

HIGH RESOLUTION SPECTROSCOPIC STUDIES OF OPEN-SHELL VAN DER WAALS COMPLEXES: A SENSITIVE PROBE OF MOLECULAR INTERACTIONS

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The high resolution spectroscopy of weakly bound clusters provides a valuable source of information on the nature of intermolecular forces. It provides details of the preferred relative orientation of molecules and hence information on the geometry of the minimum of the potential minimum. In favourable cases it all gives details of the intermolecular potential energy surface. What is less obvious is the effect of complex formation on the electron distributions of the molecules involved. Is there any incipient chemical bond formation?

In this talk I shall present recent results on the microwave fourier transform spectroscopy and infrared diode laser absorption spectroscopy of clusters containing the stable open-shell molecules NO, NO₂ and O₂.

The microwave spectra of the complexes Ar-NO₂, Kr-NO₂ and Xe-NO₂ exhibit well resolved hyperfine structure. In the first two complexes, the spectral constants can be explained in terms of the appropriate projections of the monomer constants along the axes of the complex. For the xenon complex serious perturbations are observed. There are two magnetic isotopic forms of Xe, namely ¹²⁹Xe and ¹³¹Xe. These isotopic forms of the complex show Xe magnetic hyperfine structure which indicates significant unpaired electron transfer between the molecules.

Spectra of the complex NO-HF have been analysed. These show that the presence of the HF significantly perturbs the orbital motion of the NO molecule. The barrier to free orbital motion is about 300 cm⁻¹, with the electron preferring to be in the plane of the complex. Hyperfine structure due to the hydrogen and fluorine magnetic nuclei also indicates significant unpaired electron transfer from NO to HF.

The oxygen complexes OCS-O₂ and N₂O-O₂ have been observed and analysed.

In addition models for the observed electron transfer and correlation effects will be presented.

INFRARED SPECTROSCOPY OF VAN DER WAALS CLUSTERS:
THE CO-SIDEBAND SPECTROMETER - FIRST MEASUREMENTS
OF THE FORMIC ACID DIMER

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We have built up a CO-sideband spectrometer using optothermic detection in a molecular beam. The CO-laser was mixed in a CdTe cristall with microwaves (8-18 GHz) in order to generate tunable infrared radiation. A sealed off CO-laser was chosen in order to be able to use different CO laser isotopes. We achieved a 50 % frequency coverage between 1600 and 2000 cm^{-1} .

A tunable resonant microwave cavity was designed, which yielded an increase of sideband power by a factor of 5-10. The typical output is 2-3 mW per sideband with a linewidth of ca. 1 MHz. The laser covers the chemically important region of the CO stretch. Using this setup we were able to measure the first high resolution spectrum of the formic acid dimer. The obtained spectrum indicates the existence of a large amplitude motion.