NOVEL METHODOLOGY FOR CONSTRUCTING EFFECTIVE *AB INITIO*-BASED HAMILTONIAN AND DIPOLE MOMENT OPERATORS TO ASSIST THE SPECTROSCOPIST IN HIGH-RESOLUTION ANALYSIS

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Precise knowledge of high-energy molecular states and absorption spectra is of primary importance because it gives access to the determination of the physical properties of various planetary object and clearly demonstrates the necessity of having consistent line-by-line molecular databases. Empirical effective Hamiltonians have greatly contributed to the golden age of the high-resolution molecular spectroscopy but may fail to describe congested spectra. Conversely, extensive first-principles quantum mechanical calculations are generally preferred for planetary and astrophysical applications because of their completeness but in turn may fail to describe high-resolution spectra due to their lack of accuracy.

Starting from selected variational eigenpairs, a novel methodology will be presented for the construction of global ab initio effective rotation-vibration spectroscopic models[1]. The current researches in the study of various planetary atmospheres require knowledge of increasingly complex molecular systems over wide wavenumber and temperature ranges. Unfortunately, the empirical models are beginning to reach their limits for studying molecules with complex rovibrational energy-level structures and for which the successive polyads contain many vibrational bands and numerous degeneracies and quasi-degeneracies. Modelling of the dark states is one of the major obstacles in the ordinary empirical effective approach. The model we propose turns out to be a clear alternative to the rather involved Van Vleck perturbation method. We will see how to transform first-principles calculations into a set of spectroscopic parameters to be further refined on experiment. It is demonstrated that crucial information is provided within a very short time compared to more traditional spectroscopic models (few hours, days or weeks against few months, years or decades), even for a seven-atomic molecule. Undoubtedly, the proposed approach brings a new insight into high-resolution spectra analysis and will be of great help, not only in current or future infrared spectra analyses of semirigid polyatomic molecules but also in the modelling of hot atmospheres for which completeness is crucial. The case of nonrigid molecules will be also discussed.

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