Raman Spectroscopy and Molecular Polarizabilities at Finite Temperature from First Principles

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Abstract:
Knowledge of molecular polarizabilities in condensed phases provides important information about molecular crystals, and in general about materials composed of molecular or nano-building blocks. It is of great importance for the Raman spectroscopy. We propose a first-principles method based on electronic densities to compute molecular polarizabilities in condensed phases. The method includes all multipole interactions in addition to the dipole-dipole one, and it is applicable to any semiconductor or insulator. We present results for molecular polarizabilities of water in a wide pressure-temperature range. We found that at ambient conditions, the dipole-induced-dipole approximation is sufficiently accurate and the Clausius-Mossotti relation may be used, e.g. to obtain molecular polarizabilities from experimental refractive indexes. However, with increasing pressure this approximation becomes unreliable and in the case of ice X, where covalent bonds are present, the dipole-induced-dipole approximation breaks down. Further, we calculated the Raman spectra of (bi)carbonate aqueous solutions at supercritical conditions, and obtained the Raman scattering cross sections of carbon species at high pressures and high temperatures from first principles. We will discuss how to use our results to interpret and guide spectroscopic measurements.

References

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