A theoretical line list for the hydrogen sulphide molecule

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Hydrogen sulphide is one of the molecules to be studied as part of the ExoMol project (see www.exomol.com [1]). A theoretical, high temperature (2000 K), accurate, and complete list of line positions and line strengths for $H_2{}^{32}S$ (ATY2013) is presented, covering the spectral range up to 9000 cm^{-1}. This line list is an important addition to the databases which are considered as source of information for astrophysical applications. ATY2013 is the first comprehensive line list which gives predictions for hot spectra of $H_2{}^{32}S$ molecule up to 2000 K for $J \leq 40$ with 36×10^6 transitions. At room temperature, ATY2013 results in around 5×10^5 absorption transitions with the intensity cut-off of 10^{-31} cm^{-1}/(molecule×cm^{-2}) comparing to only 2.8×10^4 transitions available in the spectroscopic databases. The standard deviation of the residuals for the line positions is about 0.066 cm^{-1}, where 82% of the transitions have the absolute error less than 0.1 cm^{-1}. The standard error of the ratios of the calculated to the experimental intensities is 1.08, where 83% of the transition intensities have the error of 20% or less. Our analysis suggests problems in some experimentally predicted transitions in the region below 4500 cm^{-1}. The ATY2013 ro-vibrational energy levels and dipole moment transition strengths were computed using the DVR3D [2] program in conjunction with an empirically refined potential energy surface (PES) and an *ab initio* dipole moment surface (DMS). Our 'spectroscopic' PES predicts experimentally known energy levels with a standard deviation of 0.11 cm^{-1} for the energy levels with $J \leq 10$ and below 15000 cm^{-1}. The intensity distribution of H_2S exhibits a known anomaly, which represents a challenge for accurate construction of an *ab initio* DMS for this molecule[3]. To this end we have tested different levels of the *ab initio* theory as implemented in the MOLPRO program. We found that especially the fundamental vibrational bands are very sensitive to the *ab intio* method used. Our best DMS (ALYT2013) used to compute the line list was constructed using the CCSD(T)/aug-cc-pV(6+d)Z level of theory covering the energy range up to 10 000 cm^{-1}.

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