Response of Carbon Fullerene Clusters to Electromagnetic Fields (*).

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The long-standing interest in carbon clusters [1] has strongly increased following the recent successful synthesis [2] of bulk quantities of carbon fullerenes, especially the most abundant C_{60} «buckyball». The hollow structure of this molecule is obtained by decorating the vertices of a soccer ball by carbon atoms [3]. This uncommon geometry, reminiscent of a «rolled-up piece of graphite», is the origin of unusual properties for the C_{60} molecule and other fullerenes with a similar topology.

In the following, I will address two important questions which are related to the response of these clusters to external electromagnetic fields. First, I will briefly discuss the static polarizability of the C_{60} structure, focussing on the importance of nonlinear terms. Then, I will discuss the possibility of collective electronic excitations in response to external electromagnetic fields. At the first glance, the occurrence of collectivity in these excitations may surprise in view of the relatively large gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) found in the fullerenes. I will address the nature of these collective electronic modes and compare them to similar modes found in graphite. Most important, I will discuss the possibility of their excitation by external multipolar electromagnetic fields and inelastic electron scattering. Results for the static polarizability of C_{60} will be summarized in sect. **1**, collectivity of dipole excitations in C_{60} will be discussed in sect. **2**, the dynamic response of C_{20}, C_{60} and C_{70} to multipolar fields will be addressed in sect. **3**, and the inelastic scattering of electrons from C_{60} and C_{70} clusters will be summarized in sect. **4**. Main conclusions will be presented in sect. **5**.

(*) Work done in collaboration with G. BERTSCH, A. BULGAC, NENG-JIU JU and YANG WANG.

1. – Static polarizability of C_{60}.

Our work on the static polarizability of C_{60} [4] has been motivated by a recent experimental report [5] of a very large absolute value [6] of the third-order optical polarizability $|\gamma| = 1.5 \cdot 10^{-42}\ \mathrm{m^5/V^2} = 1.07 \cdot 10^{-28}$ e.s.u. for C_{60} molecules in benzene solution. This value would make these systems prime candidates for a direct application in nonlinear optical devices. Subsequent experimental studies [7, 8] indicated a substantially smaller value of the hyperpolarizability than the initially observed.

We note that in an external electrostatic field $\mathcal{E}$ the induced dipole moment p of an isolated C_{60} molecule is given (to the lowest three orders) by

$$p = \alpha \mathcal{E} + \gamma \mathcal{E}^3 \,. \tag{1}$$

Here, α is the (linear) polarizability and γ is the (third-order) hyperpolarizability. We have taken into account the fact that the second-order hyperpolarizability is zero in centrosymmetric systems such as the C_{60} cluster. These polarizabilities can be determined from the energy change of a molecule due to an external field $\mathcal{E}$

$$\Delta E = -\frac{1}{2}\,\alpha \mathcal{E}^2 - \frac{1}{4}\,\gamma \mathcal{E}^4 \,. \tag{2}$$

To evaluate the energy change ΔE in eq. (2) due to an applied electric field, we use a tight-binding Hamiltonian

$$H = \sum_{i,\alpha} \varepsilon_i c^{\dagger}_{i,\alpha} c_{i,\alpha} + \sum_{i,j,\alpha,\beta} t_{i\alpha,j\beta} c^{\dagger}_{i,\alpha} c_{j,\beta} + \mathrm{h.c.} \tag{3}$$

which can be used directly in perturbation theory. Our parametrization of bulk *ab initio* density-functional results [9] for different carbon bulk structures has been used successfully to describe the equilibrium geometry [10] of carbon fullerene structures. The calculation of α requires a second-order, that of γ a fourth-order perturbation theory.

We find a very large *positive* value for the bare third-order hyperpolarizability $\langle \gamma_{\mathrm{bare}} \rangle$ which is within the range of two of the experiments (ref. [7] and [8]). However, when considering the screening of the external field by the induced dipole field in the C_{60}, this value gets reduced to a value for $\langle \gamma_{\mathrm{screened}} \rangle$ which is comparable to that of smaller aromatic molecules such as benzene. While the origin of this discrepancy is presently not resolved, we suspect the high laser frequency $\hbar\omega \approx 1.2$ eV used in the experiments to be a possible origin of this discrepancy.

2. – Collectivity of dipole excitations in C_{60} clusters.

As mentioned before, the C_{60} cluster is held together by strong covalent sp^2 bonds of similar character as in graphite. The strong hybridization within the cluster leads to a very large spread of the electronic states of more than 30 eV, as shown in fig. 1. The large HOMO-LUMO gap $E_{gap} \approx 2$ eV suggests a response to external electromagnetic fields which is typical for insulators. An intriguing question is whether, at larger energies, there is a possibility of a collective response to an external electric field, such as in a classical metal sphere.

Stimulated by a recent measurement of the photon absorption strength in C_{60} clusters [11], we have calculated the electromagnetic response of this remarkable system [12]. As I will discuss in the following, our calculated spectrum is in quantitative agreement with the experiment in the observed region. Moreover, we predict a giant Mie-type resonance at large excitation energies which has only recently been confirmed by photoionization experiments [13].

Our calculations are based on linear-response theory, which is most appropriate for large systems with mobile electrons where screening can be significant. The single-particle spectrum of the system is obtained using the tight-binding Hamiltonian discussed above [10]. The dipole operator has two contributions, from the charge on a site and from the dipole moment on a site. We

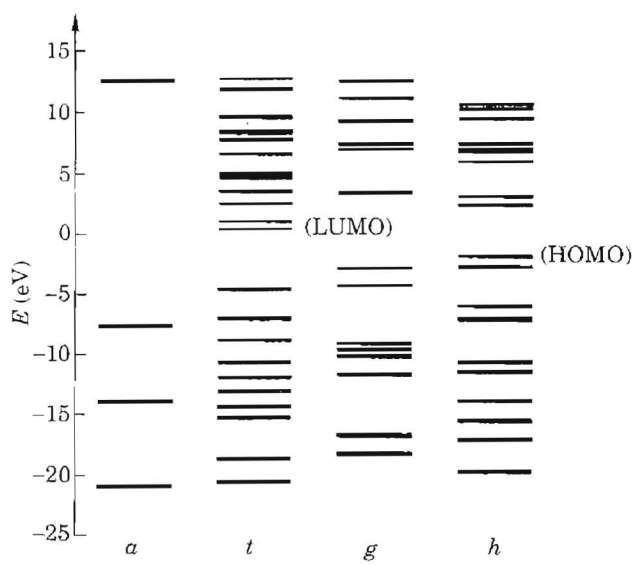

Fig. 1. – Single-particle energy level spectrum of a C_{60} cluster, as obtained using the tight-binding Hamiltonian described in ref. [10]. The levels have been sorted by symmetry (from ref. [12], © Americal Physical Society 1991).

write it as

$$D_z = D_z^{(1)} + D_z^{(2)} = \sum_{\alpha, i} a_{\alpha, i}^{\dagger} a_{\alpha, i} z(i) + d \sum_{i} (a_{s, i}^{\dagger} a_{p_z, i} + a_{p_z, i}^{\dagger} a_{s, i}) , \tag{4}$$

where $z(i)$ is the z-coordinate of the i-th 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 [14]

$$\Pi_{D_z}^{(0)}(\omega) = \sum_{p, h} |\langle p | D_z | h \rangle|^2 \frac{2(\varepsilon_p - \varepsilon_h)}{(\varepsilon_p - \varepsilon_h)^2 - (\omega + i\eta)^2} . \tag{5}$$

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, $e^2/|\boldsymbol{r} - \boldsymbol{r}'| = e^2 \sum_l r_<^l / r_>^{l+1} P_l(\cos\theta)$. The response is dominated by the dipole term, for which we only consider the fields generated by $D_z^{(1)}$ and $D_z^{(2)}$. As we see in the following section, this approximation reproduces correctly the overall response, but misses out some important details. The calculation of the RPA response is straightforward and has been described in ref. [12].

For C_{60}, we find the lowest optically allowed transitions to be $h_u \rightarrow t_{1g}$, $h_g \rightarrow$ $\rightarrow t_{1u}$ and $h_u \rightarrow t_g$, with tight-binding excitations energies of 2.8 eV, 3.1 eV and 4.3 eV. These values compare well with the LDA values 2.9 eV, 3.1 eV and 4.1 eV [15] 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 transition strengths.

Our results for the screened response, based on the RPA treatment of the tight-binding Hamiltonian and the charge dipole operator $D_z^{(1)}$, are shown in fig. 2*b*). A comparison to 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 [11, 16] value of 3.1 eV (see fig. 2*c*)). The oscillator strength [17] 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 [16] oscillator strength of 0.004. The higher excitations shown in fig. 2*b*) are found 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 [11, 16] dipole excitations. These transitions are also screened, but the screening factor is only in the range $10 \div 30$. They thus appear relatively strong compared to the low transition, in agreement with the experimental data of ref. [16].

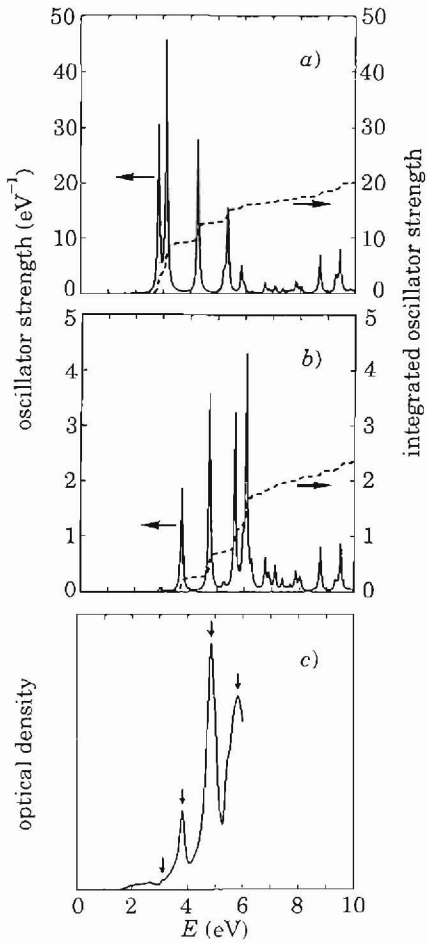

Fig. 2. – Free response (*a*)) and RPA response (*b*)) of C_{60} clusters to an external electromagnetic field (solid line). The sharp levels have been broadened by adding an imaginary part $\hbar\eta = 0.2$ eV to the energy. The dashed line indicates the integrated oscillator strength. *c*) Observed photoabsorption spectrum of ref. [11] (from ref. [12], © American Physical Society 1991).

Since the integrated oscillator strength in the region below 10 eV is substantially below the theoretical upper bound of 240 (based on the *f*-sum rule and ignoring the core electrons), we expect substantial oscillator strength at higher energies. Figure 3 displays the excitation spectrum of C_{60} extending up to 40 eV, 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 $\hbar\omega \approx (10 \div 20)$ 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 strongly collective excitation. The spectrum shown in fig. 3*b*) has

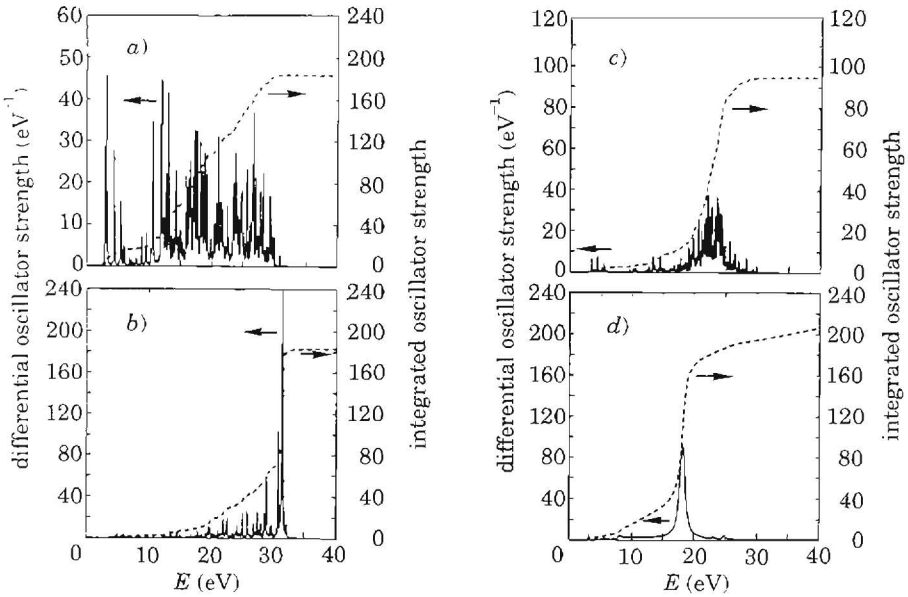

Fig. 3. – Dipole response of C_{60} clusters to an external electromagnetic field, shown in an expanded energy region. *a*) Free response, *b*) RPA response based on the charge term $D_z^{(1)}$, and *c*) RPA response based on both the charge and the dipole terms $D_z^{(1)}$ and $D_z^{(2)}$ in eq. (5). *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 (from ref. [12], © American Physical Society 1991).

this giant resonance at an unusually high frequency $\hbar\omega \approx 30$ 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, as shown in fig. 3*c*). The total integrated oscillator strength is reduced from 180 to 71, leaving most of the total strength outside the model space. We find that these extra terms shift the energy of the giant resonance 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*). These predictions are in agreement with the recently observed giant resonance in isolated C_{60} clusters [13]. Collective excitations at frequencies ranging within $(20 \div 30)$ eV have also been observed in C_{60} films [18-20].

The high-frequency collective mode 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 [21], and show the results in fig. 3*d*). The energy of the collective mode agrees with fig. 3*c*), allowing an interpretation of the high-frequency collective mode of C_{60} at ≈ 20 eV as a Mie plasmon of

a shell. We also note that this frequency is close to the Mie plasmon frequency of a solid metal sphere with 240 free electrons and the radius of the C_{60} cluster, $\hbar\omega_{\text{Mie}} = \hbar[4\pi\varrho e^2/3m]^{1/2} \approx 25$ eV.

3. – Dynamic response to multipolar fields: C_{20}, C_{60} and C_{70}.

The presence of the strongly collective dipole mode in C_{60}, which has been discussed above, suggests the existence of higher multipolar (quadrupolar, octupolar, etc.) excitations as well. We are especially interested in the frequency dependence of the excitation spectra, the nature of collective excitations and the cut-off of collective response for fields with a large multipolarity.

The results presented in the following have been published in ref. [22]. The calculations are based on the tight-binding model of ref. [10] for the single-particle states and the linear-response theory, and are not affected by the approximations used in sect. 2. The free response is given by the particle-hole propagator

$$G_0(\boldsymbol{r}, \boldsymbol{r}'; \omega) = \sum_{p,h} \frac{\langle \boldsymbol{r}|ph\rangle 2(\varepsilon_p - \varepsilon_h)\langle ph|\boldsymbol{r}'\rangle}{(\varepsilon_p - \varepsilon_h)^2 - (\omega + i\eta)^2}\,, \tag{6}$$

where p and h are the particle and hole states, $\varepsilon_{p,h}$ their corresponding energies, ω the excitation energy and η a (small) imaginary part. The random-phase approximation (RPA) Green function is determined as the solution of the integral equation $G = G_0 - G_0 VG$, where $V = e^2/|\boldsymbol{r} - \boldsymbol{r}'|$ is the Coulomb interaction among electrons. The response (transition strength) of the system to a weak external single-particle field $F(\boldsymbol{r})$ is given by $S = \operatorname{Im}\langle F|G|F\rangle/\pi$.

In fig. 4*a*), we present the free and the RPA response of a C_{60} cluster to an external multipolar field $F(\boldsymbol{r}) = r^l Y_{l,m}(\hat{\boldsymbol{r}})$, for $l = 0, \ldots, 8$ ($F(\boldsymbol{r}) = r^2$ for $l = 0$). The corresponding results for the C_{20} and C_{70} clusters are given in fig. 4*b*) and *c*), respectively. Fragmentation of the oscillator strength due to the coupling to more complicated states cannot be described by RPA. Here the Landau damping is approximated by an imaginary part in the energy $\eta \propto \omega$ in eq. (6), similar to ref. [23], which should describe the coupling of the RPA modes to surface electronic oscillations.

The multipolarity L of the external field is given by the ratio of the circumference of the fullerene and the wavelength of the surface mode, $L = 2\pi R/\lambda = qR$. The maximum expected multipolarity of a collective electronic excitation $L_{\max}$ can be estimated by comparing the C-C bond length d to $\lambda/2$, yielding $L_{\max} = \pi R/d$. This criterion gives $L_{\max} \approx 5$ for C_{20} and $L_{\max} \approx 8$ for C_{60} and C_{70}. This estimate agrees very well with the RPA results in fig. 4. The states with higher angular momentum are essentially single-particle in nature and show no collective behaviour. Except for the

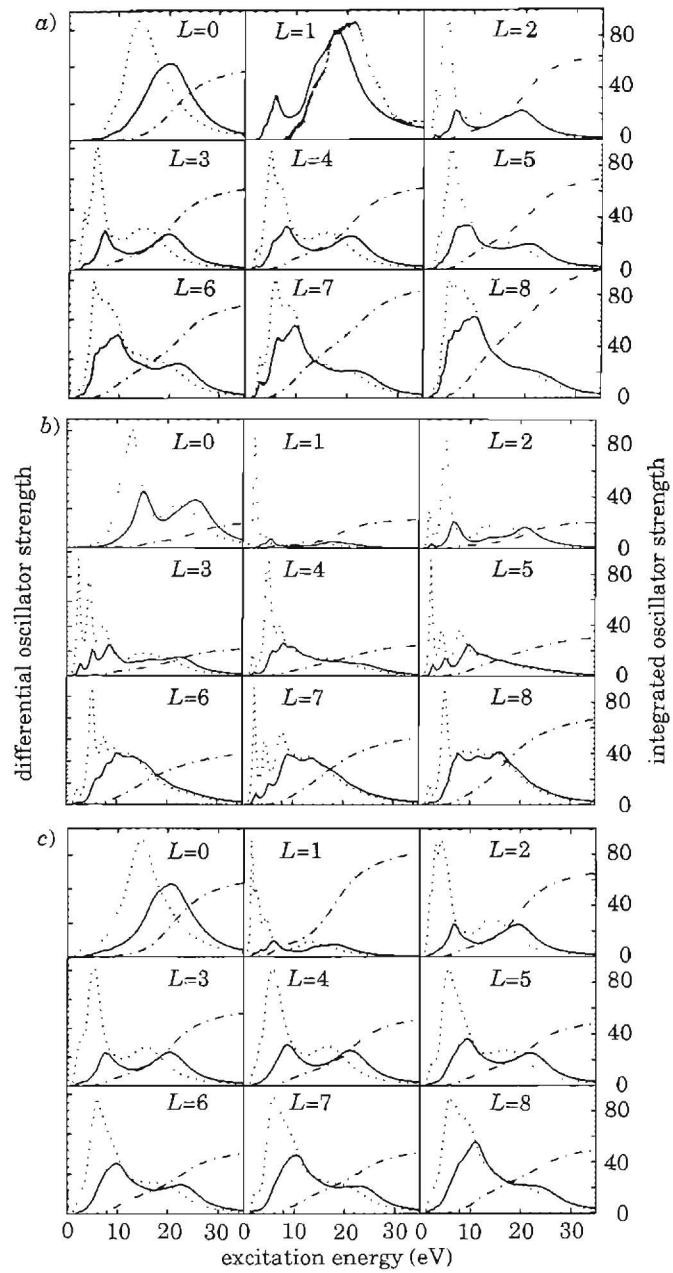

Fig. 4. – Free (dashed lines) and RPA (solid lines) response of *a*) C_{60}, *b*) C_{20} and *c*) C_{70} to external multipolar fields $F(\boldsymbol{r}) = r^l Y_{l,m}(\hat{\boldsymbol{r}})$, for $l = 0, \ldots, 8$ ($F(\boldsymbol{r}) = r^2$ for $l = 0$), using $\eta = \omega/8$ eV. For $l = 1$, the RPA photoexcitation probability is given by the solid line and the measured photoexcitation cross-section by the dotted line (arbitrary units)[13]. The dash-dotted line represents the integrated oscillator strength (from ref. [22], © American Physical Society 1992).

monopole, all the other multipoles have a very similar structure, a low-energy mode around $(6 \div 10)$ eV and a high-energy mode around $(18 \div 22)$ eV.

These two modes, which have been also observed in electron energy loss spectroscopy of C_{60} fullerite films [20], are the obvious analogues of the π and σ plasmons in graphite [24]. In graphite the low-frequency π mode has been interpreted by the in-plane response of the weakly bound p_π system to a field parallel to the layers. The high-frequency σ mode has been discussed by the out-of-plane motion of the strongly bound σ system of s and p electrons in response to a field perpendicular to the layers. A simple jellium plane model of a graphite monolayer would show the π plasmon at $\omega = 0$ and the σ plasmon at $\omega > 0$ frequency.

The high-frequency σ mode, which has been already discussed in sect. 2 (albeit in a more approximate way), agrees quite well with the giant resonance observed in the photoionization spectrum [13]. The slight red-shift by $(2 \div 3)$ eV of the observed peak with respect to the experiment could be partly due to an insufficiently precise parametrization of the tight-binding Hamiltonian underlying this calculation, or the fact that ω_σ lies very close to $3\omega_\pi$, opening the possibility of a resonant coupling between these modes. A more precise treatment of the excitation spectrum including multiparticle-hole excitations, which are responsible for the Landau damping, would require a formalism beyond the framework of the RPA.

4. – Inelastic electron scattering of C_{60} and C_{70}.

Since a plane wave representing a monochromatic electron beam has contributions from all multipoles, we expect that collective excitations with large multipolarities can be observed in an electron energy loss spectroscopy (EELS) experiment. The theoretical description, given in ref. [22], is based on the differential cross-section for electron excitation in the Born approximation,

$$(7) \qquad \frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega} = \left(\frac{e^2 m}{\hbar^2}\right)^2 \frac{4p'}{pq^4} \left|\langle\omega| \sum_n \exp[-i\boldsymbol{q}\cdot\boldsymbol{r}_n] |0\rangle\right|^2 = \left(\frac{e^2 m}{\hbar^2}\right)^2 \frac{4p'}{pq^4} S(\omega, \boldsymbol{q}).$$

Here, p and p' are the initial and final linear momenta of the electron, m is the mass of the electron, $\boldsymbol{q} = \boldsymbol{p} - \boldsymbol{p}'$ is the momentum transfer, ω is the energy transfer. $S(\omega, \boldsymbol{q})$ is the spectral function of the scattering fullerene which depends solely on the properties of this molecule and which contains the response to external fields of different multipolarities, discussed in sect. 3. This function, computed including all excited states with angular momentum up to $L = 20$ within free and RPA response, is shown for C_{60} as a contour plot in fig. 5. For a given momentum transfer $\boldsymbol{q}$ one can clearly see two peaks, one at an excitation energy around $(6 \div 10)$ eV and a second one around $(18 \div 22)$ eV, corresponding to the π and σ plasmons. A similar two-peak spectrum has recently been observed on C_{60} gas target [25].

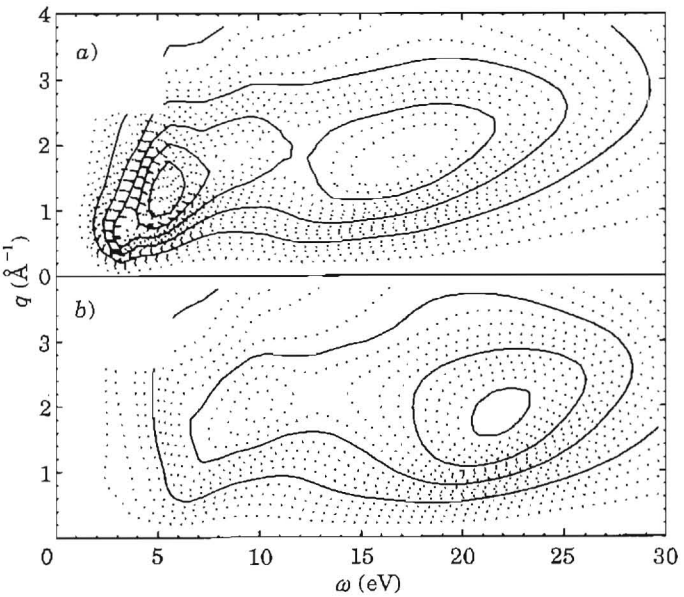

Fig. 5. – The *a*) free and *b*) RPA spectral function for an isolated C_{60} cluster ($\eta = \omega/8$ eV) (from ref. [22], © American Physical Society 1992).

5. – Summary and conclusions.

In summary, we have used the tight-binding formalism to study the polarizability and electronic excitations in C_{20}, C_{60} and C_{70} clusters. The linear and third-order nonlinear polarizability of C_{60} clusters is relatively large, but much smaller than proposed originally. Screening reduces the polarizability significantly. In response to an electromagnetic dipole field, isolated C_{20}, C_{60} and C_{70} clusters show a collective Mie-type plasmon excitation at $\hbar\omega_p \approx 20$ eV. In response to an electromagnetic multipole field, isolated C_{20}, C_{60} and C_{70} clusters show collective excitations up to $L_{max} \approx 8$. The spectra are dominated by collective modes at $\hbar\omega \approx 6$ eV and $\hbar\omega \approx 20$ eV reminiscent of the π and σ plasmons in graphite. The spectral function for electron scattering on C_{60} clusters shows two prominent features which correspond to π and σ plasmons in graphite.

The presently used formalism, in spite of its success, has certain limitations. The single-particle spectrum of the fullerenes has been determined by parametrized one-electron tight-binding Hamiltonian which spans a finite-dimensional model space. Even though such a description seems to account very well for the electronic response of the systems investigated, sum rules are strongly violated [12]. Effects of the exchange and correlation energy on the excitation energies have only approximately been addressed in the tight-binding parametrization, and treatment of self-consistency in the excitation spectra is

only approximate. Finally, the fragmentation of the collective excitations into multiparticle-hole excitations has not been included explicitly. In spite of these limitations, the overall agreement with available experimental data is surprisingly good.

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