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A particularly interesting class of organic solids are the polydiacetylenes. The most heavily studied of these is poly-2, 4-hexadiyne-1, 6 diol bis (*p*-toulene sulfonate), PTS. In solid PTS, lack of effective cross linking between polymers chains renders it a nearly one-dimensional system for electron transport. The evaluation of wave functions for this system requires data on its electronic energetics. Although the bandgap (E_g) of PTS is known to be 2.1 ± 0.1 eV,[1] its ionization energy I_c (determined from ESCA) has been reported to be 7 ± 1 eV.[2,3] This measurement gives PTS a considerably higher electron affinity (A_c of 5 ± 1 eV) than is normally associated with conjugated organics. Recent *ab initio* calculations[4] indicate that PTS should be far from irregular with A_c ~3 eV. In addition, the observation that Na injects electrons into PTS with an activation energy of 0.2 eV[5] implies $I_c \gtrsim 4.5$ eV. Clearly, still another measurement of I_c is appropriate.

Instead of ESCA, which contains intrinsic problems for insulators, we have chosen to use the Millikan–Pope–Arnold technique (MPA).[6] Through this technique, one obtains the ionization energy of a levitated microcrystal. Since this approach is electrodeless, it avoids contact potential problems associated with ESCA, and, in as much as the levitated crystal can be negatively charged, retardation effects due to the positive surface charge buildup associated with ESCA are reduced. There are inherent problems associated with knowing the orientation of the crystallite; however, orientation is not expected to perturb I_c significantly. The character of the photoemission onset may change with orientation since the probability of escape for an internally ionized electron is expected to be anisotropic in a system such as PTS, and the orientation of the crystallite with respect to the exciting light is presently unknown.

The microcrystals used in the photoemission experiments were prepared by grinding a diacetylene crystal and polymerizing the powder under 200 Torr N_2.[7] Aside from the polymerization step, the same procedure has been used in preparing molecular crystals of polyacenes for which reasonable ionization energies are obtained.[6]

Since the yield at onset of ionization is understood to be[8]

$$Y \propto (E_p - I_c)^n , \qquad (1)$$

log Y vs $(E_p - I_c)$ should give a straight line. Individual best fits were obtained on each of five particles (particle size ~ 20 μ), from which we arrived at a mean value for I_c of 5.2 ± 0.1 eV and an exponent of $n = 2.8 \pm 0.2$. The uncertainty in these values represent the standard deviation of the mean. Some particles showed a tail in the excitation spectrum. Figure 1 is an example of the excitation spectrum for such a particle. As one can see, even in this case most of the data can be fit to an ionization energy of 5.2 eV with an exponent of approxi-

mately 3. Unfortunately, the signal in the region of the tail was insufficient for establishing its origin.

We conclude that the results of the MPA technique on PTS support an ionization of 5.2 ± 0.1 eV, in agreement with recent calculations.[4] An exponent of 3 is not expected in such a broad band system unless the transition is indirect.[9] However, such an exponent has been observed in photoconductivity experiments and explained from the standpoint of an indirect transition.[1]

It is interesting to note that the yield found in PTS at 0.4 eV beyond threshold was approximately 1/20 of the yield 0.4 eV beyond threshold in anthracene. This small yield may be expected from the relatively small density of states at the valence band edge in PTS. Knecht[2] has reported a 5 eV width for the valence band in PTS, as compared with a bandwidth < 0.1 eV for anthracene.

The correspondence between theory and experiment in PTS suggest that the MPA technique can be used for examining the effect which changes in the polymeric backbone have on ionization energy. It is well known that changing the substituent groups on the diacetylenes can perturb the backbone from acetylenic to butatrienic.[10] The effect which various substituents have on the ionization energy of the polydiacetylenes is currently under investigation in our laboratory.
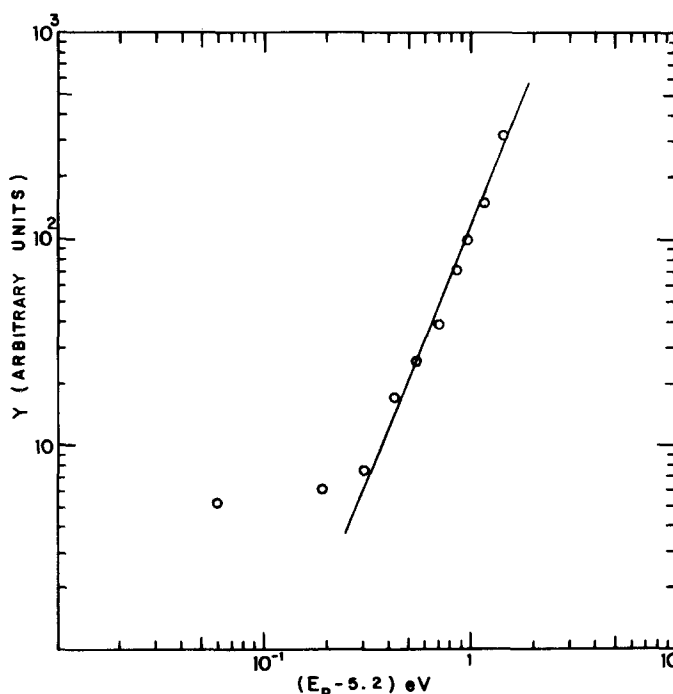
FIG. 1. The photoelectric yield Y from PTS vs $E_p - 5.2$ eV.

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The stability of the phase III structure in solid CH₄–CD₄ mixtures

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The understanding of the complex solid methane system (CH_4, CH_3D, CH_2D_2, CHD_3, CD_4) had advanced rapidly in recent years.[1] With the exception of CH_4, all of the methanes have three solid phases at zero pressure.[2] The highest temperature phase (I) is a fcc structure with no orientational order, while the next phase (II) is a partially ordered fcc phase with only two of the eight sublattices orientationally disordered.[3] The exact structure of the lowest temperature phase (III) is not known, and efforts to determine it have been hampered by the absence of a stable phase III in CH_4. Phase III in CH_4 can, however, be stabilized by the application of a pressure of ~500 bar at 10 K.[4] Direct structure determinations on single crystals of phase III CD_4, using neutron diffraction,[5] and on powders using x-ray diffraction[6] have suggested different space groups, but both do indicate that the lattice has undergone a tetragonal distortion.

The determination of the structure of phase III and of its relationship to phase II, if any, are two of the major problems remaining in the study of the solid methanes. The extent to which phase III in CH_4 can be stabilized by the addition of CD_4 should provide some insight to these problems. The low temperature phase diagram of CH_4–CD_4 has been partially investigated previously[7] but experimental limitations prevented the completion of the diagram. Unfortunately, the unaccessible portion of the diagram was the region where the phase II to phase III phase line must show some abnormal behavior. The current experiments explore, in detail, this region at low CD_4 concentrations (< 30% CD_4).

The locations of the phase boundaries were determined by a sensitive heating curve method which can detect enthalpy changes of the order of 0.5 J/mol. The temperature was measured with a four lead, calibrated, germanium resistance thermometer.[8] The experiments were all performed at constant power, the level of which was adjusted such that the sample warmed from 4.2 to 25 K in approximately 4 h. The samples used were quite large (~0.03 mol) and all mixtures were prepared in a high vacuum system using high purity CH_4 and CD_4 that was 97% deuterated.[9]

The phase diagram is shown in Fig. 1. The earlier, more limited results agree well with the present data.

The I–II phase transition varies smoothly with composition and this has been shown to be consistent with the best theoretical model for the solid methanes—the extended James and Keenan model (EJK).[10] The behavior of the II–III phase transition is not so straightforward to interpret.

As the CD_4 concentration is decreased, the II–III transition temperature drops and the enthalpy change associated with the transition decreases rapidly. For CD_4 concentrations below 15 mol%, phase III appears to be metastable. The phase line below 15% CD_4 concentration, shown in Fig. 1, is only obtained if the sample is cooled rapidly from phase I (~25 K) to 4.2 K and the heating curve started immediately. The longer a sample stays at 4.2 K, the smaller the observed enthalpy change at the II–III transition becomes until finally it disappears. The transition temperature and the shape of the anomaly do not change appreciably during this process. The time constant associated with the metastability decreases from several hours for a 12.5 mol% CD_4 sample to a few minutes for a 2 mol% sample. A hint of a II–III transition was also observed in
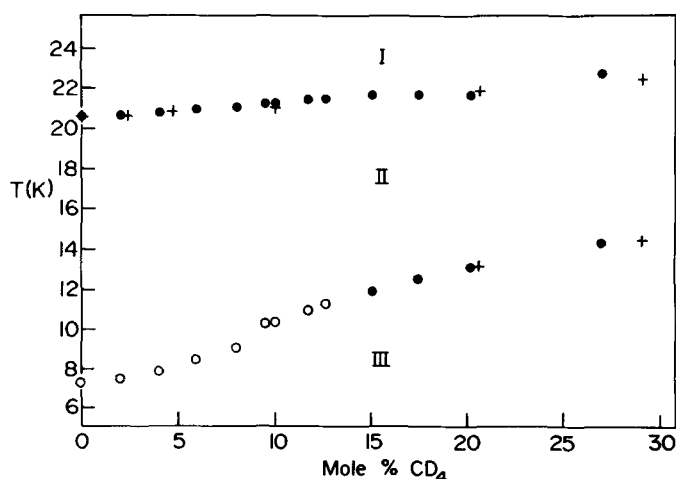

FIG. 1. The partial temperature–composition phase diagram for CH_4–CD_4 mixtures. ●, stable transition temperatures; ○, metastable transition temperatures; and +, transition temperatures from Ref. 7.

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