

Theses of the Ph.D. Dissertation

JÁNOS SARKA

# Study of exotic molecular phenomena via variational nuclear motion computations

Supervisor:

Prof. Dr. Attila G. Császár

MTA-ELTE Complex Chemical Systems Research Group

Laboratory of Molecular Structure and Dynamics, Institute of Chemistry

Eötvös Loránd University

Chemistry Doctoral School

Head of the doctoral school: Prof. Dr. György Inzelt

Theoretical and Physical Chemistry, Materials Science Research Doctoral  
Programme

Head of the doctoral programme: Prof. Dr. Péter Surján

Eötvös Loránd University

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# 1 Introduction

By the adiabatic separation of the motions of the nuclei and the electrons the Born–Oppenheimer (BO) approximation, one of the cornerstones of computational quantum chemistry, defines two fields for computational quantum chemistry, the electronic structure and the nuclear motion theories, and also introduces the concept of the potential energy surface (PES), upon which most chemical events appear to take place.

During my doctoral research I focused on exotic phenomena of quantum systems: tunneling and the dynamics of astructural molecules. The computation of accurate rotational-vibrational energy levels of exotic molecular systems require to take full advantage of the unique capabilities of GENIUSH, a universal variational nuclear motion code developed in our laboratory. Utilization of GENIUSH required certain developments in the source code in order to be able run the code for the systems studied as quickly and effectively as possible. In addition, I have developed three different, more or less automatic tools allowing the analysis of the rotational-vibrational wave functions in a post-processing step after a successful GENIUSH computation.

I also attempted to push the boundaries of computational quantum chemistry in the field of nuclear motion theory by performing variational nuclear motion computations on systems larger and more complex than before, utilizing code developments allowing the use of large amounts of memory and a large number of cores.

Besides the development and application of the GENIUSH code I derived model Hamiltonians to understand and characterize the extensive rotational-torsional coupling present in astructural molecules and be able to predict the effect of the torsional potential barrier on rotational-vibrational energy levels.

# 2 Methods

One of the principal goals during my doctoral research was the development of the GENIUSH code and several related analysis tools. Now we can use the available computational resources for the study of systems displaying exotic quantum mechanical phenomena quite effectively. To this end I used the Fortran90, C++, Bash and Mathematica programming languages, the OPENMP paralellization algorithm, and the freely available MKL library.

### 3 Results and discussion

#### Method developments

1. I implemented and added an effective and parallel Lanczos iterative diagonalization algorithm to the GENIUSH code, which uses memory to store the working vectors of the Lanczos eigensolver to avoid the intensive I/O otherwise required for larger than four-atomic molecules. My current implementation works with the shift-fold (SF) filtering and the conjugate gradient (CGM) iterative linear solver with and also without the thick-restart of Lanczos iterations.
2. To be able to assign vibrational labels efficiently in GENIUSH, I have developed and implemented several analysis tools which uses the rovibrational wave functions in a post-processing step. These analysis tools work in a post-processing step and can be used in a semiautomatic way. Using 2D wave function plots allows us to determine the extent of vibrational excitation along the different vibrational coordinates.<sup>3-5</sup> Coordinate expectation values are very helpful when the studied system has multiple minima with noticeably different structure.<sup>5</sup> The energy decomposition scheme, which can also be applied for rovibrational wave functions, is useful for studying complex systems, where the internal rotation of the monomer units has large effect on the structure of the rovibrational-energy levels.<sup>5</sup>
3. I have derived one- and two-dimensional model Hamiltonians to understand the extensive torsional-rotational coupling present in several astructural molecules resulting in anomalous, reversed rovibrational-energy level ordering and negative rotational “excitation” energies.<sup>2</sup> These modeling efforts explain the different manifestation of the rotational-vibrational coupling in the different embeddings and provide a clear and simple physical interpretation of some of the highly peculiar characteristics of the energy level structure of  $\text{H}_5^+$ , and its deuterated isotopologues and the differences in the rovibrational energy level patterns and the related degeneracies of  $\text{H}_5^+$  and dimethyl acetylene, two molecules characteristic of what we call “the zero-barrier” limit, as compared to methanol and ethane, two molecules corresponding to the large-barrier limit.

## Numerical results

1. Variational nuclear-motion computations were performed with the modified version of GENIUSH using two *ab initio* PESs to compute the ZPVE of the  $\text{H}_5^+$  molecular ion and all of its possible deuterated isotopologues and isotopomers.<sup>3</sup> The existence of 12 different isotopomers from the six possible  $\text{H}_{5-n}\text{D}_n^+$ ,  $n = 0 - 5$  isotopologues was confirmed, one for  $n = 0$  and 5, two for  $n = 1$  and 4, and three for  $n = 2$  and 3. This simplification is due to the fact that of the three large-amplitude motions of  $\text{H}_5^+$ , only the  $\text{H}_3^+$  rotation has a large enough barrier to prevent facile exchange of the atoms involved. This unfeasible permutation lowers the apparent symmetry of the systems. Our results show that the stability order of the isotopomers is determined by the following two rules: first, when possible, H prefers to stay in the middle of the ions rather than at the sides, and, second, the isotopomer with a homonuclear diatomic at the side is always lower in energy.
2. The first 50 vibrational energy levels of all of the deuterated isotopomers of the  $\text{H}_{5-n}\text{D}_n^+$  system were computed covering all of the eigenstates up to about half of the first dissociation energy of the system.<sup>3</sup> The mostly benchmark-quality vibrational energies were fully assigned using 2D wave function plots.
3. The rotational-vibrational eigenstates of the  $\text{H}_5^+$  molecular ion have been studied for  $J = 1, 2, 3$ , where  $J$  is the rotational quantum number.<sup>1</sup> The very unusual rotational-vibrational energy level structure including negative rotational energy increments have been analyzed and explained in detail.
4. Several hundred rotational-vibrational eigenstates have been computed for the  $\text{F}^-(\text{H}_2\text{O})$  and  $\text{F}^-(\text{D}_2\text{O})$  complexes using a new *ab initio* PES.<sup>4</sup> Precise tunneling splittings of the rovibrational energy levels have been determined for these complexes for the first time.
5. Using the rigid monomer approximation,  $J = 0, 1, 2$  rotational-vibrational energy levels and wave functions of the  $\text{CH}_4\cdot\text{H}_2\text{O}$  dimer were computed and assigned up to ca.  $65\text{ cm}^{-1}$  using two high-quality *ab initio* PESs.<sup>5</sup> Excellent, quantitative agreement is obtained between the computed and the experimentally reported far-infrared transitions of this complex, which were previously left unassigned by the experimentalists. Anomalous, reversed rovibrational-energy level ordering, *i.e.*, negative rotational excitation energies, is observed

both in the experimental and in the computed transitions. Thus,  $\text{CH}_4\cdot\text{H}_2\text{O}$  is another representative member of the class of astructural molecules.

## 4 Publications

### Research articles

- [1] C. Fábri, J. Sarka, and A. G. Császár, Communication: Rigidity of the molecular ion  $\text{H}_5^+$ , *J. Chem. Phys.* **140**, 051101 (2014).
- [2] J. Sarka, C. Fábri, T. Szidarovszky, A. G. Császár, Z. Lin and A. B. McCoy, Modeling rotations, vibrations, and rovibrational couplings of astructural molecules – A case study based on the molecular ion  $\text{H}_5^+$ , *Mol. Phys.* **113**, 1873–1883 (2015).
- [3] J. Sarka, and A. G. Császár, Interpretation of the vibrational energy level structure of the astructural molecular ion  $\text{H}_5^+$  and all of its deuterated isotopomers, *J. Chem. Phys.* **144**, 154309 (2016).
- [4] J. Sarka, D. Lauvergnat, V. Brites, A. G. Császár, and C. Léonard, Rovibrational energy levels of  $\text{F}^-(\text{H}_2\text{O})$  and  $\text{F}^-(\text{D}_2\text{O})$  complexes, *Phys. Chem. Chem. Phys.* accepted for publication (2016).
- [5] J. Sarka, A. G. Császár, S. C. Althorpe, D. J. Wales, and E. Mátyus, Rovibrational transitions of the methane-water dimer from intermolecular quantum dynamical computations, *Phys. Chem. Chem. Phys.* submitted for publication (2016).

## Conference posters

- [P1] J. Sarka, C. Fábri, and A. G. Császár, Higher-lying vibrational states of the  $H_{(5-n)}D_n^+$  ( $n = 0-5$ ) molecular ions, Anharmonicity in medium-sized molecules and clusters (AMOC2015), Madrid, Spain, April 2015.
- [P2] J. Sarka, C. Fábri, and A. G. Császár, How rigid is a quasimolecule? A case study of the molecular ions  $H_5^+$  and its isotopologues, 23th High Resolution Molecular Spectroscopy 2013 (HRMS, Dijon conference series), Budapest, Hungary, August 2013.

## Conference talks

- [E1] J. Sarka, The rovibrational spectroscopy of  $H_5^+$ , French-German Summer school SPECMO 2014, Marana Center, Corsica, France, September 2014.
- [E2] J. Sarka, The rovibrational spectroscopy of  $H_5^+$ , 23th International Conference on High Resolution Molecular Spectroscopy (HRMS, Praha conference series), Bologna, Italy, September 2014.
- [E3] C. Fábri, J. Sarka, and A. G. Császár, Rigidity of the molecular ion  $H_5^+$ , 69th Internal Symposium on Molecular Spectroscopy, Champaign-Urbana, Illinois, United States, June 2014.
- [E4] J. Sarka, The rovibrational spectroscopy of  $H_5^+$ , MTA Material and Molecular Structure Working Committee Meeting, Mártrafűred, Hungary, October 2013.