ref. [48] and references therein) it was argued that there is a preferential bond rupture at the $F1s$ core hole site in CF_4 , SiF_4 , and SF_6 . However, the fragmentation observed in these measurements could not be connected unequivocally with nuclear motion of the intermediate core-excited state, since the fragmentation could very likely also arise from the Auger-final electronic state.

Triggered by these studies, Ueda et al. [49] studied the resonant Auger decay of $F1s \rightarrow a_1^*$ excited, ultrafast dissociating CF_4 molecules, and found that the $F1s^{-1}$

atomic-like Auger line is split into two Doppler-shifted components due to the emission of the Auger electrons by a fragment in motion, when the electron emission is detected along the polarization vector of the light. Since the Doppler shift is inherently connected to the photoabsorption process and the nuclear motion before the Auger decay takes place, and since ultrafast fragmentation is initiated on the core-excited state potential surface, the observation of the Doppler splitting constitutes a direct proof that in the case of CF_4 the asymmetric nuclear motion proceeds in the $F1s$ -excited state, along the direction of the polarization vector of the incident light, leading to symmetry lowering from T_d to C_{3v} .

Interestingly, in comparing the results for the asymptotic kinetic energy value for the F fragment, as obtained from the Born-Haber cycle type model of Wiesner et al. [46], to the average kinetic energy of the F fragments, as estimated from the Doppler splitting, Ueda et al. [49] found that in the case of ultrafast dissociating CF_4 , the fragments are not fully accelerated when the Auger decay takes place, which is in contrast to what has been seen for the HF/DF case. This finding suggests that the residual energy is kept in the fragment of CF_3 in the form of vibrational energy.

In the work of Kitajima et al. [50], the study of the dynamic Auger-Doppler effect was extended to the highly symmetric O_h molecule SF_6 . Fig. 19 taken from Ref. [50] shows enlarged spectra (after subtraction of the baseline) of the F^* atomic-like Auger line ($1s\ 2p^6\ ^2S \rightarrow 2p^4\ ^1D$) measured for five different photon energies across the $F1s \rightarrow a_{1g}^*$ resonance in SF_6 . In the left panel of this figure, the splitting characteristic of the Doppler effect expected at the angle of 0° with respect to the polarization vector of the ionizing radiation is clearly observed. Let us focus on the 90° spectra where the Doppler splitting is absent. The line profiles measured at 90° with respect to the polarization vector of the light exhibit apparently a flat peak shape when the photon energy is tuned to the vicinity of the resonance peak (688.28 eV and 686.80 eV), and a shallow dip appears at the centre when it is tuned on top of the resonance (687.55 eV; cf. Ref. [50] for the corresponding photoabsorption profile). These peak shapes contrast with the more Gaussian-like sharp peak shapes for the corresponding F^* atomic-like Auger lines observed at 90° geometry for DF (see Ref. [46]) and CF_4 (see Ref. [49]).

As shown in the work of Kitajima et al. [50] by profound theoretical analysis, the observed energy-dependent flat peak shapes at 90° geometry contain important information about the anisotropy of the atomic-like Auger emission in the molecular frame. The Auger anisotropy is found to decrease with an increase in the F- SF_5 internuclear distance, which is a natural consequence since the Auger anisotropy is a pure

FIG. 19. Doppler profiles of the F atomic-like Auger line of F1s-excited SF_6 emitted in the directions parallel and perpendicular to the polarization vector of the ionizing radiation. The spectra were recorded across the $\text{F1s} \rightarrow a_{1g}^*$ resonance of SF_6 for five different photon energies. Baselines are subtracted. See Ref. [50] for details.

molecular effect [50].

In all works discussed so far within this section, we have seen that resonant Auger decay of core-excited molecules undergoing ultrafast dissociation may lead to a Doppler shift of the emitted electrons, depending on the direction of the electron emission relative to the dissociation axis. In the work of Kugeler et al. [51] further light was shed on this process by an angle-resolved electron-fragment ion coincidence experiment on $\text{O1s} \rightarrow \sigma^*$ core-excited O_2 . This spectroscopy technique has the potential to reveal further details of the intramolecular relaxation dynamics, which are otherwise hidden to non-coincident measurements. Indeed, with their experiment, Kugeler et al. [51] could show that a significant fraction of the autoionizing electrons emitted in the atomic region undergoes scattering on the other, neutral fragment atom after emission and that electron transfer between the two fragments is possible even after dissociation and the primary autoionization. Similar findings were very recently reported by Prümper et al. [52] for the polyatomic CH_3F system.

FIG. 20. The resonant Auger electron spectrum recorded at the photon energy 541.80 eV plotted on a kinetic energy scale in comparison to the normal Auger electron spectrum obtained at the photon energy 650 eV. See Ref. [53] for details.

RESONANT AUGER DECAY NEAR THRESHOLD

Sorensen and coworkers [53] performed recently a study where $\text{O1s} \rightarrow \text{Rydberg}$ excited resonant Auger spectra of O_2 , recorded at the photon energies 541.80 and 541.97 eV (see e.g. Ref. [53] for the corresponding absorption curve), were compared to the normal Auger spectrum of O_2 recorded well above the O1s ionisation thresholds at the photon energy of 650 eV. Interestingly, the resonantly excited electron spectra revealed in the inner valence region above 35 eV binding energy, which is governed by spectator decay, quite some reminiscence to the ordinary Auger electron spectrum as exemplary shown in Fig. 20.

Based on this finding, an interpretation of the resonant Auger electron spectra was made in terms of Rydberg series in the cation converging towards the dicationic ionisation limits. The interpretation involves a relaxation model introduced earlier for atomic resonant Auger spectra [54]. The assignments of the resonant spectra assume that the relevant intermediate neutral states at 541.80 and 541.97 eV governing the Auger decay are essentially the $\nu = 0$ and 1 vibrational components of the $(\text{O1s})^{-1} ({}^4\Sigma_u^-) 4p\sigma$ Rydberg state, and reasons for this assumption are given in Ref. [53].

In a follow-up work, Tanaka et al. [55] investigated a series of resonant Auger-electron spectra excited at ten selected photon energies across the $\text{O1s} \rightarrow \text{Rydberg}$ resonances in O_2 between 538.95 eV and 542.72 eV. Applying the spectator-electron shake relaxation model from Refs. [53, 54], and using, to a large extent, the assignments for the core-excited resonances as available from the literature, many of the observed spectator Auger-electron final states could be assigned

in terms of cationic Rydberg series. Vice versa, the resonant Auger-electron spectra were used for consistency tests of the literature assignments for the core-excited intermediate Rydberg states. For some of the latter, alternative assignments were proposed for reasons discussed in Ref. [55].

As mentioned above at the end of the section on Ultrafast Dissociation, and as Refs. [53, 55] indicate, the O1s near-edge X-ray absorption region of O_2 is quite complex. In order to obtain a deeper insight, Feifel et al. [56] investigated the valence character of this resonance region by means of participator Auger decay spectroscopy, performed at selected photon energies, and by means of partial ion yield x-ray absorption spectroscopy. For several of the excitation energies studied, a substantial $\sigma^*(^4\Sigma_u^-, ^2\Sigma_u^-)$ valence character being mixed with $ns\sigma$ and $np\sigma(^4\Sigma_u^-, ^2\Sigma_u^-)$ Rydberg states was found. Furthermore, an experimental indication of a coupling between the channels associated with quartet and doublet ion cores in form of a Fano interference has been considered and discussed in this work.

In a subsequent study, Feifel et al. [57] investigated, both experimentally and theoretically, in further detail the $O1 \rightarrow \sigma^*$ region. This work shows that core excitation takes place in a region with multiple crossings of potential energy curves of the excited states. A complete breakdown of the diabatic picture for this part of the X-ray absorption spectrum was found, which allowed Feifel et al. [57] to assign an hitherto unexplained sharp fine structure in this spectral region to bound Rydberg states.

ABOVE THRESHOLD RESONANCES

While below-threshold resonances are typically described as transitions of a core electron to an empty state such as a virtual molecular orbital or a Rydberg state (or a mixture of the two in more complex cases as just discussed), the above-threshold region is characterized by the presence of an ionization continuum. However, resonant features are still possible, superimposed on this continuum. In particular, a gross distinction can be made between one-electron processes, namely shape resonances, and multi-electron processes such as neutral states created by the simultaneous excitation of a core and a valence electron.

Shape resonances have been the subject of a vast and sometimes controversial literature, and we refer to already existing review works for a detailed description of these phenomena [58]. In particular, the effect of shape resonances has been described on the vibrational distribution of photoelectron lines, which changes sensibly at the shape resonance energy position due to non-Franck-Condon effects (see e.g. Ref. [59] for recent measurements with state-of-the-art resolution). Here we report

FIG. 21. A comparison of the N_2 K-LL Auger spectrum after ionization through the shape resonance at 420 eV and well above the shape resonance at 465 eV. The energies of the final two-hole states are indicated with bars in the figure. The sharp features indicated by arrows in the figure arise for excitation in the shape resonance. See Ref. [60] for details.

only one example, which concerns the appearance of a perturbed vibrational structure due to a shape resonance not in photoelectron lines, but in Auger lines [60].

Auger spectra of N_2 were measured after N1s photoemission at the photon energy of 420 eV (corresponding to the shape resonance position) and at a photon energy of 465 eV, well above it. These spectra are shown in Fig. 21 taken from Ref. [60]. The higher photon-energy spectrum (dashed line) resembles earlier published Auger spectra. The two spectra in Fig. 21 taken from Ref. [60] are generally very similar, but the 420 eV spectrum has more than twice the intensity of the off-resonance spectrum and certain features exhibit intensity changes within the bands. These peaks are indicated with arrows in the figure. The sharp peaks in the 420 eV spectrum appear just above an Auger feature with vibrational structure. Peak 4 at a kinetic energy of 359 eV is associated with the $D^1\Sigma_u^+$ state; a sharp peak appears when the photon energy is tuned to the shape resonance region. Another state which exhibits similar behavior at the shape resonance is the X-state with two vacancies in the $3\sigma_g$ orbital $^1\Sigma_g^+$.

Measurement of the N1s photoelectron spectrum of N_2 as a function of photon energy distinguished the gerade and ungerade components and followed the cross sections for each component separately [61]. A later study confirmed that the shape resonance has σ_u symmetry and couples primarily to the σ_g channel, but inter-channel coupling leads to resonant behavior even in the σ_u channel [62]. The intensity increase in the Auger spectrum at 420 eV reflects the increase in ionization cross section due to the shape resonance affecting the photoelectron channel.

With the aid of simulations, it was shown that for the X-state the peak arising from the superposition of the decay from the gerade and ungerade $\nu = 0$ levels produces a $\nu = 0$ peak with an energy of 366.9 eV. The increased intensity in the higher-energy peak arises from the shape-resonance induced enhancement of the $\nu = 1$ peaks in the core-ionized states. For the X-state additional peaks are discerned which arise from $\nu = 2$ vibrations in the intermediate state. The fine structure in the Auger spectrum is analyzed taking lifetime vibrational interference and the existence of two separate components in the core-ionized state into account. The analysis is consistent with a picture where the gerade and ungerade channels do not interfere.

In the following we will provide some examples of decay properties of multiply excited states embedded in ionization continua. Water is a special case, since in the above-threshold region the photoabsorption curve is rather flat, without pronounced resonant features. However, in one specific experiment, namely, negative ion yield spectroscopy, it was possible to identify a resonant feature ~ 10 eV above the ionization threshold [63]. This feature has been related to doubly excited states, since it is well known that there are no shape resonances in H_2O .

Electron spectra were recorded at several photon energies across the broad resonance that appeared only in the O^- yields above the threshold [64]. Fig. 22 taken from Ref. [64], shows electron spectra, $I(0^\circ)$ and $I(90^\circ)$, recorded at angles 0° and 90° , respectively, with respect to the polarization vector of the ionization radiation, and it shows also the angle-integrated spectrum as given by $I(0^\circ) + 2 I(90^\circ)$. The photon energy of 550 eV corresponds to the maximum of the resonance identified in the negative ion yield curves. The spectra exhibit a broad feature at a binding energy of 32 eV, which corresponds to the electron binding energy of inner-valence molecular orbital $2a_1$. Superimposed on it, some sharp structures with vibrational substructure appear in the binding energy range between 36 and 40 eV. The relative position of the features and their vibrational spacing are consistent with the Auger spectrum of the OH fragment [38]. As a further test, the spectrum was measured at several different photon energies across the broad resonance. The broad molecular feature at a binding energy of 32 eV changes its electron kinetic energy linearly as a function of photon energy, thus remaining at a constant binding energy. The electron kinetic energies corresponding to the sharp structures, on the other hand, stay constant, even though the photon energy is changed. Such behavior is typical of spectral features related to fragments (see the section devoted to Ultrafast Dissociation). These sharp peaks were assigned in Ref. [64] to the electronic decay of the OH radical, as indicated in Fig. 22 taken from Ref. [64]. The conclusion was that the resonant state

FIG. 22. Resonant Auger spectrum of H_2O recorded on top of the resonance at 550 eV photon energy. See Ref. [64] for details.

at ~ 10 eV above the threshold, evident only in the O^- yields, is dissociative, as proven by the appearance of fragment-related spectral features.

Decay of doubly excited states above an ionization threshold has been reported for CO [65]. The leading configurations of the most prominent doubly excited Rydberg states are assigned by analysis of the ion-yield spectra and the final-state spectra. Analysis of the resonant Auger spectra provides an assignment of several two-hole/one-particle final states.

The carbon K-shell ion-yield spectrum exhibits well-resolved features arising from core to Rydberg excited states below the carbon K edge, while above threshold both broad resonant features and narrow well-defined peaks have been identified in many experiments. The broad feature at ~ 305 eV has been assigned to the σ^* shape resonance, while the sharp features at slightly lower energy are attributed to vibrational progressions of doubly excited Rydberg states converging to satellite states of the C1s ionization threshold.

The decay pathways of doubly excited core hole states can be classified into several types. As these states lie in the core-ionization continuum, they can autoionize into singly-ionized core hole states, which subsequently decay by the normal Auger process. In addition, three different types of radiationless decay channels are possible for the core hole: participator Auger decay, in which both of the excited electrons participate in the Auger decay leads to singly-ionized final states with 1 hole in the valence shell and no excited electrons, i.e., a $1h-0e$ state. Single spectator Auger decay, in which one of the excited electrons remains as a spectator electron in its orbital during the decay, results in a final state with two holes in the valence shell, and one excited electron, i.e., they are $2h-1e$ states. These states are also accessible via spectator Auger decay of core-excited states. The third decay path is double spectator

FIG. 23. Angle-independent resonant Auger spectra measured via resonant excitation of the doubly excited Rydberg states. For comparison, the photoelectron spectrum measured on top of the σ^* shape resonance ($h\nu = 306$ eV) is also shown. See Ref. [65] for details.

decay, i.e., both excited electrons remain as spectator electrons in their orbitals. The final state has a $3h-2e$ configuration.

Resonant Auger spectra following the decay of above-threshold doubly excited states are shown in Fig. 23 taken from Ref. [65]. The overall shape of this spectrum closely resembles inner-valence photoelectron spectra obtained at photon energies around 45 eV.

Symmetry-resolved ion-yield spectra identify the doubly excited Rydberg states at ~ 300 eV to be of Π character. The leading configurations for the doubly

excited Rydberg states are derived by using a simple model to compare states with similar configurations, and are confirmed by the analysis of the corresponding resonant Auger spectra. The excitation of these states can be explained by a conjugate shake-up process with a $C1s \rightarrow 2\pi$ excitation accompanied by a $5\sigma \rightarrow n\sigma$ shake transition.

From the resonant Auger spectra a large number of the $2h-1e$ final states were assigned which are also present in published inner-valence photoelectron spectra (see Ref. [65] for the detailed assignment). Therefore the majority of the decay processes involve one of the above mentioned patterns, namely the formation of $2h-1e$ final states.

Other studies on doubly and triply excited states above an ionization threshold have been reported for N_2 [66, 67]. In the ionization continuum above the $N1s$ threshold there are several resonances, identified by symmetry-resolved absorption technique combined with *ab initio* calculations [66]. The resonances at ~ 410 eV and ~ 415 eV are assigned to doubly excited states and the one at ~ 419 eV, which appears only in the $^1\Pi_u$ -symmetry spectrum, to a triply excited state with a $1s \rightarrow 1\pi_g$ core hole ground configuration and two valence electrons promoted into the $1\pi_g$ lowest unoccupied molecular orbital. The resonance at ~ 419 eV is embedded in the well-known broad $N1s \rightarrow 3\sigma_u$ shape resonance located between ~ 416 eV and ~ 422 eV and thus has not been observed earlier in any ordinary absorption measurement.

In the experiment by Feifel et al. [67], 419 eV photons were used to excite two valence electrons simultaneously with a $N1s$ core electron into the $1\pi_g$ orbital borrowing intensity via initial and/or final state correlation and thus reaching a triply excited neutral intermediate state. This triply excited intermediate state predominantly decays via an Auger process to three-hole/two-particle ionic state configurations in the broad $2\sigma_g^{-1}$ inner valence band.

Fig. 24 taken from Ref. [67], shows decay spectra recorded at several photon energy values close to 419 eV. In all previous works, the band in the 34 - 42 eV binding energy region is identified as the direct $2\sigma_g^{-1}$ photoionization band. Configuration interaction calculations predict the presence of several three-hole/two-particle states in this binding energy region. These highly correlated configurations have, however, never been experimentally disentangled before.

Looking more closely at Fig. 24 taken from Ref. [67], one can see that at the isolated energy of 419 eV a band marked by the dashed line binding energy of 37.6 eV appears in the 90° spectrum, showing an anisotropic electron emission behaviour of $\beta < 2$ for this band. Correspondingly, the vibrational feature at 37.6 eV is strongly enhanced in the 0° spectrum. No significant resonant enhancement is observed for any other pho-

FIG. 24. Angle-resolved electron spectra recorded at five different photon energies across the $N1s \rightarrow 3\sigma_u$ shape resonance. See Ref. [67] for details.

toelectron bands in the entire binding energy region between 15 eV and 35 eV for all photon energies used in this study.

One possible interpretation is that this behaviour is due to the shape resonance, which is usually described as a one-electron process, but could induce changes in the angular distribution of final states. However, the response of the 37.6 eV peak at 419 eV photon energy with respect to both relative intensity and angular distribution is indicative of the presence of a much narrower intermediate state than the $3\sigma_u$ shape resonance. The sharp resonant enhancement of this photoelectron band agrees with the resonant $^1\Pi_u$ state associated with a triply excited configuration assigned in Ref. [66]. Two triply excited configurations are proposed, $1\sigma_u^{-1} 3\sigma_g^{-2} 1\pi_g^3$ and $1\sigma_u^{-1} 1\pi_u^{-2} 1\pi_g^3$. The triple excitation is forbidden within an independent particle approximation. Thus the excitation process becomes possible only via initial-state correlations, where $3\sigma_g^{-2} 1\pi_g^2$ and/or $1\pi_u^{-2} 1\pi_g^2$ configurations are mixed into the ground-state configuration, and/or final-state correlations, where the singly-excited configuration $1\sigma_u^{-1} 1\pi_g^1$ is mixed into the final-state configurations. The leading configuration of the triply excited state is most likely $1\sigma_u^{-1} 1\pi_u^{-2} 1\pi_g^3$. The decay from the triply excited

FIG. 25. The triple excitation schemes and one of the possible deexcitation channels leading to a three-hole/two-particle final state of the cation ("double spectator" decay). See Ref. [67] for details.

state is expected to be governed by the main configuration. Note that the Auger decay is a two electron transition. Thus, the most favorable decay channels should be such that one electron from the outermost orbitals fills the created core hole whilst another electron from one of the outermost orbitals is released into the continuum leaving the system in a three-hole/two-particle final-state configuration. Such a decay process would be referred as double spectator within the independent particle model. The fact that a significant enhancement of the single-hole main band or the two-hole/one-particle bands was not observed strongly confirms that the triply excited state decays into three-hole/two-particle configurations. Such configurations exist in the binding energy range of interest. The triple excitation schemes and one of the possible deexcitation channels leading to a three-hole/two-particle final state of the cation (double spectator decay) are shown in Fig. 25 taken from Ref. [67].

In conclusion, the work of Feifel et al. [67] shows that at 419 eV photon energy the new pathway via a triply excited resonant state enhances strongly the population of multiply excited cationic states. This observation shows how to preferentially probe such excited configurations of cations by means of resonant Auger-electron spectroscopy via multiple resonant excitation.

RECOIL EFFECTS

An important new phenomenon which has been observed in some selected systems is the ion recoil during photoelectron emission. Experimental work on core ionization in CH_4 and CF_4 (see Refs. [68, 69] and references therein) and valence ionization in N_2 [70] has shown that the recoil of the atom where the vacancy is created causes non-Franck-Condon effects well above the ionization threshold, and induces the excitation of

vibrational or rotational modes otherwise inactive.

In general, the analysis of the vibrational distribution in core-level photoelectron spectra is based on the Franck-Condon factors between the ground and core-ionized states. However, there are a number of effects that can distort the result, such as the post-collision interaction (PCI) and the influence of shape resonances or of Cooper minima. In Ref. [68], the C 1s photoemission from methane is studied over a broad photon energy range. The presence of non-Franck-Condon effects well above the ionization threshold is demonstrated, and a theoretical explanation is provided for the observed long-range change of the intensity ratios of the various vibrational components, based on photoelectron recoil effects.

According to momentum conservation, during the photoemission process a molecule receives a recoil momentum transfer from an ejected photoelectron. In a simple model, the whole molecule receives this momentum rigidly (elastic recoil). In the case of core-level photoemission, however, the electromagnetic field interacts primarily with the atom at which the core orbital is localized, on a time scale much shorter than the vibrational period of the molecule. This indicates that the molecule is unable to receive the recoil momentum rigidly, but it is rather given to the primary electron emitter. As a consequence, the photoelectron recoil is similar to inelastic collision processes that lead to vibrational excitations [68]. Such effect increases with increased photon energy, since the momentum transfer depends upon the kinetic energy of the ejected electron. In CH_4 , a variation in the intensity ratio of the first two vibrational peaks of the symmetric stretching progression was observed as a function of photon energy in the range 480-1200 eV. Such finding is reported in Fig. 26 which is taken from Ref. [68]. Furthermore, the authors in Ref. [68] could model the experimental spectra at a photon energy of 1050 eV by including the excitation of vibrational modes which are not active within a Franck-Condon picture but are related to the motion of the core-ionized carbon atom due to the recoil, namely the asymmetric stretching and one bending mode. They conclude that the apparent increase of the intensity ratios at high kinetic energies is not due to a change in the dominant symmetric stretching progression itself, but reflects an additional underlying structure of other vibrational modes that appears due to the recoil excitations. Such result constitutes a violation of the Franck-Condon principle, which states that neither the positions nor the momenta of the nuclei change during the ionization event.

Although the recoil excitations give minor contribution to the overall vibrational envelope in the methane case, in molecules where the electron emitter is surrounded by heavier atoms, the modifications could be much stronger. The extent of the effect is related to

FIG. 26. Intensity ratios of the symmetric stretch progression in C1s photoelectron spectra of methane. Solid line - recoil model. Dashed line - prediction without recoil. See Ref. [68] for details. Reproduced with permission.

the ratio of the mass of the excited atom versus the molecular mass. In methane the atomic mass of the excited atom is only slightly different from the molecular mass, and therefore only a small fraction of the recoil energy goes into internal excitation. The same authors have reported a similar experiment concerning CF_4 [69]. In tetrafluoromethane the ratio of mass of the ionized atom to the mass of the molecule is low, the Franck-Condon excitation is weak, and the natural linewidth is small. Therefore in Ref. [69] the recoil effect is shown to be much more evident in CF_4 than in methane.

In Fig. 27, taken from Ref. [69], the change in line-shape of the C1s photoelectron line in CF_4 is shown as a function of the photoelectron kinetic energy. The changes in the spectra as the photon energy and thus the photoelectron kinetic energy is increased are quite relevant. Those are mostly due to the excitation of the antisymmetric stretching mode which is not excited within a Franck-Condon picture.

It is apparent that recoil excitation of vibrational modes can have a significant effect on the photoelectron spectra. In CF_4 at a photon energy of 400 eV (about 100 eV above threshold) the recoil excitation is comparable to the Franck-Condon excitation, and at higher photon energies the recoil induced excitation is the dominant source of the vibrational structure.

The recoil excitation, in addition to being an inter-

FIG. 27. Carbon 1s photoelectron spectra of CF_4 at the photon energies indicated. For (a) - (i) the open circles represent the data, the heavy solid lines represent least-squares fits to the data using theoretical predictions of the recoil-induced vibrational excitation, and the light solid lines show the contribution from the vibrationally unexcited state. See Ref. [69] for details. Reproduced with permission.

esting phenomenon in itself, allows one to derive additional information on the vibrational frequencies of the core-ionized molecule. In particular, the recoil excitation involves modes that are not excited by the Franck-Condon process. In the case of CF_4 it was possible to obtain an experimental value for the frequency of the asymmetric stretching mode.

A different approach was used by the same authors in Ref. [70], where the recoil effect has been observed in valence spectra, and in which the momentum transfer leads to the excitation of rotational rather than vibrational modes. The system under investigation is N_2 , and valence photoelectron spectra are reported as a function of photoelectron kinetic energy and compared with previous fluorescence data. In particular, in the photoelectron spectrum of N_2 the apparent ionization energy to form the $\text{B } ^2\Sigma_u^+$ state increases linearly with the photon energy. Rotationally resolved measurements of the fluorescent decay of this state show a linear increase of rotational heating with increasing photon energy. These results are in quantitative agreement with the prediction of the theory of recoil-induced rotational excitation, indicating that the rotational heating that has been observed previously arises primarily from such recoil-induced excitation. Together with other results that have been reported they show that recoil-induced internal excitation is significant in many situations, including near threshold. In Fig. 28, taken from

FIG. 28. Mean apparent ionization energy to produce the $\nu=0$ B-state of N_2^+ as a function of photoelectron kinetic energy. Solid circles, left-hand axis: From photoelectron spectroscopy. Squares and triangles, right-hand axis: From fluorescence measurements. See Ref. [70] for details. Reproduced with permission.

Ref. [70], the rotational heating in the singly-ionized B valence final state of N_2 is shown as a function of photoelectron kinetic energy due to the increased population of rotational levels caused by the recoil.

An interesting point is that while for core ionization the proposed model is based on emission from a localized atom, similar arguments hold for valence ionization, where the electrons are delocalized. Both the photoelectron spectroscopic measurements and the fluorescence measurements can be understood quantitatively in terms of a model in which the photoelectron originates at a localized atom even though the valence orbital from which the electron is ejected is delocalized. These results indicate that photoelectron recoil-induced internal excitation is a widespread phenomenon and can have a significant effect even for energies not far above threshold.

CONCLUSION

Recent results on core-level electron spectroscopy and dynamics of free molecules were reviewed. The examples given enlightened the inherent interplay of the timescales of the Auger electron decay with nuclear motion, and comprised ultrafast dissociation processes, the occurrence of interference phenomena and recoil. The capability of such studies to reveal important information on the light-matter interaction, the electronic structure and the evolution of the short-lived states

thus created was enlightened, and it should be regarded as driving force for more future studies of related kinds, both at state-of-the-art synchrotron radiation facilities and Free-Electron-Laser sources.

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- * Corresponding author: raimund.feifel@fysik.uu.se
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