COLLECTIVE ELECTRONIC EXCITATIONS ON C₆₀ MOLECULE

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Collective electronic excitations on the novel fullerenes play an important role in cohesion of C₆₀ crystal. We use the dispersive hydrodynamic model for the collective electronic excitations to study surface plasmons on a model of the C₆₀ molecule. This simple model consists of a spherical metallic jellium shell of finite thickness. We find four molecular surface plasmons of energy between 15 eV < ω < 32 eV for the shell thickness corresponding to our quantum chemical calculations. Our results are compared with the electron-energy-loss spectroscopy studies and with other complementary theoretical calculations.

THE C₆₀ FULLERENE molecular solid is a new allotropic form of carbon which exhibits remarkable properties [1, 2]. Sitting on the lattice sites of a cubic crystal, a cluster of 60 carbon atoms form a soccer ball-like structure with the symmetry of a truncated icosahedron. Each cluster has 60 vertices, 20 hexagonal faces, 12 pentagonal faces, 30 double and 60 single bonds. All carbon sites on the surface of the spherical fullerene are equivalent. The ball is hollow inside. On doping with the alkalines the fullerene solid exhibits superconductivity and a host of other interesting properties [3].

One can think of a C₆₀ molecule as being constructed by wrapping a graphite layer with 12 pentagonal defects. It is now known [4] that the nuclear cage of C₆₀ has a diameter of 7.1 Å with 2 bond length (6–6 ring) 1.4 Å and (6–5 ring) 1.46 Å. The distance of the nearest approach in the molecular solid is 3.1 Å. In comparison, the graphite has intralayer bond length 1.42 Å and interlayer bond length 3.35 Å. The curvature of the network of the C₆₀ mixes states of some *sp*³ character to the mostly *sp*² hybridization. Out of 4 valence electrons on each carbon atom, 3 electrons participate in the 90 σ bonds (180 electrons) along the edges of the truncated icosahedron. The remaining 60 electrons are in the π orbitals. The short bond (6–6 ring) has more charge compared to the other bond (6–5 ring). The bonding

in C₆₀ has a closer relationship to graphite than to diamond. Because of the large diameter of the C₆₀ sphere, the electron density is localized near the surface of the sphere with zero density in the central region. The nonresonant nature of the single and double bonds (unlike on graphite) makes the charge distribution along the bonds spatially inhomogeneous.

Figure 1 depicts the hollow nuclear cage of C₆₀ molecule and the 2D cross section of the total electronic density at the mid-section of the molecule, parallel to the pentagonal face. The electronic density was obtained from MNDO90 semi-empirical program [5]. MNDO Hamiltonian was used for geometry optimization and calculations of electronic density and molecular orbitals. The structure obtained this way is in very good agreement (within 0.1%) with the experimental results quoted above. It is also seen that the distribution of charge is nonuniform along (6–5 ring) and (6–6 ring) bonds. The spread of electron gas normal to the sphere surface, (the thickness of the electron gas), clearly seen on the Fig. 1, will serve as the only parameter of our model. We will return to this point shortly.

The electronic spectra of C₆₀, obtained from numerous experiments, is rich in structure. There are now empirical and *ab-initio* electronic structure calculations of the C₆₀ [6–8]. Although the *ab-initio*

Fig. 1. Two dimensional cross-section along the plane parallel to the pentagonal face of the C₆₀ molecule showing the total density of valence electrons. The thickness parameter α is estimated to be $0.4 \leq \alpha \leq 0.7$. The density was calculated using MNDO method [5]. The contour lines are plotted every $0.02 \text{ e}\text{\AA}^{-3}$. The highest electron density in the vicinity of carbon cores is $2.14 \text{ e}\text{\AA}^{-3}$.

local density theory underestimates the correlation effects, it is found that the valence electrons are delocalized on the surface of the sphere. The results conform to the photoemission and inverse photoemission, optical and UV absorption data reasonably well. The inhomogeneous distribution of electrons makes the C₆₀ molecule highly electronically polarizable. The high polarizability giving rise to dispersion forces is responsible for the dominant part of the cohesion in the solid phase [6, 9, 10].

It is our purpose in the present work to understand how the collective excitations of the itinerant valence electrons on C₆₀ molecule give rise to the plasmon peak losses observed in electron-energy-loss spectroscopies (EELS) and in photoionization studies.

Without much apology we adopt the hydrodynamic model [11–17], which proved to be capable of describing plasmon modes on minute metallic particles [18, 19]. The electron gas is modelled by a spherical jellium shell of finite thickness. Jellium is defined here as a uniform positive charge density that confines electrons within spherical shell volume. The discussion of the applicability of the simple hydrodynamic model in *non-dispersive* limit of an infinitely thin shell can be found in Ref. [13].

In Ref. [19] we discussed the relative merits and shortcomings of the hydrodynamic model compared with the time-dependent local density approximation. Here we use the *dispersive* hydrodynamic description.

The linearized hydrodynamic equation of motion for the time dependent first order electron density fluctuation n_1 is written as

$$[\omega^2 - \omega_p^2 + \beta^2 \nabla^2] n_1(\mathbf{r}) = 0 \quad (1)$$

where $\omega_p^2 = 4\pi e^2 n_0 / m$ (in dimensional units), n_0 is the ground state electron density of valence electrons, ω_p is the plasmon frequency and β is the dispersion parameter, which at high frequencies is $\sqrt{\frac{2}{3}} v_F$. Equation (1) was solved in the spherical geometry. The details of derivation, expressions for the electrostatic potentials induced by plasmons and the density fluctuations, as well as the discussion of implications of this model on the number and type of solutions will be presented elsewhere [20].

The usual boundary conditions of vanishing normal current at inner, R_1 , and outer, R_2 , surface lead to the general dispersion relation for the shell of finite thickness:

$$\begin{aligned} & \left\{ \left[\frac{x^2}{l} - \frac{1}{2l+1} \right] m_{l+1}(\alpha xy) + \frac{\alpha^{l-1}}{2l+1} m_{l+1}(xy) + \right. \\ & \quad \left. [x^2 - 1] \frac{m_l(\alpha xy)}{\alpha xy} + \frac{\alpha^{l-1} m_l(xy)}{xy} \right\} \\ & \times \left\{ \left[x^2 \frac{2l+1}{l+1} - 1 \right] g_{l+1}(xy) - \left[x^2 \frac{l(2l+1)}{l+1} \right] \frac{g_l(xy)}{xy} + \right. \\ & \quad \left. \alpha^{l+2} g_{l+1}(\alpha xy) \right\} \\ & - \left\{ \left[x^2 \frac{2l+1}{l+1} - 1 \right] m_{l+1}(xy) + \left[x^2 \frac{l(2l+1)}{l+1} \right] \frac{m_l(xy)}{xy} + \right. \\ & \quad \left. \alpha^{l+2} m_{l+1}(\alpha xy) \right\} \\ & \times \left\{ \left[\frac{x^2}{l} - \frac{1}{2l+1} \right] g_{l+1}(\alpha xy) + \frac{\alpha^{l-1}}{2l+1} g_{l+1}(xy) - \right. \\ & \quad \left. [x^2 - 1] \frac{g_l(\alpha xy)}{\alpha xy} - \frac{\alpha^{l-1} g_l(xy)}{xy} \right\} = 0 \quad (2) \end{aligned}$$

where

$$\begin{aligned} x^2 &= \frac{\beta^2 \kappa^2}{\omega_p^2} = 1 - \frac{\omega_l^2}{\omega_p^2}, \quad xy = \kappa R_2, \quad \kappa^2 = \frac{\omega_p^2 - \omega^2}{\beta^2}, \\ \alpha &= \frac{R_1}{R_2} \quad \text{and} \quad y = \frac{R_2}{\beta} \omega_p. \end{aligned}$$

Here, m_l is the modified spherical Bessel function of the first kind and g_l the modified spherical Bessel function of the third kind [21].

It can be shown [20] that the above dispersion relation can be reduced to a dispersion relation for a sphere [18, 19] or a spherical void. The only parameter of the model, for the fixed value of valence electrons (both π and σ) of 240, and for the diameter of nuclear cage of C₆₀ molecule being $2R_0 = 7.1$ Å, is the $\alpha = R_1/R_2$. The external radius is expressed in terms of the radius of the nuclear cage as $R_2 = R_0[2/(1 + \alpha)]$. The bulk plasmon energy according to the Drude formula is $\omega_p^2 = 27.2 [720g_0/R_2^3(1 - \alpha^3)]$ eV. The radius of a sphere available for one electron, r_s , is given as $r_s = R_2[(1 - \alpha^3)/240]^{1/3}$ Å.

The dispersion relation (2) was solved numerically. The calculated dispersion curves for surface plasmons ω vs α are presented on Fig. 2. Precisely four surface plasmons can be supported on a shell of thickness $\alpha \leq 0.7$. The formal solution of equation (2) in the limit of a very thin shell gives up to 12 surface plasmons, with the plasmons of low "azimuthal number" $l = 1, 2$ and 3 disappearing for $\alpha > 0.9$. This obviously corresponds to unphysical situation of a system of very small volume and high electron density.

It is now desirable to have an estimate of the thickness of the electron gas shell that supports surface plasmons. There are two ways of estimating this quantity. The first is to consider the diffraction data on the crystalline structure of C₆₀. The lattice constant of the fcc lattice is 14.2 Å. This gives the closest approach of 3.1 Å. Assuming there is no

overlap of electronic shells, the outer radius is $R_2 = 5.1$ and $\alpha = 0.39$ in the solid. By inspection of contour map of the valence electron density of fcc C₆₀ crystal obtained on the basis of density functional theory in local density approximation [6], we get $\alpha \sim 0.33$. The second estimate is from our MNDO quantum chemistry calculations. From Fig. 1, and similar results for cross-section along different planes we see that the parameter $0.4 \leq \alpha \leq 0.7$. The outer contour of constant electronic density was at 0.02 eÅ^{-3} for the lower limit and up to 0.2 eÅ^{-3} for the upper limit of α . The separation between the contour lines was 0.02 eÅ^{-3} and the maximum valence density in the vicinity of carbon cores was 2.14 eÅ^{-3} .

Finally, we compare the eigenenergies of the four plasmons with the electron-energy-loss spectroscopy data. Recently, EELS study [22–31] has been pursued actively. The sample is usually a solid C₆₀. EELS probes both single and collective electronic excitations. It shows highly structured excitations of collective nature related to the high degree of molecular symmetry. Even on a free molecule the delocalized valence electrons exhibit collective oscillations at high frequency.

In a number of papers [22–31] the high energy peak (in solids) has been shown to occur in the range of 25–30 eV. The detailed spectra was presented by Kuzuo *et al.* [28] and Sohmen *et al.* [26]. In both cases the spectra exhibits broad peak with maximum between 25 and 27 eV. There are less pronounced shoulders at about 15, 18 and 20 eV. Those features could perhaps be attributed to surface plasmons, which in our model for $\alpha = 0.44$ appear at 15.6, 20.4, 23.7 and 26.5 eV. This is to a certain extent speculative, Kuzuo *et al.* claim that those features originate from interband transitions. But it is not yet clear if these could be signals from $l = 1, 2, 3$ and 4 surface plasmons. Saito *et al.* [27] observed the double plasmon loss at 52 eV but the peak is broadly smeared and it is difficult to see if 30, 36, 40 eV features due to harmonic plasmon effects are present. Sohmen *et al.* [26] removed contributions due to multiple scattering from their results. It is interesting to note that the outer radius corresponding to $\alpha = 0.44$ is $R_2 = 4.93$ Å. The volume of the shell is then 440 Å³ and $r_s = 0.77$. The Drude "bulk" plasmon is then $\omega_p = 26.8$ eV. This is in contrast with other estimates [26], where the volume of the valence electron was estimated on the basis of diffraction data to be 710 Å³. If that was the volume of the valence electron gas, the Drude plasmon would have energy $\omega_p = 21.2$ eV and the thickness of the shell would have to be parametrized by $\alpha = 0.26$.

Fig. 2. The dispersion curves ω_l vs α for the four surface plasmons obtained from equation (2). The values of the thickness parameter α correspond to the estimates based on Fig. 1 and other estimates discussed in the text.

The giant plasmon resonance have been reported in the photoionization spectra around ~ 20 eV [32] for which microscopic calculations based on the linear-response theory have been done [33, 34]. Lambin *et al.* [10] have performed calculations of a spherical dielectric shell of finite thickness. They have shown that multipolar surface plasmons arise in the energy range 20–30 eV. However, their model had an adjustable resonance energy parameter fixed at the value which would reproduce the strong VUV absorbance of C₆₀ around 20 eV. An empirical infinitely thin spherical shell model has been discussed by Barton and Eberlein [13] within the framework of two fluid hydrodynamic description. There are few important differences in our treatment and that of Ref. [13]. Barton and Eberlein neglected the hydrostatic pressure, this is equivalent to the *nondispersive* model. The dynamics of π and σ electrons was separated, hence the density of electron gas was lower, and consequently the Drude plasmon energy was lower as well. Our present model is similar in spirit to that of Lambin *et al.* They solved the problem of collective modes through the dielectric function structure. High energy peak around 28 eV was interpreted as the molecular property [10] in contrast to that due to solid state effects [23, 31].

Our model can be treated as a guiding tool in studies of collective electronic excitations on C₆₀ molecule. There is no complication of the single particle excitations, which makes the experimental structure so rich. The only parameter is the thickness of the electron gas shell. The model gives exactly four surface plasmons on the shell (coupled on both inner and outer surface), this is in good agreement with Barton and Eberlein estimates on the basis of dimensional analysis. In Ref. [13] they quoted $L < 6$, but the more conservative value of $L = 3$ was emphasized. Our model does not account for the 6.0–6.5 eV plasmon found in EELS experiments in both solid [22–30] and gas phase [31]. It could be related to the tangential character of this mode [13, 30] which is not taken into account by the type of boundary conditions used.

The final word in the debate on the molecular or crystal solid nature of various plasmon modes, as well as complete deconvolution of single particle and collective structure will have to await even more detailed and focussed studies of electron-energy-loss spectroscopy, photoionization, photoemission and others.

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