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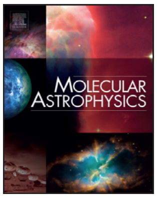

Review article

Weakly bound molecular complexes in the laboratory and in the interstellar medium: A lost interest?

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ABSTRACT

Weakly bound molecular complexes have been studied in the laboratory for more than 40 years. Interest in them was heightened when they were predicted to be important species in the chemistry of the atmosphere and the interstellar medium (ISM) and also because of their unusual rotational dynamics, described in some cases by nearly free rotation of monomers within the complex. About 15 years ago the interest was heated by the observation of microscopic superfluidity in small helium clusters. On the other hand, a number of unsuccessful tries to detect weakly bound complexes in the ISM considerably lowered the interest in their further investigations for astrophysicists. With this short review I would like to show a perspective for future studies of astrophysically relevant weakly bound molecular complexes in the laboratory and for their potential search in the ISM.

1. Introduction

To understand the evolution of our environment and the Universe it is necessary to expand our knowledge of the dynamics, physical-chemistry, and biological processes as they happen on different time and size scales. Weakly bound molecular complexes can be considered to be a bridge between individual isolated molecules and the bulk phase, a bridge along which properties of matter change dramatically. Intermolecular interactions in molecular complexes affect optical properties and reaction dynamics of molecular systems and, thus, are of a general importance.

Molecular complexes have been considered to play a large role in the chemistry of the ISM, in particular in dense and cold molecular clouds, and also at the higher density and higher temperatures found in planetary atmospheres, where they can contribute to the atmospheric chemistry and climate (Vaida and Headrick, 2000; Klemperer and Vaida, 2006). Molecular dimers have been proposed to be a major constituent of cometary matter (Krasnopolsky et al., 1988) and to be contained in interstellar grain mantles (Scherer et al., 1998). However, up until now only the $(O_2)_2$ and $(H_2)_2$ dimers have been detected in the atmospheres of Earth (Pfeilsticker et al., 1997; Solomon et al., 1998) and Jupiter and Saturn (Mckellar, 1988; Trafton and Watson, 1992). One more work, which can be mentioned in this context, is the first laboratory observation of a rotationally resolved millimetre-wave spectrum of the water dimer recorded under atmospheric conditions (Tretyakov et al., 2013).

There is a direct connection between laboratory and astronomical studies. Transition frequencies and dynamical and structural parameters obtained by using laboratory spectroscopic techniques are the data needed to make astronomical searches for "new" molecules and molecular complexes in the ISM possible and also to be able to decode already available astronomical spectra. These data are then used to test intermolecular interaction potentials, and, by merging all together, they provide necessary and unambiguous information for the development of reliable astrochemical models.

The purpose of this paper is to provide an overview of laboratory and observational studies of weakly bound molecular complexes that are of particular astrophysical or astrochemical interest in order to aid the parameterization of the search for these complexes in space and to note gaps in the laboratory and calculational data so that areas of future emphasis can be identified. Weakly bound complexes are discussed below in the context of spectroscopic studies and include hydrogen bonded and van der Waals complexes. Strongly bound molecular aggregates involving ions are also of great interest and importance (see, for example Herbst, 1985; Klemperer and Vaida, 2006) but are out of the scope of this paper. With this short review I do not aim to discuss all studied and to be studied systems, but will focus on the most interesting and promising, from my point of view, complexes of astrophysical and astrochemical relevance. Also I will not try to mention all existing works and references for specific systems, concentrating not

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on past works, but rather on those not yet well-understood systems that promise to yield the most interesting results.

2. Weakly bound complexes in the laboratory

The binding energy of weakly bound complexes is usually much smaller than room temperature thermal energy. For this reason, the low temperature of a gas phase supersonic jet, rare-gas solid matrix, or liquid helium droplet is the environment in which weakly bound complexes are typically studied in the laboratory. Low and high resolution spectroscopy, mainly in the infrared (IR), terahertz (THz), millimetre-wave (MMW), and microwave (MW) spectral regions, has been performed. The “high” resolution experiments refer to measurements taken at resolution good enough to interpret data from radio telescopes, namely, as defined by the Doppler linewidth, which is hundreds of kHz at a frequency of 100 GHz. Interaction between a complex and a solid matrix or droplet surface leads to inhomogeneous shifts and broadening of the spectral lines and also hinders free rotation of the complex. Thus, the laboratory data best suited for comparison to astronomical observations is that determined in the gas phase. They are the primary subject of the discussion below.

Typically, MW spectroscopy gives access to information about ground state rotational energy levels of the entire complex, MMW to internal rotor states, THz probes intermolecular vibrations, and IR -intramolecular vibrations. As one can see, different techniques probe different parts of the intermolecular potential, and, when merged, provide a complete picture of the interaction between sub-units in the complex. Gas phase high resolution data can be used directly as reference spectra to match data in radio-astronomical searches for ISM species, and also give unambiguous information on the dynamics, composition, and structure of the complex. Moreover, they are the best data to use for testing intermolecular potential energy surfaces (PES). For details about the relation between PES and the spectra of weakly bound complexes the reader is referred to the review by Wormer and van der Avoird (Wormer and van der Avoird, 2000). Examples of testing of PESs for molecular complexes with high resolution data are available (Fellers et al., 1999; Potapov et al., 2009; van der Avoird and Nesbitt, 2011; Jankowski et al., 2013).

A huge number of weakly bound complexes have been probed spectroscopically in the gas phase (see, for example, Novick; Xu et al., 2005; Tanaka et al., 2011; Potapov and Asselin, 2014; Herman et al., 2016). But in spite of this “huge number” a large amount of necessary information for many important species is not available. Below I give a few interesting examples, but, for sure, the reader can find more on his/her own. The future tasks for the mentioned below complexes are: to obtain spectroscopic signatures in different spectral ranges; to reveal their internal dynamics; to understand the role of hydrogen and van der Waals bonds in the dynamics, structure, and reactivity of the complexes; to build reliable interaction potentials; and, finally, to include new data into new astrochemical models.

2.1. Complexes involving water

Water molecule is a particularly interesting binding partner because of its omnipresence (it exists on Earth, on the Sun, in interstellar molecular clouds, and on outer planets) and its important role in many chemical, physical, biological, and astrophysical processes.

Weakly bound complexes involving water are suspected to significantly affect Earth’s atmospheric chemistry and, thus, to influence Earth’s climate. As this review is devoted to astrophysics, I just mention below for the interested reader a number of papers describing the role of hydrated complexes in the atmospheric chemistry (Murphy et al., 1998; Daniel et al., 1999; Vaida and Headrick, 2000; Pfeilsticker et al., 2003; Vaida et al., 2003; Vaida, 2011).

Water in its gaseous form acts as a coolant that allows interstellar gas clouds to collapse to form stars, whereas water ice facilitates the sticking of small dust particles that eventually grow to planetesimals and planets. The development of life requires liquid water and even the most primitive cellular life on Earth consists primarily of water (van Dishoeck et al., 2014). Water has been detected in spectra of the Sun (Wallace et al., 1995) and those of other cool stars. In interstellar space, gaseous water was detected more than 40 years ago in the Orion nebula (Cheung et al., 1969) and water ice was discovered a few years later through its infrared bands in protostars (Gillett and Forrest, 1973). Water vapour and ice have now been observed in many star- and planet-forming regions throughout the galaxy (Bergin and van Dishoeck, 2012).

Molecular complexes involving water may play a large role in the chemistry of the ISM, in particular in dense and cold molecular clouds (Klemperer and Vaida, 2006). In astrochemical media, as well as in planetary atmospheres, hydrogen bonding plays an important role in the evolution of many chemical species by affecting their stability as well as their reactivity (Burke and Brown, 2010; van Dishoeck et al., 2014). Many weakly bound complexes with H_2O have been probed spectroscopically in the laboratory, mostly in the MW range, and more rarely in the IR, THz, and MMW regions. For details the reader is referred to the recently published review on high resolution jet spectroscopy of weakly bound complexes involving water by Potapov and Asselin (2014).

Despite nearly forty years of study (Dyke et al., 1977; Jankowski et al., 2015) work continues on the water dimer. The interaction potential for $(H_2O)_2$ is being continuously improved, and further high resolution spectroscopic data are desired. The same concerns the larger water clusters, $(H_2O)_N$ with $N > 2$, on which fewer results have been presented than for the dimer (see, for example, Paul et al., 1999; Perez et al., 2012,2013).

The H_2–H_2O complex plays important roles in processes in the interstellar medium, such as the pumping of the H_2O maser, which is observed in regions of active star formation (Rowland and Cohen, 1986), and the recombination of H atoms to form H_2 on icy interstellar dust grains (Buch, 1990). H_2O masers tend to be highly localized, thus providing an excellent tool for pinpointing and perhaps better understanding star formation phenomena. However, the actual pumping process behind the maser radiation is as yet unknown. The intensity of the H_2O maser radiation was assumed to depend strongly on the interaction of cold water and hot gas molecules, particularly H_2 (Rowland and Cohen, 1986). One of the interesting aspects of the spectroscopic studies of the complex is that the *ortho*H_2–H_2O spin modification has been probed (Weida and Nesbitt 1999; Harada et al., 2014), but up to now there have been no measurements of the *para*H_2–H_2O spin modification.

The NH_3–H_2O and CH_4–H_2O complexes are important in astrophysical processes: the most stable carbon, nitrogen, and oxygen containing species at the temperatures and pressures that characterize protostellar nebulae, are methane, ammonia, and water. These species may therefore play critical roles in the origin and evolution of outer solar system bodies (Miller, 1973; Ellsworth and Schubert, 1983; van Dishoeck, 2014). For example, in the Saturnian system, it has been estimated that the initial ice budgets of Titan as well as the smaller satellites may have contained as much as 15% ammonia-water hydrate (Ellsworth and Schubert, 1983). The literature appears to have only two works concerning spectroscopy of these complexes (Stockman et al., 1992; Dore et al., 1994).

Various astronomical and laboratory chemical studies have shown that amino acids could be synthesized in some meteorites and cometary ices (Cronin and Pizzarello, 1983; Bernstein et al., 2002; Caro et al., 2002; Burton et al., 2012). Because of the