

Characteristic Electronic Structures of Organic Solids Classified in Terms of Molecular Electronic Relaxation

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Organic solids can be grouped into three classes in accordance with their characteristics of the electronic structure in terms of molecular electronic relaxation, which is examined using ultraviolet photoelectron spectroscopy (UPS). The molecular identity is preserved in weakly bound solids, where the polarization energy for a molecular ion in them works as a key parameter determining the energy levels in the solid. In mesoenergetically bound solids it is reduced and quasi-delocalized electronic states are realized. In strongly bound solids an anisotropic energy band formation is confirmed by angle-resolved UPS.

Keywords: Molecular solid/ UPS/ Polarization energy/ Delocalization/ Energy dispersion

The electronic structure of organic molecular and polymeric solids are characterized by the fact that their constituent has structural and/or electronic 'molecular identity' more or less. In other words, those solids consist of molecular units. Here we do not restrict the meaning of the word a 'molecular unit' only to a practical molecule, but extend it even to an undefined entity such as a repeating unit in a polymeric chain. On the basis of such an idea of the molecular unit, organic solids can be grouped into three classes in terms of the molecular electronic relaxation in them, which is examined by ultraviolet photoelectron spectroscopy (UPS) [1].

The first group of materials are typical molecular solids, in which molecular units identical to constituent molecules are bound by a weak intermolecular interaction or the van der Waals force. The molecular identity is preserved most obviously in these solids, the energy levels of which are settled by the polarization energy evaluating the degree of electrostatic stabilization for an extra charge

on a constituent molecule induced on its surrounding molecules. These solids are recognized by their UPS spectra whose features correspond well to those of the constituent molecule in the gas phase. The polarization energy, represented in the first approximation by a simple relation comprising a mean molecular polarizability and a molecular packing density in the solid, can disclose the energy structure with relation to the intermolecular interaction when it is examined more carefully. Thus the polarization energy works as the key parameter in the weakly bound organic solids.

The second group of materials are mesoenergetically bound systems, in which some inter-unit or intermolecular interactions extra to the van der Waals force work efficiently in the solid or the molecular identity is reduced to some extent to form quasi-delocalized electronic states over the molecular unit. These systems show a poor correspondence of UPS spectral features between the gaseous and solid states and are

INTERFACE SCIENCE —Molecular Aggregates—

Scope of research

The research at this subdivision is devoted to correlation studies on structures and properties of both natural and artificial molecular aggregates from two main standpoints: photoelectric and dielectric behaviors. The electronic structure of molecular and/or polymeric thin films is studied in connection with the former, and its results are applied to create novel molecular systems with characteristic functions. The latter is concerned with heterogeneous structures in microcapsules, biopolymers, biological membranes and biological cells, and the nonlinearity in their dielectric properties is also studied in relation to molecular motions.



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characterized by an only apparently large polarization energy. The polarization energy, however, has no longer original physical meaning, and should be regarded as the solid-state relaxation energy including the contribution from additional interactions which are not observed in the weakly bound systems. Such additional inter-unit interactions are caused by 1) a multipole interaction, 2) a charge-transfer interaction, 3) a valence electron mixing, and so on. Now that these interactions are found to work efficiently, those systems have high potentialities to exhibit novel and/or eminent physical properties. As an example of so-called molecular design in expectation of an additional interaction working in the crystal, polythienoacenes are synthesized and examined [2, 3].

As the last group of organic systems classified here, strongly bound ones will be referred. Strong inter-unit interactions with a high anisotropy are characteristic of these systems, which consist predominantly of organic polymeric solids and include a few organic molecular solids confirmed so far [4]. Such systems often show the energy dispersion along the strongly coupled direction, e.g., one-dimensional energy band formation along the chain axis of long-chain alkanes, as could be examined by

the angle-resolved ultraviolet photoelectron spectroscopy (ARUPS). Further, electronic relaxation energies in these systems are evaluated to be no less than those of mesoenergetically bound systems [5].

Thus, the magnitude and the dimensionality of inter-unit interactions will determine the nature of a particular system concerned. Information on the electronic structure of organic solids is therefore useful in developing new organic-based molecular systems with a view to realizing molecular electronic devices.

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The Scanning Dielectric Microscope

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A new instrument has been developed to image the local capacitance (or permittivity) and conductance (or conductivity) of colloidal particles and membranes in an aqueous environment.

Keywords: Dielectric image/ Dielectric relaxation/ Capacitance/ Conductance/ Colloidal particle/ Membrane

Electrical properties of colloidal particles including biological cells have been extensively studied by the dielectric technique referred to as suspension method. The method provides average electrical properties of colloidal particles which are extracted from the dielectric data of their suspension using an appropriate dielectric mixture equation. This method, however, is difficult to characterize individual particles. Hence, a new dielectric technique, termed scanning dielectric microscopy, has been developed. Capacitance and conductance are measured by the three-terminal method with a coaxial probe electrode, which is laterally scanned over samples on a plate electrode. The images of the local capacitance and conductance are obtained at frequencies between 1 kHz and 10 MHz, which enables the study of dielectric relaxation of individual particles and local areas of membranes.

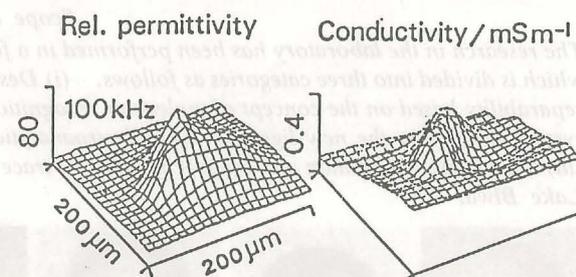


Figure 1. Dielectric images of a cultured MDCK cell in 0.3 M mannitol obtained at 0.1 MHz. The image area is 200 mm by 200 mm.