

## Infrared Spectra of $\text{CH}_3\text{Cl} + \text{H}_2\text{O}$ and $\text{NO} + \text{H}_2\text{O}$ Isolated in Solid Neon at 5 K

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The infrared spectra of  $\text{H}_2\text{O} + \text{X}$  ( $\text{X} = \text{NO}, \text{CH}_3\text{Cl}$ ) isolated in solid neon at low temperature have been investigated. The  $\text{H}_2\text{O} + \text{NO}$  and  $\text{H}_2\text{O} + \text{CH}_3\text{Cl}$  systems are remarkable due to its propensity to form  $\text{X-H}_2\text{O}$ ,  $(\text{X})_2\text{-H}_2\text{O}$ ,  $\text{X-(H}_2\text{O)}_2$  and  $\text{X-(H}_2\text{O)}_n$ , and IR spectroscopy reveals a variety of phenomena far from being fully understood.

### **$\text{CH}_3\text{Cl} + \text{H}_2\text{O}$**

Detailed vibrational assignments are made on the observed spectra of water and deuterated water engaged in the  $\text{CH}_3\text{Cl:H}_2\text{O}$  and  $\text{CH}_3\text{Cl:(H}_2\text{O)}_2$  complexes. With the use of MP2 calculations, geometrical and vibrational properties of each complex have been estimated.

The  $\text{CH}_3\text{Cl:H}_2\text{O}$  complex is found to have a cyclic structure, where the chlorine atom is weakly bonded to one of the hydrogen atoms of water, while oxygen atom is weakly bonded to one of the hydrogen atoms of  $\text{CH}_3\text{Cl}$ . The calculated and observed vibrational frequencies of partially deuterated complex established that only  $\text{CH}_3\text{Cl:DOH}$  species is formed with hydrogen bonding to D. This is a consequence of the preference for HDO to form a deuterium bonding rather than a hydrogen bonding complex.

High concentration studies of water and subsequent annealing leads to formation of the 1:2  $\text{CH}_3\text{Cl:H}_2\text{O}$  complex. The complex has a cyclic form with two hydrogen-bonds: first between the chlorine atom and one of the hydrogens of  $\text{H}_2\text{O}$  PA of water dimer, and second between the oxygen atom of the  $\text{H}_2\text{O}$  PD of water dimer and one hydrogen of  $\text{CH}_3\text{Cl}$ . Each molecule of  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{Cl}$  acts as a proton acceptor and as proton donor. The binding energy of  $\text{CH}_3\text{Cl:(H}_2\text{O)}_2$  is 49.2 kJ/mol while that of water dimer is 19.9 kJ/mol and that of  $\text{CH}_3\text{Cl:H}_2\text{O}$  is only 12.7 kJ/mol.

### **$\text{NO} + \text{H}_2\text{O}$**

Low concentration studies (0.01 % - 0.2 %), H/D isotopic substitution and subsequent annealing leads to the formation of  $\text{NO-H}_2\text{O}$ ,  $\text{NO-D}_2\text{O}$  and  $\text{NO-HDO}$  complexes. A detailed vibrational analysis of the deuterated species shows two sets of 1:1 molecular complexes labelled  $\alpha$  and  $\beta$ . Only the structure of the  $\text{NO-D}_2\text{O}(\beta)$ ,  $\text{NO-HDO}(\beta)$  species where the water deuterium and the NO nitrogen are weakly bonded, has been predicted by DFT calculations. While in the  $\text{NO-H}_2\text{O}(\alpha)$ ,  $\text{NO-HDO}(\alpha)$  and  $\text{NO-D}_2\text{O}(\alpha)$  case, the potential surface has been explored systematically at the B3LYP level but no stable species reproducing the experimental data is found. This shows that the structure of the observed  $\text{NO-H}_2\text{O}(\alpha)$  and  $\text{NO-D}_2\text{O}(\alpha)$  complexes results from columbic attractions between the water and NO and is stabilized only in neon matrix.