A CASPT2 study of the dipole moment surfaces of hydrogen sulphide molecule

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Abstract

The ability of the CASPT2 method to yield accurate H₂S dipole moment surfaces that could be further used for conclusive predictions about rovibrational calculations, has been evaluated using ANO-L basis set. The optimised geometry, permanent dipole moment, linearity barrier as well as general features of the \( \mu_x \) and \( \mu_z \) dipole moment components in the vicinity of the equilibrium configuration agree favourably with available empirical determination and with recent accurate ab initio calculations. Dipole moment functions behaviour is also well reproduced for those geometrical configurations which are far from equilibrium in dissociation path. Computational technical aspects are discussed.

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1. Introduction

A theoretical study of dipole moment functions (DMF) of hydrogen sulphide (H₂S) molecule is a particular challenging task for ab initio electronic structure calculations in view of further studies of intensities anomalies observed in infrared high-resolution spectra [1–4]. Theoretical calculations of rotational–vibrational energy levels and intensities require an accurate knowledge of both the potential energy surface (PES) [5–7] and the dipole moment surfaces (DMS) [8–10] of the considered system. The H₂S DMS obtained previously by the CEPA ab initio method [8] modelled only some rotational anomalies concerning the P-branch and R-branch regions in the \( v_1 \) and \( v_2 \) bands. There was, however, a large discrepancy between the calculated and the experimental intensities of fundamental bands. Previous studies [8–10] have shown that the dipole moment functions are extremely shallow near the equilibrium geometry and consequently first derivatives of the DMS with respect to the stretching displacement are very small. A comparison of previous calculations [8,9] with observations indicates that the DMS near the equilibrium geometry of H₂S should be very accurately describe to avoid large errors in intensities calculations. Recently the accuracy of rovibrational intensity calculations for fundamental and \( \Delta v = 2 \) bands of H₂S has been largely improved.