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EXPLOITING STRUCTURE IN THE DESIGN OF ORGANIC NON-LINEAR OPTICAL MATERIALS

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There exists an inherent link between atomic structure and non-linear optical (NLO) behavior. The overview presented here shows how such structure / property relationships can be exploited in order to assess the relative merits of a series of NLO precursors and to predict better NLO contenders. The knowledge acquired from these results can be used to optimize the material by judicious chemical tuning. This pertains to the ultimate goal of being able to 'structurally engineer' materials for a given NLO application.
This presentation concentrates on a series of tetracyanoquinodimethane (TCNQ) derivatives that exhibit varying degrees of quinoidal (neutral) and zwitterionic (charge-separated) character, these two electronic states being very close energetically. Bond-length alternation studies show that the relative balance between the neutral and charge-separated states provides a measure of their intrinsic potential for second-harmonic generation (SHG) applications. The bond-length alternation (BLA) study is presented both in a classical manner, and by using a new topological approach, which exploits ellipticity values from a charge-density study. The ability to predict better TCNQ-based NLO precursors by calculating BLA through the Cambridge Structural Database is also illustrated.
Pseudoatomic charges derived from the charge-density study were used to evaluate the nature of the molecular charge transfer and the solid-state dipole moment, μ. Whilst high dipole moments are advantageous for SHG on a molecular scale, they tend to render a crystal lattice centrosymmetric, which precludes SHG. The inclusion of TCNQ derivatives into zeolite hosts is shown to be a possible method to circumvent this problem.

Keywords: CHARGE DENSITY NON LINEAR OPTICS BOND LENGTH ALTERNATION

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PHOTOEMISSION-MONITORED NORMAL INCIDENCE X-RAY STANDING WAVES: STRUCTURAL STUDIES OF LOW-Z MOLECULAR ADSORBATES WITH CHEMICAL-STATE SPECIFICITY

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X-ray standing wave studies of the surface of surfaces using normal incidence to the Bragg scatterer planes (NIXSW) are now well-established as having a wide applicability to the determination of adsorbate structures on the surfaces of metals and semiconductors. Monitoring the X-ray absorption via core level photoemission offers the potential of obtaining structural data, which are both element and chemical-state specific (through photoelectron binding energy chemical shifts) and is also the only viable way of studying low atomic number species (e.g. C, N and O), which only have very shallow core levels. Such studies do, however, demand the combination of high photon flux and spectral resolution only available on a third-generation synchrotron radiation source. It is also important, when monitoring the photoemission signal, to take account of the effect of non-dipole transitions in the angular dependence of the photoemission. We have made systematic measurements of these non-dipole effects from 1s photoemission from most 1st and 2nd row elements based mainly on multilayer (incoherent) molecular thin films on Cu and Al substrates, and use these in our interpretation of NIXSW structural data. Recent studies of CO, NO and O adsorption and co-adsorption on Ni(111) confirm our ability to tackle these chemically-important adsorbate systems using NIXSW at the ESRF, allowing is to measure CO local site changes due to O co-adsorption and site-specific desorption, as well as dissociation, associated with extended exposure to the soft X-radiation.

Keywords: X-RAY STANDING WAVES, SURFACE STRUCTURE, SURFACE ADSORPTION

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NON-DIPOLE EFFECTS IN PHOTOELECTRIC SCATTERING STUDIED WITH X-RAY STANDING WAVE

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General theoretical description of non-dipole effects in the photoelectric scattering process excited by an x-ray standing wave (XSW) field which is generated by two plane, coherent waves is presented. The contributions of different multipole terms are analyzed for a distribution of atoms within the interference field. Solutions for the angular integrated and differential cross-sections are obtained. It is shown that particularly strong effects due to the presence of two coherent waves can be observed for angular resolved photoemission.

Theoretical analysis revealed that each multipole term shows a different dependence on the polarization vectors and wave vectors of the direct and diffracted beam. The favorite geometries for measurements of non-dipole contributions are discussed. It is shown, that contrary to one-beam scattering experiment the phase shift of photoelectron wave can be measured uniquely. An overview of recent experiments on measuring non-dipole contributions in XSW field is given.

Keywords: X-RAY STANDING WAVE, NON-DIPOLE EFFECTS, PHOTOELECTRIC SCATTERING

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LOCATION OF ATOMS USING ELECTRON STANDING WAVES TO EXCITE X-RAYS (ALCHEMI)

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M. von Laue's interpretation of the Borrman effect in 1949 led to the exploitation of standing-wave (SW) effects on characteristic X-ray production for the location and identification of atoms in crystals by Knowles, Batterman, Cowley and others in the fifties. Similar things may be done using electron diffraction in the transmission geometry to excite X-rays in a thin film. Nodes lie in planes normal to the film, in registry with a known host lattice, while the focused probe of the electron microscope used allows SW analysis of nanometer-size regions. By comparing X-ray emission from host atoms on known sites with that from substitutional impurities, as dynamical diffraction conditions are varied (shearing the SW laterally), the site of the impurity can be found. Applications of this Alchemi technique to geology, semiconductors, intermetallic turbine-blade alloys and ceramics are reviewed.(Atom Location by Channeling Enhanced Microdiffraction). Recent work, in which angle-integrated X-ray emission is collected as a function of the two-dimensional angular incident electron beam coordinate, will be reviewed. Then similar 2-D X-ray patterns from different species indicate that they are on equivalent sites, allowing simple pattern matching. Recent research aimed at determining diffusion pathways and interstitial sites will also be reviewed.
More details in Tafto and Spence, Science (1982) 218, p.49; Spence and Tafto, J. Micros. (1983) 130,p 147, and Rossouw et al, Acta (2001) A57 p.321.
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