

ATTENUATED STABILITY OF DEUTERIUM-BOUND COMPLEXES AT ROOM TEMPERATURE

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We have recorded gas-phase Fourier transform Infrared spectra at room temperature of several hydrogen (H) and deuterium (D) bound bimolecular complexes. These complexes were formed using methanol and ethanol as OH donors, and methanol- d_1 and ethanol- d_1 as OD donors, to compare isotopic effects in H/D-bond stability. The stability of these complexes are governed by the Gibbs energy of complex formation. By combining experimental and calculated intensities, the pressure of the complex can be determined, and from that and monomer pressures the Gibbs energy of complex formation. At room temperature, we find similar Gibbs energies for corresponding H/D-bound complexes. For the pair of H/D-complexes, methanol-dimethylether (OH·O) and methanol- d_1 -dimethylether (OD·O), Gibbs energies of 8.3 and 7.7 kJ/mol were determined, and for methanol-trimethylamine (OH·N) and methanol- d_1 -trimethylamine (OD·N) were determined Gibbs energies of 3.2 and 2.7 kJ/mol. Our findings of similar Gibbs energies for H/D-bound complexes at room temperature, is in contrast to what has been observed in spectra recorded in cold conditions. The deuterium bound complex is heavily favored, at low temperatures due to a lower zero-point vibrational energy. From calculations, we find that the difference in stability of the H/D-bound complexes become smaller with increasing temperature. The change in stability with temperature, arise from changes in both the rotational and vibrational entropic contributions.[1]

[1] A. Kjaersgaard, E. Vogt, N. F. Christensen, H. G. Kjaergaard, *J. Phys. Chem. A.*, **2020**, DOI: 10.1021/acs.jpca.9b11762.

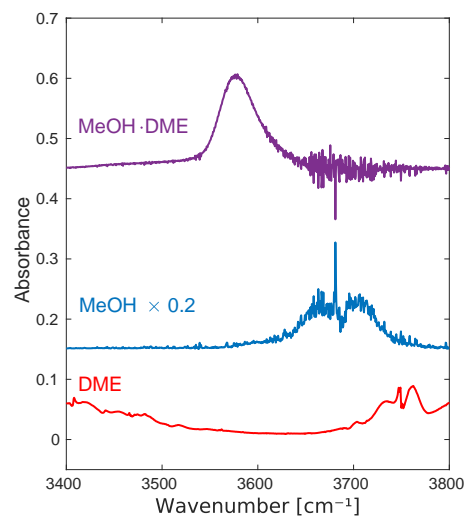


Figure 1: Spectrum of methanol (MeOH), dimethylether (DME) and the bimolecular complex (MeOH·DME).