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**Dynamics of ultrafast dissociation of hydrogenic molecules by resonant antibonding core
electron excitation: Conclusions from detuning dependence of H^+ - kinetic energy
distributions from condensed films.**

R. Weimar, R. Romberg, B. Naydenov¹, D. Menzel², P. Feulner*

Physikdepartment E20, TU-München, 85747 Garching, Germany

¹Trinity College Dublin, Dublin 2, Ireland

²also at Fritz-Haber-Institut, Dept. CP, 14195 Berlin, Germany

Abstract

The ultrafast dissociation dynamics of condensed water and ammonia by resonant core electron excitations have been studied by measuring the kinetic energy distributions of H^+ -ions desorbed by $[N1s]4a_1$ and $[O1s]4a_1$ excitations as a function of detuning, $\Delta h\nu$, from the center of the resonance. While the most probable ion energy varies monotonically with $\Delta h\nu$ for both systems, the centers of gravity of the kinetic energy distributions are minimal at resonance and shift to higher kinetic energy with detuning to either lower or higher $h\nu$. This behavior is explained by contributions from bond evolution processes before and after the core hole decay.

*corresponding author

Introduction

Excitations of core electrons can cause dissociation of molecules before the core holes decays [1], in particular if the core electron is resonantly excited into an antibonding molecular orbital and one of the fragments is very light. This so-called ultrafast bond-breaking (UFD) was first observed for halogen hydrides [2]. For these materials, the Z+1 analogue of the resonantly core excited state is a rare gas hydride that is unstable and dissociates into a hydrogen atom and a core excited halogen atom. Because core hole decay and bond breaking occur on comparable time scales, a superposition of atomic and molecular core decay spectra is observed [2]. The final kinetic energy of the dissociation fragments depends on the starting point of the reaction on the antibonding potential energy surface (PES) of the core resonance, which is a function of the excitation energy. Detuning from the center position of the resonance to its red side decreases, and detuning to its blue side increases the energy available for fragment acceleration. This was demonstrated by detuning dependent Doppler shifts of decay electron spectra from F* atoms *after* UFD of HF and DF at the F1s threshold resonance [3]. Hydrogen or deuterium and halogens are the optimum partners for UFD: the low masses of the first enable rapid acceleration and preferential energy deposition on the light fragment due to momentum conservation; and the Z+1 behavior of the latter warrants antibonding core-excited states. UFD was, however, also observed for other molecules, e.g. for antibonding core-to-bound states of di- [4-6] and triatomic molecules [7], and for hydrides of chalcogens and pnictogens. Apart from H₂S [8], H₂O is the chalcogen hydride which attracted most interest. Resonantly O1s excited H₂O corresponds in the Z+1 approximation to H₂F which is not stable. For isolated H₂O molecules UFD into OH and H by excitation of the antibonding [O1s]4a₁ threshold resonance was first concluded from ion yield data [9,10]. Experimentally, a relative lack of H⁺ photo ions was observed for this resonance when photon energy dependent ion yield and x-ray absorption (XA) signals were compared. This

lack was explained by production of neutral fragments via UFD [9,10]. Resonant Auger spectra that showed a contribution of $\sim 7\%$ from the OH fragment to the H_2O decay spectrum supported this interpretation [11]. Calculations of decay spectra including the dissociation dynamics reproduced the spectroscopic results well and supplied quantitative data for the fragment ratios [12]. Moreover, they indicated that the yield of fragments should depend on detuning, i.e. on the starting point of the reaction on the $[\text{O}1s]4a_1$ PES [12]. An example for UFD of pnictogen hydrides by core excitations is the $[\text{N}1s]4a_1$ state of the NH_3 molecule. As for H_2O , the existence of UFD was concluded from fragment signals in the decay spectra [13]. Compared to H_2O , however, the fragment contribution was very small, below 1%, indicating that only a small fraction of N1s holes survived dissociation that according to this number occurred approximately 32fs after the excitation compared to 11 fs for H_2O (ref.13; H_2O values from ref.10 are shorter). As for H_2O , calculations of the coupled nuclear and electronic dynamics [14] agree well with the experimental findings although they yield even longer dissociation times [14]. The reasons for the increasing contributions of UFD when going from NH_3 via H_2O to HF are according to ref.14 not only the increasingly steeper PES of the antibonding core-resonant state, but also the varying complexity of the dissociation dynamics. In particular, coupling between the electronic excitation and vibrational modes with dissociative asymptotic behavior is important. For HF only one bond is available which is rapidly elongated and quickly broken during the lifetime of the core hole. For H_2O , two bonds exist. In the first step the excitation elongates them both symmetrically before in a second step one H returns to the O atom and the other proceeds towards bond breaking [12,14]. For ammonia with its 3 hydrogens the coupling to an asymmetric dissociative vibration is even less efficient, explaining the rather low UFD yield for the unperturbed molecule [14]. According to [14], this yield is enhanced dramatically for deformed molecules with unequal N-H bond lengths.

Before UFD by [core]4a₁ excitations was investigated for isolated H₂O and NH₃, photon stimulated desorption (PSD) of H⁺ from condensed H₂O [15-17] and NH₃ [18] caused by this resonance was interpreted as an indication of UFD. Here, an enhanced yield of H⁺-ions was observed compared to photo absorption. On first glance, this is a contra-intuitive result because UFD of these molecules should yield neutral H atoms (see above); however, no such preferential desorption of H⁰ was experimentally observed, neither for H₂O nor for NH₃ [19]. To be sure, one has to keep in mind that electronically stimulated desorption from condensed matter is a more complicated process than electronically stimulated bond breaking of isolated molecules. The surrounding matrix which is absent in the gas-phase is a very efficient drain for excitations and charge [15-18]. In most cases the PSD yield is reduced for solid surfaces, and the fragment charges differ from the gas phase analogues. For condensed water even the two holes of the Auger final states can separate quickly in the network of hydrogen bonds [20]. The combination of these effects favors those excitations and their fragmentation patterns that break bonds particularly rapidly. For NH₃ and H₂O films these are multi shake-off states far above the [N1s] / [O1s] thresholds, the [core]2b₂ state for A_{xy}-polarization (\hat{E} -vector \parallel surface), and, most pronounced, the [core]4a₁ excitation for A_z-polarization (\hat{E} -vector \parallel surface normal [19]). Concerning the different H⁰/H⁺ ratio observed for isolated and condensed molecules, we note that even for the gas phase this value is not understood well. From ion yield data dissociation times of 4 to 5.2 fs are derived for the [O1s]4a₁ resonance of H₂O [10], whereas the more direct decay electron experiment yields 11 fs [11,13]. Another difference between both phases is the size of the UFD effect. For NH₃ and H₂O similar enhancements of H⁺-PSD are seen for the condensates [19], whereas for the isolated molecules rather different dissociation times of 32fs (NH₃) and 11fs (H₂O) are found by equivalent experiments [11,13]. This hints at a deformation of the surface NH₃ due to the reduced symmetry in the ground state, resulting in a more efficient coupling of

the electronic excitation to dissociative, asymmetric N-H modes, as has been proposed by [14]. This reduced symmetry becomes obvious from XAS. The [core]4a₁-resonances of condensed NH₃ and H₂O are split into bulk and surface contributions, and the surface contributions show polarization dependent splitting of 0.1eV for both molecules [19].

In pioneering Auger electron-photo ion coincidence (AEPICO) experiments Mase et al. investigated H⁺-PSD from condensed NH₃ [21] and H₂O [21-23]. They found H⁺ emission for both molecules correlated to blue-shifted decay electron spectra that they assigned to spectator contributions [21-23]. Based on this model they suggested a four step process for resonant H⁺-PSD for both systems: i) [core]4a₁ excitation; ii) bond elongation, iii) spectator decay of the core hole, iv) H⁺-desorption. They also found for NH₃ that H⁺-ions desorbed on resonance are slower than those desorbed off resonance [24]; a similar result has been obtained for water [16]. All these studies were done either on or off resonance; as yet, no investigations of detuning effects as done for isolated HF [3] exists for the condensates. With our study we aim at closing this gap by monitoring the kinetic energy of reaction products.

Experiment

We investigated amorphous multilayers of NH₃ and H₂O condensed onto atomically clean and well-ordered Ru(001) surfaces [19] (it should be noted that the metal substrate does not have any influence on the layers). To avoid charging, we restricted the film thicknesses to 10 monolayers. The experiments were performed at soft x-ray beam lines of the synchrotron sources HASYLAB and BESSY with A_z-light (\hat{E} -vector \parallel to surface normal), and H⁺-ions were also detected along the surface normal. Our detuning spectra below are related to the center positions of the A_z components of the surface [core]4a₁ resonances at 400.7eV and 532.9eV for NH₃ and H₂O, respectively [19]. All kinetic energy distributions (KEDs) of desorbing ions were recorded with a

hemispherical energy analyzer. To discriminate different masses, we chopped the ion flux with an electrostatic chopper positioned in front of the analyzer's entrance aperture and accumulated the signals from the 5 channeltrons of this analyzer in a time resolved fashion with a 5-fold multichannel scaler. From such 2-dimensional time-of-flight & kinetic energy data sets we extracted mass resolved KEDs [25]. To avoid any distortion of the trajectories of slow ions by patch field effects from work function differences of the environment, the sample was positively biased by 6V, thus accelerating all ions. This bias voltage and the work function differences between sample and analyzer were taken into account in our calibration of the energy scale. We note that the application of a dispersive energy analyzer removes most of the zero point and slope calibration problems inherently related to time-of-flight detectors.

Results

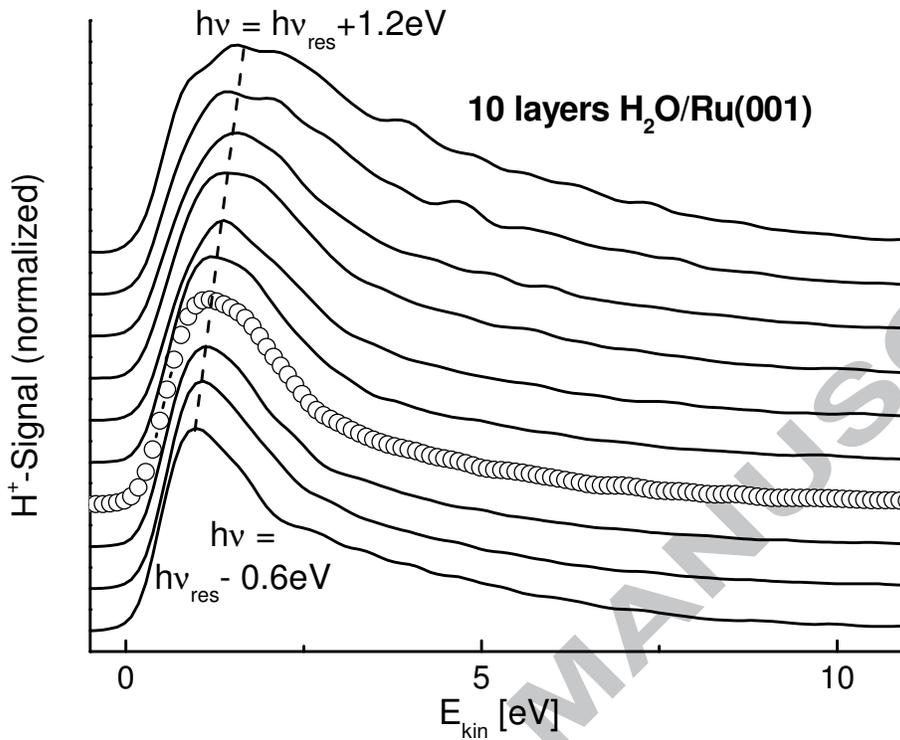


Fig.1: Kinetic energy distributions of H^+ -ions desorbed by $[O1s]4a_1$ excitation from the surface of a 10 monolayer thick H_2O film condensed onto a $Ru(001)$ substrate, as a function of detuning from the center energy of the resonance (curves arranged upwards with increasing excitation energy). The center of the resonance is indicated by the line & symbol trace. $\Delta h\nu$ between the individual curves is 200meV. To ease comparison of the shapes, all traces have been normalized at their maxima.

Fig. 1 shows KEDs of H^+ ions obtained from 10 monolayer thick films of amorphous water. In agreement with [16], we find narrow KEDs for resonant excitation. The maxima \hat{E}_{kin} of the KED curves show clearly shift with detuning, lying at ~ 1 eV at the red side of the resonance ($\Delta h\nu = -0.6$ eV), at 1.15 eV at the center ($h\nu = 532.9$ eV), and at 1.7 eV at the blue side ($\Delta h\nu = 1.2$ eV). So, a change of the excitation energy by 1.8 eV transforms into a shift of the KED maxima of 0.7 eV (Fig3a).

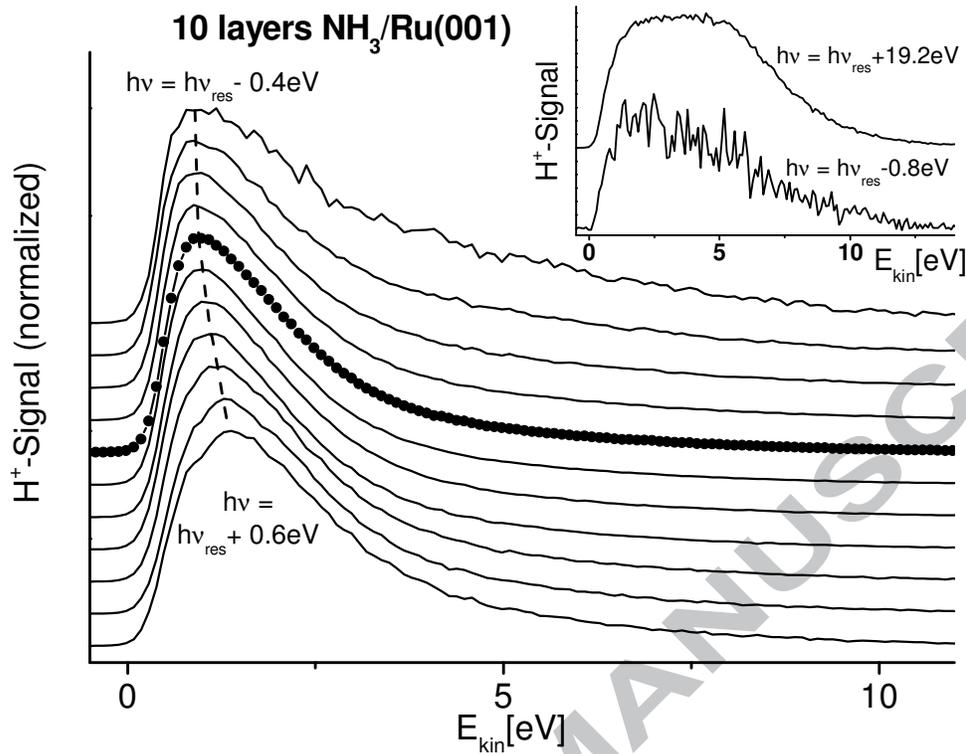


Fig.2: KEDs of H^+ -ions desorbed by $[N1s]4a_1$ excitation from a 10 monolayer thick NH_3 film condensed onto a $Ru(001)$ substrate as a function of detuning from the center energy of the resonance (note that for better visibility the curves are arranged with increasing energy downwards). The center of the resonance is indicated by the line & symbol trace. $\Delta h\nu$ between the individual curves is 100meV. All traces have been normalized at their maxima. The inset shows KEDs obtained at the onset and well above the $[N1s]4a_1$ resonance.

We observe a similar effect for NH_3 films at the $[N1s]4a_1$ resonance (Fig.2). The KED narrowing described by [24] is clearly seen by comparing KEDs obtained at and above/below the $[N1s]4a_1$ transition (Fig.2 and inset). We disagree with [24] concerning the onset of the KED which here is at 0 eV with respect to the vacuum level and in [24] at 1.3eV. Although we believe that our result is the correct one because i) our hemispherical energy analyzers was well calibrated by photoemission, and because ii) the leading onsets of our KEDs coincide perfectly, also for excitation energies below and above the resonances (Fig.2), we note that such an overall shift of the kinetic energy scale would not change the arguments given below which are exclusively

based on differential effects. As for water, the peak of the KED, \hat{E} , shifts from 0.9 to 1.37 eV for a detuning range of -0.4 to $+0.6$ eV. Compared to the water case, the $\Delta\hat{E}/\Delta h\nu$ ratio is less constant and gets larger at the blue edge of the resonance (Fig.3a). The width of the resonance is also smaller for NH_3 compared to H_2O , reflecting the decreasing antibonding nature of the K-shell to LUMO excitation for NH_3 [14]. In summary, \hat{E} varies monotonically with detuning for both systems (Fig.3a).

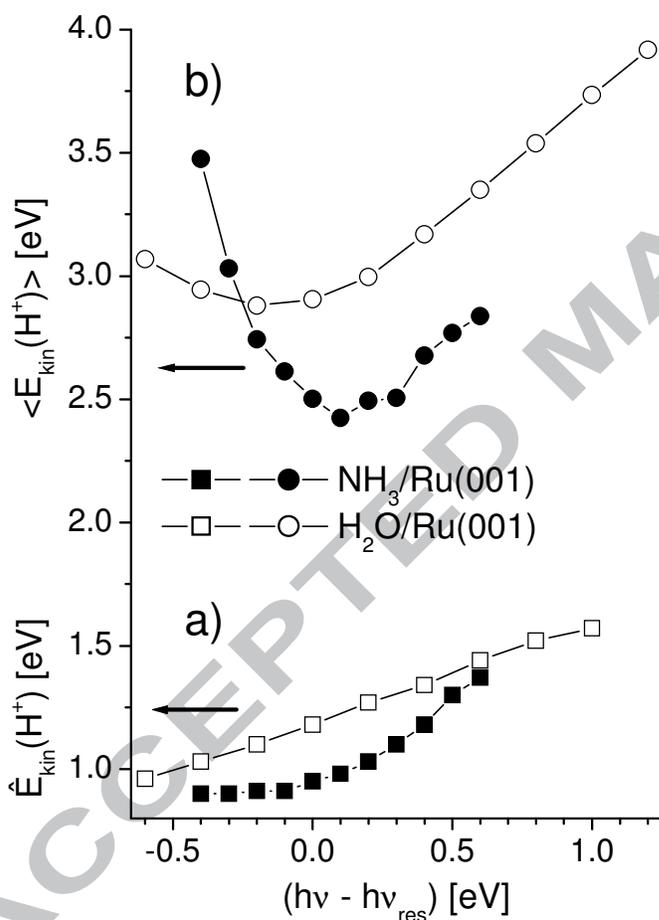


Fig.3: a) Most probable kinetic energies, \hat{E}_{kin} , and b) center of gravity values, $\langle E_{\text{kin}} \rangle$, as a function of detuning for the KEDs of Figs.1 and 2.

This is not the case for the centers of gravity of the KEDs, $\langle E_{\text{kin}} \rangle$ (Fig.3b). Here, two trends in opposite directions compete. For water as for ammonia minimal values of $\langle E_{\text{kin}} \rangle$ are obtained

around the center of the resonance, in agreement with the narrowing effect described previously for water [16] and ammonia [24]. At the red as well as at the blue side of the resonance $\langle E_{\text{kin}} \rangle$ increases. This behavior is only slightly different for H_2O and NH_3 , even the minima of $\langle E_{\text{kin}} \rangle$ coincide within 0.5 eV. For NH_3 the negative slope at the red side wins whereas for H_2O the positive slope at the blue side dominates. Comparing $\langle E_{\text{kin}} \rangle$ and \hat{E}_{kin} traces at the blue side of the resonance, we find for NH_3 nearly identical slopes of both traces in Fig.3; for H_2O , the slope of \hat{E}_{kin} is smaller than the slope of $\langle E_{\text{kin}} \rangle$.

Interpretation and discussion

In [24] the KED narrowing for resonant excitation was explained as follows: the second step after excitation of the $[\text{core}]4a_1$ state is bond elongation due to the antibonding nature of the resonance [21-23]. Only a single potential energy surface (PES) exists for this state; no further inelastic channels are available; vibrations in the ground state are not excited because their energy is well above $k_B T$, and in the excited state no vibrations exist because of its antibonding nature [12,14,16]. Upon de-excitation by core hole decay, a multitude of highly valence-excited final states with different PESs is populated [12,14,21-24]. These PESs will have different slopes in the Franck Condon region related to core hole decay, causing broad KEDs. The slopes of all these final state PESs will approach zero at large bond length, as will the slope of the intermediate core-excited state [24]. Two limiting cases exist therefore (see Fig. 4 for a schematic depiction):

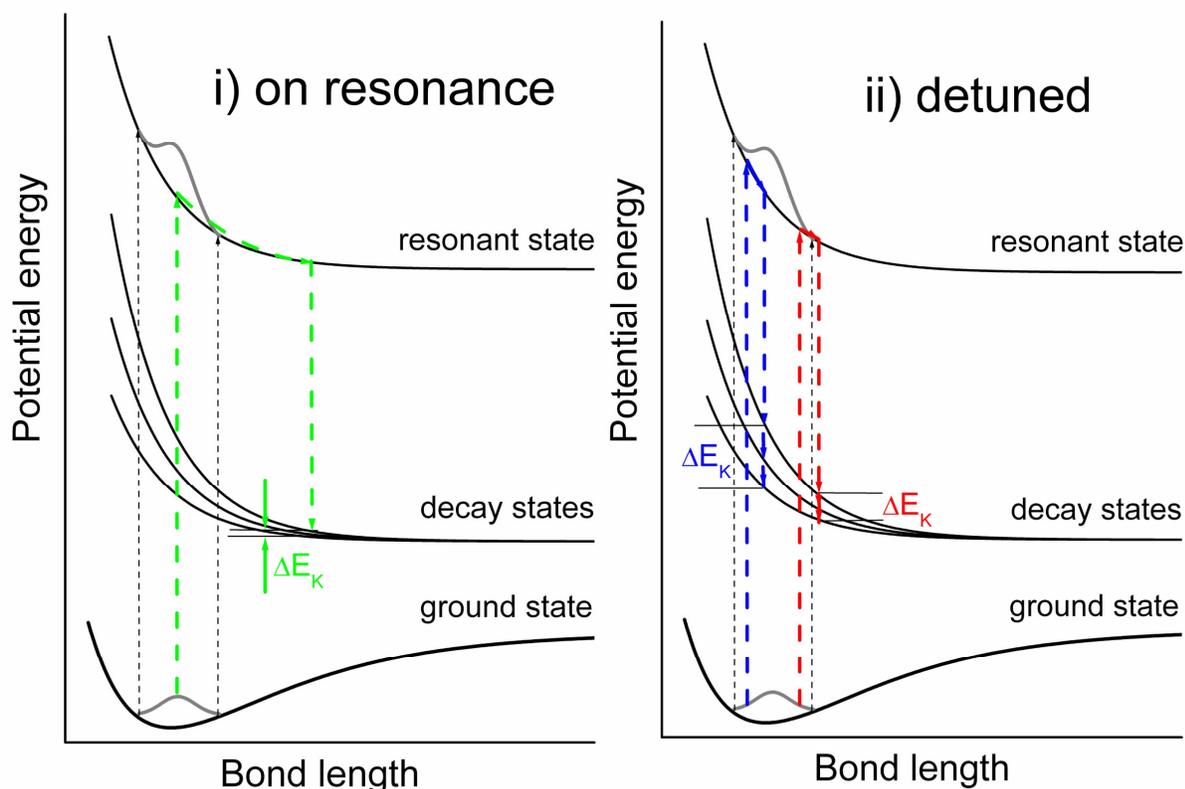


Fig.4 Schematic illustration of the shifting and broadening of the ion kinetic energy distribution caused by detuning. Schematic potential energy curves for the ground state, the resonantly excited state and a schematic ensemble of states reached by decay of the resonance are shown (for the latter the energy offsets in the asymptotic dissociation limits are set to zero). The wave packet in the resonance is shown as the projection of the ground state wave packet onto the potential energy curve of the resonant state. No attempt is made to depict the wave packets in the decay states.

i) For resonant excitation the lifetime of the resonance is maximal, so that bond elongation occurs to a large extent on the potential energy surface of the resonant state. The broadening ΔE_k of the kinetic energy distribution due to the multiplicity of decay states is small.

ii) If de-tuned to the red or to the blue side of the resonance, the resonance lifetime is shortened and contribution of the decay states to bond elongation and multiplicity induced broadening becomes large. At the same time the ion energies change correspondingly.

i) If bond elongation and acceleration of the fragments towards dissociation occur mainly during the lifetime of the intermediate resonant state, a KED representing the projection of the ground state wave packet onto the PES of the resonance and its further evolution on this PES is expected.

Because only a single state is involved in the acceleration process, this KED should be rather

narrow [24]. As for the HF case [3], the fragment energies will be larger for detuning to the blue side, and smaller for detuning to the red side of the resonance. This would be the case for an antibonding intermediate state that is long-lived compared to the dissociation time.

ii) For short-lived intermediate states where acceleration and bond elongation are dominated by the evolution on the post-decay PESs the situation is different. Here, a multiple of states (see, e.g., [13,14,21] for NH₃ and [11,12,23] for H₂O) with different and still large slopes is occupied at bond lengths close to the equilibrium values; KEDs will therefore become broad [24].

Because core hole lifetimes and dissociation times are not too different for our systems, we expect contributions of both cases in Figs.1 and 2. Case i) contributes narrow KEDs and dominates the detuning related shift of \hat{E}_{kin} for both systems; they are monotonic with $h\nu$. Case ii) contributes broad KEDs for short lifetimes of the resonance and /or Franck-Condon regions of minor slope of the PES of the intermediate state. Because core holes decay exponentially with time, both alternatives mix. The wellknown fact that detuning changes the lifetime of the resonance [26-28] explains the changing mixtures. At the center of the resonance its lifetime is maximal and route i) wins [26-28]. The widths of the KEDs are at their minima. Detuning reduces the lifetime of the resonances and changes the starting point of the dissociation reaction on the PES of the intermediate state [26]. This admixes contributions from ii), decreasing and changing the KED due to process i) (see above). We believe that both effects can be seen in the KEDs of Figs.1,2. At the red side ii) is dominant and amplitude as well as \hat{E}_{kin} due to i) are small; large values for $\langle E_{kin} \rangle$ are obtained. Reducing the detuning increases the contribution of i), therefore the KED gets narrower and $\langle E_{kin} \rangle$ decreases despite the increase of \hat{E}_{kin} . At the blue side of the resonance i) as well as ii) increase $\langle E_{kin} \rangle$ as well as \hat{E}_{kin} . The similarity of the KEDs obtained for NH₃ and H₂O as a function of detuning underlines the general validity of these considerations. The detailed shapes of the traces in Fig.3 depend on the individual shapes of the

PESs of the intermediate and the post-decay states, which for the surface molecules of NH_3 and H_2O films are not available as yet.

In summary we found that tuning through the antibonding O1s and N1s core excitation threshold resonances of condensed H_2O and NH_3 , respectively, changes the KEDs of desorbing H^+ -ions in a characteristic way. These results, which agree well with previous findings and extend them, contain fingerprints of the bond evolution during the lifetime of the intermediate antibonding core excited state, as well as of the dynamics due to the final states of the core hole decay. The change of resonance lifetime with detuning explains the varying contributions of the evolution in the intermediate and final states. As soon as PESs for the different states will be available from theory also for the condensed phase, our results should be usable to disentangle the dynamics occurring during the whole sequence of states following the initial core excitation.

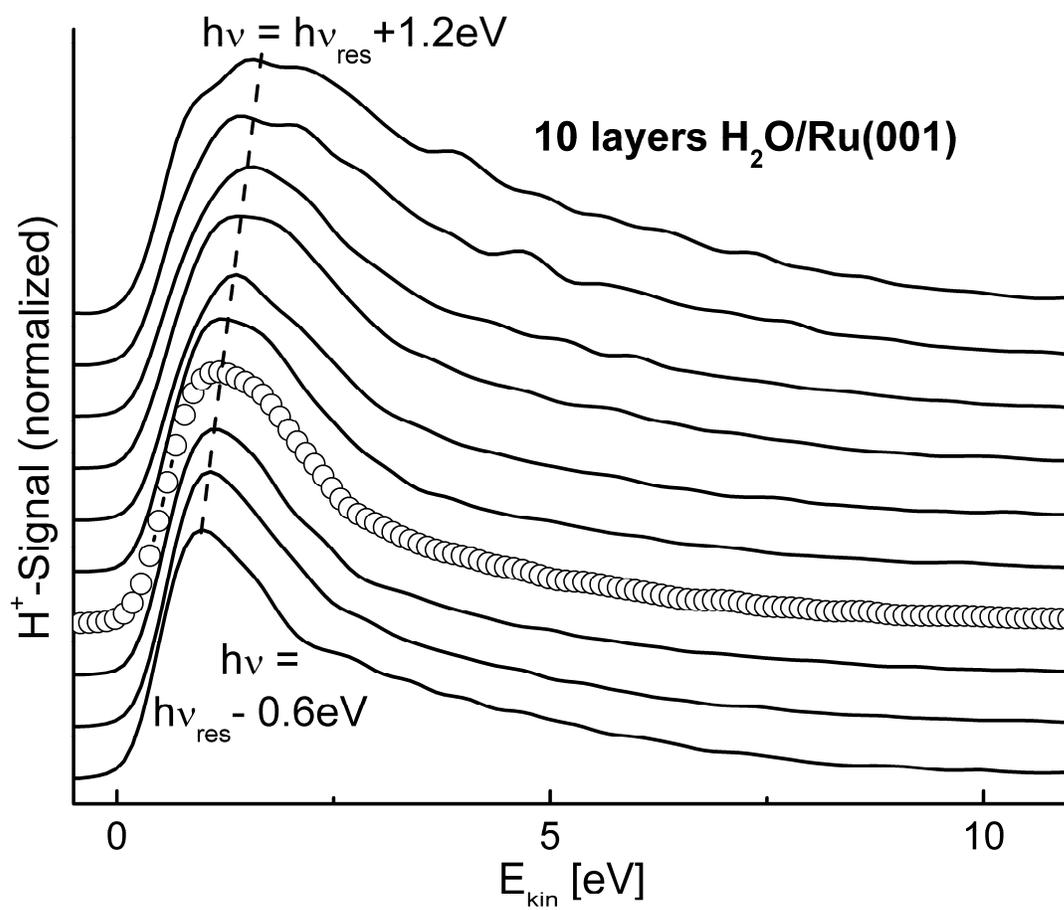
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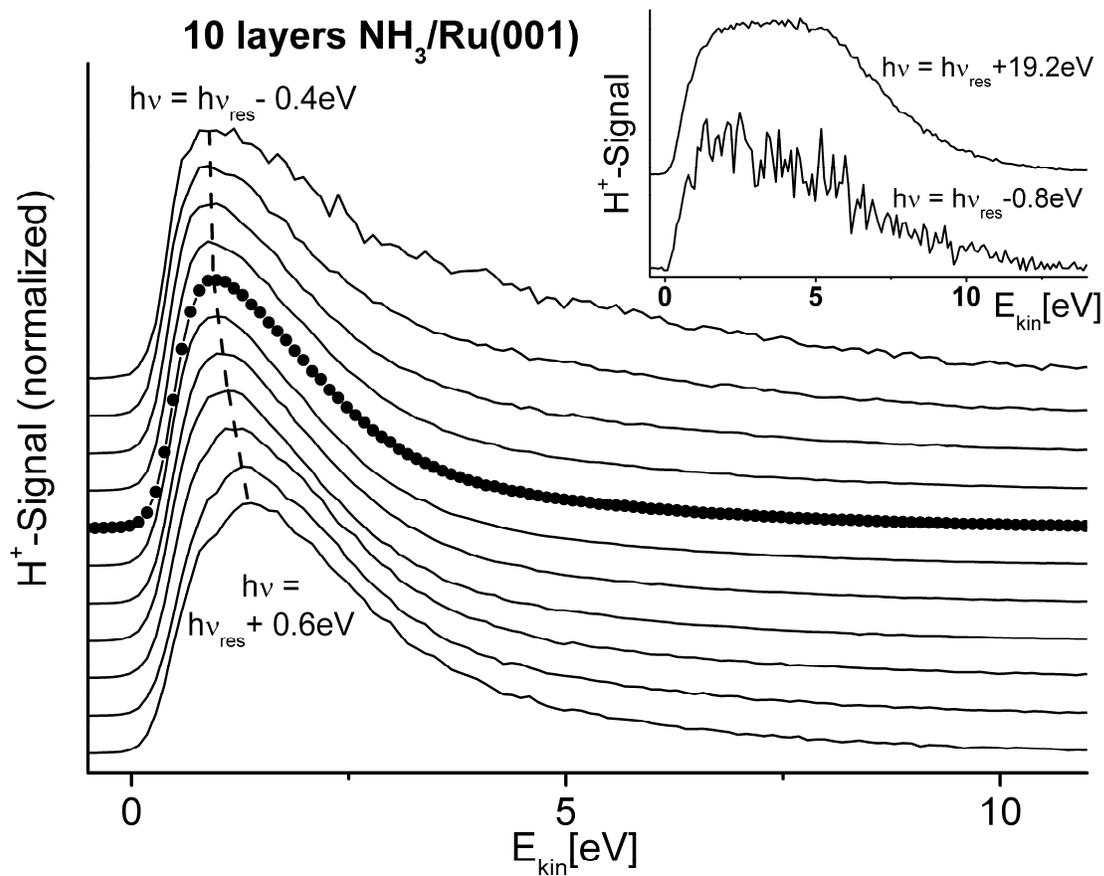
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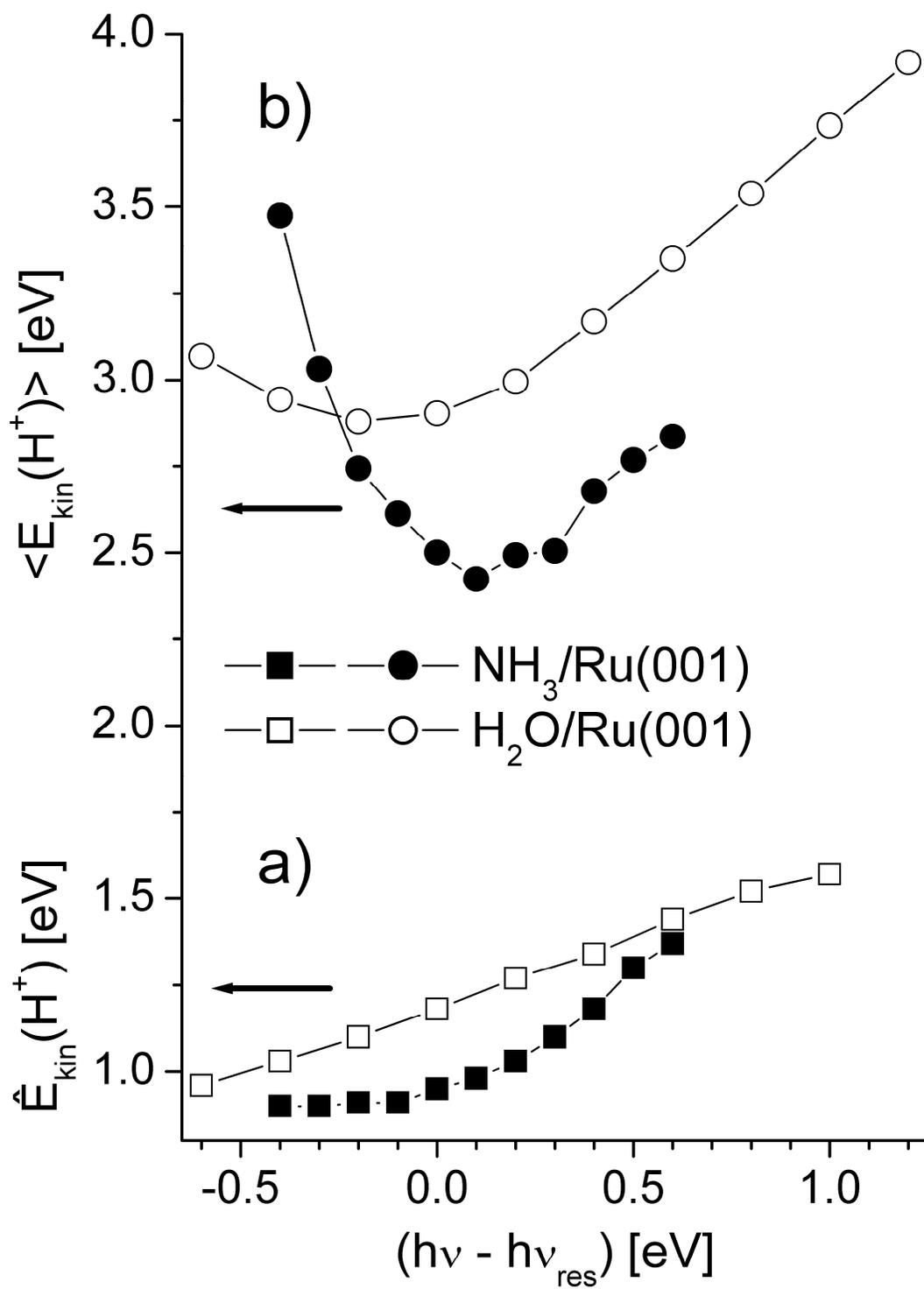
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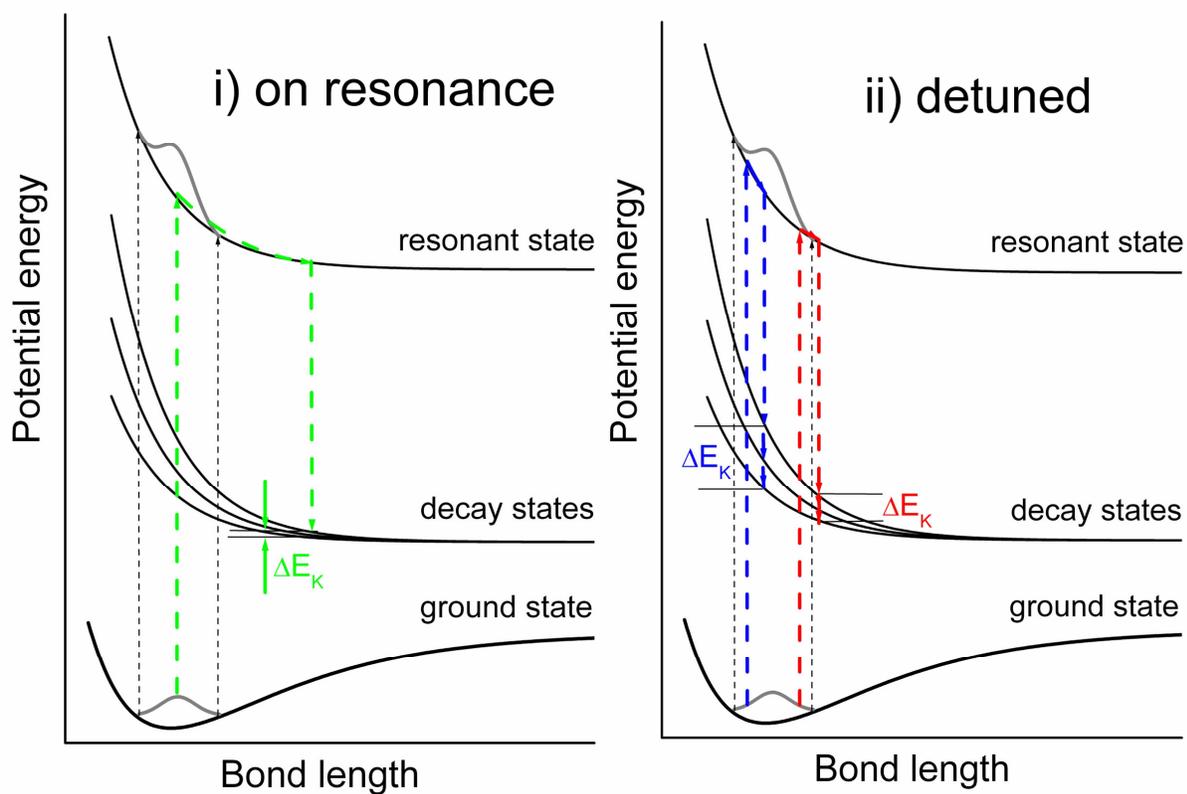


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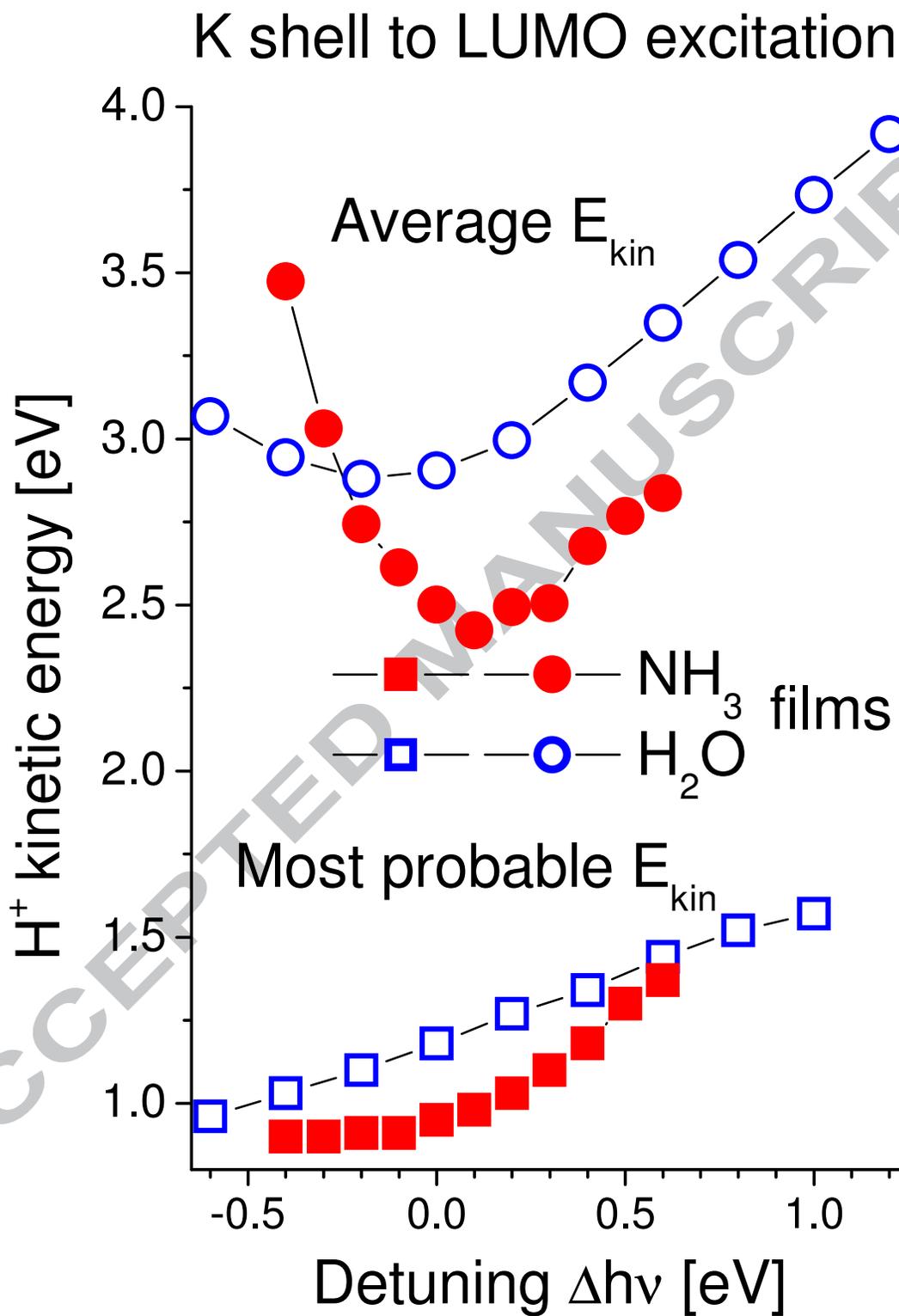


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Dynamics of ultrafast bond breaking by resonant inner shell excitation

Detuning dependent fragment energy distributions

Different behavior of average and most probable kinetic energy

Signatures of bond evolution during core excited and post-decay states discernible

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