Extension of MOL_CT program suite to high orders for polyatomic molecules: application to methane polyads

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Effective Hamiltonians (EH) and dipole transition moment operators (DTM) are widely used in many domains of chemistry, physics and molecular spectroscopy. The MOL_CT (“Molecular Contact Trasformations”) program package [1,2] aims at building accurate effective models of strongly interacting vibration-rotation states for molecular spectroscopy and dynamics using a generalised formulation of Contact Transformations (CT) [3-5]. In practical terms CTs provide links between molecular potential energy surface and effective constants involved in empirical EH models. CTs also apply to other molecular properties relating dipole moment surfaces with effective transition moment band parameters [2]. Recent advances in the algebra of vibration-rotation transformations allow an extension of MOL_CT calculations for higher orders and for larger number of atoms. This was achieved using an optimised techniques of handling the commutator CT calculations and similar terms reductions according to the algorithms of „bi-colored trees” ranging of the terms arrays in the transformed Hamiltonian. A comparison of vibration and vibration-rotation energies, line positions and intensities for successive polyades of methane predicted from the new NRT methane potential energy and dipole moment surfaces [6] with experimental data [7], with spectroscopic databases [8,9] and with recent variational calculations [10,11] will be presented.

[1] Vl.G. Tyuterev, S. A. Tashkun, H.Seghir, SPIE, Issue N° 5311, pp164-175 (2004)
[2] J. Lamouroux, S.A. Tashkun and Vl.G. Tyuterev, Chem. Phys. Lett., 452, p225–231 (2008)
[3] Vl. G. Tyuterev, V. I. Perevalov, Chem. Phys. Lett. 74, 494-502 (1980)
[4] M. R. Aliev, J. K .G. Watson, in "Molecular Spectroscopy: Modern Research", vol III, Academic Press (1985)
[5] X. G. Wang and E. L. Sibert III, Spectrochim Acta A, 58, 863–872 (2002)
[6] A.N. Nikitin, M. Rey, Vl.G. Tyuterev, Chem. Phys. Lett.501,179–86 (2011); ibid 565,5–11,(2013)
[7] L. Brown et al, JQSRT, 2013, in press
[8] Ch. Wenger, J-P. Champion. JQSRT, 59:471-80, (1998)
[9] Y.A.Ba, et al JQSRT 2013, in press
[10] M. Rey, A. V. Nikitin, Vl. G. Tyuterev, J Mol Spectrosc (2013), in press http://dx.doi.org /10.1016/ j.jms.2013.04.003
[11] M. Rey, A. V. Nikitin, Vl. G. Tyuterev, Phys. Chem. Chem. Phys. 136, 244106 (2013)