Preface

During the last five years Spectrochimica Acta Part A (SAA) has devoted two special issues (SI) to theoretical molecular spectroscopy. The first SI, vol. 53(8), was published in July 1997 and had the title 'Ab Initio and Ab Initio Derived Force Fields: State of the Science'. The second theoretically oriented SI, vol. 55(3), was published in March 1999 with the title 'Theoretical Spectroscopy: State of the Science'. These developments in a journal traditionally devoted to experimental aspects of spectroscopy are not at all surprising given the enormous advances in the field of theoretical spectroscopy and in the computer hardware employed to assess the new and ever more sophisticated theoretical/computational approaches. Given this background, we present here a third solely theoretically oriented SI, entitled 'First Principles Rovibrational Spectroscopy'.

For many decades rovibrational spectroscopy treated nuclear motion in terms of near-rigid rotation and small-amplitude vibration, relying heavily on perturbation theory (PT). While the formulas resulting from PT, even at second order, as usually applied, are often rather complex, they are easy to program: the resulting methods require almost no CPU time to run, especially on today's sophisticated hardware, and, last but not the least, they are extremely successful in reproducing many experimental data obtained at low to medium excitation (for some of the recent developments in this area one can consult the SI 'Ab Initio and Ab Initio Derived Force Fields: State of the Science', vol. 55 (3), and paper #16 by Atkinson and Law). Nevertheless, from the very beginning, perhaps starting from the insight-ful suggestions of Professor Boys of Cambridge University, there have been attempts to calculate rovibrational spectra of polyatomic molecules by more computationally intensive first-principles techniques. This usually means that the electronic structure calculations, necessary to compute potential energy and property hypersurfaces, are performed by convergent ab initio electronic structure methods and variational, nearly variational, or higher-order perturbational techniques are employed for the nuclear motion calculations. This combined technique can be made, at least in principle and within the Born–Oppenheimer approximation, arbitrarily accurate. For the first-principles approach to rovibrational spectroscopy to be really successful one has to utilize sophisticated procedures at all stages of the calculation. This means that one needs not only highly accurate electronic structure techniques but also sophisticated ways to represent the surfaces, as well as numerically efficient ways to determine intermediate quantities arising from the variational— or nearly variational—nuclear motion treatments. Recent developments suggest that these novel approaches can be even more successful than their predecessors and, in favorable cases, the results obtained can approach spectroscopic accuracy. This SI, comprising 17 papers from most of the leading experts in this field of natural science, not only reviews the latest developments in first-principles rovibrational spectroscopy but is also a testimony to the success of the field.

Due to the positive response of so many colleagues, most aspects of first-principles rovibrational spectroscopy are represented and the

leading edge of this science is covered in this SI. Paper #1, by Makarewicz and Skalozub, presents the difficulties encountered during determination of rovibrational Hamiltonians in internal coordinates and gives the Hamiltonian, derived independently by Handy and co-workers earlier, for ammonia-like molecules. Another prerequisite of most first-principles rovibrational calculations, representation of potential energy hypersurfaces (PES), is the topic of paper #2 by Varandas and Rodriguez. A simplified, one-dimensional approach to the bending modes of the [H, C, N] system by Chapuisat and co-workers in paper #3 shows the successes and difficulties encountered when simplified treatments are applied. Papers #4 to #9 present high-accuracy rovibrational results for closed- and open-shell triatomic molecular systems, including light (H_3^+), intermediate ([H, C, N], H_2O, NH_2), and heavier ones (CS_2 and He_2Si^{2+}). Different difficulties during solution of the full rovibrational problem are encountered in these papers, including the proper treatment of the Renner (sometimes called Renner–Teller) effect (paper #9) and of resonances (paper #7), inclusion of energy corrections due to special relativity (paper #4), as well as treatment of effects beyond the Born–Oppenheimer approximation (papers #4 and #6). New tetratomic paradigms (most notably H_2O_2, H_2CO, and ammonia-like systems) are treated in papers #10 to #13. Mladenovic describes the discrete variable representation (DVR) approach, she developed further for four-particle systems, in paper #10 and state-of-the-art applications of this approach in paper #11. A somewhat similar approach is used in the paper by Leonard, Handy, Carter, and Bowman (paper #12) and results are presented for the vibrational levels of ammonia. Results obtained with a complementary strategy embodied in the code MULTIMODE, which can be applied

straightforwardly to larger molecular systems, are given for H_3O^+ and D_3O^+ in paper #13 by Bowman, Huang, and Carter. The rovibrational level of possibly the most important pentatomic molecule, CH_4, is the subject of papers #14 and #15. Schwenke (paper #14) describes results obtained with his fully variational approach based on a highly sophisticated ab initio PES, while Wang and Sibert (paper #15) use, with similar success, high-order perturbative techniques for treatment of the nuclear motion problem. The anharmonic potential energy surface of CH_3F is the subject of paper #16, which gives an excellent overview of the remarkably successful perturbation-resonance approach, which again can be applied to larger systems. Paper #17 shows how anharmonic vibrations of large molecules (e.g. $(HF)_n$, $(H_2O)_n$, $n = 1, 2, 4$) can be treated from first-principles.

It is my belief that this collection of first-rate research papers will convince all readers of SAA that the future of theoretical rovibrational spectroscopy is even brighter than its past or present.

Here I would like to express again my sincere appreciation and gratefulness to all colleagues for their positive response to the request for papers for this SI, for the high quality of their manuscripts, and for their co-operation during the process of reviewing and editing the SI. Finally, I'd like to thank Professor Sidney Kettle for his guidance and patience in helping to put together this Special Issue.

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