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Electron propagator calculations on C₆₀ and C₇₀ photoelectron spectra

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Vertical ionization energies of C₆₀ and C₇₀ fullerenes are calculated with semidirect implementations of electron propagator methods and a triple- ζ plus polarization basis set. These predictions are in close agreement with photoelectron spectra for final states in which the Koopmans description is qualitatively valid. Many correlation states, where the latter description fails, are predicted by methods with nondiagonal self-energies. © 2008 American Institute of Physics.

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I. INTRODUCTION

Since their discovery,¹ fullerenes and C₆₀, in particular, have received extraordinary attention from experimentalists and theoreticians. This interest became especially pronounced when synthesis of large amounts of species such as C₆₀ and C₇₀ became feasible.^{2–5} Prospective employment of fullerenes in organic solar cells and other electronic devices also has stimulated study.^{6–11}

Recent achievements in thin-film photovoltaic devices have led to development of the so-called tandem solar cells based on heterojunctions of small molecular donors and acceptors.¹⁰ C₆₀ has become one of the most popular components for photovoltaic pair elements in combination with copper phthalocyanine^{10,11} or pentacene.¹² To optimize the efficiency of photovoltaic elements,^{11–18} reliable determinations of electron binding energies and associated Dyson orbitals are needed. Whereas information on molecular energy levels can be obtained from photoelectron (PE) experiments, assignment of spectra often requires additional information from electronic structure calculations.

II. EXPERIMENTS

PE spectra of C₆₀ were measured in the gas phase¹⁹ as well as in thin films of 1–3 ML deposited on gold.^{19,20} The gas-phase and thin-film PE spectra are qualitatively similar. The He I PE spectrum of gaseous C₆₀ consisted of two well-resolved bands in the energy range up to ~10 eV, followed by three unresolved bands at higher energies.¹⁹ The first ionization energy (IE) was estimated to be 7.61 ± 0.02 eV. One ionized state resulting from electron removal from a fivefold degenerate h_u molecular orbital (MO) was anticipated under the first envelope. A shoulder to the left of the main peak was ascribed to Jahn–Teller distortion following the ionization. Two ionized states were predicted for the second envelope. The second and third IEs were placed at 8.89 and 9.12 eV, respectively. The rest of the gas-phase spectrum remained unresolved. A somewhat more extensive assignment²⁰ accompanied a surface ultraviolet (UV) PE spectrum of a thin film of C₆₀. The second band in this spectrum was separated

from the first peak by 1.35 eV. Two final states corresponding to g_g and h_g MOs were assigned to the second envelope. The band centroid was placed at 8.95 eV. An energy range of 10.82–11.59 eV was given for the third band. Three final states were anticipated. The MOs corresponding to the first two of these were thought to be g_u and t_{2u} . The symmetry of the third participating MO was not determined. Four final states were assigned to the fourth envelope, which extends from 12.43 to 13.82 eV; none of these states was identified. Although only one peak was recognized in the fifth band (15.81 eV), there was evidence of other transitions.

In the PE spectrum of gaseous C₇₀ taken at ~400 °C,²¹ three separate bands range from ~7.3 to ~8.8, from ~8.9 to ~10.3, and from ~10.3 to ~12 eV, respectively. The first feature was assigned to two nearly degenerate a_2' and e_1' levels and its peak was placed at 7.47 ± 0.02 eV. Four additional transitions were recognized under this envelope. Of these, only one peak at 7.68 eV was assigned to an a_2' MO. Three, higher energy transitions were assigned to the e_2' , e_2'' , and e_1' levels. All peaks overlapped significantly. The second band consisted of a separate peak at 9.04 eV that was assigned to an e_1' level and a broad, unresolved feature between ~9.2 and ~10.2 eV. The unresolved feature was analyzed in terms of asymmetric Gaussian functions, three of which were used to fit the experimental contour. All three functions were assigned to twofold degenerate levels. All assignments were based on canonical Hartree–Fock orbital energies and Koopmans' theorem (KT).²² Final states corresponding to the third band were not described.

Since these pioneering works, there have been few publications on the PE spectra of C₆₀ and C₇₀. Most works on gaseous fullerenes considered only the first IE. An adiabatic threshold of 7.57 ± 0.01 eV was observed in vacuum-UV, photoionization mass spectrometry of gaseous C₆₀ at ~600 °C.²³ The first IEs of C₆₀ and C₇₀ have been determined by single-photon ionization with synchrotron radiations to be 7.58 ± 0.04 and 7.3 ± 0.2 eV, respectively.^{24,25} An adiabatic ionization potential of 7.36 eV for C₇₀ was measured by Knudsen cell mass spectrometry.²⁶ The first two peaks in another PE spectrum occurred at 7.61 and 8.89 eV, respectively, and were assigned to the highest occupied MO (HOMO) and HOMO-1.²⁷ Only tentative maxima were

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TABLE I. C_{60} and C_{70} IEs (eV).

Method	C_{60}	Ref.	C_{70}	Ref.
MNDO	9.1	28	8.7	28
Hückel	7.45	29		
	8.41	29		
DV- X_α	6.4	30		
PRDDO	4.5	31		
HF, Δ SCF, (7s3p)/[4s2p]	7.92	32		
HF, KT, (7s3p)/[4s2p]	8.24	32		
DVM, BH	7.8	33 and 34		
DVM, X_α	6.9	34		
MNDO, KT	9.13	35		
HF, KT, (10s6p1d)/[5s3p1d]	8.0	36		
LDF	5.94	37	5.99	37
PM3, Δ SCF			9.01	38
LSDA, Δ SCF	7.59	39	7.59	39
BLYP, Δ SCF	7.04	39	7.04	39
B3LYP, Δ SCF, 6-31G*	7.24	40		

shown for the other three bands in the higher energy part of the spectrum. Peaks in the spectrum of C_{70} (Ref. 27) were not discussed.

III. PREVIOUS CALCULATIONS

Some of the calculations on the lowest IE of C_{60} (Refs. 28–40) published prior to or shortly after the first PE experiment¹⁹ are given in Table I. Depending on the method, the first IE values vary from 4.5 to 9.1 eV. The closest correspondence with the experimental value of 7.64 ± 0.02 eV was obtained with a local spin-density approximation (LSDA), Δ SCF procedure.³⁹ Significantly fewer data are available for the C_{70} ionization potential. Published values range from 5.99 to 9.01 eV.

An analysis of occupied levels in the C_{60} molecule was performed on the basis of local density functional (LDF) calculations.³⁷ Although the value of the first IE (5.94 eV) was far above experiment, these calculations did facilitate assignments. Ionization from the upper $6h_u$ level was placed at 5.94 eV. Two levels were assigned to the second band.

Four energy levels were placed under the third envelope, whereas seven final states were predicted under the fourth band. (See Table II.) Similar analysis predicted a 5.99 eV value for the first IE of the C_{70} molecule. A broad feature arising from five states with a 0.7 eV intervals was predicted to be the first peak in the PE spectrum of the C_{70} . Transition-state (TS) and Δ SCF calculations with the same LDF (Ref. 41) produced closer agreement with experimental peak positions.^{19,20} C_{60} IEs from closed-shell and restricted Hartree–Fock calculations with a (9s5p)/[4s3p] basis⁴² are notably higher than experiment at the Koopmans and Δ SCF levels.

Significant data were obtained with the INDO/S (intermediate neglect of differential overlap/spectra) method.⁴³ Although Koopmans and configuration interaction (CI) values for the first IE were in poor agreement with experiment, correlation (i.e., shakeup) final states were predicted in the latter calculations. (See Table III.) INDO-based, second-order Green’s function (GF) calculations exhibited large correlation and relaxation effects.⁴⁴

Semiempirical methods give poor agreement between calculated^{45–47} and experimental IEs. The outer valence GF (OVGF) in combination with several semiempirical Hamiltonians was used to obtain vertical IEs of C_{60} and C_{70} .^{45,46} The results vary widely with respect to the model Hamiltonians.

Ab initio calculations on C_{70} IEs are limited to Koopmans results.²² The closest agreement with experiment was achieved with a double- ζ plus polarization basis. A deviation of only 0.12 eV was obtained for the first IE. Differences between calculated and experimental IEs increased markedly for higher final states.

With the exception of the INDO/CI results, all theoretical predictions were obtained within the one-electron picture of ionization. In this work, we employ correlated *ab initio* electron propagator methods to study the nature of ionization events in the C_{60} and the C_{70} molecules.

IV. PRESENT CALCULATIONS

Electron propagator methods^{48–52} can generate IEs without evaluation of total energies or state functions. For closed-

TABLE II. SCF vertical IEs of C_{60} (eV).

MO	LDF (11s/7p1d)/[5s3p1d]		Δ SCF ^c	RHF (9s5p)/[4s3p] ^a	
	KT ^b	TS ^c		KT	Δ SCF
$6h_u$	5.94	7.49	7.60	8.32	8.14
$10h_g$	7.24	8.79	8.88	9.99	9.81
$6g_g$	7.12	8.68	8.78	10.36	10.17
$6g_u$	8.83	10.38	10.47	13.04	12.85
$6t_{2u}$	9.38			13.33	13.14
$5h_u$	8.77	10.40	10.48	13.78	13.54
$9h_g$	9.08			14.16	13.92
$8h_g$	10.70			15.65	15.47
$5g_u$	10.10			16.26	15.71
$2t_{2g}$	10.57			16.26	16.03
$5g_g$	10.85			16.98	16.75

^aReference 42.

^bReferences 37 and 41.

^cReference 41.

TABLE III. INDO IEs of C₆₀ (eV).

MO	KT	INDO/S ^a		INDO ^b	
		CI (30 × 30)	CI (48 × 48)	KT	GF
6 <i>h_u</i>	6.57	6.36	6.36	9.99	8.85
10 <i>h_g</i>	7.89	7.42	7.48	10.80	9.71
6 <i>g_g</i>	8.05	7.46	7.50	11.12	9.82
6 <i>g_u</i>	10.38	9.96	9.91	12.86	11.17
			10.17		
			10.64		
			10.70		
6 <i>t_{2u}</i>	10.97	10.37	10.43	13.10	11.53
		11.39	10.95		
5 <i>h_u</i>	10.84	11.19	11.02	13.38	11.66
		11.23			
9 <i>h_g</i>	11.05	10.93	10.82	13.44	11.76
			10.85		
8 <i>h_g</i>	13.84			15.23	13.86
5 <i>g_u</i>	12.29		12.55	14.23	12.62
			12.57		
2 <i>t_{2g}</i>	13.66			14.30	12.74
5 <i>g_g</i>	13.67			14.53	13.17

^aReference 43.^bReference 44.

shell initial states, spin contamination in final doublet states is absent. Efficient computer codes have facilitated electron propagator calculations with triple- ζ plus polarization basis sets for molecules as large as octamethyl porphyrin.^{53,54}

Three approximations are used below: the OVGf,^{51,55} the third-order algebraic diagrammatic construction, or ADC(3) method,^{51,55–57} and nondiagonal, renormalized, second-order theory (NR2).⁵⁸

V. METHODS

A. Theory

For each vertical IE calculated with electron propagator methods, there corresponds a Dyson orbital defined by

$$\phi^{\text{Dyson}}(x_1) = N^{-1/2} \int \Psi_{\text{cation}}^*(x_2, x_3, x_4, \dots, x_N) \Psi_{\text{molecule}} \times (x_1, x_2, x_3, \dots, x_N) dx_2 dx_3 dx_4 \dots dx_N,$$

where N is the number of electrons in the molecule and x_i is the space spin coordinate of electron i . The Dyson orbital represents the change in electronic structure accompanying the detachment of an electron from a molecule. The pole strength (PS) associated with a given IE is related to the corresponding Dyson orbital by

$$P_q = \int |\phi_q^{\text{Dyson}}(x)|^2 dx.$$

PSs may vary between 0 and 1. Values between 0.85 and unity indicate that one-electron descriptions of final states (e.g., via Koopmans's theorem) are qualitatively valid and that methods that assume a diagonal self-energy operator such as OVGf are applicable.⁵¹ Nondiagonal self-energy methods, such as ADC(3) and NR2, are needed to describe final states in which the one-electron picture collapses.

VI. COMPUTATIONS

All calculations were performed with the GAUSSIAN 03 suite of programs.⁵⁹

Equilibrium structures were obtained with the B3LYP density functional⁶⁰ and the 6–31G(d) basis with five d components. Because of high symmetry and compact arrangement of carbon atoms, improvement of the basis is unlikely to influence the optimized geometries. The I_h and D_{5h} point groups were imposed, respectively, on the C₆₀ and C₇₀ optimizations.

Electron propagator calculations were performed at the OVGf, ADC(3), and NR2 levels. Semidirect, symmetry-adapted algorithms for electron propagator calculations were employed.^{61–65} The 6–311G(d) basis⁶⁶ was used. The total numbers of basis functions are 1080 for the C₆₀ and 1260 for the C₇₀. For C₆₀, two sets of OVGf calculations were performed: one with a full active virtual space and another one with an active space of 120 occupied and 645 virtual MOs. ADC(3) calculations required a somewhat smaller active orbital space of 84 occupied and 465 virtual MOs. The active orbital space for C₇₀ is discussed below.

VII. RESULTS AND DISCUSSION

A. C₆₀ IEs

IEs obtained with the OVGf, ADC(3), and NR2 methods are compiled in Table IV together with experimental values.^{19,20} PSs also are given in parentheses.

Truncation of the virtual space did not have any significant effect upon the first ten IEs of the C₆₀. The largest deviation was 0.06 eV. For the last two IEs under consideration, the differences were 0.10 and 0.20 eV, respectively.

The lowest state of C₆₀⁺ is ²H_u. An IE value of 7.65 eV is obtained with the OVGf method. The PS of 0.89 indicates a one-electron process, where the Koopmans description of the

TABLE IV. Vertical IEs of C_{60} (eV).

MO	KT	OVGF ^a	OVGF ^b	IEs (eV)		Expt. ^c
				ADC(3)	NR2	
$6h_u$	7.87	7.65(0.89) ^d	7.67(0.89)	7.68(0.87)	7.47(0.83)	7.64 ± 0.02
$10h_g$	9.65	9.18(0.88)	9.18(0.88)	9.07(0.83)	8.85(0.80)	8.95 ^e
				10.49(0.002)		
				10.54(0.02)	10.48(0.01)	
$6g_g$	9.91	9.21(0.86)	9.23(0.87)	9.16(0.84)	8.82(0.80)	
				10.46(0.003)	10.47(0.003)	
$6g_u$	12.59	11.32(0.78)	11.33(0.78)	11.32(0.70)		10.82–11.59 ^f
				9.84(0.02)	9.79(0.07)	
				10.45(0.02)	10.34(0.06)	
$6t_{2u}$	13.06	11.86(0.79)	11.88(0.79)	10.40(0.006)	10.38(0.02)	
				10.66(0.002)		
$5h_u$	13.68	11.73(0.86)	11.79(0.89)		11.29(0.85)	
$9h_g$	14.03	12.06(0.89)	12.13(0.89)		11.65(0.80)	
$8h_g$	15.29	13.53(0.66)	13.54(0.66)	10.49(0.007)		12.43–13.82 ^f
$5g_u$	15.58	13.30(0.89)	13.37(0.89)			
$2t_{2g}$	16.15	14.03(0.82)	14.13(0.81)			
$5g_g$	16.56	14.84(0.64)	15.04(0.58)			15.81

^aFull virtual space.^b645 virtual orbitals retained.^cReference 19.^dPS values are given in parentheses.^eBand centroid.^fUnresolved band.

final state is qualitatively valid. The ADC(3) method produces 7.68 eV with a PS value of 0.87, thus confirming the one-electron nature of this transition. Both methods are in excellent agreement with experiment. Two almost degenerate IEs are obtained for the second band. The OVGF and ADC(3) values are very close. The corresponding MOs are of h_g and g_g symmetries. These results correspond qualitatively to experimental estimates.^{19,20} No essential satellite lines are predicted. However, many satellites with very small PS values do appear. Of these, two are represented in Table IV for the ionization from the $10h_g$ MO.

Four ionized states corresponding to the $6g_u$, $6t_{2u}$, $5h_u$, and $9h_g$ MOs are predicted for the third band. Ionizations from the first two MOs are characterized by low PSs in the OVGF calculations. Thus, exact positions of the main lines might be quite different from the energy values given in Table IV. The OVGF predicts the 2G_u ionized state at 11.32 eV. The ADC(3) value is essentially the same and the PS for this energy is 0.70, thus implying that it is the main spectral line. Numerous shakeups with very small PS values appear for this ionization. ADC(3) calculations on a system of this size are feasible only from -15 to 2 eV. Whereas a collapse of the one-electron picture of ionization is anticipated for these two energy levels, the current ADC(3) calculations revealed only two satellite lines for the ${}^2T_{2u}$ state. A state with a large PS may exist within a larger energy range, or there may be a complete breakdown of the one-electron picture of ionization from this MO.

The OVGF PS values for ionizations from the $5h_u$ and $9h_g$ levels are high and therefore the one-electron picture of ionization is indicated. ADC(3) calculations fail to find any IEs for these levels.

Three ionized states are predicted for the fourth experi-

mental envelope by OVGF. These include ionizations from the $8h_g$, $5g_u$, and $2t_{2g}$ MOs. Of these, only ionization from the $5g_u$ level with its high PS can be considered to be a one-electron process. The IE, 13.37 eV, fits well into the experimental range. A complete breakdown of the one-electron picture is expected for the $8h_g$ level where the OVGF PS value is only 0.66. ADC(3) finds a shakeup at 10.49 eV with a PS of only 0.007. Numerous shakeups with even smaller PS values are revealed. In attempts to find the energies missed by the ADC(3) procedure, NR2 calculations were performed. The NR2 procedure usually converges faster than ADC(3) and produces IE values that are somewhat smaller than the ADC(3) values.^{54,67} Indeed, two IEs were found: ionization from the $5h_u$ was placed at 11.29 eV and ionization from the $9h_g$ level appeared at 11.65 eV. Both processes seem to have one-electron character.

Electron propagator results presented in the Table IV clearly show the many-electron nature of ionizations from deeper g_u , t_{2u} , h_g , t_{2g} , and g_g levels. Improved methodology is needed for a proper description of the very complicated higher energy part of the experimental PE spectrum.

VIII. C_{70} IEs

Vertical IEs of C_{70} are compiled in Table V. The table contains two sets of OVGF energies obtained with different truncations of the active orbital space. In the first truncation scheme, 610 virtual MOs out of 1050 are retained. Virtual MOs with energies exceeding 61.9 eV are dropped. In the second truncation, all but 100 virtual MOs are kept. Discrepancies between the two sets of OVGF results are small. Good agreement with the experimental assignment²¹ is achieved for the first seven transitions. PSs are high for the first six IEs

TABLE V. Vertical IEs of C₇₀ (eV).

MO	IEs (eV)				
	KT	OVGF ^a (PS)	NR2 ^a (PS)	OVGF ^b (PS)	Expt. ^c
14a ₂ ''	7.54	7.47(0.90)	7.73(0.81) 9.86(0.02)	7.45(0.90)	7.47
19e ₁ ''	7.60	7.49(0.89)	7.69(0.81)	7.47(0.89)	7.47
7a ₂ '	8.06	7.59(0.88)	7.97(0.82)	7.63(0.88)	7.68
23e ₂ '	8.48	7.90(0.88)	8.22(0.80)	7.94(0.88)	7.96
19e ₂ '	8.58	8.11(0.88)	8.13(0.79)	8.09(0.88)	8.12
23e ₁ '	8.82	8.44(0.88)	8.51(0.80)	8.42(0.88)	8.43
22e ₁ '	10.01	9.14(0.84)	9.22(0.73) 10.11(0.05)	9.17(0.84)	9.04
18e ₂ '	10.63	9.67(0.82)	9.70(0.38) 9.36(0.17) 9.62(0.08) 9.82(0.03)	9.69(0.81)	9.28
18e ₁ '	11.03	9.90(0.81)	9.93(0.35) 9.69(0.29)	9.92(0.81)	9.60
22e ₂ '	11.20	10.03(0.81)	9.73(0.32) 9.79(0.07) 10.16(0.06)	10.06(0.80)	9.60

^a610 virtual MOs retained in the active space.^b950 virtual MOs retained in the active space.^cReference 21.

and indicate that the Koopmans description of the corresponding final states is qualitatively valid. Nearly degenerate energies for the 14a₂' and 19e₁' orbitals pertain to the first spectral feature. (The energy difference is only 0.02 eV.) The third IE (7.63 eV), assigned to a ²A₂' final state, is in excellent agreement with the experimental value of 7.68 eV.²¹ For the subsequent transitions associated with e₂', e₂'', and e₁' MOs, there is also an excellent agreement with the experimental PE spectrum. For the remaining transitions, PSs are somewhat lower than those for ionizations discussed above and indicate stronger correlation effects in the final states.

Propagator approximations with a nondiagonal self-energy offer a more definitive test of the qualitative validity of the Koopmans description of final states and are capable of revealing the presence of correlation (shakeup) final states. For C₇₀, the relatively low memory requirements of the NR2 approximation facilitate calculations with the smaller active orbital space that was used in the OVGF calculations discussed above. No correlation satellite states with essential PS values appeared for the first six transitions. Starting with the seventh final state, satellite lines are predicted. Complete breakdowns of the one-electron picture of ionization occur for the 18e₂' and 18e₁' MOs where two ionized states of comparable PSs arise. Some of these energies correspond rather well to experimental values. Thus, the experimental feature at 9.28 eV matches an 18e₂' satellite at 9.36 eV with a PS of 0.17. Three shakeup states at 9.70 eV (18e₂''), 9.69 eV (18e₁''), and 9.73 eV (22e₁') might be responsible for the IE at 9.60 eV.

IX. CONCLUSIONS

PE spectra of the C₆₀ and the C₇₀ molecules are assigned with *ab initio* electron propagator methods. The lowest IE of C₆₀ corresponds to a one-electron process with a high PS.

Two final states with one-electron character pertain to the second experimental envelope. Calculations are in close agreement with experimental data. For higher final states, markedly lower PSs indicate the qualitative importance of correlation effects. For C₇₀, the first seven final states have one-electron character. Excellent agreement with experimental data is achieved for these IEs. Correlation effects are qualitatively more important for higher final states.

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