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The dielectric function of dimerised $C_{59}N$

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Abstract:

We present electron energy-loss spectroscopy studies in transmission of the electronic structure of $(C_{59}N)_2$. The overall broadening observed for the π -derived structures in the low energy-loss function of $(C_{59}N)_2$ when compared to C_{60} is due to the reduced symmetry of the heterofullerene. The optical gap of $(C_{59}N)_2$ is about 1.4 eV, slightly smaller than that of C_{60} (1.8 eV). Using a Kramers-Kronig analysis the dielectric function in the low energy region was calculated. A static dielectric function at zero energy of ~ 5.6 is found.

Keywords: Electron energy-loss spectroscopy, fullerenes and derivatives

The preparation and mass spectroscopic identification of fullerene cages with carbon atoms substituted by heteroatoms was reported in molecular beam experiments by several groups as early as 1991 [1]. However, only the synthesis and isolation of bulk quantities of $(C_{59}N)_2$ [2] has allowed the first investigation of the physical and chemical properties of these heterofullerenes [2-5].

The electronic structure of a $C_{59}N$ monomer was calculated long before the first successful bulk synthesis [6]. The calculations propose that the "extra" electron is to a large extent localised on the nitrogen atom, with only a small charge transfer to the surrounding carbon atoms of the same molecule. Very recently, the electronic structure of $(C_{59}N)_2$ has been probed using electron-energy loss spectroscopy (EELS) in transmission and photoemission spectroscopy [7]. The C_{60} HOMO-derived band in valence band photoemission which is at ~ 2.2 eV binding energy was found to be influenced by the nitrogen substitution. A broad shoulder about 0.5 eV below the HOMO of C_{60} is found but there is no clear in-gap structure from a donor impurity level from the substituted nitrogen at low binding energy. For the matrix element weighted unoccupied π^* -derived density of states, as measured by the Cls excitation edges in EELS, the width of the LUMO-derived states is about twice as large as in C_{60} . However, the overall shape of the Cls excitation spectra for $C_{59}N$ dimers remains very similar in comparison with C_{60} . The spectral weight of all carbon- π^* -derived structures is within the experimental error identical, which demon-

strates that the extra electron is strongly localised on the nitrogen with at most a small charge transfer to the neighbouring carbon atoms. The measured occupied and unoccupied electronic structure have been compared to band structure calculations of the $C_{59}N$ dimer [8] and are in qualitatively good agreement.

In this contribution we report on the dielectric function of $(C_{59}N)_2$ as derived from the measured low energy-loss function performing a Kramers-Kronig analysis (KKA).

The preparation of $(C_{59}N)_2$ was described previously [2]. After purification by multi-cycle high-performance liquid chromatography, solid $(C_{59}N)_2$ grains were obtained after evaporation of o-dichlorobenzene followed by recrystallization from a CS_2 solution. For the EELS measurements, thin films of $(C_{59}N)_2$ were prepared by sublimation of degassed material under ultra high vacuum conditions at about 560° C onto NaCl crystals. The film thickness was chosen to be about 1000 - 1500 Å. Additional characterisation using mid infrared and optical absorption spectroscopy showed no features from remaining CS_2 solvent or from C_{60} . The films were then floated off the substrate in distilled water, mounted on electron microscope grids and transferred into the 170 keV EELS spectrometer which is described elsewhere [9]. An energy and momentum resolution of 110 meV and 0.05 Å^{-1} were chosen. In the low energy region of the loss function, contributions from the quasi-elastic line have been subtracted. Additional characterisation of the film quality was provided by electron diffraction in our spectrometer and in a transmission

electron microscope. The observed diffraction profile is consistent with the reported monoclinic structure [5].

Fig. 1: Loss function ($Im(-1/\epsilon)$), real part (ϵ_1) and imaginary part (ϵ_2) of the dielectric function of $(C_{59}N)_2$ (solid line) and C_{60} (dotted line).

Fig. 1 shows the the loss function at low momentum transfer ($0.1 \text{ \AA}^{-1}$) between 0 and 7 eV for $(C_{59}N)_2$ (solid line) and C_{60} (dotted line). At this low momentum transfer the loss function measures dipole allowed transitions (matrix element weighted excitations of the (σ, π) electrons into empty (σ^*, π^*) states) and can therefore be compared with optical measurements. In particular, the onset of the spectral weight is a direct measure of the optical gap. Additionally, the real and imaginary part (ϵ_1, ϵ_2) of the dielectric function, as derived by a KKA, are depicted in Fig. 1, for which the loss function was normalised using the oscillator strength sum rule:

$$n = N/V = \frac{m_e}{2\pi^2 e^2} \int_0^\infty E \epsilon_2(E) dE \quad (1)$$

E denotes the energy and m_e the mass of the electron, respectively. The number of valence electrons per dimer is $N = 482$ and the volume of the primitive unit cell is $V = 1380 \text{ \AA}^3$, as calculated from the measured lattice parameters [5]. The inset of Fig. 1 shows the loss function of the $C_{59}N$ dimer in an extended region of 0 to 45 eV. The two strong maxima in the loss function at about 6.4 eV and about 25 eV are characteristic for carbon systems like graphite, conducting polymers, C_{60}

or other fullerenes [9,10,11] and can be assigned to the so-called π plasmon (6.4 eV), reflecting the collective excitation of the π electrons, and the $\pi + \sigma$ plasmon (25 eV), respectively. For $(C_{59}N)_2$ the $\pi \rightarrow \pi^*$ features between 2 and 6 eV are broadened compared to C_{60} but maxima are found at similar excitation energies. Therefore, the changes are mainly due to a lifting of the degeneracy of the molecular energy levels due to the reduction from I_h to C_{2h} symmetry and not by the small charge transfer from the donor atom into the former LUMO. From the onset of the loss function and from the onset of the imaginary part of the dielectric function we find an optical gap of about 1.4 eV which is in quantitative agreement with optical absorption measurements in solution and in the solid state [2,7], but significantly smaller than in C_{60} (1.8 eV) [10]. For the real part of the dielectric function a static dielectric constant $\epsilon_1(0) \sim 5.6$ is obtained. The larger value of $\epsilon_1(0)$ compared to C_{60} $\epsilon_0 \sim 4$ also reflects the smaller energy gap of $C_{59}N$ dimers. In C_{60} it has been shown by measuring the momentum (q) dependence of the loss function (at high q dipole allowed transitions are suppressed in favour of monopole and quadrupole transitions) that the gap transition is a dipole forbidden excitonic $h_u \rightarrow t_{1u}$ transition at about ~ 2 eV [11]. For the q -dependence of $(C_{59}N)_2$ (not shown) we find that the features in the loss function at about 2.8 and 3.8 eV decrease with increasing q and are therefore dipole allowed. However, no significant change with increasing q is found for the gap transition. This may be explained by close lying dipole allowed and forbidden transitions that cannot be resolved.

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