QUANTITATIVE ASSESSMENT OF EXTRA-MECHANICAL EFFECTS IN SPECTRA OF DIATOMIC MOLECULES

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To correct for significant deficiencies of a model of atoms in molecules that become obvious during a reduction of rotational and vibration-rotational spectra, recorded under conditions of great resolution , of diatomic molecular species in an electronic state of class $^1\Sigma$ or 0 according to a primitive hamiltonian comprising only potential energy and vibrational and rotational kinetic energies, terms are added that are described as adiabatic corrections, vibrational and rotational g factors. Because even abundant spectra of multiple isotopic variants in the absence of external fields are insufficient to define completely all these additional terms, and because typical application of the Zeeman effect on one or a few rotational transitions is likewise inadequate for this purpose, one has recourse to calculation of molecular electronic structure. For molecules containing atomic centres of small atomic number Z, these calculations are expected to be accurate without major complications from a non-relativistic approximation and from neglect of finite nuclear volume. As an application of an approach named computational spectrometry[a], we present the results of calculations for selected molecular species with a particular objective to compare with the magnitudes of parameters that are deduced from critical spectral analyses[b].

[a] J. F. Ogilvie and J. Oddershede, Advances in Quantum Chemistry, 48, 253-317 (2005)

[b] J. F. Ogilvie, The Vibrational and Rotational Spectrometry of Diatomic Molecules, Academic Press, London U.K., 1998