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## Supplemental materials to the manuscript: Adsorbate Dissociation Due to Heteromolecular Electronic Energy Transfer from Fluorobenzene Thin Films

## GAS DOSING ON SAMPLE

Deposition of molecules on the sample was done using a micro-capillary array directed doser, with the sample held normal to the doser, 25mm away. This arrangement was found to enhance the deposition by a factor of 10 compared to background dosing. The pressure in the UHV chamber was measured using uncorrected ionization gauge readings. The dosing (in Langmuirs, L) was calibrated in terms of equivalent monolayers for the different species used by Temperature Programmed Desorption (TPD) measurements as discussed below. The liquids used in this work were degassed by multiple freeze-pump-thaw cycles. Vapour from CH<sub>3</sub>I (Sigma-Aldrich, 99.5%), benzene (Sigma-Aldrich, 99.8%), mFBz (Sigma-Aldrich, 99%), dFBz (Sigma-Aldrich, >99%), triFBz (TCI, >98%), tetraFBz (Sigma-Aldrich, >99%), pFBz (TCI, >98%) and hFBz (Sigma-Aldrich, >99.5%) was obtained from the liquid in a pyrex vial a few cm from the precision leak valve used to admit the room-temperature vapour to the directed doser. The deposition of the molecules was done using substrate temperatures below 100K.

## TEMPERATURE PROGRAMMED DESORPTION

Temperature programmed desorption (TPD) measurements were made by positioning the Cu(100) sample to face a quadrupole mass spectrometer (QMS) following dosing. In early experiments, a UTI 100C QMS was used, and for later experiments it was replaced by a Stanford Research Systems RGA200 QMS. The QMS ionizer was located  $\sim 80$ mm away from the sample and behind an aperture that limits the ionizer line-of-sight to the central region of the sample. The sample was heated using a filament at ground potential, located a few mm behind the sample mount.

The dose corresponding to the completion of 1ML was estimated by measuring the area of the second layer peaks and extrapolating that to zero signal. This was found to agree well with the observed onset of the second layer peaks in the spectra. The dose amounts shown in the spectra are the doses (initially in Langmuirs) converted to equivalent monolayers, rounded to the nearest 0.05ML.

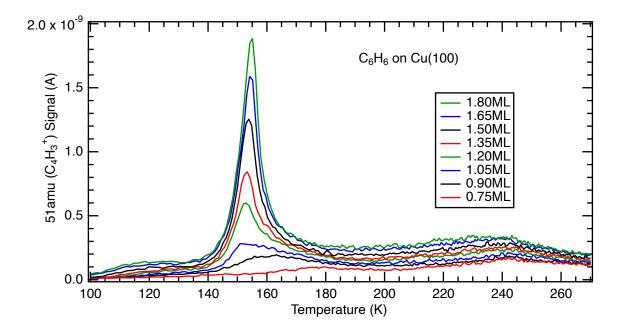


FIG. 1: Temperature programmed desorption spectra from benzene adsorbed on Cu(100). These spectra were obtained with the UTI 100C QMS.

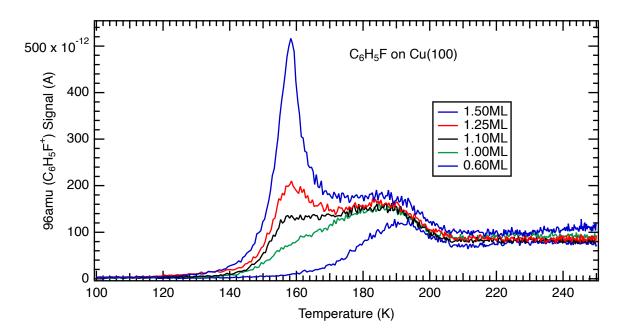


FIG. 2: Temperature programmed desorption spectra from mFBz (monofluorobenzene) adsorbed on Cu(100). These spectra were obtained with the SRS RGA200 QMS.

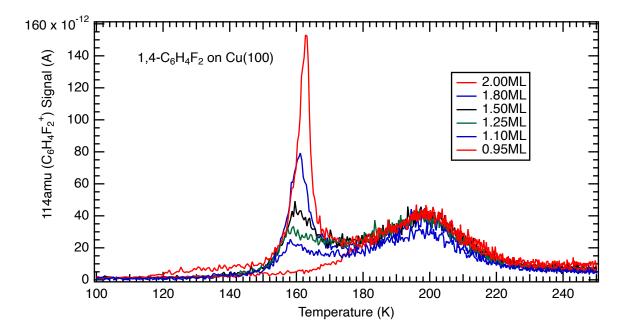


FIG. 3: Temperature programmed desorption spectra from dFBz (1,4-difluor obenzene) adsorbed on Cu(100). These spectra were obtained with the SRS RGA200 QMS.

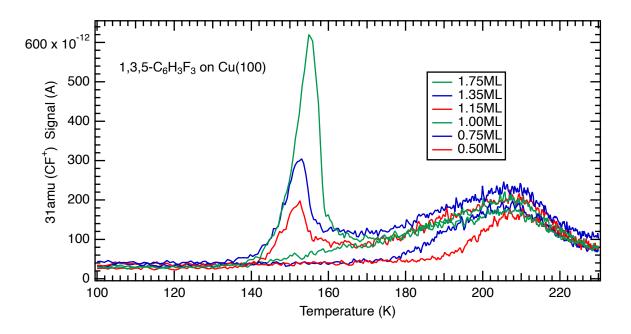


FIG. 4: Temperature programmed desorption spectra from triFBz (1,3,5-trifluorobenzene) adsorbed on Cu(100). These spectra were obtained with the UTI 100C QMS.

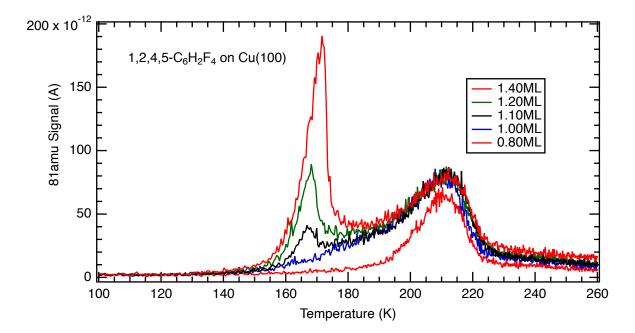


FIG. 5: Temperature programmed desorption spectra from tetra FBz (1,2,4,5-tetrafluorobenzene) adsorbed on Cu(100). These spectra were obtained with the SRS RGA200 QMS.

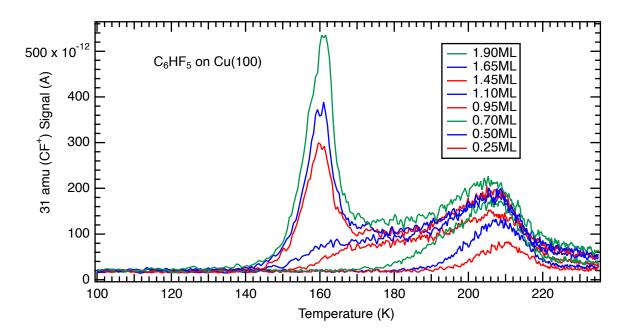


FIG. 6: Temperature programmed desorption spectra from pFBz (pentafluorobenzene) adsorbed on Cu(100). These spectra were obtained with the UTI 100C QMS.

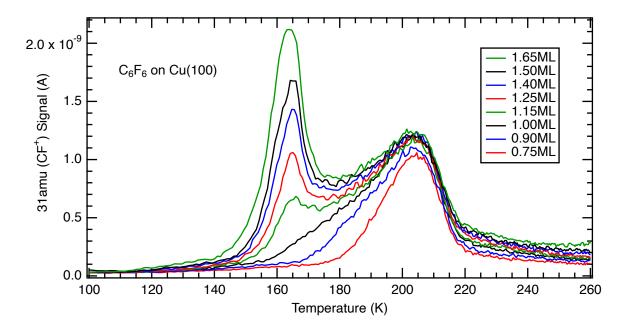


FIG. 7: Temperature programmed desorption spectra from hFBz (hexafluorobenzene) adsorbed on Cu(100). These spectra were obtained with the UTI 100C QMS.