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The spectroscopy of water vapor: theory and applications

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Although the strong absorption spectrum of water vapor has been studied under high-resolution for several decades, this triatomic molecule still is a challenge for molecular theorists. The water molecule being involved in many physical, chemical, and atmospherical processes, the best possible modeling of its spectrum is required in order to build the spectroscopic databases used, for instance, to understand the energy balance of the earth, to interpret remote sensing experiments, or to monitor combustion processes. In the present paper we will focus on two key issues related to the spectroscopy of the water molecule and to the building of databases for this molecule: the calculation of line positions and line intensities.

The calculation of line position is particularly difficult in the case of the water molecule because it is so light. We will try to understand why the rotational energy levels of water are different from those of a usual molecule by studying the interaction of the large amplitude bending ν_2 mode with the overall rotation of the molecule[1] and by showing that this gives rise to the so-called anomalous centrifugal distortion. As a result, usual spectroscopic techniques can not be applied to the case of the water molecule and special theoretical treatments must be developed. The approaches which have been set-up so far can be divided into two types depending on the number of degrees of freedom considered in the Hamiltonian. There are effective approaches in which the bending ν_2 mode and the overall rotation are treated together[2] and first principle variational calculations[3] in which energy levels are calculated from a 3-dimensional potential energy surface.

The calculation of line intensities is the other important issue when modeling the water vapor spectrum. For this purpose there also exist two types of approaches. In effective approaches, the dipole moment function is obtained by fitting experimental data. Other approaches are based on a dipole moment surface obtained through *ab initio* calculations.[4] In the present paper, special emphasis will be given to results obtained recently with the Bending-Rotation approach, belonging to the first type of approaches, which allowed us to reproduce satisfactorily[5] new accurate experimental values for the intensities of transitions occurring in the 10μm atmospheric window and belonging to the ν_2 band. These new results made it possible to compute a new line list for water which will be used to update the HITRAN and GEISA databases.

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