The dipole moment surface for hydrogen sulfide H2S

Abstract

In this work we perform a systematic ab initio study of the dipole moment surface (DMS) of H2S at various levels of theory and of its effect on the intensities of vibration-rotation transitions; H2S intensities are known from the experiment to display anomalies which have so far been difficult to reproduce by theoretical calculations. We use the transition intensities from the HITRAN database of 14 vibrational bands for our comparisons. The intensities of all fundamental bands show strong sensitivity to the ab initio method used for constructing the DMS while hot, overtone and combination bands up to 4000cm^{-1} do not. The core-correlation and relativistic effects are found to be important for computed line intensities, for instance affecting the most intense fundamental band (ν2) by about 20%. Our recommended DMS, called ALYT2, is based on the CCSD(T)/aug-cc-pV(6+d)Z level of theory supplemented by a core-correlation/relativistic corrective surface obtained at the CCSD[T]/aug-cc-pCV5Z-DK level. The corresponding computed intensities agree significantly better (to within 10%) with experimental data taken directly from original papers. Worse agreement (differences of about 25%) is found for those HITRAN intensities obtained from fitted effective dipole models, suggesting the presence of underlying problems in those fits.