Frenkel and charge transfer excitons in $C_{60}$

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Abstract

We have studied the low energy electronic excitations of $C_{60}$ using momentum dependent electron energy-loss spectroscopy in transmission. The momentum dependent intensity of the gap excitation allows the first direct experimental determination of the energy of the $^1H_g$ excitation and thus also of the total width of the multiplet resulting from the gap transition. In addition, we could elucidate the nature of the following excitations - as either Frenkel or charge transfer excitons.

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$C_{60}$ has attracted a lot of attention during the last years due to its remarkable physical properties such as superconductivity \cite{1,2}, non-linear optical properties \cite{3,4}, or magnetism \cite{5}. Despite the large number of studies devoted to $C_{60}$ there remain unanswered question regarding a complete microscopic understanding of its properties. Since it also acts as a model substance for the description of $\pi$-electron systems in general and their interaction in solids and interfaces, its properties are also of general value with respect to the entire class of molecular materials with $\pi$-governed electronic structures.

One of the questions which has remained unanswered up to now is connected with the electronic excitations across the energy gap in $C_{60}$ at about 1.8 to 2 eV. For the icosahedral point group the gap transition of $C_{60}$ splits into a multiplet with 4 components having $^1T_{1g}$, $^1T_{2g}$, $^1G_g$ and $^1H_g$ symmetry \cite{6}. While there exist several studies of the low energy components and their excitation energies \cite{7,8}, the energy of the highest lying $^1H_g$ excitation and thus the total width of the multiplet have not been experimentally determined yet, although it has important consequences for the understanding of optical properties such as e.g. second or third harmonic generation (SHG, THG) \cite{9,10}. Additionally, it also provides an important test quantity regarding the applicability of different theoretical approaches to describe these electronic excitations. Theoretical predictions for the multiplet width spanning a wide range from 150 meV to 600 meV have been reported \cite{9,11,12}. Furthermore, the nature of the energetically higher lying excitations that are observed as absorption maxima at about 2.4 eV and 2.7 eV is still under discussion. From a number of experiments both have been controversially assigned to either Frenkel excitons (on-ball) or charge transfer excitons \cite{9,13,14–18}.

In this study we present a detailed analysis of the momentum dependent electronic excitations of $C_{60}$ as obtained using electron energy-loss spectroscopy (EELS) in transmission. We show that the intensity variation of the low lying excitation can be used to derive the excitation energy and the mean extension of the $^1H_g$ excitation. This additionally gives the first experimental determination of the multiplet width arising from the gap transition. Furthermore, the nature of the two excitations at about 2.4 and 2.7 eV could be clarified.
For our EELS studies C\textsubscript{60} films with a thickness of about 1000 Å have been prepared by evaporation onto KBr single crystals under high vacuum conditions. After deposition, the films are floated off in destilled water, mounted on standard electron microscopy grids and transferred into the spectrometer. Prior to the measurements the films were characterized using electron diffraction showing that they were polycrystalline. The electron diffraction and EELS measurements were performed in transmission at room temperature using a 170 keV spectrometer described elsewhere. The energy and momentum resolutions were chosen to be 110 meV and 0.05 Å\textsuperscript{-1}. The raw data have been corrected for contributions from the elastic line. In order to obtain the optical conductivity from the measured loss functions we have performed a Kramers-Kronig analysis. Our results for low momentum transfers (optical limit) are in very good agreement with those obtained from optical measurements.

The response function in EELS in transmission is proportional to the dynamic structure factor \( S(q, \omega) \), i.e. EELS can provide information on the spatial structure of the electronic excitation under consideration. The matrix element, \( M \), for EELS is proportional to \(< 1 | \exp(\text{i}qr) | 0 >\) which can be expanded to

\[
M \propto \sum_{n} \frac{i^{n}}{n!} (q < r >)^{n} < 1 | (\frac{r}{< r >})^{n} | 0 >.
\]

Hereby, the introduction of a mean radius \(< r >\) allows one to separate the characteristic dimensionless \((q < r >)-\text{dependence of the matrix element from the (now also dimensionless)}\) constant excitation probability \(< 1 | (r/< r >)^{n} | 0 >\). In the case of excitations with a specific multipole character (e.g. dipole excitations) the latter has a finite value only for the corresponding \( n \) (e.g. \( n = 1 \)), i.e. one can derive the mean radius of the excitations from their moment dependence. The mean radius \(< r >\) gives a measure for the extension of the electron-hole wave function \( \Psi_{eh}(r) \) in the excited state which represents the probability amplitude to find the electron at a certain distance \(< r >\) assuming that the hole is fixed. Thus, the momentum dependence of the excitation intensity \( I_{n} \propto |M|^{2} \) of an excitation with a specific multipole character can be written as
\[ I_n \propto \frac{n!^2 (q < r >)^{2n}}{N}, \quad N = \sum_n \frac{(q < r >)^{2n}}{n!^2}. \]  \hspace{1cm} (2)

\( N \) is a normalization factor which guarantees the oscillator strength sum rule.

In Fig. 1 we show the intensities \( I_n \) as a function of \( q < r > \) for \( n = 1 \) (dipole excitations) and \( n = 2 \) (quadrupole excitations). Fig. 1 demonstrates that from the intensity variation of an excitation with, for example, quadrupole character as a function of momentum transfer, \( q \), one can derive the mean radius of the excited electron-hole pair (exciton).

In Fig. 2 the optical conductivity, \( \sigma \), of \( C_{60} \) is shown between 0.6 and 3.2 eV for various momentum transfers. The optical conductivity has been derived performing a Kramers-Kronig analysis of the loss function which was published previously \[22\]. We now demonstrate how these results can be used to determine the multiplet width of the gap excitation and the nature of the two following excitations. In Fig. 2 strong intensity variations with increasing momentum transfer are visible. At low momentum transfers the spectrum consists of a small shoulder at about 2.1 eV and two further structures located at about 2.45 and 2.8 eV. While the 2.1 eV shoulder develops into a clear peak with increasing momentum transfer the intensity of the two higher lying excitation decreases. At a momentum transfer of about 0.8 Å\(^{-1}\) the feature at 2.1 eV reaches its maximal intensity before it starts to decrease again, whereas the other two structures show the opposite behavior.

In order to obtain the momentum dependent intensity variation of the electronic excitations as observed in Fig. 2 quantitatively, we have modelled the optical conductivity with a sum of Lorentz oscillators:

\[ \sigma(\omega) = \epsilon_0 \sum_j \frac{\omega^2 f_j \gamma_j}{(\omega_j^2 - \omega^2)^2 + \omega^2 \gamma_j^2}, \]  \hspace{1cm} (3)

with \( \omega_j \) being the energy position, \( \gamma_j \) the width and \( f_j \) the oscillator strength of the corresponding excitation. The energy positions were fitted to obtain a best agreement within the entire \( q \)-dependent series and kept the same for all \( q \). The width of the excitations was also kept constant for all \( q \) and models the finite lifetime as well as phonon satellites of the electronic excitations. The result of this fit for the momentum dependent intensity of the low energy features seen in Fig. 2 is shown in Fig. 3.
Fig. 3a depicts the intensity variation of the gap transition at 2.1 eV. As expected, it clearly shows the behavior of a dipole forbidden excitation. The EELS response function in the gap region is almost solely caused by the $^1H_g$ excitation because it can be reached via an electric quadrupole transition while the other multiplet components can only be reached via magnetic dipole or even higher order transitions \[3\]. Consequently, a comparison of the intensity variation of the gap transition shown in Fig. 3a and Fig. 1 gives a direct measure of the mean radius of the $^1H_g$ excitation of $<r> \sim 2.8$ Å. This value is somewhat smaller than one would expect for the mean distance $\bar{d}$ of two particles moving independently on a sphere with the radius, $R$, of a $C_{60}$ molecule which is $\bar{d} = (4R_{C_{60}}/\pi) \sim 4.5$ Å. This indicates that the electron-hole pair is considerably excitonic in agreement with other results and predictions \[23\]. From the mean radius one can also derive an estimate for the exciton binding energy, $E_B$:

$$E_B \sim \frac{1}{4\pi\varepsilon_0\varepsilon_r} \frac{e^2}{<r>},$$

which is screened by the static dielectric constant $\varepsilon_r$ ($\sim 4$ for $C_{60}$ \[20,21\]). This simple consideration leads to a binding energy $E_B$ of about 1.3 eV also in good agreement with other results \[23\]. We note that local, unconventional screening effects, which have been discussed for finite size systems \[12,24\], play a minor role for the binding energy derived above as the bare and the effective Coulomb repulsion are very similar at a distance of 2.8 Å \[24\].

Moreover, the fact that the $^1H_g$ excitation dominates the EELS response function in the region of the energy gap yields a first direct experimental access to its excitation energy which can be derived from the first maximum in Fig. 2 ($q$ around 0.8 Å$^{-1}$) to be 2.1 eV. Together with optical studies of the other multiplet components \[8\], we can determine the total width of the gap excitation multiplet of $C_{60}$ to be about 260 meV. Thus, the multiplet width of the gap transition of $C_{60}$ is significantly smaller than predictions from calculations \[11,12\] which indicates that, independent of the exact approach, the models used to describe the electronic excitations of $C_{60}$ (and other $\pi$ electron systems) tend to overestimate electron
interaction effects.
In Fig. 3b and 3c we show the $q$-dependent intensity changes of the excitations visible at about 2.45 and 2.8 eV. The excitation occurring at 2.45 eV does not show any significant momentum dependence which suggests that it is not of a pure multipole but of mixed character. Since intra-molecular excitations in C$_{60}$ can all be classified as either gerade or ungerade we conclude that the electronic excitation appearing at 2.45 eV in C$_{60}$ is a charge transfer excitation resulting in the final state hole and electron sitting on different molecules. In contrast, the spectral weight of the excitation at 2.8 eV decreases with increasing momentum transfer which is consistent with a dipole allowed excitation. We therefore attribute the 2.8 eV feature in the optical conductivity to an intra-molecular or Frenkel exciton. The second intensity maximum visible in Fig. 3c at about 1.3 Å$^{-1}$ is probably caused by a resonance effect in the solid. Provided the mean radius of an excitation is commensurate with the lattice spacing further intensity maxima can occur at $q \sim 2\pi/ <r>$. Our assignment of the two excitations at 2.45 eV and 2.8 eV to charge transfer and Frenkel excitons, respectively, is in agreement with a recent comprehensive analysis of the excited states of C$_{60}$ using optical absorption and luminescence, electroabsorption and photoconductivity [17]. It is also qualitatively in line with theoretical calculations [12] which predicted the charge transfer excited states to occur about 150 meV above the $^1H_g$ excitation.
To summarize, analyzing the momentum dependent intensity variation of the low lying electronic excitations of C$_{60}$ we could determine the total multiplet width of the gap transition to be about 260 meV, which is smaller than predictions from calculations. Additionally, the mean radius ($\sim$ 2.8 Å) and the binding energy of the $^1H_g$ exciton ($\sim$ 1.3 eV) could be derived. The nature of the next higher lying excitations could also be elucidated; the excitation at 2.45 eV gives a charge transfer exciton while at 2.8 eV a Frenkel exciton is formed.

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FIGURES

FIG. 1. Intensity of a pure dipole or quadrupole excitation in EELS as a function of the reduced parameter $q < r >$ (see text).

FIG. 2. Low energy optical conductivity $\sigma$ of C$_{60}$ as a function of momentum transfer $q$ in steps of 0.1 Å$^{-1}$. The curves are offset in y-direction.

FIG. 3. The experimentally determined intensity variation of (a) the gap excitation and (b,c) the following electronic excitations of C$_{60}$ as a function of momentum transfer $q$. The excitation energies are given in the corresponding panel. The solid line in panel (a) represents the theoretical expectation for a quadrupole excitation with a mean radius of 2.8 Å (see also Fig. 1).
Optical conductivity (arb. units)
E = 2.1 eV

E = 2.45 eV

E = 2.8 eV

M. Knupfer and J. Fink, Fig. 3