

# RAMAN AND INFRARED SPECTROSCOPIC INVESTIGATION OF $\text{In}(\text{OH}_2)_6^{3+}(\text{aq})$ .

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**Abstract:** Raman and infrared spectra of aqueous *In(III)- perchlorate*, *nitrate* and *sulfate* solutions have been measured and the different aqua  $\text{In}^{3+}$  complexes with *nitrate* and *sulfate* have been characterised. The modes of the  $[\text{In}(\text{OH}_2)_6^{3+}]$  ion (in acidified perchlorate solution only) have been assigned. *Ab initio* geometry optimizations and frequency calculations are reported for *In(III) – water clusters* including a second hydration sphere.

The behaviour of metal ions in aqueous solution is of quintessential interest in many fields, including biochemistry, mineralogy and geochemistry, industrial chemistry, and environmental chemistry. The measurement of Raman spectra of aqueous solutions, supplemented by *ab initio* computational chemistry [1-9], has helped to resolve many uncertainties regarding the nature of the metal ion in aqueous solution, such as the coordination number of lithium [1] and scandium [6], and supported traditional physicochemical and structural measurements of other metals. For ion pairing [6b], it is also important to understand the nature of the anion [10-11]. We report here our studies of the aqueous indium(III) cation.

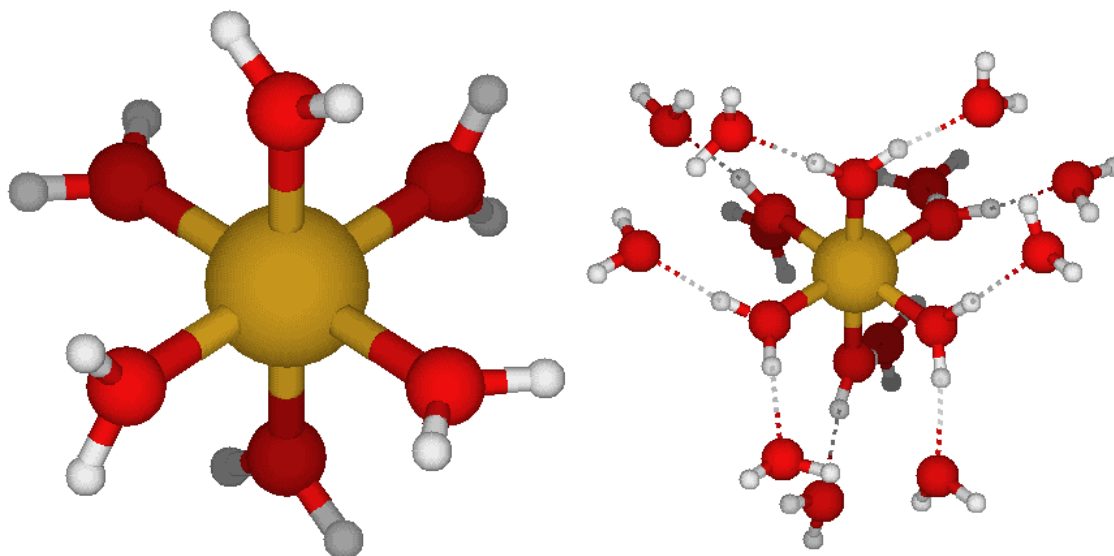
Raman and infrared spectra of aqueous *In(III)- perchlorate*, - *nitrate* and -*sulfate* solutions were measured. The Raman spectrum on *In(III)- perchlorate* solutions reveals a strongly polarized mode of medium intensity at  $487\text{ cm}^{-1}$  and two depolarized modes at  $410\text{ cm}^{-1}$  and  $306\text{ cm}^{-1}$ . These modes have been assigned to  $\nu_1(\text{a}_{1g})$ ,  $\nu_2(\text{e}_g)$  and  $\nu_5(\text{f}_{2g})$  of the hexaaquaindium(III) ion,  $[\text{In}(\text{OH}_2)_6^{3+}]$  ( $\text{O}_h$  symmetry), respectively. The infrared active mode at  $472\text{ cm}^{-1}$  has been assigned to  $\nu_3(\text{f}_{1u})$ . The Raman spectroscopic data suggest that the hexaaquaindium(III) ion is thermodynamically stable in acidified perchlorate solutions (no inner-sphere complex formation and no polyhydroxo species) over the concentration range measured.

In a concentrated  $\text{In}(\text{NO}_3)_3$  solution, indium(III) can exist in the form of both an inner-sphere complex,  $[\text{In}(\text{OH}_2)_5\text{ONO}_2]^{2+}$  and an outer-sphere complex  $[\text{In}(\text{OH}_2)_6^{3+} \text{NO}_3^-]$ . Upon dilution the inner-sphere complex dissociates and the amount of the outer-sphere complex increases. In a dilute solution most indium occurs as  $[\text{In}(\text{OH}_2)_6^{3+}]$  and unbound nitrate. The nitrate complex is thermodynamically weak and completely disappears upon dilution.

Indium sulfate solutions show a different picture and a thermodynamically stable indium(III) sulfato complex could be detected using Raman spectroscopy and 115-In NMR. The formation of the sulfato complex is favoured with increase in temperature and thus entropically driven. At higher temperatures a basic indium(III) sulfate of the alunite type is precipitated and was characterised by wet chemical analysis and X - ray diffraction (XRD). *Ab initio* geometry optimizations and frequency calculations of  $[\text{In}(\text{OH}_2)_n^{3+}]$  clusters with *n* equal to 1 to 6 were carried out at the Hartree-Fock and second order Møller- Plesset levels of theory, using various basis sets up to 6-31+G\*. The global minimum structure of the aqua *In(III)* species was reported. The unscaled

vibrational frequencies of the  $[\text{In}(\text{OH}_2)_6]^{3+}$  cluster were reported and do not correspond well with experimental values because of the missing second hydration sphere. The theoretical binding enthalpy for  $[\text{In}(\text{OH}_2)_6]^{3+}$  was calculated and accounts for ca. 60 % of the experimental single ion hydration enthalpy for In(III).

*Ab initio* geometry optimizations and frequency calculations are also reported for the  $[\text{In}(\text{OH}_2)_{18}]^{3+}$  cluster ( $[\text{In}[6+12]]$ ) with 6 water molecules in the first sphere and 12 water molecules in the second sphere (T symmetry). The calculated  $\nu_1(\text{InO}_6)$  mode of the Indium [6+12] cluster occurs at  $483\text{ cm}^{-1}$  (HF/6-31G\*), and is in good agreement with the experimental value at  $488\text{ cm}^{-1}$ , as are the other frequencies. The theoretical binding enthalpy for  $[\text{In}(\text{OH}_2)_{18}]^{3+}$  was calculated and slightly underestimates the experimental single ion hydration enthalpy of In(III).



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