

Calculation of Ro-vibrational Spectra: State-of-the Art

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Abstract

The state-of-the art in the calculation of ro-vibrational spectra of small molecules of interest in astronomy and astrophysics is demonstrated through several examples. The highly accurate quantum chemistry method, singles and doubles coupled-cluster theory with a perturbational correction for triple excitations, denoted CCSD(T), is used to compute a purely ab initio potential energy surface (PES). Corrections for correlation of core electrons, higher-order correlation effects, and scalar relativistic effects, among others, are incorporated into the final purely ab initio PES. Ro-vibrational calculations show that such potentials are highly accurate and, for example, can produce fundamental vibrational frequencies to within 1 cm⁻¹. It is shown that further refinement of the potential using high resolution experimental data, can decrease errors for ro-vibrational energy levels by several orders of magnitude. In fact, potentials constructed in this way lead to the most reliable opacity data for small molecules available. Examples of this work will be shown for several small molecules.

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