Electronic Supplementary Information

Vibrational excitation of adsorbed molecules by photoelectrons of very low energy: acrylonitrile on Cu(100)

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Parameters influencing the 2PPE spectroscopy

The main parameters influencing the 2PPE spectra in our measurement approach include (i) the coverage of the Cu(100) surface with (layers of) ACN, i.e. the number of molecules partaking in the interaction process; (ii) the polarisation of the exciting laser radiation, which finds its way into the dipole excitation probabilities; (iii) the laser pulse energy, which is associated with the number of electrons being available for the interaction; and (iv) the wavelength of the laser, which is linked to the maximum electron excess kinetic energy in the 2PPE process, i.e. it determines which vibrational modes of the molecule might be excited.

i. The coverage of Cu(100) with ACN.

We carried out brief experiments to ascertain the influence of the thickness of the adsorbate on the 2PPE signals. For this, the exposure of the surface to ACN was varied in the range 0.5–12.0 L. For sub-mono layer coverage, and up to ~1.5 L, the behaviour is “linear”, i.e. electron signal attenuation is proportional to the adsorbate coverage, indicating largely elastic scattering out of the acceptance cone for the electron analyzer. For higher ACN coverage, “shielding” effects start to become evident, and multiple scattering of electrons sets in (this was evident from some simple angular-resolved measurements – however, the related setup was only crude, and no full angular scans could be performed).

Since it was the goal of our investigation to have to consider only single scattering processes in the analysis, the majority of experimental results discussed in the paper were obtained for an exposure of our Cu(100) substrate to 0.5L – 1.0 L of ACN.

ii. The polarization of the 2PPE excitation laser beam.

As shown in Fig. 1 of the main paper, in our experiments the laser beam was (normally) p-polarised, with respect to the plane of incidence onto the Cu(100) surface. This polarisation orientation is in accordance with the accepted knowledge that the selection rules for dipole excitation / scattering are at their optimum.

In a brief cross-check we established that indeed the 2PPE signals decreased significantly when altering the laser beam polarisation to the s-orientation. Note that this check was done only for a single laser wavelength, namely λ = 488 nm, which corresponds to an energy of E_{2PPE} = 5.08 eV (associated with a maximum 2PPE-electron kinetic energy of ~0.5 eV). Note also that the polarization-change experiment was performed for a clean Cu(100) surface, i.e. no ACN adsorbate.

iii. The change in laser pulse energy.

The available laser pulse energy, E_p, within the wavelength range of our studies was above 10 mJ. This already surpasses the damage threshold of the copper surface, when the laser beam is focussed to a spot size well below 1 mm^2. Hence, care was taken never to even approach the aforementioned damage threshold, in order to preserve the integrity of the Cu(100) surface (and the adsorbate layers). For the tests, the laser pulse energy was varied in the range 10-100 μJ (laser beam attenuation ÷1000 to ÷100). As expected, the 2PPE signal increased proportional to the square of E_p, saturating at the higher pulse energies.

For comparison, we also repeated the pulse energy experiments using UV-photons (with $h\nu_{UV} = 2\times h\nu_{VIS}$). Not surprisingly, now the single-photon (UV) PE-signal increases linearly with E_p, again saturating at the highest pulse energies. This latter experiment was performed to ascertain that no secondary electrons contributed to the photo-electron signals. Indeed, secondary electron contributions are seen in the 1PPE signals, while they were by and large absent from the 2PPE signals, at least in the range of wavelengths relevant to our studies. This finding is in agreement with other photo-electron studies of copper surfaces (see e.g. ref. 20 of the main paper).

It should be noted that for comparative studies at different wavelengths one could adopt two different strategies, namely (a) to keep the photon flux equal for all wavelengths, or (b) to adjust it so that the total number of generated photoelectron remains constant. We opted for always adjusting the laser pulse energy to be equal for all measurements in a series, so that either approach, (a) or (b), could be applied for the correction of the experimental raw data. We also would like to note that we kept the laser pulse conditions at about the middle of the range for which the 2PPE signal was proportional to E_p^2. On the one hand this served not to saturate the signal accidentally but on the other hand to maintain a good signal-to-noise ratio.

iv. Wavelength range for the 2PPE experiments.

In our studies of inelastic scattering loss, δE, into the vibration excitation of ACN, $E_{v,}$ we aimed at an energy loss ratio of $\delta E/E_v \sim 1$. This guarantees – as pointed out in the introduction to the main paper – that elastic scattering, which normally dominates for electrons with high kinetic energy (as e.g. encountered in EELS), may not any longer

mask the inelastic transfer processes of interest. Note that the observed maximum (final state) kinetic energy of the electrons is related to the two-photon absorption process in Cu(100), taking into account its published work function value of ϕ = 4.59 eV,[21] i.e. $E_{kin,max} = 2\times h\nu - \phi$. This maximum value for the electron kinetic energy distribution increases with photon energy.

The output wavelength range of our OPO system, from the near IR down to about 425 nm, completely covers the range of energies required in our 2PPE experiments with $\delta E/E_v \sim 1$. These include the 2PPE threshold given by the work function ($2\times h\nu \sim 4.6$ eV $\leftrightarrow \lambda_{OPO} \sim 540$ nm) and all fundamental vibrational modes of ACN (up to $2\times h\nu \sim 4.6+1$ eV $\leftrightarrow \lambda_{OPO} \sim 450$ nm); selected wavelength / $E_{kin,max}$ values of relevance to our work are collected in Table 1 of the main paper.

Note that, as expected, all recorded 2PPE spectra exhibited a sharp edge at about the tabulated $E_{kin,max}$ values, with a width which is governed by the thermal energy distribution at the Fermi edge. An example 2PPE electron kinetic energy distribution revealing this notion was shown in Fig. 2 of the main paper.

References

20. V.M. Shalaev, C. Douketis, T. Haslett, T. Stuckless and M. Moskovits; *Phys. Rev. B* 1996, **53**,193-206.

21. P.O. Gartland, S. Berge and B.J. Slagsvold, *Phys. Rev. Lett.* 1972, **28**, 738-739.