MOLECULAR STRUCTURE AND CHEMICAL PROPERTIES OF ATMOSPHERIC WATER

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Contents

Summary

This chapter gives a brief overview of molecular properties and the chemical fate of individual water molecules. Particular attention is paid to the aggregation of water molecules to form small hydrogen-bonded associates or clusters. The latter are extensively studied nowadays in laboratory controlled conditions by virtue of sophisticated spectroscopic tools. The involvement of a number of these minor water aggregates in atmospheric processes is still a matter of discussion. There is no doubt, however, that water molecules in pairs, interacting with molecular perturbers, play a key role in transmission of short-wave radiation through the atmosphere. Also minor neutral and ion clusters are of importance in atmospheric photochemistry, nucleation processes, and cloud physics and chemistry. Aqueous and solid water particles of larger size play a vital role in various atmospheric processes since these are major constituents of aerosol, haze, fog and precipitation. Heterogeneous chemical reactions on the surface of condensed water particles is recognized to be of prime importance in stratospheric photochemistry. The rates of reactions increase significantly when the reactants are stuck to the surface of tiny water droplets and ice crystals. To understand the molecular mechanisms which govern aqueous and surface chemistry in particles and drops it is necessary to possess reliable knowledge of elementary pairwise and many-body interactions of individual water molecules. To achieve this goal the consideration and

modeling of small water clusters is inestimable. This will allow unambiguous incorporation of the concept of interacting water molecules in a variety of atmospheric models.

1. Introduction

Water is among the most abundant molecular species in nature. Water molecules are ubiquitous in the universe: the spectroscopic signature of water is found in the spectra of the sunspots, in interstellar media, in cometary environments, and, of course, in the planetary atmospheres. Although water in the atmosphere represents only a minor admixture to more abundant constituents, the role played by water molecules in atmospheric processes is inestimable. This primarily concerns radiative properties of the Earth's atmosphere, since water vapor is recognized among the principal absorbers of radiation in the atmosphere. Atmospheric chemistry and photochemistry are also strongly affected by the presence of water. The water molecule gives rise to a good deal of members of the atmospheric water family, which extends from separate hydrogen and oxygen atoms to condensed phase, i.e. liquid, water and ice. Products of both fragmentation and aggregation of atmospheric water are of particular importance for organic life on Earth. Detachment of the hydrogen atom from the water molecule is possible under the action of short-wave UV radiation (with λ shorter than 242 nm). Direct photolysis of water happens readily only in the upper atmosphere, since at lower altitudes UV-radiation is strongly depleted by oxygen Herzberg absorption. Consequently, chemical decomposition and transformations of H_2O prevail below 50 km. Aggregation of water occurs mainly in the troposphere where the partial density of water vapor is significant. This aggregation is due to very weak inter-molecular forces arising at close distance between water-water and water-foreign gas molecules. The so-called hydrogen bonding is among the key features characterizing the interaction of water molecules. Interestingly, the hydrogen bonding is a cornerstone of organic life in general, since a multiplicity of hydrogen bonds is responsible for unique rearrangements in complicated nucleotic acids and bases. The present survey concentrates mainly on water species built up from several to numerous individual water molecules (monomers). Water aggregates may have no definite structure in a common sense. In other words the loose binding of these molecules results in significant distortion of their structure as a function of thermal excitation. Broad distribution over geometric and energetic characteristics is appropriate to these species at ambient temperature. That is why the detailed study of the complete potential energy surface is of crucial importance for modeling of the water molecule in interaction with other molecular or particulate atmospheric species. Prior to consideration of the water aggregates, basic properties of the isolated water monomers seem worth of characterizing.

2. The Water Molecule

The fact that water is composed of oxygen and hydrogen was established by Lavoisier and Cavendish at the end of the eighteenth century. In a few decades (1805) it was realized by Gay-Lussac and Humboldt that the ratio of oxygen to hydrogen constituents in water amounts to 1:2. About fifty years later Dumas proved the validity of the 2:16 ratio for the weights of hydrogen and oxygen in water. To establish the structure of the H_2O molecule it then took almost a century. Successful assignment of the early

molecular spectra (Mecke et al, 1933) allowed identification of molecular rotational constants thus making it possible to deduce a nonlinear triangle-shape geometry for the water molecule (see Figure 1).
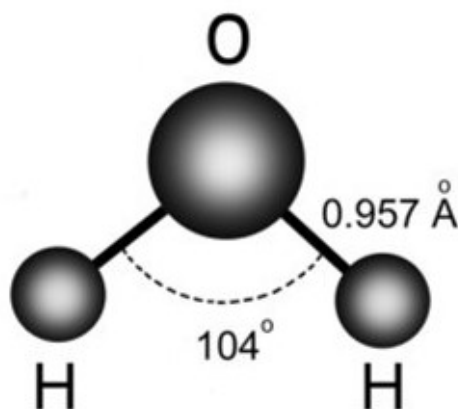

Figure 1. Schematic view of H_2O molecule

Directions of OH bonds are roughly determined by geometry of the oxygen atom electronic clouds which relate to a couple of electrons occupying 2p orbitals. That the angle among OH bonds slightly exceeds 90° can be understood in terms of hybridization of the oxygen 2s and 2p orbitals which results in an increase of the wave functions overlap leading to formation of a stronger OH bond. Two regions of the so-called unshared lone electron pairs (formed due to the former 2s and 2p orbitals) occur on the oxygen atom directed upward and downward relative to molecular plane. Lone pairs play a very important role in hydrogen bonding since each water molecule may act both as a double donor and a double acceptor of protons. This determines, in particular, nearly tetrahedral coordination of water molecules in ice, liquid water, and water clusters.

Electronic charge redistribution upon formation of a triangle-shape H_2O unit causes appearance of a significant permanent dipole moment in a globally neutral water molecule (see Table 1).

Parameter		Value
r_{OH}, Å		0.9572
α, degrees		104.52
Dipole moment μ, D		1.855
Dissociation energy,[a] kJ mole^{-1}		493
Polarizability tensor, Å^3	α_{xx}	1.4679
	α_{yy}	1.4146
	α_{zz}	1.5284
Rotational constants,[b] cm^{-1}	A	27.79
	B	14.51
	C	9.29
Vibrational fundamentals, cm^{-1}	asymmetric stretch	3755.79
	symmetric stretch	3656.65
	bending	1594.59

[a] The energy for the dissociation to $H^+ + OH^-$

[b] The frequency ω expressed in cm^{-1} means $\omega[cm^{-1}] = (\lambda[cm])^{-1}$, where λ is the wavelength

Table 1. Molecular properties of the individual H_2O molecule

Generally, electrical properties of a molecule in a gas, e.g. dipole moment, are subject to temporal variations. In a laboratory fixed frame of reference, the molecular dipole permanently changes its direction due to three-dimensional rotations of a free molecule in space. Thermal excitation of intra-molecular vibrations results in the oscillatory change of molecular dipole, thus causing emission of electromagnetic radiation by the heated gas. Inversely, molecular vibrations can be induced in the course of absorption of radiation in the oscillating external electromagnetic field. Absorption of radiation by atmospheric water vapor is mainly caused by pure rotational and rotation-vibrational transitions. Water in the gas phase possesses a very rich and complicated spectrum which covers a very wide spectral range extending from radio frequencies to near infrared and spotting in the visible and UV ranges. Water is known to account for some 70% of absorption in the Earth's atmosphere. Figure 2 shows that the absorption spectra of pure H_2O and the atmosphere are very much alike. This means that the water vapor absorption alters significantly the spectrum of incoming solar radiation.
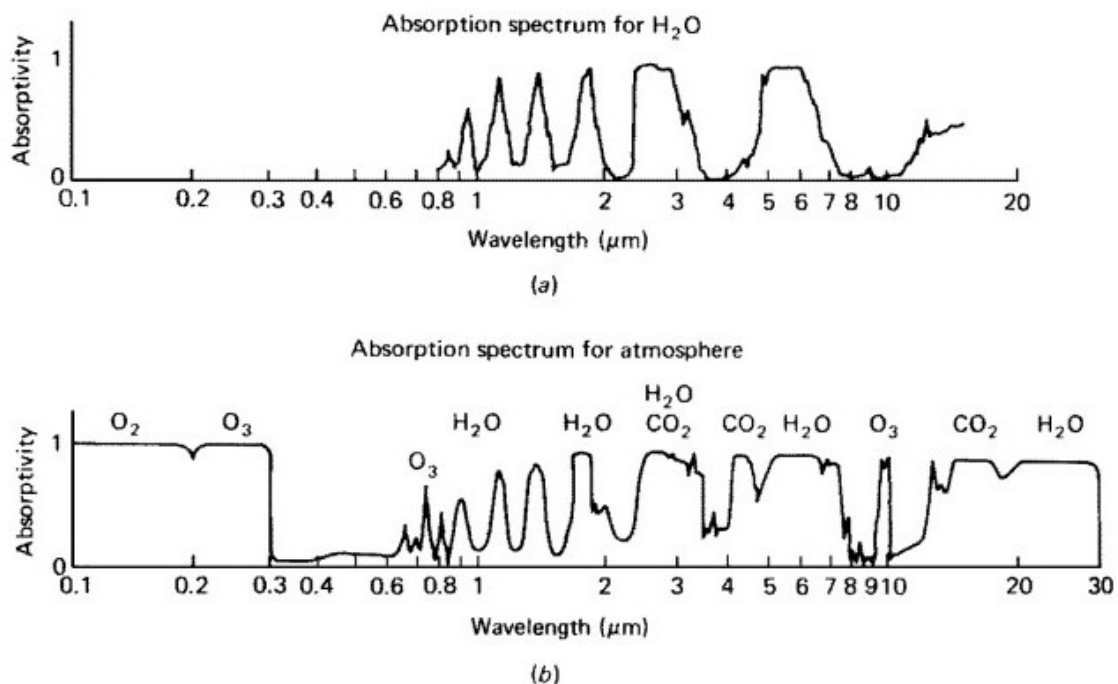

Figure 2. Absorption spectra for (a) water and (b) the atmosphere
(Redrawn with changes from Seinfeld J.H. (1986). Atmospheric Chemistry and Physics of Air Pollution, 738 pp. New York: Wiley)

Most outgoing thermal radiation from the Earth's surface falls in the important atmospheric "window" of relative transparency at 8–13 mcm. Despite the weakness of the underlying absorption by water vapor in this spectral range it is, however, of principal value for atmospheric radiative balance. The nature of this weak continuum absorption by water vapor in the real atmosphere is still a matter of controversy. One of

the popular hypotheses links this absorption to the water dimers, i.e. to pairs of water molecules tightly held together by the so-called hydrogen bond.

Capacity for hydrogen bonding is one of the key features of the water molecule which determines its chemical and physical properties, in any phase. The very term "hydrogen bond" was first introduced by Latimer and Rodebush in 1920 in order to characterize weak inter-molecular interaction which occurs in a number of chemical compounds as if the end hydrogen atom of one molecule forms a weak bond with an atom of a neighboring molecule with an unshared lone electron pair, such as O, F, N, S, etc. The energy of formation typical for the hydrogen bond between two water molecules is of the order of 15 kJ/mole, a figure which is about 30 times less than the energy of formation of the covalent OH bond in the water molecule. These weak H-bonds allow easy formation of an open-worked net of almost tetrahedra-coordinated water molecules. This network is clearly represented by molecular arrangements in the structure of low-temperature ice crystals. As temperature rises, some hydrogen bonds break down, the net only partially conserves the order, and the ice melts and transforms into a liquid phase. Evaporated from the bulk are mainly water monomers with some admixture of dimers, as well as more developed minor aggregates of water molecules, i.e. hydrogen-bonded water polymers. Conversely, homogeneous condensation of the water vapor occurs when isolated monomers combine with each other to form water polymers transforming progressively into condensed liquid or solid phase. This process is of particular importance for aerosol formation and growth in the atmosphere, as well as for cloud physics and chemistry.

Generally, isolated water molecules are apt to combine with any other molecular constituents due to extremely weak van der Waals inter-molecular interactions. The properties of individual water-water and some water-foreign gas complexes have now been subject to thorough laboratory studies. These are carried out at very low temperature (of the order of 10 K), not typical of the ambient atmosphere. Major characteristics for a variety of van der Waals dimers in their ground state are established in detail thus making it possible to incorporate the concept of van der Waals association in atmospheric modeling. This task is, however, very difficult to accomplish in an explicit way. To include a multiplicity of inter-molecular weakly bound pairs in theoretical considerations of atmospheric processes, one has to possess a set of complete multi-dimensional inter-molecular potential energy surfaces characterizing various pairwise interactions. Despite the outstanding capabilities of modern computer chemistry this goal can hardly be reached at the present time. Knowledge of dimer properties in the vicinity of its ground-state seems insufficient for any of the possible atmospheric applications since, as temperature rises, the average geometric and other dimeric characteristics notably change. It is clear, however, that the concept of isolated water monomers in the atmosphere can no longer be admitted beyond very initial and rough approximation. In reality, the isolated H_2O molecules are always in a bath of polymerized species due to weak binding to neighboring water or foreign gas molecules. The equilibrium content of these aggregates is usually several orders of magnitude lower than that of their parent molecules. As we shall see in the following paragraphs, however, some weakly bound water complexes are as abundant in the atmosphere as major trace or even minor "normal" constituents which are recognized to notably contribute to the atmospheric radiation balance.

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Biographical Sketch

Andrei Vigasin graduated from the Physical Faculty, Moscow State University in 1972. He received his Candidate of Sciences degree (equivalent to PhD) in nonlinear optics in 1978 at the Physical Faculty and a Doctor of Sciences degree in physical chemistry in 1995 at the Chemical Faculty, Moscow State

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