

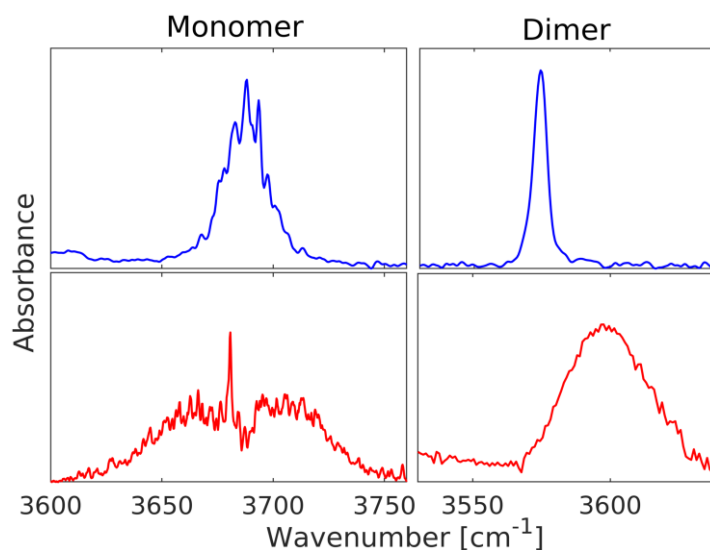
Vibrational Band Shapes in Hydrogen Bound Complexes: From Jet-Cooled to Room Temperature

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The infrared spectra of molecules vary continuously with temperature, from sharp individual transitions under cold conditions to broader bands at room temperature. In isolated molecules (figure, left), the broader bands observed at elevated temperatures are typically centered around the transitions observed under cold conditions. This variation with temperature is a consequence of the large number of thermally accessible rotational states. In addition, thermally populated excited vibrational states of low-frequency modes can also contribute to the observed spectra (i.e. hot bands).

In bimolecular complexes, six low-frequency intermolecular vibrations arise upon complex formation. For weakly bound complexes like the methanol dimer (figure, right), many excited states of the low-frequency intermolecular modes are thermally accessible. As a consequence, the population of the vibrational ground state quickly diminishes relative to the population of all the excited vibrational states [1,2]. This leads to a very different spectral temperature dependence for weakly bound complexes, compared with that of isolated molecules, with clear shifts in band maxima of certain bands. A physical picture of the temperature dependent vibrational band shapes in hydrogen bound complexes will be presented.



Jet-cooled (blue lines) and room temperature (red lines) spectra of the OH-stretching fundamental band of methanol (left) and the bound OH-stretching fundamental band of the methanol dimer (right). For methanol, the elevated temperature results in a broadening of the band due to transitions from excited rotational states. For the methanol dimer, the elevated temperature results in a blueshift of the band maximum due to transitions from excited vibrational states

References:

- [1] A. S. Hansen, E. Vogt & H. G. Kjaergaard, *Int. Rev. Phys. Chem.* **38**, 115-148 (2019).
 [2] E. Vogt & H. G. Kjaergaard, *Annu. Rev. Phys. Chem.* **73**, (2022).