Molecular interactions in complexes and nanodroplets

A J Boatwright, A Musgrave, D Bergeron, R R Wright, A J Stace, T G Wright

Department of Physical Chemistry, School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK

Main contact email addresses: *tony.stace@nottingham.ac.uk, tim.wright@nottingham.ac.uk*

Introduction

The interactions between a rare gas atom and a molecule are one of the simplest, owing to the closed-shell nature of the ground electronic state of the rare gases. Consequently, 1:1 complexes of molecules with rare gases have been used as a probe to see what happens when two "molecules" interact. As well as small perturbations in electronic structure, there is also the formation of weak bonds, which allow vibration of the rare gas (intermolecular bends and stretches). There have been many studies of, for example OH and SH with rare gases, since these allow the probing of the interaction of an open-shell species with the closed-shell rare gas. In the first section below, we report some of our new results on another common open-shell molecule, NO, that is stable and found throughout the Earth's atmosphere, with both rare gases and the methane molecule.
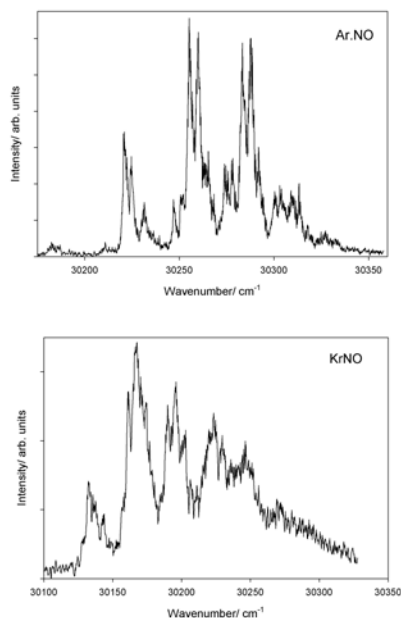

Figure 1. (1 + 1) REMPI spectra of the Ar·NO and Kr·NO complexes, obtained when the π^* electron on NO is excited to the 4s Rydberg state.

Rare gas atoms, and inert molecules, such as N_2, have been used to isolate molecules for many years. The rationale is that if a molecule can be surrounded by a number of rare gas atoms, then it is unable to interact with other species, and consequently it can be studied in isolation; in addition, even very reactive species (such as radicals) are then able to be studied since they can only react when they meet another molecule. Matrix isolation spectroscopy is one of the widespread methods that has been used to study a wide range of species by infrared, Raman and electronic spectroscopy. In this method, the molecules are codeposited in a solid matrix of (for example) argon. Although this has proven to be very useful, even the weak interactions between the Ar atoms and the molecule of interest lead to broadening of the lines, shifts in absorption frequencies, and the observation of multiple lines, caused by the presence of different absorption sites within the matrix. Very recently, a strong push has been made into using helium nanodroplets as a "matrix" in which to trap molecules and hence to study them under isolated, and very cold, conditions. In the second section below, we describe some of our recent experiments on trapping benzene and substituted benzene in helium nanodroplets, and studying them using electronic spectroscopy.

(1) Nitric oxide molecules interacting with rare gases and molecules

Experiment

We form molecular complexes involving argon and nitric oxide by premixing 0.5–1% of NO in 5 atm of argon. The mixture is then allowed to expand through a small orifice (~750 μm) into a vacuum. This expansion is supersonic and leads both to the rotational cooling of the NO molecule (down to ~ 1 K), and the formation of cold Ar·NO complexes. These complexes are then interrogated using the frequency-doubled output of a dye laser (Sirah Cobra-Stretch, Photonics Ltd) and a repetition rate of 10 Hz, in this case operating at 225 nm (Coumarin 450), or ~ 325 nm (DCM).

The energy of the radiation is in the correct energy range to excite the $\tilde{A} \leftarrow \tilde{X}$ transition on the complex, which is an excitation of the π^* electron into the 3s Rydberg orbital of NO. The radius of this Rydberg orbital is such that the Ar atom cannot exist inside it, and so (as a result of the Pauli repulsion), is forced to remain outside of the orbit, and form a very weak van der Waals species. We have previously published and discussed the spectrum of the $\tilde{A} \leftarrow \tilde{X}$ transition [1]. The spectrum appears rather simple, but in fact its interpretation is complicated as the floppiness of the molecule means that the NO rotational angular momentum is partially coupled to the internuclear axis. As the Rydberg orbital becomes larger, and as the nature of the Rydberg electron changes (from a penetrating s electron to a non-penetrating d electron), then it is of interest to see how the interaction of the argon gas atom evolves. This change in interaction can also be studied as a function of the rare gas atom, and to this end work is in progress to record spectra of the electronic states formed when Ar, Kr and Xe interact with Rydberg states of NO, where the Rydberg electron is in the 3s, 3p, 4s, 3d, 5s and 6s orbitals. By analyzing the intermolecular vibrational frequencies observed, it is possible to make deductions regarding the bonding of these species, and in particular how strongly the rare gas atom is able to interact with the NO^+ core, in spite of the presence of the Rydberg electron. We only have preliminary data for Ar and Kr atoms interacting with 4s (see Figure 1) and 3d Rydberg states at present, and these are presently being analysed, Meyer and coworkers have recorded such spectra for Ne and Ar [2]. Although there are theoretical data available on the cations [3], it would be very useful to have experimental spectra, and to this end, we wish to record two-colour ZEKE spectra of the Rg·NO complexes, using intermediate Rydberg states to change the vibrational activity observed in the ZEKE spectra.

Finally, we note that the interaction of the NO molecule with a molecule is also of interest, but is much more complicated as there are more degrees of freedom. We have recorded spectra of a number of NO·molecule complexes, but just show recent spectra we have recorded for various isotopomers of the NO·methane complex excited via the $\tilde{A} \leftarrow \tilde{X}$ transition (Figure 2) — this work is ongoing, and again we wish to

explore higher Rydberg states, and use these to record two-colour ZEKE spectra.
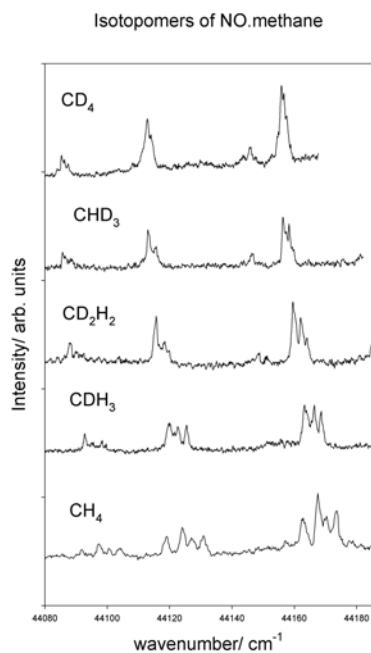

Figure 2. Origin region of various isotopomers of NO·methane — notice how the structure changes in each band as the deuteration increases.

(2) Substituted benzene molecules trapped in helium nanodroplets

Electronic spectra from a wide range of organic molecules embedded in helium nanodroplets have now been recorded, and for each of the molecules studied, the $S_1 \leftarrow S_0$ electronic transition exhibits a small spectral shift of between 10 and 100 cm^{-1} with respect to the frequency for the same transition in the gas phase. Neither the sign nor magnitude of these shifts follows any form of systematic pattern. Part of an on-going program of experiments involves recording the electronic spectra of series of substituted benzene molecules trapped in helium nanodroplets containing ~ 10^4 atoms.

Helium droplets were generated by the expansion of pure helium (99.9999%) at a pressure of ~ 30 bar through a 5 μm nozzle. Prior to expansion, the helium and the nozzle were cooled to ~ 12 K using a two-stage closed cycle cryogenic refrigeration system (APD Cryogenics Inc.). The droplet beam was collimated by a 0.5 mm skimmer (Beam Dynamics) before entering a pick-up chamber, where they could collide with molecules of spectroscopic interest. A 2 mm skimmer further collimated the doped droplet beam before entering a detection chamber, which housed a quadrupole mass spectrometer (Extrel ELQ-400). Photon absorption was detected and recorded as a function of wavelength using laser-induced depletion (LIDS). A laser beam was aligned coaxial and antiparallel to the droplet beam, which provided a depleted signal with a duration of 3 ms. A pulsed dye laser (Sirah Cobra-Stretch, Photonics Ltd) with a frequency-doubling unit and a repetition rate of 10 Hz were used in conjunction with Coumarin dyes to generate tuneable UV radiation suitable for the excitation of $S_1 \leftarrow S_0$ transitions in benzene, fluorobenzene, chlorobenzene, bromobenzene, benzonitrile, and toluene. Depletion spectra were recorded with the quadrupole mass spectrometer set to transmit either the parent ions of the molecules identified above or, in some cases, such with chlorobenzene, the most intense fragment ion. Figure 3 shows an example of a depletion signal recorded for benzene at 258.83 nm. The depleted region of the time profile would be monitored as a function of laser wavelength to provide an absorption spectrum.
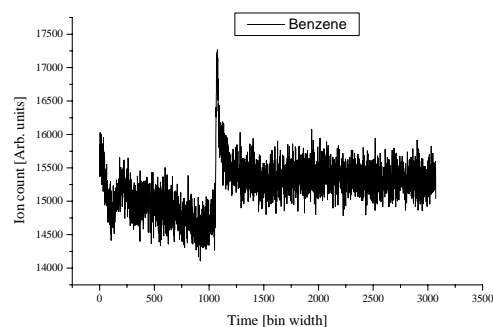

Figure 3. Section of a depletion signal recorded for benzene molecules trapped in helium nanodroplets. The time scale is such that 1000 bins corresponds to approximately 3 ms.

Figure 4 shows a section of an electronic spectrum recorded for trapped molecules of bromobenzene. The profile is characteristic of many such spectra. The sharp, narrow feature corresponds to a zero phonon line, which is an electronic transition in the molecule alone, and the broad feature is a phonon wing, which corresponds to simultaneous excitation of low frequency modes within the helium droplet.
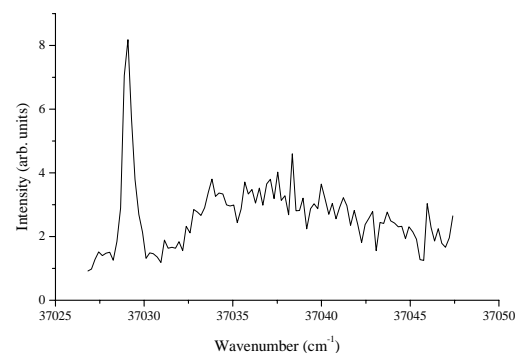

Figure 4. Part of an electronic spectrum recorded from bromobenzene molecules trapped in helium.

From results recorded for a range of substituted benzenes, it has been possible to offer an explanation for the origin of spectral shifts in the electric spectra of trapped molecules [4]. In addition, the shifts have been interpreted in terms of the amount of energy required either to pick-up a molecule, or to vaporize all of the He atoms prior to ion detection [5]. We are progressing two-colour experiments to investigate the energy dependence of the ion signal, by tuning the energy of the ionization laser independently of the excitation laser.

References

1. J Lozeille *et al.*,
   J. Chem. Phys., 113, 7224 (2000).

2. J Fleniken, Y Kim, H Meyer,
   J. Chem. Phys. 109, 8940 (1998).

3. E P F Lee, P Soldán, T G Wright,
   J. Phys. Chem. A 102, 6858 (1998).

4. A Boatwright *et al.*,
   J. Chem. Phys. in press.

5. S Curtis, A Boatwright, R R Wright, A J Stace,
   Chem. Phys. Lett. 401, 254 (2005).