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Franck–Condon Coupling in Anthracene Isomer Self-Assembled Layers and Symmetry Effects on the High Resolution Ultraviolet Photoemission Spectra

Luis G. Rosa,^{*,†,‡,§} Jinyue Jiang,^{||} Freddy Li Wong,^{†,‡} Jie Xiao,[§] Emmanuel Utreras,^{†,‡} Ocelio V. Lima,^{||} Jose Alvira,^{†,‡} Ya. B. Losovyj,^{§,⊥} and Li Tan^{||}

Department of Physics and Electronics, University of Puerto Rico-Humacao, 100 Road 908 CUH Station, Humacao, PR 00791, Institute for Functional Nanomaterials, University of Puerto Rico-Rio Piedras, Facundo Bueso Building, Rio Piedras, PR 00931, Department of Physics and Astronomy and the Nebraska Center for Materials and Nanoscience, University of Nebraska-Lincoln, P.O. Box 880111, Lincoln, Nebraska 68588-0111, Department of Engineering Mechanics, W306 Nebraska Hall, University of Nebraska, Lincoln, Nebraska 68588-0526, and Center for Advanced Microstructure and Devices, Louisiana State University, 6980 Jefferson Highway, Baton Rouge, Louisiana 70806

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Franck–Condon coupling to the electronic structure of anthracene silane isomer complexes self-assembled on a silicon oxide surface has been measured by high-resolution photoelectron emission spectroscopy. Our results are in strong agreement with theoretical semiempirical calculations and gas phase measurements. The Franck–Condon vibronic fine structure observed in the high resolution photoemission spectra exhibits a strong dependence on the isomer, in particular, the anthracene functional group orientation with respect to the surface normal.

Introduction

In recent years, Franck–Condon coupling of the vibrational structure on the electronic spectra for an organic polymer system has been obtained^{1–3} for systems with large dipoles and a strong preferential orientation along the surface normal. The existence of vibrational fine structure contribution to the photoemission spectra has been long recognized experimentally for gas phase and adsorbed molecules,^{4–9} but symmetry selection rules that can be attributed to the electronic initial states symmetry have been hard to demonstrate for adsorbed molecular systems until recently.¹ In general, for large molecular systems and solids, vibrational coupling within the valence band electronic structure has proven to be difficult to observe by ultraviolet photoemission (UPS).^{6,10,11}

The Franck–Condon principle requires an electronic transition that takes place almost instantaneously on the time scale of the vibration, implying a nearly constant value of the internuclear separation. To be able to observe the vibronic coupling to the electronic spectra is necessary to have a system with a sufficiently large electronic band gap that reduces the damping effects of the free electron density of states (DOS), as in metals, and further, the electronic state must share a common symmetry with the vibrational mode.

In this work we will examine the effects of structural symmetry and selection rules on the Franck–Condon coupling on a photoemission fine structure for (4-(anthracen-2-yl)butyl)diethoxy(methyl)silane and (4-(anthracen-9-yl)butyl)diethoxy(methyl)silane (referred to in this paper as vertical and horizontal anthracene isomers, respectively).

One of the general issues in molecular electronics is the transport through organic molecules. The study of the details of transport mechanisms in organic systems has demonstrated that, not only do interface dipoles and valence band electronic structure symmetry play a role, but that there is a strong dependence on molecular vibrations^{12–18} that couple to the transport properties through electronic structure. In the electronic excitation processes that occur in organic semiconductors and dielectrics, the vibronic interactions resemble Franck–Condon coupling. High-resolution photoemission (HRUPS) is able to resolve the vibronic coupling and is a means to indirectly probe electron–phonon coupling in molecular systems that accompany electronic excitations.

The organic molecules (4-(anthracen-2-yl)butyl)diethoxy(methyl)silane and (4-(anthracen-9-yl)butyl)diethoxy(methyl)silane show vibronic coupling in the low valence band region measured by HRUPS. These molecules' main terminal group contains anthracene, a well-known organic semiconductor, which can be oriented as a functional end-group in two very different orientations, as schematically illustrated in Figure 1. By comparing the vibronic fine structure intensities for these different isomers, we are able to show a strong influence of initial state molecular orientation on the Franck–Condon vibronic fine structure. Unlike the prior study of the symmetry dependence of the vibronic fine structure in photoemission, the effects observed here are largely temperature independent and not as strongly affected by anharmonic in-plane vibrational modes.

Experimental Section

The polished p-type Si(100) wafers were precleaned to remove organic contamination particles and were immersed in piranha solution ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2 = 1:1$ by volume) to hydroxylate the silicon wafer surfaces, making them extremely hydrophilic. The native oxide surface was untouched by this procedure. The hydrophilic wafers were then immersed in a toluene solution

* Corresponding author. E-mail: luis.rosa13@upr.edu.

[†] University of Puerto Rico-Humacao.

[‡] University of Puerto Rico-Rio Piedras.

[§] Department of Physics and Astronomy and the Nebraska Center for Materials and Nanoscience, University of Nebraska-Lincoln.

^{||} Department of Engineering Mechanics, University of Nebraska-Lincoln.

[⊥] Louisiana State University.

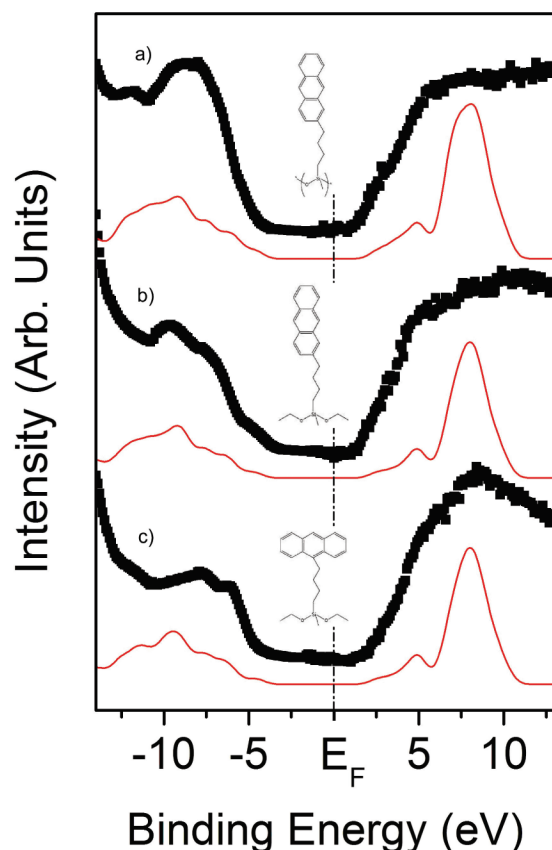


Figure 1. Combined UPS and inverse photoemission spectroscopy for (a) polymer system of (4-(anthracen-2-yl)butyl)diethoxy(methyl)silane thin film, (b) self-assembled monolayer (SAM) on silicon oxide of (4-(anthracen-2-yl)butyl)diethoxy(methyl)silane, and (c) SAM on silicon oxide of (4-(anthracen-9-yl)butyl)diethoxy(methyl)silane. For a, b, and c, respectively, the calculated DOS is shown (red lines).

of (4-(anthracen-2-yl)butyl)diethoxy(methyl)silane and (4-(anthracen-9-yl)butyl)diethoxy(methyl)silane, and the excess molecules were removed by rinsing and sonicating in a fresh toluene solvent. After repetition, the wafers were annealed at 50 °C in high humidity (~80% relative humidity) for 8 h and immersed once more in the same silane solution and rinsed and sonicated and then finally baked at 115 °C. The latter step aims to convert the hydrogen bonds of the adsorbed (4-(anthracen-2-yl)butyl)diethoxy(methyl)silane and (4-(anthracen-9-yl)butyl)diethoxy(methyl)silane to the silicon oxide surface to covalent bonds. The process from the first immersion until baking was repeated twice more, leading to a more complete filling of the monolayer molecular film.¹⁸

The 3 m normal incidence monochromator (NIM) at the Center of Advanced Microstructures and Devices, Baton Rouge, LA (CAMD), combined with a high-resolution angle-resolved ultraviolet photoemission (ARUPS) endstation, equipped with an electron energy analyzer (Scienta SES200 electron energy analyzer), is more than suitable for the HRUPS spectra, with a combined resolution of better than 10 meV,^{1,2} necessary for the identification of vibronic fine structure in photoemission. The NIM beamline consists of a water-cooled ellipsoidal entrance mirror with a 70 mrad acceptance angle for horizontal radiation from a dipole magnet at the CAMD, and spectra were taken at a photon energy of 21 eV.

Combined photoemission and inverse photoemission spectra were also obtained by means of a helium lamp He I radiation (21.2 eV) for the photoemission, with inverse photoemission spectra taken using a variable energy electron gun producing

TABLE 1: Comparison Table of the Calculated Modes (Frequency Units of cm^{-1}) for the Free Anthracene Molecule and the Horizontal Isomer of the Silane Complex

anthracene	horizontal molecule	symmetry
1828.72	1834.57	9 B3G
1819.80	1823.66	9 AG
1802.59	1800.56	8 B1U
1775.73	1775.67	9 B2U
1703.91	1706.69	8 B3G
1701.76	1715.33	8 AG
1653.05	1661.38	8 B2U
1563.67	1578.34	7 B1U
1516.61	1525.02	7 AG
1489.86	1485.75	7 B2U
1458.20	1471.58	7 B3G
1433.01	1491.40	6 B1U
1396.78	1715.33	6 AG
1218.60	1211.21	6 B3G
1119.78	1122.47	5 AG
1108.55	1112.86	4 B2U
1091.61	1089.54	4 B1U
1007.19	1026.16	2 B2U
975.57	977.39	6 B2G
907.54	912.17	3 B3G
546.168	574.45	2 B3G

electron kinetic energies from 5 to 20 eV, incident normal to the surface. Photons were detected by means of a Geiger–Muller detector, as done in previous studies.^{19,20}

Evidence of Vibronic Fine Structure on (4-(Anthracen-2-yl)butyl)diethoxy(methyl)silane and (4-(Anthracen-9-yl)butyl)diethoxy(methyl)silane. Combined photoemission and inverse photoemission of the (4-(anthracen-2-yl)butyl)diethoxy(methyl)silane and (4-(anthracen-9-yl)butyl)diethoxy(methyl)silane compounds are shown in Figure 1. These combined photoemission inverse photoemission spectra are in good agreement with expectations based on the calculated electronics structure of these anthracene silane compounds from NDO-PM3 (neglected differential overlap, parametric method 3), as seen in Figure 1. Geometric optimization of the system was performed by obtaining the lowest unrestricted Hartree–Fock (UHF) energy states. The calculated DOS, shown in Figure 1 (red lines), was obtained by applying equal Gaussian envelopes of 1 eV full width half-maximum to each molecular orbital (to account for the solid-state broadening in photoemission) and then summing. This model DOS is also combined with a rigid energy shift applied to the calculated electronic structure in large measure to account for the energy difference between the vacuum level and the chemical potential. We find that the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) gap is smaller for the species with a “vertical” anthracene functional of (4-(anthracen-2-yl)butyl)diethoxy(methyl)silane (Figure 1b) compared with the “horizontal” anthracene functional of (4-(anthracen-9-yl)butyl)diethoxy(methyl)silane isomer (Figure 1c). This suggests a stronger intermolecular interaction for the (4-(anthracen-2-yl)butyl)diethoxy(methyl)silane isomer or the “vertical” isomer.

The key goal is to identify differences in the vibronic fine structure associated with the anthracene functional of each isomer. In fact, differences are readily observed. Terminal groups attached to the ninth carbon of the (4-(anthracen-9-yl)butyl)diethoxy(methyl)silane isomer causes a shift in the IR modes, if compared to the (4-(anthracen-2-yl)butyl)diethoxy(methyl)silane isomer, whose IR vibrational modes are close to the gas phase theoretical values shown in Tables 1 and 2. Vibronic fine structure is evident in the HRUPS spectra as

TABLE 2: Comparison Table of the Calculated Modes (Frequency Units of cm^{-1}) for the Free Anthracene Molecule and the Vertical Isomer of the Silane Complex

anthracene	vertical molecule	symmetry
1828.72	1828.007	9 B _{3G}
1819.812	1820.748	9 A _G
1802.585	1804.477	8 B _{1U}
17775.735	1777.759	9 B _{2U}
1701.761	1704.277	8 A _G
1653.051	1659.113	7 B _{1U}
1516.607	1528.901	7 A _G
1489.864	1512.541	7 B _{3G}
1458.196	1460.408	7 B _{3G}
1433.01	1432.32	6 B_{1U}
1396.779	1424.89	6 A _G
1218.607	1218.079	6 B _{3G}
1178.875	1185.25	5 B _{1U}
1124.179	1122.248	5 B _{2U}
1108.551	1097.69	4 B _{2U}
1044.463	1051.877	3 B _{2U}
975.5673	971.3102	6 B _{2G}
926.456	921.47	6 B _{3U}
915.1673	917.5866	3 A _G
674.9827	676.4628	2 B _{1U}
615.53	618.14	1 B _{2U}
546.168	539.3717	2 B _{3G}

shown in Figure 2, corresponding to final-state vibrational mode excitations in the infrared region of 1871 cm^{-1} (a vibrational energy of about 232 meV) for the horizontal and vertical anthracene compounds. This fine structure corresponds to the excitation of possibly several vibrational modes for each anthracene isomer compound, but is most apparent with the horizontal anthracene functional of the (4-(anthracen-9-yl)-butyl)diethoxy(methyl)silane isomer (Figure 2a). This vibronic fine structure can be better observed on the energy range of 6.7 to 10.7 eV binding energy in Figure 2.

The Franck–Condon coupling of this particular vibration into the electronic spectra is most likely ascribed to one dipole active mode. The mode measured for the horizontal and vertical anthracene compounds of 1871 cm^{-1} corresponds to a vibration intrinsic to the anthracene terminal of these anthracene silane complex isomers. The likely mode is a vibrational (C–C) stretching mode with a calculated value of approximately 1433

cm^{-1} for a single free anthracene molecule in the electronic ground state, and occurs at about 1491 cm^{-1} for the horizontal anthracene functional of (4-(anthracen-9-yl)butyl)diethoxy-(methyl)silane (Table 1) and 1432 cm^{-1} for the vertical anthracene functional of (4-(anthracen-2-yl)butyl)diethoxy-(methyl)silane (Table 2). In comparison with gas-phase photoelectron emission measurements, the HOMOs $D_0(^2B_{2g})$ and $D_2(^2A_u)$ measured by Sanchez⁴ and collaborators are coupled to the vibrations of 1548 cm^{-1} and 1492 cm^{-1} , respectively.

The free molecule semiempirical calculation shows shifts of 380 cm^{-1} (horizontal) and 438 cm^{-1} (vertical) with respect to the value obtained from the vibronic fine structure in HRUPS spectra of the anthracene silane isomers. In a similar manner, the gas phase measurement⁴ shows a shift of 323 cm^{-1} for $D_0(^2B_{2g})$ and 379 cm^{-1} for $D_2(^2A_u)$ with respect to the value measured in the HRUPS (1871 cm^{-1}) of the silane complex SAM layers. The differences in the values could be ascribed to the formation of a temporary positive ion on the anthracene end group of the silane compound, causing a stiffness of the vibrational mode energy to measured higher values.^{1,2} This correction to the photoemission spectra is a result of a photohole left from the photoemission process, caused by a hole vibrational coupling as in the dipole-mode excitation observed for the polymer poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)].^{1,2}

The Role of Structural Symmetry and Selection Rules. A striking difference is observed in the vibronic fine structure in HRUPS, due to the Franck–Condon coupling, for the two isomers of the anthracene derivatives. As seen in Figure 2, the relative amplitude of the vibronic fine structure due to Franck–Condon coupling is far stronger for the horizontal anthracyl silane complex isomer, and is suppressed for the vertical anthracyl silane isomer complex, as noted above. Since the synchrotron light source is highly plane polarized with an incidence angle of 45° , it is possible to observe that selection rules play a role in the photoemission spectra due to the different anthracene orientations, with respect to the surface normal, of these two isomers.

The Franck–Condon coupling measured in Figure 2 originated from the vibrational mode 1871 cm^{-1} , which corresponds to the theoretical value of 1433 cm^{-1} and an irreducible representation of B_{1u} of the D_{2h} point group of the free anthracene calculation. The dynamic of vibration is illustrated in the Figure 2 inset, a vibration which is along the anthracene minor axis (z axis or along the surface normal) of its molecular structure. In order to account for the contribution of symmetry to this measurement, the dipole transition matrix element is split in two contributions: the electronic dipole (d_e) transition matrix plus the molecular dipole (d_N) transition matrix. This can be written as

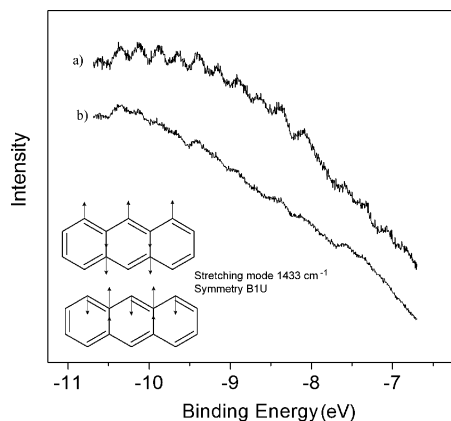


Figure 2. HRUPS spectra of (a) (4-(anthracen-9-yl)butyl)diethoxy-(methyl)silane (horizontal) and (b) (4-(anthracen-2-yl)butyl)diethoxy-(methyl)silane (vertical), measured from -6.7 to -10.68 eV binding energy. Inset shows the dynamic of the C–C stretching vibrational mode 1433 cm^{-1} of the calculated free anthracene molecule. The mode oscillations are along the z axis of the molecule, which has an assigned symmetry of B_{1u} , an irreducible representation of the D_{2h} point group.

$$\langle \psi'_e \psi'_v \psi'_s | d | \psi_e \psi_v \psi_s \rangle = \langle \psi'_e \psi'_v \psi'_s | d_e + d_N | \psi_e \psi_v \psi_s \rangle$$

$$\underbrace{\langle \psi'_e | d_e | \psi_e \rangle}_{\text{Electronic Orbital Selection Rules}} \underbrace{\langle \psi'_v | \psi_v \rangle}_{\text{Franck-Condon factor}} \underbrace{\langle \psi'_s | \psi_s \rangle}_{\text{Vibrational Structure Selection Rules}} + \langle \psi'_e | \psi_e \rangle \underbrace{\langle \psi'_v | d_N | \psi_v \rangle}_{\text{Vibrational Structure Selection Rules}} \underbrace{\langle \psi'_s | \psi_s \rangle}_{\text{Vibrational Structure Selection Rules}}$$

The suppression and enhancement of the vibronic fine structure in the observed photoemission spectra (Figure 2) of the electronic structure is due to the vibrational selection rules that are applied to the molecular dipole transition matrix $\langle \psi'_v | d_N | \psi_v \rangle$. The radiation polarization along the z axis makes our dipole operator d_N of B_{1u} symmetry: this irreducible representation symmetry is in terms with z parallel to the anthracene plane. On the other hand, for light polarization

parallel to the surface or along the x -axis, our dipole perturbation operator acquires B_{3u} symmetry.

For this particular Franck–Condon coupling with the vibrational mode 1871 cm^{-1} (associated with the theoretical value of 1433 cm^{-1} in the electronic ground state), our initial vibrational wave function has an irreducible representation of B_{1u} . It should be noted that, with respect to the surface normal, the direction in which the photoelectrons are collected, the final state irreducible representation is B_{1u} or A_{1u} : the necessary change of coordinate systems with respect to the surface normal and the normal to the anthracene plane makes the B_{1u} symmetry of anthracene an allowed final-state symmetry and an allowed transition. For light polarization parallel to the surface (or along the x axis) the dipole operator acquires a B_{3u} irreducible representation symmetry. As a consequence, the dipole operator is orthonormal to B_{1u} of the initial and final state of the vibrational wave function, and this transition $\langle \psi_f | d_N | \psi_i \rangle$ is not allowed, corresponding to the observed reduction of intensity in the vibronic fine structure observed in the HRUPS spectra of the vertical anthracene silane isomer complex.

Summary

Organic semiconducting systems, such as anthracene, on the other hand, are characterized by their high degree of electron localization and molecular polarization that dominates the physics of excited states and transport phenomena. These organics have small intermolecular overlap, low dielectric constant, localized charges on individual molecules, and large polarizabilities involving charges and induced and permanent electric dipoles.^{21–24} This can be enhanced by suitable functionalization, as we have demonstrated here for the horizontal and vertical anthracene isomers of the silane complexes (Figure 1).

There is one vibrational mode that contributes to the Franck–Condon coupling of the electronic structure spectra for (4-(anthracen-2-yl)butyl)diethoxy(methyl)silane and (4-(anthracen-9-yl)butyl)diethoxy(methyl)silane. As a result of the structural orientation adopted by these anthracene compounds on the surface, one expects to observe an enhancement of intensity of the fine structure features for the (4-(anthracen-9-yl)butyl)diethoxy(methyl)silane and a intensity suppression for the (4-(anthracen-2-yl)butyl)diethoxy(methyl)silane. We associate this difference in the spectra with the initial state symmetry conditions and selection rules from the molecular dipole transitions.

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