Auger Lineshapes of Solid Surfaces - Atomic, Bandlike or Something Else?

by

Brett I. Dunlap, Fred L. Hutson, and David E. Ramaker

Prepared for Publication

in the

Journal of Vacuum Science and Technology

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

Reproduction in whole or in part is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited
# Auger Lineshapes of Solid Surfaces: Atomic, Bandlike or Something Else?

## Authors
Brett I. Dunlap, Fred L. Hutson, and David E. Ramaker

## Title
Auger lineshapes of solid surfaces—atomic, bandlike or something else?

## Type of Report & Period Covered
Technical Report

## Contract or Grant Number
N00014-78-C-0496
N00014-80-K-0852

## Program Element, Project, Task Area & Work Unit Numbers
Chemistry Department, George Washington University, Washington, D.C. 20052

## Distribution Statement
This document has been approved for public release and sale; its distribution is unlimited.

## Distribution Statement (of the abstract entered in Block 20, if different from Report)

## Supplementary Notes
Submitted for publication in the Journal of Vacuum Science and Technology.

## Abstract
A simple model is presented to predict the level of localization (i.e., localization onto an atomic, bonding lobe, molecular, or band orbital) of the two and three hole final states in Auger lineshapes. In the spirit of the Hubbard model, the extent of localization is predicted from the one- and two-center Coulomb interaction potentials and the relevant valence bandwidths. Results from the model are compared with experiment for the N KVV lineshapes from NaN0₃, and the S and Si L₂-₃VV lineshapes from Li₇SO₄ and SiO₂.
These lineshapes exhibit a wide range of localization consistent with the model.
Auger Lineshapes of Solid Surfaces - Atomic Bandlike or Something Else?

by

B. I. Dunlap, F. L. Hutson and D. F. Ramaker
Chemistry Department
George Washington University
Washington, DC 20052

Abstract

A simple model is presented to predict the level of localization (i.e., localization onto an atomic, bonding lobe, molecular, or band orbital) of the two and three hole final states in Auger lineshapes. In the spirit of the Hubbard model, the extent of localization is predicted from the one- and two-center Coulomb interaction potentials and the relevant valence bandwidths. Results from the model are compared with experiment for the N KVV lineshape from NaN$_3$, and the S and Si L$_{23}$VV lineshapes from Li$_2$SO$_4$ and SiO$_2$. These lineshapes exhibit a wide range of localization consistent with the model.
Often the core-valence-valence (CVV) Auger lineshapes can be successfully interpreted as the self-convolution of the valence band density of states, particularly for conductors with wide valence bandwidths $\Gamma$. Matrix element effects and initial state screening can alter this picture to some extent. If the lifetime of the core hole is short enough, the Auger electron can interact with the particles and fields present during the creation of the core hole. Near threshold, when the kinetic energy of the Auger electron is low, post-collision interactions can effect the lineshape. A more detailed and balanced discussion of these and other factors affecting Auger lineshapes in solids has been given in the excellent review by Fuggle.

The most dramatic departures from the valence-band self-convolution lineshape occurs if two (or more) holes are trapped locally in their mutual Coulomb repulsion. For example, two conduction band holes in the final state of the Auger process are trapped rendering the $\text{L}_3\text{M}_{45}\text{M}_{45}$ Auger lineshape atomic-like for the elemental solids Cu, Fe, Ga and Ge. Similarly, a valence hole created via shakeoff during the initial state ionization process can become trapped locally due to the core-valence Coulomb repulsion $U_{cv}$ leading to a shake-Auger satellite contribution to the total Auger lineshape. The three-hole final state of the shake-Auger process may be localized even though the two-hole final state from the normal Auger process is not because of the increased Coulomb repulsion of the 3-holes.

In the Cini-Sawatzky (CS) model of the Auger process in elemental solids, two parameters determine the degree of
localization of the CVV two-hole final state. Since inter-atomic Auger matrix elements are negligible\textsuperscript{13}, except where intra-atomic transitions are blocked\textsuperscript{14}, the Auger process picks out a local density of states (DOS), i.e., the Auger intensity is proportional to the probability that the two holes are local to the atom with the initial core hole. This local DOS experiences an effective one-center Coulomb repulsion $U$. The energy of this state is degenerate with that of two delocalized band electrons if $U < \Gamma$, and thus to a good approximation the Auger lineshape is quasiantomic provided $U > \Gamma$ and a self-convolution of the valence band provided $U < \Gamma$. In regions where $U \approx \Gamma$ both atomic and bandlike contributions are evident in the lineshape; i.e., correlation effects are present.

The CS model has been applied only to mono-elemental solids, primarily metals. Consequently the localization can be described as either atomic or bandlike. A very interesting question arises; are there systems where intermediate levels of localization exist, i.e., localization on some sub-cluster of the system? Some ionic solids contain covalently bonded sub-clusters such as the oxygen anions (e.g., $\text{NO}_3^-$ and $\text{SO}_4^{2-}$) where it is easy to envision delocalization within the molecular anions. Recently, we reported Auger contributions resulting from localization onto a $\text{Si}-\text{Si}$ bond orbital cluster in $\text{SiO}_2$, a covalently bonded system.

We report in this work a summary of studies on the solids $\text{LiNO}_3$\textsuperscript{5} and $\text{Li}_2\text{SO}_4$\textsuperscript{16} along with conclusions from our study.
In these systems there are a wide range of possible localized initial and final Auger states. They could involve localization onto an atomic orbital (AO), onto a bonding lobe orbital (LO), onto a subcluster molecular orbital (MO), or delocalized throughout the band orbital (BO). A simple semiempirical model is presented here for determining the extent of localization and its effects on the experimental Auger lineshapes. This model is presented in the next section. Application of this model to the systems under study are presented in Sec. 3.

2. Theoretical Model

For the poly-elemental solids such as those under study, a cluster configuration interaction (CI) approach, such as that described previously by one of us is appropriate. The results of that approach and the necessary definitions of the parameters involved is best summarized by presenting a simple two-orbital model problem.

For the moment, we assume the system has two holes present which is appropriate for the initial shake-Auger or final (normal) Auger state assuming an initially closed shell or filled band state (e.g., an insulator). We describe the holes by the one-electron orbitals $\phi_a$ and $\phi_b$ and proceed to diagonalize the hamiltonian $H=h_1 + h_2 + r_{12}^{-1}$ (We consider only the singlet spin states and assume $\langle \phi_a | \phi_b \rangle = 0$.)

$$
\begin{pmatrix}
\phi_a^2 & \phi_b^2 & \frac{1}{2}(\phi_a \phi_b + \phi_b \phi_a) \\
2\varepsilon_a + U_{aa} & 0 & H_{ab} \\
0 & 2\varepsilon_b + U_{bb} & H_{bb} \\
\frac{1}{2}(\phi_a \phi_b + \phi_b \phi_a) & H_{ab} & H_{ab} + \varepsilon_a + \varepsilon_b + U_{ab}
\end{pmatrix}
$$

\[1\]
where \( \epsilon_a = \epsilon_b \) are the one-electron orbital energies (e.g. \( \epsilon_a = \langle \phi_a | \hat{H} | \phi_a \rangle \)), \( U_{aa} = U_{bb} \) and \( U_{ab} \) are the one- and two-center Coulomb repulsion interaction integrals, \( \langle \phi_a \rho | \hat{r}_iz^{-1} | \phi_a \rho \rangle \) and \( \langle \phi_a \phi_b | \hat{r}_iz^{-1} | \phi_a \phi_b \rangle \) respectively, and \( H_{ab} = \langle \phi_a | \hat{H} | \phi_b \rangle \) is the hopping matrix element. Clearly if \( H_{ab} \ll U_{aa} - U_{ab} \), very little mixing occurs and the hole states \( \phi_a^\pm, \phi_b^\pm \), and

\[
\phi_a \phi_b + \phi_b \phi_a
\]

essentially diagonalize \( H \), i.e., the orbitals \( \phi_a \) and \( \phi_b \) properly describe the localization of the two holes. If \( H_{ab} \gg U_{aa} - U_{ab} \), the mixing of the configurations is complete and the eigenstates are

1) \( \frac{1}{2} \left( \phi_a^\pm + \phi_b^\pm + \phi_a \phi_b + \phi_b \phi_a \right) = \frac{1}{2} (\phi_a + \phi_b)^\pm \)

2) \( \frac{1}{\sqrt{2}} \left( \phi_a^\mp - \phi_b^\pm \right) = \frac{1}{\sqrt{2}} \left[ (\phi_a + \phi_b)(\phi_a - \phi_b) - (\phi_a - \phi_b)(\phi_a + \phi_b) \right] \)

3) \( \frac{1}{2} \left( \phi_a^\pm + \phi_b^\pm - \phi_a \phi_b - \phi_b \phi_a \right) = \frac{1}{2} (\phi_a - \phi_b)^\pm \)

with eigenvalues

\[
E_1 = 2\epsilon_a + (U_{aa} + U_{ab})/2 + H_{ab}
\]

\[
E_2 = 2\epsilon_a + U_{aa}
\]

\[
E_3 = 2\epsilon_a + (U_{aa} + U_{ab})/2 - H_{ab}
\]

In this instance the linear combinations \( \phi_a \pm \phi_b \) properly describe the localization of the two holes.

We now use an 'Aufbau' principle to determine the extent of delocalization. Consider first the possibility of localization into AO's vs. LO's. The Auger process prepares the holes locally in an atomic orbital, say AO\(_a^2\). In this instance \( H_{ab} = V/2 \) (\( V \)=bonding-antibonding separation) is the covalent interaction between neighboring atoms (e.g., between the central atom \( X \) and \( O_{2p} \) in \( XO_n \)), \( U_{aa} \) is the one-center Coulomb repulsion (\( U_{xx} \) or
and $U_{oo}$, $U_{ab}$ is a two center repulsion integral which we approximate by the Klopman approximation:

$$U_{ab} = e^2 \left[ \frac{R_{ab}}{2} + \frac{e^4}{(U_{aa} - U_{bb})} \right]^{-1/2}.$$  \hspace{1cm} (4)

If $V > U_{xx}-U_{xo}$ the holes delocalize onto the orbital $aAO_x + bAO_o$ which we refer to as a bonding lobe orbital (LO).

A CI involving the LO's proceeds similarly with $\xi_a$ now the energy of the LO. We assume here that $AO_x$ is an sp$^3$(or sp$^2$ in the case of NO$_3$) hybrid orbital, thus $H_{ab}$, $U_{aa}$ and $U_{ab}$ are now the covalent and Coulomb interactions between lobe orbitals.

$$H_{ab} = \gamma/n = a^2 h_{xx} + b^2 h_{oo} + 2ab h_{xo},$$

$$U_{aa} = U_{ll} = a^2 U_{xx} + b^2 U_{oo} + 2ab U_{xo},$$

$$U_{ab} = U_{ll} = a^2 U_{xx} + b^2 U_{oo} + 2ab U_{xo},$$  \hspace{1cm} (5)

where $n$ is the number of lobes on the MO cluster. We assume $h_{oo}$ and $h_{xo}$ are negligible; $h_{xx} = 2(a_s - \alpha_p)$, where $\alpha_s$ and $\alpha_p$ are the empirical one-electron atomic s and p orbital binding energies of the central atom. $\gamma$ can be obtained empirically from the spread in energy of the X s and p orbitals in the O$_2p$ bonding band of the system; information which can be obtained from x-ray emission data. If $\gamma > U_{ll} - U_{ll'}$, the holes delocalize onto clusters involving the $n$ LO's on the X atom, $\MO = \sum_{k=1}^{n} C_k \ LO_k$.

A CI involving MO's on different molecular clusters requires the quantities $H_{ab} = \Gamma/N$, $U_{vv} = (U_{ll} + (N-1) U_{ll'})/N$, and $U_{vv} = e^2/R$, where $\Gamma$ is the orbital band width, $N$ is the number of nearest neighbor clusters, $R$ is the X-X' nearest neighbor distance, and $U_{vv}$ and $U_{vv'}$ are the Coulomb interactions between holes on the same and neighboring MO clusters (e.g., XOn). If $\Gamma > U_{vv} - U_{vv'}$, the holes delocalize in the BO's.
Summarizing the results of the CI approach we have:

\[ V < U_{xx} - U_{x0} \quad \phi \rightarrow \text{AO} \]
\[ V > U_{xx} - U_{x0} \quad \gamma < U_{\ell\ell} - U_{\ell\ell'} \quad \phi \rightarrow \text{LO} \]
\[ \delta > U_{\ell\ell} - U_{\ell\ell'} \quad \Gamma < U_{\nu\nu} - U_{\nu\nu'} \quad \phi \rightarrow \text{MO} \]
\[ \phi > U_{\nu\nu} - U_{\nu\nu'} \quad \phi \rightarrow \text{BO} \]

where \( \phi \) describes the appropriate localization of the two holes. By defining the U's appropriate to the 3-hole Coulomb interaction, we can describe the localization in the 3-hole shake-Auger final state. If the U's are defined as a core-valence Coulomb interaction, we can determine the localization of the core-valence state initiating the shake-Auger process.

A quantitative comparison of theory and experiment is made by deriving a theoretical Auger lineshape. The Auger transition energies are given by

\[ E_{\text{cnn'}} = E_c - E_n - E_{n'} - U_{nn'} \]

where \( E_c \) is the core one-electron binding energy and \( E_n \) and \( U_{nn'} \) are the valence one-electron binding energy and Coulomb interaction appropriate for the extent of localization, i.e., for the atomic, lobal, molecular, or band orbital. Auger intensities are computed from the local AO populations \( a^2_{\text{xn}} \) and atomic Auger matrix elements \( M_{\text{cxx'}} \),

\[ I_{\text{cnn'}} = a^2_{\text{xn}} a^2_{\text{x'n'}} M_{\text{cxx'}} \]

both determined as described previously. The Auger widths are approximated as a sum,

\[ \Gamma_{\text{cnn'}} = \Gamma_c + \Gamma_n + \Gamma_{n'} + 2K \]

of core \( \Gamma_c \) and valence \( \Gamma_n \) level widths plus a singlet-triplet spin splitting term obtained as described previously.
A large contribution (20 to 40%) to the total Auger line-shape results from shake-Auger satellites. These contributions arise from shake-off during the initial core ionization process, the additional valence state hole causing a shift in the Auger energy. The shake-up process (valence excitation instead of valence ionization) is not significant in the insulating systems studied here due to the large band gaps at the Fermi level.\(^{20}\) The probability for shake resulting from core ionization can be determined from the sudden approximation

\[
P_n = 1 - \left( \langle \phi_n \phi'_n \rangle \right)^{2N},
\]

where \(\phi_n (\phi'_n)\) is the unrelaxed (relaxed) orbital describing the proper localization of the valence hole. We approximate eq. (10) with the expression

\[
P_n = 1 - (1-a^2 + a^2 \left( 1-P_a \right)^{1/2n})^{2N},
\]

where \(a^2\) is the local orbital population and \(P_a\) the atomic shake-off probability for the atom with the core hole. A comparison of the results using eqs. (10) and (11) for the \(\text{NH}_3\) molecule\(^{21}\) indicates eq. (11) is a good approximation. The resultant satellite intensity is

\[
I_{cs-snn'} = \frac{(N-i) P_n}{N \left( 1-\frac{1}{\xi^2} \right)} \mathcal{I}_{cnn'},
\]

where \(i=1\) if \(s=n \neq n'\), \(i=2\) if \(s=n=n'\) and \(i=0\) otherwise. (Eqs. (11-12) correct eqs. (1-2) in ref. 22.) The shift in energy between the parent Auger and shake satellite contributions is approximated by\(^{22}\)

\[
\Delta E_{cs-snn'} = U_{cs} - U_{sn} - U_{sn'} = U_{cs} - U_{snn'} + U_{nn'}
\]

where the \(U\)'s must be evaluated with the properly localized orbitals, and the sum of pairwise potentials has been assumed.
3. Results and Discussion

As seen from Table I, $U_{xx} - U_{xo}$ is generally less than 10eV. The X-O covalent interaction $V$ is $\approx 10$-12eV, for the systems under study, thus delocalization from the central atom X is expected. On the other hand, $\Gamma$ ($U_{vv}$, for Li$_2$SO$_4$ and NaNO$_3$) is less than $U_{vv} - U_{vv}'$ ($U_{vv}'=3$eV), thus delocalization from the anion is not expected. However, if two holes are created in adjacent Si-O-Si lobes, they can delocalize ($U_{x\alpha}'(\text{adjacent}) - U_{x\alpha}''$ (non-adjacent) $\gamma = \Gamma$). Thus, the focus of this discussion is localization on a lobe verses delocalization onto the molecular anion $XO_n^-$ or throughout the system for SiO$_2$. It is evident from Table I that two holes will remain localized on a Si-O-Si lobe ($U_{x\alpha} - U_{x\alpha}'$ $\gamma$); two holes will delocalize onto the NO$_3$ molecular anion ($U_{x\alpha} - U_{x\alpha}'$ $\gamma$). The situation is unclear in SO$_4$ since $U_{x\alpha}' - U_{x\alpha}'' \not\approx \gamma$; however, we will proceed to use SO$_4$ MO's. Therefore, the two hole final state will be described by the $XO_n^-$ cluster MO approach for oxyanion systems and by the Si-O-Si bond orbital approach in SiO$_2$. Local Si-O-Si and non-local Auger contributions (correlation effects) should be seen in SiO$_2$, only NO$_3$ MO contributions will be seen in NO$_3$. Large correlations effects should be present in SO$_4$, however the local and non-local contributions will not be resolved since $U_{x\alpha}' - U_{x\alpha}'' \not\approx \gamma$, thus they will not significantly alter the normal Auger lineshape.

The shake-Auger satellites follow a similar trend. First, note that because of the size of $U_{cv}$, the shake hole cannot get off of the oxyanion or off the Si-O-Si bond orbital. (If the shake hole could delocalize, all shake satellites would be
absent from the Auger lineshape.) The three-hole final state resulting from the shake–Auger process has a larger Coulomb interaction energy, hence localization and correlation effects are expected to be more important. As revealed in Table I, however, even the three holes should delocalize throughout the NO$_3$ anion; little correlation effects are expected since $U_{111} - U_{111'}$ and $U_{222} - U_{222'} < \gamma$. In SO$_4$, $U_{222} - U_{222'} > \gamma \approx U_{111} - U_{111'}$; thus one might proceed with a SO$_4$ MO picture for the 3-hole state, but large correlation effects should again be expected.

In SiO$_2$ $U_{111} - U_{111'}$ and $U_{222} - U_{222'}$ so the Si–O–Si LO gives the proper description of shake–Auger satellites.

The upper set of curves in Figs. 1–2 compare experimental and total theoretical N KVV LiNO$_3$ and S L$_{23}$VV Li$_2$SO$_4$ Auger lineshapes respectively. The N lineshape was obtained via x-ray excitation, the S by electron excitation; both were background subtracted and loss deconvoluted by a method described elsewhere.

The middle curves compare the separate Auger and shake–Auger theoretical contributions, the latter 35% for N and 34% (including Coster-Kronig) for S of the total as determined from eq. (11). These curves have been obtained using eqs. (6) through (13) and NO$_3$ and SO$_4$ MO energies and populations as derived and reported elsewhere. The total theoretical lineshape was normalized and shifted in energy $\Delta$ for principle peak alignment with the experiment. The required energy shifts $\Delta (+3eV$ and $+2eV$ respectively) may be attributed to charging of the insulating samples and thus this absolute energy shift
is not a good test for correlation effects in the two-hole state. The lower curves compare the theoretical shake-Auger lineshape with the difference between the total experimental and the theoretical normal Auger lineshapes; the latter may be referred to as the 'experimental' shake-Auger lineshape. Differences between the theory and experiment in the upper and lower curves (by definition the differences are the same) are largest at the higher energies. These may be attributed to damage of the sample since in both NO$_3$ and SO$_4$ the higher energy region grows with electron beam exposure. Note, as one might expect, more structure is seen in the shake-Auger than in the normal Auger lineshape.

We focus our attention on the lower curves of Fig. 1-2 and the shift $\delta$ required to bring the theoretical and "experimental" shake lineshapes into alignment. This additional shift $\delta = -1$eV for NO$_3$ may be regarded as an adjustment in $\Delta E_{CS-SVV}$ (a relative energy shift between the Auger and shake-Auger); we can allow this flexibility due to the approximate nature of eq. (13). However, the $\delta = +6$eV for SO$_4$ is larger than the uncertainty in eq. (13), and we attribute it to the large correlation effects expected in the three-hole final states of SO$_4$.

Assuming the SO$_4$ MO's describe the proper localization, eq. (13) gave $\Delta E(MO) = -8$eV. If we assume instead that the LO's are more proper, we might expect a shake-Auger contribution at each level of localization; at $\Delta E(LLL) = -17$eV, $\Delta E(LLL') = -7$eV, and $\Delta E(LLL") = -2$eV. However, the LLL contribution is forbidden by the Pauli principle, and the LLL' contribution is reduced in
magnitude by matrix element\textsuperscript{11} and statistical (the \(\frac{(N-i)}{N}\))
factor in eq. (12)) effects. Thus, we might expect the dominant
shake contribution at \(\Delta E = -2\text{eV}\) which accounts for the \(J\) shift of
\(+6\text{eV}\). We conclude the LO gives the more proper localization
for the \(\text{SO}_4\) three hole final state.

A similar comparison of theory and experiment for the
\(\text{Si } L_{23}\text{VV}\) and 0\text{ KVV lineshapes in } \text{SiO}_2\) have been given previous-
ly.\textsuperscript{11} Significant correlation effects were evident in these
lineshapes already in the two-hole final state as expected from
the data in Table I.

In conclusion, it is clear intermediate levels of localiza-
tion are evident in Auger lineshapes in both the two- and three-
hole final states. Our simple model as outlined above is helpful
in understanding and predicting the extent of this localization.

\textbf{Acknowledgements}

We thank Jim Murday for discussions which stimulated this
work. This work supported in part by the Office of Naval Research.
References

TABLE I. Summary of covalent and Coulomb interactions in NO$_3$, SO$_4^-$, and SiO$_2$\(^a\)

<table>
<thead>
<tr>
<th>Interaction</th>
<th>NO$_3^-$</th>
<th>SO$_4^-$</th>
<th>SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$</td>
<td>9</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>$U_{xx}$</td>
<td>12</td>
<td>12</td>
<td>9</td>
</tr>
<tr>
<td>$U_{xO}$</td>
<td>eq. (4)</td>
<td>9</td>
<td>8</td>
</tr>
<tr>
<td>$U_{oo}$</td>
<td>eq. (4)</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>$U_{ll}$</td>
<td>eq. (5)</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>$U_{ll'}$</td>
<td>eq. (5)</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>$U_{VV} = (U_{ll} + (N-1)U_{ll'})/N$</td>
<td>9</td>
<td>9</td>
<td>6</td>
</tr>
<tr>
<td>$U_{cv}$</td>
<td>13</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>$U_{llll}$</td>
<td>$= 3U_{ll}$</td>
<td>36</td>
<td>36</td>
</tr>
<tr>
<td>$U_{llll'}$</td>
<td>$= U_{ll} + 2U_{ll'}$</td>
<td>28</td>
<td>26</td>
</tr>
<tr>
<td>$U_{llll''}$</td>
<td>$= 3U_{ll'}$</td>
<td>24</td>
<td>21</td>
</tr>
</tbody>
</table>

\(^a\)All quantities (in eV) evaluated assuming the electron population on the central atom $a^2$ is .38, .25, and .25 respectively for N, S, and Si. We assume $a^2 + b^2 = 1$ and utilize the zero differential overlap approximation. All numbers have uncertainties of the order \(\pm\) 1eV.

\(^b\)Evaluated empirically from an analysis of x-ray emission and photoemission data (11, 15-16) and from $2(w_\phi - a\rho)a^2$. Agreement to within 1eV is obtained.

\(^c\)\(U_{nn} = F^0_{nn} - r_{nn}\) where $F^0$ is the Slater integral tabulated by Mann\(^25\) and $r$ is a relaxation energy\(^26\) estimated to be 6,6,1 and 1eV for N, O, S, and Si. $U_{oo} = 15$eV
TABLE I (continued)

\[ d \text{Evaluated using } R_{xO} = 1.2, 1.4, \text{ and } 1.6, \quad R_{oo} = 2.1, 2.4, \]
\[ \text{and } 2.6 \AA \text{ respectively for NO}_3, \text{ SO}_4, \text{ and SiO}_2 \]

\[ eU_{cv} = a^2 U_{cx} + b^2 U_{co} \text{ where } U_{cx} \text{ is determined using the equivalent cores approximation}^{26}. \]
Figure Captions

Fig. 1
Upper curves: the total experimental (solid line) and theoretical (dotted line) N KVV Auger lineshape for NaNO₃. The theoretical lineshape has been normalized and shifted by Δ = 3eV to align with the principle experimental peak.
Middle curves: the normal Auger (solid) and shake-Auger (dotted) contributions to the total Auger lineshape.
Lower curves: the "experimental" (solid) and theoretical (dotted) shake-Auger lineshape. The "experimental" was obtained by subtracting the theoretical normal Auger lineshape from the total experimental lineshape. The theoretical lineshape was shifted by $\delta = -1eV$ for better alignment.

Fig. 2
Same as Fig. 1 for LiSO₄, except $\Delta = +2eV$ and $\delta = +6eV$. 
<table>
<thead>
<tr>
<th>Office of Naval Research</th>
<th>Copies</th>
<th>U.S. Army Research Office</th>
<th>Copies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Attn: Code 472</td>
<td>2</td>
<td>Attn: CRD-AA-IP</td>
<td>1</td>
</tr>
<tr>
<td>800 North Quincy Street</td>
<td></td>
<td>P.O. Box 1211</td>
<td></td>
</tr>
<tr>
<td>Arlington, Virginia 22217</td>
<td></td>
<td>Research Triangle Park, N.C. 27709</td>
<td>1</td>
</tr>
<tr>
<td>ONR Branch Office</td>
<td>1</td>
<td>Naval Ocean Systems Center</td>
<td>1</td>
</tr>
<tr>
<td>Attn: Dr. George Sandoz</td>
<td></td>
<td>Attn: Mr. Joe McCartney</td>
<td></td>
</tr>
<tr>
<td>536 S. Clark Street</td>
<td></td>
<td>San Diego, California 92152</td>
<td>1</td>
</tr>
<tr>
<td>Chicago, Illinois 60605</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ONR Area Office</td>
<td>1</td>
<td>Naval Weapons Center</td>
<td>1</td>
</tr>
<tr>
<td>Attn: Scientific Dept.</td>
<td></td>
<td>Attn: Dr. A. B. Amster,</td>
<td></td>
</tr>
<tr>
<td>715 Broadway</td>
<td></td>
<td>Chemistry Division</td>
<td></td>
</tr>
<tr>
<td>New York, New York 10003</td>
<td></td>
<td>China Lake, California 93555</td>
<td>1</td>
</tr>
<tr>
<td>ONR Western Regional Office</td>
<td>1</td>
<td>Naval Civil Engineering Laboratory</td>
<td>1</td>
</tr>
<tr>
<td>1030 East Green Street</td>
<td></td>
<td>Attn: Dr. R. W. Drisko</td>
<td></td>
</tr>
<tr>
<td>Pasadena, California 91106</td>
<td></td>
<td>Port Hueneme, California 93401</td>
<td>1</td>
</tr>
<tr>
<td>ONR Eastern/Central Regional Office</td>
<td>1</td>
<td>Department of Physics &amp; Chemistry</td>
<td>1</td>
</tr>
<tr>
<td>Attn: Dr. L. H. Peebles</td>
<td></td>
<td>Naval Postgraduate School</td>
<td></td>
</tr>
<tr>
<td>Building 114, Section D</td>
<td></td>
<td>Monterey, California 93940</td>
<td>1</td>
</tr>
<tr>
<td>666 Summer Street</td>
<td></td>
<td>Dr. A. L. Slafkosky</td>
<td></td>
</tr>
<tr>
<td>Boston, Massachusetts 02210</td>
<td></td>
<td>Scientific Advisor</td>
<td></td>
</tr>
<tr>
<td>Director, Naval Research Laboratory</td>
<td>1</td>
<td>Commandant of the Marine Corps</td>
<td>1</td>
</tr>
<tr>
<td>Attn: Code 6100</td>
<td></td>
<td>(Code RD-1)</td>
<td></td>
</tr>
<tr>
<td>Washington, D.C. 20390</td>
<td></td>
<td>Washington, D.C. 20380</td>
<td>1</td>
</tr>
<tr>
<td>The Assistant Secretary</td>
<td>1</td>
<td>Office of Naval Research</td>
<td>1</td>
</tr>
<tr>
<td>of the Navy (RE&amp;S)</td>
<td></td>
<td>Attn: Dr. Richard S. Miller</td>
<td></td>
</tr>
<tr>
<td>Department of the Navy</td>
<td></td>
<td>800 N. Quincy Street</td>
<td></td>
</tr>
<tr>
<td>Room 4E736, Pentagon</td>
<td></td>
<td>Arlington, Virginia 22217</td>
<td>1</td>
</tr>
<tr>
<td>Washington, D.C. 20350</td>
<td></td>
<td>Naval Ship Research and Development Center</td>
<td>1</td>
</tr>
<tr>
<td>Commander, Naval Air Systems Command</td>
<td>1</td>
<td>Attn: Dr. G. Bosmajian, Applied</td>
<td></td>
</tr>
<tr>
<td>Attn: Code 310C (H. Rosenwasser)</td>
<td></td>
<td>Chemistry Division</td>
<td></td>
</tr>
<tr>
<td>Department of the Navy</td>
<td></td>
<td>Annapolis, Maryland 21401</td>
<td>1</td>
</tr>
<tr>
<td>Washington, D.C. 20360</td>
<td></td>
<td>Naval Ocean Systems Center</td>
<td>1</td>
</tr>
<tr>
<td>Defense Technical Information Center</td>
<td>1</td>
<td>Attn: Dr. S. Yasamoto, Marine</td>
<td></td>
</tr>
<tr>
<td>Building 5, Cameron Station</td>
<td></td>
<td>Sciences Division</td>
<td></td>
</tr>
<tr>
<td>Alexandria, Virginia 22314</td>
<td></td>
<td>San Diego, California 91232</td>
<td>1</td>
</tr>
<tr>
<td>Dr. Fred Saalfeld</td>
<td>15</td>
<td>Mr. John Boyle</td>
<td>1</td>
</tr>
<tr>
<td>Chemistry Division, Code 6100</td>
<td></td>
<td>Materials Branch</td>
<td></td>
</tr>
<tr>
<td>Naval Research Laboratory</td>
<td></td>
<td>Naval Ship Engineering Center</td>
<td>1</td>
</tr>
<tr>
<td>Washington, D.C. 20375</td>
<td></td>
<td>Philadelphia, Pennsylvania 19112</td>
<td>1</td>
</tr>
<tr>
<td>No.</td>
<td>Copies</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>--------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Dr. Rudolph J. Marcus  
Office of Naval Research  
Scientific Liaison Group  
American Embassy  
APO San Francisco 96503  

Mr. James Kelley  
DTNSRDC Code 2803  
Annapolis, Maryland 21402  

1
<table>
<thead>
<tr>
<th>Name</th>
<th>Institution</th>
<th>Location</th>
<th>Copies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dr. D. A. Vroom</td>
<td>IRT</td>
<td>San Diego, California</td>
<td>1</td>
</tr>
<tr>
<td>Dr. G. A. Somorjai</td>
<td>Department of Chemistry</td>
<td>University of California</td>
<td>1</td>
</tr>
<tr>
<td>Dr. L. N. Jarvis</td>
<td>Surface Chemistry Division</td>
<td>Washington, D.C.</td>
<td>1</td>
</tr>
<tr>
<td>Dr. J. B. Hudson</td>
<td>Materials Division</td>
<td>Troy, New York</td>
<td>1</td>
</tr>
<tr>
<td>Dr. John T. Yates</td>
<td>Surface Chemistry Section</td>
<td>National Bureau of Standards</td>
<td>1</td>
</tr>
<tr>
<td>Dr. Theodore E. Madey</td>
<td>Surface Chemistry Section</td>
<td>National Bureau of Standards</td>
<td>1</td>
</tr>
<tr>
<td>Dr. J. M. White</td>
<td>Department of Chemistry</td>
<td>University of Texas</td>
<td>1</td>
</tr>
<tr>
<td>Dr. Keith H. Johnson</td>
<td>Department of Metallurgy and Materials Science</td>
<td>Massachusetts Institute of Technology</td>
<td>1</td>
</tr>
<tr>
<td>Dr. J. E. Demuth</td>
<td>IBM Corporation</td>
<td>Thomas J. Watson Research Center</td>
<td>1</td>
</tr>
<tr>
<td>Dr. C. P. Flynn</td>
<td>Department of Physics</td>
<td>University of Illinois</td>
<td>1</td>
</tr>
<tr>
<td>Dr. W. Kohn</td>
<td>Department of Physics</td>
<td>University of California</td>
<td>1</td>
</tr>
<tr>
<td>Dr. R. L. Park</td>
<td>Director, Center of Materials Research</td>
<td>University of Maryland</td>
<td>1</td>
</tr>
<tr>
<td>Dr. W. T. Peria</td>
<td>Electrical Engineering Department</td>
<td>University of Minnesota</td>
<td>1</td>
</tr>
<tr>
<td>Dr. Narkis Tzoar</td>
<td>City University of New York</td>
<td>10031</td>
<td>1</td>
</tr>
<tr>
<td>Dr. Chia-wei Woo</td>
<td>Department of Physics</td>
<td>Northwestern University</td>
<td>1</td>
</tr>
<tr>
<td>Dr. D. C. Mattis</td>
<td>Polytechnic Institute of New York</td>
<td>11201</td>
<td>1</td>
</tr>
<tr>
<td>Dr. Robert M. Hexter</td>
<td>Department of Chemistry</td>
<td>University of Minnesota</td>
<td>1</td>
</tr>
<tr>
<td>Dr. R. P. Van Duyne</td>
<td>Chemistry Department</td>
<td>Northwestern University</td>
<td>1</td>
</tr>
<tr>
<td>No. Copies</td>
<td>No. Copies</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dr. M. G. Lagally</td>
<td>Dr. J. Osteryoung</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Department of Metallurgical and Mining Engineering</td>
<td>Chemistry Department</td>
<td></td>
<td></td>
</tr>
<tr>
<td>University of Wisconsin</td>
<td>SUNY, Buffalo</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Madison, Wisconsin 53706</td>
<td>Buffalo, New York 14214</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dr. Robert Gomer</td>
<td>Dr. G. Rubloff</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Department of Chemistry</td>
<td>I.B.M.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>James Franck Institute</td>
<td>Thomas J. Watson Research Center</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5640 Ellis Avenue</td>
<td>P. O. Box 218</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chicago, Illinois 60637</td>
<td>Yorktown Heights, New York 10598</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dr. R. G. Wallis</td>
<td>Dr. J. A. Gardner</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Department of Physics</td>
<td>Oregon State University</td>
<td></td>
<td></td>
</tr>
<tr>
<td>University of California, Irvine</td>
<td>Corvallis, Oregon 97331</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dr. P. Ramaker</td>
<td>Dr. G. D. Stein</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemistry Department</td>
<td>Mechanical Engineering Department</td>
<td></td>
<td></td>
</tr>
<tr>
<td>George Washington University</td>
<td>Northwestern University</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Washington, D.C. 20052</td>
<td>Evanston, Illinois 60201</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dr. P. Hansma</td>
<td>Dr. K. G. Spears</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemistry Department</td>
<td>Chemistry Department</td>
<td></td>
<td></td>
</tr>
<tr>
<td>University of California, Santa Barbara</td>
<td>Northwestern University</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Santa Barbara, California 93106</td>
<td>Evanston, Illinois 60201</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dr. P. Hendra</td>
<td>Dr. R. W. Plummer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemistry Department</td>
<td>University of Pennsylvania</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Southampton University</td>
<td>Department of Physics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>England 509JNH</td>
<td>Philadelphia, Pennsylvania 19104</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Professor P. Skell</td>
<td>Dr. E. Yeager</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemistry Department</td>
<td>Department of Chemistry</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pennsylvania State University</td>
<td>Case Western Reserve University</td>
<td></td>
<td></td>
</tr>
<tr>
<td>University Park, Pennsylvania 16802</td>
<td>Cleveland, Ohio 41106</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dr. J. C. Hemminger</td>
<td>Professor George H. Morrison</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemistry Department</td>
<td>Cornell University</td>
<td></td>
<td></td>
</tr>
<tr>
<td>University of California, Irvine</td>
<td>Department of Chemistry</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irvine, California 92717</td>
<td>Ithaca, New York 14853</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dr. Martin Fleischmann</td>
<td>Professor N. Winograd</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Department of Chemistry</td>
<td>Pennsylvania State University</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Southampton University</td>
<td>Chemistry Department</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Southampton 509 SNH</td>
<td>University Park, Pennsylvania 16802</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hampshire, England</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Professor Thomas F. George</td>
<td>The University of Rochester</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Chemistry Department</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rochester, New York 14627</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>