New insights in low-energy electron-fullerene interactions

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ABSTRACT

The robust Regge-pole methodology has been used to probe for long-lived metastable anionic formation in C_n (n = 20, 24, 26, 28, 44, 70, 92 and 112) through the calculated electron elastic scattering total cross sections (TCSs). All the TCSs are found to be characterized by Ramsauer-Townsend minima, shape resonances and dramatically sharp resonances manifesting metastable anionic formation during the collisions. The energy positions of the anionic ground states resonances are found to match the measured electron affinities (EAs). We also investigated the size-effect through the correlation and polarization induced metastable resonances as the fullerene size varied from C_{20} through C_{112}. The C_{20} TCSs exhibit atomic behavior while the C_{112} TCSs demonstrate strong departure from atomic behavior attributed to the size effect. Surprisingly C_{24} is found to have the largest EA among the investigated fullerenes making it suitable for use in organic solar cells and nanocatalysis.

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1. Introduction

The discovery of the now most studied C_{60} fullerene by Kroto et al. [1] inspired vigorous searches for new fullerenes. Of particular interest here was the subsequent discovery of the smallest fullerene thought to exist C_{20}; its electron affinity (EA) was measured as well to be 2.25 eV [2]. Other small fullerenes of interest here are C_{24}, C_{26}, C_{28} and C_{44}, which have measured EAs available. The EA provides a stringent test of theory when the calculated and measured EAs are compared. Indeed, it was concluded that the EAs of fullerenes are relatively very high and almost size-independent [3]. This and their rich resonance structures explain the tendency of fullerenes to form compounds with electron-donor anions and their vast applications [4], including in nanocatalysis through their anions.

The present investigation has been motivated by the following: (1) Amusia concluded that fullerenes can be viewed as "big atoms" [5]; (2) Rich resonances have been observed to characterize low-energy electron-fullerene interactions [6–9]; (3) The availability of high quality measured EAs [10–16]; (4) The Regge pole calculated low-energy electron elastic total cross sections (TCSs) for fullerene ground states were found to be characterized by dramatically sharp resonances located at the second Ramsauer-Townsend (R-T) minima of their TCSs [17]. The energy positions of these sharp resonances generally matched excellently the measured EAs for the investigated fullerenes, from C_{60} through C_{92}; (5)

The need for fullerenes with large EAs for organic solar cells and nanocatalysis of water to peroxide and (6) The Regge pole-calculated electron-fullerene scattering TCSs revealed polarization induced long-lived metastable fullerene anions [17,18], also demonstrated in this paper. The Regge pole approach implemented here represents a theoretical breakthrough in low-energy electron scattering investigations of fullerenes/clusters.

Except for C_{60}, where resonances have been investigated [19–22], low-energy electron elastic scattering TCSs for fullerenes are sparse. In C_{20} low-energy resonant structures were explored and identified [23] while geometry effects in elastic scattering and capture of electrons by C_{60} were studied [24]. Electron elastic scattering from endohedral C_{60} has been investigated [25–27] while scattering phases in electron collision with multi-atomic systems have been studied [28]. Experimentally, low-energy electron elastic scattering differential cross sections for C_{60} were measured [29]. Elhamidi et al. [6] considered low-energy electron attachment in the gas-phase C_{60} and C_{70} and identified several resonant states as well as determined the lifetimes of the formed negative ions. Regge pole-calculated low-energy electron scattering TCSs for ground and first excited states of fullerenes are generally robust; for C_{20} they resemble those of atomic Au, consistent with the conclusion that fullerenes can be viewed as "big atoms" [5]. Here we explore the variation of R, the ratio of the second to first R-T minima of the first excited states TCSs, from C_{20} through C_{112}. We find that for C_{20} the ratio R (1.41) is close to that for atomic Au while for C_{24} R is about unity. For C_{112} R is 0.20 demonstrating strong departure from atomic behavior due to significant polarization interaction in C_{112}; which also induces long-lived metastable C_{112}^- anions.

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Indeed, the ratio R together with the electron affinity provides a powerful instrument for identifying stable fullerenes. The energy positions, corresponding to the ionic binding energies (BEs) of the ground state resonances, located at the second R-T minima of the investigated fullerenes TCSs, are found to be comparable to the EAs of C_{60} and C_{70}, consistent with the findings in [3,17]. For the fullerenes under consideration, their ground-state TCSs resemble those of atomic Au and C_{60}. However, the first excited state TCS and the attendant sharp resonance for C_{20}, sensitive to the polarization interaction, also resemble those of the Au atom. Consequently, this TCS can be used as a sensitive probe of the size effect. In the results we also include the data for Au to represent and reflect the atomic perspective.

2. Method of calculation

For the electron-neutral fullerene collisions the TCS is calculated using the Mulholland formula [30] in the following form wherein is fully embedded the electron-electron correlation effects (atomic units are used throughout) [31]:

$$\sigma_{tot}(E) = 4\pi k^{-2} \int_0^\infty \text{Re}[1 - S(\lambda)]\lambda d\lambda$$
$$- 8\pi^2 k^{-2} \sum_n \text{Im} \frac{\lambda_n \rho_n}{1 + \exp(-2\pi i \lambda_n)} + I(E) \qquad (1)$$

In Eq. (1) S is the S-matrix, $k = \sqrt{(2mE)}$, with m being the mass and E the impact energy, ρ_n is the residue of the S-matrix at the nth pole, λ_n and I(E) contains the contributions from the integrals along the imaginary-axis; its contribution has been demonstrated to be negligible [32].

Consistent with the previous work [27], here we consider the incident electron to interact with the fullerene without consideration of the complicated details of the electronic structure of the fullerene itself. For the calculation of the TCSs within the Thomas-Fermi theory, Felfli et al. [33] generated the robust potential, now known as the Avdonina-Belov-Felfli (ABF) potential,

$$U(r) = \frac{-Z}{r(1 + \alpha Z^{1/3} r)(1 + \beta Z^{2/3} r^2)} \qquad (2)$$

where Z is the nuclear charge, α and β are variational parameters. Notably, our choice of the ABF potential, Eq. (2) is adequate as long as we limit our investigation to the near-threshold energy regime, where the elastic cross section is less sensitive to short-range interactions and is determined mostly by the polarization tail. Note also that the ABF potential has the appropriate asymptotic behavior, *viz.* $\sim -1/(\alpha\beta r^4)$ and accounts properly for the polarization interaction at low energies. The advantage of the well-investigated [34–36] Eq. (2), is that it is a good analytic function that can be continued into the complex plane. The effective potential, V(r) = U(r) + L (L + 1)/ ($2r^2$), is considered here as a continuous function of the variables r and L (complex).

The potential, Eq. (2) has been used successfully with the appropriate values of α and β. It has been found that when the TCS as a function of β has a resonance [32], corresponding to the formation of a stable long-lived negative ion, this resonance is longest lived for a given value of the energy which corresponds to the EA of the system (for ground state collisions) or the BE of the excited anion. This was found to be the case for all the systems we have investigated thus far, including fullerenes. This fixes the optimal value "β" in Eq. (2) when the optimum value of α = 0.2.

Im L plays an important role in our calculations. It is used to distinguish between the shape resonances (short–lived resonances) and the stable bound, both ground and excited, states of the negative ions (long-lived resonances) formed as Regge resonances in the electron-fullerene scattering [32,37]. In Connor [37] and the applications [32] the physical interpretation of Im L is given. A small Im L implies that the system orbits many times before decaying, while a significant Im L value denotes a short-lived state. For a true bound state, namely E < 0, Im L ≡ 0 so that the angular life, 1/ (Im L) → ∞, implying that the system can never decay.

The numerical details of the evaluations of the TCSs are described in Ref. [31] and further details of the calculations may be found in Ref. [38].

3. Results

Additional to providing first time TCSs for the C_{20}, C_{24}, C_{26}, C_{28} and C_{44} fullerenes, the results presented here are primarily in the context of answering the important simple questions: (a) Can we determine when the atomic and fullerene pictures merge together, if at all? (b) Can we readily identify fullerene negative ion resonances that correspond to stable anionic formation as was done for the case of the fullerenes, C_n (n = 60, 70, 76, 78, 80, 82 and 92)? [17] (c) Can we extract unequivocally from the TCSs the BEs of the formed fullerene anions for comparison with the measured EAs? Indeed, each TCS presented here conveys its own unique and interesting story. This notwithstanding, the subtle differences among these results will not be discussed here. Importantly, the internal region of zero potential provided by the hollow cage structure of the fullerenes is conducive to metastable states C_n^- (n = 20, 24, 26, 28, 44, 70, 92 and
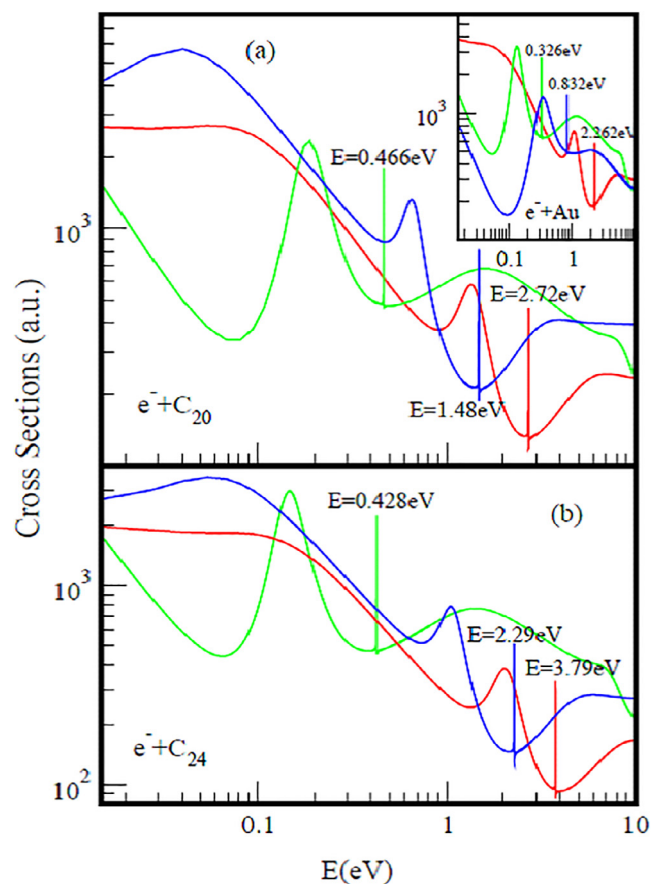
Fig. 1. (a) Total cross sections (a.u.) for electron elastic scattering from C_{20}. The red, blue and green curves represent TCSs for the ground, first and second induced metastable states, respectively. The dramatically sharp resonances correspond to the C_{20}^- anions formation during the collisions. The inset represents the TCSs for atomic Au for comparison. (b) Total cross sections (a.u.) for electron elastic scattering from C_{24}. The red, blue and green curves represent TCSs for the ground, first and second induced metastable states, respectively. The dramatically sharp resonances correspond to the C_{24}^- anions formation during the collisions.