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Atmospheric applications of vibrational local modes

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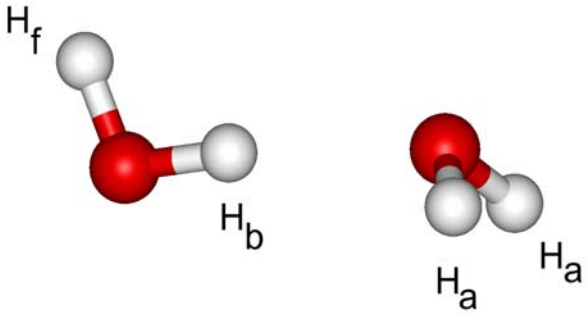
We have calculated fundamental and overtone OH-stretching vibrational band positions and intensities of molecules and mono-hydrated complexes of atmospheric interest. The spectral intensities were determined with a harmonically coupled anharmonic oscillator local mode model and ab initio calculated dipole moment functions. The basic principles of the local mode model will be outlines and the effect of various ab initio methods on these types of calculations discussed. Atmospheric implications of our results are highlighted.

The water dimer is a weak van der Waals complex consisting of a hydrogen doner and a hydrogen acceptor unit.



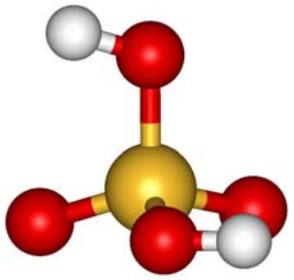
Our calculations predict that the frequencies of the hydrogen-bonded OH-stretching transitions are red-shifted compared to those of the monomers and that the shifts increase with increasing overtone. For the fundamental region, we see a significant increase in intensity for the hydrogen-bonded transitions compared to the monomer transitions. For the first overtone, the hydrogen-bonded transitions are weaker than the monomer transitions, and for the higher overtones the intensities are comparable. Our calculated water dimer spectrum compares well with recent matrix isolation spectra in the fundamental and first overtone region. The OH_b bond of the hydrogen donor unit is the bond mostly affected by the complexation. We show that transitions to higher overtones in the OH_b-stretching vibration are well seperated from water monomer transitions.

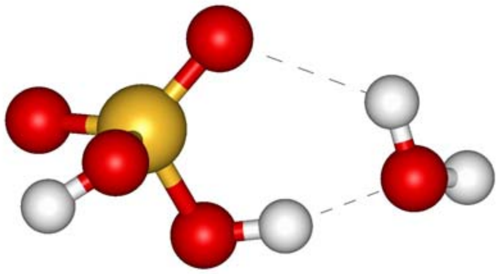
Resent atmospheric observation of one of these OH_b-stretching transitions has provided the first atmospheric detection of the water dimer. Our calculated spectra of water dimer and hydrated complexes of oxygen, nitrogen, and argon combined with estimates of their atmospheric abundance have been used to access the impact these complexes have on absorption of solar radiation.

Sulfuric acid is one of the major sulfur species in our upper atmosphere. The concentration and distribution of sulfur compounds in the stratosphere have been of increasing interest due to the important role they play in the formation of atmospheric aerosols. Atmospheric field measurements and models of the stratospheric sulfate aerosol layer led to the suggestion that sulfuric acid must photolyze at high altitudes.

High level ab initio calculations found that the lowest lying electronic transition in sulfuric acid occurs at wavelengths of about 144 nm. However, very few photons with this much energy are available in our atmosphere and thus photolysis via electronic transitions is not very likely.

We propose that excitation of vibrational overtones of sulfuric acid and its hydrate leads to photolysis forming sulfur trioxide and water in the near infrared and visible.





The calculated spectra of fundamental and overtone OH-stretching transitions in sulfuric acid are in very good agreement with observed OH-stretching transition in vapor phase sulfuric acid spectra. Based on our calculated spectra, the measured stratospheric and mesospheric sulfur dioxide concentrations and the observation of the sulfate layer can be explained.

These findings will allow scientists to improve their models of the Earth's atmosphere and will no doubt change our understanding of the atmosphere.
It is likely to affect climate modelling and our planet's energy budget through radiative and chemical effects.