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Comment on "Low-frequency Raman-scattering study of the liquid-glass transition in aqueous lithium chloride solutions"

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A conclusion arrived at by Tao *et al.* [Phys. Rev. **44**, 6665 (1991)] related to the assignment of the *nominal* 60-cm^{-1} feature from liquid water is corrected. The 60-cm^{-1} band from liquid water due to the O—O—O bending mode is nearly degenerate with the O—O—Cl bending mode from aqueous LiCl solutions.

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Low-frequency Raman scattering from aqueous lithium chloride solutions has been examined by Tao, Li, Chen, Du, and Cummins (TLCDC) [1]. This Comment corrects the conclusion of TLCDC dealing with the origin of the *nominal* 60-cm^{-1} feature from liquid water. We emphasize, however, that we do not wish to express any opinion of, and that we neither support nor contest, the mode-coupling aspects of the paper by TLCDC.

TLCDC conclude (pp. 6667–6668) that the 60-cm^{-1} band from liquid water *cannot* refer to O—O—O bending because the Raman intensity does not decline near 60 cm^{-1} as lithium chloride is added to water. However, the O—O—O and O—O—Cl bending frequencies are essentially degenerate, and of similar intensities. The broad O—O—O bending mode occurs near 55 cm^{-1} [2], whereas the broad O—O—Cl bending mode occurs near 42–57 cm^{-1} [3]. Accordingly, the failure to observe a marked intensity decline near 60 cm^{-1} as lithium chloride is added to water cannot be used as an argument to negate the 60-cm^{-1} O—O—O bending assignment for liquid water.

Recent normal-coordinate analysis [4] of intermolecular modes of concentrated aqueous lithium chloride (see C_s model for aqueous HCl [3]) yields values near 51–54 cm^{-1} for the O—O—Cl bending mode, and near 43–56 cm^{-1} for the O—O—O bending mode. Moreover, the O—O—O bending and TA phonon interpretations are *different aspects of the same effect,* for the specific case of liquid water.

Walrafen [2,5] and Rousset, Duval, and Boukenter [6] assigned the 60-cm^{-1} band of water to a TA phonon, and Walrafen [2,5] has shown that this TA phonon involves O—O—O bending. Specifically, the 60-cm^{-1} (43–56 cm^{-1}) water band is a transverse spherical rotary shear mode (*S* wave or TA phonon) involving O—O—O bending [2,5], whereas the O—O stretching mode (~ 160 cm^{-1}) is a longitudinal spherical dilatational mode (*P* wave or LA phonon) [2,5]. Evidence has also been presented recently that shows that the *S* and *P* modes may be damped [7]. Moreover, the *S* and *P* modes may contain some contributions from standing waves [8].

The O—O—Cl bending mode (51–54 cm^{-1}) is probably also a TA phonon or *S* wave. A normal-coordinate C_s point-group approach based on an accurate x-ray radial distribution function has yielded a clear and detailed understanding of the microscopic motion of this mode [3].

Workers other than Walrafen have assigned the 60-cm^{-1} band of water to O—O—O bending, see [9], and to a damped harmonic oscillator involved in (perpendicular) restricted translation (hence O—O—O bending) [7]. Moreover, the classic 1959 book on hydrogen bonding by Pimentel and McClellan indicates that $A\text{-H}\cdots B$ bending of hydrogen-bonded $R\text{-}A\text{-H}\cdots B$ structures ($R\text{-}A\text{-H}$ bent) occurs near 50 cm^{-1}, see pp. 68 and 71 of Ref. [10]. Even more important, however, is the work of Bertie and Whalley [11] who used a nearest-neighbor, bond-stretching, angle-bending force field to assign a TA phonon in ice *Ic* at 65 cm^{-1} to *pure* O—O—O bending, $6K_{\Theta}=(0.058\,894)(18.02)[(65)]^2]$, where the bending force constant, $K_{\Theta}=747$ dyn/cm (see Note at end of p. 1284 of Ref. [11]). They assigned ice *Ic* LA phonons to the 165–181-cm^{-1} region, in agreement with [2], and recent normal coordinate calculations [4].

Modified interpretations of the 60-cm^{-1} mode from liquid water may be developed in the future which, for example, could involve mixing of the *S* and *P* modes, that is, either or both of the ≈ 60- and ≈ 160-cm^{-1} features from water could involve TA and LA contributions, but because of the O—O—O and O—O—Cl frequency degeneracy, it is clear that an intensity argument related to aqueous LiCl should not be used to refute the O—O—O bending assignment for liquid water.

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