INVESTIGATIONS ON THE EXISTENCE OF WELL DEFINED METALLIC CATION HYDRATES IN ELECTROLYTICAL SOLUTIONS (*)

M. ALVES MARQUES
Centro de Física da Matéria Condensada

Raman bands assigned to internal vibrations of cation hydrates in concentrated aqueous solutions of aluminium chloride [1] were investigated. The author considered, in the bulk of a concentrated aqueous solution, cation hydrates with a (defined) structure independent of the anion in order to calculate the isotopic shift of these bands when the ordinary water, in the solution, is replaced by deuterium oxide. No coupling of the internal vibration of the water molecule with the oscillations of the hydration complex was noticed in liquid solutions. The approach that H_2O and D_2O molecules are rigid ones was admitted. In the cation hydrate, assumed as octahedral, the interactions of each water molecule with the surrounding particles were considered cilindrically symmetric around the axis of its valence angle. Besides the vibration modes, already investigated, in which the six bonds from the cation to the six water molecules stretch or shorten, four triply degenerate oscillation modes, Raman active, are possible [1] — fig. 1. Three different non zero values for these frequencies are in general obtained for assumed values of the force constants of the oscillations of the water molecules about their equilibrium positions.

The simplified potential of the aggregate used here was:

$$V = \frac{1}{2} k \left\{ (\phi_1 - \theta_1)^2 + (\phi_2 - \theta_2)^2 \right\} + \frac{1}{2} k' (\theta_1 + \theta_2)^2$$

(*) Results presented at the Conference of the Portuguese Physics Society (Lisbon, February, 1978).

For low values of the ratio k'/k, up to $k'/k \sim 7$, the isotopic ratio of the lowest (non-zero) value of the frequencies of the above normal modes was calculated (*).

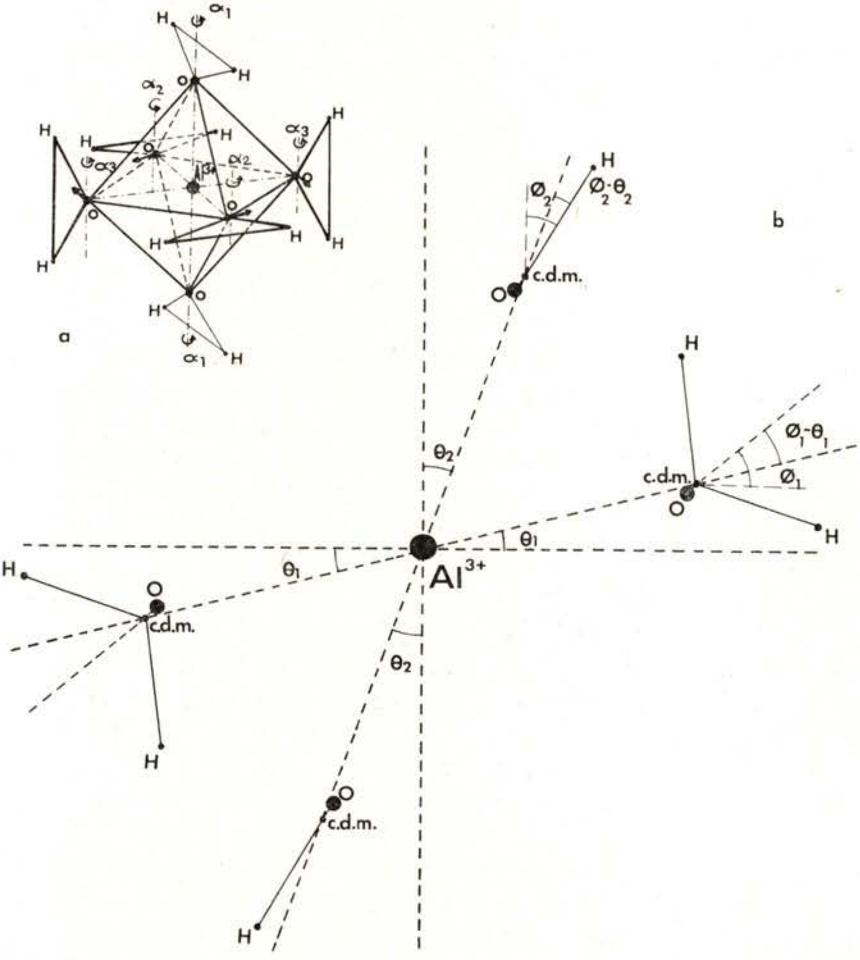

Fig. 1a. — Triply degenerate Raman active normal vibrations are different combinations of the indicated oscillations. 1b. — Bending and librational angles of the octahedral hydrate; ϕ_i are measured about the center of mass of the water molecule. Only the four water molecules drawn with a heavy line in the upper picture (1a) are represented here.

(*) The upper limit was obtained by considering only the interaction of the electrostatic field with the dipole moment of each coordinated water molecule, the short-range intermolecular forces being ignored.

Comparing the calculated ratio with the observed isotopic shift of the band that lies about 340 cm^{-1}, in the Raman spectra of the concentrated aqueous solutions of aluminium chloride, a reasonable agreement is obtained (fig. 2). As the isotopic shift was calculated without considering the anion interactions, the hypothesis about the existence of a *well-defined* coordinated hydration shell of Al^{3+} in aqueous solutions of aluminium salts [1] seems plausible. For indium chloride solutions, at the moment of the experiments, the results were not yet sufficient for elaborate conclusions [2]. Positional correlations between the electrons of the In^{3+} and the electrons

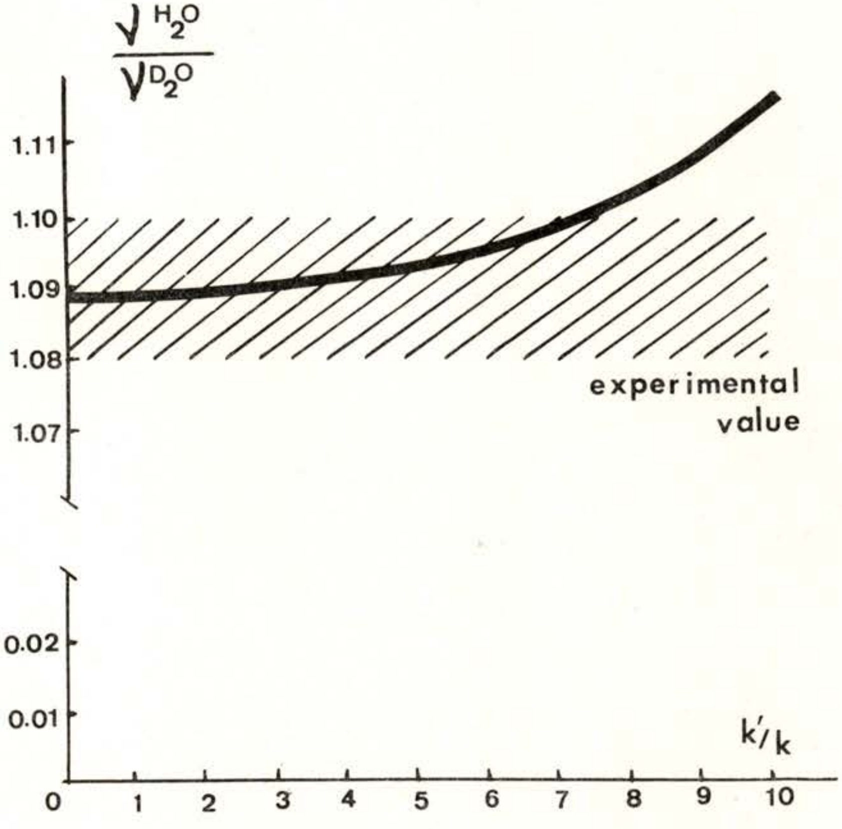

Fig. 2 — Isotopic ratio ν^{H_2O} / ν^{D_2O} of the frequency of the lowest wavenumber Raman band corresponding to the normal vibrations indicated (Fig. 1).

of the neighbour water molecules, obtained from X-ray diffraction investigations [3] point out the presence of six water molecules in the first hydration shell.

The author wishes to thank Prof. Dr. N. Macias Marques and Dr. J. Resina Rodrigues for stimulating discussions. M. C. Carreiro da Costa did the necessary calculations.

REFERENCES

[1] M. ALVES MARQUES, thesis, Univ. T. Lisboa, 1962; A. DA SILVEIRA, M. A. MARQUES and N. M. MARQUES, *Mol. Phys*, **9**, 271 (1965). In this article only the investigations on the Raman active vibration modes of the octahedral hydrate where the water molecules are considered as punctual are reported.

[2] M. A. MARQUES, *Proc. 6th Int. Conf. on Raman Spectroscopy*, Bangalore Sept. 1978.

[3] M. A. MARQUES and M. I. B. MARQUES, *Proc. K. Ned. Akad. Wet.* **B77**, 286 (1974). M. A. SOUSA OLIVEIRA, M. I. CABAÇO e M. A. MARQUES, following research note.