Work plan for the STSM

Theory and implementation of rovibrational Raman intensities

Text books address rovibrational Raman intensities in a rough and abstract way leaving out (important) details [1]. Few scientific articles exist [2], but lack the depth and completeness of a text book. On the other hand Raman spectroscopy can be a complementary technique to IR spectroscopy filling in gaps in experiments and theoretical studies. We want to develop a more complete theoretical basis, including expressions for transition moments, ratios of isotropic and anisotropic Raman scattering in potential experimental setups and understand the aspects of group theory in this topic.

With this theoretical foundation the next step will be to incorporate techniques and approximations needed for the numerical treatment, e.g. (truncated) expansions of potential energy surfaces and polarizability surfaces. Working equations will have to be developed and effects and problems of methods for the numerical treatment will have to be addressed. However the basic properties needed for Raman intensities are available, e.g. within the Molpro program system in whose development our group takes part: energies, nuclear spin statistical weights and polarizability surfaces. Since we use other frameworks and programs (normal mode expansion, Molpro) than the group of the host, Dr. Sergey Yurchenko, (full PES in internal coordinates, TROVE [3] program and other) we will have to adjust the equations to fit both our needs. But in this way we will be able to compare results, especially intermediate numbers which is a huge help in the implementation for checking the code. Another challenge is the tremendous numbers of transitions making up the spectra which may easily reach numbers of millions to billions [4, 5]. Efficient schemes have to be developed and applied to be able to treat that problem. The host Dr. Yurchenko has extensive experience in the field of computational rovibrational infrared spectra and he and his coworkers have developed and employed numerous sophisticated methods [6].

In conclusion our work plan is as follows: completing the theory, derive working equations, begin the implementation and discuss occurring and possible future problems.

[1] Philip R. Bunker and Per Jensen. *Molecular Symmetry and Spectroscopy, 2nd Ed.* NRC Research Press, Jan. 2006.

[2] William F. Murphy. "Intensities of rotation and vibration-rotation Raman transitions in asymmetric top molecules". In: *J. Raman Spectrosc.* 11.5 (1981), pp. 339–345.

[3] Sergei N. Yurchenko, Walter Thiel, and Per Jensen. "Theoretical ROVibrational Energies (TROVE): A robust numerical approach to the calculation of rovibrational energies for polyatomic molecules". In: *J. Mol. Spectrosc.* 245 (2007), pp. 126–140.

[4] Jonathan Tennyson and Sergei N. Yurchenko. "ExoMol: molecular line lists for exoplanet and other atmospheres". In: *MNRAS* 425.1 (2012), p. 21.

[5] A. Owens et al. "ExoMol line lists – XXII. The rotation-vibration spectrum of silane up to 1200K". In: *MNRAS* 471.4 (2017), pp. 5025–5032.

[6] Ahmed F. Al-Refaie, Sergei N. Yurchenko, and Jonathan Tennyson. "**G**PU **A**ccelerated **IN**tensities MPI (GAIN-MPI): A new method of computing Einstein-A coefficients". In: *Comput. Phys. Commun.* 214 (2017), pp. 216–224.

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