Plasmon-Frenkel-exciton in a clustered solid

Slava V. Rotkin, Robert A. Suris

Ioffe Physico-Technical Institute, 26 Politekhnicheskaya Street, 194021 St. Petersburg, Russia

Abstract

The standard theory of the Frenkel exciton (a small radius exciton) is applied to a fullerene 2D solid. It is the dipole collective electron excitation of a single cluster which forms the delocalized plasmon-Frenkel-exciton (PFE) in a crystal. The PFE retarded interaction is taken into account. We present transverse PFE-polariton dispersion curves along with the Coulomb problem solution for longitudinal excitation in the 2D plane. © 1998 Elsevier Science B.V.

PACS: 36.20−r; 36.20.Kd; 36.40.+d

1. Introduction

A large number of different stable carbon nanoclusters bearing the common name of "fullerenes" have attracted attention during the last decade [1]. The most stable cluster C_{60} with a nearly spherical symmetry will be considered below. This cluster shows an interesting physics due to its large size, high symmetry and large number of highly mobile electrons. The high frequency single cluster excitation of the whole valence electron density in the fullerene is usually called a "plasmon". For the hollow fullerenes it was shown that this plasmon is a surface one [4,5]. The plasmon peaks were observed in electron energy loss spectra. A review of the experiment and theory can be found in Refs. [1–6].

A very attractive spherical-shell-quantum-well approach gives a quantum mechanical description of the single cluster plasmon [7]. However, the high polarizability of the cluster leads to the coincidence of the quantum mechanical result and the simple classical calculation [8] if one includes the interaction between electrons accurately, at least in the RPA. The spherical plasmon has a definite angular momentum, hence its electric field is the field of a definite charge multipole. Of course, this simplification fails in any lower-symmetry case, for example in the crystal. This means that all the spherical single cluster plasmons must interact. We will discuss the Coulomb interaction in C_{60}, using the result of Ref. [9]. Only the dipole plasmon will be of interest to us below, therefore we will consider the dipole plasmon frequency splitting due to the interaction and drop the mixing with other excitations having a higher multipole index. A reason to neglect this mixing was given in Ref. [9].

Despite being localized on the surface of the clusters, the single cluster plasmons in the solid are mixed via their electric field. This results in a new crystal excitation – the plasmon-Frenkel-exciton (PFE). We consider

here the retarded field for the special problem of the polariton. The dipole–dipole interaction between the plasmons in the solid determines the PFE band dispersion. As usual this calculation faces the lattice sum problem, hence here we will consider analytic asymptotes only. The method is well known to give the dielectric function ϵ of the solid [10]. Here we obtained ϵ in the approximation of a single oscillator strength. It works since for the clustered solid all other dipole oscillator frequencies are split off and lie far below our plasmon frequency.

The characteristic wavelength is about 400 Å, which proves the continuous dielectric function harnessing. The PFE band structure and the dielectric function calculation are very routine, except in the excitation frequency region. Since in our case the Frenkel exciton is constructed on the basis of the plasmon, the corresponding energy lies around 25–28 eV. The optical response of the cluster system should be in the X-ray or vacuum ultraviolet (VUV) region.

2. Frenkel exciton in the plane

The Coulomb interaction between fullerene clusters belonging to the dimer, considered in Ref. [9], results in new modes with slightly shifted and split-off frequencies. These dipole plasma modes have different (odd and even) symmetries. What will happen in the case of a 2D lattice of interacting clusters? According to the simplest group consideration, the plasmons in these systems have a quasimomentum (or wave vector) since the Hamiltonian is invariant to translation. The allowed plasmon frequencies depending on the plasmon wave vector form a band with a width determined by the characteristic interaction energy which is much lower than the plasma frequency. So we obtained a new 2D crystal excitation (1D case is considered in Ref. [11]) exhibiting a slight dispersion owing to Coulomb intercluster interaction. One writes the expression for the coupled modes as

$$\sigma_z(x, y) = -\chi \left(\varphi_z(x, y) + \varphi_z^{\text{latt}}(x, y) \right), \qquad \sigma_x(x, y) = -\chi \left(\varphi_x(x, y) + \varphi_x^{\text{latt}}(x, y) \right),$$
$$\sigma_y(x, y) = -\chi \left(\varphi_y(x, y) + \varphi_y^{\text{latt}}(x, y) \right), \tag{1}$$

where φ_M^{latt} are components of the lattice sum of the dipole potentials φ_M; here $M = x, y, z$ denotes the polarization. It is very natural to choose σ_z as normal variables with polarization along the z-axis perpendicular to the plane; $\sigma_{||}$ with polarization along $\boldsymbol{k}$, the wavevector of a collective excitation which lies in the plane; and $\sigma_\perp$ with polarization orthogonal to the first two.

Here χ is the high frequency single molecule response function given by [8]

$$\frac{4\pi R}{3} \chi(\omega) \simeq -\omega_1^2/\omega^2, \tag{2}$$

where

$$\omega_1 = \omega_P \sqrt{\tfrac{2}{3}} = \sqrt{\tfrac{2}{3}} \sqrt{Ne^2/m^* R^3} \tag{3}$$

is the characteristic frequency of the dipole component of the response and the single cluster surface plasmon frequency. R is the C_{60} radius, $N = 240$ is the valence electron number, m^* and e are the electron mass and charge.

One needs to calculate the lattice sum of the fields from all the interacting dipoles. The problem is the same as for the Frenkel exciton [12] when the dipole–dipole lattice sum arises. The motion equation system reads

$$\left(\frac{\omega^2}{\omega_1^2} - 1 \right) \varphi_z(\boldsymbol{A}) + \frac{3R}{4\pi} \sum_B \left(\frac{R}{r_{AB}} \right)^3 \varphi_z(\boldsymbol{B}) = 0,$$

$$\left(\frac{\omega^2}{\omega_1^2} - 1\right)\varphi_{||}(\boldsymbol{A}) - \frac{3R}{4\pi}\sum_B\left(\frac{R}{r_{AB}}\right)^3\left(\frac{3x_{||}^2}{r_{AB}^2}\varphi_{||}(\boldsymbol{B}) - \varphi_{||}(\boldsymbol{B}) + \frac{3x_\perp x_{||}}{r_{AB}^2}\varphi_\perp(\boldsymbol{B})\right) = 0,$$

$$\left(\frac{\omega^2}{\omega_1^2} - 1\right)\varphi_\perp(\boldsymbol{A}) - \frac{3R}{4\pi}\sum_B\left(\frac{R}{r_{AB}}\right)^3\left(\frac{3x_\perp^2}{r_{AB}^2}\varphi_\perp(\boldsymbol{B}) - \varphi_\perp(\boldsymbol{B}) + \frac{3x_\perp x_{||}}{r_{AB}^2}\varphi_{||}(\boldsymbol{B})\right) = 0. \tag{4}$$

The calculation can be carried out in the continuum approximation. After some cumbersome integration one gets the dispersion of the Frenkel excitons:

$$\omega_{||} = \omega_1\sqrt{1 + \tfrac{3}{2}(R/H)^3[\tfrac{3}{2} - 2|k|H + \tfrac{5}{16}(kH)^2 + \mathrm{o}((kH)^4)]},$$

$$\omega_z = \omega_1\sqrt{1 - \tfrac{3}{2}(R/H)^3[1 - |k|H + \tfrac{1}{4}(kH)^2 + \mathrm{o}((kH)^4)]},$$

$$\omega_\perp = \omega_1\sqrt{1 - \tfrac{3}{2}(R/H)^3[\tfrac{1}{2} - |k|H - \tfrac{1}{16}(kH)^2 + \mathrm{o}((kH)^4)]}, \tag{5}$$

where the result is written up to the second power of the parameter kH at small wave number k. Here $H \simeq 10$ Å is the nearest neighbor distance. Let us check that in the region of interest the wavenumbers are small. The characteristic wavenumber $k_0 = \omega_1/c = \alpha\sqrt{Na_B}/R\sqrt{R}$ is determined by the point of intersection of the light line $\boldsymbol{ck}$ and the VUV Frenkel exciton frequency $\omega_1 \simeq 28$ eV, where $\alpha = 1/137$ is the fine structure constant, and $a_B = \hbar^2/me^2$ is the effective Bohr radius of the electron. The characteristic value of k_0 corresponds to a very long wavelength ~ 450 Å compared with R and H.

We emphasize that the dispersion of the VUV-plasmon-Frenkel-exciton is linear in its wave number in the interesting region of small k.

3. Polariton

It is well known that the standard Frenkel exciton couples with light. We calculated this retardation effect, following Ref. [10]. Since the longitudinal excitation does not interact with the transverse field and the scalar and longitudinal Coulomb interaction are included in Eq. (5) (except the transverse retarding interaction), its first branch will not change.

The eigenfrequencies of new exciton polaritons look especially simple for the case of a very small wave number $k \ll k_0$. The frequencies of the z and transverse branches are

$$\omega_z \simeq \omega_1\sqrt{1 - (R/H)^3\tfrac{3}{2}(1 - kH) + 2\pi(P^2/\omega_1 H^3)kH},$$

$$\omega_\perp \simeq \omega_1\sqrt{1 - (R/H)^3\tfrac{3}{2}(\tfrac{1}{2} - kH) + 2\pi(P^2/\omega_1 H^3)kH}. \tag{6}$$

Here $P^2 \sim e^2 R^2$ is the dipole matrix element of the PFE. Here the first root corresponds to the PFE normal to the plane, and the second corresponds to the exciton–polariton with transverse polarization. The standard experimental parameters of the polariton effect in semiconductors are the splitting between the transverse and longitudinal branches due to the retarding Coulomb interaction, $\Delta\omega_{LT}$, and the change of the phase velocity of the lower straight-line photon-like part of the PFE spectrum. The first parameter can be extracted from independent transverse and longitudinal probing of the system. The second shows that the light velocity is slowed via interaction with the plasmons. The theoretical estimation of these parameters reads

$$\left(\frac{\partial\omega}{c\partial k}\right)^{-1}_{k=0} \simeq 1 + (2\pi\alpha + \tfrac{3}{4}k_0 R)(R/H)^2 \simeq 1.044,$$
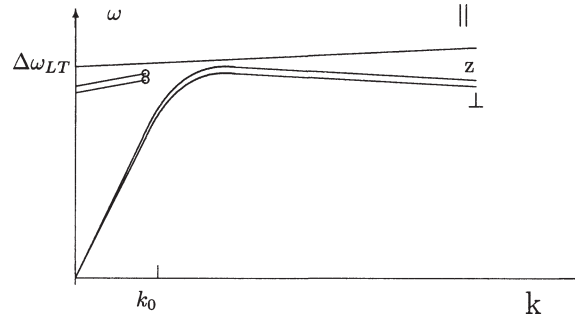
Fig. 1. Long wavelength part of the plasmon-Frenkel-exciton polariton dispersion for the fullerene plane. The $\perp$ and z-polarized retarded polariton exciton spectrum has two branches. The photon-like straight line of the lower branch lies below the ck, hence its light velocity is less than c. For small k the dispersion of the unperturbed Coulomb Frenkel exciton is weak and linear in k. This is clearly seen for the longitudinal branch and two upper branches. Their frequencies are not changed significantly by the retarded interaction. The circles denote the disappearance of the transverse excitation due to radiative decay.

$$\Delta\omega_{LT} = \omega_1 \left[\sqrt{1 + \tfrac{9}{4}(R/H)^3} - \sqrt{1 - \tfrac{3}{4}(R/H)^3} \right] \simeq \omega_1 \tfrac{3}{2} \left(R/H \right)^3 \simeq 1.6 \text{ eV}. \tag{7}$$

The spectrum of transverse polarized retarded polariton excitons is presented in Fig. 1 in comparison with the unchanged longitudinal branch. It is seen that at small k the dispersions of the Coulomb excitons are weak and linear in k. Each transverse polariton has two branches, its straight-line photon-like velocity being less than c for the lower branch.

4. Summary and discussion

We obtained a dispersion law for collective electron excitations in a 2D crystal of fullerene clusters. Let us consider the most striking points.

Usually, in solids the induced field related to the collective excitation is completely longitudinal, that is why the solid state plasmons are inactive in optical experiments. Unlike the standard plasmons, the "plasmon" in the fullerene solid is more an exciton of small radius (i.e. Frenkel exciton) than a wave of excess electron density.

We distinguish the surface plasmon on the single cluster and the Frenkel excitation in the lattice of the fullerene clusters (1D, 2D or 3D crystal). The excitation of the single cluster has a definite dipole momentum and is localized in the volume of the cluster. It looks like a simple dipole excitation of the fullerene super-atom.

Similarly to the dipolar insulator, the single cluster plasmon mixes with all the neighbors. The resulting wave of the dipole momentum in the cluster medium is a new delocalized excitation which has a VUV frequency owing to the large number of electrons within a single cluster participating in the charge oscillation. This excitation is the VUV plasmon-Frenkel-exciton.

To conclude, we present a microscopical model predicting the VUV polariton phenomenon in the polymerized fullerene plane. The frequency dispersion laws for the 2D excitations with transverse and longitudinal polarization were derived in the continuum approximation for the non-retarded part of the Coulomb interaction. Considering the retardation effect the polariton splitting $\Delta\omega_{LT} \simeq 1.6$ eV was evaluated along with the effective PFE phase velocity, to be compared with future experiments in VUV optics.

Acknowledgement

References

[1] S.V. Kozyrev, V.V. Rotkin, Sov. Semiconductors 27 (1993) 777.
[2] G.F. Bertsch, A. Bulgac, D. Tomanek, Y. Wang, Phys. Rev. Lett. 67 (1991) 2045.
[3] G. Barton, C. Eberlein, J. Chem. Phys. 95 (1991) 1512.
[4] Ph. Lambin, A.A. Lucas, J.-P. Vigneron, Phys. Rev. B 46 (1992) 1794;
    A.A. Lucas, G. Gensterblum, J.J. Pireaux, P.A. Thiry, R. Caudano, J.-P. Vigneron, Ph. Lambin, W. Kratschmer, Phys. Rev. B 45 (1992) 13 694.
[5] M.T. Michalewicz, M.P. Das, Sol. State Comm. 84 (1992) 1121.
[6] A. Bulgac, N. Ju, Phys. Rev. B 46 (1992) 4297.
[7] V.V. Rotkin, R.A. Suris, Mol. Mat. 5 (1994) 87.
[8] V.V. Rotkin, R.A. Suris, Fiz. Tverd. Tela (Sov. Phys. Sol. State) 36 (1994) 1899.
[9] V.V. Rotkin, R.A. Suris, Sol. State Comm. 97 (1995) 183.
[10] V.M. Agranovich, Exciton Theory (Nauka, Moscow, 1968).
[11] V.V. Rotkin, R.A. Suris, unpublished.
[12] Ya.I. Frenkel, Phys. Rev. 37 (1931) 17; 1276.