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

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We present recent results obtained with an analytic approach to reduction of numerous frequencies of spectral lines of diatomic molecules in gaseous samples, for comparison with external data. 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[a]. An analytic basis bestows not only an advantage in reduction that parameters appear in well defined expressions, of generally simple form, 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 for a polar molecular species or rotational g factor for any species.

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