



# Molecular structures and thermodynamic properties of monohydrated gaseous iodine compounds: Modelling for severe accident simulation



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## ABSTRACT

Monohydrated complexes of iodine species (I, I<sub>2</sub>, HI, and HOI) have been studied by correlated ab initio calculations. The standard enthalpies of formation, Gibbs free energy and the temperature dependence of the heat capacities at constant pressure were calculated. The values obtained have been implemented in ASTEC nuclear accident simulation software to check the thermodynamic stability of hydrated iodine compounds in the reactor coolant system and in the nuclear containment building of a pressurised water reactor during a severe accident. It can be concluded that iodine complexes are thermodynamically unstable by means of positive Gibbs free energies and would be represented by trace level concentrations in severe accident conditions; thus it is well justified to only consider pure iodine species and not hydrated forms.

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## 1. Introduction

Behaviour of iodine and iodine compounds in the reactor coolant system (RCS) as well as in the containment of a pressurised water reactor (PWR) during a severe accident has been a subject of several experimental programmes and modelling [1–4] because <sup>131</sup>I is one of the most important radiotoxic fission products that may be released through the RCS and next in the nuclear containment building and further possibly into the environment by the leakages. A detailed understanding of the evolution of the chemical speciation of all iodine compounds formed is necessary to assess the radiological consequences during the accident progress for a wide range of accidental scenarios.

In the case of a PWR accident, the gaseous radio-iodine is present either in atomic or in molecular forms. Atomic hydrogen and oxygen, hydroxyl radical and water may also be present in the gas phase due to thermal and radiolytic reactions and react with iodine species. Some of these reactions were theoretically studied previously [5–7]. Except for high temperatures and pressures, in addition of thermochemical stability, microhydration of reactants and products may also have an effect on the kinetics of the chemical reactions. This phenomenon was mainly studied in the field of atmospheric chemistry [8]. Presence of water molecules may influence the overall profile of the reaction, because it may assist in forming different pre-reactive molecular complexes and transition

states comparing to the “water-free” reaction, and therefore can change its activation energy and kinetics [9–11].

Bimolecular complexes of H, O, OH and iodine chemical species with one water molecule were studied both experimentally and theoretically to determine their geometrical structure, energetic stability and other properties. Hydrogen atom is capable of forming weakly bound complexes with one water molecule stabilized by the interaction of the free hydrogen atom with the oxygen atom or one of the hydrogen atoms in the water [12]. Vibrational spectra of the bimolecular van der Waals complex of oxygen atom and one water molecule were observed in UV photolysis of hydrogen peroxide in solid argon, krypton and xenon matrices by Pehkonen et al. [13,14]. Other experimental studies dealing with reactions of oxygen with water include mostly crossed-beam technique capable to estimate the activation energy barrier of these reactions, but they do not allow to study weak molecular complexes [15,16]. To the best of our knowledge, experimental value of the dissociation energy of the complex of oxygen atom in its ground triplet state and one water molecule is not available. Only a few theoretical studies are focused directly on the structure, properties and stability of this complex [17,18]. Hydroxyl radical forms stable hydrogen bonded complexes with water as confirmed by several experimental [19–22] and theoretical [11,23–28] studies. Analysing infrared spectra, Engdahl et al. concluded that the hydroxyl radical should be a donor in this hydrogen bond. Brauer et al. [20] and Ohshima et al. [21] determined H...O bond length by means of microwave spectroscopy. Dissociation energy with respect to HO and H<sub>2</sub>O molecules was estimated by Soloveichik et al. [22].

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There are only a few experimental and theoretical works on bimolecular complexes of I, I<sub>2</sub>, HI and HOI with water. Experimental works [29–31] on the bimolecular complex of iodine with water were rather focused on I<sup>−</sup>...H<sub>2</sub>O since it is easily accessible to experimental techniques such as photoelectron spectroscopy. Theoretical studies of iodine–water complexes were concentrated on calculations of geometrical parameters of the most stable structures, character of the intermolecular interactions, vibrational properties and energetics [31,32]. Engdahl and Nelander studied spectroscopically complexes of halogens and hydrogen–halogens with water and concluded that complexes of HI with H<sub>2</sub>O are probably planar, but I<sub>2</sub>...H<sub>2</sub>O is not and the intermolecular interaction is weaker in comparison with the first ones [33,34]. To our knowledge, only one theoretical study deals with the complexes of I<sub>2</sub> molecule with water. Pathak et al. [35] studied microhydration of iodine molecule by performing a series of calculations with one to eight water molecules.

In the most stable HI...H<sub>2</sub>O complex H<sub>2</sub>O acts as proton acceptor [36–39]. The most recent theoretical study of the HI...H<sub>2</sub>O complex was performed by Kołaski et al. [39] who identified three different structures (minima). HOI complexes with one water molecule may be stabilized by hydrogen bond formed between the hydrogen atom in HOI and oxygen atom in H<sub>2</sub>O, weak interaction between the oxygen in H<sub>2</sub>O and iodine or between the hydrogen in H<sub>2</sub>O and oxygen in HOI [40,41].

In this paper, we calculated the complexes of atomic (H, O, I) and molecular species (HO, HI, I<sub>2</sub>, HOI) with one water molecule which may be formed in the gas phase either in the RCS or in the containment of a PWR during an accident to provide accurate thermochemical data at unified level of theory. Calculated thermodynamic quantities (heat capacity at constant pressure, entropy and enthalpy) are used to derive Gibbs free energies of the complexes formation. Simulations of a severe nuclear accident are performed by the SOPHAEROS module [42] of ASTEC software (Accident Source Term Evaluation Code) [43] to study the possible effect of microhydration of iodine containing species on the iodine equilibrium speciation. Briefly, ASTEC is a software package dedicated to the simulation all the phenomena that occur during a severe accident in a pressurised water-cooled nuclear reactor, from the initiating event to the possible release of radioactive compounds outside the containment.

## 2. Computational methods

Geometry optimizations of all species were performed at the Møller-Plesset second-order perturbation theory (MP2) [44] as implemented in Gaussian program [45]. We used Dunning's augmented triple-zeta correlation consistent basis sets (aug-cc-pVTZ) for hydrogen and oxygen atoms [46] and basis set of the same class with effective core potential incorporating scalar relativistic effects for iodine atom by Peterson et al. [47]. The latter one was improved from the first published version by the same group [48] to give better performance for iodine atom, which was confirmed by high level ab initio calculations of molecular constants of IO and IO<sup>−</sup> species and comparison with their experimentally determined values [47]. Basis set used in this work was chosen with respect to the previous theoretical studies on the systems containing iodine that provided adequate results in comparison with experiment [6,7,49]. Geometry optimizations were accompanied with vibrational frequency analysis to confirm the minima on the potential energy surface.

In the second step single point energy calculations at coupled-cluster theory including single, double and non-iterative triple substitutions (CCSD(T)) [50] as implemented in Molcas suite [51–53] were performed. Here we used all-electron relativistic

ANO-type basis sets [54,55] suitable for estimation of the scalar relativistic effects on all atoms in two contractions: (1) “valence quadruple-zeta plus polarisation”-type of contraction (ANO-RCC-VQZP) and (2) “LARGE” contraction ((8s4p3d1f)/[6s4p3d1f] for H, (14s9p4d3f2g)/[8s7p4d3f2g] for O and (22s19p13d5f3g)/[10s9p8d5f3g] for I). Douglas–Kroll–Hess 2-nd order model was used to account for scalar relativistic effects [53]. CCSD(T) interaction energies of all complexes were corrected for the basis set superposition error (BSSE). This error originates from unbalanced description of the monomers with respect to the complex. We used the Boys–Bernardi counter-poise method [56] modified by Xanthreas [57] to account for geometry relaxation when forming complexes from the separate monomers.

Thermodynamic properties were calculated from molecular partition functions using standard statistical thermodynamics expressions and the ideal gas assumption. We paid special attention to low-frequency vibrational modes which may be a source of errors in the molecular partition functions in the harmonic oscillator/rigid rotor (HO/RR) approximation as they may represent internal rotations in the system [58,59]. Such a low frequency mode can be considered as torsional vibration at low temperatures (with the internal rotation barrier  $V_0 \gg kT$ ) or as free rotation at high temperatures ( $V_0 \ll kT$ ). At room temperatures ( $V_0 \approx kT$ ) the rotation of a group of atoms around a single bond with respect to the rest of a molecule has to be often treated as hindered rotation (HR) [60]. It is well known that HO/RR approach is insufficient in such cases and corrections to the vibrational partition function of the molecule are needed. Methods capable of treating HR have been introduced in the last few decades to improve theoretical thermochemistry predictions [61,62].

In our calculations, we adopted one-dimensional hindered rotor approach developed by Pfaendtner et al. [59,63] and implemented in Calctherm code. First of all, detailed inspection of the low frequency vibrational modes is essential to determine possible internal rotations in the molecule. After the identification of rotating groups of atoms and the respective axis of internal rotation the one-dimensional potential energy scans were performed with 10° step (dihedral angle). We preferred relaxed scans to take into account the coupling to other motions. Frequency calculation as well as the relaxed scans were used as inputs for Calctherm code which (1) fitted the energy profiles to a Fourier series expansion, (2) calculated the reduced moments of inertia for the rotating tops from the stationary point geometry, and (3) solved the 1D Schrödinger equation to obtain the energy levels of the internal rotations used for calculating the partition function. For the remaining modes, the harmonic approximation was adopted. All vibrational frequencies were scaled by an appropriate scaling factor (0.95) to compensate the effects of anharmonicity [64].

To check the quality of the CCSD(T)/ANO-RCC-LARGE approach the dipole moments and dipole polarizabilities for selected monomers were determined. Selected components of electric properties were obtained as numerical derivatives of the total energy with respect to the weak electric field. To keep the numerical stability and accuracy we used the Romberg procedure [65,66]. The minimum external electric field ( $F_0$ ) was set to  $2 \times 10^{-4}$  a.u. ( $1 \text{ a.u.} = 5.1422 \times 10^{11} \text{ V m}^{-1}$ ) and the other field amplitudes were given by  $\pm 2^k F_0$  with  $k = 1, 2, \dots, 7$ .

Severe nuclear accident simulations were performed using one functionality of the SOPHAEROS module [42] of ASTEC [43] that allows us to perform some gas phase equilibrium calculation as a function of temperature and pressure, based on a minimisation of the total Gibbs free energy of the system. For the mono-hydrated iodine species, the  $C_p$  values were fitted with the usual polynomial relationship:  $C_p = a + bT + cT^2 + d/T^2$  (Table 1). Gaseous Gibbs free energy was derived from  $C_p$  relationship and from calculated standard enthalpies at 298 K. These species with their Gibbs free en-

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