Ab initio calculations of the vibrational spectrum of ethylene

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Infrared spectra of small polyatomic molecules play an important in the study of exoplanets and looking for signs of life. Ethylene (C_2H_4) is thought to be an important constituent of solar system, gas giant and "hot-Jupiter" exoplanets. Lack of the experimental information on the weak overtone bands puts demands on theoretical methods. As part project ExoMol [1] we have calculated vibrational band centres and intensities of an IR absorption spectrum of ethylene.

The calculation of the equilibrium geometry of the molecule was performed *ab initio* using the CCSD(T)/aug-cc-pVQZ level of theory. The potential energy and dipole moment functions of this molecule were represented by fourth-order polynomials in terms of Morse coordinates (stretching modes) and angle displacements (bending modes). The calculation of the centres of the vibrational absorption bands and their intensities in the IR spectrum was carried out using the vibrational Hamiltonian from Ref. [2] as implemented in the variational program ANGMOL [2]. Vibrational energy levels are found within 5 cm^{-1} and 10 cm^{-1} from the experimentally derived values for the fundamental and overtone bands, respectively. The vibrational band intensities are within 5% from the experiment. This is the first step towards calculating a hot line list for ethylene molecule and its isotopologues within the ExoMol project.

Additionally we present a new global potential energy surface (PES) of C_2H_4 computed *ab initio* by means of the explicitly-correlated coupled-cluster theory CCSD(T)-F12* in conjunction with the cc-pVTZ(F12) basis set. This PES is qualitatively correct at the long and short ranges of the nuclear coordinate domain. The long range part is made up from four CH and CC Morse oscillator functions, while the short range part is represented by a damped 4-mode polynomial expansion of the 8th order depending on all twelve coordinates. We could usefully vary less than 1500 parameters by fitting to 130000 *ab initio* points resulting in the root-mean-square error within 1 cm^{-1}. This global *ab initio* PES will serve as a good initial guess in a successive empirical refinement process. These calculations will be performed with an enhanced version of TROVE and compared with the above IR calculations.

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[1] J. Tennyson and S. N. Yurchenko, *Mon. Not. R. Astron. Soc.* **2012**, *425*, 21.
[2] L.A. Gribov, A.I. Pavlyuchko, Variational Methods for Solving Anharmonic Problems in the Theory of Vibrational Spectra of Molecules, Nauka, Moscow, **1998** (in Russian).