ELUCIDATION OF EXTRA-MECHANICAL EFFECTS IN REDUCTION OF INFRARED AND RAMAN SPECTRA OF SMALL MOLECULES IN GASEOUS SAMPLES

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Initiated by Born and Huckel, Dunham and van Vleck, an analytic approach to reduction of numerous frequencies and intensities of spectral lines of diatomic molecules in gaseous samples has become intensively developed during the past century, as reviewed elsewhere.[a] To reproduce faithfully these frequencies, an effective hamiltonian must contain parameters not only associated with vibrational and rotational motions of atomic centres putatively constituting a molecule but also to take into account that electrons fail to follow perfectly motion of one or other atomic nucleus; the latter we describe as extra-mechanical effects. An analytic basis bestows not only an advantage in reduction that parameters appear in well defined, and generally simple, expressions that one can employ to fit frequencies to these parameters but also that these parameters yield predictions of molecular properties not directly employed in analysis of frequencies, such as molecular electric dipolar moment. We present several instances of application of an analytic approach to evaluate parameters for comparison with external data.

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