Electronic Shell Structure and Relative Abundances of Cesium-Coated C_{60}

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(Received 11 July 1995)*

The relative abundances of $C_{60}Cs(N)$, $N \leq 500$, determined from mass spectra measurements, are presented and explained in terms of the successive filling of the electronic shells by the cesium valence electrons. The motion of the Cs valence electrons, confined to a metal layer surrounding the C_{60} molecule, is described within the jellium model, with Cs spread into a uniform positive background. The electronic shell structure is calculated with the local approximation to density-functional theory and is shown to correspond to measured abundances. Strong Friedel oscillations in the electronic density are found and closed forms for them are given for jellium spheres both with and without the void. [S0031-9007(96)00807-1]

PACS numbers: 73.20.Dx, 61.46.+w

Recently alkali clusters have been shown to exhibit an electronic shell structure, which can be described in a jellium model where the alkali valence electrons move in the uniform positive background of the ions [1–5]. The stability of these clusters as a function of size (i.e., as a function of the number of jellium electrons) is described in terms of occurrence of closed electronic shells.

In this paper we describe a new system, $C_{60}Cs(N)$ (a buckyball coated with N Cs atoms), for which relative abundances are also shown to be described reasonably well in terms of the electronic shell structure within the jellium model.

These metal-coated buckyballs were produced by co-evaporation of fullerenes and cesium metal in a gas aggregation cell [6]. They were subsequently ionized with monochromatic photons and analyzed with a time-of-flight mass spectrometer. The ionization energy of the cluster oscillates with the size of the cluster, which is caused by the successive filling of the electronic shells of the $C_{60}Cs(N)$ system. For certain values of the total number of electrons, all electronic shells are either completely filled or completely empty. Addition of just one more electron causes a new shell to open up leading to a drop in the ionization energy. It is tedious and virtually impossible to ionize each individual cluster and measure its ionization energy. Fortunately, the shell oscillations can be observed in a much simpler experiment where the clusters are ionized with photons followed by a measurement of a single mass spectrum. The photon energy is chosen in such a way that it is large enough to ionize the open-shell clusters, but is too small to ionize the closed-shell clusters. Clusters with closed-shell structures are therefore not ionized and do not appear in the mass spectra.

Thus dips in the mass spectra correspond to closed-shell clusters.

Figure 1(a) shows the measured mass spectra of $C_{60}Cs(N)$ clusters ionized at different photon energies. The dips in the mass spectra are indicated by the corresponding number N of cesium atoms.

The $C_{60}Cs(N)$ system is a very complicated system for exact electronic-structure studies and it is therefore desirable to develop approximate models that can describe its main features and which, furthermore, provide general insight into its properties. We shall here show that this is achieved with the jellium model.

We model the $C_{60}Cs(N)$ clusters as a metal-coated buckyball, which is suggested from the fact that Cs is known to wet graphite so that one would also expect C_{60} to be surrounded by the Cs metal. We describe the system as a jellium sphere with a “void” at the center (Fig. 2). In this model, the Cs s valence electrons are considered to move freely within the volume of the jellium outside the “void,” with the metal ion cores smeared out into a uniform positive and rigid background. The background density is given by $n = n_0$ for $a \leq r \leq b$ and $n = 0$ otherwise. Here n_0 is the valence electron density of the corresponding metal, b is the outer radius of the cluster, and a is the inner radius, which we have taken to be $a = 4.5 \text{ \AA}$. This value was chosen to be slightly larger than the geometrical radius of C_{60} ($3.5 \text{ \AA}$) so as to model the repulsive interaction of the π -electron charge cloud on the surface of the buckyball. In terms of the standard electron gas parameter r_s ($r_s = 2.98 \text{ \AA}$ for Cs), the quantity b is given by the expression $b = r_s[N + (a/r_s)^3]^{1/3}$.

The ground-state electronic properties are then obtained by solving the Kohn-Sham equations within the

FIG. 1. (a) Photoionization mass spectra of $C_{60}Cs(N)$ clusters, ionized with photons of various energies. (b) The total energy differences $\Delta(N)$ calculated from the density-functional theory. Peaks in the energy difference correspond to the complete filling of the electronic shells giving rise to dips in the photoionization mass spectrum. The abscissa in (a) gives the number of Cs atoms whereas in (b) it gives the number of electrons in the jellium. Assuming that $Cs(N)$ donates six electrons to C_{60} , the two axes are displaced relative to each other by 6.

density-functional theory

$$[-(\hbar^2/2m)\nabla^2 + v_{\text{eff}}(r)]\psi_i(r) = \epsilon_i\psi_i(r), \quad (1a)$$

$$\rho(r) = \sum_i |\psi_i(r)|^2, \quad (1b)$$

where ϵ_i and $\psi_i(r)$ are, respectively, the one-electron eigenvalues and the wave functions. With these the elec-

FIG. 2. Jellium model for the cesium-coated buckyball. The cesium valence electrons are confined to move in the metal shell surrounding the C_{60} molecule.

tron density $\rho(r)$ and the energy functional are evaluated to obtain the total energy $E(N)$ for the cluster. The density-functional equations were solved self-consistently for each value of N .

Figure 1(b) shows the variation of the electronic energy, $\Delta(N) = E(N+1) + E(N-1) - 2E(N)$, as calculated with this jellium model, with $E(N)$ being the total energy of the jellium containing N electrons. A peak in $\Delta(N)$ indicates the presence of a closed shell and therefore predicts a dip in the mass spectra.

We estimate that the minimum number of Cs atoms for the jellium model to work is given by $N \geq 20$, which is the number needed to coat a full monolayer of cesium on the C_{60} surface, based on the Cs atomic size of about 3 Å. The thickness of the Cs layer is then large enough to screen off any Coulomb potential due to the charge on the C_{60} sphere, as indicated by the small value of the Thomas-Fermi screening length, $\lambda_{\text{TF}} \approx (r_s/a_0)^{1/2}/(2.95 \text{ Å})$, which is about 0.80 Å for Cs. Thus for $N \geq 20$, the jellium model should work and, in addition, the Coulomb potential of the C_{60} sphere may be neglected. Further support for this comes from additional calculations on a $Cs(N)C_{60}$ system with either (i) an infinite potential barrier or (ii) a repulsive Coulomb potential due to the charged C_{60} sphere, which gave results only marginally different from those reported here.

Because of the spherical symmetry, the eigenfunctions can be labeled by the angular momentum quantum numbers l, m and the principal quantum number n just as in the case of the free atom. The calculated self-consistent one-electron eigenvalues as a function of the number N of electrons in the jellium are shown in Fig. 3, from which the opening of new shells as N is increased is clearly noticeable. The opening of a new shell corresponds to the observed dip in the mass spectra. The occurrence of nearly degenerate subshells, e.g., $2p + 2d$,

FIG. 3. One-electron eigenvalues ϵ_i for the $C_{60}Cs(N)$ cluster with a neutral carbon cage (a) and the pure $Cs(N)$ cluster (b) obtained from self-consistent density-functional calculations. The zigzag line showing the highest-filled electronic orbital indicates the opening of successive new shells as the number of Cs atoms is increased. Also shown are the (n, l) quantum numbers of the orbitals.

$1g + 1h + 2s$, etc. for $N \approx 100$ in Fig. 3(a), may be a sign of the existence of larger shells which are more pronounced for considerably larger values of N [7].

We now address the issue concerning the number of electrons transferred from the Cs atoms to the C_{60} cage. As is well known from the electronic structure of the single C_{60} molecule [8–11], the lowest unoccupied molecular orbital consists of the threefold t_{1u} molecular orbitals that can accommodate up to six electrons in total when taking spin into account. According to conventional wisdom, this is the number of electrons transferred from the Cs atoms to the C_{60} molecule. The net increase of energy by the transfer of ν electrons from the alkali region to the carbon cage is given approximately by the expression $\Delta E = \nu\phi_{\text{metal}} - \nu A(C_{60}) + [\nu(\nu - 1)/2]U$, where ϕ_{metal} is the work function for Cs (≈ 2.14 eV), $A(C_{60})$ (≈ 2.7 eV [12]) is the electron affinity of the C_{60} molecule, and U is the screened Coulomb interaction for two electrons on C_{60} . According to the above expression, U must be ≤ 0.22 eV. if as many as six electrons are transferred. Now the bare value of the Coulomb interaction $U_0 \approx 2.7$ eV [13] for the isolated C_{60} molecule is expected to be significantly reduced by screening from the jellium electrons. If we approximate the system by a cavity of radius r in a

bulk metal ($r \approx 6$ Å), then it can be seen that in the classical electrostatic model, the bare U_0 is reduced by the amount of e^2/r or about 2.4 eV. Thus a low U value is entirely reasonable and we will assume that six electrons are transferred to the C_{60} molecule.

With this assumption, Table I shows a comparison between the predicted and the observed values for the shell closing (see Fig. 2). The large N spacing in the table is an indirect evidence for a system with high symmetry. The agreement between theory and experiment is remarkably good considering the simplicity of the jellium model and is comparable to that found for pure alkali clusters. According to the calculations, the electronic levels of the jellium are filled in the order $1s, 1p, 1d, 1f, 1g + 2s, 2p, 1h + 2d, 1i + 2f, 3s + 1j + 2g + 3p, 3d + 1k + 2h, 3f + 1l + 2i + 4s, 1m + 3g + 2j + 4p, 4d + 1n + 3h + \dots$, where levels close in energy (supershells) are grouped together. The near degeneracies lead to special stability of the cluster only when a whole group of near-degenerate levels is filled and therefore to large spacing between the magic numbers as seen from Table I. The discrepancy between the predicted and observed magic numbers is hardly surprising since small perturbations in the potential seen by the jellium electrons may easily modify some of these near degeneracies leading to slightly different magic numbers. These perturbations may be caused by deviations from either the spherical symmetry or the uniform positive background (both of which are assumed in our model) as well as from electronic and electrostatic interactions between the C_{60} molecule and the Cs electrons.

The electronic charge density decays roughly exponentially outside the jellium sphere (see Fig. 4), mimicking both the case of the sphere without the void and the case of jellium terminated by a flat surface. To describe the charge-density oscillations (Friedel oscillations) seen in the Cs bulk, we model the jellium surface by a repulsive δ -function potential shell of strength V_0 and located at a distance β outside the surface. The magnitude of β is of the order of the electron gas parameter rs and the quantity V_0 has the units of energy $\times$ length.

We then find that for the jellium sphere *without* the void, the oscillatory part of the electron density $\delta\rho$ inside the sphere at a distance x from the potential shell is given by the expression

$$\delta\rho(R, x) = -V_0 2k_F^2 \frac{m}{h^2} \frac{R}{R - x} [f(x) - f(2R - x)], \quad (2)$$

where

$$f(x) = \sin \lambda/\lambda^2 - \cos \lambda/\lambda + \pi/2 - \text{Si}(\lambda) \quad (3)$$

is the same function that enters in the expression for the Friedel oscillations of a two-dimensional planar surface [14]. Here $\lambda = 2k_F x$, k_F is the Fermi momentum of the electron gas, R is the radius of the potential shell (i.e., R

TABLE I. Comparison of the experimentally observed shell closing with the prediction of the jellium model for $C_{60}Cs(N)$.

Theory	14	24	38	58	64	96	136	192	258	338	434
Expt.	12 ± 0	27 ± 1	33 ± 1	44 ± 0	61 ± 1	98 ± 1	146 ± 2	198 ± 0	255 ± 5	352 ± 10	445 ± 10

is the radius of the jellium sphere $+\beta$), and the Si function is defined as $Si(\lambda) = \int_0^1 dz \sin(\lambda z)/z$. Equation (2), obtained from perturbation theory, should be more accurate for larger spheres. It reduces to a particularly simple form for the electronic density at the center of the jellium sphere, viz., $\delta\rho = V_0(2m/h^2)[2k_F R \cos(2k_F R) - \sin(2k_F R)]/R^2$, which is consistent with the standard expression for the Friedel oscillations produced by a point impurity. For a large sphere $R \gg r_s$, this means that as the sphere radius is increased the oscillations die out, but only as slowly as $\delta\rho(R) \sim \cos(2k_F R)/R$. Such large Friedel oscillations have been observed by earlier authors [4,5] for the jellium clusters. If we now take the integral strength of the potential shell to be $V_0 \equiv \eta r_s$ with $\eta \approx 2.5$ eV, a reasonable value for the repulsive surface potential, we find that the potential shell is located about $\beta \approx 1$ Å outside the boundary of the jellium sphere.

For the jellium sphere with the void, the oscillations arise from both the inner and outer surfaces bounding the jellium. We find that the electronic density oscillations

inside the jellium are then given by

$$\delta\rho = \delta\rho(b + \beta, x_2) + \delta\rho'(a - \beta, x_1), \quad (4)$$

where x_1 and x_2 are the distances of a point inside the jellium from the inner and the outer boundaries of radii a and b , respectively. The functional form of $\delta\rho'$ is the same as in Eq. (2) except that the two “ $-x$ ” appearing there are to be replaced by “ $+x$.” Expression (4) agrees reasonably well with the calculated charge oscillations for the $C_{60}Cs(N)$ spheres, with the above values for η and β . The wavelength λ of the Friedel oscillations is of course specific to the metal (Cs), being independent of the presence of the C_{60} molecule, and the stable clusters occur for radii differing by approximately a third of λ .

In conclusion, we have experimentally produced the metal-coated buckyballs $C_{60}Cs(N)$ and have explained the mass abundance spectra in terms of the successive filling of the electronic shells within the jellium model.

M.S. and S.S. would like to thank the Research Board of the University of Missouri for partial financial assistance.

FIG. 4. Electronic density profile $\rho(r)$ for $C_{60}Cs(400)$ (a) and $Cs(400)$ (b). The uniform positive background density is indicated by $n(r)$. Dashed lines indicate the self-consistent potential seen by the electrons and the energy of the highest occupied electronic level. Strong Friedel oscillations in the electronic density profiles are visible in both cases.

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