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Summary of Doctoral Dissertation entitled

Selected aspects of theoretical prediction of spectra of van der Waals complexes with spectroscopic accuracy.

A reliable theoretical description of intermolecular interactions is of paramount importance for understanding the natural world around us. Progress in the development of theoretical methods and the increase in computational power in recent years have made it possible to go beyond mere qualitative agreement. The accuracy of calculated physical properties for small molecular complexes has increased to the extent that, in some cases, theory can support the interpretation of experiments and even provide data when the necessary experimental information is lacking. However, at the same time, we are reaching for increasingly demanding systems, whose precise description once again brings us closer to the current performance limits of methods and equipment. The research conducted as a part of the doctoral thesis aimed to demonstrate how accurate theoretical results can be used to resolve interpretative problems in experiment, and to propose an approximate method for modeling interactions that enables a reduction in the computational cost of calculating the spectroscopic properties of complexes without significant loss of accuracy.

This work considered the complex of H_2 and CO molecules, which is of primary importance in astrophysics due to the widespread occurrence of these molecules in the Universe. The author's goal was to fully interpret the experimental spectra for *ortho*H_2–CO, which were measured as early as 1998, but the energy level structure of the complex had not yet been deduced. To improve the precision of the theoretical description, the positions of low-energy resonances, which are crucial for spectral interpretation, were identified. This opportunity was also used to investigate the resonances for other isotopologues and spin isomers of this complex: *para*H_2–CO, HD–CO, *ortho*D_2–CO, and *para*D_2–CO, and thus supplement the literature data. Thanks to information about the energies of bound states and resonances, as well as their corresponding wave functions, a theoretical spectrum was generated for *ortho*H_2–CO. Comparison with the experimental spectrum enabled the assignment of individual lines and even the refinement of experimental transition energies. In

the next step, 84% of the experimental vibrational-rotation levels for *ortho*H_2–CO were deduced from these energies using the originally prepared algorithm. It was also shown that the remaining levels could not be determined based on the available experimental data. Using the aforementioned algorithm and the calculated spectra for *ortho*D_2–CO, an analysis of the experimental spectrum for this complex, which had been partially interpreted previously, was also performed. This allowed for minor corrections to those results and the determination of additional energy levels, including all previously missing bound states. The presented studies have shown that the theoretical description of complexes of weakly interacting molecules, if performed with sufficient accuracy, can be effectively used for detailed analysis of experimental results.

Furthermore, this dissertation also proposes a new method to account for the effects of molecular nonrigidity on the intermolecular interaction energy when constructing surfaces of reduced dimensionality. This procedure, named adiabatic averaging, was tested for the demanding HF–HF complex, characterized by a significantly stronger interaction and greater anisotropy than H_2–CO. The tests showed that the adiabatic surface yields results closer to the reference data than the previously used surface obtained by simple averaging over molecular vibrations. This finding opens the prospect of creating interaction energy surfaces that, combined with an approximate description of the dynamics, will lead to spectra of very high accuracy.