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Electronic transitions and excitations in solid C₇₀ studied by reflection electron energy loss spectroscopy

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The electronic transition and excitation properties of highly ordered C₇₀ films have been studied by reflection electron energy loss spectroscopy (EELS). The EELS study revealed a total of eleven features in the energy loss range 1–40 eV. These include a prominent peak at 2.55 eV revealing the first dipole allowed transition across the band gap in C₇₀ fullerite; a feature at 2.20 eV correlated with the electron transition between the highest-occupied-molecular-orbital- and lowest-unoccupied-molecular-orbital-derived bands; two excitonic levels corresponding to a tight-binding Frenkel exciton in C₇₀ fullerite at 1.53 and 1.88 eV; and a doublet at 5.2 and 5.9 eV showing evidence of the π -plasmon splitting in fullerite C₇₀. A broad hump at ~ 28 eV corresponds to the excitation of the ($\sigma + \pi$) plasmon. © 1995 American Vacuum Society.

We report on a reflection electron energy loss spectroscopy (REELS) study of highly ordered C₇₀ films. The experiments were performed in a two-chamber ultrahigh vacuum (UHV) system equipped with a high-resolution spectrometer (ISA-Riber).¹ The spectrometer consists of two identical hemispherical electrostatic selectors, one acting as monochromator, the other as analyzer. The energy of the incident electron beam can be varied from 0 up to 150 eV. For the study of electron transitions and excitations, the instrumental resolution is set to 0.03–0.06 eV. The base pressure in the analysis and preparation chambers was 6×10^{-11} and 3×10^{-10} mbar, respectively.

Purified C₇₀ powder ($\geq 98\%$) was sublimed at ~ 450 °C from a Knudsen cell on two lamellar materials, MoS₂ and GeS that were cleaved in vacuum. The substrate was held at ~ 150 °C during C₇₀ deposition. The typical evaporation rate, monitored by a quartz oscillator, was 2 Å/min. Highly ordered C₇₀ films were obtained on both substrates, as evidenced by the sharp electron diffraction (LEED) patterns characteristic of the close packed C₇₀ molecular arrangement with 10.8 ± 0.02 Å interspacing. Subsequent high resolution transmission electron microscopy (TEM) studies have indicated a fcc arrangement of the C₇₀ molecules in these films with the $\langle 111 \rangle$ direction normal to the substrate surface.² For simplicity, we will hereafter denote the sample as C₇₀(111). The thickness of the C₇₀ films used in our experiment was estimated to be ~ 1000 Å.

Figure 1 displays a spectrum recorded with a primary electron energy of 8.0 eV (resolution 0.04 eV). The first prominent group of loss structures in the near infrared and visible range has an onset at ~ 1.8 eV and culminates at ~ 2.55 eV, with two shoulders on the ascending slope at ~ 1.9 and ~ 2.2 eV, respectively. We assign the feature at ~ 2.2 eV to the first electron transition across the band gap in C₇₀ fullerite (i.e., the solid state analog of the highest-occupied-molecular-orbital–lowest-unoccupied-molecular-orbital (HOMO–LUMO) transition in a C₇₀ molecule). It is dipole forbidden in a C₇₀ molecule but weakly allowed in the solid phase. We should note that, due to the

correlation effects, the onset of the interband transition measured in EELS does not directly provide the fundamental energy gap of C₇₀ fullerite in its ground state.

The weak shoulder at ~ 1.9 eV, as well as the clear feature at 1.53 eV loss energy shown in the EEL spectrum presented in the inset of Fig. 1, reveal molecular excitonic structures in C₇₀ fullerite. They reflect, respectively, the singlet state and the triplet state of a tight-binding Frenkel exciton in C₇₀ fullerite. In fact, in highly correlated molecular solids such as C₆₀ and C₇₀ where the Hubbard U correlation energy is greater than the typical band width W , the existence of tight-binding Frenkel-type excitons has been theoretically predicted in the energy range 1.5–2 eV.³

The outstanding peak at 2.55 eV loss energy clearly corresponds to the optical absorption band of C₇₀ centered at 468 nm (2.64 eV), considering the similarity in their peak positions for line shapes.^{4,5} It constitutes the first dipole allowed electronic transition. From the direct and inverse photoemission (PES-IPES) measurements, a center-to-center separation of 3.8 ± 0.2 eV was found between the highest occupied band and the lowest unoccupied band in C₇₀ fullerite,⁶ corresponding to the ($N \pm 1$) electron system. Comparing these two transition energies, measured by EELS and PES-IPES, respectively, gives a direct measure of the Hubbard correlation energy ($U \approx 1.2 \pm 0.2$ eV) for charged particles on the same molecule. Indeed, for a molecular solid like C₇₀ fullerite, the individual molecule wave functions are only weakly delocalized. Consequently, the interband electron transitions, particularly those between the energy bands close to the energy gap, should retain their largely localized character. Therefore, the energy to separate an electron-hole pair on the same site (as in the case of EELS) to infinite (as in the case of PES-IPES) is appreciable and it constitutes the main contribution to the Hubbard correlation energy.

The peak at 3.2 eV is another dipole allowed transition across the energy gap; it correlates with the sharp AS peak at 378 nm (3.28 eV).^{4,5} We note that the energy separation between this peak and the prominent peak at 2.55 eV corresponds to the energy separation between the first and second

FIG. 1. Electron energy loss spectrum of C₇₀ fullerite in the near-infrared to visible region. It exhibits electronic transitions across the energy band gap (the shoulder at 2.20 eV and the peaks at 2.55, 3.2, and 4.7 eV) as well as two excitonic levels at 1.53 and 1.88 eV. The spectrum in the inset shows the details of the feature at 1.53 eV, assigned to the triplet level of a tight-binding Frenkel exciton. The two features at 5.2 and 5.9 eV probably correspond to the double split of the π plasmon of C₇₀.

empty bands of C₇₀ fullerite as measured by both inverse photoemission⁶ and x-ray absorption spectroscopy.⁷ Accordingly, we assign the peak at 3.2 eV as revealing the transition from the highest occupied band to the second lowest unoccupied band envelope in C₇₀ fullerite.

Further above in loss energy, the next group of peaks is composed of at least three distinct features: at 4.7, 5.2, and 5.9 eV. An analysis of their intensity dependence with the primary electron energy indicates that the 4.7 eV peak stems from the interband transitions of individual electron while the two peaks at 5.2 and 5.9 eV result from collective excitations.⁸ We interpret the two latter peaks as revealing the two split levels of the π plasmon of C₇₀, a direct consequence of its ellipsoidal molecular shape—the collective dipolar excitation of the π electrons along the long molecular axis has a different resonance frequency from those along the short axes.

An estimation of the magnitude of this π -plasmon splitting in the C₇₀ molecule could be made by employing a simple model based on the Mie theory describing bulk excitations of small particles.^{9,10} In this model, the π electrons of a C₇₀ molecule were considered to be homogeneously distributed in a solid ellipsoidal object immersed in a medium. Classical electrostatics was used to calculate the polarizability of this object as a function of its dielectric constant and geometric parameters. Two different plasmon modes, corresponding to the excitation along the long and short axes of

FIG. 2. Lower panel: EEL spectrum of C₇₀ fullerite taken at primary electron energy of 100 eV. The broad hump culminating at ~ 28 eV results from the $(\sigma + \pi)$ -plasmon excitation, the collective excitation of all valence electrons of C₇₀. Upper panel: XPS C 1s satellite structures of C₇₀ fullerite. The broad hump at ~ 28 eV corresponds to the $(\sigma + \pi)$ plasmon. The first shakeup peak, at 2.5 eV from the C 1s main line, probably reveals the electronic transition from the highest occupied band to the lowest unoccupied band in the ionized species C₇₀⁺. The peak at ~ 6 eV correlates with the excitation of the C₇₀ π plasmon.

the molecule, have been found. By using this model and introducing the commonly accepted geometrical parameters of the C₇₀ molecule, it was found that the ratio of the plasmon energies along the long and short molecule axes was 1:1.2,¹⁰ in good agreement with the experimental value of 1:1.13 (i.e., 5.2:5.9).

The lower panel of Fig. 2 displays an EEL spectrum recorded at the primary electron energy of 100 eV. The $(\sigma + \pi)$ plasmon, i.e., the collective excitation of all valence electrons, was revealed by a broad hump at ~ 28 eV. Its broadness precludes any observation of possible plasmon level splitting in contrast to the case of π plasmon. This $(\sigma + \pi)$ plasmon of C₇₀ fullerite was also observed in the x-ray photoelectron spectroscopy (XPS) C 1s satellite structure, shown in the upper panel of Fig. 2. A few other features are visible in the XPS C 1s satellite structure. The peak at 2.5 eV from the C 1s main line probably corresponds to the electronic transition between the highest occupied and the lowest unoccupied bands in the ionized species C₇₀⁺. The next group of peaks, extending from 4.5 to 6.5 eV, culminates at 6.0 eV with a pronounced shoulder at ~ 4.7 eV. In analogy to EELS, we interpret the feature at ~ 4.7 eV as revealing the interband transitions of individual electrons and the compo-

ment at higher binding energy side (~ 6 eV) as the excitation of the π plasmon of C₇₀. Here, the splitting of the π -plasmon levels is not resolved, probably by the limited instrumental resolution in XPS. Moreover, the intermixing character of the two sorts of loss mechanism, i.e., the on-site contribution coming from the excited states of the ionized molecule from which the photoelectron is ejected and the off-site contribution from the inelastic scattering that the photoelectron experiences when it propagates through the lattice, could also have some smearing effect. The separation between the 9.6 eV peak and the peak corresponding to the center-to-center transition between the HOMO- and LUMO-derived bands (at 2.55 eV) agrees with the x-ray absorption spectroscopy (XAS) data which located the σ^* band at ~ 7 eV above the LUMO-derived bands.⁷ Therefore, we assign the peak at 9.6 eV to the electronic transition from the highest occupied band into the lowest-lying σ^* band.

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