Temperature-Dependent Ultraviolet Photoemission Linewidths of Molecular Solids: Isopropyl Benzene

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The temperature (T) dependence of the width of the first ionization potential of condensed films of isopropyl benzene has been measured by ultraviolet photoelectron spectroscopy with use of synchrotron radiation. Over the range $15°K \lesssim T \lesssim 150°K$, the linewidth exhibits the form $\delta^2(T) = \delta^2(0) + c^2T$, where $c = 4.4$ (± 0.8) $\times 10^{-2}$ eV/(°K)$^{1/2}$. This T dependence originates from the interaction of the photogenerated localized molecular hole states with low-energy vibrational modes of the film.

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In this Letter we report the first observation of the temperature dependence of a linewidth in the ultraviolet photoelectron spectroscopy (UPS) of a condensed organic molecular solid. The origin of the surprisingly large (~1 eV) widths of valence-electron photoemission lines from molecular solids has been a puzzle for many years,[1-5] and only recently has been identified with variations in the relaxation energies of localized photo-generated hole states.[3-5] The detailed microscopic origin of these variations has remained a mystery, however, because both site-to-site alterations in local environment[3,4] and the interaction of the photoinduced holes with longitudinal polarization fluctuations[1,2] can generate suitable changes in the relaxation energies. In this paper we report a study of the dependence on the temperature, T, of the full width at half maximum, $\delta(T)$, of the first ionization potential of isopropyl benzene, $C_6H_5CH(CH_3)_2$. The results, i.e., $\delta^2(T) = \delta^2(0) + c^2T$, $c = 4.4$ (± 0.8) $\times 10^{-2}$ eV/(°K)$^{1/2}$, permit us to identify the zero-temperature residual 0.4 eV $\lesssim \delta(0) \lesssim 0.6$ eV as being caused by site-to-site relaxation-energy variations whereas the T-dependent contributions are accounted for by the interaction of the photogenerated holes with vibrational modes of the isopropyl benzene film. These results constitute the first experimental verification of hole-vibration coupling as a major contributor to the widths of valence-electron photoemission lines from molecular solids.

The measurements were performed with use of the University of Pennsylvania angle-resolved photoelectron spectrometer at the University of Wisconsin Synchrotron Radiation Center. A liquid helium cryostat allowed sample temperatures to

be varied over the range $15°K \lesssim T \lesssim 600°K$. The spectra were obtained at 32 eV photon energy, where the combination of the toroidal grating monochromator and synchrotron light source has a maximum photon flux. The data presented here correspond to light incident at 45° to the sample normal, the light vector $\vec{A}$ in the plane of incidence, and the electrons collected in a direction parallel to the vector $\vec{A}$, i.e., at about 45° to the sample normal and about 90° relative to the incident light direction. To monitor the vapor deposition of the sample, a slightly different geometry, illustrated in the inset in Fig. 1, was used. Data were recorded digitally by multiple scanning with a Tracor Northern multichannel analyzer.

Isopropyl benzene, $C_6H_5CH(CH_2)_3$ or cumene, was used as received from Aldrich Chemical. A vapor of isopropyl benzene was exposed to a palladium surface which had been cleaned by standard sputtering and annealing techniques. The Pd substrate was mounted directly on the end of a special helium Dewar in the vacuum chamber and was cooled by liquid He from a transfer tube. Temperatures were monitored by a thermocouple spot welded directly onto the surface of the metal crystal substrate. A low temperature of $T = 15$ °K could be reached, and by adjusting a flow of cold He gas, temperatures up to about 200 °K could be maintained. The base pressure of the spectrometer with all components at room temperature was 1×10^{-10} Torr, while when the Dewar column was cold, pressures below 5×10^{-11} Torr (nude ion gauge) were obtained.

In order to make a condensed molecular film of isopropyl benzene on the Pd substrate, repeated exposures were made with the substrate
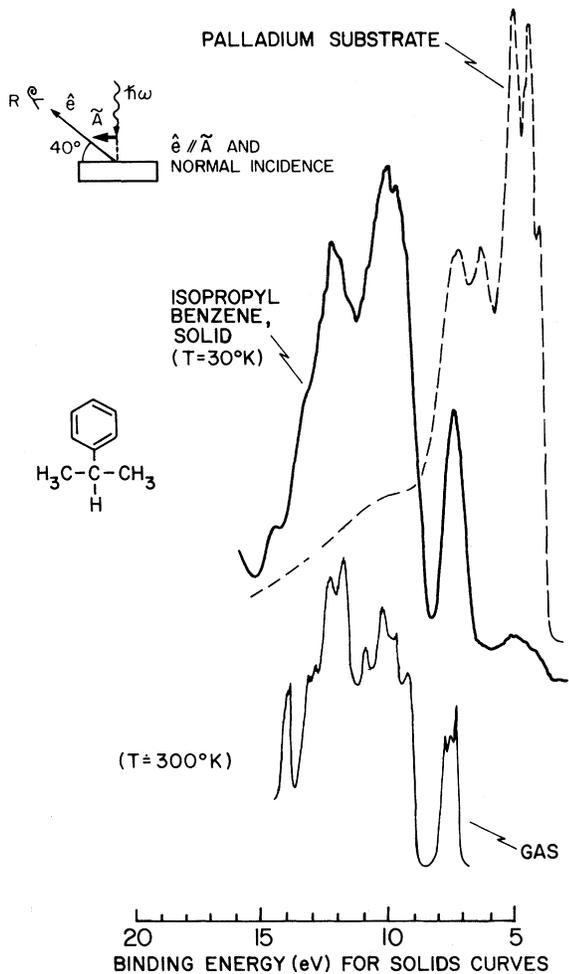
FIG. 1. From top to bottom are shown the UPS spectra of the clean palladium substrate, of a molecular solid thin-film sample of isopropyl benzene, and of isopropyl benzene in gas phase (redrawn from Ref. 7). The photon energies are 32, 32, and 21.2 eV, respectively. The scale is for the solid-state spectra and should be shifted to read higher building energy by 1.5 eV for the gas-phase spectrum. The isopropyl benzene film in this case is only about 15 Å thick, and consequently the Pd d band can still be seen. The data of Fig. 2, however, are for approximately 25-Å-thick films.

at about 30 °K and a vapor pressure of isopropyl benzene at 1×10^{-7} Torr. Typically 20 L (langmuir) total exposure was necessary to reduce the Pd d-band emission to about 0.2% of its original intensity (1 L = 10^{-6} Torr sec). The d-band attenuation was used to estimate the overlay thickness. Using a photoelectron escape depth[4,6] of $\lambda = 4$ Å, the films were estimated to be 15–25 Å thick.

The UPS spectrum for a 15-Å-thick film of
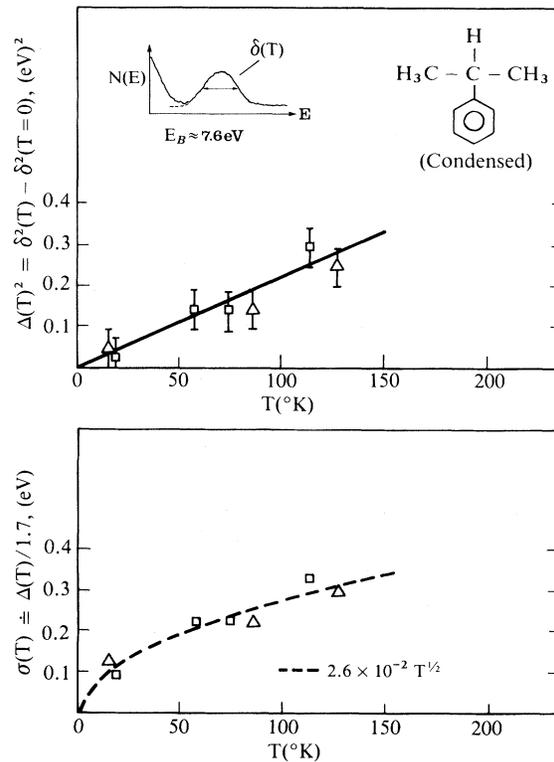
FIG. 2. The square of the experimental temperature contribution to UPS linewidth, $\Delta^2(T)$, is plotted as a function of temperature for two totally independent runs (triangles and squares) in the top panel. The large error bars reflect the signal-to-noise ratio relative to the magnitude of the total observed linewidths. In the lower panel, a dashed line is drawn for the standard deviation of a Gaussian linewidth, σ, using the slope from the upper panel, where $\sigma = 2.6 \; (\pm 0.5) \times 10^{-2} T^{1/2}$. The linewidth data points plotted in the lower panel show consistency with the $T^{1/2}$ behavior predicted by a molecular-ion model calculation (Refs. 1 and 2).

isopropyl benzene at 30 °K is shown in Fig. 1. Also shown in the figure is the clean Pd substrate signal obtained at 32 eV photon energy, and the gas phase isopropyl benzene UPS spectrum[7] obtained at 21.2 eV photon energy. The data on the temperature dependence of the width of the first ionization potential (at about 7.6 eV) from approximately 25-Å-thin films of isopropyl benzene are summarized in Fig. 2. The data are analyzed by assuming that the observed full width at half maximum is given by the square root of the sum of the squares of the individual contributions to $\delta(T)$:

$$\delta(T) = \left[\Delta_N{}^2 + \Delta_{res}{}^2 + \Delta_0{}^2 + \Delta^2(T) \right]^{1/2}, \qquad (1)$$

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where Δ_N is the 0.65 eV linewidth of the peak in the gas phase[7]; Δ_{res} is the instrumental resolution estimated at 0.1 eV from the width of the Fermi level of the clean metal substrate; $\Delta(T)$ is the T-dependent contribution that is extracted from the data; and Δ_0 is a residual T-independent solid-state contribution obtained by extrapolating to $T = 0$. We plot $\delta^2(T)$ vs T, extrapolate to $T = 0$, and then subtract $(\Delta_{res}^2 + \Delta_N^2)^{1/2} = 0.71$ eV in order to determine Δ_0^2. We find $\Delta_0 \simeq 0.4$ eV, but somewhat dependent upon the vapor deposition conditions. For example, slow, multiple exposures to total about 20 L yield $\Delta_0 \simeq 0.4$ eV. However, a fast 20-L exposure yielded $\Delta_0 \simeq 0.6$ eV. This latter case most probably corresponds to a greater degree of molecular disorder in the resultant sam-sample. After determining the specific Δ_0^2 contribution for each separate run, the data are plotted as $\Delta^2(T) = \delta^2(T) - \delta^2(T = 0)$ in Fig. 2 for two totally independent runs. The data can be converted to the standard-deviation parameter of a Gaussian curve, σ, and plotted as a function of T, as also shown in Fig. 2, with $\sigma(T) = \Delta(T)/(2 \ln 2)^{1/2}$. If one takes the square root of the slope of the $\Delta^2(T)$ curve, a plot of $\sigma = 2.6 \, (\pm 0.5) \times 10^{-2} T^{1/2}$ is found to be consistent with the data as shown in Fig. 2(b).

A linear temperature dependence of $\Delta^2(T)$ is predicted by any model in which a low-frequency vibrational mode, $\hbar\omega \ll kT$, is strongly coupled to the molecular-ion state.[8-12] The most obvious such coupling, however, is to intramolecular modes, a phenomenon which causes structure in photoionization lines in the gas phase as well as the condensed phase.[2,10,13] Evaluation of the relevant coupling constants for benzene-based molecular ions[13] suggests that the coupling to the intramolecular modes is too weak to explain quantitatively the coefficient of T in $\Delta^2(T)$, i.e., the observed value of c^2, although we cannot experimentally exclude this coupling mechanism. The most probable mechanism, therefore, is the coupling of the molecular-ion state to dipole-active normal modes of neighboring via long-range Coulomb interactions.[1] The consequences of this interaction can be described by a generalization of the Huang-Rhys model.[14,15] The Huang-Rhys model has been applied previously to interpret x-ray photoemission spectroscopy studies of alkali halides,[9] and small molecules adsorbed or condensed onto the surfaces of metals.[11,12] The generalized model was developed to interpret UPS spectra of aromatic pendant group polymers.[1,2,5,13,16,17] A numerical estimate, based upon utilizing the known vibrational parameters

of benzene molecules in this model, yields a σ value for a Gaussian linewidth of $\sigma = 4 \times 10^{-2}$ eV/$(°K)^{1/2}$, which corresponds to a full width at half maximum of about 6.8×10^{-2} eV/$(°K)^{1/2}$ for condensed molecular solid films of benzene.[16] From the close correspondence between the experimental value and numerical estimate, we infer that coupling of a given isopropyl benzene molecular ion state to infrared active vibrations involving neighboring neutral isopropyl benzene molecules is the most probable cause of the observed temperature-dependent linewidth.

Finally, we attribute the origin of the temperature-independent residual solid-state broadening, 0.4 eV $\lesssim \Delta_0 \lesssim 0.6$ eV, to spatial variations in the electronic contributions to the intermolecular relaxation energies in the vicinity of the surface.[3-5] There are two sources that contribute: (1) the depth-dependent effect, where surface molecules experience a lower value of the intermolecular relaxation energy gas-to-solid spectral shift because of the existence of a smaller number of nearest neighbor molecules[3,4]; and (2) the local site-to-site variations in ion-state energies due to nonequivalent local environments in the non-single-crystalline film.[2,5] In (1), a study involving anthracene molecules yielded an intermolecular relaxation energy of 1.2 eV for surface molecules and 1.5 eV for molecules in the bulk.[4] Thus, a contribution on the order of 0.3 eV is expected, which can be subtracted appropriately from Δ_0. The remaining 0.25 to 0.5 eV for Δ_0 is collected into effect (2), which seems reasonable considering that the value is found to be dependent upon sample preparation. Similar widths have been observed in a variety of other contexts, including condensed thin films of N_2 and CO molecules[18] and the submonolayer adsorption of these molecules on metal surfaces.[19] Interatomic Auger and electron-hole shakeup processes have been found to be too small to account for the observed widths in these cases,[18,20,21] in which a temperature dependence was not investigated. Such processes are expected to occur for inner valence orbitals and not for the outermost ionization potential studied here. Thus, spatial variations in the relaxation energies are the only extant interpretation of the temperature-independent (inhomogeneous) broadening.

In summary, we have observed a temperature-dependent contribution to the UPS linewidth of the lowest–binding-energy state of condensed molecular solid films of isopropyl benzene. This contribution is caused by the interaction of the photo-

induced holes (molecular cations) with low-energy vibrational modes of the isopropyl benzene film. The modes involved are those which correspond to longitudinal polarization fluctuations in the molecular solid film. A temperature-independent contribution to the linewidth also was observed, which we attribute to the inhomogeneous line broadening caused by spatial variations in the relaxation energies in the vicinity of the molecular solid surface, as well as site-to-site variations in local cation environment.

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Long-Wavelength Surface Spin Waves on Antiferromagnets

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The first discussion of a long-wavelength, magnetostatic, surface spin-wave mode on uniaxial antiferromagnets is presented. In the absence of an applied field, the frequency of the surface wave depends on the angle between the direction of propagation and the easy axis. With a magnetic field applied parallel to the surface, and along the easy axis, the surface mode does not propagate in all directions, but is limited to a restricted set of angles.

Recent Brillouin-scattering experiments[1-3] have elegantly probed the properties of the Damon-Eshbach[4] (DE) mode. The DE mode, a long-wavelength surface spin wave on ferromagnets, is interesting because of its unusual properties. For instance, the DE mode does not propagate in all directions, but is restricted to a specified set of angles with respect to the magnetic field. This is nicely demonstrated in the light-scattering experiments and has also been examined theoretically.[5,6]

The properties of the DE mode are governed, not by the short-range exchange interaction, but by macroscopic dipole fields set up by the motion of the spins precessing around the magnetic field. These dipole fields are calculated through the use of the magnetostatic form of Maxwell's equations, and thus the resulting spin waves are often known as magnetostatic modes. When one considers the unusual properties of the DE mode, it is sur-