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Two-Center, Two Electron Excitations Identified
in NEXAFS for Solid Ne

by

H. Sambe, X. Qian and D.E. Ramaker

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### Title and Subtitle
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### Authors
H. Sambe, X. Qian, and D.E. Ramaker

### Performing Organization Name(s) and Address(es)
Chemistry Department  
George Washington University  
Washington, D.C. 20052

### Sponsor's/monitoring agency name(s) and address(es)
Office of Naval Research  
800 N. Quincy Street  
Arlington, VA 22217-5000

### Abstract
Experimental K-edge NEXAFS (near edge X-ray absorption fine structure) data for solid Ne are compared with theoretical results. Seven features in the experimental spectrum that are not reproduced by the theoretical results are found to be attributable to two-electron excitations. Five of them are usual one-center excitations, but the remaining two are found to be novel two-center excitations involving resonant orbitals as opposed to the usual bound orbitals. In contrast, two-center, two-electron excitations involving only bound orbitals are found to be absent in the experimental spectrum.
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H. Sambe, X. Qian, and D.E. Ramaker

Chemistry Department, George Washington University, Washington, D.C. 20052

Experimental K-edge NEXAFS (near edge X-ray absorption fine structure) data for solid Ne are compared with theoretical results. Seven features in the experimental spectrum that are not reproduced by the theoretical results are found to be attributable to two-electron excitations. Five of them are usual one-center excitations, but the remaining two are found to be novel two-center excitations involving resonant orbitals as opposed to the usual bound orbitals. In contrast, two-center, two-electron excitations involving only bound orbitals are found to be absent in the experimental spectrum.

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In photo-absorption spectra, one-electron (1-e) excitations normally dominate the spectra for obvious reasons. Much weaker two-electron (2-e) shakeup excitations, nevertheless, have been observed in many atomic, molecular, and solid systems. In solids and molecules, these 2-e excitations can be either one-center (1-c) or two-center (2-c), i.e., two holes can be located at the same or different atoms. Most of the observed 2-e excitations are 1-c. Only a few 2-c excitations have been identified, for example, in alkali halides [1], PrCl$_3$ crystal [2], (O$_2$)$_2$ dimers isolated in solid Ne [3], and Ar solid [4]. All of these observed 2-c excitations are associated with two identical valence excitations (except that of Ref. [2] which involves different valence excitations) and are observed in the UV region well below 30eV. This begs the question: Are 2-c excitations restricted to valence excitations, when strong mutual interactions are guaranteed due to the large hole size and similar excitation energies? In this Letter, we shall identify, for the first time, 2-c excitations involving a core excitation in the X-ray region. Another novel aspect of the identified 2-c, 2-e excitations is involvement of resonant rather than bound orbitals, i.e., quasi-stationary orbitals in the continuum.

Figure 1 compares experimental K-edge NEXAFS (near edge X-ray absorption fine structure) data for solid Ne with our theoretical results. The experimental data were recently measured by Hiraya et al. [5] with high energy resolution (0.46eV) for a thick Ne film condensed at 6.3K. A dramatic "thickness effect" is observed for the sharpest peak, E$_1$. To reduce this effect, Hiraya et al. also measured spectra on thin Ne films, which illustrated that the E$_1$ peak intensity is about eight times stronger than the R$_2$ peak intensity, contrary to Fig. 1: The E$_1$ peak actually dominates the spectrum. Our theoretical results are calculated utilizing a curved-wave, multiple-scattering (MS) approach (FEFF6) recently developed by Rehr and co-workers [6,7]. The input data for these calculations include the coordinates for 87 atoms (which form 6 shells with an fcc lattice constant of 4.463Å [8]), the sample temperature (6.3K), the Debye temperature (66.0K) [9], and a choice for the self-energy as
described below. All other information, including the core lifetime, are internally provided by
the code. We have performed full MS calculations incorporating the maximum number of
paths that the code allows. In Ne solid, the inelastic mean free path of the photoelectrons is
very long (>80Å) for electron energies less than 20eV but rapidly decreases to 20Å above
30eV [10]. In order to include this large variation in the mean free path, we have performed
two calculations, one without inelastic loss [theory (a)] and one with inelastic loss [theory
(b)]. We employed the ground-state, exchange-correlation potential with a zero imaginary
part for (a) and the complex Hedin-Lundquist self-energy for (b). Thus, the theoretical result
(a) simulates the experimental spectrum below 30eV and (b), above 30eV. These sections of
the spectra are indicated by solid lines in Fig. 1 and represent our theoretical spectrum.

The sharpest peak (E₁) in the experimental solid Ne spectrum closely resembles the
1s→3p excitation peak for gaseous Ne, so that peak E₁ has been attributed to the 1s→3p
exciton [5]. The FEFF6 model is limited to an "extended" continuum spectrum above the
Fermi level, and hence excitonic peaks are not well reproduced with this model [6]. A small
kink near the threshold in the theoretical spectrum does suggest a trace of the 1s→3p
exciton. Peaks Rᵢ for i=1-8 in the experimental spectrum, which are well reproduced by the
theoretical spectrum, are attributable to l-e excitations, 1s→εᵢp, where εᵢp are resonant
orbitals arising from scattering interference. The experimental features that are not
reproduced by the theoretical spectrum are shaded in the figure and labeled Dᵢ for i=1-7.
Below we shall discuss the origins of those Dᵢ features.

The structure comprising the D₃-D₅ features is virtually identical to the structure
observed in the NEXAFS of gaseous Ne [11] except for a uniform shift of 1.8eV to higher
energy. This structure in the gas phase has been attributed to ¹P states arising from the
1s¹2s²2p⁵3p² configuration, final states in the 1s2p→3p3p excitation. These localized 2-e
excitations are expected to survive in the solid phase, just as the 1s→3p excitation does, so
the D₃-D₅ features can be attributed to those ¹P states [12]. Similarly, we can show that the
D₆ and D₇ peaks are due to two ¹P states resulting from the 1s2s→3s3p excitation. The separation between the two ¹P states is large, because they are almost pure states of 
[(1s2s)³S(3s3p)³P]¹P and [(1s2s)¹S(3s3p)¹P]¹P and the 2s orbital is substantially relaxed due to creation of the 1s hole. All of these assignments involving 1-c, 2-e excitations will be discussed and justified in detail elsewhere [13] together with similar 1-c, 2-e excitations observed in Ar and Kr solids.

The D₁ and D₂ features are enlarged and shown in Fig. 2. Removing a smooth background with straight lines in two reasonable ways, the D₁ and D₂ contributions are isolated. Their peak energies are found to be insensitive to the background removal procedure. These contributions cannot be due to 1-c, 2-e excitations, because the lowest 1-c, 2-e excitation (i.e., 1s2p→3s3s) is well above 900eV [13]. They must be due to 2-c, 2-e excitations of the monopole shakeup type, such as the 1sₐ→3pₐ dipole excitation accompanied with monopole excitation 2p₉→3p₉ or 2p₉→ε₉p₉, where the subscripts a and b denote different atomic centers. Alternative excitations, the 1sₐ→ε₉pₐ dipole excitations accompanied with the 2p₉→3p₉ monopole excitation, should be much weaker than the above-mentioned excitations, because the R₉ intensities due to the 1sₐ→ε₉pₐ excitations are much weaker than the E₁ intensity due to the 1sₐ→3pₐ excitation. Recall that the E₁ peak actually dominates the absorption spectrum. Thus, the probable excitations for the D₁ and D₂ contributions are 1sₐ2p₉→3pₐ3p₉ or 1sₐ2p₉→3pₐε₉p₉.

The energies of these probable 2-c, 2-e excitations are approximately given by the 1sₐ→3pₐ excitation energy (i.e., the E₁ peak energy) plus the 2p₉→3p₉ or 2p₉→ε₉p₉ excitation energy on a neighboring Ne atom. The 2p→3p excitation energy in solid Ne is, in a very good approximation, equal to that (18.5eV [14]) in the gas phase plus the "solid-state" shift (∼1.2eV [5]) due to the Pauli repulsion of the 3p electron by the neighboring Ne atoms. Further, the difference between the 2p→3p and 2p→ε₉p excitation energies should be approximately equal the energy separation between the E₁(1s→3p) and R₉(1s→ε₉p) features.
in Fig. 1. (In fact, a more detailed spectrum [5] than that in Fig. 1 was used for these energy separations.) The estimated energies of the probable excitations are included in Fig. 2, which suggests that the $1s_a2p_b \rightarrow 3p_a\varepsilon_d p_b$ excitation energies for $i=1$ and 2 agree with the $D_1$ and $D_2$ peak energies except for a uniform downward shift of about 1.4eV. One can attribute this downward shift to the Coulomb attraction between the positive $1s_a$ hole and an electron that occupies the $\varepsilon_d p_b$ orbital, $U(1s_a, \varepsilon_d p_b)$, which has not been included in the theoretical estimates. This agreement on the energies suggests that the $D_1$ and $D_2$ contributions are due to the $1s_a2p_b \rightarrow 3p_a\varepsilon_d p_b$ excitations for $i=1$ and 2, respectively.

Figure 2 also shows that the 2-c, 2-e shakeup process is selective, because the $1s_a2p_b \rightarrow 3p_a3p_b$ and $1s_a2p_b \rightarrow 3p_a\varepsilon_d p_b$ excitations are apparently absent in the experimental spectrum. One can explain the absence of the localized excitation $1s_a2p_b \rightarrow 3p_a3p_b$ by invoking a well-known shakeup mechanism. That is, a shakeup peak appears only when the orbitals relax upon creation of a hole, so that the monopole overlap integral does not vanish, (i.e., $<2p_b|3p_b'>$ in the present case, where the prime indicates a relaxed orbital of the excited state). In the $1s_a^{-1}2p_b^{-1}3p_a3p_b$ excited state, however, the 2-c attraction $U(1s_a, 3p_b)$ is negligible, because the $1s_a$ core hole is shielded by the $3p_a$ electron from the view point of an electron in the $3p_b$ orbital localized around another atomic center. On the other hand, the more delocalized $\varepsilon_d p_b$ and $\varepsilon_2 p_b$ resonant orbitals do sense the attractive potential as revealed by the 1.4eV downward shift already mentioned above, i.e., $U(1s_a, \varepsilon_d p_b) \approx 1.4eV$ for $i=1$ and 2. The lower-energy resonant orbitals $\varepsilon_d p_b$ for $i=1$ and 2 apparently penetrate into the atomic region of center $a$, but the higher energy orbitals for $i \geq 3$ are expected to stay outside of the atomic regions. More importantly, additional nodal planes in the higher-energy orbitals tend to make the overlap integral, $<2p_b|\varepsilon_d p_b'>$, much smaller. These trends can account for the absence of the $1s_a2p_b \rightarrow 3p_a\varepsilon_d p_b$ and higher 2-c, 2-e excitations.

In conclusion, one can attribute the $D_1$ and $D_2$ contributions to the $1s_a2p_b \rightarrow 3p_a\varepsilon_d p_b$ monopole-shakeup excitations for $i=1$ and 2, respectively. The relaxation of the delocalized
resonant orbitals $\varepsilon_d^P_b$ upon creation of the $1s_a$ core hole is responsible for the appearance of these 2-$c$ shakeup excitations. It should be noted that these excitations involve a resonant orbital $\varepsilon_d^P$ embedded in the continuum, unlike commonly known 2-$e$ shakeup mechanisms that involve only bound orbitals. If $\varepsilon_d^P$ were completely delocalized in the continuum, on the other hand, the 2-$e$ excitations would represent the normal shakeoff process; these features appear step-like or disappear into the background in absorption spectra. Thus, the 2-$e$ excitations identified here are novel, for they involve not only two centers but also resonant orbitals. To our knowledge, this is the first identification of 2-$c$ shakeup excitations involving a core hole.

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References


[12] Recently Soldatov et al. [A. V. Soldatov, T.S. Ivanchenko, S.D. Longa, and A. Bianconi, Phys. Rev. B 47, 16155] attributed the $D_3$ and $D_4$ features to $1s2p \rightarrow 3p3p$ and $1s2p \rightarrow \varepsilon_1 \varepsilon_1 p$ excitations, respectively, based on the similarity between the $(D_3, D_4)$ and $(E_1, R_1)$ energy separations, which we reject.


Figure Captions

Fig. 1. Comparison of experimental K-edge NEXAFS for solid Ne with theoretical results. Solid lines of theory (a) and (b) represent our theoretical spectrum as described in the text. The experimental spectrum is interpreted as follows: $E_1$ is an excitonic excitation; $R_1$-$R_8$ are one-electron excitations; $D_3$-$D_7$ are one-center, two-electron excitations; and $D_1$-$D_2$ are two-center, two-electron excitations.

Fig. 2. Experimental spectrum (Fig. 1) in the 880-900 eV range. The $D_1$ and $D_2$ contributions are isolated from the spectrum by removing a smooth background using straight lines in two reasonable ways. Solid bars represent predicted energy positions for $1s_a2p_b \rightarrow 3p_a3p_b (3p)$ and $1s_a2p_b \rightarrow 3p_aE_d p_b (E_d p)$ excitations.
K-edge NEXAFS of Ne solid

Absorption coefficient (relative units)

Photon energy (eV)

experiment

theory (a)

theory (b)

Fig. 1