Challenges in spectroscopy: accuracy versus interpretation from isolated molecules to condensed phases

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Molecular spectroscopy can be considered a discipline underlying all areas of chemistry because of its ability to investigate the stereo-electronic, dynamic and environmental effects of molecular systems in a non-invasive fashion. In the last decade, we have been witnessing relevant advancements of well-established techniques together with the blooming of new ones. If, on the one side, these accomplishments have opened the way toward deeper investigations and characterizations, also for systems of increasing complexity, on the other side, the analysis and interpretation of these experiments have been posing a great challenge. In such a scenario, computational studies play an essential role in the prediction of spectroscopic properties that can be directly compared with the experimental information or can even challenge the experiment itself, at least for small isolated semi-rigid systems. However, the analysis of experiments is seldom straightforward because of the subtle interplay of several different effects and/or the complexity of the system under consideration. For example, when moving to large systems, difficulties in the application of accurate quantum-chemical protocols are paralleled by the need of extensive configurational sampling.

While the recent developments of hardware and software have moved computational spectroscopy from a highly specialized research area limited to theoreticians to a general tool for researchers in different fields of chemical science, this branch of quantum chemistry has been characterized from the very beginning by the dichotomy of qualitative and quantitative descriptions. Such dichotomy has led to that of interpretation and accuracy. However, an increasing number of researchers have been giving significant contributions to their reconciliation in the field of molecular spectroscopy and this collection of papers tries to provide a picture of the current state-of-the-art.

As a matter of fact, the disentanglement of the different effects contributing to the overall spectrum requires synergic contributions from experiment and computation, thus starting from semi-rigid isolated molecules, then proceeding toward flexible systems, and – with the proper treatment of intermolecular interactions – ending up with a deep understanding of condensed phases. This kind of effort has been at the center of the scientific career of Vincenzo Barone, to whom this collection is dedicated in occasion of his 65th birthday. The most significant contributions of Vincenzo Barone range from density functional theory [1,2], to solvent effects [3-6] and vibrational modulation of different spectra [7]. He also devoted huge efforts in software developments and pilot applications for EPR [8], vibrational [9,10] and electronic [11,12] spectroscopies. In the last years, the virtual multifrequency spectrometer

(VMS) project has led to a general tool with powerful graphical user interfaces for both theoretically and experimentally oriented spectroscopists [13,14]. Finally, the role of immersive of virtual and augmented reality is being explored with the aim of building an integrated cyber-infrastructure, which, besides enabling a number of applications well beyond the state of the art in the field of molecular spectroscopy, will represent a revolutionary proof of concept [15].

This themed issue collects a series of articles that cover the most relevant aspects of experimental (from low to high resolution) and computational spectroscopy, with a special emphasis on gas-phase investigations, but also facing important challenges in condensed-phase. Starting from the radio-frequency regime, it has been shown that EPR can be successfully used to study complexation in supramolecular systems of relevant complexity when traditional methods based on NMR or fluorescence cannot be applied (DOI: 10.1039/c8cp04362k). Proceeding to higher frequencies, thus moving to the microwave region, it is pointed out the high precision that characterizes rotational spectroscopy, which is therefore suitable for guiding astronomical investigations (DOI: 10.1039/c8cp04498h, DOI: 10.1039/c8cp05311a, DOI: 10.1039/c8cp04532a) and for dynamic studies (DOI: 10.1039/c8cp04462g, DOI: 10.1039/c8cp04455d).

To reconcile accuracy and interpretation in the field of molecular spectroscopy and dynamics, a fundamental role is played by state-of-the-art computational methodologies (DOI: 10.1039/c8cp04455d, DOI: 10.1039/c8cp01721b, DOI: 10.1039/c8cp04451a, DOI: 10.1039/c8cp04672g, DOI: 10.1039/c8cp04490b, DOI: 10.1039/c8cp05169k). In this respect, in the perspective article (DOI: 10.1039/c8cp04990d) quantum approaches applied to vibrational dynamics and infrared (IR) spectroscopy, also describing their extension to molecular clusters and even condensed phase applications, are addressed in detail. An important step forward for the reconciliation mentioned above is the synergic interplay of experiment and theory (DOI: 10.1039/c8cp04327b, DOI: 10.1039/c8cp04480e, DOI: 10.1039/c8cp06288a) that can lead, for example, to accurate structural determination (DOI: 10.1039/c8cp04888f). Moving to the field of electronic spectroscopy, an important issue is the proper account of the underlying vibrational structure required to correctly describe the dynamic and spectroscopic behavior (DOI: 10.1039/c8cp04707c, DOI: 10.1039/c8cp02845a). Spectroscopy plays a fundamental role for the elucidation of aggregation processes (DOI: 10.1039/c8cp04386h), solvation (DOI: 10.1039/c8cp06527f) and quantum confinement effects (DOI: 10.1039/c8cp04109a), also allowing the investigation of peculiar quantum effects such as those, e.g., characterizing the photoexcitation dynamics of atoms from the surface of helium nanodroplets (DOI: 10.1039/c8cp05253k). Furthermore, computational spectroscopy permits to shed light on complex quantum behavior, like, e.g., the photodynamic activity of complex systems (DOI: 10.1039/c8cp04848g).

Among the various techniques, the chiral spectroscopies deserve to be mentioned because they enable unique characterizations of the peculiar properties, effects and behavior of chiral molecules (DOI: 10.1039/c8cp02395f, DOI: 10.1039/c8cp04748k, DOI: 10.1039/c8cp04107e). Finally, the integration of quantum-chemical and stochastic methods for the determination of transport properties of molecules, and in particular of proteins, are relevant to model and interpret their chemical-physical activity in solution and thus

provide an important step for the correct reproduction of the corresponding spectra (DOI: 10.1039/c8cp04879g).

In summary, even if a number of other aspects and/or techniques are of course important in computational and experimental spectroscopy, we think that the collected papers represent a significant and comprehensive account of the state of the art in this very active field.

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