

High resolution infrared laser jet-cooled spectroscopy of small van der Waals clusters with rare gases

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Weak intermolecular van der Waals (vdW) interactions play an essential role within large systems such as the bulk phase and macromolecules, because of the significant effect on structural and internal dynamics properties induced by many possible interactions. High resolution (HR) spectroscopy has proved to be a suitable method, primarily in the microwave and millimeter-wave regions to characterize finely the vibration-rotation-tunnelling (VRT) ground states of complexes with large amplitude motions and any other transitions due to the non-rigidity of the complex. More recently, the advent of HR infrared (IR) laser spectroscopy coupled to supersonic jets opened the way to a direct determination of the potential energy surface (PES) of linear triatomic molecules[1] interacting with rare gases (Rg) based on precise structural parameters derived from the fitting of spectra to provide ground and excited state rotational constants. Dynamic and structural data could be more challenging to extract in the case of floppy complexes with internal rotor or umbrella inversion motions, or with heavy rigid partners having small rovibrational constants.[2]

Taking advantage of an IR tunable laser spectrometer recently implemented at MONARIS, which combines a pulsed supersonic jet with a quantum cascade laser in the 10.5 μm region, two recent HR IR laser jet-cooled studies involving mixed vdW clusters will be presented: the first one about the $\text{NH}_3\text{-Ar}$ complex in the ν_2 umbrella region of NH_3 reports the measurement of five ortho and para bands unambiguously assigned on the grounds of rovibrational analysis for the ortho ones and by comparison with *ab initio* VRT levels from a four-dimensional PES surface for the para bands. The *ab initio* results turn out to be very predictive in terms of band centres, upper state rotational constants, tunnelling frequencies and relative weight of Coriolis couplings in the ground and excited ν_2 states.[3] The second one about small $\text{SF}_6\text{-Rg}$ (Rg = Ne, Ar, Kr, Xe) clusters exploits the precise S-Rg bond lengths derived from the rovibrational analysis of jet-cooled laser spectra to evidence that vibrational band shifts measured with respect to the SF_6 monomer can be modeled by a radial Buckingham intermolecular potential containing both long-range attractive and short-range repulsive contributions. Also, signatures of larger clusters containing up to three Rg atoms are shown to be consistent with the additivity of vibrational shifts, in particular for Ar.[4]

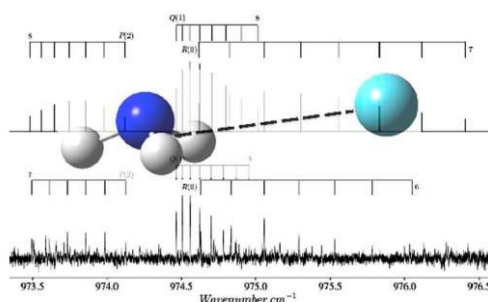


Fig. 1: Jet-cooled laser spectrum of the highest transition $\Pi_{\text{vib,rot}}(J = 1, k = 1) \leftarrow \Sigma_{\text{vib}}(j = 1, k = 1)$ in *para*- $\text{NH}_3\text{-Ar}$ compared to the theoretical spectrum of the same transition at a rotational temperature of 3 K, generated with our VRT levels and transition line strengths.

[1] G. D. Hayman et al. J. Chem. Phys. 86, 1670 (1987).

[2] G. T. Fraser et al. J. Chem. Phys. 94, 7061 (1991).

[3] P. Asselin et al., Mol. Phys. DOI 10.1080/00268976.2018.1471533.

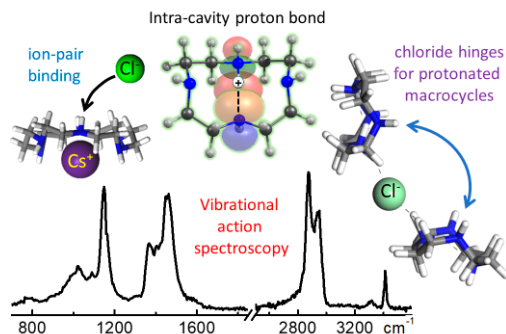
[4] P. Asselin et al., submitted to Phys. Chem. Chem. Phys. (2018).

Insights into the binding of protons, cations and anions by azamacrocycles

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Supramolecular complexes formed by the N-substituted crown ethers cyclen and hexacyclen with protons, alkali and transition metal cations and halogen anions, are investigated with action vibrational spectroscopy, ion mobility, high resolution mass spectrometry and quantum-chemical computations. Several benchmark effects are addressed, such as intra- and intermolecular proton bridges, ditopic ion-pair binding, or the oligomerization of the macrocycles in linear arrangements mediated by halide hinges. Specific spectroscopic signatures of proton delocalization or proton-halide interactions are exposed, plausibly involving anharmonic behavior, which poses important challenges for the accurate molecular modelling of these systems.



Infrared spectroscopy and quantum–chemical calculations on diacetylene complexes: a joint experimental study and theoretical investigation on OCS–H₂C₄ and N₂O–H₂C₄ dimers

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In this contribution we present the results of a joint experimental study and theoretical investigation recently carried out on the weakly bound complexes of diacetylene, H₂C₄, with OCS and N₂O. By using both a tunable diode laser and a QCL source coupled to a pulsed supersonic slit–jet expansion, the infrared spectra of OCS–H₂C₄ and N₂O–H₂C₄ were recorded around 4 mm, and the bands located in the region of the n₁ fundamental band of OCS (about 2050 cm⁻¹) and N₂O (about 2200 cm⁻¹), respectively, were analyzed. These bands have hybrid rotational structure which allows for estimates of the orientation of OCS and N₂O in the plane of their respective dimers. From the rovibrational analysis both OCS–H₂C₄ and N₂O–H₂C₄ dimers were found to have planar structure with nearly parallel monomer units; analogous bands for OCS–D₂C₄ and N₂O–D₂C₄ were also measured and analyzed. Quantum–chemical calculations were carried out to identify the stationary points on the potential energy surface of both the dimers, and to characterize them in terms of structures and binding energies. From this analysis we identified four stable geometries for OCS–H₂C₄ and three for N₂O–H₂C₄; on the most stable structure of both OCS–H₂C₄ and N₂O–H₂C₄ dimers we performed additional calculations at coupled cluster level of theory to further refine their structural parameters. The predicted data, obtained by computations carried out at both CCSD(T*)–F12c/VTZ–F12 and CCSD(T)/CBS levels of theory, corrected by anharmonic effects computed at DFT level, were in very good agreement with those experimentally obtained from the rovibrational analysis of the infrared spectra.

Infrared spectra of the carbon monoxide – water dimer and larger clusters

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The CO–water dimer has been studied previously in the microwave [1] and millimeter-wave [2] regions. Infrared spectra have also been observed accompanying the CO [3] and H₂O ν_2 [4] and ν_3 [5] fundamental vibrations. We have now observed the $K = 1 - 0$ subbands for CO–H₂O and –D₂O in the CO region, thus determining A rotational constants for the excited ($\nu(\text{CO}) = 1$) state. These bands are the exact analogs of the $K = 1 - 0$ millimeter bands studied by Bumgarner et al. [2].

Further b -type $K = 1 - 0$ subbands are observed around 2200 (H₂O) and 2198 (D₂O) cm⁻¹ which we assign to the combination band involving the C–O stretch plus the intermolecular in-plane CO rocking mode. The observed bands do not give us direct values for the intermolecular mode frequencies since we do not (yet) know the excited state A -values. But it appears that this frequency must be higher than the value of 19 cm⁻¹ predicted for CO–H₂O by Rivera-Rivera et al. [4]. There is also an apparent anomaly in that the CO–H₂O and –D₂O subbands are closer together than might be expected.

Finally, two bands which must involve larger CO – water clusters are observed. For CO–D₂O, they can be rotationally assigned, but for CO–H₂O they are broadened ($\gg 0.02$ cm⁻¹) by predissociation. Neither band corresponds to the previously observed trimer, (CO)₂–H₂O [6]. The first band, near 2158 cm⁻¹, involves a planar or near-planar species which is probably the other possible trimer, CO–(D₂O)₂. The second band, near 2150 cm⁻¹, involves a non-planar species which may be another isomer of the (CO)₂–D₂O trimer, or possibly the CO–(D₂O)₃ tetramer.

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