GLOBAL ANALYSIS OF THE WATER MOLECULE SPECTRUM BEYOND THE SECOND TRIAD

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The spectrum of the water molecule has been the subject of a very large number of theoretical investigations. These are motivated by the importance of this molecule, by the availability of a large body of high-resolution data, and by the fact that it is a theoretically challenging molecule displaying a strong vibration-rotation coupling leading to an anomalous centrifugal distortion.

In this paper, using the same ideas as in several previous investigations[a] in which satisfactory analyses of the water molecule rovibrational energy were performed up to the second triad, an effective rotation-vibration Hamiltonian will be built and used to account for the rovibrational energy of water up to the the first hexad.

In agreement with Bunker and Moss,[b] this effective rotation-vibration Hamiltonian is obtained starting from the exact Hamiltonian of the molecule written with Radau coordinates and adding the kinetic energy-like terms arising from the breakdown of the Born-Oppenheimer approximation. The effective Hamiltonian thereby obtained accounts for all three vibrational modes of the molecule and for the overall rotation. Making use of the potential energy function obtained by Partridge and Schwenke,[c] the Schrödinger equation for this effective Hamiltonian is then solved and rovibrational levels are obtained.

In the paper, the theoretical formalism will be introduced and we hope to be able to show results concerning a global analysis of the rovibrational levels of water up to the first hexad.

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[a]Lanquetin, Coudert, and Camy-Peyret, *J. Molec. Spectrosc.* **195,** 54 (1999); Lanquetin, Coudert, and Camy-Peyret, *J. Molec. Spectrosc.* **206,** 83 (2001); *and* Coudert, Pirali, Vervloet, Lanquetin, and Camy-Peyret, *J. Molec. Spectrosc.* 2004, *submitted.*

[b]Bunker and Moss, *J. Molec. Spectrosc.* **80,** 217 (1980).

[c]Partridge and Schwenke, *J. Chem. Phys.* **106,** 4618 (1997).