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Synchrotron Radiation Studies of the *K*-Edge Photoabsorption Spectra of Kr, Br_2, and $GeCl_4$: A Comparison of Theory and Experiment

Brian M. Kincaid*†
W. W. Hansen Laboratories of Physics, Stanford University, Stanford, California 94305

and

P. Eisenberger
Bell Laboratories, Murray Hill, New Jersey 07974

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The *K*-edge photoabsorption spectra of Kr, Br in Br_2, and Ge in $GeCl_4$ were measured using synchrotron radiation from SPEAR, Stanford's e^+e^- storage ring, which provides a factor of 5×10^4 improvement in intensity over a conventional x-ray source. The agreement between theory and experiment is only qualitative.

The structure of x-ray absorption edges has been of interest for some time.[1] Measurements using conventional x-ray sources have been made on a wide variety of atomic systems, including crystalline and amorphous solids, liquids, and gases.[2-7] The current view of the origin of the extended x-ray-absorption fine structure (EXAFS), above about 50 eV from the edge, is that the normal atomic photoabsorption matrix element is modulated as a result of interference of backscattered photoelectrons with the outgoing photoelectrons. This model has led to several recent theoretical works on EXAFS in solids.[8-10] One of the major goals of the theory has been the extraction of accurate interatomic-distance information from the experimental data. The most serious limitation in the past has been the low intensity available from conventional x-ray sources at the output of a suitable monochromator. A high-resolution *K*-edge-absorption study using a conventional x-ray tube can take typically 2 weeks to obtain a signal-to-noise ratio of about 300. At SPEAR the intensity improvement over a powerful conventional source is a factor of 50 000, making possible EXAFS measurements with a signal-to-noise ratio of 10^4 taking only 30 min. This work represents the first use of the high x-ray intensity available from a storage ring for high-resolution EXAFS measurements.

It is the intent of this work to compare *ab initio* theoretical calculations with new experimental data. Other work[11] has focused on empirical methods for extracting interatomic-distance information. We find only qualitative agreement between theory and experiment, yielding only a 5% accuracy in the interatomic distances in simple molecules. This disagreement does not preclude, of course, more accurate empirical determination. In order to test the validity of the theory on the simplest possible system, the *K*-edge EXAFS of Br_2 gas was measured. This is the first time that EXAFS modulation has been observed in a diatomic molecule. In Br_2 there is only one interatomic distance so the absorption spectrum should have a single sine-wave modulation with a small amplitude. Similarly, in a system like $GeCl_4$ gas, multiple-scattering effects are expected to be negligible for high enough photoelectron energies, allowing us to treat the four chlorine atoms separately from the point of view of EXAFS. A monatomic gas like Kr should have no oscillatory absorption structure, as there are no nearest neighbors.

In an x-ray-absorption experiment with our apparatus, described in detail elsewhere,[12] the x-ray beam leaves the SPEAR vacuum through a beryllium window and travels through a helium atmosphere to an entrance slit and a channel-cut silicon-crystal monochromator using the (220) Bragg planes located 20 m from the SPEAR source point. After passing through the monochromator the beam intensity I_0 is monitored in a transmission ion chamber. The beam then passes through the sample and is absorbed in another ion chamber, which measures the transmitted intensity I. The ion-chamber currents are digitized and a PDP-11/05 minicomputer stores the ratio I_0/I. Under typical operating conditions roughly 10^8 photons per eV of bandwidth hit the sample. The high flux makes possible a signal-to-noise ratio of $\sim 10^4$ with an integration time of 1 sec/point. The sample cell, approximately 30 cm long with thin Kapton windows, is filled with gas and pumped out until roughly 2–3 absorption lengths of gas (measured just above the K edge) remain, yielding the optimum signal-to-noise ratio. The energy resolution of the computer-controlled monochromator is determined mainly by the angular divergence of the input x-ray beam. The fractional energy resolution is given by $\Delta E/E = \cot\theta\Delta\theta$, where θ is the Bragg angle and $\Delta\theta$ is the angular divergence. In this experiment the resolution was always on the order of 1 eV.

The data for Br_2, Kr, and $GeCl_4$ are shown in Figs. 1 and 2, where $\mu X = \ln(I_0/I)$ is plotted against photon energy. The energy scale for Kr has been shifted and the curve displaced to allow comparison with the data for Br_2. The larger EXAFS modulation in the case of $GeCl_4$ is consistent with the larger number of nearest neighbors and smaller interatomic distances than in Br_2. Near-edge data are shown on an expanded scale in the insets. The curves for Kr and Br_2 are somewhat similar and as expected there is no oscillatory structure for Kr.

Kronig[13] proposed the first theory of EXAFS in solids. The failure of the early Kronig theory to explain EXAFS in gases and amorphous materials prompted a number of other theoretical studies of EXAFS, including a detailed calculation of EXAFS in $GeCl_4$.[14] The assumptions of the current theories[8-10] differ from those of Kronig in that short-range order, rather than a well-defined crystal lattice, is all that is necessary for the existence of EXAFS. In the current view, the modulation of the x-ray absorption, $\chi = (\mu - \mu_0)/\mu_0$, is due to interference between the backscattered and outgoing photoelectrons in the photoabsorption matrix element, where μ_0 is the absorption coefficient of an isolated atom with no fine-structure modulation. Using the "golden rule" and assuming the same density of final states in the molecular-absorption process as in

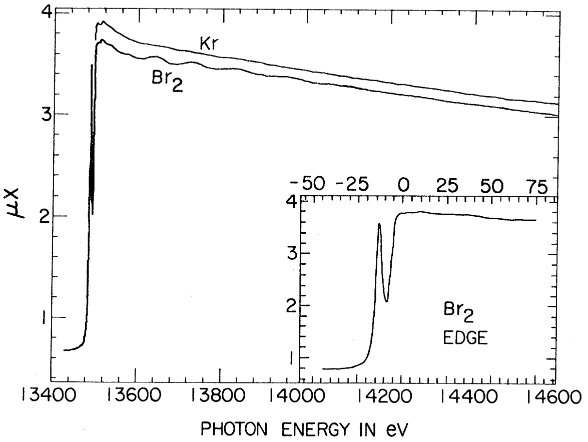

FIG. 1. K-edge x-ray-absorption spectra for Kr and Br_2 gases. The Kr energy scale has been shifted and the curve displaced for comparison with Br_2. Near-edge data for Br_2 in inset.

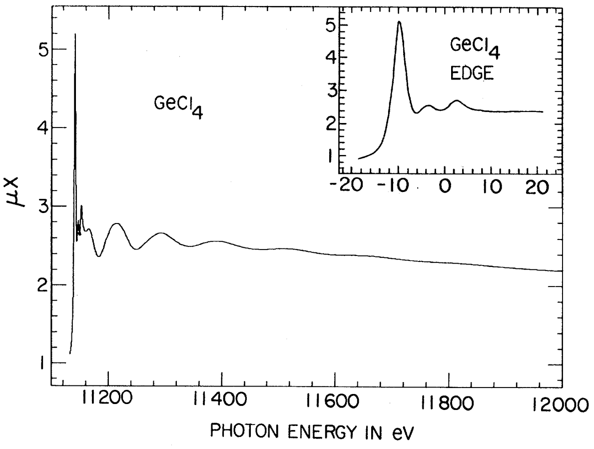

FIG. 2. Germanium K-edge-absorption spectrum of $GeCl_4$ gas. Near-edge data in inset.

the isolated-atom case, one is led to[8]

$$\chi = \frac{|\langle f_0 + f_{sc}|H_i|K\rangle|^2}{|\langle f_0|H_i|K\rangle|^2} - 1. \qquad (1)$$

$|K\rangle$ is the initial K-shell atomic wave function and H_i is the dipole-approximation interaction Hamiltonian. The final state in the isolated-atom case after the absorption of the photon is $|f_0\rangle$ and $|f_0 + f_{sc}\rangle$ is the final state in the molecular-photoabsorption process, where an electron scattered from the nearby environment is included. We assume that the outward wave may be considered to be a plane wave near a scattering atom and the backscattered wave returning to the absorbing atom may also be treated as a plane wave. It is also assumed that the scattering from neighboring atoms is elastic and can be treated independently of the other atoms. These assumptions lead to the formula[9]

$$\chi(k) = -\frac{|f(k,\pi)|}{kR^2} \times \exp(-2\sigma^2 k^2)\sin[2kR + \alpha(k)], \qquad (2)$$

for molecules like Br_2 and $GeCl_4$ with only one significant interatomic spacing. Here k is the wave vector of the outgoing electron, R is the atomic spacing, 2.28 Å for Br_2 and 2.09 Å for $GeCl_4$, $f(k,\pi)$ is the backscattering amplitude from the neighboring atoms, σ^2 is the mean square fluctuation in the distance R due to the vibration of the molecule, and $\alpha(k) = 2\eta_1(k) + \arg[f(k,\pi)]$ is the phase shift, with $\eta_1(k)$ the outgoing p-wave phase shift for the photoelectron. The backscattering amplitude $f(k,\pi)$ is then calculated from the phase shifts δ_l according to the partial-wave formula

$$f(k,\pi) = (1/k)\sum_{l=0}^{\infty}(-1)^l(2l+1)\exp(i\delta_l)\sin\delta_l.$$

In this work the phase shifts are calculated in the static-exchange Hartree-Fock approximation assuming a fixed set of atomic wave functions. The radial Schrödinger equation is solved iteratively to produce phase shifts for the nonlocal exchange potential. The atomic wave functions used are double-ζ analytic Hartree-Fock wave functions[15] generated using a program similar to that of Roothan and Bagus.[16] The fully relaxed ion with a single K-shell vacancy is taken for the absorbing atom and the ground state is used for the scattering neighbors. This neglects all molecular properties except for the internuclear distance. The value of σ^2 is computed from the vibrational parameters of Br_2,[17] and is estimated for $GeCl_4$ based on the known vibrational modes and frequencies of the molecule,[18] and the Debye-Waller factor is found to be significant only at the highest photoelectron energies. No parameters of the theory have been adjusted to improve agreement with the data.

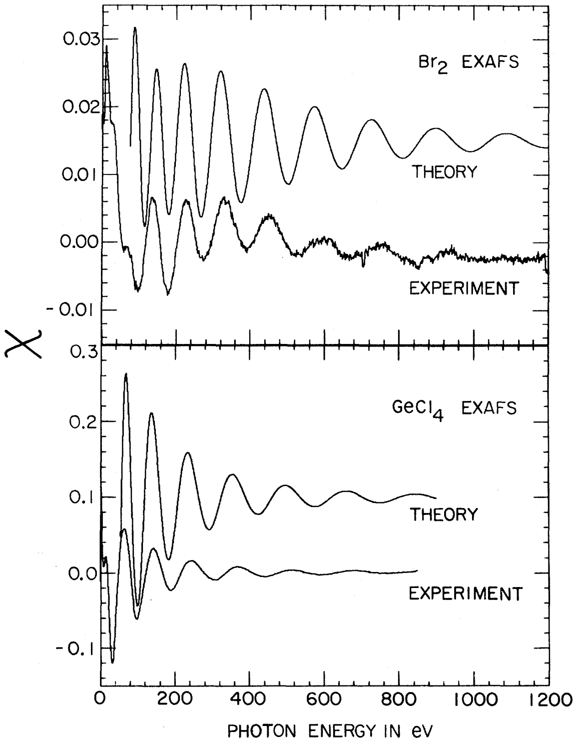

FIG. 3. Comparison of theory and experiment. The theoretical curves have been displaced for clarity.

The results of the theory calculations are compared with experiment in Fig. 3. The oscillatory part of the experimental absorption curve has been separated from the background atomic absorption and normalized by assuming the smooth background absorption to be the same as the isolated-atom absorption curve. The theory curves have been displaced upward for clarity. The zero of the energy for the experimental curves was chosen by calculating (with the Hartree-Fock program mentioned previously) the difference in energy between the continuum limit and the atomic excited state presumed to be responsible for the first large peak in the absorption spectra. For Br this difference is 13.3 eV and for Ge it is 9.8 eV. This neglects any possible molecular effects on the zero of energy. As can be seen from Figs. 3(a) and 3(b), the theory predicts EXAFS roughly a factor of 2 larger than the data. Also, there are disagreements of peak positions that are well outside the experimental error limits. If one adjusts the starting value of the interatomic spacing, which is the most sensitive parameter in the theory, to improve the peak-position agreement, the distance so determined is in error by 5%.

The large discrepancy in amplitude between theory and experiment is probably due to the assumption of elastic scattering and neglect of inelastic processes in core-hole production. Also, the additional phase shift due to inelastic scattering could possibly account for the peak-position disagreement. Another possible problem is the choice of initial wave functions, since agreement of peak positions between theory and experiment requires quite accurate values for the scattering and outgoing-wave phase shifts. The removal of other assumptions of the theory, specifically the plane-wave approximation, lack of multiple scattering, and the static-exchange approximation, have been treated by others.[8-10] While these effects should be important for low photoelectron energies, it is difficult to understand how they could modify the amplitude by a factor of 2 over an energy range of more than 1000 eV.

It is concluded that the theory of EXAFS as outlined in this paper and other theories used to date are inadequate to produce quantitative agreement with the experimental data available using synchrotron radiation. One can still use a combination of theory and empirically determined phase-shift and amplitude curves to determine atomic-shell spacings around an absorbing atom.

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†Currently associated with Bell Laboratories, Murray Hill, N. J. 07974.

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Measurement of Slow Vibrational Relaxation and Fast Vibrational Energy Transfer in Solid N_2

K. Dressler, O. Oehler, and D. A. Smith
Physical Chemistry Laboratory, Federal Institute of Technology (ETH), 8006 Zürich, Switzerland

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The decay rates of the vibrational levels $v=3$ to $v=13$ in ground-state N_2 have been measured in solid nitrogen between 4.2 and 18 K. In N-atom-doped but otherwise highly purified solid N_2, the vibrational relaxation rates are found to be fitted by the expression $P_{v\rightarrow v-1}=A_v+B_v\exp(-\Delta E_v/kT)$. The rate $A_v\cong v\times(1\ \mathrm{sec}^{-1})$ is interpreted as the multiphonon creation rate in the $v\rightarrow v-1$ relaxation, while $B_v\cong 6\times 10^8\ \mathrm{sec}^{-1}$ near $v=10$ describes the intermolecular transfer of a vibrational quantum, $N_2(v)+N_2(0)\rightarrow N_2(v-1)+N_2(1)$, with energy mismatch $\Delta E_v=E_1-E_0-E_v+E_{v-1}$.

We have investigated the vibrational relaxation of ground-state N_2 in vapor-deposited pure solid nitrogen at temperatures from 4.2 to 18 K. The vibrational levels $v=3$ to $v=13$ have been observed after excitation by a pulsed 10-keV electron beam. Examples of the decays of the indi-