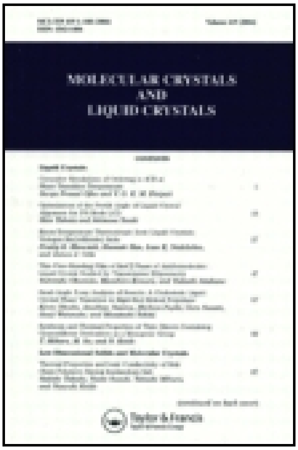

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Electron Correlation Effects in Multicharged Ions of Icosahedral C_{60} Fullerene

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Electron Correlation Effects in Multicharged Ions of Icosahedral C_{60} Fullerene

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The SCF–CI calculations of the many-electron states of high-symmetry molecules are discussed with the application to icosahedral fullerene C_{60}. *A method is elaborated that successively takes full advantage of the relations between the integrals and CI matrix elements defined on molecular orbitals (MO) of the symmetry. The results of the SCF–CI calculations for* C_{60} *ions with charges* -4 *to* $+3$ *are reported. Four different parametrizations for the electron-electron (e-e) potential are used within the spatial* π*-electron model, two of them are proposed to account for the polarization of carbon atoms in* C_{60}. *The manifestations of electron correlation in ion excitation spectra and correlation functions are discussed in the relation to the e-e potential shape. It is shown that all the e-e potentials can lead to a correct prediction of the energies of* C_{60}^{-N} *anions providing for the three e-e parametrizations, the correction of the carbon valence ionization potential by* $\sim$*2.5 eV.*

Keywords: electron correlation; fullerene ions; high-symmetry molecules; icosahedral symmetry; many-electron states

INTRODUCTION

The electronic characteristics of hollow carbon clusters, fullerenes and nanotubes, are of great interest due to unique physical properties of these systems. Particularly, the fullerene C_{60} intercalated by some metals shows superconductivity [1], and carbon nanotubes as quantum wires are considered to be perspective systems for applications in molecular devices [2]. In spite of the intense investigations of these

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systems, the physical picture in them seems to be far from completeness. Especially, it concerns the effects of electron-electron (*e-e*) interaction that are known to play an important role in forming the electronic properties of fullerenes [3,4] and, as expected, it is also the case for nanotubes. It should be noticed that the available studies of the electronic states of fullerenes are focused mainly on the energies of states, whereas the other properties characterizing the *e-e* interaction effects seem to be also of importance for a deeper comprehension of the real physical situation.

Because of a large size of fullerenes and nanotubes, the three-dimensional quasi-π-electron model is commonly used to treat the effects of *e-e* interactions. By essence, one deals with a spatial modification of the widespread Pariser–Parr–Pople (PPP) model for conjugate molecular systems. In its applications to carbon clusters, the crucial point is the choice of *e-e* potential consistent with the real physical picture of *e-e* interactions in the systems with specific multi-atom structure.

A number of *e-e* parametrizations available in the literature differs by the magnitude of on-site potential and by the shape of the distance dependence for intersite interactions. Particularly, the calculations of fullerene have been performed by using the Ohno-Yukawa potential with varied screening [5], and another analytic *e-e* parametrization was used in the study [6] of fullerene ions by the extended Hartree–Fock method. The next two potentials proposed in [7,8] take into account the screening of *e-e* interaction arising from the polarization of carbon atoms [8] or due to the electronic polarization effect [7]. So, the comparative calculations with these potentials are of special interest. We also mention the comprehensive study [9] of C_{60} anions based on other *e-e* potential.

The present study aims to clarify specific features in the electronic characteristics of C_{60} positive and negative ions originated from the shape of *e-e* potential, basing on the calculations of positive and negative multicharge ions with different *e-e* potentials. To get comparable results, the same model Hamiltonian and unified approximations for wave functions are used in the calculations of many-electron states. We apply the configuration-interaction (CI) approach using the molecular-invariant technique [10,11] to take full advantage of the high fullerene symmetry. This approach provides a unified treatment of the different C_{60} charge forms, and the results easily tabulated for different potentials are equivalent to those obtained within the straightforward CI approach. The symmetry-based technique is developed and applied also for obtaining the correlation functions that are important visual characteristics of electron interactions.

MODEL

A fullerene molecule is described by the Pariser–Parr–Pople (extended – Hubbard) Hamiltonian

$$H = -\sum_{m}\left(I_{\mathrm{C}} + \sum_{n(\neq m)} U_{mn}\right)n_m - \sum_{mn\sigma} t_{mn}a^{+}_{m\sigma}a_{n\sigma} + H_2, \tag{1}$$

where the operator $a^{+}_{m\sigma}(a_{m\sigma})$ creates (destroys) an electron with spin σ $(\sigma = \uparrow, \downarrow)$ at site (atom) m, $n_m = a^{+}_{m\uparrow}a_{m\uparrow} + a^{+}_{m\downarrow}a_{m\downarrow}$, I_{C} is the valence ionization potential for carbon, t_{mn} and U_{mn} are hopping (resonance) and electron-repulsion integrals, respectively, and H_2 is the two-electron operator contribution,

$$H_2 = \frac{1}{2}\sum_{mn} U_{mn}n_m n_n - \frac{1}{2}\sum_{m} U_{mm}n_m. \tag{2}$$

Assuming the icosahedral geometry for C_{60}, for the bond lengths $r_{mn} = 1.40\,\text{Å}$ (in hexagons between pentagons) and $1.45\,\text{Å}$ (in pentagons) [12], t_{mn} are set to $t_0 = 2.5\,\text{eV}$ and $t_1 = t_0/1.1$, correspondingly, the rest of t_{mn} being neglected.

To define H_2, we account for the C_{60} symmetry. By the symmetry, there are only 23 nonequal interatomic distances r_α and, correspondingly, 24 different values of potentials $U_\alpha = U(r_\alpha)$, $\alpha = 0, 1,\ldots, 23$, from 1830 possible one- and two-center U_{mn}. Correspondingly, H_2 can be written as

$$H_2 = \sum_{\alpha} U_\alpha H_\alpha + \frac{1}{2}\sum_{m} U_0(n_m^2 - n_m), \quad H_\alpha = \sum_{m\geq n}^{\alpha} n_m n_n, \tag{3}$$

where the index α over the sum symbol means that the sum involves only the pairs m, n corresponding to the distance r_α.

The calculations are performed with four different e-e potentials mentioned above, denoting them as OY [5], MK [6], GRZ [7], and BS [8]. They are displayed in Figure 1.

With on-site $U_0 = 11.13\,\text{eV}$, the OY potential combines the Ohno and Yukawa expressions

$$U_r = U_0 \exp(-ar_{mn})\left[1 + (U_0 r/e_0^2)^2\right]^{-1/2}. \tag{4}$$

At the screening parameter $a = 0$, long-range interactions are taken into account with Coulomb-type decay e_0^2/r at large r. In the opposite

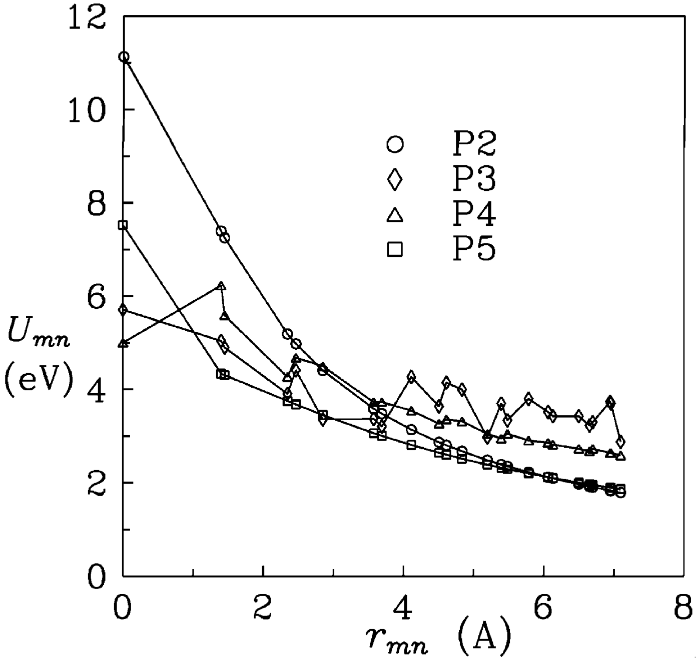

FIGURE 1 Electron-electron potentials (for notations, see the text) are shown for discrete intersite distances in C_{60}. Lines are depicted to follow by eye.

limit $a \to \infty$, potential (4) turns into the Hubbard one, $U_r = U_0\delta_{0r}$. The MK potential is defined analytically as

$$U_r = 14.1954/\sqrt{9.4864 + r^2} + 0.2044/\sqrt{0.0049 + r^2}. \tag{5}$$

The GRZ and BS potentials are determined numerically for specified interatomic distances in C_{60}. These potentials are distinguished by nonmonotonic and shallow r-dependence with essentially reduced on-site interactions and, in the case of the BS potential, by antiscreening which causes some increase of U_r at large r. It should be noted that we consider the CI calculations with the GRZ potential as rather formal because some part of electronic correlations are taken into account by the RPA approach used in [7] to construct a potential.

METHOD

For the ground state of neutral C_{60} the Hartree–Fock energy and self-consistent molecular orbitals are determined using the self-consistent procedure [13] that supports the preassigned irreducible representations for orbitals. To calculate correlated electronic states and evaluate energies $E(Q_A)$ for a fullerene ion with charge Q, we use the CI approach taking into account the most essential electron correlations within the correspondent active spaces adjacent to the lowest unoccupied molecular orbital (LUMO). The space envelops five components of the highest occupied molecular orbital (HOMO) with h_u symmetry for cations or six components of unified $t_{1u}-t_{1g}$ LUMO and LUMO + 1 for anions, the orbitals being the most important for the fullerene states with $N = -Q$ extra electrons. The correlated wave function of the C_{60}^N electronic state is expressed as the full CI expansion in Slater determinants originating from all the electronic configurations $(h_u)^Q$ or, correspondingly, $(t_{1u})^k(t_{1g})^l$, $k + l = -Q$, over the closed electron shells. In the case of cations, the lowest-charge ions are the most interesting. Thus, for convenience, the CI problem is reformulated to considering N_h holes in the Hartree-Fock 60-electron ground state instead of 10–N_h particles above 50 closed-shell electrons. In such a way, both cations and anions are treated uniformly and the desired energies of all ions measured from the Hartree–Fock ground state are directly identified with the eigenvalues of the correspondent CI matrices **H**.

The CI matrix **H** is formed from the Hamiltonian matrix elements over the determinants. The CI matrix elements, in turn, are constructed from the matrix elements of the Fock operator in the orbital representation and two-electron integrals $(ij|kl)$ representing the Coulomb interaction of electron distributions ij and kl (in the general six-orbital case, there are 231 different integrals). Commonly, the molecular symmetry in CI calculations is taken to account by the transformation of the CI matrix **H** constructed on Slater determinants by any many-electron symmetry basis functions. Then **H** matrix, mostly large, is reduced to a block-diagonal form with blocks that are small matrices $\mathbf{H}_{[k]}$ for each type of symmetry marked by the set [k] of spin-symmetry quantum numbers. We take full advantage of C_{60} high symmetry basing on the molecular-invariant theory. According to [10], the elements of $\mathbf{H}_{[k]}$ are determined by simple expressions that are linear combinations of molecular invariants defined via a few molecular integrals. Only the integrals depend on the specific parameters of the model whereas the coefficients are defined only by the symmetry and multiplicity of a molecular state. Specifically, in the considered case of cations (h_u active space), any of integrals or CI matrix elements M in some symmetry-MO basis is expressed by the formula

$$M = c_1 E_{\mathrm{B3MO}} + (d_1 J_{11} + d_2 J_{22} + d_3 J_{21} + d_4 J_{31} + d_5 J_{32})/6, \qquad (6)$$

Whereas, for anions [the $(t_{1u}+t_{1g})$ active space: six LUMO and LUMO + 1], they are represented by the expression

$$M = c_1\,E_{\text{HBMO}} + c_2\,E_{\text{HBMO}+1} + (d_1J_{11} + d_2J_{44} + 2d_3J_{21} + d_4J_{41} + 2d_5K_{41} + 4d_6K_{42})/4, \tag{7}$$

where E_{HOMO}, E_{LUMO}, and $E_{\text{LUMO}+1}$ are the Hartree–Fock orbital energies. Note that expressions (6) and (7) involve only the Coulomb and exchange integrals, $J_{ij} = (ii|jj)$ and $K_{ij} = (ij|ij)$, over the orbitals involved in the correspondent active spaces.

The coefficients c_i are zeros for integrals and nondiagonal CI matrix elements whereas, for diagonal elements, they are the correspondent occupation numbers of orbitals in the electronic configuration (negative in the case of holes). The coefficients d_i are tabulated for all terms derived from given active spaces. They do not depend on specific values of the t_{mn} and U_{mn} parameters and are integers for all integrals and most of CI matrix elements.

The same expansions are also valid for matrix elements of any full-symmetry one- and two-electron operator. We use them to estimate the average distance between extra electrons or holes and obtain the charge-charge correlation function $P(r_\alpha)$ defining it by averaging, within active spaces, the operators H_α that are all full-symmetric in the correspondent many-body states as

$$P(r_\alpha) = N_\alpha^{-1}\langle|H_\alpha|\rangle, \tag{8}$$

where N_α is the number of atom pairs relating to the distance r_α. The quantity $P(r_\alpha)$ thus normalized represents the two-particle probability that the extra electrons or holes are separated by the distance r_α.

RESULTS AND DISCUSSION

All the states of ions with charges $-4e$ to $+3e$ are calculated with each of the four *e-e* potentials. By different qualitative characteristics of the *e-e* interaction effects, the latter can be conveniently considered as slightly correlated and strongly correlated. This can be exemplified by the energy spectra of C_{60}^{-3} for the OY and GRZ potentials. Their multiplet structures that are representative for the rest of potentials are displayed in Figure 2.

As seen from Figure 2a, the spectrum with the GRZ parametrization retains, to a great extent, electron features to be independent. Specifically, well separated narrow groups of levels can be easily related to one-electron spectra in a simple orbital model with two three-fold degenerate orbitals, t_{1u} and t_{1g}. The lowest group of slightly

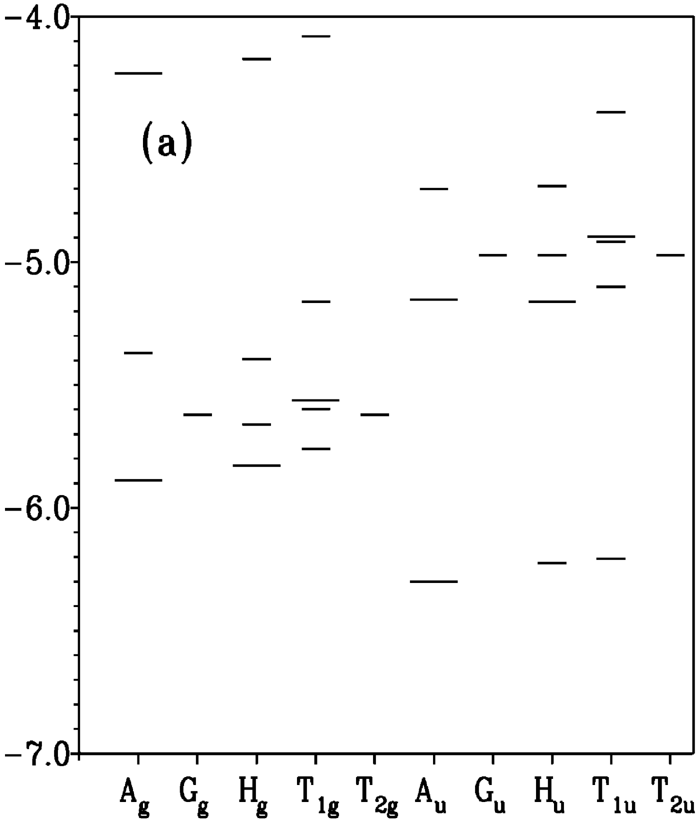

FIGURE 2 Many-electron energy spectra of C_{60}^{-3} calculated with the GRZ (a) and OY (b) *e-e* potentials. Longer lines – quartet states, shorter lines – doublet states.

splitted three-electron levels corresponds to the degenerate ground state in the orbital model. The next groups alternating by parity can be related with mono, doubly, and triply excited states.

Contrary to this, in the spectrum calculated with the OY potential (Fig. 2b), levels are uniformly distributed within the range from 0 to 6 eV. The energy intervals occupied by gerade and ungerade states alternate but without distinct gaps, moreover, they partly overlap. Thus, the *e-e* interaction with the OY potential strongly modifies the orbital picture.

Another characteristic visualizing the *e-e* interaction effects is a shape of the charge-charge correlation function defined by Eq. (8).

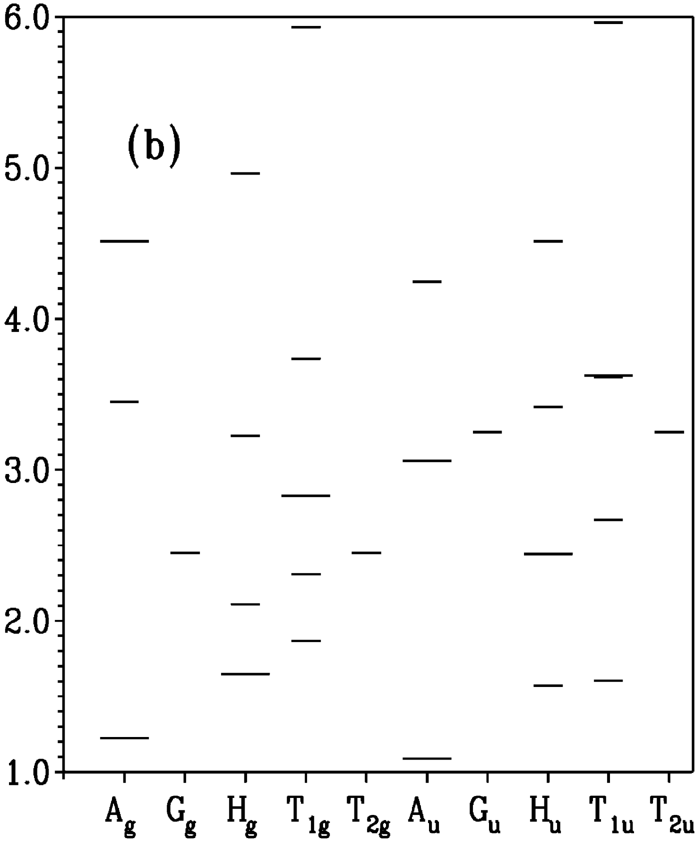

FIGURE 2 (Continued).

Typical patterns are displayed in Figure 3 for the CI ground state of C_{60}^{-2} ion with two potentials of different correlation ranges.

For the sake of comparison, we calculate the correlation functions also for the state without CI, i.e. described by the single configuration of the lowest energy for the correspondent ion. In the case of the GRZ potential, the correlation functions with and without CI are very close (Fig. 3a). They both do not show any trend of electrons being apart. On the contrary, this trend is apparent in the case of a correlated C_{60}^{-2} with the OY potential, but the correlation function without CI is quite similar to one obtained with the GRZ potential.

Now we turn to the qualitative results obtained for the ground-states of C_{60} ions with different *e-e* potentials. The numerical data for ions with charges $Q = -4, \ldots, +3$ are given in Table 1. Together

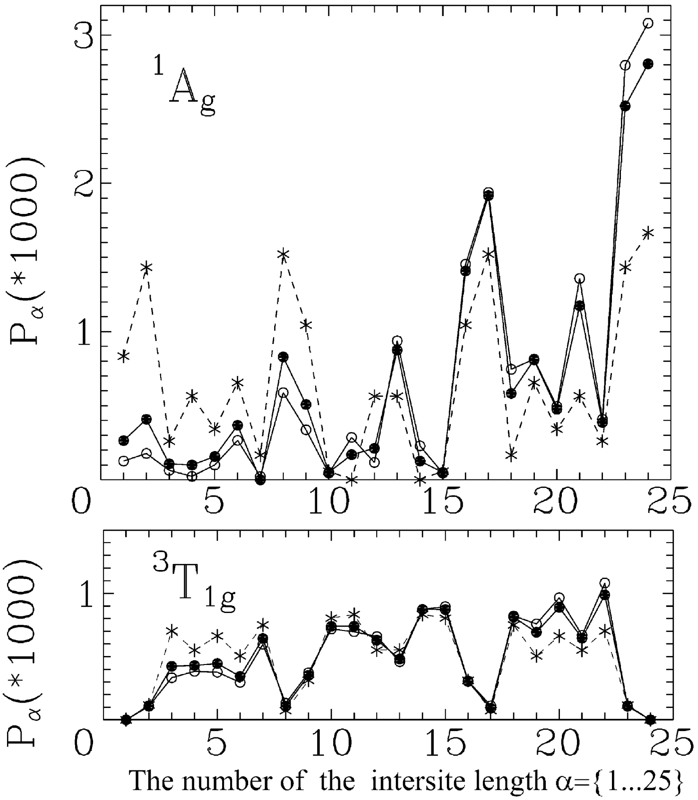

FIGURE 3 Correlation functions of extra electrons for two ground states of C_{60} dianions obtained with two *e-e* potentials: white circles correspond to the OY potential and black circles – BS. Solid lines – CI; dotted lines – the single configuration approximation.

with the ground-state energies of ions (measured from the Hartree–Fock energies of a neutral C_{60}), we present the correlation contributions. They are defined as differences between the CI energies and the energy of the main one-configuration state involved in the correspondent CI state with maximal weight. The weights are estimated as the squares of coefficients in the CI expansions and also given in Table 1. For cations, the most of them are unit due to that the CI active space involves here only the single HOMO. So, the cation ground-state terms turn out to be single (the GRZ C_{60}^{3} double term is the only exception). In these cases, the CI states are reduced to monoconfigurational ones.

TABLE 1 Calculated Properties of C_{60} Ions in the Lowest-energy State with Different Electronic-interaction Potentials U_{mn} (see text)*

	Ion charge and ground-state symmetry						
U_{mn}	$+3$ $^4T_{1u}$	$+2$ $^3T_{1g}$	$+1$ ^2H_u	-1 $^2T_{1u}$	-2 ^1A_g	-3 ^4A_u	-4 $^3T_{1g}$
			CI ground-state energy of ions (eV)				
OY	38.37	22.49	9.72	−2.74	−2.74	0.22	6.91
MK	39.98	24.00	10.68	−5.24	−7.92	−8.02	−5.20
BS	48.06[a]	28.62[b]	12.61	−5.76	−8.26	−7.36	−2.89
GRZ	46.63[c]	27.37[d]	11.86	−5.77	−7.87[e]	−6.30	−0.94
experim.	...	19.0[16]	7.6[15]	−2.7[14]	−2.7[14]	...	...
			Correlation contribution (eV)				
OY	0	0	0	0	−0.72	−0.74	−0.90
MK	0	0	0	0	−0.32	−0.25	−0.37
BS	0	0	0	0	−0.25	−0.31	−0.41
GRZ	−0.02	0	0	0	−0.01	−0.04	−0.09
			Weight of the main configuration				
OY	1	1	1	1	0.76	0.63	0.72
MK	1	1	1	1	0.84	0.80	0.82
BS	1	1	1	1	0.87	0.77	0.80
GRZ	0.91	1	1	1	0.99	0.96	0.94

*Symmetry of ion ground states differing from those indicated in the heading: [a]($^2T_{1u}$), [b] (^1G_g), [c](^2H_u), [d] (^1H_g), [e]($^3T_{1g}$).

For C_{60} negative ions, whose six-dimensional CI active space involves two orbitals, the CI takes into account not only the orbital degeneracy but also the electron correlation. Data in Table 1 show that both the increasing magnitudes of correlation contributions to the anion energies and the decreasing weights of main configurations suggest that the *e-e* potentials should be ranged by the correlating degree as OY > MK > BS > GRZ. The above consideration of correlation functions and excitation spectra is consistent with this order.

Let us turn now to the calculated ion energies. As seen from Table 1, they are sharply depend on the shape of *e-e* potential, especially in the case of anions. The OY potential with the chosen screening parameter $a = 0.015\,\text{Å}^{-1}$ leads to the agreement with available observed energies of free ions (without screening, the calculated Ohno energies are shifted by about 0.5 eV). Particularly, the predicted energies are consistent with the observation of stable C_{60}^- and C_{60}^{-2} anions only with the ionization energy $I_- = 2.7\,\text{eV}$ and the electron affinity $A_- \approx 0$ for C_{60}^- [14]. It should be mention that the OY cation energies turn out to be overestimated as compared with the measured ionization potentials [15,16]. Evidently, an expansion of the active space, too restricted just for cations and accounting for the geometry relaxation, must improve the agreement by lowering the energy.

Contrary to the OY case, the other *e-e* potentials lead to much greater discrepancies with the available experimental data for anions: the predicted anion energies are negative and overestimated. Because the calculations for all potentials are performed with fixed other parameters, we try to improve the predictions changing the standard value $I_C^{10} = 11.16\,\mathrm{eV}$ for the carbon ionization potential I_C in (1) by $I_C = I_C^0 + \Delta$. Using the evident relation for the ion energies $E(I_C^0 - \Delta) = E(I_C^0) + Q\Delta$ we estimate Δ by the mean-square fit to the measured monoanion and dianion energies. With Δ thus obtained, the calculated ion energies are presented in Figure 4. As seen, the parabola-like charge dependences of the corrected energies with all potentials turn out to be very close and are in qualitative agreement with the experimental data. The energies predicted for higher anions

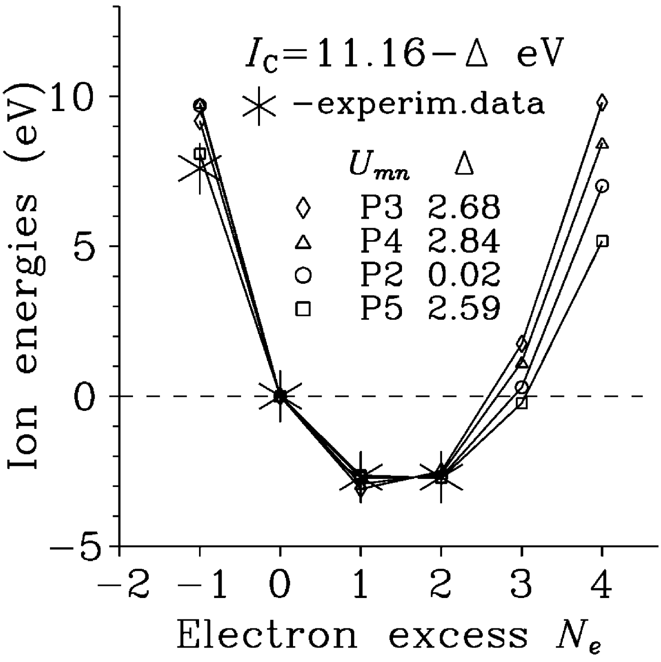

FIGURE 4 Ground-state energies of C_{60} ions calculated with the corrected ionization potential I_C of a carbon atom at different *e-e* potentials U_{mn}.

are positive, which is consistent with the observations of stable mono- and dianions only.

CONCLUSIONS

The following conclusions can be drawn from this study.

(i) Correlation regimes of C_{60} anions, manifested in the characteristics of electronic spectra, correlation functions, and ion energies are related to the *e*-*e* potential slope. Correspondingly, the interelectronic potentials considered here can be ranged by correlation strength. Only the conventional Ohno potential provides the strong correlation regime even with chosen small screening. The other ones are slightly correlated.

(ii) Slightly correlated potentials result in discrepancies in the estimations of the second C_{60} affinity predicting too lower negative energies for higher anions. We should mention, in this relation, the similar effect of the *e*-*e* interaction considered in [17]. As is shown, the right order of the ground-state energies of C_{60}^{-N} anions with respect to N, ascending with the Ohno potential, changes for opposite with a sufficient screening of *e*-*e* interactions. Just the descending order is a characteristic of the independent-electron model at the negative energy of the degenerate LUMO, in which the anion energy lowers proportionally to the orbital occupation. To some extent, this feature persists also at a strongly screened potential.

The energy rising with N is provided by the sufficient electron repulsion, whose energy contribution rises evidently with N.

(iii) The above discrepancy for anion energies can be removed by the correction of the carbon ionization potential relative to its standard value commonly used for conjugate systems. However, the great magnitude of corrections needs a separate substantiation.

(iv) For all potentials, the anion $E(Q)$ curves are concave. Sequently, $E(C_{60}^{-2}) + E(C_{60}^{-4}) - 2E(C_{60}^{-3}) > 0$, thus, the free-anion energy contribution is deficient to provide, by itself, the interfullerene electron transfer in superconducting fulleride compositions A_3C_{60}.

The results of this study are supposed to be of use not only for a better understanding of the correlation effects in fullerenes but also for adjusting the *e*-*e* model potentials for other carbon clusters, particularly, nanotubes.

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