



## Introduction to the Special issue Spectroscopic Tests of Fundamental Physics



This special issue of the Journal of Molecular Spectroscopy highlights the recent advances in the use of molecular spectroscopy to test fundamental physics. It follows a special session on the same subject at the 68th International Symposium of Molecular Spectroscopy held on 17–18 June 2013 at The Ohio State University.

Due to the possibilities of achieving increased precision in frequency measurements, the development of ultrastable lasers, extremely accurate atomic and molecular clocks, and techniques to produce and control ultracold samples of molecules, spectroscopic methods are now being employed to test our physical understanding of the Universe as laid out in General Relativity (GR) and the Standard Model (SM), and search for physics beyond these grand schemes. The principal idea is that the effects of new physics (e.g. that beyond the tenants of GR and SM) manifest themselves in minute shifts in quantum level structure of atoms and molecules. Physics that is normally associated with the TeV-scale can be probed in measurements at the feV level. Molecules, and molecular spectroscopy, is currently shifting to the forefront, because some phenomena and effects searched for are specifically enhanced in some of the nearly infinite variety of molecular species. Four, interrelated, facets of fundamental physics are strongly impacted by molecular spectroscopy:

1. Symmetry violating interactions that lead to a permanent electric dipole moment of the electron (eEDM,  $d_e$ ) and nuclear anapole moments ( $k_A$ ).
2. Parity violations in chiral molecules associated with the weak force.
3. Test of quantum electrodynamics (QED) in molecular systems and the quest for fifth forces.
4. Search for temporal and spatial variations of fundamental constants of nature.

These are topics covered in the 22 contributed papers to this special issue. Some papers highlight novel methods for cooling and manipulating molecules, either in neutral or ionized form, to be of relevance for future precision experiments, or for the development of molecular clocks. While part of the contributions focus on experiments, there are also a number of theoretical papers suggesting specific molecules as a sensitive test ground to probe symmetry violations or variation of fundamental constants.

More than 50 years ago Wu et al. measured a non-symmetrical spatial distribution of beta decay from  $^{60}\text{Co}$  establishing non-conservation of parity, or P-symmetry. As a second step CP violation was experimentally demonstrated in the decay of neutral K-mesons, for which the 1980 Noble Prize in Physics was awarded to Cronin and

Fitch. CP violation implies a time reversal T-asymmetry under the assumption of the CPT theorem (i.e. the invariance under simultaneous transformation of charge conjugation, parity transformation, and time reversal). Measurement of a non-zero electric dipole moment EDM in spin  $\frac{1}{2}$  particles, such as the electron, proton or neutron provides direct evidence of both P and T symmetry violations. The Standard Model of particle physics only incorporates a very limited amount of CP or T violation and hence predicts very small EDM values: for the proton,  $d_p$ , and neutron,  $d_n$ ,  $\sim 10^{-32}$ – $10^{-31}$  e cm, and for the electron  $d_e < 10^{-38}$  e cm. If an EDM value was to be measured that were significantly larger than these feeble values, than there is evidence for physics beyond the Standard Model.

The advantages of utilizing metal containing polar molecules for Parity Non-Conservation and electron-EDM measurements were recognized approximately 40 years ago and primarily stem from the very large obtainable internal electric fields,  $E^{\text{int}}$ , and the closeness of levels with opposite parity. The latter implies that the molecule can be fully polarized under application of a modest external field. The energy contribution due to  $d_e$  is the product  $d_e P(E_a) E^{\text{int}}$ , where  $P(E_a)$  is the degree of polarization achieved under the application of an applied electric field,  $E_a$ . The energy contribution due to the  $d_e$  is a nuclear spin independent process and all isotopologues are potential venues. Effectively this means that in some molecular systems the sensitivity for probing an electron-EDM is greatly enhanced, notably in YbF and ThO neutral molecules and in HfF<sup>+</sup> ions. The contributions by Smallman et al. and by Glasmann et al. serve to further characterize the YbF system, while Ni et al. present an experimental study on improved detection methods for the EDM-sensitive HfF<sup>+</sup> system. The study of Fleig and Nayak focuses on improved theoretical calculations for the ThO system.

Apart from the spin-independent phenomena there also exist nuclear spin-dependent parity violations arising from interactions between electrons and nucleons under the weak force and from nuclear anapole moments,  $k_A$ . The anapole moment couples to the spin of penetrating electrons and is thus detectable via molecular spectroscopy. Heavy, paramagnetic molecules such as  $^{87}\text{SrF}$  are particularly useful candidates because levels of opposite parity can be Zeeman tuned into near coincidence. This area of research is a combined effort of experimentalists and theorists because the coupling coefficients in the effective Hamiltonians that describe the interaction of  $d_e$  or  $k_A$  with the electrons can only be derived from electronic structure calculations. The work of Van den Berg et al. describes recent progress on an experiment of SrF, while the work of Isaev and Berger presents theoretical calculations of enhancement effects in certain classes of diatomic molecules.

The weak interaction responsible for eEDM and  $k_A$  is also at play in molecular systems and predicts a small energy difference between enantiomers of chiral molecules. Right- and left-handed molecules cease to be exact mirror images. The small parity violating energy difference corresponds to a reaction enthalpy of approximately  $10^{-11} \text{ J mol}^{-1}$ . In their work Shubert et al. describe an experimental effort based on three-wave mixing for enantiomer differentiation in the microwave regime using rotational transitions.

The description of the quantum level structure of low-mass atoms and molecules is fully governed by accounting only for a single interaction: electromagnetism. The weak and strong forces do not play a role at the present level of accuracy, while gravitational forces are many orders of magnitude out of range. Hence, quantum electrodynamics (QED), the fully quantized and relativistic approach to electromagnetism, must provide a full description of atomic and molecular structure. The observation of the Lamb shift in atomic hydrogen in the late 1940s for the first time revealed specific QED effects. Currently, highly accurate calculations including relativistic and QED effects can be performed for the smallest molecular systems: hydrogenic ions  $\text{H}_2^+$  and  $\text{HD}^+$ , and the neutral hydrogen molecules  $\text{H}_2$ ,  $\text{HD}$  and  $\text{D}_2$ . The work of Karr aims at further studies of the hydrogenic ions, with an added suggestion that these systems could operate as molecular clocks. The new *ab initio* calculations by Pachucki and coworkers on neutral hydrogen are put to a test in precision experiments: Niu et al. perform a highly accurate measurement of the fundamental vibration (1,0) in all three isotopomers, Kassi and Campargue measure the (2,0) first overtone in  $\text{H}_2$ , and Tan et al. measure the (3,0) second overtone in  $\text{H}_2$ . Niu et al. further explain how these QED tests in calculable molecular systems can be interpreted in terms of a probe for fifth forces at the Angstrom scale beyond the Standard Model. In the work by Salumbides et al. this concept is extended to the exotic molecular systems anti-protonic helium and the muonic deuterium ion probing fifth forces at the sub-Angstrom length scale.

The possibility that fundamental constants of nature may evolve over time touches upon the heart of science. Since the days of Galileo scientists have strived to cast the workings of natural phenomena in quantitative relationships of universal validity. Drifting constants imply that physical law is no longer eternal and incontestable. There are two dimensionless constants, the fine structure constant,  $\alpha$ , and the proton-electron mass ratio,  $\mu$ , for which spectroscopy is a test ground to probe temporal and spatial variations. While  $\alpha$  is an important parameter in electronic structure, and can be tested in atoms, molecules form a natural and sensitive venue to probe  $\mu$ . Tests can be performed on a cosmological time scale, with the advantage of time intervals of billions of years, or on a laboratory time scale, with the advantage of exploiting the modern tools of molecular spectroscopy and freedom to choose exotic molecular systems.

For probing a drifting  $\mu$  on a cosmological time scale, accurate laboratory frequencies must be determined for comparison with astronomical data. Two studies are presented demonstrating highly accurate Ramsey spectroscopy in the microwave domain; Truppe et al. measured transitions in the CH radical; De Nijs et al. measured a microwave transition in metastable CO.

Certain transitions in molecules are particularly sensitive to possible variations of the proton-electron mass ratio. Calculations of such sensitivity coefficients for spectral lines to be targeted in radio astronomical studies were performed by Ilyushin on acetone and by Viatkina and Kozlov on ethylene glycol.

A variation of the proton-electron mass ratio may be probed on a laboratory time scale in a wide variety of spectroscopic studies on molecules. In these studies extreme accuracy is of relevance, and methods include control of molecular motion, as well sensitive state-selective detection of species. Kajita et al. describe routes to accurate measurements on a variety of neutral and ionic diatomic molecules using laser cooling and ion trapping methods. Similarly, Seck et al. propose to perform precision experiments on  $\text{AlH}^+$  ions. Two studies focus on the application of the Stark-deceleration technique on polar molecules with the perspective of searching for  $\mu$ -variation: Quintero-Perez et al. demonstrate the preparation of ultracold ammonia samples, and Santamaria et al. propose to produce a cold beam of  $\text{CF}_3\text{H}$ , both for the purpose of assessing  $\mu$ -variation. Gacesa and Côté describe an alternative method to probe a varying proton-electron mass ratio via Feshbach resonances in ultracold molecules.

Finally, a study by Castrillo et al. is presented, describing a route to a novel definition of a fundamental constant, the Boltzmann constant  $k_B$ , through molecular spectroscopy.

These contributions provide an exciting overview of the subject of "Spectroscopy Tests of Fundamental Physics" and may serve as a reference for future investigations and developments.

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