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Determination of Interionic Potentials in Molecules

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Abstract

Virtually all of the important state-to-state processes undergone by molecules (excitation, relaxation, ionization, dissociation, and combination) and the selection among these different pathways are determined by the ion-ion potentials and the resulting degree of overlap between molecular vibrational states for different electronic and atomic configurations. Although the depths of these potentials can be obtained from thermodynamic data and the separations between the vibronic states from spectroscopic measurements, the use of these potentials in the *ab initio* calculation of state-transformation outcomes is limited by the absence of any direct method for determining their extent and shape. We have recently developed a generalization of x-ray absorption fine structure (XAFS) and a related set of experimental and analysis procedures that, in principle, will allow us to obtain such potentials from XAFS data. We have undertaken the analysis of temperature-dependent XAFS data of Cu, Ag, and Au to test the accuracy of existing analytical forms (the Morse potential for metals) in predicting the details of pair distributions and to determine the range of validity of a temperature-independent effective pair-potential approximation. This is the final report of a three-year Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL).

1. Background and Research Objectives

Quantum mechanically, state transformations in molecules are described by $\langle \psi_i | O | \psi_f \rangle$, where the probability of this given channel is determined by the overlap of the initial state and the final state after its modification by the operator for the process. In principle, knowing the spatial extent of the initial and final states is sufficient to calculate all of the outcomes from an interaction of an atom or molecule with, for example, itself, radiation, or another set of atoms.

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Limitations are imposed by the fact that more than two states may be involved in such a transformation and that the higher, more energetic and less populated vibronic levels of a given electronic state with the greatest spatial excursions of the ions may be the states actually involved in a given reaction. These higher levels are, however, not only the most important but also the ones for which the greatest errors in standard analytical forms occur, restricting their use in calculations of this type. Experimental determination of the potentials would ameliorate this problem, but no direct methods for obtaining these data have been developed. This project describes such a method.

An example is the competition between different processes in simple diatomic molecules, which has been the subject of recent laser excitation and photodissociation studies [1-4]. The vibrational autoionization depends on the direct coupling of the initial and final vibronic Rydberg states, and consequently on the ion-ion potential for the different Rydberg states. Similarly, the predissociation of the molecule is determined by the decay of excited vibrational states (corresponding to the electronic ground state configuration) to continuum vibrational states of the ion-ion potential (corresponding to excited electronic configurations). Consequently, the relative rate of these two processes is a function of the ion-ion potential. It has been shown that *ab initio* theoretical calculations of the ion-ion potentials in simple systems as Ar^{2+} and Kr^{2+} yield incorrect values for the dissociation energy [5] and that simple forms of the potential (e.g., Morse potentials) lead to significant errors in the calculation of Franck-Condon factors for ionizing transitions [5]. These problems in the fundamental photophysics, even for homo-diatomic molecules, illustrate the shortcomings of existing theoretical approaches and the need for reliable ion-ion potentials obtained with actual experimental results.

We have concentrated on the forms and characteristics of potentials in simple metals. Traditional analysis of XAFS spectra in metals, even at ambient temperatures, often lead to near-neighbor distances that differ from those measured by diffraction techniques by up to 0.02 Å. Now that reliable calculations of the photoelectron scattering factors exist, it is apparent that these differences originate in the approximation of using harmonic pair potentials in the quantitative analysis of XAFS spectra of these materials. It has been shown that a model Morse pair potential describes in an adequate manner many macroscopic properties of simple bcc and fcc metals. Among these properties are the energy of vaporization and compressibility. Consequently, we have chosen these systems to test the use of a model pair potential in the quantitative analysis of XAFS data. In this case we have independently derived potentials that can be compared with those extracted from the XAFS spectra.

The objective of this project was to demonstrate a method for the direct, experimental determination of ion-ion potentials. These potentials will be of use in the calculation of initial

and final state overlap and the resulting paths and probabilities of state-to-state transformations in molecules, and can ultimately result in the development of a rational approach to the accurate prediction of molecular reactivities and relaxation mechanisms. We focused on the measurement and analysis of some pure metals, determination of the best analytical model for the pair potential, calculation of thermodynamic and vibronic parameters and comparison with known data, comparison of two-body with many-body potential, and determination of the range of validity of a temperature-independent effective pair-potential approximation.

2. Importance to LANL's Science and Technology Base and National R&D Needs

The rationale underlying materials by design is that properties are determined by structure (which is determined by synthesis) so that, if the relationships between structure and properties are understood, an appropriate material can be designed and fabricated to meet any set of criteria. Since ion-ion potentials determine state transformations and reactivity, they are essential to the entire concept of materials and molecules by design. The work performed under the auspices of this project explored the ability to refine and measure such potentials.

The development of the methods of analysis and the interpretation paradigms have already had a substantial impact in our work on other projects. In our studies of technologically significant metal oxides such as superconductors and colossal magnetoresistance materials, our analysis software and experience in examining potentials and distributions have allowed us to determine the distributions of the oxygen atoms around the transition metals with a high degree of accuracy, thereby obtaining information on structural distortions that are critical in understanding the interesting properties of these materials. We have also used these methods in studying local structure in plutonium alloys, and have found the existence of a local "phase transition" induced by age. Disorder and local "phase transitions" apparently play critical roles in aging processes in these materials and the application of accurate paradigms is essential in this work because of the apparent complexity of the statics and dynamics of structure in plutonium.

3. Scientific Approach and Results

XAFS is typically used to obtain information on the average local structure around selected absorber elements in a sample. A photoelectron is produced by the absorption of an

x-ray by a core-level electron of the element; the scattering of this photoelectron from neighboring atoms modulates the absorption cross section above the ionization threshold. Analysis of this modulation provides the types and numbers of neighboring atoms and their distances and mean-square fluctuations with respect to the central absorber to chemically significant accuracies. This scattering process is very fast compared to ionic motions; XAFS thus provides a snapshot of the structure averaged over all of the atoms of that element in the sample.

Extraction of the structural information is facilitated by assuming a harmonic distribution of the neighbor atoms. If the population of higher vibronic states is non-negligible, this approximation results in significant errors; i.e., a contraction in the apparent bond length and a reduction in the number of neighbor atoms. This problem has typically been solved by a cumulant expansion of the disorder term. We have pioneered an alternative approach, generalizing the XAFS equation by relaxing the harmonic motion condition, yielding the correct structural parameters, and incorporating the determination of the ion-ion potential.

This is accomplished by including the effect of the relative motion of the ions in a molecule, interacting via a potential, $V(z)$, by taking the statistical average of the XAFS from a single bond

$$\langle \chi \rangle = \int dz g(z) \chi(k, r(z)) \quad (1)$$

where $\chi(k, r)$ denotes the single scattering XAFS contribution arising from an atom located at a distance r from an absorbing atoms, and the photoelectron momentum, $k = [(2m/\hbar^2)(E - E_0)]^{1/2}$ is referenced to the ionization threshold, E_0 . The radial distribution function (RDF), $g(z)$, is expressed in terms of single-particle wavefunctions, $\{\Psi_i(z)\}$, and single-particle energy levels, $\{\epsilon_i\}$:

$$g(z) = \frac{\sum_i |\Psi_i(z)|^2 e^{-\beta \epsilon_i}}{\sum_i e^{-\beta \epsilon_i}}. \quad (2)$$

The temperature of the system, T , is introduced through $\beta = 1/k_B T$, and z denotes the relative displacement along the bond from the equilibrium position, i.e., $\mathbf{r} = \mathbf{R} + z\mathbf{R}$. The wavefunctions, $\{\Psi_i(z)\}$, are determined by solving the Schrödinger equation using the reduced mass for the isolated pair of interest, and a model potential, $V(z)$. For the Fe-O bonds discussed below, we found that the Lennard-Jones form,

$$V(z) = -V_0 \left[\left(\frac{r_0}{r} \right)^\alpha - 2 \left(\frac{r_0}{r} \right)^\beta \right] \quad (3)$$

leads to the best fit to experiment and yields consistent results for the observed bond-length expansion, bond-dissociation energies, and available optical spectroscopic data. Here, V_0 , r_0 , α , and β are used as parameters determined by fitting $\langle \chi(k, r) \rangle$ to the experimental data at the highest available temperature. The form of the potential is then explored by keeping these parameters fixed when calculating $\langle \chi(k, r) \rangle$ at lower temperatures.

We applied this method to the analysis of the Fe K-edge XAFS of the mineral andradite ($\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$). The analysis of the Fe-O contributions to the XAFS at high temperatures yields the potential and energy levels for the Fe^{+3} -O bond. Using this potential, the XAFS can be calculated at different temperatures, leading to very good agreement with experiment [6]. In this system, the accuracy in the bond dissociation energy is better than 2 percent, and the energy between the ground and first excited states measured by Raman spectroscopy differs by less than 10 percent from the value obtained by XAFS. It is important to note that the application of this method to a molecule is expected to yield better accuracy, since, in a condensed system, the derived effective potential takes into account the presence of other ions beyond the first coordination shell only in an average sense. We have also applied this method in magnesiowustite ($\text{Mg}_{0.9}\text{Fe}_{0.1}\text{O}$), obtaining the Fe^{+2} -O potential and observing the expected softening of the potential as the formal valence state of the Fe ion is reduced.

Despite the agreement with thermodynamic and spectroscopic data, the significance of the measurements on these condensed systems is problematic because we do not understand the meaning of a pair potential in extended systems of this type. It is likely that the parameters defining the potential are used to accommodate the many body effects, with the result that the derived shapes of the potentials will be in error. The only way to circumvent this problem is to investigate simpler systems, i.e., diatomic molecules, and then extend these results to more complex molecules and materials.

Measurements up to 400–500° C on platinum and copper have shown that, although the distribution is adequately modeled by the standard Morse potential, and that this potential also gives the correct distribution at low temperatures, the calculated potential fails to correctly calculate the XAFS between the endpoints. There are two possible origins to this problem. The first is that this analytical form is incorrect and, although possessing sufficient accuracy in terms of the potential depth and the shape on the proximal side (so that it correctly gives such parameters as the energy of vaporization and the compressibility), it fails on the side away from the other atom of the pair. If so, it will not be useful in calculations depending on the

magnitude of these less hindered vibrational excursions that are involved in the breaking of the bond between the pair. The alternative explanation is that the potential is temperature dependent even over a limited range. We have very high quality data for Cu, Ag, and Au, and, in combination with molecular dynamics simulations of the pair distribution function from which the potential can be derived, are now completing the analysis that will determine which of these models is correct.

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