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1s x-ray-absorption spectroscopy of C₆₀: The effects of screening and core-hole relaxation

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The C 1s near-edge absorption spectrum of C₆₀ has been studied experimentally and theoretically. An assignment of the C 1s transitions to unoccupied states below the continuum threshold is suggested on the basis of multiple-scattering $X\alpha$ local density and semiempirical intermediate-neglect-of-differential-overlap self-consistent-field calculations, including effects of screening and relaxation of the symmetry-breaking core hole. The present work shows that modeling the core hole is necessary for understanding the absorption spectrum of C₆₀. Thus excitonic interactions between the excited electron and the core hole left behind give a final state that is significantly different from the ground state.

Since the discovery of a method for producing macroscopic quantities of C₆₀,¹ there has been an ongoing experimental and theoretical effort to understand electronic and optical properties of this novel form of carbon. The use of different experimental methods such as photoelectron spectroscopy,²⁻⁵ inverse photoemission,⁶ electron-energy-loss spectroscopy (EELS),^{7,8} and x-ray-absorption spectroscopy^{9,10} have given an extensive amount of experimental data about the electronic structure of C₆₀. From structural studies it is known that at room temperature C₆₀ is a molecular solid with face-centered-cubic structure in which the individual molecules are rotating.¹¹ Studies thus far indicate that delocalized π -like electrons within the molecule and van der Waals intermolecular interactions characterize the electronic structure of solid C₆₀.¹²

Band structure calculations in the local density approximation (LDA) predict nearly isolated C₆₀ molecules in the solid and an electronic structure typical for a molecular solid with narrow bands ($\sim 1/2$ eV).¹² The low-energy EELS of solid C₆₀ shows a peak at 1.55 eV,⁷ interpreted as an excitation across the h_u-t_{1u} HOMO-LUMO gap, where HOMO is the highest occupied molecular orbital and LUMO is the lowest unoccupied molecular orbital, which seems to be consistent with the calculated band gap of ~ 1.6 eV (Ref. 12) using LDA. However, it is well-known that LDA usually underestimates the band gap and experimental values could be considerably larger, particularly for semiconductors and insulators. In recent work Lof *et al.*¹³ determined the band gap to be indeed considerably higher, 2.3 eV, consistent with earlier experimental results.^{3,14} They suggested that the low-

energy features in the optical spectrum of C₆₀ should in fact be assigned to Frenkel molecular excitons, indicating strong electron-hole interactions and supporting the picture of a highly correlated system.

Inner shell excitation spectroscopy is proving to be a powerful technique for obtaining information on the electronic structure of molecules and solids. The suggestion of excitons in the optical spectra of C₆₀ indicates that this type of effect, sometimes referred to as a final state effect, might be important in C 1s absorption spectroscopy of C₆₀. The "excitonic effect" in this context is considered to be the interaction between the excited electron and the core hole, which gives a final state of one core hole and 241 valence electrons which may be quite different from the ground state of 240 valence electrons. The electronic structure of molecular C₆₀ is characterized by delocalized and highly degenerate orbitals due to the π -bonding and icosahedral geometry. A 1s hole will break the symmetry and create an attractive potential to which all electrons of the system must respond. There has recently been some question as to the magnitude of the effect of the localized hole on π states,¹⁵ which centers on the case of graphite. The core-hole interaction was introduced to explain the shape and position of the graphite π^* peak in calculations for a single layer of graphite, including relaxation near the core hole, suggesting a strong excitonic effect,¹⁶ but more recent workers have challenged that picture.^{17,18} It is therefore of high interest to test a mesoscopic case such as C₆₀.

In this work we report an experimental study of the near-edge carbon 1s x-ray-absorption spectrum of molecular and

solid C_{60} , and compare to the results of two theoretical analyses: self-consistent calculations of molecular C_{60} using the multiple-scattering $X\alpha$ (MS- $X\alpha$) method, including effects of broken symmetry, static screening, and relaxation, and the more easily implemented intermediate-neglect-of-differential-overlap-self-consistent-field (INDO-SCF, or INDO) method. Our results show that the main effects of the core-hole-valence-electron interaction can be described qualitatively within a one-electron model including effects of relaxation and static screening of the core hole. These effects are pronounced, and essential for understanding the $1s$ near-edge x-ray-absorption spectrum of C_{60} .

The experimental data were taken at Beamline 22 at MAX-lab¹⁹ in the total electron yield mode. For the data presented here, the samples were a thick film of C_{60} deposited on Au(110), and C_{60} molecules isolated in a Xe matrix. The data were calibrated by comparing first and second order light-excited photoemission spectra, and after many measurements we find a threshold peak of 284.45 ± 0.05 eV. The shape of the spectra is comparable to earlier results.⁸⁻¹⁰ Comparison of the two experimental spectra shows that the primary effect of neighboring fullerenes on the near-edge x-ray-absorption fine structure (NEXAFS) is a slight broadening of the features, consistent with weak intermolecular bonding. This conclusion is also supported by high-temperature gas phase NEXAFS data.²⁰

The self-consistent MS- $X\alpha$ oscillator strengths were calculated using a local density type of exchange-correlation potential, i.e., the $X\alpha$ potential with $\alpha=0.7$. The volume of the constant muffin-tin potential was substantially reduced by introducing a number of extra "empty sphere potentials" which minimizes the effect of the muffin-tin approximation on the calculated result. The core-hole relaxation and static screening were modeled by using the transition state procedure introduced by Slater.²² It is well-known in density functional theory that differences in total energies between electronic states can be calculated by considering a specified occupancy of one-electron orbitals by using the relation between the total energy functional E and the eigenvalues

$$\varepsilon_i = \partial E(n_1, \dots, n_i, \dots, n_N) / \partial n_i, \quad (1)$$

where n_i are the occupation numbers. Consider a transition $A \Rightarrow B$ with the initial occupation $A = [n_i = n_i(0), n_j = n_j(0)]$ and the final occupation $B = [n_i = n_i(0) - 1, n_j = n_j(0) + 1]$ after an excitation from i to j . By introducing a reference state, the "transition state" T , in which both the orbitals i and j have occupancies $1/2$, i.e., $T = [n_i = n_i(0) - 1/2, n_j = n_j(0) + 1/2]$, all second order terms vanish and the energy difference to third order between the initial and final state simply is

$$E^{\text{INITIAL}} - E^{\text{FINAL}} = E(A) - E(B) \approx \varepsilon_i(T) - \varepsilon_j(T), \quad (2)$$

where $\varepsilon_i(T)$ and $\varepsilon_j(T)$ are the one-electron eigenvalues calculated by using the transition state T . This approach was extended for calculating the oscillator strengths

$$f = 2m/\hbar^2 |\langle \phi_a | r | \phi_{1s} \rangle|^2 (\varepsilon_a - \varepsilon_{1s}), \quad (3)$$

shown as the theoretical spectrum in Fig. 1(b), by using tran-

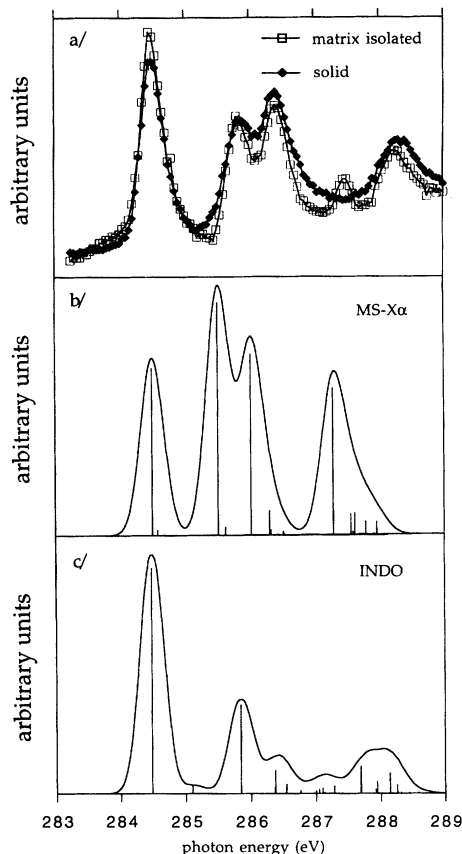


FIG. 1. C $1s$ absorption spectra of C_{60} : (a) Experimental data for solid and matrix isolated (molecular) C_{60} —the matrix isolation data contain a small contribution from CO, leading to the extra peak at 287.4 eV; theoretical results for molecular C_{60} : (b) MS- $X\alpha$ and (c) INDO. The oscillator strengths are broadened with a Gaussian function.

sition state eigenvalues and wave functions corresponding to $1s$ transitions to unoccupied valence orbitals.

Computational schemes based explicitly on the Hartree-Fock Hamiltonian, including, e.g., the complete neglect of differential overlap and INDO methods, have the well-known property that the virtual orbital energies corresponding to excited states are placed at artificially high energies, because of an unbalanced treatment of the electronic self-repulsion.²³ In an early paper, Mulliken²⁴ suggested that these states are better obtained as eigenstates of the so called "ionic Hamiltonian"

$$F_i = h_1 + \sum_{j \neq i}^N \langle \phi_j | (1 - P_{12}) | \phi_j \rangle, \quad (4)$$

where N is the number of electrons, h_1 the kinetic energy plus nuclear attraction, ϕ_j the occupied Hartree-Fock spin orbitals, and ϕ_i the initial orbital of the excited electron. It was later shown^{25,26} that the Hamiltonian (4) can be derived from a configuration interaction treatment between all singly-excited configurations which have ϕ_i as initial orbital, yielding the excitation energies directly as orbital energy differences.

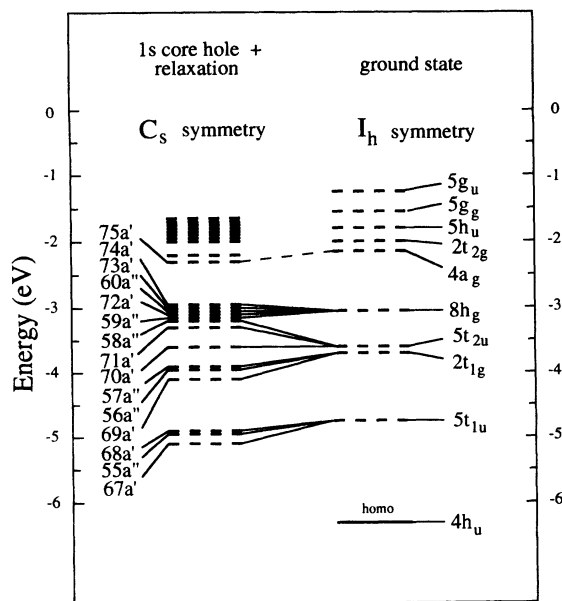


FIG. 2. Energy level diagram for unoccupied states of C₆₀ calculated with the MS- $X\alpha$ method. To the right are the ground state orbital energies calculated in I_h symmetry. To the left are the transition state energies presented for transitions from the 1s core of a C atom in the C₆₀ molecule in C_s symmetry. The energy scale for the transition state energies is defined as relative to the C 1s ionization potential.

In the present application, ϕ_i is a 1s orbital on one of the carbon atoms. In a valence electron approximation such as INDO, the removal of ϕ_i from the Fock operator in (4) is then equivalent to an increase of the nuclear charge from Z to $Z + 1$, whereas the number of occupied valence MO's included in (4) is unchanged. The appropriate Fock operator to use in the present case is thus the ordinary INDO Hamiltonian for C₅₉N⁺. The theoretical spectrum in Fig. 1(c) was shifted to align the first peak with experiment, and scaled uniformly by a factor of 1.28 in order to fit the positions of the two lowest peaks in the experimental spectrum.

The intensities of the 1s \Rightarrow valence transitions have in the present INDO treatment been calculated within a one-center approximation, using the expression

$$I(1s \Rightarrow \phi_a) \propto |c_{A,2p_x}|^2 + |c_{A,2p_y}|^2 + |c_{A,2p_z}|^2, \quad (5)$$

where A is the core-ionized atom, the expansion coefficients refer to the excited orbital ϕ_a , and the slight variation in $(\epsilon_a - \epsilon_{1s})$ in Eq. (3) has been neglected. Formula (5) was used to calculate the relative intensities shown in Fig. 1(c).

The ground state energy levels obtained from the MS- $X\alpha$ calculations are presented in Fig. 2. Most of the published calculations agree about the ordering of the four lowest unoccupied electronic states in the ground state but there is some uncertainty about the higher states. The LUMO is $5t_{1u}$ followed by $2t_{1g}$, $5t_{2u}$, $8h_g$, and $4a_g$. The $4a_g$ state of the MS- $X\alpha$ calculation does usually not occur in calculations of linear combination of atomic orbitals (LCAO) type. This state has a pronounced spherical electron density inside the cage and is likely to be missed in calculations using LCAO type basis sets, as pointed out by Jost *et al.*⁶ Shown to

TABLE I. Energies and oscillator strengths for 1s- ϵ_i transitions of C₆₀ calculated in C_s symmetry with the transition state procedure (Ref. 22). Calculated transition energies are shifted -4.63 eV to give better correspondence with the experimental transition energies.

	MO	Transition energy (eV)	Oscillator strength $f \times 10^{-3}$
$5t_{1u}$	67A'	284.50	32.37
	55A''	284.58	0.9
	68A'	284.68	0.05
$2t_{1g}$	69A'	285.51	45.03
	56A''	285.62	1.51
	57A''	285.64	<0.01
$5t_{2u}$	70A'	286.02	34.96
	71A'	286.30	4.59
	58A''	286.32	0.96
$8h_g$	59A''	286.35	<0.01
	72A'	286.43	0.05
	60A''	286.44	0.02
	73A'	286.51	0.64
$4a_g$	74A'	286.52	0.30
	75A'	287.28	28.29
$4a_g$	76A'	287.34	<0.01
	61A''	287.55	3.84
	62A''	287.58	0.55
	63A''	287.59	0.14
	77A'	287.61	4.00
	78A'	287.72	0.05
	64A''	287.78	2.42
	65A''	287.80	0.02
	66A''	287.90	0.15
	67A''	287.92	0.03
	79A'	287.95	2.35
	80A'	287.96	0.88
	68A''	288.23	<0.01
81A'	288.29	0.07	
82A'	288.30	<0.01	
83A'	288.31	<0.01	

the left in Fig. 2 are the transition state electron energies in C_s symmetry. The valence electrons of C₆₀ are grouped in the final state into 66 orbitals of A' symmetry and 54 orbitals of A'' symmetry. Orbitals of initial state T symmetry are split into two A' orbitals and one A'' orbital if the symmetry is "ungerade" and in one A' and two A'' if the symmetry is "gerade." Orbitals of G and H symmetry are split in a corresponding manner.

The theoretical oscillator strengths in Figs. 1(b) and 1(c) were broadened with a Gaussian linewidth to mimic the experimental data. The MS- $X\alpha$ oscillator strengths and transition energies are given in Table I. Four prominent peaks of A' symmetry appear and the suggested assignment is based on our calculations by referring to the ground state. The first peak originates from the $5t_{1u}$ state and only one of the three components, the 67a' orbital, gives any substantial contribu-

tion. The next two peaks originate from the $2t_{1g}$ and the $5t_{2u}$ states, with contributions from the $69a'$ orbital and the $70a'$ orbitals, respectively. The last peak originates from the $4a_g$ state which corresponds to the $75a'$ orbital in C_s symmetry. There is almost no contribution from orbitals originating from the $8h_g$ state which indicates that the absorption spectrum deviates strongly from the ground state density of states. There is a good overall agreement between experimental and calculated spectra although the intensities are somewhat different. Broadening of the peaks due to band formation between the core-excited molecule and its neighbors occurs, but has a small effect on the peak heights.²¹ It can be noted that the experimental intensity for the $1s-2t_{1g}$ transition is weaker relative to the $1s-5t_{1u}$ transition, while the opposite holds true for the theoretical intensities using the MS- $X\alpha$ method. The INDO result is in this regard in agreement with experiment, but is noticeably less accurate in the spacing of the energy levels derived from a given ground state level, and also in terms of absolute intensities. In particular, the intensity of the fourth peak is much too low, which can be traced to the above-mentioned inability of LCAO methods to describe the $4a_g$ state.

We have calculated the oscillator strength of $1s$ transitions to Rydberg states by including a $1/r$ tail potential in the MS- $X\alpha$ calculation. Weak Rydberg transitions ($<0.1 \times 10^{-3}$) occur in the $-1-0$ (eV) energy range which is above the last $1s-4a_g$ peak. The Rydberg states play a role in C $1s$ near-edge absorption spectroscopy of aromatic molecules with planar π bondings as benzene and pyridine.^{27,28} Benzene has at least two visible Rydberg peaks, the $1s-3s$ and $1s-3p$ transitions, but C_{60} has none. Otherwise there are some similarities between the $1s$ absorption spectrum of benzene and C_{60} , e.g., benzene is dominated by the $1s-e_{2u}$ transition in a similar way as C_{60} is by the (first) $1s-5t_{1u}$ transition. The effect of core-hole interactions in C $1s$ absorption of aromatic molecules is important, as has previously been demonstrated,^{27,28} and is similar to C_{60} as this work shows.

It is important to note that the core-hole relaxation can be

divided into a static and a dynamic part in the real space picture. If the core hole is stationary and localized we are talking about static screening and static relaxation, but if the charge distribution of the hole has a time dependence, the electron cloud will follow the motion of the hole and the screening involves dynamic relaxation. In this work we have only considered static relaxation induced by a localized core hole, but dynamical screening could be included by calculating the dielectric response function and introducing the effect perturbatively using linear response theory.²⁹ By considering the bare core hole as a localized charge distribution, the relaxation process leads to a correlation between the position of the hole and the position of the screening cloud. As a result, the concepts of relaxation and correlation become inseparable.³⁰

To summarize, in this paper we have demonstrated the importance of final state relaxation effects in core photoabsorption spectroscopy of delocalized π -electron systems in general, and C_{60} in particular. We have also given a comparison between two widely different computational approaches, the semiempirical INDO method and the local density MS- $X\alpha$ method, which give coinciding interpretations of the first three peaks. Of these two methods, MS- $X\alpha$ gives the best overall agreement with the experimental spectrum, but both methods can serve as the basis for an assignment of near-edge peak structures in the C $1s$ absorption spectrum. The importance of final-state interactions found here and for benzene elsewhere suggests that the system size required to quench such effects is at least orders of magnitude larger than C_{60} .

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