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SRI 2007 Conference Proceedings

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High Resolution Photoemission of Organic Systems at 3m NIM Beamline at CAMD

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Abstract

The 3m NIM VUV beamline at CAMD was designed for novel high resolution photoemission experiments. Both solid state samples and gas phase resolution tests demonstrate that high resolution photoemission is possible below 10 meV, and vibronic fine structure in the photoemission final state can be observed: the first direct experimental identification of symmetry dependence in electron-phonon coupling in a solid state system: the vibrational fine structure observed in photoemission from crystalline copolymer poly-vinylidenefluoride with trifluoroethylene.

PACS: 87.61.Ff, 87.64.Lg, 63.20.Kr

Key words: high resolution photoemission, phonon-electron interactions, Franck-Condon scattering

1. Introduction

The 3m NIM VUV beamline at CAMD was designed to deliver high resolved, high flux VUV synchrotron radiation for investigations in the basic and material surface science field. The beamline is equipped with endstation consisting of two separate chambers consisting of basic ARUPS chamber with Scienta SES200 electron analyzer connected through a sample transfer system with the preparation chamber.

We show here results, recently performed, of vibronic final states effects in photoemission of a solid state organic system. These results provide evidence of a symmetry dependence in electron-phonon coupling in poly(vinylidene fluoride) (70%) and trifluoroethylene (30%).

2. Experimental details

The 3m normal incidence (NIM) beamline consists of water cooled ellipsoidal entrance mirror with a 70 mrad acceptance angle of horizontal radiation from a dipole magnet at CAMD. Two cylindrical mirrors produce a coma-free image on the entrance slit because of opposite sign comas for each mirror in the vertical direction. Two interchangeable gratings (Richardson Grating Laboratory, Rochester, NY) with different blaze angles and surface coatings housed in monochromator utilizing a McPherson mount [1], as described elsewhere [2].

This normal incidence monochromator is combined with an angle-resolved ultraviolet photoemission (ARUPS) endstation (as schematically indicated in Figure 1), which consists of a magnetic field shielded UHV chamber with the electron energy analyzer (Scienta SES200 electron energy analyzer). The ARUPS chamber is connected to a preparation chamber equipped with capabilities for LEED/AES/STM as well as sputtering/deposition/dosing facilities, by a 36 inch McAlister translator. Both chambers can be exploited independently and are equipped with sample holders providing heating/cooling capabilities. The polar rotation of the sample is accomplished by a differentially pumped rotary feedthrough with the liquid helium/liquid nitrogen cooled cryostat housed at XYZ McAlister manipulator with a rotational accuracy is 0.5˚. With the liquid He cooled cryostat, the sample temperature can be controlled from 30 K to 450 K with better than one degree accuracy.

3. Experimental results and discussion

Both gas phase resolution tests (see inset in Figure 1) and solid state sample (Figure 2) show that the demonstrated resolution is seen to be 9 meV or less for the combined beamline/electron analyzer (in transmission mode for the latter) for the Fermi edge of gold films on the silicon and better than 5 meV ultimate electron energy analyzer resolution for Ar 3p level using He I radiation. As it is seen from the inset in the Figure 2, measured Fermi edge broadening of gold films at about of 30 K at 12-88% of the step width appears to be less than 15 meV. This corresponds to better than 9 meV combined analyzer/beamline resolution after deconvolution of the Fermi-Dirac distribution (3 $k_B T$ at a given temperature). Our gas phase results, with 500 μm analyzer slits, show FWHM (7-8 meV) for the Ar gas 3p level. This comparable to reported previously for these Scienta SES200 electron energy analyzers at SSRL and ALS. The combination of the same 2 eV pass energy and the narrowest (200 μm) slit does not significantly improve the measured peak widths. Possible reasons of this limitation is much wider line width of our conventional He I radiation source compared to high resolution microwave discharge VUV sources, or regular discharge sources employing space charge compensation electrodes. Considering the Doppler broadening [3] of ~4.62 meV for the Ar-He gas combination suggests 6 meV for our combined analyzer/source resolution. Assuming value of 4.3 meV broadening introduced by our conventional He I radiation source (the best sources have close to 1.2 meV line width), we can estimate 4.2 meV for ultimate analyzer resolution. In the angular mode, the photoemission data both for gold film on the silicon and for Au(111) single crystal show parabolic shaped dispersion of the well known gold surface state (see insets on the Figure 1), consistent with expectations.

This relatively high combined resolution permits the identification of vibronic fine structure in the photoemission final state. We identified (see Figure 2) two different vibrational contributions to the photoemission fine structure of the ferroelectric copolymer poly(vinlylidene fluoride) with trifluoroethylene, (CH_2-CF_2: CHF-CF_2, 70%: 30%) [3], as denoted in Figure 2. Surprisingly, the contribution of one vibrational mode (denoted ν_1 in Figure 2) to the photoemission fine structure decreases with decreasing temperature. We associate this temperature dependence to the importance of symmetry in vibronic coupling to the photoemission process and increased dipole ordering with decreasing temperature in this ferroelectric system, as noted elsewhere [4].

Studies like this one demonstrate that vibronic contributions to valence band photoemission of large *adsorbed* organic species are now possible a synchrotron light sources [4-6].

Acknowledgements

This work was supported by the National Science Foundation through grant CHE-0415421 and the NSF “QSPINS” MRSEC (DMR-0213808).

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Figure captions:

Figure 1. The layout of Micro/Nanofabrication and Characterization System at 3m NIM beamline at CAMD. Insets show angular mode tests results for Au(111) single crystal and the resolution tests fo rAr gas phase target.

Figure 2. The first direct experimental identification of symmetry dependence in electron-phonon coupling in a solid state system observed in the crystalline polymer P(VDF-TrFE) [4]. Inset shows the resolution tests using the Au Fermi edge, at 21 eV photon energy.

Figure 1.

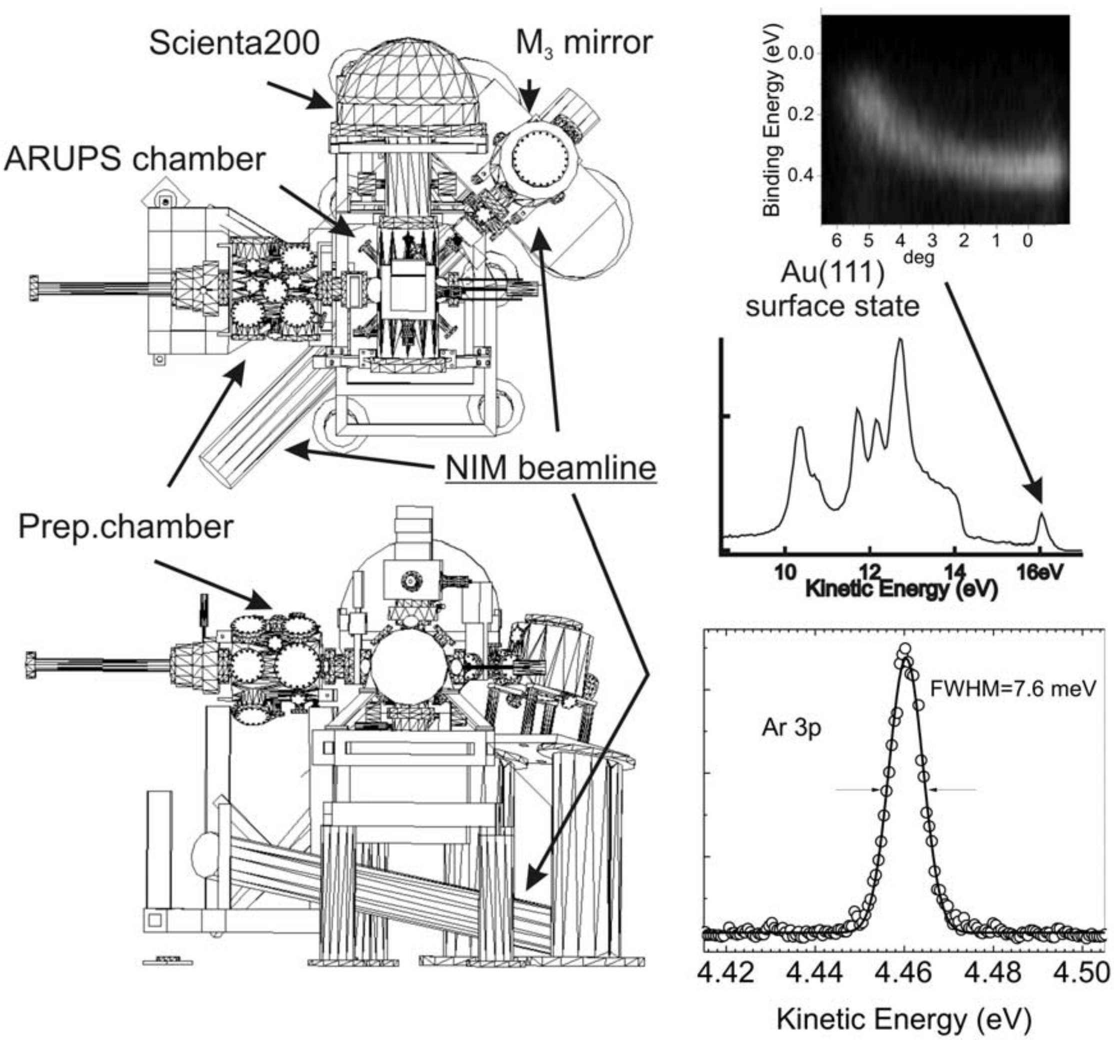
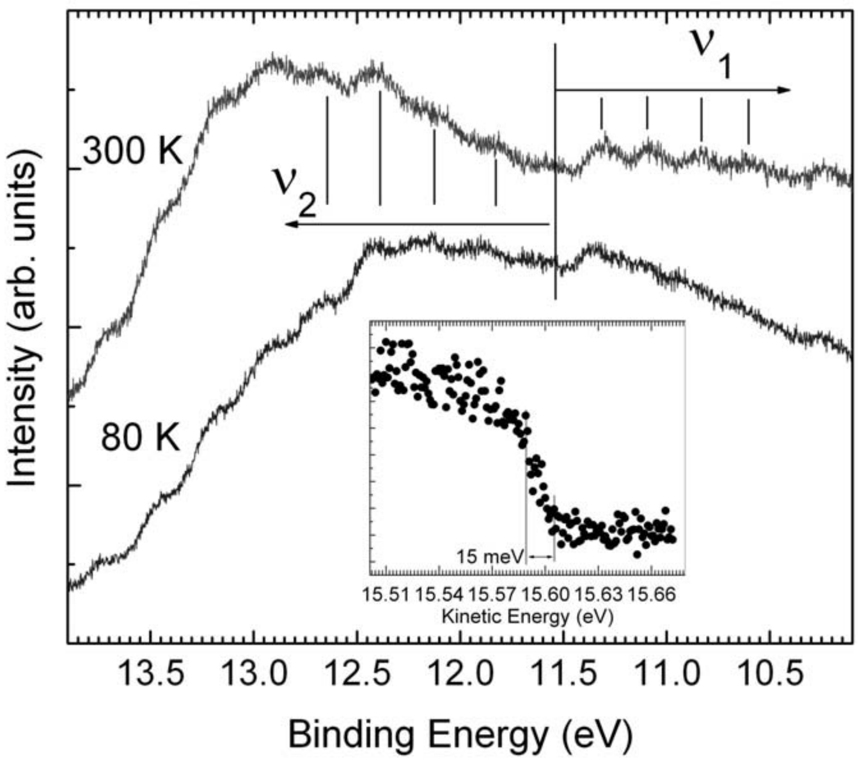

Scienta200
M3 mirror
ARUPS chamber
NIM beamline
Prep.chamber
Binding Energy (eV)
0.0
0.2
0.4
6 5 4 3 2 1 0
deg
Au(111)
surface state
10 12 14 16eV
Kinetic Energy (eV)
Ar 3p
FWHM=7.6 meV
4.42 4.44 4.46 4.48 4.50
Kinetic Energy (eV)

Figure 2.



300 K
80 K
ν_1
ν_2
Intensity (arb. units)
13.5 13.0 12.5 12.0 11.5 11.0 10.5
Binding Energy (eV)
15 meV
15.51 15.54 15.57 15.60 15.63 15.66
Kinetic Energy (eV)