

Localized Auger final states in covalent systems

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We report an experimental and theoretical analysis of localized valence two-hole excitations in covalent systems. The theoretical interpretation suggests that the factors which produce the effect are commonly found and include geometric constraints upon dynamical screening.

While states with two valence holes localized upon one site have previously been observed to be produced by core-valence-valence (CVV) Auger decay in ionic solids¹ and in "narrow band" metals such as nickel² and copper,^{3,4} previous analyses of covalent decays, both in solids⁵ and in the gas phase,⁶ have shown only delocalized (independent hole) Auger final states. We show below, both experimentally and theoretically, that in covalent systems as well, there exist two-hole states which are spatially localized, even though all one-hole states are delocalized and are appropriately described by band or molecular orbital (MO) theory.

Previous theoretical attempts^{7(a),7(b),8} to understand the localized two-hole resonance (L) phenomenon have all concluded that in filled band solid-state systems, strong correlation effects should occur whenever a parameter which describes the strength of the hole-hole interaction U becomes significant when compared to the total^{7(a)} bandwidth W , $U/W > 1-2$. However, it has been clear to many workers⁹ that U may not universally (i.e., for partially filled bands) be equated to the relevant bare (i.e., atomic) interaction, or else localization would occur almost everywhere.¹⁰ For example, while there is little difference between the atomic $3d-3d$ interaction or the $3d$ bandwidths in cobalt and copper metals [U (bare)/ W is ~ 12 vs ~ 18], there is a complete transition between an observed U , i.e., U_{eff} , appropriate to delocalized (bandlike) behavior and one appropriate to localized (atomiclike) CVV Auger behavior as one proceeds from Co to Cu⁴ [U_{eff} may be empirically determined using Eq. (1) below.] A strong indication that other factors are important was provided by Cini^{7(a)} who showed a rapid change in the localized resonance upon the slight unfilling of the band. His analysis was restricted, however, to the solid-state case in which the number of holes per site, $n_h \ll 1$.

We show theoretically below, using a configuration-interaction formalism, that in order for localization to occur in molecules or in solids, the dynamical screening response of the system (i.e., the ability to screen the holes from each other) must be ineffective. This may be due to the existence of filled or almost filled atomic shells (as in ionic solids and copper). We find that this also may occur due to geometrical constraints imposed by the molecular structure and may lead to localization over units larger than atomic (e.g., functional groups). We suggest that similar geometrical constraints may permit the existence of L states upon a covalent surface, even if no such states occur in the bulk.

The observation of these localized states in the two-particle excitation spectrum is most distinct in gas-phase molecules. (We use the term "localized states," appropriate for molecules, interchangeably with "localized resonances," appropriate for surfaces.) In an independent-particle theory, the position in the Auger spectrum of the vertical transitions to the possible two-hole final states with holes in the j and k molecular orbitals are given by

$$E_a = I_c - I_j - I_k - U_{\text{eff}}(j, k, s), \quad (1)$$

where E_a is the Auger electron kinetic energy, the I 's are experimental (photoemission) ionization potentials, U_{eff} (the effective hole-hole interaction energy) is either experimentally derived using Eq. (1) or theoretically calculated from the appropriate ground-state orbitals,⁶ and s is the final-state spin. U_{eff} has been shown to have a size component due to the finite extent of molecule. This component often vanishes in the limit of the infinite system.^{5,11}

Clear *experimental evidence* for localized two-hole states has been found in several systems^{11,12} by the use of photoemission results, calibrated Auger peak positions, and Eq. (1). However, an understanding of the effect and an analysis of the localization were previously lacking.

For example, in the series of alkanes, if the final-state holes were independent, U_{eff} would monotonically decrease with increasing molecular size. The experimental results¹¹ for the normal alkanes C_1-C_6 show that the highest amplitude feature remains at constant U_{eff} , thus directly indicating the existence of a two-hole final state whose energy is relatively independent of molecular size. However, except for the smallest molecules in the series, the number of final states prevents the resolution of the experimental spectra into individual components, thus prohibiting a more complete understanding.

We now further the alkane analysis in order to locate the geometric position of the L states. The resolution of largely localized and delocalized components is enhanced in neopentane, $C(CH_3)_4$, due to high symmetry. Note the formal resemblance to a hydrogen-covered small diamond. The experimental neopentane $C(KVV)$ spectrum¹¹ is given in Fig. 1. For a molecule of this size, U_{eff} is $\sim 7-9$ eV with 7.5 eV typical of the shallow valence region upon which we focus. We report in Fig. 1 independent-particle calculations,¹³ which produce spectra for both the central carbon and terminal methyl carbons which are in agreement with the experimental high-energy Auger features, but are in great disagreement with the dominant experimental peak. By comparing $Si(CH_3)_4$, where one can experimentally resolve¹⁴ the spectra of the central and methyl atoms, to neopentane, we find that the major feature in Fig. 1 is produced by the methyl carbons, while the dominant portions of the central atom spectrum are well given by the independent-particle theory [as in the bulk spectrum of Si (Ref. 5)]. This suggests no localization on carbon atoms or in the C-C bond, while the discrepancy in the major peak implies a localized two-hole final state on the methyl group. This peak has a U_{eff} of ~ 12 eV compared to a methane value of 13.4 eV.⁶ Since this difference can be ascribed to polarization effects, we conclude that there exist both largely localized and largely delocalized states in the two-hole spectrum of neopentane, even though the single-hole spectrum from UPS shows only delocalization.¹⁵

The rigorous solution of this problem is quite formidable. Therefore, our theoretical approach is to model the construction of a correlated "quasi-particle" (i.e., bare particle plus polarization cloud) two-hole wave function. Because only two holes are involved, it is convenient to proceed via a configuration interaction (CI) approach and consider

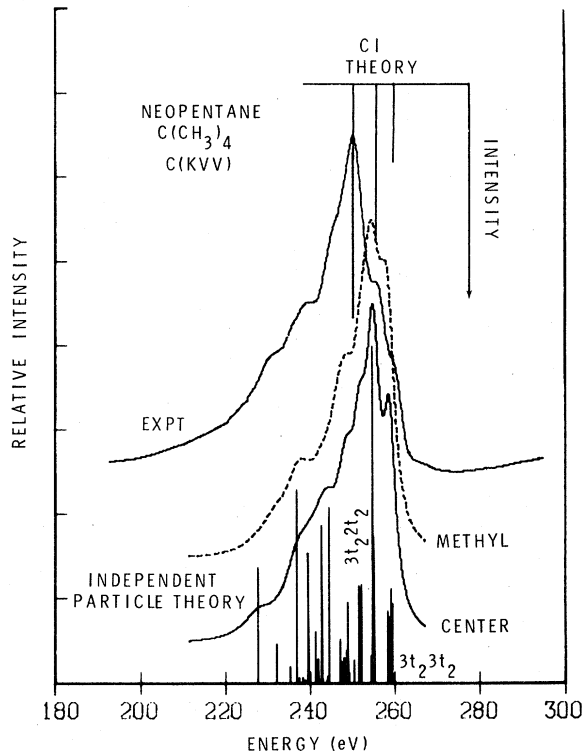


FIG. 1. Experimental (Ref. 11) neopentane $[C(CH_3)_4]$ $C(KVV)$ spectrum is compared to theoretical methyl carbon (center) and center carbon (bottom) spectra calculated by assuming independent final-state holes (see Ref. 13). The smooth curves result from normalized broadening of the vertical transitions to optimize the agreement with experiment. Vertical transition results of the CI formalism with static limit screening (top) reproduce the shallow valence region of the spectrum.

all possible configurations (arrangements) of the two holes within the system. Thus the electrons in the system are treated as providing a background potential and source of screening for the two holes.

A diatomic example will explain notation. Independent-particle theory yields for a diatomic molecule $a-b$ (with atomic orbitals a and b) bonding ($B \propto a+b$) and antibonding ($A \propto a-b$) orbitals. (We omit normalization and the spin part of the wave functions.) While orbitals such as these (or Bloch functions in the bulk) may be used as CI basis functions, better bases for our two-hole CI analysis are single site, $L_{\pm} \propto a_1 a_2 \pm b_1 b_2$, and two site $D_{\pm} \propto a_1 b_2 \pm b_1 a_2$ bases, where the subscripts indicate the hole indices. We note that D_- is a spin triplet, the rest are singlets. D_+ and L_+ are even with respect to inversion and mix to produce the lowest and highest two-hole states which in a

one-electron model are $B^2 \propto D_+ + L_+$ and $A^2 \propto D_+ - L_+$. L_- cannot mix except with higher configurations, and we note that the singlet $AB \propto L_-$. This shows the equivalence of the two types of bases. [Localization in the singlet AB -like state has been observed by an analysis similar to the above in CO, CO₂ (Ref. 16), and ethane.¹⁷]

In extended systems, whether localized states in fact exist depends upon the degree of CI mixing of the L and D bases in each block of the spin and symmetry-factored CI Hamiltonian matrix. This matrix has, as the largest components of the diagonal elements (i.e., to first order in overlap, S_{ab}), $E(L) \cong 2I + U^L$ and $E(D) \cong 2I + U^D$, where U^L and U^D are the screened hole-hole interactions and I is the ionization potential of the relevant valence level.

L states will exist if and only if $E(L)$ differs from $E(D)$ by an amount large compared to the off-diagonal elements $H_{LD} \equiv \langle L | H | D \rangle$ [to first order in overlap, given by $2IS_{ab} + \langle a | f | b \rangle + 2(aa | ab)$, where f is the single-particle part of the Hamiltonian operator and $(aa | ab)$ is a two-electron integral]. However, we see that the difference, $\Delta H \equiv E(L) - E(D) = \Delta U \equiv U^L - U^D$ is entirely determined by the effectiveness of the screening response of the remaining electrons. In the bulk cases described above, it seems that ΔU largely depends upon whether the site has filled shells. If the holes are in a filled shell, the screening charge can only be on another atom or in a higher shell on the relevant site, thus producing a significant residual ΔU . If, however, the shell is, say, half-filled, screening charge may exist in the same shell as the holes, thus killing ΔU so that $E(L) \cong E(D)$. Since the energy "band" width W , of the canonical valence orbitals spanned by the local structure is $\sim H_{LD}$, $\Delta H/H_{LD} \sim \Delta U/W$. Thus we find by our CI analysis formally the same criterion for the degree of localization in finite systems (size dependencies cancel out in ΔH), as Cini⁷ and independently Sawatzky⁸ found for their analyses of solids. However, our ΔU (screened) may differ by many electron volts from ΔU (bare), e.g., ~ 12 eV in copper.³

The degree of mixing between the L and D configurations results in the resonance width which is expressed as the partial density of the L basis in the two-hole spectrum of the finite system. If the screening is effective, the near degeneracy of the D and L bases, as in the above diatomic case, produces the independent-particle solution. That this is indeed a common situation is the reason for the

reported successes^{5,6,11} of the independent-particle Auger theory.

The above CI formalism may be easily evaluated to first order in overlap. I and $\langle a | f | b \rangle$ may be set to duplicate the single-particle (i.e., photoemission) spectrum. The remaining quantities may be calculated from first principles, with U^L found from the total energy of self-consistent calculations performed with and without two-localized holes (Δ SCF). This includes screening in the static approximation. We have performed this calculation on the shallow valence region of neopentane and have obtained the vertical transitions shown at the top of Fig. 1. This duplicates the energy position and amplitude of the major spectral features. Details of this calculation will be submitted soon.

The requirement of filled atomic shells (bands) is consistent with all localization observed to date in bulk Auger spectra.¹⁻⁴ For example, silicon has half-filled bands from the point of view of localization within an atomic orbital and the relevant W includes both valence and conduction bands^{7(a)}; $W \sim 24$ eV. The neopentane example suggests, however, that we might expect localization to occur at a covalent surface even if none occurs in the bulk, provided that a surface structure exists into which we may place two holes such that they are decoupled from the efficient screening response which exists in the bulk material.

The molecular systems we are considering seem upon first impression to resemble bulk saturated covalent systems such as diamond and silicon. However, their finite extent and irregular shapes lead to differences. If we relax our definition of "shells" to include spatially distinct group orbitals, then again the criterion of filled shells predicts all localization observed to date^{11,12,16} in molecules. The ϵ -group orbital of a CH₃ unit and the b_2 -orbital of a CH₂ unit are spatially distinct from the other group orbitals and both are full (the geometric inhibitors of screening). No corresponding orbitals exist to permit C or C-C localization.

While our estimate of the screening effectiveness in the static limit allows us to rank sites for the degree of localization, the correct quantitative evaluation of the screening is a more difficult dynamical problem. However, if our static limit screening produces localization, we may have confidence that it indeed exists, since dynamical screening is less effective.

There has been considerable recent interest in simulated desorption phenomena, principally due to the discovery in ionic systems of an Auger

electron-stimulated desorption (ESD) mechanism by Knotek and Feibelman¹⁸ and the subsequent observation by Knotek *et al.*¹⁹ of photon-stimulated desorption (PSD). However, ESD and PSD have been observed from covalent surfaces also.²⁰ A major unanswered question is how in extended covalent systems electronic excitation energy can be localized for times long enough to permit desorption. While detailed calculations of lifetime and resonance width remain to be done, we find that the present results provide a link of similarity to the ionic case and indicate that these localized states *may* provide a detailed mechanism for desorption and/or dissociation events in extended

systems. Since these two-hole states may be produced without an Auger decay via a shakeup mechanism,²¹ they may explain observed ESD and PSD events below Auger thresholds. One immediate test of their relevance to stimulated desorption would be to compare observed desorption thresholds to the energy of the relevant localized states. This work is under way.

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who concluded that they exist in bulk SiO₂. However, this work assumed a bare hole-hole interaction, did not evaluate the system screening response or allow charge to flow into the cluster, and used only the occupied bandwidths (*W*), in conflict with Ref. 7.

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