

Electron irradiation damage to aromatic compounds

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Radiation damage is of continuing interest to electron microscopists, most recently in connection with aberration-corrected TEM's and low-voltage scanning microscopes. It has been suggested that damage to π -bonded organic compounds requires carbon K-shell excitation, based on similarity of the cross sections for damage and for K-shell ionization [1] or on the rate of fading of the diffraction pattern as a function of incident-electron energy E_0 [2,3]. If so, a low-voltage SEM could examine such materials without damage, while at higher E_0 there would be negligible effect from low-energy secondary electrons, leading to high spatial resolution if these materials were used as electron-beam resists.

We have investigated the radiation damage in coronene, rubrene and other aromatic compounds according to several criteria. Loss of long-range order (crystallinity) was monitored from fading of electron-diffraction patterns. Disruption of the aromatic ring within each molecule was measured from decay of the 6eV energy-loss peak, representing $\pi - \pi^*$ transitions. These measurements were performed a TEM equipped with a PEELS system and CCD camera. Radiation sensitivity can be represented by a damage cross section $\sigma = e / D_c$ where e is the electronic charge and D_c is a characteristic dose for diffraction or π -peak fading. Results for $E_0 = 200$ keV are shown in Fig. 1. Loss of crystallinity is seen to be less rapid when the irradiation takes place at lower temperature [4]. As expected for aromatic molecules [1], though not for C_{60} [5], loss of the π -resonance peak has a lower cross section, i.e. a higher dose than needed for loss of crystallinity.

Decay of the cathodoluminescence (CL) signal was measured using a Philips 505 SEM operated with accelerating voltages between 1 kV and 30 kV. Landing energies below 1000 eV were obtained by applying negative voltage to the specimen stage. Emitted light was collected by a fibre-optic spectrometer system or by a photomultiplier tube. Cross sections for CL decay are shown as solid circles in Fig. 1. The dashed curve represents the cross section *per molecule* for all inelastic scattering; its approximate match with the CL data suggests that the molecular energy-level structure can be disrupted (leading to loss of light emission) by a *single* inelastic event occurring within each molecule. The fact that CL cross sections (for $E_0 > 1$ keV) are *higher* than the total-inelastic cross section may be due to plural scattering and the fact that some inelastic collisions generate several secondary electrons, which then damage adjacent molecules [6]. The decrease in CL cross section for $E_0 < 1$ keV reflects the lower energy (per primary electron) available for bond breakage and the production of secondaries.

Open circles in Fig. 1 show cross sections for loss of crystallinity measured for coronene by the Cavendish group [2,3]. They match (in absolute value) the calculated cross section for one K-shell ionization per molecule (solid curve in Fig. 1), suggesting that a *single* K-ionization *per molecule* is sufficient to cause randomization of the *intermolecular* spacing and orientation (loss of crystallinity). This argument is supported [2,3] by the sharp reduction in cross section which was observed as the incident energy was reduced to values approaching the K-shell ionization energy (~ 285 eV). However, care must be exercised in interpreting measurements in which crystallinity is determined subsequent to irradiation, using electrons of higher energy. For $E_0 < 500$ eV, the electron range becomes less than the specimen thickness, so electron irradiation can be expected to leave an undamaged layer which is subsequently detected by transmission diffraction and could be mistaken for lack of damage. This

possibility occurs at higher E_0 (for a given *average* thickness) if the specimen has a porous granular structure. To produce specimens with constant thickness, we vacuum-deposited the organic materials onto a cooled (100 K) substrate. However, this procedure results in amorphous films which cannot be used for diffraction measurements.

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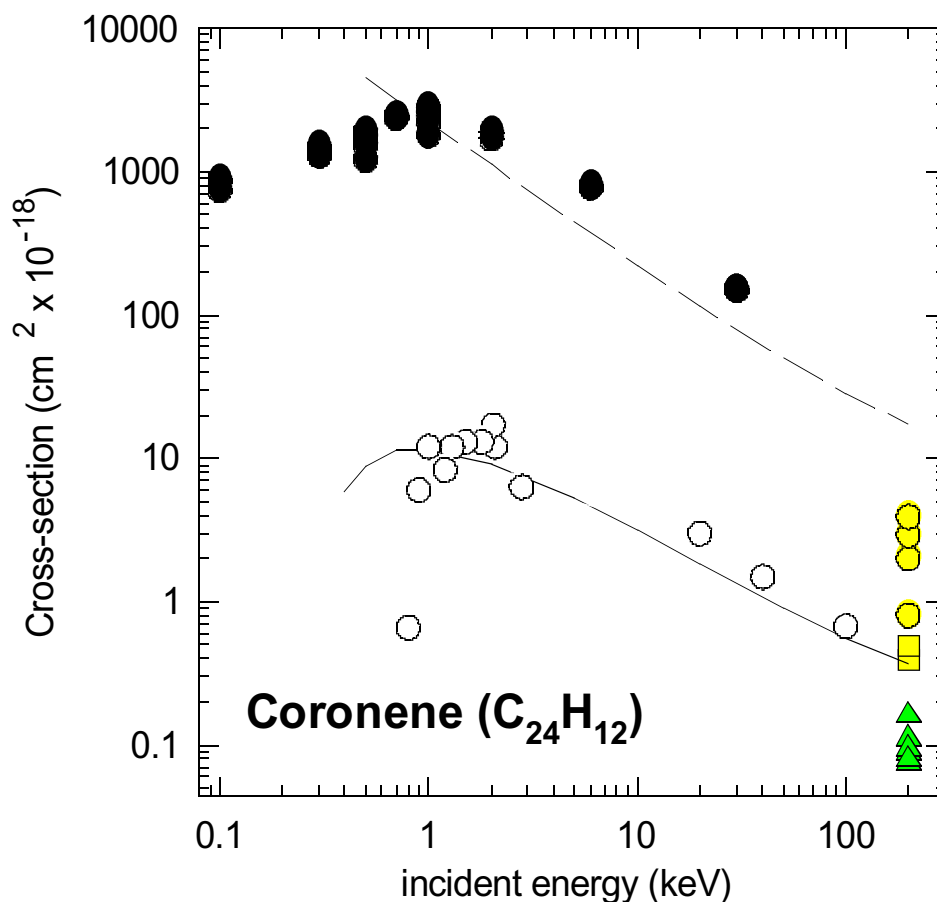


FIG. 1. Cross sections for cathodoluminescence decay (black circles), loss of crystallinity (open circles and squares) and decay of the 6eV energy-loss peak (triangles), compared with calculated cross sections for a single K-shell (solid curve) or valence-electron (dashed curve) excitation per molecule.