X-Ray Photoelectron Spectroscopy of Some β-Quinol Clathrates

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Summary The β-quinol clathrates of SO_2, MeCN, N_2H_4, H_2S, HCl, and Ar have been examined by XPS, and the valence band of the hydrogen chloride compound indicates substantial modification of the outer orbitals of HCl upon clathration.

THE β-quinol clathrates, first characterised by Powell,[1] form a convenient series for the study of small molecules by solid-state photoelectron spectroscopy. In these molecular compounds quinol (*p*-dihydroxybenzene) crystallises in the 'β-modification,' a large interpenetrating lattice held together by hydrogen bonds, and containing vacancies of the size required to enclose small gas molecules. *X*-Ray diffraction,[2] vibrational,[3] thermodynamic,[4] and n.m.r.[5] data have been used to investigate the interaction between the lattice and the guest molecule.

The clathrates were examined as fine powders in an AEI ES200B photoelectron spectrometer, using un-monochromatised Al-K_α radiation. Samples were cooled with liquid nitrogen and the spectra were recorded at pressures of *ca.* 10^{-7} Torr. The composition of the residual atmosphere within the sample chamber was monitored with an MAT AMP3 quadrupole mass analyser. Binding energy calibration of the spectra was effected either by taking the binding energy of the C(1*s*) line equal to 284·0 eV, or pressing samples onto Au foil and monitoring both the Au($4f_{7/2}$) peak (binding energy = 83·8 eV), and the core-level peak of interest, as the clathrate sample sublimed. Satisfactory analyses were obtained for all the compounds.

The valence band regions of the photoelectron spectra of β-quinol,[6] the β-quinol clathrate of hydrogen chloride, and gaseous HCl, all on the same energy scale, are shown in the Figure. The gaseous data, and the assignment of the molecular ions, are taken from the work of Turner *et al.*,[7] who used u.v. exciting radiation. Clearly the two intense peaks in the clathrate spectrum at binding energies of 10·0 and 16·2 eV must originate from the HCl, and the drastic modification of these valence orbitals implies a strong interaction between the guest molecule and the quinol cage. An X-ray structural analysis of this compound[9] could only be successfully refined using the space group $R3$, in contrast to the corresponding sulphur dioxide clathrate, which was solved[1] using the space-group $R\bar{3}$. This non-centrosymmetric space group in the HCl clathrate provides further evidence for a specific interaction.

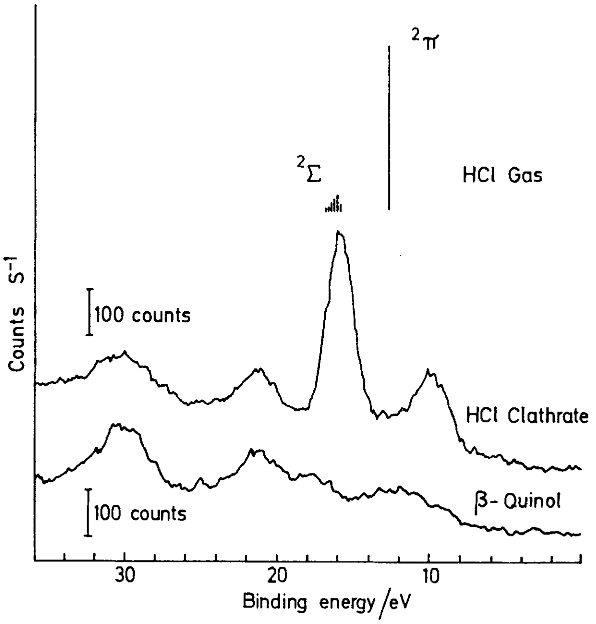

FIGURE. The valence band photoelectron spectrum of β-quinol (the empty cage structure), the hydrogen chloride clathrate (shown by analysis to have *ca.* 87% of available spaces filled with HCl), and a superimposed gaseous HCl spectrum of arbitrary absolute intensity (all to the same energy scale).

The volatility of the β-quinol clathrates (the quinol parent molecular ion $m/e = 110$ and the ion fragments $m/e = 81, 55, 54, 53$, and 39; together with the various guest molecule species, were detected in all cases), coupled with the high concentration of guest species in the solid clathrate, might suggest that a sufficient number of gaseous molecules are present in the region of the sample surface to yield a detectable photoelectron spectrum. We believe, however, that our measurements actually originate from guest molecules within the β-quinol framework for the following reasons: (i) the measured core-level for each guest molecule in the series studied has a PWHM (peak-width at half maximum) of the magnitude observed in solid state measurements; this increase over the gas-phase values[8] is probably due to polarisation of the core-level by the β-quinol lattice. (ii) The $S(2p)$ region of the photoelectron spectrum of the SO_2 clathrate develops an extra peak at *ca.* 4·5 eV lower binding energy from the original peak; since the intensity of this extra peak increases with time of exposure to the X-ray beam, we believe that this is due to photoreduction of the SO_2 molecule within the β-quinol cage.

We are extending these studies to include u.v. excitation and detailed calculation of the polarisation effect of the β-quinol cage on the valence levels of the guest molecule.

(*Received*, 25*th May* 1976; *Com.* 595.)

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