Anomalous Intensity Effects in the Matrix Isolated Infrared Spectra of Acrylic Acid and Related Compounds Produced by Traces of Nitrogen Impurity

By STUART W. CHARLES,* FRANCES C. CULLEN, and NOEL L. OWEN
(*School of Physical and Molecular Sciences, University College of North Wales, Bangor, Gwynedd* LL57 2UW)

Summary The presence of trace quantities of nitrogen or air produces dramatic intensity changes in some of the i.r. absorption bands of acrylic and acetic acids in argon matrices.

WE have recently studied the i.r. spectrum of monomeric acrylic acid in order to ascertain whether the *s-cis/s-trans* rotamer equilibrium, reported in the microwave studies,[1] can be detected by i.r. spectroscopy. The presence of dimeric forms of acrylic acid complicates the i.r. spectrum[2] and for this reason matrix isolation experiments, where the amount of dimer could be minimised, were carried out. Details of the results of these experiments will be reported elsewhere, but here we report an interesting observation arising from this work.

In our initial experiments, acrylic acid vapour was mixed with pure argon at various matrix ratios and deposited onto the precooled optical window of an ACL-3 cryotip, held at 20 K, using both pulsed and slow-spray-on methods of deposition. The recorded i.r. spectra are very complex with a doubling of many of the bands which are obviously associated with monomeric forms of acrylic acid. (Dimer and monomer peaks are easily distinguished by studying a series of spectra of different matrix concentrations).

From a comparison of many spectra from different runs we noticed that many of the bands which showed doubling also showed surprisingly large changes in relative intensity, but it was not possible to correlate the intensity changes with spray-on conditions or with any other obvious experimental factor. However, from the spectra, we were able to distinguish two separate sets of associated frequencies (henceforth referred to as A and B), such as would be expected to occur if two rotameric monomers were present. However, the intensity variation was so great that in some instances spectra were obtained which contained only those bands from set A or from set B. We would not expect such a situation to arise for two rotamers of approximately equal energy, as suggested for acrylic acid.[1]

When the experiments were repeated using nitrogen as the matrix gas only one set of bands resulted on every occasion, with frequencies virtually identical to one of the sets of bands obtained for argon matrices (set B). This prompted us to repeat the argon matrix experiments and in addition, to 'dope' the matrix by introducing small amounts of (a) air, (b) nitrogen, and (c) water into the matrix mixture before deposition.

Matrix isolation studies of the hydrogen halides and other small molecules in inert gas matrices have shown that the addition of small quantities of nitrogen and other 'impurities' can produce additional absorptions due to the presence of the molecule in a distorted lattice site.[3] The main interest of many of these previous studies has been the effect of distortion of the inert gas lattice on the rotation of the molecule within the site.

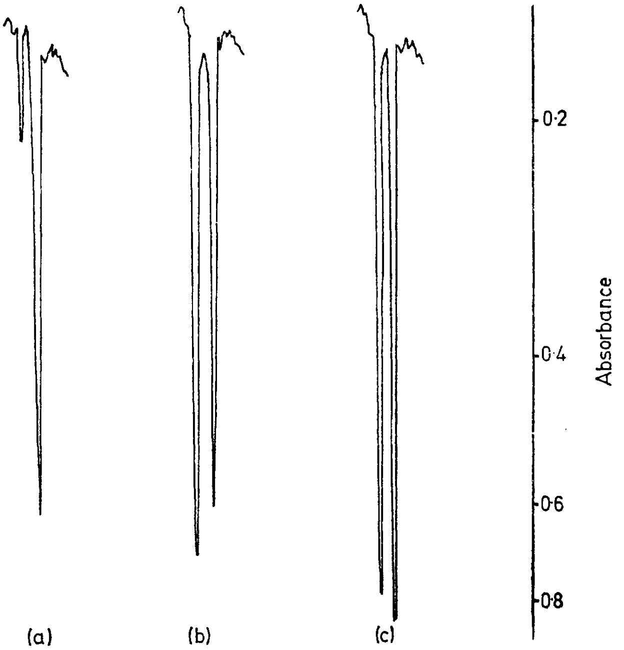

FIGURE. Demonstration of complete reversal of intensity which occurs on doping an acrylic acid–argon sample (M/R 2000) with 1% air impurity (1160—1110 cm^{-1} region). (a) After spraying on 7 mmol of acrylic acid–argon mixture. (b) After spraying on to (a) a further 3 mmol acrylic acid–argon–air impurity mixture. (c) After spraying on to (b) a further 3 mmol acrylic acid–argon mixture.

On doping acrylic acid–argon matrices with water, the spectra remain unchanged, apart from showing bands characteristic of the presence of water as an impurity in a matrix. The effect of doping with both air and nitrogen causes dramatic increases in intensity of those bands belonging to set B. Depositing further 'undoped' matrix samples on top of doped samples resulted in the other set of bands (set A) increasing in intensity relative to bands from set B. We conclude, therefore, from these data that the set of bands (B) observed in argon matrices arises from the presence of nitrogen introduced as an impurity from air leaks in the spray-on system. The presence of oxygen in the air may also produce a similar effect but this has not been the subject of a separate investigation. It is interesting that the presence of minute amounts of nitrogen is sufficient to cause dramatic spectral changes. For example, when a sample M/R 2000 is doped with a 1% air impurity, the bands associated with the presence of nitrogen, which were hardly visible before doping, increased dramatically and became dominant (Figure). This in itself explains why such a wide variety of spectra, intermediate between set A and set B, were obtained during the original experiments in argon.

In order to establish whether this effect was peculiar to acrylic acid or of a more general nature, amongst similar organic molecules, we studied three closely related substances *viz.* acetic acid, methyl acrylate, and acrylyl chloride and recorded their i.r. spectra in (a) argon matrices, (b) nitrogen matrices, and (c) argon matrices doped with air or nitrogen.

For methyl acrylate, the fundamental vibrational frequencies in argon and nitrogen matrices are rather similar (all within 7 cm^{-1}). However, doping the argon matrices with nitrogen or air has no observable effect on the i.r. spectra. Similarly, for acrylyl chloride where the vibrational absorptions in the two matrices differ in frequency more than for methyl acrylate, the spectra of matrix-isolated samples in argon are unchanged after doping either with air or with nitrogen.

For acetic acid, previous matrix isolation studies[4] have established the positions of the fundamental frequencies in argon and nitrogen matrices. In this case, doping with small amounts of air or nitrogen again shows dramatic increases in relative intensity of those bands associated with a nitrogen-isolated sample, whilst the argon-isolated frequencies remain unchanged. This parallels the results of doping acrylic acid–argon matrices and indicates that it is perhaps the interaction of the carboxylic acid group, rather than the vinylic group of the molecule, 'associating' with nitrogen, which is responsible for the observed intensity changes.

Our results suggest that the carboxylate group may have a strong affinity for nitrogen in a matrix and that some form of association exists between the two groups. Thus the presence of very small amounts of nitrogen (*e.g.* from air leaks) can, in some cases, have dramatic effects on i.r. spectra. This is especially important when studying systems capable of exhibiting rotational isomerism where doubling of bands is anticipated. In such cases, effects such as these described here can easily lead to erroneous conclusions.

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[1] K. Bolton, D. G. Lister, and J. Sheridan, *J.C.S. Faraday II*, 1974, **70**, 113.

[2] W. R. Feairheller Jr. and J. E. Katon, *Spectrochim. Acta*, 1967, **23A**, 2225.

[3] M. T. Bowers and W. H. Flygare, *J. Chem. Phys.*, 1966, **44**, 1389; D. E. Mann, N. Acquista, and D. White, *ibid.*, 3453; A. J. Barnes, H. E. Hallam, and G. F. Scrimshaw, *Trans. Faraday Soc.*, 1969, **65**, 3172; H. Dubost and L. Abouaf-Marguin, *Chem. Phys. Letters*, 1972, **17**, 269.

[4] C. V. Berney, R. L. Redington, and K. C. Lin, *J. Chem. Phys.*, 1970, **51**, 1713.

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