Resonances in low-energy electron transmission through organized organic films: Evidence for molecular quantum wells

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Energy-resolved transmission spectroscopy of low-energy photoelectrons through self-assembled monolayer films on a gold cathode are used to identify electron resonances in the film. For films composed of benzene, naphthalene, and anthracene aromatic moieties, the transmission spectra reveal well-defined vibronic structure, which is quite similar to that found for the corresponding aromatic molecules in the gas phase. In contrast, the electronic state positions are not molecular and indicate a ''quantum-well'' structure formed by the monolayer film. [S0163-1829(99)01044-9]

It is well established that transient anion states, or electron resonances, play an important role in low-energy electron-molecule scattering in the gas phase.[1] Such resonances have also been observed when electrons are scattered from adsorbed molecules.[2,3] When electrons are transmitted through thin molecular films, structure is observed in the energy-dependent transmission probability. This spectral structure can have several origins. The broad features have been related to the electronic band structure of the film.[4,5] Namely, they correspond to states in which an excess electron is delocalized in the film. These broad features display a strong dependence on the degree of order in the film.[6] Another type of spectral feature can arise from localized resonance states of the electron with either traps or impurities in the film.[7] In this case, the electrons can be localized at the ''trap'' site. Because of the charge localization in this process, strong electron-vibrational coupling can exist and inelastic processes may occur.

Here, we present evidence for a new type of resonance in the transmission probability of electrons through organized organic films. These resonances result from the two-dimensional character of the organized organic films and correspond to states in which the electron is delocalized in two dimensions but localized in the third one. This picture is similar to the situation occurring in semiconductor quantum wells. Hence, the structure in the transmission probability does not result from complete delocalization of the electron in three dimensions nor from complete localization of the electron on a single molecule, as in the case of trap sites or as in gas phase resonances. The feature of these resonances, when compared to inorganic quantum well structures, is the strong vibronic structure in the transmission probability's spectrum.

The molecules shown in Fig. 1 were self-assembled on a glass slide that was coated with a 100-nm polycrystalline Au film Fourier transform infrared isotherms showed that under these conditions one monolayer of the organic molecules is adsorbed. The structural features of these organic films have been well characterized in an earlier study.[8] A 193 nm, 20-ns laser pulse (Lambda Physics Compex) was used to eject photoelectrons from the substrate. This photon energy is low enough that the organic molecules are not directly ionized. The photoelectrons from the substrate passed through the organic films and their kinetic-energy distribution was measured by a time of flight electron energy analyzer.[9] Details of the apparatus have been described elsewhere.[4]

Figure 2 presents the electron energy distributions obtained for electrons that are transmitted through films comprised of molecules I, II, and III (see Fig. 1). Each of the spectra in Fig. 2 consists of two broad bands that are centered at about 0.7 and 1.4 eV. Superimposed on these bands is a fine structure that is well resolved on the low energy band but less defined on the high-energy band (i.e., only clearly evident for the case of molecule I). For molecules I and II, the fine structure on the low-energy band can be clearly assigned to vibronic structure in the electron resonances of their aromatic moieties. For the case of molecule I, which has two benzene units, a progression in the fine structure with an energy separation of 0.12 ± 0.01 eV can be identified. In the case of molecule II, which has two naphthalene units, the progression is composed of two energy intervals, 0.08 ± 0.01 and 0.16 ± 0.02 eV. These progressions are in excellent agreement with the vibronic resonances reported for electron transmission studies of benzene and naphthalene in the gas phase. In the gas phase, the electron resonances have well-defined vibronic structure with an energy spacing of 0.123 eV for benzene and an energy spacing of 0.78 and 0.170 eV for naphthalene.[10] In the case of molecule III, which has two anthracene units, a long and strong anharmonic progression is observed with energy gaps of $\Delta E = 0.18, 0.15, 0.11, 0.09,$ and 0.08 eV. No gas phase data is available for the anthracene system. The vibronic structure becomes better defined through the series: benzene, naphthalene, anthracene. This trend indicates a longer lifetime for
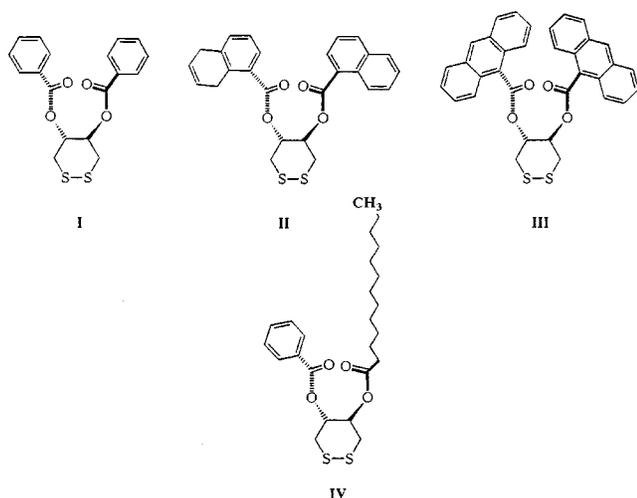
FIG. 1. Structures of the molecules that are adsorbed on the gold surface are shown.

the resonances as the aromatic system becomes larger.

Electron transmission studies were performed on derivatives of molecule I in which the benzene ring was substituted in the *para* position by CN, NO$_2$, and CF$_3$. In these cases, the fine structure in the electron transmission spectra disappeared. A similar sensitivity to substitution is found for electron transmission spectra in the gas phase. In that case, the loss of structure has been traced to a reduction in the electronic state's symmetry that results in a smaller barrier to the decay of the anion resonance and a shortening of the reso-
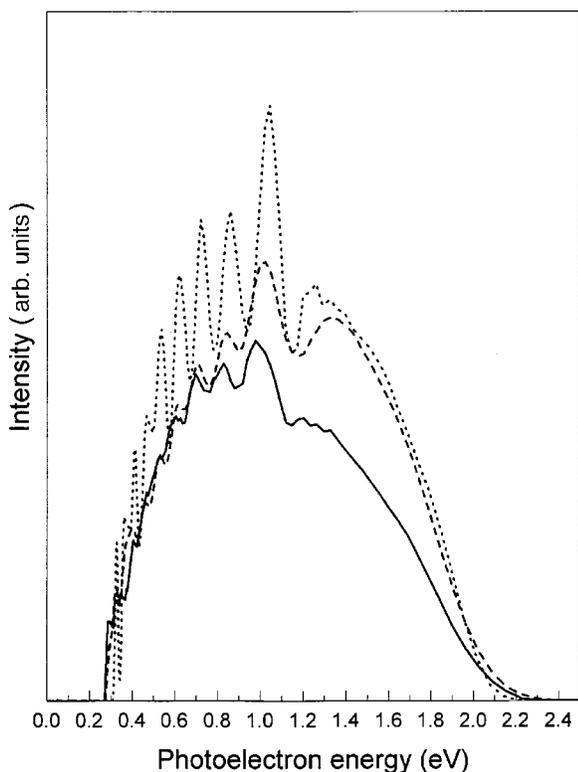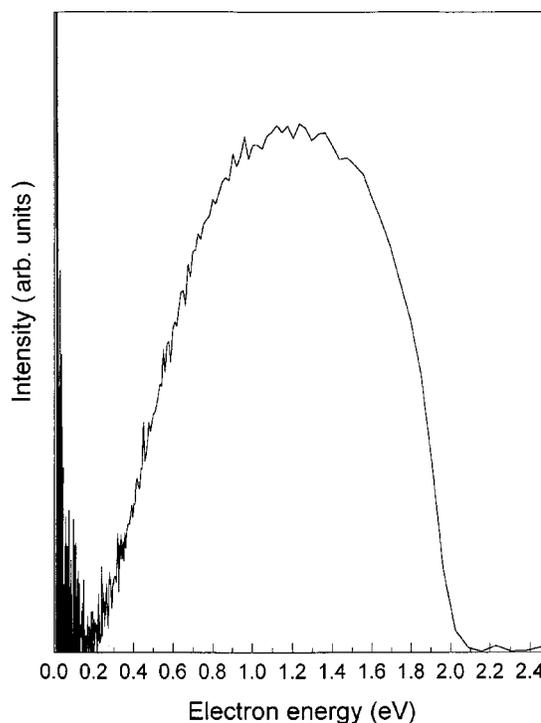
FIG. 3. The electron energy distribution obtained for electrons transmitted through an organized monolayer film comprised of molecule IV.

nance lifetime.[10] We performed studies also on molecules that had one of the benzenes replaced by an alkyl chain, molecule IV in Fig. 1. Figure 3 shows the distribution obtained for a monolayer composed of molecule IV. The lack of vibronic structure in this spectrum demonstrates that resonances are only observed when the molecule contains two unsubstituted aromatic systems. More generally, this results suggests that the vibronic structure is sensitive to the film order in the lateral direction, either energetic, structural or both. Whereas it was possible to distinguish two electronic bands in the Fig. 2 spectra because of the change in the vibronic structure, it is not possible to determine if the spectrum in Fig. 3 possesses more than one electronic band. In general, we found that the vibronic structure in the spectrum is extremely sensitive to the properties of the film (its mode of preparation) and its molecular constituents.

The observation that the fine structure in the spectra of Fig. 2 is related to the vibrational states of the aromatic part of the molecular anion, indicates that the electron is located near the aromatic groups. However, two other findings do not support the presence of a localized anion state on the aromatic groups. First is the observation that the electronic energies (the two broad bands) occur at nearly the same energy for the three different molecular substituents. From studies of electron scattering in the gas phase it is known that the first two resonances occur at 1.12 and 4.8 eV for benzene, 0.19 and 0.9 eV for naphthalene, and 0.6 and 1.13 eV (Ref. 10) for anthracene. Second is the observation that if one aromatic ring in each molecule is replaced by an alkyl chain (molecule IV), the vibronic resonances disappear, see Fig 3. Hence, we must conclude that despite the fact that the vibronic structure relates to the negative aromatic ions, the

FIG. 2. The electron energy distribution obtained for electrons transmitted through an organized monolayer film comprised of molecule I (solid line), II (dashed line), and III (dotted line).
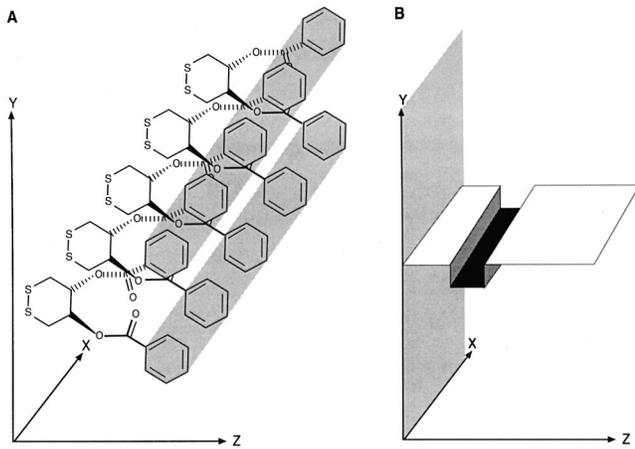
FIG. 4. An idealized scheme of the ''molecular quantum well'' formed by monolayers comprised of molecules I is shown in the left panel. The right panel provides an energy scheme for a two dimensional quantum well.

electron is not localized on a single aromatic moiety and the energy of the electronic state has a different origin.

We propose a simple model that explains all the observations. We hypothesize that the electrons are localized on the aromatic rings in the direction perpendicular to the film, but are delocalized between the molecules in the layer. In other words, the photoemitted electron exists in a state that is delocalized in the XY plane parallel to the substrate (see Fig. 4), but is localized along the Z axis (normal to the substrate). The second panel of Fig. 4 depicts a two dimensional potential well that is short along the Z axis and unbounded along X. The electronic resonances that are observed will be localized above the well in Fig. 4 and their energy will be determined by the length of the ''box'' along the Z direction (i.e., the size of the aromatic moiety) and the depth of the well.

To calculate the energy position of the electronic states the following two assumptions were made:

(1) The width of the quantum well corresponds to the length of the aromatic rings, taking into account their tilt angle vs surface normal.

(2) The depth of the quantum well between the three systems is shifted by the polarization energy between the electron and the aromatic moiety.

In this simple model the electronic energy levels of systems are given by

$$E_n = \frac{n^2 h^2}{8mL^2} - \frac{\alpha' e^2}{4\pi\varepsilon_0}, \tag{1}$$

where L is the length associate with the localization of the electron in the direction parallel to the surface normal, m is the mass of a free electron, e is the charge on an electron, and α' is the effective polarization such that

$$\alpha' = \frac{\text{const}\,\alpha}{r^4}, \tag{2}$$

where α is the polarizability of the aromatic system and r is the range of the polarization arising from the electron

charge.[11] It is interesting to note that this expression is similar to that suggested for a polaron, and it contains both the localization energy and the polarization energy.[12] However, for polarons an isotropic structure is usually assumed (L and r are the same) and the polarization energy contains both ionic and electronic contributions. In the present model, only the electronic polarization is considered to play a role.

The following procedure was taken in calculating the energy levels of the three different systems. In all cases, m was taken to be the mass of a free electron. For the benzene substituted molecules, L and r were chosen so that the first two resonance states, above the electron affinity energy of the quantum well (namely with positive energy), coincided with the experimental observation of the two electronic state positions. Values of $L = 12\,\text{Å}$ and $\alpha' = 3.9 \times 10^6\,\text{cm}^{-1}$ give the first two electronic resonances at 0.5 and 1.8 eV for benzene. For the naphthalene and anthracene substituted molecules, the length of the well was taken to be 24 and 36 Å (factors of two and three), respectively. The parameter α' was scaled by the molecular polarizability (10 Å^3 for the benzene system, 16.5 Å^3 for the naphthalene system, and 25.4 Å^3 for anthracene). These parameters give resonances at 0.7 and 1.4 eV for naphthalene and at 0.9 and 1.5 eV (Ref. 13) for anthracene. Considering the simplicity of the model, it is quite surprising that the results fit so well to the experimental values of about 0.7 and 1.5 eV for all three molecules.

The mechanism for the vibronic structure could be either elastic or inelastic. The elastic mechanism corresponds to an enhanced transmission of electrons at energies, determined by the vibronic structure arising from the aromatic groups. This mechanism would be similar to that used in understanding electron transmission experiments in the gas phase. The inelastic mechanism involves the energy dependent scattering of electrons and the loss of energy into vibrational modes. This mechanism is found to be operative in energy-loss studies.[14] The observations here do not distinguish between these two mechanisms, although the vibronic structure observed for molecule I is in better agreement with the elastic experiments in the gas phase than with the inelastic measurements.

It is important to realize that the delocalization in the XY plane does not have to be macroscopic in scale. Rather, it is enough that the scale of delocalization be larger than a few electron wavelengths for the effect to be observed. Since the wavelength of the electrons in these experiments is of the order of 1-5 nm, it is enough to have delocalization on the scale of 50 nm. Since the domain size, in the organized films, is expected to range from tens of nanometers to microns,[15] no macroscopic scale delocalization is required in order to observe the effect. It is also important to consider that some fraction of the electrons may not experience resonances, because of inhomogeneties and defects in the film. These electrons would contribute a background signal that is unstructured. From the signal to noise in Fig. 2, it is clear that even if 50% of the electrons are not trapped, the structure would still be evident. These two factors, the relatively short length scale required for the delocalization and the high sensitivity of the spectrum to resonances, enable us to observe the effect.

To conclude, these data display well-defined vibronic structure in the energy spectrum of photoelectrons that are transmitted through monolayer films of aromatic molecules. The vibronic spacing is associated with the vibrational structure of the aromatic molecules, and the electronic state positions are determined by the electronic resonance that is highly localized along the surface normal but delocalized in the plane of the film.

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