Collective Plasmon Excitations in C_{60} Clusters

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The electromagnetic response function of a C_{60} cluster is calculated using linear-response theory. We find that the valence electrons are quite delocalized and show collective excitations. In the low-energy part of the excitation spectrum, the lowest allowed transition at $\hbar\omega \approx 3$ eV is strongly screened, and the other transitions below 6 eV are moderately screened, in agreement with experiment. We also predict a giant collective resonance at an unusually high energy of ≈ 20 eV.

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The long-standing interest in carbon clusters [1] has greatly increased following the recent successful synthesis [2] of bulk quantities of C_{60} clusters. The uncommon hollow "buckyball" (or "fullerene") structure, which has been originally postulated for this cluster [3], promises unusual properties for C_{60}. So far, the interest in this novel form of carbon has been focused primarily on structural properties, with less experimental effort devoted to electronic excitations. Stimulated by a recent measurement of the photon absorption strength in C_{60} clusters [4], we have calculated the electromagnetic response of this remarkable system. As we discuss in the following, we can calculate the spectrum and obtain quantitative agreement with the experiment in the observed region. Moreover, we predict a giant Mie-type resonance at large excitation energies where no data are available so far.

We use linear response theory, which is most appropriate for large systems with mobile electrons where screening can be significant. Within the one-electron theory, for which we shall use mostly a tight-binding model, the dipole operator has two contributions, from the charge on a site and from the dipole moment on a site. We write it as

$$D_z^{\star} = D_z^{(1)} + D_z^{(2)} = \sum_{a,i} a_{a,i}^{\dagger} a_{a,i} z(i) + d \sum_i (a_{s,i}^{\dagger} a_{p_z,i} + a_{p_z,i}^{\dagger} a_{s,i}) , \quad (1)$$

where $z(i)$ is the z coordinate of the ith carbon atom and d is the $s \rightarrow p_z$ dipole matrix element on a carbon atom.

Starting from an independent-particle picture, we define the polarization propagator for the free dipole response by [5]

$$\Pi_{D_z}^{(0)}(\omega) = \sum_{p,h} |\langle p|D_z|h\rangle|^2 \frac{2(\epsilon_p - e_h)}{(\epsilon_p - \epsilon_h)^2 - (\omega + i\eta)^2} . \quad (2)$$

Here, p and h label particle and hole eigenstates of the single-particle Hamiltonian and ϵ_p and ϵ_h are the corresponding particle and hole energies.

The full response requires the interaction between electrons. We approximate it as a pure Coulomb interaction, and make a spherical expansion of the potential about the center of the cluster, $e^2/|\mathbf{r} - \mathbf{r}'| = e^2 \sum_l r_<^l / r_>^{l+1} P_l(\cos\theta)$. The response is dominated by the dipole term, for which we only consider the fields generated by $D_z^{(1)}$ and $D_z^{(2)}$ [6]. In a first simple approximation, we shall keep only the charge operator $D_z^{(1)}$, and assume the atomic size to be small in comparison with the hollow buckyball radius $R \approx 3.5$ Å, $r_< \approx r_> \approx R$. Then the electron-electron interaction is $e^2 D_z^{(1)} D_z^{(1)} / R^3$, and the screened response function due to $D_z^{(1)}$ in Eq. (1) is given by [5]

$$\Pi_1^{\mathrm{RPA}}(\omega) = \left(1 + \Pi_1^{(0)}(\omega) \frac{e^2}{R^3}\right)^{-1} \Pi_1^{(0)}(\omega) . \quad (3)$$

Note that in the present approach the Π's are ordinary functions and the equation is algebraic and easily computed. We shall later consider a more refined approximation by including the dipole moments on the sites, described by $D_z^{(2)}$. The effect will be to replace Eq. (3) by a 2×2 matrix equation

$$\tilde{\Pi} = (\tilde{1} + \tilde{\Pi}^{(0)} \tilde{V})^{-1} \tilde{\Pi}^{(0)} , \quad (4)$$

which separates the charge and the internal dipole operators. The elements of the 2×2 free response matrix are

$$\tilde{\Pi}_{nm}^{(0)}(\omega) = \sum_{p,h} \langle p|D_z^{(n)}|h\rangle \times \langle h|D_z^{(m)}|p\rangle \frac{2(\epsilon_p - \epsilon_h)}{(\epsilon_p - \epsilon_h)^2 - (\omega + i\eta)^2} . \quad (5)$$

$\tilde{V}$ in Eq. (4) is the 2×2 matrix of the interaction, with the elements $\tilde{V}_{11} = e^2/R^3$, $\tilde{V}_{12} = \tilde{V}_{21} = e^2/2R^3$, and $\tilde{V}_{22} = e^2/2dR^2$.

We determine the single-particle wave functions and energy levels using a tight-binding model which has been recently developed [7] to study the relative stability of different carbon cluster structures. The tight-binding Hamiltonian, which considers only the s and p valence electrons of C, is given by

$$H = \sum_{\alpha,i} \epsilon_\alpha a_{\alpha,i}^{\dagger} a_{\alpha,i} + \sum_{\alpha,\beta,i,j} t_{\alpha\beta}(r_{ij}) a_{\alpha,i}^{\dagger} a_{\beta,j} . \quad (6)$$

Here, i labels the atomic site and $\alpha = s, p_x, p_y, p_z$ labels the atomic orbital. ϵ_α is the orbital energy and $t_{\alpha\beta}$ are the hopping matrix elements between different sites. The parameters, based on local-density-approximation [8] (LDA) calculations for different carbon structures, have

been given in Ref. [7].

The equilibrium nearest-neighbor distance between carbon atoms in buckyballs is 1.453 Å on pentagons ("single bonds") and 1.369 Å between pentagons ("double bonds") [9], corresponding to a buckyball radius $R \approx 3.5$ Å. We computed the spectrum of the tight-binding Hamiltonian using this geometry, and obtained the energy levels shown in Fig. 1. The total width of the occupied band is 19.1 eV, to be compared with the LDA values of 18.8 eV of Ref. [10] and 19.2 eV of Ref. [11]. The level ordering near the Fermi level agrees with results based on the LDA and other methods [10,12–14]. We find a gap of 2.2 eV between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) level, to be compared with the LDA values of 1.8 eV from Ref. [10] and 1.7 eV from Ref. [11] and the experimental value [13] of 1.9 eV.

The HOMO to LUMO transition is forbidden by parity, and the lowest optically allowed transitions are $h_u \rightarrow t_{1g}$, $h_g \rightarrow t_{1u}$, and $h_u \rightarrow h_g$, with tight-binding excitation energies of 2.8, 3.1, and 4.3 eV. These values compare well with the LDA values of 2.9, 3.1, and 4.1 eV [10] and are reflected in the free response shown in Fig. 2(a). As we discuss in the following, the electron interaction changes the excitation energies significantly and is essential for even a qualitative understanding of the transitions strengths.

Our results for the screened response, based on the

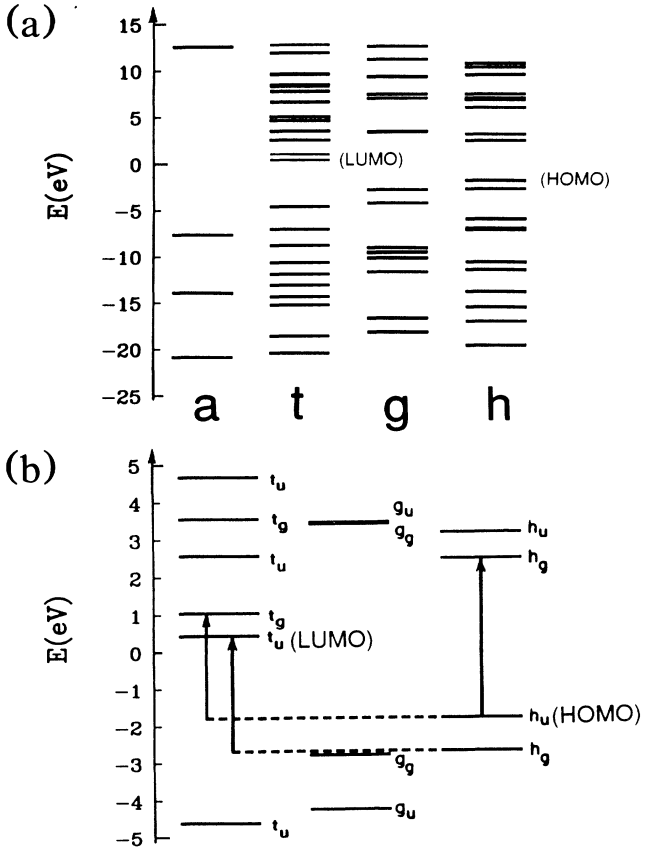

FIG. 1. (a) Single-particle energy-level spectrum of a C_{60} cluster, as obtained using the Hamiltonian described in Eq. (6). The levels have been sorted by symmetry. (b) Expanded region of the energy-level spectrum near the Fermi level. Allowed transitions between states with gerade (g) and ungerade (u) parity are shown by arrows.

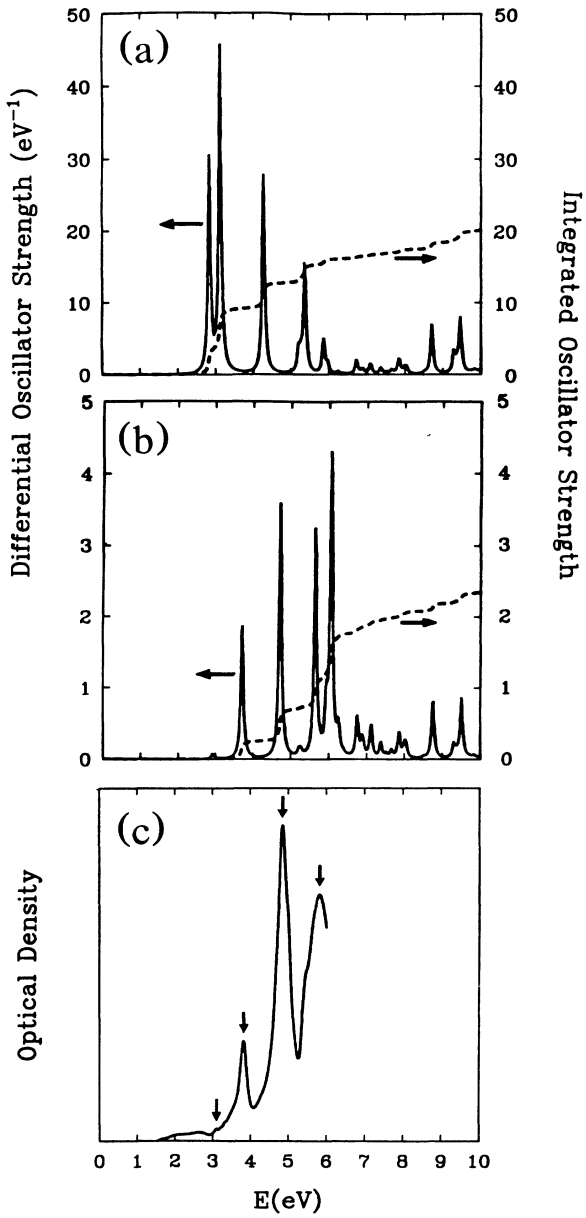

FIG. 2. (a) Free response and (b) RPA response of C_{60} clusters to an external electromagnetic field (solid line). The sharp levels have been broadened by adding an imaginary part $\hbar\eta = 0.2$ eV to the energy. The dashed line indicates the integrated oscillator strength. (c) Observed photoabsorption spectrum of Ref. [4].

RPA treatment of the tight-binding Hamiltonian and the charge dipole operator $D_z^{(1)}$, are shown in Fig. 2(b). A comparison with the free response shows that the lowest allowed particle-hole transition is slightly shifted in energy to 2.9 eV and agrees well with the observed [4,15] value of 3.1 eV. The oscillator strength [16] of this transition is drastically reduced by a factor of 400 from the value 3.8 in the free response to 0.010 in the RPA. This brings the transition strength close to the measured [15] oscillator strength of 0.004. An independent calculation of the interacting response has been performed using the quantum-chemical CNDO/S (complete neglect of differential orbitals) method [17], but this method yielded an oscillator strength of 0.08, which is considerably less screening than in RPA.

Turning to the next few excitations, we find the transitions to be shifted substantially upward in energy as compared to the free response shown in Fig. 2(a). This brings them into fair agreement with the observed [4,15] dipole excitations at 3.76, 4.82, and 5.85 eV. These transitions are also screened, but the screening factor is only in the range 10–30. They thus appear relatively strong compared to the low transition, in agreement with the experimental data of Ref. [15] [see Fig. 2(c)].

The results for the low-lying excitations are essentially unaffected when the on-site dipole operator $D_z^{(2)}$ is added to the response [18]. As we will discuss below, the effect of $D_z^{(2)}$ on the higher excitations is much more pronounced.

Turning to the plasmonlike transitions at high energy, we first note that the tight-binding Hamiltonian with the operator $D_z^{(1)}$ has a total oscillator strength of $N = (2m/\hbar^2)\sum_{p,h}|\langle p|D_z^{(1)}|H\rangle|^2(\epsilon_p - \epsilon_h) \approx 180$, which is, of course, the same in both the free response and the RPA. This value is close to the theoretical upper bound of 240, ignoring the core electrons, giving some credibility to the model for the entire energy range. Figure 3 displays the excitation spectrum of C_{60} extending up to plasmon energies, obtained using several approximations. The $D_z^{(1)}$ free response function, shown in Fig. 3(a), has a broad band of transitions in the "intermediate" energy range $\hbar\omega \approx 10$–20 eV. With the electron-electron interaction present, the main effect of the Coulomb field is to collect the strength of these transitions into a single collective excitation, a Mie-type plasmon. The spectrum

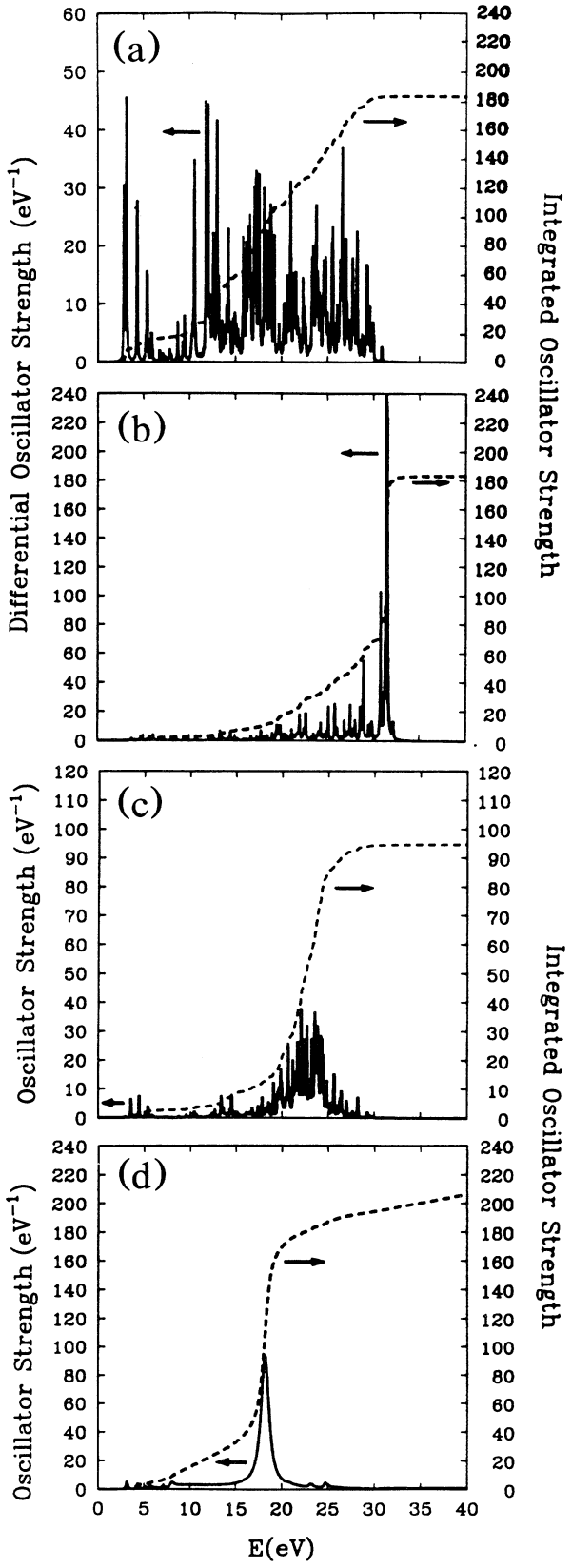

FIG. 3. Dipole response of C_{60} clusters to an external electromagnetic field, shown in an expanded energy region. (a) Free response, (b) RPA response based on the charge term $D_z^{(1)}$, and (c) RPA response based on both the charge and the dipole terms $D_z^{(1)}$ and $D_z^{(2)}$ in Eq. (1). (d) Interacting response of a thin jellium shell, describing the electron-electron interactions in LDA. The response function is given by the solid line, and the integrated oscillator strength is shown by the dashed line.

shown in Fig. 3(b) has this giant resonance at an unusually high frequency $\hbar\omega \approx 30$ eV, well beyond the typical plasmon range ($\hbar\omega < 10$ eV). In contrast to the low-energy region, the inclusion of the on-site dipole term $D_z^{(2)}$ has a substantial effect on the high-frequency response. The total integrated oscillator strength is reduced to 71, leaving most of the total strength outside the model space. We find that these extra terms shift the plasmon energy to $\hbar\omega \approx 20$ eV and decrease the oscillator strength by a factor of ≈ 2 when compared to the results in Fig. 3(b).

This high-frequency Mie-type plasmon has its origin in the large valence electron density ρ in the C_{60} cluster, and can be understood qualitatively by considering a conducting spherical shell with a radius $R \approx 3.5$ Å and 240 conduction electrons. We have calculated the optical transition strength function for this system using the program JELLYRPA [19], and show the results in Fig. 3(d). The energy agrees with Fig. 3(c), but in the jellium model the total oscillator strength is concentrated in the plasmon. An additional plausibility argument for the jellium picture of C_{60} follows from the static polarizability α. We find the classical conducting sphere value $\alpha = R^3 = 290$ a.u. to be in good agreement with the tight-binding value of 250 a.u. and the quantum-chemical result [14] $\alpha \approx 300$–400 a.u., depending on the basis set.

In summary, we have calculated the electromagnetic response function of C_{60} using linear response theory. We found the valence electrons to be quite delocalized and to show collective excitations. The lowest allowed excitation at $\hbar\omega = 3$ eV is strongly screened by a large factor of 400 when compared to the free response. The higher-lying excitations in the region below 6 eV experience much weaker screening. An unexpected result of our calculation is a giant collective resonance at $\hbar\omega \approx 20$–30 eV which has not been observed before and can be viewed as a Mie plasmon in a conducting sphere with a high charge density.

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Note added.—Our calculated spectra are in very good agreement with the recently observed giant plasmon in isolated C_{60} clusters [20]. Plasmon frequencies ranging between 20 and 30 eV have also been observed in C_{60} films [13,21].

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