PSEUDO-r_e STRUCTURES FROM EXPERIMENTAL ROTATIONAL CONSTANTS AND *AB INITIO* VIBRATION-ROTATION CONSTANTS

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The determination of accurate molecular structures from spectroscopic data has been and remains a formidable challenge. Inspired by the close agreement of experimental and theoretical centrifugal distortion constants and inertial defects [a], we explored the possibility of using vibration-rotation constants from *ab initio* calculations together with experimental ground state constants to derive approximate r_e structures. In the past, this has been done successfully for (very) small molecules with large basis sets at high levels of calculation (for an example, see [b]). We were interested in finding out whether MP2 calculations with small basis sets yield sufficiently accurate vibration-rotation constants for larger molecules. This method was tested with MP2/6-31G(d) calculations for the $COCl_2$, HCOCl, FCOCl, and HCOOH, for which near equilibrium structures derived from experimental data are available in the literature. It was subsequently used to re-evaluate the structures of CF_2NH, CF_eNCl, CH_3OCOCl, CH_3OCOCN, and two conformers of $CH_3CH_2PH_2$. Many, but not all, problems encountered in deriving meaningful structures are significantly reduced. It appears that the structures are comparable to r_m^{ρ} [c] and $r_m^{(1)}/r_m^{(2)}$ [d] structures.

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[b] M. Oswald, J. Flügge, and P. Botschwina, J. Mol. Struct. 320, 227 (1994).

[c] M. D. Harmony, in: J. R. Durig (Ed.), Vibrational Spectra and Structure, (Elsevier, Amsterdam, 2000) Vol. 24.

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