Magnetic Circular Dichroism Evidence for the Paramagnetism of Tetracarbonyliron(0): Low-temperature Matrix Studies

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Summary The temperature dependence of the magnetic circular dichroism spectrum of matrix-isolated $[Fe(CO)_4]$ shows that the molecule is paramagnetic.

A NUMBER of aspects of the solution behaviour of $[Fe(CO)_4]$ could be explained if the compound were paramagnetic, for instance its similarity in reactions to $:CCl_2$.[1] The M.O. calculations of Burdett[2] and the i.r. work of Poliakoff and Turner[3] have led to the prediction of a triplet ground state for $[Fe(CO)_4]$. Magnetic circular dichroism (m.c.d.)[4,5] offers an elegant method for proving this predicted paramagnetism.

The Figure shows the m.c.d. spectra of $[Fe(CO)_5]$ in an Ar matrix {$[Fe(CO)_5]$: Ar, 1 : 500} before and after photolysis with a mercury lamp. The m.c.d. spectrum of the unphotolysed $[Fe(CO)_5]$ is very similar to the room temperature solution m.c.d. spectrum,[6] and correlates well with the published absorption spectrum.[7] The m.c.d. spectrum of a diamagnetic molecule should not be temperature dependent and the spectrum of $[Fe(CO)_5]$ shows no change as the temperature of the matrix is varied. After u.v. photolysis the m.c.d. signal changes sign and becomes temperature dependent. This shows that the photolysis product is paramagnetic.

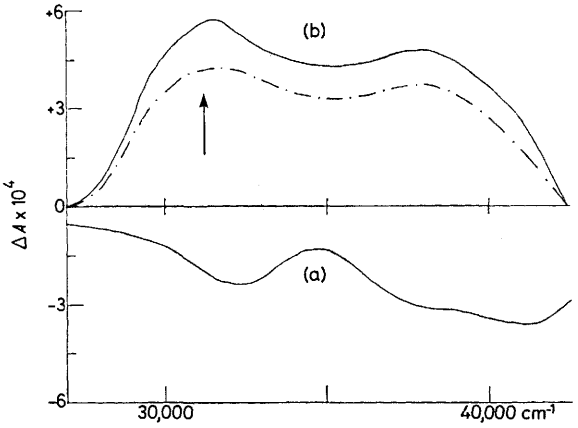

FIGURE. The m.c.d. spectrum of $[Fe(CO)_5]$ in an Ar matrix. {$[Fe(CO)_5]$: Ar, 1 : 500}; (a) after deposition, superimposed spectra taken at 5 and 25 K. (These are sample-block temperatures and may not accurately represent the matrix temperature. Diagrams of the apparatus may be found in refs. 4 and 5); (b) After 130 min photolysis with a medium-pressure Hg arc: —, 5 K, -·-·-·-, 25 K. The arrow indicates the reported[8] absorption maximum of $[Fe(CO)_4]$. Magnetic field = 7 T. The ordinate axis is plotted in measured units of ΔA ($=A_L-A_R$), where A_L and A_R are absorbances for left and right circularly polarised light, respectively.

I.r. experiments under similar conditions[7,8] show that the predominant photolysis product is $[Fe(CO)_4]$. Furthermore, one of the m.c.d. maxima corresponds closely to the previously reported[8] absorption maximum of $[Fe(CO)_4]$, see Figure. Thus m.c.d. has provided positive evidence for the paramagnetism of $[Fe(CO)_4]$, and confirmed the conclusions of the earlier matrix experiments[3] and M.O. calculations.[2]

This is the first example of the determination of the paramagnetism of an unstable species in a matrix by m.c.d. It is especially useful in this case, since it is unlikely that a transition metal compound, having C_{2v} symmetry and an even number of electrons in the ground state, could be detected by e.s.r. spectroscopy.

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