GAS-PHASE CR^+ COMPLEXES OF AROMATIC LIGANDS: SITE OF BINDING AND SPIN STATE OF THE METAL ION CHARACTERIZED BY INFRARED SPECTROSCOPY USING THE FELIX FREE-ELECTRON LASER

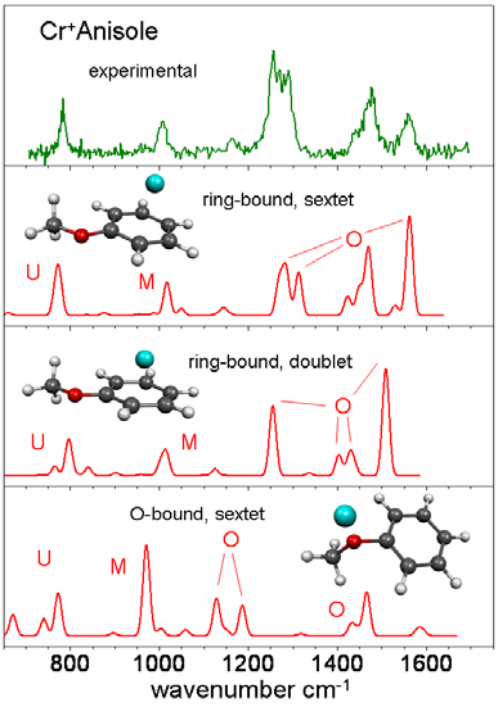
R.C. Dunbar (Case Western Reserve U., Chemistry); J. Oomens (FOM Institute); D. T. Moore (FOM Institute); G. von Helden (Fritz-Haber-Institut der Max-Planck-Gesellschaft); G. Meijer (Fritz-Haber-Institut der Max-Planck-Gesellschaft); J. R. Eyler (UF, Chemistry)

Introduction

The combination of a Fourier-transform ion cyclotron resonance (FT-ICR) spectrometer with the Free Electron Laser for Infrared eXperiments (FELIX) at FOM Institute in Nieuwegein, Netherlands [1] has been found to give remarkable new capabilities for characterizing gas-phase organometallic complexes of transition metal ions. In initial work described in the 2003 NHMFL Research Report (Dunbar, R. C.. *et al*., p. 76) and subsequently published [2] it was found that the site of binding of the Cr^+ ion to a bi-functional ligand (aniline) could be identified with confidence. In new work including additional ligands (anisole, acetophenone) it has been shown that not only the site of complexation, but also the spin state of the metal ion can be identified.

Experimental

The FELIX laser provides continuously tunable IR radiation over the IR fingerprint region, typically 10 macropulses of pulse energy 35 mJ. Light is directed into the cell of the FT-ICR spectrometer (4.7 T actively shielded magnet). Atomic metal ions are produced external to the magnet by laser desorption/ionization, and guided into the cell. Organometallic complexes are formed by ion chemical processes within the cell, isolated by selective ion ejection, and their signal intensity is monitored both with and without FELIX irradiation to determine dissociation rate versus wavelength.



Results and Discussion

The Figure shows the results for anisole, as an example. In the top panel is shown the infrared photodissociation spectrum from the FT-ICR/FELIX instrument. The other panels show the computed predictions for high-spin ring-bound, low-spin ring-bound, and high-spin side-chain-bound complexes. The high-spin ring-bound prediction clearly gives by far the best fit to the experiment.

Among these three ligands, ring binding has been proven for anisole and aniline, while acetophenone binds at the oxygen. The bis-complexes of aniline and anisole were shown to be low-spin, whereas the respective mono-complexes, as well as the acetophenone bis-complex, are high-spin.

Acknowledgements

Establishment of the FT-ICR facility at FELIX was made possible by funding (NSF #CHE-9909502) from the NHMFL. This work was financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO). RCD acknowledges the support of the donors of the Petroleum Research Fund, administered by the American Chemical Society.

References

[1] van Heijnsbergen, D. *et al*., J. Am. Chem. Soc.**, 124**, 1562-63 (2002).
[2] Oomens, J. *et al*., J. Am. Chem. Soc., **126**, 724-25 (2004).