

AD-A089 454

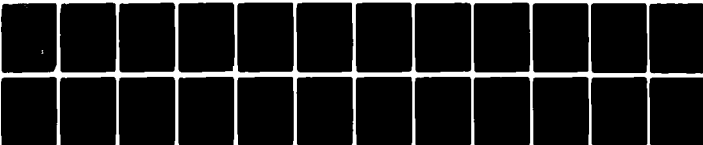
GEORGE WASHINGTON UNIV WASHINGTON D C DEPT OF CHEMISTRY F/G 7/4  
AUGER LINESHAPES OF SOLID SURFACES - ATOMIC, BANDLIKE OR SOMETH—ETC(U)  
AUG 80 B I DUNLAP, F L HUTSON, D E RAMAKER N00014-78-C-0496

UNCLASSIFIED

TR-4

NL

Fig 1  
Aug 80



END  
DATE  
FILMED  
10-80  
DTIC

**LEVEL** #

12

AD A089454

OFFICE OF NAVAL RESEARCH

Contracts ~~N00014-78-C-0496~~ and ~~N00014-80-K-0852~~

Task No. 056-681

Technical Report No. 4

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

DTIC  
S ELECTRIC  
SEP 24 1980

A

August 1980

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

FILE COPY

80 9 24 01.

REPORT DOCUMENTATION PAGE		READ INSTRUCTION: BEFORE COMPLETING FORM
1. REPORT NUMBER No. 4	2. GOVT ACCESSION NO. A089 454	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) AUGER LINESHAPES OF SOLID SURFACES-ATOMIC, BANDLIKE OR SOMETHING ELSE ?		4. TYPE OF REPORT & PERIOD COVERED Technical Report
		5. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Brett I. Dunlap, Fred L. Hutson, and David E. Ramaker.		8. CONTRACT OR GRANT NUMBER(s) N00014-78-C-0496 N00014-80-K-0852
9. PERFORMING ORGANIZATION NAME AND ADDRESS Chemistry Department George Washington University Washington, D.C. 20052		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Prog. Elem. No. 61153N Task Area No. PP 013-08-01 Work Unit No. NR 056-681
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research, Dept. of Nav. 800 N. Quincy Street. Washington, D.C. 22217		12. REPORT DATE August 1980
		13. NUMBER OF PAGES 25
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Submitted for publication in the Journal of Vacuum Science and Technology.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Auger electron spectroscopy, surface oxides, electron correlation		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) 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 $\text{NaNO}_3$ , and the S and Si $L_{2,3}$ VV lineshapes from $\text{Li}_2\text{SO}_4$ and $\text{SiO}_2$ .		

These lineshapes exhibit a wide range of localization consistent with the model.

Unclassified

Accession For	
NEIS	<input checked="" type="checkbox"/>
DLC	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Institution/	
Approved for Files	
Dist	Special
A	

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

by

B. I. Dunlap, F. L. Hutson and D. E. 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  $\text{NaNO}_3$ , and the S and Si  $L_{23}^{VV}$  lineshapes from  $\text{Li}_2\text{SO}_4$  and  $\text{SiO}_2$ . 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,<sup>1</sup> particularly for conductors with wide valence bandwidths  $\Gamma$ . Matrix element effects<sup>2</sup> and initial state screening<sup>3</sup> 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.<sup>4-6</sup> Near threshold, when the kinetic energy of the Auger electron is low, post-collision interactions can effect the lineshape.<sup>7</sup> A more detailed and balanced discussion of these and other factors affecting Auger lineshapes in solids has been given<sup>in</sup> the excellent review by Fuggle.<sup>8</sup>

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.<sup>9-11</sup> For example, two conduction band holes in the final state of the Auger process are trapped rendering the  $L_3M_{45}M_{45}$  Auger lineshape atomic-like for the elemental solids Cu, Fe, Ga and Ge<sup>12</sup>. 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<sup>9-10</sup> (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<sup>13</sup>, except where intra-atomic transitions are blocked<sup>14</sup>, 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 quasiatomic 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 oxy-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 Si-O-Si bond orbital cluster in  $\text{SiO}_2$ ,<sup>11</sup> a covalently bonded system.

We report in this work a summary of studies on the solids  $\text{LiNO}_3$ <sup>15</sup> and  $\text{Li}_2\text{SO}_4$ ,<sup>16</sup> along with conclusions from our study

in  $\text{SiO}_2$ .<sup>11</sup> 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.<sup>11</sup> 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  $\langle \phi_a | \phi_b \rangle = 0$ .)

$$\begin{array}{c}
 \phi_a^2 \\
 \phi_b^2 \\
 \frac{1}{\sqrt{2}}(\phi_a\phi_b + \phi_b\phi_a)
 \end{array}
 \left|
 \begin{array}{ccc}
 2\varepsilon_a + U_{aa} & 0 & H_{ab} \\
 0 & 2\varepsilon_b + U_{bb} & H_{ab} \\
 H_{ab} & H_{ab} & \varepsilon_a + \varepsilon_b + U_{ab}
 \end{array}
 \right|
 \quad 1)$$



where  $\epsilon_a = \epsilon_b$  are the one-electron orbital energies (e.g.  $\epsilon_a = \langle \phi_a | h | \phi_a \rangle$ ),  $U_{aa} = U_{bb}$  and  $U_{ab}$  are the one- and two-center Coulomb repulsion interaction integrals,  $\langle \phi_a^2 | r_{12}^{-1} | \phi_a^2 \rangle$  and  $\langle \phi_a \phi_b | r_{12}^{-1} | \phi_a \phi_b \rangle$  respectively, and  $H_{ab} = \langle \phi_a | h | \phi_b \rangle$  is the hopping matrix element. Clearly if  $H_{ab} \ll U_{aa} - U_{ab}$ , very little mixing occurs and the hole states  $\phi_a^2$ ,  $\phi_b^2$ , 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

$$\begin{aligned}
 1) & \frac{1}{2} (\phi_a^2 + \phi_b^2 + \phi_a \phi_b + \phi_b \phi_a) = \frac{1}{2} (\phi_a + \phi_b)^2 \\
 2) & \frac{1}{\sqrt{2}} (\phi_a^2 - \phi_b^2) = \frac{1}{\sqrt{2}} [ (\phi_a + \phi_b)(\phi_a - \phi_b) + (\phi_a - \phi_b)(\phi_a + \phi_b) ] \quad 2) \\
 3) & \frac{1}{2} (\phi_a^2 + \phi_b^2 - \phi_a \phi_b - \phi_b \phi_a) = \frac{1}{2} (\phi_a - \phi_b)^2
 \end{aligned}$$

with eigenvalues

$$\begin{aligned}
 E_1 &= 2\epsilon_a + (U_{aa} + U_{ab})/2 + H_{ab} \\
 E_2 &= 2\epsilon_a + U_{aa} \\
 E_3 &= 2\epsilon_a + (U_{aa} + U_{ab})/2 - H_{ab} .
 \end{aligned} \quad 3)$$

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  $X_p$  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:<sup>17</sup>

$$U_{ab} = e^2 [R_{ab}^2 + e^4/(U_{aa} U_{bb})]^{-1/2} \quad 4)$$

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  $\epsilon_a$  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.

$$\begin{aligned} H_{ab} &= \gamma/n = a^2 h_{xx'} + b^2 h_{oo'} + 2ab h_{xo'} \\ U_{aa} &= U_{\rho\rho} = a^2 U_{xx} + b^2 U_{oo} + 2ab U_{xo} \\ U_{ab} &= U_{\rho\rho'} = a^2 U_{xx'} + b^2 U_{oo'} + 2ab U_{xo'} \end{aligned} \quad 5)$$

where  $n$  is the number of lobes on the MO cluster. We assume  $h_{oo'}$  and  $h_{xo'}$  are negligible;  $h_{xx'} = 2(\alpha_s - \alpha_p)$ , where  $\alpha_s$  and  $\alpha_p$  are the empirical one-electron atomic s and p orbital binding energies of the central atom.<sup>18</sup>  $\gamma$  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  $\gamma > U_{\rho\rho} - U_{\rho\rho'}$ , the holes delocalize onto clusters involving the  $n$  LO's on the X atom,  $MO = \sum_{\lambda} c_{\lambda} LO_{\lambda}$ .

A CI involving MO's on different molecular clusters requires the quantities  $H_{ab} = \Gamma/N$ ,  $U_{vv} = (U_{\rho\rho} + (N-1) U_{\rho\rho'})/N$ , 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.,  $XO_n$ ). If  $\Gamma > U_{vv} - U_{vv'}$ , the holes delocalize in the BO's.

Summarizing the results of the CI approach we have:

$$\begin{array}{ll}
 V < U_{xx} - U_{xo} & \phi \rightarrow AO \\
 V > U_{xx} - U_{xo} , \quad \gamma < U_{\ell\ell} - U_{\ell\ell}' & \phi \rightarrow LO \quad 6) \\
 \gamma > U_{\ell\ell} - U_{\ell\ell}' , \quad \Gamma < U_{vv} - U_{vv}' & \phi \rightarrow MO \\
 \Gamma > U_{vv} - U_{vv}' & \phi \rightarrow BO
 \end{array}$$

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

$$E_{cnn'} = E_c - E_n - E_{n'} - U_{nn'} \quad 7)$$

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, lobar, molecular, or band orbital. Auger intensities are computed from the local AO populations  $a_{xn}^2$  and atomic Auger matrix elements  $M_{cxx'}$ ,

$$I_{cnn'} = a_{xn}^2 a_{x'n'}^2 M_{cxx'} \quad 8)$$

both determined as described previously.<sup>19</sup> The Auger widths are approximated as a sum,

$$\Gamma_{cnn'} = \Gamma_c + \Gamma_n + \Gamma_{n'} + 2K \quad 9)$$

of core  $\Gamma_c$  and valence  $\Gamma_n$  level widths plus a singlet-triplet spin splitting term obtained as described previously.<sup>19</sup>

A large contribution (20 to 40%) to the total Auger line-shape results from shake-Augur 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.<sup>20</sup> The probability for shake resulting from core ionization can be determined from the sudden approximation

$$P_n = 1 - \langle \phi_n \phi_n' \rangle^{2N}, \quad (10)$$

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

$$P_n = 1 - (1-a^2 + a^2 (1-P_a)^{1/2N})^{2N}, \quad (11)$$

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<sup>21</sup> indicates eq. (11) is a good approximation. The resultant satellite intensity is

$$I_{cs-snn'} = \frac{(N-i)}{N} \frac{P_n}{1-\sum P_n} I_{cnn'}, \quad (12)$$

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<sup>22</sup>

$$\Delta E_{cs-snn'} = U_{cs} - U_{sn} - U_{sn'} = U_{cs} - U_{snn'} + U_{nn'} \quad (13)$$

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  $\approx 10-12\text{eV}$ , for the systems under study,<sup>23</sup> thus delocalization from the central atom X is expected. On the other hand,  $\Gamma' (< U_{vv}, \text{ for } \text{Li}_2\text{SO}_4 \text{ and } \text{NaNO}_3)$  is less than  $U_{vv} - U_{vv'}$ , ( $U_{vv'} \approx 3\text{eV}$ ), thus delocalization from the anion is not expected. However, if two holes are created in adjacent Si-O-Si lobes, they can delocalize ( $U_{\lambda\lambda'}(\text{adjacent}) - U_{\lambda\lambda}'$  (non-adjacent)  $< \gamma = \Gamma'$ ). Thus, the focus of this discussion is localization on a lobe versus delocalization onto the molecular anion  $\text{XO}_n$ , or throughout the system for  $\text{SiO}_2$ . It is evident from Table I that two holes will remain localized on a Si-O-Si lobe ( $U_{\lambda\lambda} - U_{\lambda\lambda}' > \gamma$ ); two holes will delocalize onto the  $\text{NO}_3$  molecular anion ( $U_{\lambda\lambda} - U_{\lambda\lambda}' < \gamma$ ). The situation is unclear in  $\text{SO}_4$  since  $U_{\lambda\lambda}' - U_{\lambda\lambda} \approx \gamma$ ; however, we will proceed to use  $\text{SO}_4$  MO's. Therefore, the two hole final state will be described by the  $\text{XO}_n$  cluster MO approach for oxyanion systems and by the Si-O-Si bond orbital approach in  $\text{SiO}_2$ . Local Si-O-Si and non-local Auger contributions (correlation effects) should be seen in  $\text{SiO}_2$ , only  $\text{NO}_3$  MO contributions will be seen in  $\text{NO}_3$ . Large correlations effects should be present in  $\text{SO}_4$ , however the local and non-local contributions will not be resolved since  $U_{\lambda\lambda} - U_{\lambda\lambda}' \approx \gamma$ ; thus they will not significantly alter the normal Auger lineshape.

The shake-Augger 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  $\text{NO}_3$  anion; little correlation effects are expected since  $U_{\text{xxx}} - U_{\text{xxx}}'$  and  $U_{\text{xxx}}' - U_{\text{xx}'\text{x}} < \gamma$ . In  $\text{SO}_4$ ,  $U_{\text{xxx}} - U_{\text{xxx}}' > \gamma \approx U_{\text{xxx}}' - U_{\text{xx}'\text{x}}$  thus one might proceed with a  $\text{SO}_4$  MO picture for the 3-hole state, but large correlation effects should again be expected. In  $\text{SiO}_2$   $U_{\text{xxx}} - U_{\text{xxx}}'$  and  $U_{\text{xxx}}' - U_{\text{xx}'\text{x}} > \gamma$  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  $\text{LiNO}_3$  and S  $L_{23}$  VV  $\text{Li}_2\text{SO}_4$  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.<sup>24</sup> 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  $\text{NO}_3$  and  $\text{SO}_4$  MO energies and populations as derived and reported elsewhere.<sup>15-16</sup> 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  $\text{NO}_3$  and  $\text{SO}_4$  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  $\delta = -1\text{eV}$  for  $\text{NO}_3$  may be regarded as an adjustment in  $\Delta E_{\text{CS-SVV}}$  (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  $\delta = +6\text{eV}$  for  $\text{SO}_4$  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  $\text{SO}_4$ .

Assuming the  $\text{SO}_4$  MO's describe the proper localization, eq. (13) gave  $\Delta E(\text{MO}) = -8\text{eV}$ . If we assume instead that the LO's are more proper, we might expect a shake-Auger contribution at each level of localization; at  $\Delta E(\text{lll}) = -17\text{eV}$ ,  $\Delta E(\text{lll}') = -7\text{eV}$ , and  $\Delta E(\text{lll}'') = -2\text{eV}$ . However, the  $\text{lll}$  contribution is forbidden by the Pauli principle, and the  $\text{lll}'$  contribution is reduced in

magnitude by matrix element<sup>11</sup> and statistical (the  $(N-i)/N$  factor in eq. (12)) effects. Thus, we might expect the dominant shake contribution at  $\Delta E = -2\text{eV}$  which accounts for the  $\delta$  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 Si  $L_{23}\text{VV}$  and O KVV lineshapes in  $\text{SiO}_2$  have been given previously.<sup>11</sup> 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 localization 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.

#### Acknowledgements

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



## References

1. J. L. Lander, Phys. Rev. 91, 1382 (1953).
2. P. J. Feibelman, E. J. McGuire and K. C. Pandey, Phys. Rev. Lett. 36, 1154 (1976).
3. D. R. Jennison, H. H. Madden and D. M. Zehner, Phys. Rev. B 21, 430 (1980).
4. J. C. Fuggle, R. Lasser, O. Gunnarsson and K. Schonhammer, Phys. Rev. Lett. 44, 1090 (1980).
5. O. Gunnarsson and K. Schonhammer, preprint.
6. S. M. Girvin and D. R. Penn, Phys. Rev. B, to be published.
7. M. K. Bahl, R. L. Watson and K. J. Irgolic, Phys. Rev. Lett. 42, 165 (1979).
8. J. C. Fuggle, in Electron Spectroscopy, Vol. 4, eds. C. R. Brundle and A. D. Baker (Academic, New York, 1980).
9. M. Cini, Solid State Commun. 20, 605 (1976); 24, 681 (1977); Phys. Rev. B 17, 2788 (1979); Surf. Sci. 87, 483 (1979).
10. G. A. Sawatzky, Phys. Rev. Lett. 39, 504 (1977); G. A. Sawatzky and A. Lenselink, Phys. Rev. B 21, 1790 (1980).
11. D. E. Ramaker, Phys. Rev. B 21, 4608 (1980).
12. E. Antonides, E. C. Janse and G. A. Sawatzky, Phys. Rev. B 15, 1669 (1977).
13. J. A. D. Matthew and Y. Kominos, Surf. Sci. 53, 716 (1975).
14. P. H. Citrin, J. E. Rowe and S. B. Christman, Phys. Rev. B 14, 2642 (1976).
15. F. L. Hutson, D. E. Ramaker, J. D. Gangei and J. S. Murday, manuscript in preparation.

16. D. E. Ramaker, J. S. Murday and N. H. Turner, manuscript in preparation.
17. G. Klopman, J. Am. Chem. Soc. 86, 4550 (1964).
18. D. J. Chadi and M. L. Cohen, Phys. Status Solidi B 68, 405 (1975).
19. D. E. Ramaker, J. S. Murday, N. H. Turner, G. Moore, M. G. Lagally and J. Houston, Phys. Rev. B 19, 5375 (1979).
20. D. R. Jennison, J. A. Kelber and R. R. Rye, Chem. Phys. Lett., to be published.
21. D. R. Jennison, Phys. Rev. A, to be published.
22. D. E. Ramaker and J. S. Murday, J. Vac. Sci. Technol. 16, 510 (1979).
23. W. A. Harrison, Electronic Structure and Properties of Solids (W. H. Freeman, San Francisco, 1980).
24. D. E. Ramaker, J. S. Murday and N. H. Turner, J. Elect. Spectros. and Rel. Phenom. 17, 45 (1979).
25. J. B. Mann, Los Alamos Scientific Laboratory Report No. LASL-3690, 1967 (unpublished).
26. D. A. Shirley, Phys. Rev. A 7, 1520 (1973).

TABLE I. Summary of covalent and Coulomb interactions in  
 $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{SiO}_2$ <sup>a</sup>

<u>Interaction</u>		$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{SiO}_2$
$\gamma$ <sup>b</sup>		9	5	4
$U_{xx}$ <sup>c</sup>		12	12	9
$U_{xo}$ <sup>d</sup>	eq. (4)	9	8	7
$U_{oo}$ <sup>d</sup>	eq. (4)	6	6	5
$U_{\lambda\lambda}$ <sup>d</sup>	eq. (5)	12	12	11
$U_{\lambda\lambda'}$ <sup>d</sup>	eq. (5)	8	7	5
$U_{vv}$	$= (U_{\lambda\lambda} + (N-1)U_{\lambda\lambda'})/N$	9	9	6
$U_{cv}$ <sup>e</sup>		13	10	9
$U_{\lambda\lambda\lambda}$	$= 3U_{\lambda\lambda}$	36	36	33
$U_{\lambda\lambda\lambda'}$	$= U_{\lambda\lambda} + 2U_{\lambda\lambda'}$	28	26	21
$U_{\lambda\lambda'\lambda''}$	$= 3U_{\lambda\lambda'}$	24	21	15

<sup>a</sup>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  $\pm 1$  eV.

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

<sup>c</sup> $U_{nn} = F_{nn}^0 - r_{nn}$  where  $F_{nn}^0$  is the Slater integral tabulated by Mann<sup>25</sup> and  $r$  is a relaxation energy<sup>26</sup> estimated to be 6, 6, 1 and 1 eV for N, O, S, and Si.  $U_{oo} = 15$  eV

TABLE I (continued)

<sup>d</sup>Evaluated using  $R_{xO} = 1.2, 1.4, \text{ and } 1.6$ ,  $R_{OO} = 2.1, 2.4,$   
and  $2.6 \text{ \AA}$  respectively for  $\text{NO}_3$ ,  $\text{SO}_4$ , and  $\text{SiO}_2$

<sup>e</sup> $U_{cv} = a^2 U_{cx} + b^2 U_{co}$  where  $U_{cx}$  is determined using the  
equivalent cores approximation<sup>26</sup>.

## Figure Captions

### Fig. 1

Upper curves: the total experimental (solid line) and theoretical (dotted line) N KVV Auger lineshape for  $\text{NaNO}_3$ . The theoretical lineshape has been normalized and shifted by  $\Delta = 3\text{eV}$  to align with the principle experimental peak.

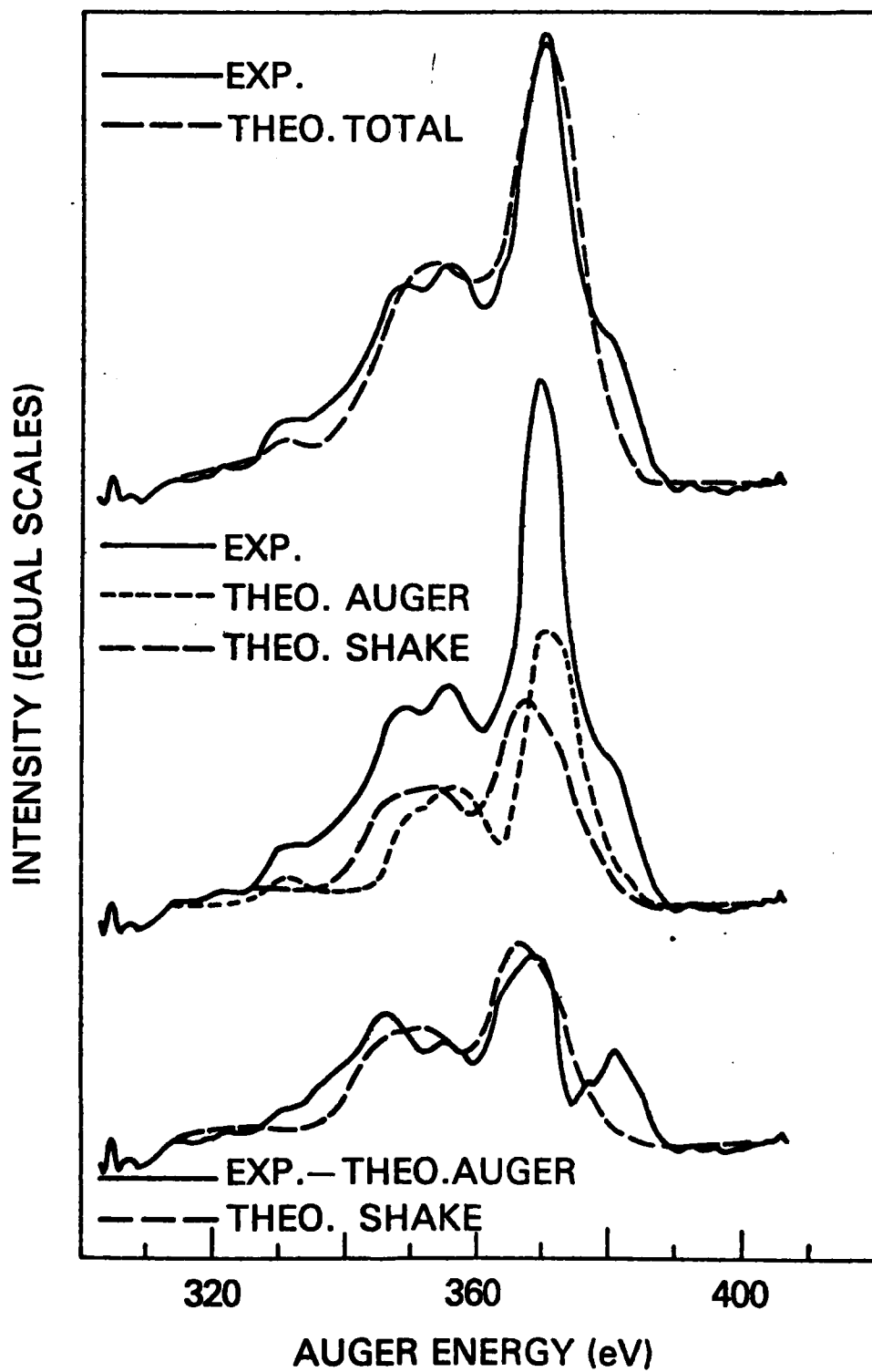
Middle curves: the normal Auger (solid) and shake-Auger (dotted) contributions to the total Auger lineshape.

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  $\delta = -1\text{eV}$  for better alignment.

### Fig. 2

Same as Fig. 1 for  $\text{Li}_2\text{SO}_4$ , except  $\Delta = +2\text{eV}$  and  $\delta = +6\text{eV}$ .

NO<sub>3</sub><sup>-</sup> N kVV

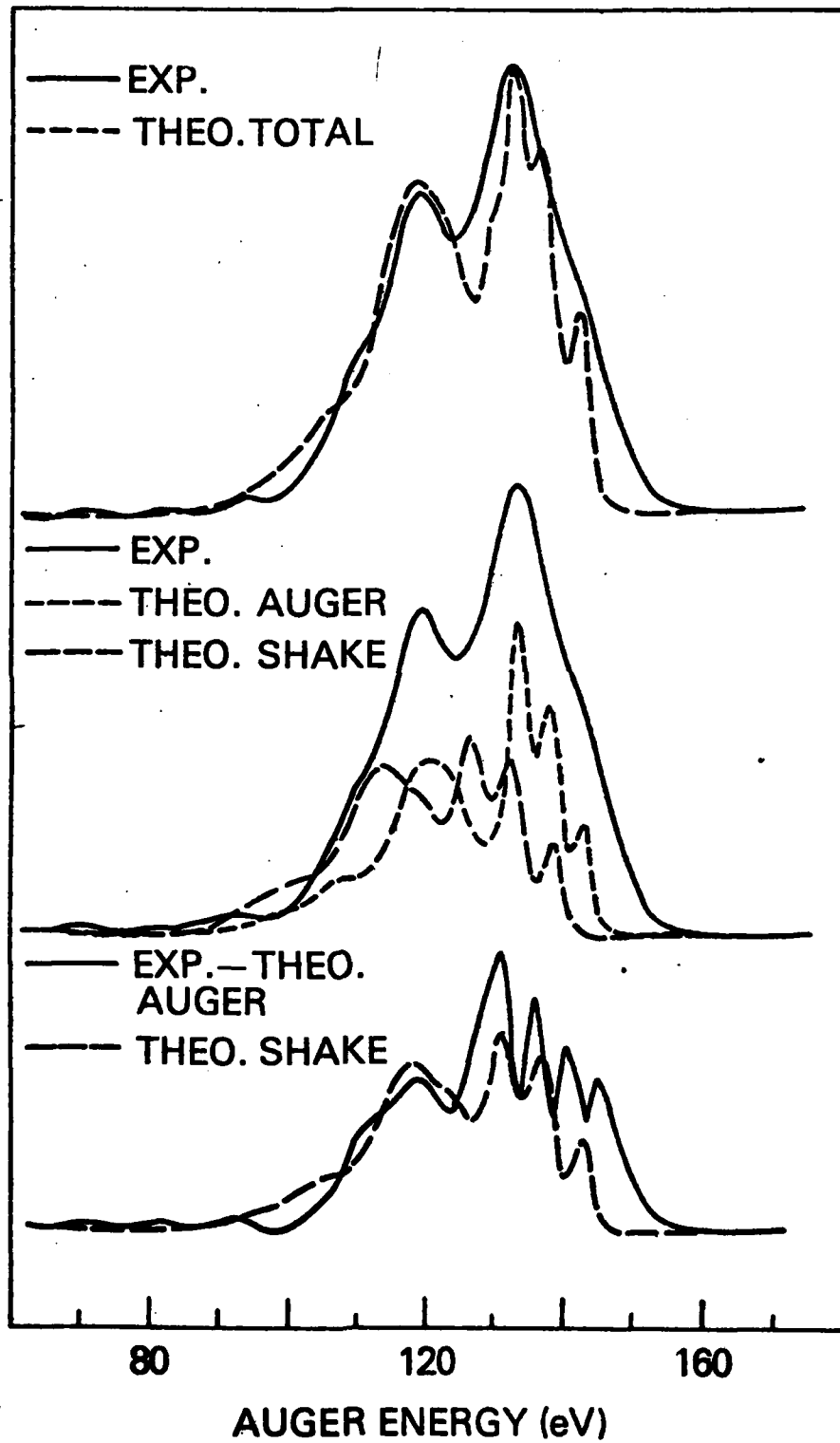


SO<sub>4</sub><sup>=</sup>

S

L<sub>23</sub> VV

INTENSITY (EQUAL SCALES)



TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Area Office Attn: Scientific Dept. 715 Broadway New York, New York 10003	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
ONR Western Regional Office 1030 East Green Street Pasadena, California 91106	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
ONR Eastern/Central Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1



TECHNICAL REPORT DISTRIBUTION LIST, GEN

No.  
Copies

Dr. Rudolph J. Marcus  
Office of Naval Research  
Scientific Liaison Group  
American Embassy  
APO San Francisco 96503 1

Mr. James Kelley  
DTNSRDC Code 2803  
Annapolis, Maryland 21402 1

TECHNICAL REPORT DISTRIBUTION LIST, 056

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. D. A. Vroom IRT P.O. Box 80817 San Diego, California 92138	1	Dr. C. P. Flynn Department of Physics University of Illinois Urbana, Illinois 61801	1
Dr. G. A. Somorjai Department of Chemistry University of California Berkeley, California 94720	1	Dr. W. Kohn Department of Physics University of California (San Diego) LaJolla, California 92037	1
Dr. L. N. Jarvis Surface Chemistry Division 4555 Overlook Avenue, S.W. Washington, D.C. 20375	1	Dr. R. L. Park Director, Center of Materials Research University of Maryland College Park, Maryland 20742	1
Dr. J. B. Hudson Materials Division Rensselaer Polytechnic Institute Troy, New York 12181	1	Dr. W. T. Peria Electrical Engineering Department University of Minnesota Minneapolis, Minnesota 55455	1
Dr. John T. Yates Surface Chemistry Section National Bureau of Standards Department of Commerce Washington, D.C. 20234	1	Dr. Narkis Tzoar City University of New York Convent Avenue at 138th Street New York, New York 10031	1
Dr. Theodore E. Madey Surface Chemistry Section Department of Commerce National Bureau of Standards Washington, D.C. 20234	1	Dr. Chia-wei Woo Department of Physics Northwestern University Evanston, Illinois 60201	1
Dr. J. M. White Department of Chemistry University of Texas Austin, Texas 78712	1	Dr. D. C. Mattis Polytechnic Institute of New York 333 Jay Street Brooklyn, New York 11201	1
Dr. Keith H. Johnson Department of Metallurgy and Materials Science Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Dr. Robert M. Hexter Department of Chemistry University of Minnesota Minneapolis, Minnesota 55455	1
Dr. J. E. Demuth IBM Corporation Thomas J. Watson Research Center P.O. Box 218 Yorktown Heights, New York 10598	1	Dr. R. P. Van Duyne Chemistry Department Northwestern University Evanston, Illinois 60201	1

TECHNICAL REPORT DISTRIBUTION LIST, 056

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. M. G. Lagally Department of Metallurgical and Mining Engineering University of Wisconsin Madison, Wisconsin 53706	1	Dr. J. Osteryoung Chemistry Department SUNY, Buffalo Buffalo, New York 14214	1
Dr. Robert Gomer Department of Chemistry James Franck Institute 5640 Ellis Avenue Chicago, Illinois 60637	1	Dr. G. Rubloff I.B.M. Thomas J. Watson Research Center P. O. Box 218 Yorktown Heights, New York 10598	1
Dr. R. G. Wallis Department of Physics University of California, Irvine Irvine, California 92664	1	Dr. J. A. Gardner Department of Physics Oregon State University Corvallis, Oregon 97331	1
<del>Dr. D. Ramaker Chemistry Department George Washington University Washington, D.C. 20052</del>	1	Dr. G. D. Stein Mechanical Engineering Department Northwestern University Evanston, Illinois 60201	1
Dr. P. Hansma Chemistry Department University of California, Santa Barbara Santa Barbara, California 93106	1	Dr. K. G. Spears Chemistry Department Northwestern University Evanston, Illinois 60201	1
Dr. P. Hendra Chemistry Department Southampton University England SO9JNH	1	Dr. R. W. Plummer University of Pennsylvania Department of Physics Philadelphia, Pennsylvania 19104	1
Professor P. Skell Chemistry Department Pennsylvania State University University Park, Pennsylvania 16802	1	Dr. E. Yeager Department of Chemistry Case Western Reserve University Cleveland, Ohio 41106	2
Dr. J. C. Hemminger Chemistry Department University of California, Irvine Irvine, California 92717	1	Professor George H. Morrison Cornell University Department of Chemistry Ithaca, New York 14853	1
Dr. Martin Fleischmann Department of Chemistry Southampton University Southampton SO9 5NH Hampshire, England	1	Professor N. Winograd Pennsylvania State University Chemistry Department University Park, Pennsylvania 16802	1
	1	Professor Thomas F. George The University of Rochester Chemistry Department Rochester, New York 14627	1