

Summary of Doctoral Dissertation entitled

## **Precise calculations of rovibrational spectra for various isotopologues of the H<sub>2</sub>–CO complex**

The weakly interacting complex of H<sub>2</sub> and CO molecules is of particular importance in astrophysics and astrochemistry because of the abundance of both molecules in the Universe. In turn, the significant presence of deuterium in the total amount of hydrogen in some regions of space requires information on HD and D<sub>2</sub> interacting with CO. These facts have been stimulating experimental and theoretical studies of the H<sub>2</sub>–CO complex for a long time, but only recently theoretical calculations have reached a level of accuracy that can genuinely assist in the interpretation of the experiment and replace experimental data where they are unavailable.

The doctoral thesis investigated five cases of the H<sub>2</sub>–CO complex, with different isotopic substitutions and spin isomers of the H<sub>2</sub> molecule: *para*H<sub>2</sub>–CO, *ortho*H<sub>2</sub>–CO, *para*D<sub>2</sub>–CO, *ortho*D<sub>2</sub>–CO and HD–CO. The main goal of the research was to obtain a pattern of rovibrational levels and then theoretical infrared spectra for *ortho*D<sub>2</sub>–CO, *para*D<sub>2</sub>–CO and HD–CO, for which such data had not been previously available. To obtain the spectra, the rigid rotator method was used in dynamic calculations, and the interaction surface dependent only on the intermolecular coordinates was obtained by averaging the full-dimensional interaction energy surface over internal vibrations of the interacting molecules. The accuracy of this approach was checked in model studies for the *para*H<sub>2</sub>–CO and *ortho*H<sub>2</sub>–CO complexes. For these cases, the energy levels were recently calculated using the full-dimensional method with the same potential so that they can be used as the reference. The agreement between the energies calculated using the approximate method and the reference energies was unprecedentedly high, at the level of 0.001 cm<sup>-1</sup>.

Successful tests of the applied spectral calculation protocol allowed us to confidently approach the calculations for the following cases. For *ortho*D<sub>2</sub>–CO, the calculated rovibrational energies and spectra agreed with the experimental ones at a similar level as in

the case of *para*H<sub>2</sub>–CO, which is an additional confirmation of the accuracy of the applied procedure. It was also shown that dedicated averaged surfaces should be used, i.e., those taking into account the isotopic composition of the molecules. Theoretical results obtained for the HD–CO complex were compared with very limited experimental data and this test was positive. The next case, *para*D<sub>2</sub>–CO, is a kind of *terra incognita*, since the theoretical results obtained in the present research are the first data on it. This system is the most spectroscopically complicated of all those considered. Taking into account potential experiments, a measurement procedure for successively changing temperature values was proposed, which would increase the chances of complete interpretation of experimental spectra.

In search of possibilities for further improvement of the interaction energy surface, the significance of corrections describing the contributions to the interaction energy from advanced correlation effects, relativistic effects, and adiabatic effects has been investigated. It has been shown that the influence of advanced correlation corrections is crucial for achieving the current good agreement between theoretical and experimental spectra. The accuracy of the calculation of this correction should be improved in the future, although this may be difficult due to high costs. On the other hand, relativistic or adiabatic corrections are more accessible to calculate at a satisfactory level of theory, but their impact on improving the accuracy of the spectra is likely to be small.

The research results presented in the dissertation significantly enriched the knowledge of the spectra of various isotopologues and spin isomers of the H<sub>2</sub>–CO complex. An achievement that goes beyond this particular complex is the demonstration that if, together with the rigid rotator approximation commonly used in dynamic calculations, we use the interaction energy surface averaged over the internal vibrations of the molecules, we obtain results very similar to those derived from expensive full-dimensional calculations. Moreover, the approximate averaging method used in the studies does not require the construction of a full-dimensional surface and allows for significant savings in numerical calculations.