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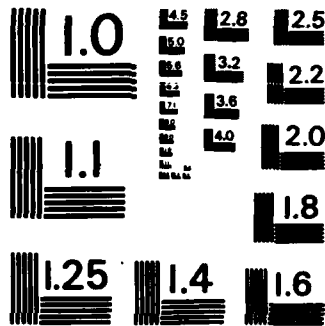
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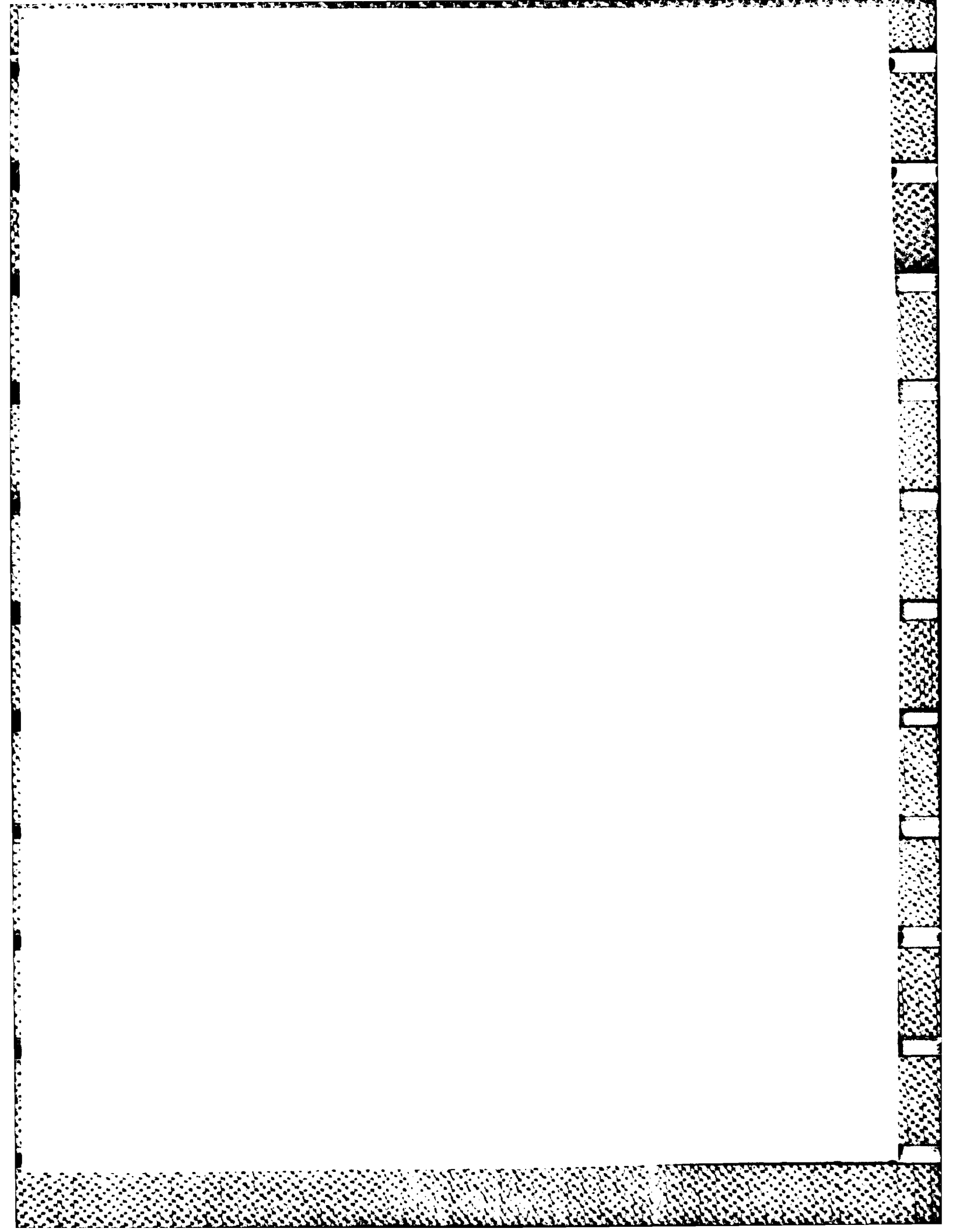
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SUMMARY ABSTRACT: A CONSISTENT QUANTITATIVE INTERPRETATION OF
THE AUGER LINESHAPES OF CARBON IN MOLECULES AND SOLIDS

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The theoretical interpretation of molecular CVV lineshapes has generally utilized results from ab-initio theories such as Hartree Fock-Self Consistent Field calculations,¹ multi-configuration interaction, or Greens function approaches² where the different two-hole final states resulting from the Auger process are described directly as approximate solutions to the Schrodinger equation. On the other hand, in metals and covalent solids, the one-electron density of states (DOS), $\rho(\epsilon)$, is most often obtained empirically from x-ray emission (XES) or photoelectron (PES) spectroscopy.³ These DOS are self-folded to obtain $N(E)$,

$$N(E) = \int \rho(\epsilon - \epsilon) \rho(\epsilon) d\epsilon \quad (1)$$

The Cini-Sawatzky expression,

$$A(E) = \frac{N(E)}{(1 - U_1(E))^2 + U_2 \pi^2 N(E)} \quad (2)$$

is then utilized to introduce final state hole-hole localization effects, where the hole-hole repulsion, U , is obtained empirically.

* Supported by the Office of Naval Research

In this work we have theoretically interpreted the C KVV spectra for benzene and cyclohexane, utilizing eqs (1) and (2) above in a procedure consistent with that used previously^{4,5} for graphite and diamond. The experimental spectra for benzene and cyclohexane are well known.^{6,7} The molecular one-electron DOS was obtained empirically utilizing XES and XPS data and theoretical SCF calculations.^{8,9}

The Cini expression was initially derived within the Hubbard model for extended metallic systems.¹⁰ We have shown that it can be applied to covalent systems by assuming localization onto bond or cluster orbitals rather than atomic orbitals as in metals. In graphite and diamond the localization effects can best be interpreted in terms of the cluster orbitals, i.e. the 3 bond orbitals arranged in a trigonal planar or 4 in a tetrahedral configuration about a single carbon atom. These can be termed the s, P_z and π , or s and P_r orbitals respectively for graphite and diamond. Multiplet structure within this picture allows for correlation effects within the cluster orbital.¹¹ The Hubbard model¹² ignores all inter-atomic hole-hole repulsions so that $U_{ij} = U$ in eq. (2) and $U_{ij} (i \neq j) = 0$. It has been shown that U_{ij} can be approximately included within the Cini expression by interpreting U in eq. (2) as the difference between the hole-hole repulsion on the same cluster orbital minus that on different neighboring clusters orbitals, $U = \Delta U = U_{ii} - U'_{ij}$. Although this interpretation is not good for large U_{ij} , U'_{ij} , and ΔU , it is adequate for the relatively small U 's involved in diamond and graphite, indeed for these systems the individual

4,5
multiplets can be merged into single ss , sp , and pp components.

The validity of the Cini expression for covalent molecules follows from the interpretation above. We have shown that a two hole configuration interaction theory (CI) applied to increasingly larger clusters eventually produces results similar to the Cini expression. Since the number of two-hole states in the six carbon atom molecules is already relatively large, the Cini expression is reasonably valid. The ΔU is interpreted exactly as that described above, but the entire lineshape must be shifted downward to account for the hole-hole repulsion, U_{hh} , in the delocalized molecular orbitals. In the band orbitals of extended systems, U_{hh} goes to zero, so this shift is not required for solids. In cyclohexane, the C-H like bonding orbitals exhibit larger ΔU 's compared to the C-C bonding orbitals similar to that found previously for ethane and other alkanes. Both the ΔU and U_{hh} are determined from the best fit to the experimental lineshapes.

Generally good agreement between theory and experiment for all four lineshapes is obtained. The molecular spectra are more highly structured,^{6,7} but even this fine structure is reasonably well reproduced. A summary of the ΔU 's and U_{hh} are given in Table 1. The similarity between the molecular and solid state results reveals that final state screening due to the extended band character of the solids is negligible. The screening that does occur, apparently results primarily from intra-ring polarization.^{2,3} The difference between the ΔU 's for the sp and sp systems is attributed to the increased intra-molecular screening

2
in the sp systems due to the delocalized π electrons. The increase in ΔU apparently arises from a greater decrease in U_{ij} than in U_{ii} , suggesting that intraorbital $\sigma\sigma$ hole screening by the π electrons is ineffective. On the other hand, short range electron screening is important for the $\sigma\pi$ and $\pi\pi$ ΔU 's, as indicated by the very small ΔU 's for these components. The value of U_{hh} for benzene and cyclohexane are consistent with that expected for two holes in molecular orbitals delocalized throughout the molecule, and again indicates the increased intra-molecular screening in benzene.

TABLE 1. Comparison of ΔU and U_{hole} Values

Lineshape	$\sigma\sigma$	ΔU (eV)	U_{hole} (eV)
Benzene } ² sp	4	1.5	0 7
Graphite	4	1.5	0 0
Cyclohexane } ³ sp	1.2 ^c		9
Diamond	1.5		0

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^a $\Delta U = U_{ij} - U_{ij}$ for the $\sigma\sigma$, $\sigma\pi$, and $\pi\pi$ components obtained empirically using eq. (2)

^b The totally delocalized, molecular, hole-hole repulsion.

^c The ΔU reported here is for the $p\pi$ orbital component corresponding to two holes in C-C like bonding orbitals. The ΔU for two holes in C-H like bonding orbitals is ~ 4-5 eV and for the cross terms 3 eV.

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