



The Interplay Between Experimental Spectroscopy, Theoretical, and Computational Quantum Chemistry

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Abstract

Advances in technology led to development of sophisticated experimental techniques for studying new chemical systems and processes on the molecular levels. Such experimental observations required advanced computational and theoretical studies to enable observations and analysis of the data. This led to evolution of new theoretical models and computational methods that have been proven valuable in aiding experimental detection and interpretation of results. Collaborative research between theorists and experimentalists became essential in the various areas chemistry, such as identification and determination of properties of new important hydrogen-bonded and chemically-bonded chemical species. These molecular systems are of importance in the atmospheric chemistry, development of new materials from large clusters, drug design, reactions and interactions in biological systems. This mini review provides examples of the author's theoretical work for two different types of new chemical systems, in collaboration with experimental spectroscopists. These selected studies will be used to emphasize importance of the interplay between theory, computational chemistry, and high-resolution molecular spectroscopy in gas phase.

Review

Laser Induced Fluorescence (LIF), Infrared (IR) laser absorption, and Fourier Transform Microwave (FTMW) high resolution spectroscopy of gaseous molecules are recognized as the most accurate methods for determination of the molecular geometry as well as detailed quantitative information about electronic, vibrational, and rotational energy levels. However, application of these spectroscopic techniques for observation and analysis of new gaseous species is experimentally and theoretically challenging. The experimental difficulties are: 1) finding the proper conditions for preparation of new molecules in supersonic expansions at very low temperatures (2-5 K); 2) knowledge of the frequency region for spectroscopic detection. The theoretical and computational challenges are due to complexity of the rotational and fine structures, large amplitude motion, electron-spin interactions, and mixing of electronic configurations. These difficulties make experimental identification and analysis of spectra as almost impossible tasks without theoretical/computational assistance. However, advanced quantum mechanical computational methods are capable of predicting the molecular

geometry, electronic excitation frequencies, vibrational frequencies, rotational constants, and molecular properties. Development of the proper quantum mechanical theoretical model for each chemical system enables analysis of observed spectra. Thus, the interplay between molecular spectroscopy, computational, and theoretical chemistry is essential for studying new molecules and clusters. Examples that demonstrate importance of collaborative interdisciplinary research between theoretical/computational chemistry and experimental high resolution spectroscopy will be briefly discussed in the next paragraphs.

High resolution IR laser spectrum of the hydrogen-bonded O₂-HF dimer in the ground electronic state was observed in a supersonic jet expansion at 2 K but assignment and analysis of the spectrum was not possible because the existed theories were not suitable for O₂-HF. Derivation of the proper quantum mechanical Hamiltonian, its matrix elements, electric dipole moment matrix elements, and expectation values of the quantum number of open-shell systems, such as O₂-HF, is a major theoretical task that needs theoretician's efforts. This is primarily attributed to complex coupling schemes between the overall molecular rotational angular momentum in the complex and the electron-spin angular momentum of the O₂ moiety. Accordingly, the author developed a new quantum mechanical Hamiltonian [1-3] and a computer code [4] that implement matrix elements of the Hamiltonian and the electric dipole moment matrix elements for calculation of energy levels and relative intensities of the allowed transitions. The theory and the computer code were successfully used to assign and analyze the observed IR spectrum [5] of O₂-HF. Detailed analysis led to determination [5] of the molecular structure and estimation of the value of the intermolecular binding energy in the complex. This work was followed by high level ab initio computational investigation of the potential energy surface [6] of O₂-HF. The computationally determined structure, binding energy, and vibrational frequencies were in almost perfect agreement [6] with conclusions of the spectroscopic analysis. This agreement provided strong validation for the theoretical model, the computer code, and the spectroscopic analysis. Furthermore, both the theoretical and the computational results [6] provided predictions for observation of the microwave spectrum of O₂-HF. The microwave spectrum was successfully assigned and analyzed [7] using the same quantum mechanical Hamiltonian [1-3] that was introduced for analysis of the IR spectrum [5].

Attempts for the first spectroscopic detection of the MgOMg species in the gas phase by means of high resolution LIF spectroscopy have been hindered by the lack of computational prediction for the electronic excitation and the vibrational frequencies. The author carried out detailed correlated ab initio calculations followed by multi-reference configuration interaction calculations for investigation of the potential energy surfaces of the ground and the excited electronic states of MgOMg. This work determined linear geometry and the ground state as a $X^1\Sigma_g^+$ state with electron configuration that is a mixture of σ_g^2 and σ_u^2 configurations. The computed potential energy curves of all possible excited electronic state (seven states) showed either crossing and/or avoided crossing of the vibronic energy levels. The calculations showed change in geometry of MgOMg upon electronic excitation from the ground state ($X^1\Sigma_g^+$) to the lowest-energy excited electronic state (A^1B_2), where the geometrical structure switches from linear to a bend configuration of C_2v symmetry. The A^1B_2 state was identified as the least perturbed state for relatively low-energy vibrational levels. Furthermore, the electronic excitation frequency of the $A^1B_2 - X^1\Sigma_g^+$ transition is the most accessible by the Frank-Condon factor and the dye laser frequency range. These conclusions provided excellent predictions for LIF spectroscopic observation [8] of rovibronic transitions upon tuning the dye laser frequency to the predicted vertical excitation frequency of the $A^1B_2 - X^1\Sigma_g^+$ electronic transition. In addition, calculation of the vibrational energy levels was carried out for assignment of the observed vibronic progression. Results of the spectroscopic analysis of the recorded transitions were in good agreement with those of the computational study [8]. Thus, the computational predictions aided the first observation of the important MgOMg hyperstoichiometric species while the experiment validated the used computational method as a good level of theory for investigation of the potential energy surface of MgOMg.

Competing Interests: The authors declare that they have no competing interests.

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