

Vacuum-ultraviolet plasma Frenkel excitons: elementary excitations of polymerized fullerene

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The high-frequency excitations of the molecular insulator C_{60} are investigated theoretically. The model of a quantum well rolled into a sphere is used to calculate the dipole (multipole in the general case) modes of an individual C_{60} cluster. If the spectrum and oscillator strengths of the collective modes of an individual cluster are known, the microscopic continuum approach can be used to calculate the spectrum of delocalized excitations in a cluster crystal. Then the ordinary dielectric constant formalism permits calculation of the optical characteristics of the material in the vacuum ultraviolet region studied. © 1998 American Institute of Physics. [S1063-7834(98)04505-5]

The molecules in a C_{60} crystal are joined by weak van der Waals forces. As a result, solid-state fullerene is readily soluble in many typical organic solvents. However, it was shown in Ref. 1 that a fullerene surface undergoes a phototransformation during prolonged illumination by incoherent UV radiation or under the action of a high-power low-frequency coherent source. After such treatment, a surface region with a thickness amounting to several C_{60} monolayers becomes practically insoluble. Such a phototransformation has been termed polymerization, in analogy to the process for unsaturated hydrocarbons, whose electronic structure exhibits some similarity to that of fullerene. Apart from photopolymerization, the transformation of fullerene into an insoluble phase at high pressures and temperatures has been reported.² X-ray structural investigations of the polymer phase have shown that the formation of linear or two-dimensional structures (apparently chains) of C_{60} clusters bonded to one another and of a united 2D network is typical. The present work examines the elementary excitations in one- and two-dimensional systems of fullerene clusters.

1. HIGH-FREQUENCY DIPOLE MODES OF A C_{60} CLUSTER: SURFACE-PLASMON APPROXIMATION

The foundation for the theory of elementary excitations in molecular insulators was laid in Ref. 3. Application of the ideas advanced by Frenkel to the solution of concrete problems involving calculations of the optical characteristics of insulating crystals has provided explanations for numerous experimental findings based on the model of an exciton of small radius, or a Frenkel exciton. In the case of crystalline C_{60} we are clearly dealing with a typical molecular insulator, whose dipole excitations are localized and migrate through the crystal as a result of dipole-dipole interactions between neighboring clusters.

Despite the fact that C_{60} is similar as a whole to the previously known molecular insulators, the theoretical description of the cluster and the cluster medium is far more

difficult. Nevertheless, the high-frequency excitations of the polyatomic electronic structure of fullerene is practically insensitive to the details of its spectrum.

Since the π -electronic system of fullerene is readily polarizable and the total number of valence electrons is high, it turns out that both the analytical quantum-mechanical model of a quantum well rolled into a sphere^{4,5} and the simple phenomenological hydrodynamic model of a charged liquid on the surface of a sphere^{6,7} can be applied successfully. The high-frequency multipole polarizability of a cluster can be determined from the continuity equation and the equation of motion for the oscillations of a charged liquid on the spherical surface of a cluster:

$$\begin{cases} \frac{\partial j}{\partial t} = -\frac{ne^2}{m} \nabla \varphi \\ \frac{\partial \sigma}{\partial t} + \nabla j = 0 \end{cases}, \quad (1)$$

where $n = 240/4\pi R^2$ is the density of valence electrons on the surface of a spherical cluster of radius R , m and e are the mass and charge of an electron, φ is the effective electric potential, which, by necessity, includes the potential of the charge induced on the cluster itself, σ is the density fluctuation, j is the current density associated with it, and ∇ is the gradient over the surface of the sphere. The solutions of these equations are naturally sought using an expansion in the spherical harmonics $P_L(r)Y_{L,M}(\Omega)$, i.e., a multipole expansion.⁸ Then the discontinuity of the field on the cluster surface is related to the amplitude of the multipole fluctuations $\sigma_{L,M}$ according to the Ostrogradsky–Gauss theorem: $(2L+1)\varphi_{L,M}/R = 2\pi\sigma_{L,M}$. Solving these equations together, we obtain the multipole dynamic response function of an individual cluster in the form

$$\alpha_L(\omega) \equiv \frac{-\sigma_{L,M}}{\varphi_{L,M}^{xt}} = \frac{R^3}{(1 - \omega^2/\omega_L^2)},$$

where $\varphi_{L,M}^{xt}$ is the spherical harmonic of the external electric potential. When $L = 1$, we are dealing with a dipole-moment

excitation in the cluster. The lack of a dependence of α on M is a consequence of the spherical symmetry of the model, and, although C_{60} actually has icosahedral, rather than spherical, symmetry, the dipole polarizability of the cluster remains isotropic. The polarizability has a resonance at the frequency of the collective mode excited in the C_{60} cluster by the external multipole potential:

$$\omega_L = \omega_p \sqrt{\frac{L(L+1)}{2L+1}} = \sqrt{\frac{4\pi n e^2}{m^* R}} \sqrt{\frac{L(L+1)}{2L+1}}. \quad (2)$$

Here ω_p is the characteristic plasma frequency of fullerene. It is the excitation frequency of a surface plasmon in a metallic sphere of radius R with a surface charge density corresponding to the valence electron density of fullerene. We see that collective modes^{4,5,7} in the vacuum-ultraviolet region, for example, the dipole mode ($\omega_1 \approx 25$ eV), are excited in C_{60} in a range of frequencies much greater than the frequencies of all the ‘‘single-electron’’ modes.

2. EXCITATIONS OF A ONE-DIMENSIONAL CRYSTAL: THE COULOMB PROBLEM

In this section we examine the spectrum of dipole modes of a chain of fullerene clusters neglecting retardation. The Coulomb interaction of the multipole plasma modes of two clusters was previously studied in detail in Refs. 9 and 10. In particular, it was shown there, for a triply degenerate dipole mode of an individual C_{60} cluster, that it is sufficient to take into account the interaction with the dipole mode of the neighboring cluster. Such an axisymmetric perturbation leads to splitting of the state with $L=1$ into longitudinally and transversely polarized modes. In a chain of fullerene molecules the solutions must be sought in the form of plane waves of the same polarizations. Therefore, an anisotropic (axisymmetric) system of C_{60} clusters has transverse modes, i.e., one-dimensional Frenkel excitons, which are formed on the basis of elementary plasma excitations of an individual fullerene cluster. We shall call such excitations ‘‘plasma Frenkel excitons.’’

The Fourier transformation

$$\sigma_M(k) = \sum_{n=-N}^N e^{-iknH} \sigma_M(x-nH),$$

where $n = -N, \dots, 0, \dots, N$ is the number of the cluster in a chain of length $2N$, k is the wave number of the excitation, and H is the distance between clusters, diagonalizes the problem, and the spectrum takes the form

$$\omega(k) \approx \omega_1 \sqrt{1 + \frac{1+3(-1)^M}{2} \left(\frac{R}{H}\right)^3 \frac{2 \sum_{n=1}^N \frac{\cos(kHn)}{n^3}}{2}}. \quad (3)$$

The spectrum is doubly degenerate for $M = \pm 1$. There is natural splitting between the $M = \pm 1$ and $M = 0$ states, which describe transversely and longitudinally polarized excitations, respectively. For small $kH \ll 1$ the dispersion of the modes is linear with respect to the wave vector:

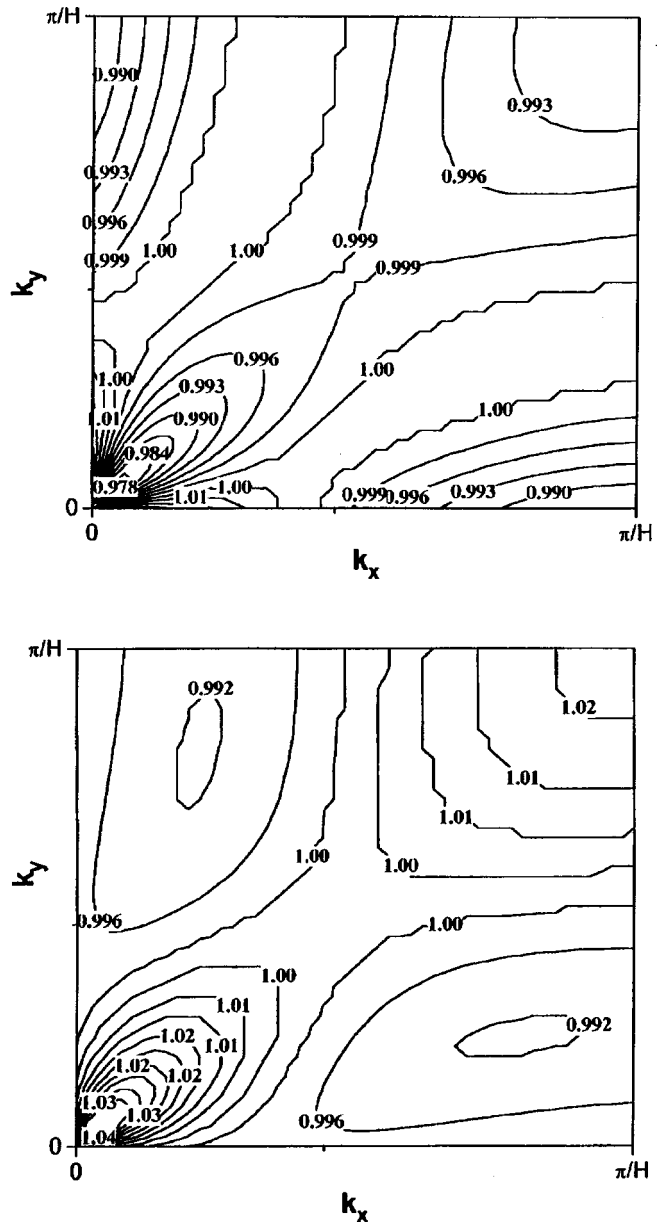


FIG. 1. Spectra of longitudinal (\parallel , upper spectrum) and transverse (\perp , lower spectrum) two-dimensional plasma Frenkel excitons obtained numerically with consideration of a concrete square lattice of polymerized C_{60} . A quarter of the Brillouin zone is shown: dependence of the normalized frequency $\omega(f)/\omega_1$ of the mode on the wave vectors $k_x H$ and $k_y H$.

$$\omega(k) \approx \omega_1 \left(1 + \frac{1+3(-1)^M}{4} \left(\frac{R}{H}\right)^3 \times \left\{ 2\zeta(3) - (kH)^2 \left[\ln \frac{1}{kH} + \frac{3}{2} \right] \right\} \right),$$

where $\zeta(x)$ is a zeta function,¹¹ which defines the lattice sum for the ground, totally symmetric state of the plasma Frenkel exciton with $k=0$ [$\zeta(3) \approx 1.202$, compare the results in Ref. 12]. It follows from (3) that the longitudinal–transverse splitting is specified by the ratio $(R/H)^3$ and amounts to 3.9 eV for $k=0$ and -3.1 eV for $k = \pi/H$ when $H \approx 10 \text{ \AA}$.¹⁾

3. TWO-DIMENSIONAL PLASMA FRENKEL EXCITONS

The theory of two-dimensional Frenkel excitons was described in detail in Ref. 13, where there are also references to experimental results in this area. Below we present the results of a microscopic calculation of the spectrum of Coulomb 2D-plasma Frenkel excitons in a monomolecular fullerene film, including results obtained analytically in the continuum approximation.

We choose the directions of the orthogonal polarizations of the eigenmodes of the two-dimensional problem in a natural manner: σ_z is a transverse mode polarized along a normal to the film surface, σ_\perp is a second transverse mode (its polarization vector lies in the plane of the film and is perpendicular to the excitation wave vector k), and σ_\parallel is a longitudinal mode with polarization along the excitation wave vector. In the continuum approximation, the two-dimensional lattice sum can be replaced by an integral, which is taken in an expansion to the second order in the small parameter of the problem $(R/H)^3 \ll 1/3$ in the approximation of small wave numbers. Neglecting retardation, the frequencies of the Coulomb 2D plasma Frenkel excitons have the form

$$\begin{cases} \omega_\parallel = \omega_1 \sqrt{1 + \frac{3}{2} \left(\frac{R}{H}\right)^3 \left(\frac{3}{2} - 2kH + \frac{5(kH)^2}{16} + o((kH)^4)\right)}, \\ \omega_z = \omega_1 \sqrt{1 - \frac{3}{2} \left(\frac{R}{H}\right)^3 \left(1 - kH + \frac{(kH)^2}{4} + o((kH)^4)\right)}, \\ \omega_\perp = \omega_1 \sqrt{1 - \frac{3}{2} \left(\frac{R}{H}\right)^3 \left(\frac{1}{2} - kH - \frac{(kH)^2}{16} + o((kH)^4)\right)}. \end{cases} \quad (4)$$

All three branches are clearly linear with respect to the wave number at small kH .

The splitting between the longitudinal and transverse modes at the Γ point is

$$\begin{aligned} \Delta\omega_{LT} &= \omega_1 \left(\sqrt{1 + \frac{9}{4} \left(\frac{R}{H}\right)^3} - \sqrt{1 - \frac{3}{4} \left(\frac{R}{H}\right)^3} \right) \\ &\approx \omega_1 \frac{3}{2} \left(\frac{R}{H}\right)^3 \approx 1.6 \text{ eV}. \end{aligned} \quad (5)$$

We also present the spectra of longitudinal and transverse modes obtained by numerical summation for a square lattice of polymerized C_{60} (see Fig. 1).

Thus, the spectra of longitudinal and transverse vacuum-ultraviolet Coulomb excitations in one- and two-dimensional periodic systems of fullerene clusters, which were calculated analytically in the continuum approximation for wave numbers that are small compared with the reciprocal lattice period and numerically in the entire Brillouin zone, have been presented in this paper. The values of the translational-transverse splitting of the elementary excitations near the Γ point, as well as on the Brillouin-zone edge in the one-dimensional case, have been determined.

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¹The distance between nearest neighbors in crystalline C_{60} .

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