Relationship of EXAFS-determined Bond Anharmonicity to Electron Delocalization
S. Calvin, J. Mimih, V. Kishinyovsky, H. Mehta, J. Ciannella, J. Waters, and M. denBoer (Hunter College, City U. of NY)
Abstract No. Calv7929
Beamline(s): X23A2, X23B

Introduction: The EXAFS cumulant expansion yields information on the anharmonicity of the pair-distribution function for bonded atoms. We have found that this anharmonicity is correlated with (and hence gives information about) the degree of electron delocalization in specific bonds.

Methods and Materials: We collected temperature-dependent EXAFS transmission data for a number of materials, including Ti2O3, V2O3, Cr2O3, Se, I2, Br2, n-butyl bromide, sec-butyl bromide, and tert-butyl bromide. Br2 and the butyl bromides were measured in the gas phase, I2 in both gas and powder phases, and all other materials as powders. Temperatures from 20 K to 500 K were used.

Results: To facilitate comparison between samples, we defined a dimensionless radial asymmetry parameter for each distinguishable pair of atoms, given by

\[ \rho = \frac{\langle (r - \overline{r})^3 \rangle}{\overline{r}^3} \]

where \( \overline{r} \) is the average distance between the atoms. A perfectly harmonic bond thus corresponds to a radial asymmetry parameter of zero.

Ti2O3 undergoes a semiconductor-metal transition with onset at 390 K. As can be seen from Figure 1, the radial asymmetry parameter for the shortest titanium-titanium bond increases substantially at that temperature.

Solid iodine, although not a conductor at standard pressure, does have substantial nanoscale delocalization of electrons. The increase in the radial asymmetry parameter for the iodine bond in the transition from vapor to solid reflects this delocalization (Table I).

Finally, t-butyl bromide is considerably more reactive than n-butyl bromide, primarily because of hyperconjugation. This is also reflected in our data (Table I).

In contrast, the bond between nearest-neighbor vanadiums in V2O3 shows no change in anharmonicity at its metal-insulator transition. Investigation continues into this compound.

<table>
<thead>
<tr>
<th>Iodine Vapor</th>
<th>Iodine Solid</th>
<th>n-butyl bromide</th>
<th>tert-butyl bromide</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho = 0.053 \pm 0.022 )</td>
<td>( \rho = 0.093 \pm 0.006 )</td>
<td>( \rho = 0.027 \pm 0.004 )</td>
<td>( \rho = 0.038 \pm 0.004 )</td>
</tr>
</tbody>
</table>

Conclusions: EXAFS-determined anharmonicities can be used to probe the degree of electron delocalization in bonds in a wide range of materials.

Acknowledgments: Support provided by the Department of Energy. Some samples provided by Jan-Peter Urbach, Peter Pfalzer, and Siegfried Horn of the University of Augsburg.