Novel explorations of bonding in diatomic van der Waals molecules: high resolution rotational spectroscopy and advanced ab initio calculations – probing sources of discrepancies

1. OBJECTIVES OF THE PROJECT

At the beginning, before main objectives of the project are introduced, an obvious statement that frequently escapes during an evaluation of the current status of knowledge on interatomic bonding in simplest molecules – diatoms - will be very appropriate. So, Let us have in mind the present development in experimental methods of laser spectroscopy that allows precise studies of molecular energy structures, and have in mind highly advanced ab initio methods (that is those that enable derive "from the beginning" at an interatomic potential between two atoms constituting a molecule without any adjustment of calculation model to the experimental data). The conclusion is that very rarely one may state that ab-initio calculated interatomic potential reproduces that derived from experimental studies of molecular (vibrational and rotational) energy structures. For many (even for a non-expert, chemist or physicist) it is a surprising news. What is worse, it seems to concern that simple physical objects. But the fact is a fact – **there is no agreement between results of experimental studies and theoretical description of the interatomic interaction, even in a simple diatom**.

Here, an experienced physicist experimentally and theoretically studying the problems of physical chemistry (or chemical physics) comes to the rescue. Together with his research team proposes the following project.

Let us narrow the class of molecules in question to these that in their ground energy state constitute two atoms with fully filled electron shells (the atoms are not excited and electron shells around their nuclei possess a spherical symmetry). As a result, a *very weak interaction* between two electrically neutral objects in the molecular ground state is created. The interaction is called van der Waals (vdW) interaction. The bond between atoms is extremely weak, so in a room temperature there is no chance for its existence. Thus, in order to be able to study the vdW molecules, it is necessary to create them in very specific environment (characterized with low temperatures) that ensures their survival, even for a short period of time needed for their interaction with a laser beam – a process that is essential to examine their energy structures. The special environment guarantees so-called *supersonic molecular beam* in which molecules travel with a speed larger than speed of sound in vacuum – hence the term "supersonic" in name of the beam.

Situation is changing when one of the atoms that constitute the molecule gets excited. Consequently, the entire molecule becomes excited and the interaction between atoms undergoes a modification: to the vdW interaction present in the ground state add contributions that characterize interaction of a distant electron with the rest of the molecule. In case of a strong electron excitation (it occurs in so-called Rydberg molecule) one deals with unusual effects that appear when the distant electron moves further away from nuclei surrounded by a cloud of the remaining electrons. In effect, interactions appear which are responsible for irregularities in the interatomic potential, the irregularities that are difficult to obtain within present ab initio calculations.

Having learned the reasons for studies of weak vdW interaction and the environment in which the studies can be performed, let us formulate the **project Objectives**.

The project proposes novel experimental studies of rotational energy structures in diatomic vdW molecules (rotational energy structure is a result of rotation of nuclei around an axis perpendicular to the internuclear axis and has an influence on interatomic bonding). The studies will be conducted with high spectral resolution enabling the detection of very subtle details of the energy structure. The experimental studies will be supported by ab initio calculations. The obtained results will contribute to general knowledge on, so far unknown, properties of molecular vdW bonds, will allow a classification of presently highly incomplete interatomic potentials of ground, low- and higher-excited (Rydberg) electronic energy states in molecules formed by two atoms with fully filled electron shells in their ground states.

The results will contribute to the understanding and (perhaps) explaining of still existing large disagreement of experimental potentials with those obtained as a result of ab initio calculations. Assumptions of the project rely on the fact that new and precise potentials determined experimentally and those being a results of new, more accurate ab initio calculations based on quantum chemistry methods are mutually stimulating sources of information leading to a full classification of interaction in vdW molecules. It will lead to interpretation of potential irregularities. Also, it will help in parameterization of vdW interaction according to the type and degree of excitation of interacting atoms constituting the molecule.

2. BASIC RESEARCH TO BE CARRIED OUT

It is easy to find out that the research proposed in the project is strictly oriented towards broadening of basic knowledge on molecular rotations, properties of molecular bonding and classification of interatomic potentials of vdW molecules by studying rotational (as well as vibrational – that is caused by a periodical change of the internuclear distance) energy structures with high spectral resolution as well as by calculating interatomic potentials using ab initio methods. The research is aimed at learning phenomena that rule a behaviour of the elementary components – two atoms when they approach each other and are able to create more complex objects – diatomic molecules. The final effect depends on to what extent the two elements can "get closer", how willingly they share electrons between each other and to what extent atomic nuclei vibrate and rotate.

The activities in the project are divided between **experimental** and **theoretical-computational** basic research. The former relies on experiments in which molecules in supersonic beam interact with laser beam from a unique laser system. Interatomic potentials will constitute the final results. The latter will provide ab-initio calculated potentials obtained according to assumptions made during the calculations. Comparison of these two approaches will provide with far-reaching conclusions for the experiments (are they executed with sufficient accuracy?) as well as for the calculations (are they sufficiently accurate in accounting for all of the

effects present in interatomic interaction?).

The mutual stimulus of the two approaches will minimize incompatibilities and still existing differences of the results obtained from these two approaches.

3. REASONS FOR CHOOSING THE PROPOSED RESEARCH TOPIC

Ground-breaking, as intended, studies of molecular spectra of relatively heavy vdW molecules performed with high spectral resolution open new possibilities in their interpretation.

First of all, the proposed studies will provide precise interatomic potentials and accurate spectroscopical constants (they allow an empirical description of molecular energy structure). Besides, results of such experiments are extremely important in verification of theoretical assumptions, development of methods of quantum-chemical calculations and testing new relativistic models of interatomic interactions (in relativistic models it is assumed that electron's speed is limited and is equal to speed of light). Secondly, particularly within the context of proposed advanced ab initio calculations, an originality of the project outcome will transfer into a possibility of modelling new materials based on vdW interaction (for instance graphen structures which interact via vdW interaction), perspective of applying the obtained results to new schemes of creation of quantum entanglement of atoms (a state in which, for instance, two atoms remember that they were "born" from one molecule via its controlled dissociation), or schemes of photo-association of molecules (that is a processes permitting creation of molecule from two distant atoms in presence of a quantum of laser light).

The proposed research goes well beyond present knowledge being focused on first-time investigation of very "dense" rotational energy structures of vdW molecules consisting of two neutral atoms (it is planned to study molecules consisting of zinc, cadmium, mercury and noble gases, such as Zn_2, Cd_2, Hg_2, CdKr, ZnAr or HgHe), and determination of precise shape of potential energy curves describing interatomic interaction that depends on distance between atomic nuclei.

The pioneering studies will be conducted by a team members who have large experience and ensure necessary "know-how", modern and unique laboratory equipment. It guarantees high-quality results and expectation for a ground-breaking results – facts that are highly anticipated by international scientific community and will bring publications in scientific journal with high impact factors.