時間分解光電子分光法によるo-ニトロフェノールの超高速光解離反応の観測

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O-nitrophenol (*o*-NP) absorbs strongly in the atmospherically important UV-regime between 300 and 400 nm and releases nitrous acid (HONO) [1] which itself is a precursor for OH-radicals. The OH radical is the key oxidant in the degradation of air pollutants and one of the defining molecules in atmospheric chemistry.

We investigated HONO formation from *o*-NP in gas phase by time-resolved photoelectron spectroscopy using 400 nm as excitation wavelength and the 19th harmonic pulses (29.5 eV) generated with a Ti:Sapphire laser pulse as a probe. *o*-NP molecules were vaporized and expanded into the interaction region by mixing with helium gas warmed at a temperature of 323 K.

Figure 1 a) shows the photoelectron spectrum without the pump pulse and the temporal evolution at selected pump-probe delays. We recognize the peaks at 11.0, 11.4, 12.2 and 12.5 eV. Most prominently, we observe the rise of a peak around 11 and 12.5 eV indicated by the arrows in Fig. 1 a). For a more detailed analysis, the difference spectrum between the spectrum taken at a delay time of 1333 fs and the spectrum without pump is shown in Fig. 1 b). This difference spectrum agrees nicely with the photoelectron spectrum of HONO taken from Ref. 2. Therefore, this provides a strong indication that HONO is formed upon irradiation of 400-nm light. The timescale of HONO formation is plotted in Fig. 1 c). Here, the time evolution of the signals around 11 and 12.5 eV is shown. The temporal behaviour of these two bands is quite similar. Directly after excitation, the intensity was reduced by the depletion of the ground state by pump or by the change of the ionization cross section in the excited states.

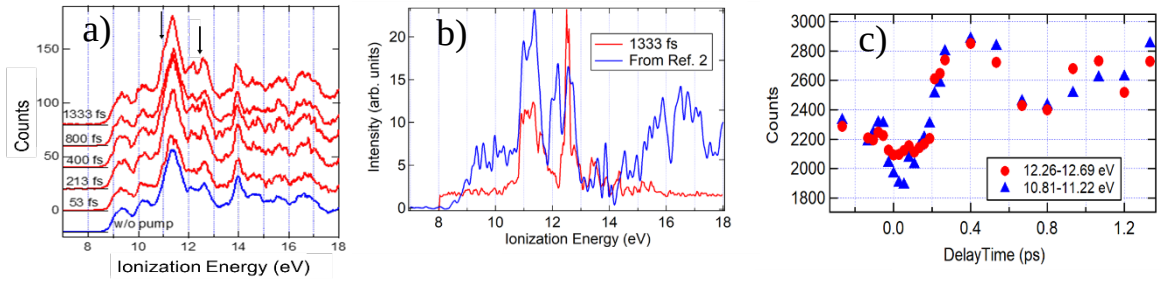

Fig. 1 a) Photoelectron spectrum of o-nitrophenol measured with probe pulse only and temporal evolution of the photoelectron spectrum following excitation at 400 nm.　b) Difference spectrum at 1333 fs and the photoelectron spectrum of HONO taken from Ref. [2], c) Temporal evolution of the HONO band at 12.5 (●) and at 11 eV (▲).

At 200 fs, the signal starts to rise and has a first maximum around 400 fs. At that delay time, the structure of the two HONO peaks are already visible (see Figure 1a). Around 600~800 fs, the spectrum becomes less intense and undergoes spectral changes. Afterwards, the intensity of the HONO band gradually increases again. The temporal evolutions of the fingerprints of HONO in photoelectron spectra suggest that HONO is formed after about 250 fs. This is the first real time observation of HONO formation. The observed timescale is consistent with an earlier study by UV pump-UV probe photoelectron spectra, in which excited state dynamics is finished after about 200 fs [3].

[Refferences]

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