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An integrated experimental and quantum-chemical investigation on the vibrational spectra of chlorofluoromethane

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Artykuł

The vibrational analysis of the gas-phase infrared spectra of chlorofluoromethane (CH_2ClF, HCFC-31) was carried out in the range 200–6200 cm^{-1}. The assignment of the absorption features in terms of fundamental, overtone, combination, and hot bands was performed on the medium-resolution (up to 0.2 cm^{-1}) Fourier transform infrared spectra. From the absorption cross section spectra accurate values of the integrated band intensities were derived and the global warming potential of this compound was estimated, thus obtaining values of 323, 83, and 42 on a 20-, 100-, and 500-year horizon, respectively. The set of spectroscopic parameters here presented provides the basic data to model the atmospheric behavior of this greenhouse gas. In addition, the obtained vibrational properties were used to benchmark the predictions of state-of-the-art quantum-chemical computational strategies. Extrapolated complete basis set limit values for the equilibrium geometry and harmonic force field were obtained at the coupled-cluster singles and doubles level of theory augmented by a perturbative treatment of triple excitations, CCSD(T), in conjunction with a hierarchical series of correlation-consistent basis sets (cc-pV*n*Z, with *n* = T, Q, and 5), taking also into account the core-valence correlation effects and the corrections due to diffuse (aug) functions. To obtain the cubic and quartic semi-diagonal force constants, calculations employing second-order Møller-Plesset perturbation (MP2) theory, the double-hybrid density functional B2PLYP as well as CCSD(T) were performed. For all anharmonic force fields the performances of two different perturbative approaches in computing the vibrational energy levels (i.e., the generalized second order vibrational treatment, GVPT2, and the recently proposed hybrid degeneracy corrected model, HDCPT2) were evaluated and the obtained results allowed us to validate the spectroscopic predictions yielded by the HDCPT2 approach. The predictions of the deperturbed second-order perturbation approach, DVPT2, applied to the computation of infrared intensities beyond the double-harmonic approximation were compared to the accurate experimental values here determined. Anharmonic DFT and MP2 corrections to CCSD(T) intensities led to a very good agreement with the absorption cross section measurements over the whole spectral range here analysed.

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