

# **Sigma\*-mediated electronic relaxation in 200 nm photoexcited ammonia and heteroaromatics**

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**Abstract:** Time-resolved photoelectron spectra of ammonia display combination bands of the umbrella and stretching modes associated with the N-H coordinate of  $\sigma^*$  relaxation. Time-resolved photodissociation studies determine timescales  $<200$ fs. Similar  $\sigma^*$  photochemistry is found in heteroaromatics.

## **1 Introduction**

The past few years have demonstrated the photochemical importance of  $\pi\sigma^*$  and  $n\sigma^*$  excited states in promoting non-radiative deactivation of many UV photoexcited molecules. These states are either populated via direct photoexcitation typically with weak intensities or indirectly via non-radiative population transfer from optically bright electronic states of  $\pi\pi^*$  character. As put forth in the theoretical work by Sobolewski and Domcke,[1]  $\pi\sigma^*$  states are repulsive along the X-H coordinate (X=N,O,...) and promote efficient molecular deactivation via non-radiative relaxation back to the neutral ground state or via X-H bond fission. Here, we demonstrate a powerful combination of time-resolved spectroscopic techniques for the characterization of  $\sigma^*$  mediated relaxation dynamics while revealing new aspects of ammonia and imidazole UV photochemistry. Time-resolved photoelectron spectra (TRPES) are analyzed for characteristic vibrational structure associated with the X-H stretch relaxation coordinate while time-resolved photofragment translational spectroscopy (TRPTS) clocks the dynamics based on appearance time of H-atoms from X-H bond fission.

## **2 Experimental technique**

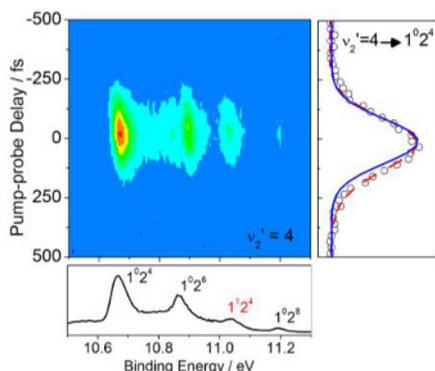
The optical set up consists of a Coherent Inc femtosecond laser system (Mira Optima 900, Legend Elite HE) with a custom-built fourth harmonic box for  $\sim 200$ nm generation as a pump pulse and a tunable optical parametric amplifier (TOPAS) that provides a UV probe pulse. The pump/probe beams are combined collinearly and focused into the ionization region of our magnetic bottle-type time-of-flight (TOF) spectrometer where they interact with a molecular beam of the sample (vapor), ammonia or imidazole, seeded in He. In a TRPES experiment the sample is ionized in a two-photon process with the  $\sim 200$ nm pump pulse tuned to an electronic excited state resonance. A TRPES spectrum is obtained by scanning the time delay between the pump and probe pulses and recording a photoelectron spectrum at each time step. In TRPTS experiments a  $\sim 200$ nm pump pulse resonantly one-photon excites the sample to the first electronic excited state. H-atoms from N-H

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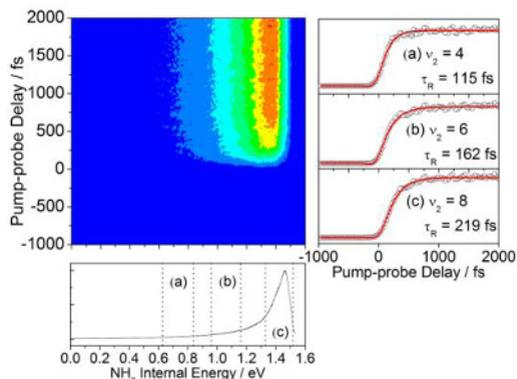
photodissociation are ionized in a 243nm (2+1) resonant multiphoton process and analyzed with respect to their kinetic energies in the magnetic bottle as the pump-probe delay is scanned. 1,3-butadiene is used for TOF to energy calibrations and characterization of the instrument response function (IRF) which is approximately 225fs.

### 3 Results and discussion

Ammonia, a prototypical amine group which appears in a number of organic molecules, is resonantly (200.8nm) excited to the  $v_2' = 4$  vibrational level of the umbrella mode in its first electronic excited state of  $\text{no}^*$  character. Three  $\sigma^*$  mediated deactivation paths are available along the N-H stretching coordinate: Non-adiabatic crossing through a conical intersection leads to either repopulation of the  $\text{NH}_3$  ground state or dissociation into ground state  $\text{NH}_2$  and H photoproducts whereas adiabatic avoidance of the conical intersection correlates with excited state  $\text{NH}_2$  and ground state H.



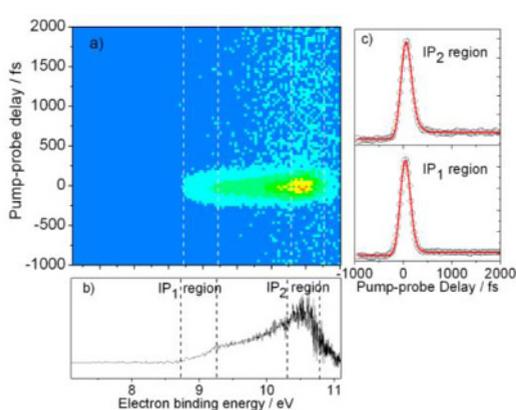
**Fig. 1.** TRPES spectrum of  $\text{NH}_3$  (2d map). The time profile of the signal integrated over all electron binding energies (circles) is shown on the right together with our IRF (solid line) and an exponential decay fit convoluted by the IRF (dashed line). The bottom graph represents the photoelectron spectrum intergrated over all pump-probe delays.



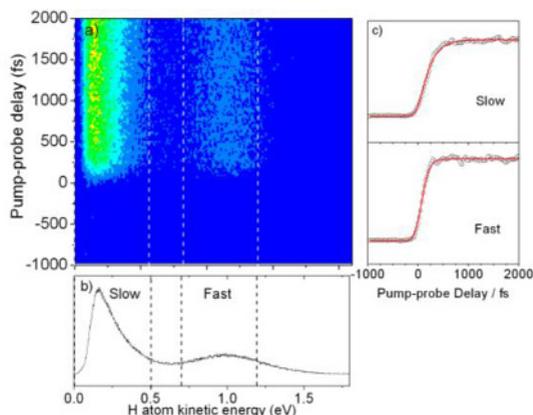
**Fig. 2.** TRPTS spectrum for H-atoms eliminated from UV excited  $\text{NH}_3$  (2d map). The bottom graph shows the H-atom signal in terms of internal energy remaining in its  $\text{NH}_2$  co-fragment. For the energy regions (a), (b), (c) timetraces are plotted in the graphs on the right.

The TRPES spectrum of the  $\text{NH}_3 \tilde{A}$  state is displayed in the 2D picture of Figure 1 with a time-integrated photoelectron spectrum and energy-integrated time profile shown in the attachments. The photoelectron spectrum shows four distinct peaks, which are labelled according to their quanta of excitation in the cationic symmetric stretch mode ( $v_1$ ) and umbrella mode ( $v_2$ ). Three peaks energetically align with an odd progression in the umbrella mode ( $1^0 2^4$ ,  $1^0 2^6$ ,  $1^0 2^8$ ). The dominant peak is associated with an  $\text{NH}_3^+(\tilde{X}) \leftarrow \text{NH}_3(\tilde{A})$  transition where the number of initially excited  $v_2'$  quanta ( $v_2'=4$ ) is preserved upon ionization. Intensities in the progression diminish toward higher quanta of vibrational excitation. The third peak is assigned to a combination band of the symmetric stretch and umbrella mode ( $1^1 2^4$ ). This vibrational pattern in the photoelectron spectrum is the result of a pyramidal to planar geometry shift from the neutral ground state to the  $\tilde{A}$  state in combination with  $\sigma^*$  mediated relaxation along the N-H stretching coordinate. All photoelectron peaks show identical time profiles and can be fit with a decay convolution with the IRF. A decay constant of  $t_{\text{dec}} < 75\text{fs}$  is extracted this however corresponds to evolution of the excited state wavepacket out of the vertical Franck-Condon window with the cation rather than the actual relaxation time on the  $\text{no}^*$  state. For the purpose of determining timescales, time-resolved translational kinetic energies of H-atoms eliminated along the N-H stretching coordinate are measured. This is shown in Figure 2 as a TRPTS spectrum plotted in terms of the internal energy of the  $\text{NH}_2$  co-fragment. H-atom appearance times of 115, 163, and 219fs are measured, respectively, when  $\text{NH}_2$  is left in its electronic ground state with 4, 6, and 8 quanta of  $v_2$  excitation. In the case of highly excited co-fragments, less energy is available to flow into the N-H dissociation and hence H-atom appearance times increase.

Imidazole, a common chromophore in biomolecules, undergoes similarly efficient  $\pi\sigma^*$  mediated relaxation in competition with ring puckering and ring opening pathways following 200nm excitation to its lowest electronically excited  $^1\pi\pi^*$  state.[2] From *ab initio* non-adiabatic dynamics simulations [3] it is known that 83% of the excited state flux proceeds along a non-radiative  $^1\pi\pi^* \rightarrow ^1\pi\sigma^*$  pathway which is the focus of the present study. The TRPES spectrum of imidazole is displayed in Figure 3 together with a time-integrated photoelectron spectrum and energy-integrated timetraces of the IP2 and IP1 regions.



**Fig. 3.** (a) TRPES spectrum of imidazole. (b) Time-integrated photoelectron spectrum. (c) Energy-integrated timetraces of the IP2 and IP1 regions.



**Fig. 4.** (a) H-atom TRPTS spectrum from imidazole. (b) Integrated H-atom kinetic energy spectrum. (c) Timetraces for the slow and fast H-atom regions.

timetraces. The photoelectron spectrum shows two steps that fall within the range of the first and second ionization potential (IP1=8.81eV, IP2=10.38eV) but lack discernable vibrational structure. Timetraces of the IP1 and IP2 region provide 50 and 74fs decay times, respectively, which are interpreted as evolution of the excited state wavepacket out of the ionization window.[3] Appearance times of H-atom photoproducts from NH-dissociation provide a better measure of these dynamics. A TRPTS spectrum is shown in Figure 4, but not enough information is known about the energetics of the imidazolyl co-fragment to allow conversion from an H-atom kinetic energy to an imidazolyl internal energy axis. The H-atom kinetic energy spectrum shows a very distinct bimodal distribution. High kinetic energy (fast) H-atoms can be associated with relaxation along the repulsive  $\pi\sigma^*$  state leading to N-H dissociation. An appearance time of 82fs is determined from the high kinetic energy timetrace. Low kinetic energy (slow) H-atoms are also eliminated on ultrafast timescales (199fs). In analogy with the ammonia study presented above, these H-atoms may be correlated with an imidazolyl co-fragment that is left with high internal energy. Alternative sources for slow H-atoms discussed in the literature include multiphoton dissociative ionization and statistical decay of vibrationally hot imidazole following relaxation back to its ground state.[3] The latter is excluded based on the timescale measured here.

## References

- [1] A. L. Sobolewski, W. Domcke, *Eur. Phys. J. D* **20**, 369 (2002)
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