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# Infrared matrix-isolation and theoretical studies of interactions between CH<sub>3</sub>I and water

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## Abstract

Gaseous iodomethane are naturally emitted in the atmosphere over oceans through the algae and phytoplankton activities. The fate of naturally emitted iodomethane is of great interest because of the oxidizing properties of iodine in the atmosphere and its impact on the catalytic destruction of the ozone layer. Additionally, iodomethane is one of the gaseous species that can be emitted in the case of severe nuclear accident. The radiological impact of gaseous iodomethane is of concerns and requires knowledge about its behavior in the atmosphere. Water is one of the major species in the atmosphere which is responsible for atmospheric aerosol nucleation and thus, for cloud condensation nuclei (CCN). The fundamental knowledge concerning the interaction between methyl iodine and water at the molecular scale contributes to the better understanding of the fate of such species into the atmosphere and their role in CCN formation. Here the microhydration of iodomethane was investigated using cryogenic matrix experiments which were supported by theoretical DFT calculations. A large excess of water regarding CH<sub>3</sub>I was used in order to mimic atmospheric conditions. Dimers and trimers of CH<sub>3</sub>I are observed despite the high water amount in the initial mixture together with hetero aggregates between CH<sub>3</sub>I and water clusters. This may be explained by the low affinity of CH<sub>3</sub>I with water. Considering the concentration of iodomethane used in our experiments, the aggregates are rather formed in gas phase and not in the matrix cage. The interaction between CH<sub>3</sub>I and H<sub>2</sub>O molecules studied experimentally and supported by DFT calculation highlights that, in the

atmosphere, gaseous iodomethane and water will likely form association between water and iodomethane aggregates instead of  $(\text{CH}_3\text{I})_n\text{-(H}_2\text{O)}_m$  hetero complexes. Our results have important consequences for the understanding of the alkyl halide solvation in primary processes and contribute to the understanding of reactive halogen species in tropospheric chemistry. In the context of a nuclear severe accident, our work is contributing to better understand the fate of nuclear species in the atmosphere and thus, the radionuclide dispersion.

**Key words:** iodomethane, hydration, nuclear accident, atmosphere, matrix isolation infrared spectroscopy

## 1. Introduction

Iodine is an important fission product of the fuel used in Nuclear Power Plants (NPPs) in terms of safety with the generation of high radioactive isotopes ( $^{131}\text{I}$  and  $^{133}\text{I}$ ) potentially released outside in case of severe accident. Indeed, radioactive gaseous iodine poses a health hazard if released into the atmosphere due to its accumulation in the human thyroid gland after inhalation, where it can locally induce cancer [1-4]. A severe accident in a NPPs as Chernobyl (Ukraine) and the more recent Fukushima- Daichi (Japan) disaster can led to gaseous molecular iodine ( $\text{I}_2$ ) and methyl iodide ( $\text{CH}_3\text{I}$ ), as main representative of organic iodides released into the atmosphere [5-7]. Particularly, it has been postulated that the removal of  $\text{CH}_3\text{I}$  with the currently used filter materials (for instance as charcoal media or liquid scrubber) is less efficient compared to  $\text{I}_2$  [3,8,9]. Hence, the reactivity of  $\text{CH}_3\text{I}$  in the atmosphere has recently gained much interest in the field of nuclear industrial safety as its interaction with atmospheric species i.e. gaseous oxidants, radicals, water or aerosols may influence the atmospheric dispersion and thus the sanitary impacts.

Iodine also occurs naturally in the ocean boundary layer and is mainly derived from algae and phytoplankton in the oceans and from heterogeneous reactions at the ocean-atmosphere interface [10-12]. The iodine species mainly emitted by these natural sources are halogenated organic compounds such as  $\text{CH}_3\text{I}$ . The atmospheric chemistry of iodine species is of great interest because of the oxidizing properties of iodine in the atmosphere and its impact on the catalytic destruction of the ozone layer. The chemistry of halogens especially the marine iodine chemistry has been extensively studied and was reviewed by Saiz-Lopez et al. [11] and Simpson et al. [12]. These previous works mainly focus on gaseous chemistry and photochemistry of iodine species such as  $\text{CH}_3\text{I}$  which leads to the formation of iodine oxide particles (IOP). Iodine oxide-driven new particle formation has been reported from both field observations and

laboratory experiments. As one of the main species present in the atmosphere, water molecules may affect the reactivity of the gaseous species. As a gas, water molecules may form some aggregates or complexes with atmospheric species. As a liquid droplet, water may dissolve gaseous components, the latter being driven by Henry's law constant [13,14]. Recently, the microhydration of n-alkyl halides has received much attention as it may affect the halide chemistry processes such as photolysis, and more generally the atmospheric halide cycle. The atmospheric gas-to-particle conversion mechanism may be also influenced by the humidity as it is reported for the IOP formation. Additionally, the effect of water on aerosol chemical processes are increasingly questioned [15 and reference herein] since water cluster growth and further, hygroscopicity properties of aerosols, are the most research concerns for understanding the cloud formation. The interaction between water and halide compounds (including iodine) has been mainly investigated using ab initio calculations [16 and ref herein] since sparse experimental data are available due to the challenging task to study water-alkyl interaction in ambient conditions. In a previous work, the structure and vibrational spectra of methyl halides dimers has been examined by ab initio calculation [17]. Besides, Ito et al. have studied the formation of CH<sub>3</sub>I clusters and CH<sub>3</sub>I-H<sub>2</sub>O (1:1) complex by using the matrix isolation technique [18-20] since the matrix isolation technique is a relevant experimental technique to study inter- and intra-molecular interactions occurring during the microhydration process. In Ito's papers, the only CH<sub>3</sub>I-H<sub>2</sub>O complex considered is the 1:1 ratio when complexes with higher number of molecules are expected in the atmosphere. The main question that remains for further atmospheric implication, i.e. the influence of water on both reactivity of halide compounds in gaseous phase and CCN formation, is: in the atmospheric conditions i.e. with high water content, is CH<sub>3</sub>I species able to form complexes (CH<sub>3</sub>I)<sub>n</sub>(H<sub>2</sub>O)<sub>m</sub> with water molecules or only aggregates of homo-clusters of (CH<sub>3</sub>I)<sub>n</sub> and (H<sub>2</sub>O)<sub>m</sub> can be observed?

In the present paper, we have investigated the interactions between CH<sub>3</sub>I and H<sub>2</sub>O to give insights on the microhydration process of CH<sub>3</sub>I, which in turn help in understanding the reactivity of CH<sub>3</sub>I in the gas phase and its molecular interaction with hydrated aerosols. Increasing the knowledge of CH<sub>3</sub>I reactivity will contribute to improve the understanding of the atmospheric iodine cycle and consequently, the prediction of the radiological consequences resulting from accidental iodine radioisotope releases. The matrix- isolation Fourier Transform Infra-Red (FTIR) spectroscopy technique was used for studying in details the formation of (CH<sub>3</sub>I)<sub>n</sub>-(H<sub>2</sub>O)<sub>m</sub> complexes or aggregates of homo-clusters. To help in the interpretation, the formation of (CH<sub>3</sub>I)<sub>n</sub> clusters were studied in similar experimental conditions and the structure,



infrared spectra and energetics of the observed species have been investigated by Density Functional Theory (DFT) calculations.

## 2. Experimental and theoretical section

**Matrix isolation experiments.** The matrix isolation system used in this work has been described in details elsewhere [21-23]. Experiments were conducted in a high vacuum experimental set up consisting in a stainless steel chamber ( $P = 10^{-5}$  mbar at room temperature) containing an IR transparent NaCl window cooled to 10K by means of a closed cycle He cryostat Cryophysics Cryodine. The sample temperature is monitored with a Si diode thermometer set on the copper holder of the NaCl window. Two sets of experiments were conducted in this work to scrutinize the  $\text{CH}_3\text{I}-\text{H}_2\text{O}$  interactions at low temperature (1)  $\text{CH}_3\text{I}$  in Ar matrix from 10 to 35 K as benchmark experiment and (2)  $\text{CH}_3\text{I}$  and  $\text{H}_2\text{O}$  in Ar matrix from 10 to 35 K. Gaseous samples of  $\text{CH}_3\text{I}/\text{Ar}$  (0.1%  $\text{CH}_3\text{I}$  - 99.9% Ar, Airproduct) were used without any further purification at a flow of 1mL/min. The matrix ratio is then  $\text{CH}_3\text{I}/\text{Ar} = 1/1000$  since various ratios were investigated in previous work [20]. For the observation of the formation of  $(\text{CH}_3\text{I})_m-(\text{H}_2\text{O})_n$  complexes, the vapor of ultrapure  $\text{H}_2\text{O}$  (conductivity of 18.2 M $\Omega$  Millipore system) was introduced from a glass flask and mixed with  $\text{CH}_3\text{I}/\text{Ar}$  in a glass reservoir in the proportion  $\text{CH}_3\text{I}/\text{H}_2\text{O}/\text{Ar} = 1/25/1500$  and injected into the chamber at a rate of 1 mL/min<sup>-1</sup>. This  $\text{CH}_3\text{I}/\text{H}_2\text{O}$  ratio is chosen to ensure both high water concentration in matrix and  $\text{CH}_3\text{I}$  signal detection since beyond this ratio, signals of water aggregates would overlap those of  $(\text{CH}_3\text{I})_m-(\text{H}_2\text{O})_n$ . Deionized water was previously subjected to multiple freeze-pump-thaw cycles under vacuum to remove dissolved gases. Thus, the concentration  $\text{H}_2\text{O}/\text{Ar}$  equal to 1/60 introduced was used to mimic the closest atmospheric conditions. A reference experiment with  $\text{H}_2\text{O}$  trapped in Ar matrix (7/1000) was also recorded at 4 K for comparison. The gaseous samples were introduced by gas nozzle inlet and deposited by diffusion directly on NaCl plate for 2 hours. This deposition mode is soft enough to limit cluster formation during the deposition process. The deposited samples at 10 K were annealed to 35 K, close to the sublimation temperature of the argon crystal. The infrared spectra of the gas-isolated samples were recorded in transmission mode using a Bruker Vertex 70V FTIR spectrometer with a DTGS detector in the spectral range 4000-400  $\text{cm}^{-1}$ , with a spectral resolution of 0.5  $\text{cm}^{-1}$  and each spectrum averaged over approximately 200 scans. Spectra were recorded at 10K for  $\text{CH}_3\text{I}$  and  $\text{CH}_3\text{I}/\text{H}_2\text{O}$  experiments.

**Theoretical Calculations.** The structure and harmonic vibrational spectra of  $\text{CH}_3\text{I}$  monomer, dimers and trimers, and  $\text{CH}_3\text{I}$ -water complexes such as  $(\text{CH}_3\text{I})_m-(\text{H}_2\text{O})_n$  (with  $m = 1,2,3$  and  $n$

= 1,2,3) were calculated with the Gaussian09 suite of programs [24] using the long range corrected functional  $\omega$ B97X-D [25] with the aug-cc-pVTZ basis set for hydrogen, carbon and oxygen atoms, while the aug-cc-pVTZ-PP basis set [26] was used for the iodine atom that incorporates a small-core relativistic pseudo potential, as previously mentioned [27]. Harmonic vibrational frequencies have been calculated at the same level of theory, and remained unscaled. Additionally, NBO analysis was performed on the isolated molecules CH<sub>3</sub>I and H<sub>2</sub>O and on CH<sub>3</sub>I.H<sub>2</sub>O (1:1a and 1:1b) complexes at the  $\omega$ B97X-D/aug-cc-pVTZ level of theory. The standard molar entropy ( $S^\circ_{10\text{ K}}$ ) and the heat capacity at constant pressure (1 bar) have been calculated with the script thermo.pl published by the National Institute of Standards and Technology [28]. The Gibbs free energy of reaction ( $\Delta_r G^0$ ) in kJ.mol<sup>-1</sup> for both CH<sub>3</sub>I clusters and complexes have been calculated at the  $\omega$ B97XD/ aug-cc-pVTZ-PP level of theory. The basis set superposition error (BSSE) correction is known to be negligible in microhydration energetics, [27, 29] therefore this correction has not been included in the energetic calculations of this study.

The IR band assignment was performed by comparing the observed and calculated shifts  $\Delta\nu$ . The frequency shifts are calculated with respect to the monomer position ( $\Delta\nu = \nu - \nu_{\text{monomer}}$ ).

### 3. Results and discussion

**Formation of (CH<sub>3</sub>I)<sub>n</sub> clusters.** Structures of CH<sub>3</sub>I monomer, dimers and trimers were investigated using experimental spectra supported by calculations presented above. Two isomers of (CH<sub>3</sub>I)<sub>2</sub>, shown in Fig. S1(a) with xyz coordinates reported in Table S2 (Supporting Information), are found to be stable and will be hereafter referred as Head-to-Tail (HT) and Head-to-Head (HH) structures. These structures were previously reported using the MP2/LanL2DZ+fdp level of theory [18]. It should be highlighted that both levels of theory using MP2/ LanL2DZ+fdp [18] and  $\omega$ B97XD/aug-cc-pVTZ-PP (this work) predict the same (CH<sub>3</sub>I)<sub>2</sub> stable isomers, i.e. HH and HT, with a difference in the intermolecular distance not exceeding 0.2 Å. A Gibbs free energy difference of 3.0 and 3.8 kJ/mol is found for HH and HT isomers respectively, between the method used in this study and the one used previously [18]. Two (CH<sub>3</sub>I)<sub>3</sub> isomers have also been found to be stable (Fig. S1(b) and Table S2 (SI)) and will be hereafter referred as Tail-to-Head-to-Tail THT<sub>1</sub> and THT<sub>2</sub>. The THT<sub>2</sub> structure was previously discussed by Ito et al. [20,30] to be the most stable structure of (CH<sub>3</sub>I)<sub>3</sub> using the MP2 method. In the present work the Gibbs free energy difference between the 2 isomers is less than 1 kJ/mol at the  $\omega$ B97X-D/ aug-cc-pVTZ-PP level of theory. As a result, THT<sub>1</sub> and THT<sub>2</sub> could be

considered as isoenergetic. The difference in the intermolecular distance between the level of theory used in this study and the one used previously [30] does not exceed 0.2 Å. Moreover, a difference of about 5 kJ/mol in the Gibbs free energy was found between the two levels of theory. As a result, the difference in binding energies shows that  $\Delta E(\omega B97X, \text{this work})$  is lower than  $\Delta E$  calculated using MP2 method [18,30] for both CH<sub>3</sub>I dimers and trimers. This interaction between CH<sub>3</sub>I molecules is more accurately evaluated using the  $\omega B97X-D$  functional, which is consistent with a recent study [17] that includes dispersion for a better characterization of the inter-molecular complexes under study. Moreover the size of the basis set is larger in our work (aug-cc-pVTZ-PP) than the one used in Ito's studies (LANDZ+fdp) [18,30].

The calculated vibrational spectra together with bands relative intensities of the monomer and the most stable HH, HT, THT<sub>1</sub>, THT<sub>2</sub> isomers are gathered in Table S8. For a more reliable analysis of CH<sub>3</sub>I clusters infrared spectra, we used unscaled IR frequencies. It should be noted that the calculated wavenumber position is likely dependent of the level of theory. For example, the wavenumber position of the monomer CH<sub>3</sub> symmetric deformation mode is calculated at 1334 cm<sup>-1</sup> using the MP2/ LanL2DZ+fdp level of theory [18], whereas it is calculated at 1297 cm<sup>-1</sup> in this work using the  $\omega B97X-D$ /aug-cc-pVTZ-PP level of theory. It is known that the shift from the monomer peak due to clustering can be evaluated by theoretical calculations. For instance, in the CH<sub>3</sub> symmetric deformation region the shift of the dimer mode, with respect to that of the monomer, ranges between -4 and 2 cm<sup>-1</sup> using the MP2/ LanL2DZ+fdp level of theory [18], against of -1 to 3 cm<sup>-1</sup> in this work using the  $\omega B97X-D$ /aug-cc-pVTZ-PP level of theory. Similar observations have been found for the trimer, where the shift ranges between -7 to -1 cm<sup>-1</sup> using the MP2/ LanL2DZ+fdp level of theory [30] and -1 to 8 cm<sup>-1</sup> using the  $\omega B97X-D$ /aug-cc-pVTZ-PP one (this work, Table S8). It shows that the bands of dimers and trimers are in close vicinity with those of monomer, what underlies that perturbation induced by CH<sub>3</sub>I homo-complexation is weak. Considering that shifts calculated at both levels of theory, that of the present work and the one used by Ito et al. [18,30] are of the same magnitude, it is more accurate to uniquely consider those shifts rather than scaled harmonic frequencies to identify present species. The calculation performed in this study will be used as a support to discriminate between monomers, dimers and trimers observed by FTIR-isolation matrix experiments. Those theoretical vibrational spectra will be studied in fingerprint regions in which they will help to identify species trapped in the matrix.

196 A typical matrix-isolation infrared (IR) spectra of CH<sub>3</sub>I in Ar matrix at 10K and at a mixing  
 197 ratio of 1/1000 is shown in Fig. S2. The spectrum shows CH<sub>3</sub>-stretching ( $\nu_1$  and  $\nu_4$ ),  
 198 deformation ( $\nu_2$ ) and rocking ( $\nu_6$ ) regions centered at 3000, 1250 and 890 cm<sup>-1</sup>, respectively  
 199 while the C-I stretching mode is outside the observed spectral region (< 600 cm<sup>-1</sup>). Additional  
 200 bands related to traces of water are observed at ~3750 cm<sup>-1</sup> and 1600 cm<sup>-1</sup> (not shown). The  
 201 fundamental bands of the CH<sub>3</sub>I monomer are observed at 3054 (not shown), 2965, 1432 (not  
 202 shown), 1245, 882 and 881(doublet) cm<sup>-1</sup> for  $\nu_4$ ,  $\nu_1$ ,  $\nu_5$ ,  $\nu_2$  and  $\nu_6$ , respectively. These band  
 203 positions are consistent with those previously reported for supersonic jet deposition for CH<sub>3</sub>I  
 204 monomer [18,31]. Some additional bands appear on both sides of monomer bands, especially  
 205 for  $\nu_1$ ,  $\nu_2$  and  $\nu_6$ , which are the most intense bands on the FTIR spectrum (Fig.S2). The observed  
 206 wavenumbers and the shifts from the monomer are listed in Table 1 and compared with those  
 207 obtained by calculations. As expected, the set of additional bands are due to the formation of  
 208 CH<sub>3</sub>I clusters. Considering the concentration 1/1000 of CH<sub>3</sub>I in Ar matrix, the observation of  
 209 the monomer bands is the most plausible. However, regarding the calculated and experimental  
 210 bands the additional ones can be assigned to both HT and HH dimers observed at 2967, 2960,  
 211 1248, 1246, 1245, 886 cm<sup>-1</sup> and 2960, 1244, 886, 881, 878 cm<sup>-1</sup>, respectively. If the 882-881  
 212 doublet is assignable to the monomer, the band at 886 cm<sup>-1</sup> and that at 879 cm<sup>-1</sup> present a blue-  
 213 shift of  $\approx +4$  and a red-shift of  $\approx -3$  cm<sup>-1</sup> with respect to the 882 cm<sup>-1</sup> one (the most intense of  
 214 the doublet). Those shifts match (CH<sub>3</sub>I)<sub>2</sub> HT (+5), and HH (-2). Even if it is more unlikely, the  
 215 blue-shift could also match with THT<sub>1</sub> and THT<sub>2</sub> trimers. These bands can also be due to Ar  
 216 sites, what is certainly the case of 882-881 doublet. The 1246-1245 cm<sup>-1</sup> bands are assigned to  
 217 two monomer sites, when other observed bands are blue-shifted by  $\approx +7$  and  $+3$  cm<sup>-1</sup> and the  
 218 two latter are red-shifted by  $\approx -2$  and  $-6$  cm<sup>-1</sup>. Those shifts allow us to identify unambiguously  
 219 THT<sub>2</sub> trimer (at 1252 cm<sup>-1</sup> and tentatively at 1243 and 1239 cm<sup>-1</sup>), and more tentatively HT  
 220 dimer and THT<sub>1</sub> trimer (at 1248 cm<sup>-1</sup>). However, we cannot discard the presence of HH dimer  
 221 because this latter one presents almost degenerated bands with monomer (see Tables 1 and 2).  
 222 No clusters larger than  $n > 3$  are observed in our experimental conditions. The bands of both  
 223 monomer and clusters are almost degenerated, which is due to the weakness of CH<sub>3</sub>I  
 224 intermolecular forces (and adopted structures) as previously reported [17]. As a result, the shifts  
 225 due to the dimer and trimer formation are close to the monomer frequencies. Iodomethane  
 226 dimers and trimers are more likely formed in the gas phase prior to deposition. The formation  
 227 of homo-clusters of CH<sub>3</sub>I is confirmed by annealing the matrix from 10 to 35K. The FTIR  
 228 spectra (Fig. S1) clearly show the decrease of the bands of monomer when the IR bands

assigned to dimer or trimer increase. The FTIR spectra (Fig. S3) clearly show the decrease of the monomer bands when those assigned to dimer or trimer increase. This behavior in matrix experiments is explained by the diffusion of CH<sub>3</sub>I molecules in the Ar matrix during the annealing. Indeed, Van der Waal radius of iodine atom is large, which results in a limited diffusion of CH<sub>3</sub>I within the Ar matrix, moreover on long distance. Thus, we can hypothesis that CH<sub>3</sub>I dimers and trimers are formed in the matrix by diffusion of monomers, which are in a close vicinity. This close vicinity may be explained by the fact that cluster of CH<sub>3</sub>I are formed in the gaseous phase and partly separated as monomers during the matrix deposition, because of translational kinetic energy relaxation. The further annealing of the close CH<sub>3</sub>I molecules is then able to re-form clusters of CH<sub>3</sub>I.

In brief, in our experimental conditions we observe CH<sub>3</sub>I dimers and trimers formation. These results complete those obtained by Ito et al. [18, 20] in previous studies performed using supersonic jet technic.

**Formation of CH<sub>3</sub>I-H<sub>2</sub>O complexes.** The structure and the vibrational spectra of various (CH<sub>3</sub>I)<sub>n</sub>-(H<sub>2</sub>O)<sub>m</sub> complexes have been calculated at  $\omega$ B97X-D/aug-cc-pVTZ-PP level of theory for n=1, 2 and m=1, 2, 3. Ito et al. [20] have demonstrated that the B971/LanL2DZ+fdp level of theory reproduces well the MP2/aug-cc-pVTZ level of theory results, while the MP2/LanL2DZ +fdp level of theory underestimates the intermolecular interaction between CH<sub>3</sub>I and H<sub>2</sub>O for 1:1 complex only. In the present work, the calculations are performed with the  $\omega$ B97X-D functional with a relativistic effective core potential and an extended valence basis-set for iodine, i.e., aug-cc-pVTZ-PP.

The 1:1, 1:2, 2:1, 2:2 and 1:3 structures were optimized revealing the predicted most stable isomers for each of them as following: 2 isomers for 1:1 and 1:2 structures, 4 isomers for 1:3 structure, 5 isomers for 2:1 structure and 10 isomers for 2:2 structure. The geometry and the standard Gibbs free energies of these isomers are presented in Fig. S4 to S8 with xyz coordinates in Tables S3 to S8 (see SI).

From this theoretical work, valuable information can be retrieved on relative stabilities of each species together with the structure of their vibrational spectra. Indeed, from those results we selected the most accurate spectral regions to discriminate between (CH<sub>3</sub>I)<sub>n</sub>, (H<sub>2</sub>O)<sub>m</sub> and (CH<sub>3</sub>I)<sub>n</sub>-(H<sub>2</sub>O)<sub>m</sub> aggregates and complexes.

The 1:1 hetero-dimer (Fig. S4 in SI) presents two stable forms, one pseudo-cyclic, referred as 1:1a, more stable than an unexpected one, 1:1b, which displays a I $\cdots$ O interaction ( $\Delta_r G^\circ_{10K}$



= -13.5 kJ mol<sup>-1</sup>, for 1:1a, against -7.5 kJ mol<sup>-1</sup>, for 1:1b). Indeed, one could have expected to observe, in 1:1b case, a I...H H-bond interaction, rather than this long distance interaction between iodine and oxygen atoms. Is it so surprising? If one compares, iodine's Pauling electronegativity of 2.66 with that of hydrogen, which is 2.2, it is then plausible to observe a halogen-bond type interaction between iodine and oxygen, this latter presenting a Pauling electronegativity of 3.44. Moreover, the iodomethane dipole moment is oriented toward carbon atom, which leads a partial positive Mulliken's charge for iodine atom in this configuration. It is thus likely that we observe this I...O interaction. The complementary NBO calculations (reported on Fig. S9) show that the distribution of NBO charges within isolated systems (i.e. CH<sub>3</sub>I and H<sub>2</sub>O monomer) do not greatly differ from those within the 1:1a and 1:1b systems. This indicates that the charge transfer is not the main process while electrostatic interactions are the main forces involved for these systems as we stated. However, the charge transfer influence the geometry of the H-bonds as we have seen on THT<sub>1</sub> and THT<sub>2</sub> structures. Our assumptions are consistent with a recent work [32]. On the vibrational spectra side, one observes a stronger perturbation for 1:1a, with respect to each monomer, H<sub>2</sub>O and CH<sub>3</sub>I, vibration frequencies, than for 1:1b (see Table S9). Water  $\nu_3$  and  $\nu_1$  modes are both red-shifted by -28 and -41 cm<sup>-1</sup>, respectively, while the most obvious shift concerning CH<sub>3</sub>I moiety seems to be that of the CH<sub>3</sub> rocking with a blue-shift of 22 cm<sup>-1</sup>. For 1:1b, water partner presents two almost equivalent free OH bonds, however red-shifted by -11 and -10 cm<sup>-1</sup>. This result illustrates the iodomethane polarity effect: while there is greater stabilization from the donor-acceptor interaction between the units of the dimer in 1:1b than 1:1a, dimer 1:1a is the lower energy species indicating that electrostatic interactions are mainly responsible for the energy difference between species 1:1a and 1:1b.

For the CH<sub>3</sub>I-(H<sub>2</sub>O)<sub>2</sub> complexes, shown in Fig. S5 (SI), there are three stable structures denoted 1:2a, 1:2b and 1:2c, with  $\Delta_r G^\circ_{10K}$  of -45.01, -25.38 and -21.61 kJ mol<sup>-1</sup>, respectively. If the former one presents a cyclic structure which can be summarized as a water dimer interacting by two H-bond type interactions with CH<sub>3</sub>I, the second one displays an almost symmetrical structure with the two water monomers on each side of the CH<sub>3</sub>I partner, i.e. a kind of double 1:1a (1:1 complex) structure with respect to the ICH iodomethane plane. Regarding the last form, it is the addition of the forms 1:1a and 1:1b (it could be noted that its  $\Delta_r G^\circ_{10K}$  is the sum of those of 1:1a and 1:1b species). As a result, on the vibrational spectra of the two first forms, one should observe in 1:2a case, a typical water dimer spectrum, with one proton acceptor, PA, and one proton donor, PD, partner, perturbed by CH<sub>3</sub>I, but with the difference

that PA partner also gives its proton to iodine atom, while for 1:2b, one should find a vibrational spectrum close to that of 1:1a. Concerning the last form, 1:2c, it should display a vibrational spectrum really close to those of 1:1a and 1:1b. From Table S10, for 1:2b species, one observes, indeed, comparable shifts with those of 1:1a, for water monomers while CH<sub>3</sub> rocking mode presents more pronounced blue-shifts, by 33 instead of 22 and 22 against 6 cm<sup>-1</sup>, with respect to 1:1a ones. Another noticeable red-shift is that of CH<sub>3</sub> symmetrical stretching which is -8 cm<sup>-1</sup>. If we come back to 1:2a species, it is clearly a water dimer spectrum perturbed by CH<sub>3</sub>I as illustrated by  $\nu_3$  and  $\nu_1$  water mode red-shifts. These red-shifts, namely that of -205 cm<sup>-1</sup> (typical of a  $\nu_1$  water dimer PD), coupled to OH...O distance of 1.87 Å (typical of a water dimer) [33], put in evidence that H<sub>2</sub>O-H<sub>2</sub>O interaction is stronger than interactions of each water monomer with CH<sub>3</sub>I partner. As a result it would be difficult to discriminate between 1:2a (in the water region) spectrum and that of the pure water dimer. For 1:2c species, it is easy to see from Tables S9 and S10, that its spectrum will be almost degenerated with those of 1:1a and 1:1b species. As a result it would be quite impossible to discriminate among those three species. Considering this fact, in the remainder of the manuscript, especially in the interpretation of the experimental spectra, if 1:1a and 1:1b are found, this will imply that potentially the 1:2c species is also present.

The CH<sub>3</sub>I-(H<sub>2</sub>O)<sub>3</sub> complex, displayed in Fig. S6 (SI), could be considered as the first step of CH<sub>3</sub>I water embedding and could lead to models of CH<sub>3</sub>I trapped in water environment as aggregates or Amorphous Solid Water (ASW). We found four different stable structures: (i) 1:3a, the most stable one ( $\Delta rG^\circ_{10K} = -86.4$  kJ mol<sup>-1</sup>) which is a cyclic water trimer perturbed by CH<sub>3</sub>I molecule which should present a vibrational spectrum close to that of cyclic water trimer; (ii) 1:3b, the least stable one ( $\Delta rG^\circ_{10K} = -37.5$  kJ mol<sup>-1</sup>), which is a kind of spinning top structure with three water molecules interacting independently from each other with a central CH<sub>3</sub>I molecule, and should exhibit a spectrum close to that of 1:1a; (iii) 1:3c ( $\Delta rG^\circ_{10K} = -59.7$  kJ mol<sup>-1</sup>) which displays a kind of “1:1a+1:2a” structure and should therefore share much in common with these two structures; (iv) 1:3d ( $\Delta rG^\circ_{10K} = -74.8$  kJ mol<sup>-1</sup>) which is a cyclic structure comprising a non-cyclic water trimer bridging both iodine and H atoms of iodomethane. It should be noted that 1:3b and 1:3c should present the strongest CH<sub>3</sub> blue-shifts. One more time, it is obvious that, the greater the number of water molecules involved in self H-bond association, the more stable the hetero-complex or hetero-aggregate is. It comes partly from H-bond interaction efficiency which induces cooperative effects. From the observation of

theoretical harmonic frequencies values (Table S11), it is clear that those signals overlap with those of the other forms.

For the  $(\text{CH}_3\text{I})_2\text{-H}_2\text{O}$  complexes, shown in Fig. S7 (SI) we count none less than five stable structures denoted, 2:1a to 2:1e, with  $\Delta_r G^\circ_{10\text{K}}$  lying in a close range of energies (-30.6 to -28.9  $\text{kJ mol}^{-1}$ , 2:1b and 2:1c being degenerated), with the exception of 2:1e one, which is a little bit disfavored at -23.8  $\text{kJ mol}^{-1}$ ). If the three first ones, 2:1a, 2:1b and 2:1c, present quite similar structures, *i.e.*  $\text{CH}_3\text{I}$  dimer interacting with a water monomer (2:1a presenting a subtle double PD, one time PA, character, which gives a small stabilization compared to 2:1b and 2:1c, whose one OH bond remains free), the 2:1d displays water molecule bridging between the two  $\text{CH}_3\text{I}$  molecules while 2:1e presents again the 1:1a moiety in interaction with the other  $\text{CH}_3\text{I}$  partner. Not surprisingly, the most “3D” interacting structures are the most stable. From a vibrational point of view (see Table S12), one can guess that indeed, in the water stretching region, 2:1e presents red-shifts comparable with those of 1:1a but also overlapping with those of 1:2b. Having regard to 2:1a and 2:1d, also in water stretching region, they present comparable red-shifts of  $-61 \text{ cm}^{-1}$  ( $\nu_3$ ), while 2:1a shares its  $\nu_1$  red-shift of  $-54 \text{ cm}^{-1}$  with 2:1b and 2:1c. In the  $\text{CH}_3$  rocking region, all the species should present the same spectrum, with blue-shifts overlapping with those of the above studied forms.

Concerning  $(\text{CH}_3\text{I})_2\text{-(H}_2\text{O)}_2$  species, shown in Fig. S8 (SI), we can easily discriminate between two kinds of complexes: those which display a water dimer part, and those which display two separated water molecules. Except for 2:2e ( $\Delta_r G^\circ_{10\text{K}} = -47.9 \text{ kJ mol}^{-1}$ ), all the former class present the most stable potentials with  $\Delta_r G^\circ_{10\text{K}}$  ranging from -70.1 (2:2b) to -53.7 (2:2j)  $\text{kJ mol}^{-1}$ . The latter class displays less stable structures with  $\Delta_r G^\circ_{10\text{K}}$  ranging from -47.0 (2:2d) to -33.2 (2:2f)  $\text{kJ mol}^{-1}$ . It could be understood in terms of H-bond type interaction strength. Indeed, in the case of the presence of a water dimer moiety, there is a strong interaction (as illustrated by short  $\text{OH}\cdots\text{H}$  bonds of 1.8-1.9 Å, see Fig S8), due to the quasi-linear interaction between the PD O-H bond and the  $\text{sp}^3$  doublet of the PA partner, while in the second category of complexes, interactions between PD and PA are less effective. On the vibrational side, from Table S13, it is obvious that one more time considering OH stretching regions and  $\text{CH}_3$  one, if all these isomers coexist, it will induce a spectral congestion. However, some blue-shifts in the  $\nu_2$  water bending mode (2:2b,  $28 \text{ cm}^{-1}$ ; 2:2e,  $32 \text{ cm}^{-1}$ ; 2:2g,  $35 \text{ cm}^{-1}$ ; 2:2h,  $26 \text{ cm}^{-1}$ ) could be of some help, even if the 1:2a isomer presents also a blue-shift in this region of  $25 \text{ cm}^{-1}$ .

The formation of all these species will induce a spectral congestion, so, a careful examination of spectral conditions (namely sample ratio) will be necessary to unambiguously identify all the forms present in argon matrices.

On the experimental vibrational spectra, the two iodomethane spectral regions, *i.e.*  $\nu_2$  (bending CH) and  $\nu_6$  (rocking mode) are displayed on Fig. 1, while the three water spectral regions, *i.e.*  $\nu_1$  (symmetric stretching),  $\nu_2$  (bending) and  $\nu_3$  (antisymmetric stretching) are presented in Fig. 2 and Fig. S10. We selected those spectral domains because the new bands related to  $\text{CH}_3\text{I}-\text{H}_2\text{O}$  interaction are well visible on the spectra in these regions. In addition, as discussed above, with the help of theoretical results, we should be able to identify which aggregates and complexes are present in those experimental conditions (with a large excess of water) supposed to mimic atmospheric ones. In Fig. 1 and 2 and Fig. S9 (SI) we present a comparison of pure  $\text{CH}_3\text{I}$  spectra with mixed  $(\text{CH}_3\text{I})_n(\text{H}_2\text{O})_m$  ones and of pure water homo-clusters for various spectral regions. New or increasing bands, observed in mixed species spectrum, with respect to those of pure water or iodomethane ones, are marked with a dashed line. The frequencies and assignment are reported in Tables 2 and 3.

It is known that iodomethane is not soluble in water, as a result, it is water self-aggregation which should be favored. However, considering that mixed aggregates and complexes will be trapped in the same matrix cage, we should be able to observe those latter subject to two conditions: they are formed in gas phase prior to sample deposition, and they survive landing on the sample carrier, or they are formed when they land. Indeed the injection mode we used in our experiments is similar to the quenching of a molecular jet when landing on the sample holder. The kinetic energy of translation must then be dissipated which can lead to the dissociation of these complexes. A third way to form those species is to anneal the samples to allow molecules in close neighborhood (few Å to nm) to diffuse through the argon matrix and aggregate. However, iodomethane concentration is so low that homo iodomethane aggregates, by extension hetero complexes with more than one  $\text{CH}_3\text{I}$  molecule, should be formed in gas phase and survive landing at sample carrier.

Considering the large excess of water we used, it seems more appropriate to start by iodomethane vibrational regions  $\nu_2$  and  $\nu_6$  (Fig. 1 and Table 2). Indeed  $\text{CH}_3\text{I}$  concentration remains 1/1000 with respect to Ar, which limits homo-iodomethane aggregation. Therefore, water addition, if there is aggregation with iodomethane, will lead to less overlapping bands than in the water zone. Between 930 and 850  $\text{cm}^{-1}$  (Fig. 1, Table 2), for pure iodomethane

(spectrum (a)), one observes bands centered at 886, 882, 881 and 879  $\text{cm}^{-1}$  that are assigned to monomer of  $\text{CH}_3\text{I}$  and  $\text{CH}_3\text{I}$  clusters (dimers and trimers) as presented in the previous part. In the case of mixed iodomethane-water sample (spectrum (b)), one observes the 886  $\text{cm}^{-1}$  increase, while 882 and 881 decrease in intensity, and new bands at 909, 903, 899 and 891  $\text{cm}^{-1}$  (Table 2). Those latter are blue-shifted by  $\approx +27, +20, +16$  and  $+9 \text{ cm}^{-1}$ , with respect to 882  $\text{cm}^{-1}$ . These shifts match totally or partially those of the following hetero-complexes and aggregates  $((\text{CH}_3\text{I})_n(\text{H}_2\text{O})_m)$ : 1:1a, 1:2a, the 1:3a, 1:3c ones, the whole series 2:1a to 2:1e and the three 2:2f, 2:2g and 2:2h species (Fig. S4 to S8 in SI).

In the  $\nu_2$  (bending CH) region (1270-1230  $\text{cm}^{-1}$ ), one observes, in the case of pure iodomethane, bands at 1248, 1246, 1245, 1243 and 1239  $\text{cm}^{-1}$  (Fig. 1, Table 2) that are attributed to  $\text{CH}_3\text{I}$  monomer, dimer and trimer as described in the previous part. In the case of mixed iodomethane-water sample (spectrum (b)), one observes the 1248  $\text{cm}^{-1}$  increase, while 1246-1245 decrease in intensity, and new bands at 1257, 1256, 1254 and 1250  $\text{cm}^{-1}$  (Table 2). Those latter are blue-shifted by  $\approx +12, 10, 9$  and  $5 \text{ cm}^{-1}$ , with respect to 1245  $\text{cm}^{-1}$ . These shifts match totally or partially those of the following hetero-complexes and aggregates  $((\text{CH}_3\text{I})_n(\text{H}_2\text{O})_m)$ : 1:1a, 1:2a and 1:2b, the 1:3a and 1:3b, the whole serie 2:1a to 2:1e and the three 2:2c, 2:2d, 2:2f and 2:2g species (Figures S4 to S8). Concerning the species 1:3b, we can already discard its presence because we did not observe blue-shifts of about  $+44 \text{ cm}^{-1}$  in the  $\nu_6$  region.

From the analysis of the iodomethane regions ( $\nu_2$  and  $\nu_6$ ), we can conveniently discriminate between the first candidates when at least two bands were identified:

$\text{CH}_3\text{I}.\text{H}_2\text{O}$  complex: 1:1a

$\text{CH}_3\text{I}.\text{(H}_2\text{O)}_2$  complex: 1:2a

$\text{CH}_3\text{I}.\text{(H}_2\text{O)}_3$  complex: 1:3a

$(\text{CH}_3\text{I})_2.\text{H}_2\text{O}$  complexes: whole serie 2:1a to 2:1e

$(\text{CH}_3\text{I})_2.\text{(H}_2\text{O)}_2$  complexes: 2:2f, 2:2g

Water spectral regions should bring decisive clues in the identification of the different isomers, despite the spectral congestion due to water aggregates.

The  $\text{H}_2\text{O}$  spectral regions (i.e.  $\nu_1$ ,  $\nu_2$  and  $\nu_3$ ) are presented in Fig. 2 ( $\nu_1$ ) and in Fig. S10 ( $\nu_2$  and  $\nu_3$ ). In the  $\nu_2$  region (1770-1510  $\text{cm}^{-1}$ ), in the case of pure water matrix (Fig. S10 (a)), one observes bands at 1663, 1658, 1637, 1627, 1625, 1620, 1616, 1612, 1611, 1608, 1602, 1599,



419 1593, 1591, and 1590  $\text{cm}^{-1}$ . They are due to water monomer and water clusters [34]. In the case  
420 of iodomethane-water mixture (trace (b)), one observes only one new band at 1600  $\text{cm}^{-1}$  (Fig.  
421 S10), blue-shifted by about  $\approx +11 \text{ cm}^{-1}$  with respect to the nrm (non rotating monomer) water  
422 bending mode at 1589  $\text{cm}^{-1}$ . It is a “poor” area because of strong overlapping between water  
423 aggregates signals and those of iodomethane-water complexes and aggregates, which should be  
424 in minority. As a consequence, the only partial matches found are: 1:3a, which should present  
425 theoretically three blue-shifts of  $\approx +32$ ,  $+16$  and  $+10 \text{ cm}^{-1}$  (the  $+32$  and  $+10 \text{ cm}^{-1}$  band are  
426 certainly overlapped by water aggregates ones), and 2:2a, 2:2e and 2:2j species.

427 In the  $\nu_1$  and water cluster region (3695-3100  $\text{cm}^{-1}$ ) (Fig. 2(a) and Table 3), one observes bands  
428 at 3670, 3662, 3654, 3648, 3647, 3640, 3630, 3628, 3617, 3612, 3574  $\text{cm}^{-1}$  (Proton Donor, PD,  
429 dimer), 3567, 3564, 3549, 3543, 3528, 3515  $\text{cm}^{-1}$  (Trimers), 3445, 3409, 3392, 3373  $\text{cm}^{-1}$   
430 (Tetramers), 3332-3325  $\text{cm}^{-1}$  (Pentamers), and 3209  $\text{cm}^{-1}$  (larger clusters and  $2\nu_2$  harmonic  
431 mode of  $\text{H}_2\text{O}$ ). The first band of interest in the case of mixed samples, is located at 3463  $\text{cm}^{-1}$ ,  
432 *i.e.* between trimers and tetramers. This band is red-shifted with respect to water trimers and  
433 blue-shifted with respect to water tetramers, *i.e.* more red-shifted (“perturbed”) than a water  
434 trimer but less than a water tetramer. This structure is undoubtedly a water trimer perturbed by  
435 an iodomethane partner. In Fig. S6, there are only two such structures, 1:3a and 1:3d.  
436 Considering that we did not find any evidence of 1:3d presence in the other regions, and that in  
437 a large excess of water, this is a cyclic conformation that will be adopted by water, we suggest  
438 that this band is assigned to 1:3a. In addition, we have reported a calculated band at 3557  $\text{cm}^{-1}$   
439 *i.e.* redshifted by 322  $\text{cm}^{-1}$  for this species (see Table S11) that is not observed on the  
440 experimental spectrum. Indeed, because water is overabundant, and considering that IR  
441 calculated intensities are indicative in matrix media, this is not surprising not seeing it. The  
442 second band of interest is the one centered at 3553  $\text{cm}^{-1}$ , red-shifted by  $\approx -85 \text{ cm}^{-1}$  with respect  
443 to  $\nu_1$  nrm mode located at 3638  $\text{cm}^{-1}$  [34]. This species is located between water dimer Proton  
444 Donor (PD) band and those of water trimers. Following the same reasoning, it is thus a water  
445 dimer perturbed by an iodomethane partner. In Fig. S5, there is only one structure which  
446 matches this water dimer type configuration, this is 1:2a. The mode we observe is the  $\nu_1$  stretch  
447 of water dimer Proton Acceptor (PA) which bridges to iodine atom. This vibrational assignment  
448 is strongly supported by the calculated shift  $\Delta\nu \approx -97 \text{ cm}^{-1}$  (Table S10), found for this species.  
449 However, one has to consider also the presence of 1:3c structure (Fig.S6) which is a “1:2a  
450 +1:1a” kind of structure. This last form presents a theoretical red-shift of  $\approx -91 \text{ cm}^{-1}$  in this  
451 region (and also a blue-shift of  $\approx +26 \text{ cm}^{-1}$  in  $\nu_6$  ( $\text{CH}_3\text{I}$ ), as mentioned above). The other bands

observed in case of iodomethane-water mixture are centered at 3582, 3603, 3607, 3609 and 3642  $\text{cm}^{-1}$ . The four first bands display red-shifts of  $\approx -56$ ,  $-35$ ,  $-31$  and  $-29$   $\text{cm}^{-1}$  against a blue-shift of  $\approx +4$   $\text{cm}^{-1}$  for the last one. The only forms which could partially or totally match with those shifts are: 1:1a, 1:3c, the whole serie 2:1a to 2:1e, and 2:2i. As already mentioned, calculated intensities, especially those of the OH modes, they are purely indicative. For instance, in the case of malonaldehyde [35], the OH intensity of the chelated form is calculated to be 0.33 of the most intense OH band among the isomers, but is not observed because of the H-bond strength, which induces a FWHM of thousands of  $\text{cm}^{-1}$ . As a result, this band is almost flat, and not observed. A similar situation is expected in our case.

In the  $\nu_3$  region (3950-3700  $\text{cm}^{-1}$ ) (Fig. S10 (a) and Table 3)), one observes bands at 3777, 3756, 3753, 3738, 3736, 3731, 3721, 3716, 3711, 3708, 3707, 3703, 3700 and 3695  $\text{cm}^{-1}$ . Those bands are mainly due to water monomer and clusters, the non rotating monomer (nrm) and rovibrational transitions [29]. Four new bands are observed in the case of mixed sample, at 3752, 3749, 3720 and 3713  $\text{cm}^{-1}$ . If the two highest ones are tentatively assigned to  $0_{00} \rightarrow 1_{01}$  water monomer rovibronic transition perturbed by iodomethane proximity, the two lowest ones present red-shift with respect to  $\nu_3$  nrm mode of water monomer, located at 3736  $\text{cm}^{-1}$  [34] of  $\approx -23$  and  $-16$   $\text{cm}^{-1}$ . Species which present possible matching with those red-shifts are: 1:1a, 1:2b, the whole (1:3) series, 2:1b, 2:1c and 2:1e, 2:2c, 2:2f and 2:2i (Tables S2-S6).

From the combined analysis of the three water regions we can conveniently discriminate between the candidates we have found. Only species presenting at least two distinct bands are considered:

CH<sub>3</sub>I.H<sub>2</sub>O complex: 1:1a

CH<sub>3</sub>I.(H<sub>2</sub>O)<sub>2</sub> complex: 1:2a

CH<sub>3</sub>I.(H<sub>2</sub>O)<sub>3</sub> complexes: 1:3a, 1:3c

(CH<sub>3</sub>I)<sub>2</sub>.H<sub>2</sub>O complexes: whole series from 2:1a to 2:1e

(CH<sub>3</sub>I)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> complexes: 2:2i

In summary, comparing the candidates identified from both CH<sub>3</sub>I and H<sub>2</sub>O regions, we can confidently state that we have identified 1:1a, 1:2a and 1:3a, 1:3c species shown on Fig. 3, together with CH<sub>3</sub>I monomer, dimers and trimers (Table 2 and 3). It should be noted that they present common bands, this is due to their close structures (see theoretical part). The 1:1a, 1:2a

and 1:3a isomers observed experimentally are consistent with calculated Gibbs free energy given them as the most stable isomers. The structures of dimer or trimer of H<sub>2</sub>O perturbed by CH<sub>3</sub>I are found in our experimental conditions. This result highlights the preferred formation of hetero aggregates rather than hetero complexes.

Concerning the other possible candidates, either they partially match the observed shifts with no decisive evidence of their presence, or CH<sub>3</sub>I being the minority product, 2:1 and 2:2 species are hard to see. The evidence of dimer of CH<sub>3</sub>I in our experiments suggests the presence of interaction with water as 2:1 and 2:2 complexes as mentioned above. Indeed, we observed for 2:2i isomer, the only form among all those calculated which present a blue-shift in the  $\nu_1$  water region, or 2:1a, 2:1b and 2:1c which could be responsible for the band at 3582 cm<sup>-1</sup>, while that observed at 3603 cm<sup>-1</sup> could be assigned to 2:1d and 2:1e species. Because we cannot confirm their presence, we do not include them in Tables 2 and 3.

#### 4. Conclusion

We have investigated the interaction between CH<sub>3</sub>I and water molecules using argon cryogenic matrix experiments. The experimental data were supported by theoretical DFT calculations. The experiments were conducted with a large excess of H<sub>2</sub>O molecules compared to CH<sub>3</sub>I in order to mimic CH<sub>3</sub>I environment in the atmosphere. Cryogenic matrices seem pretty accurate in order to describe inter molecular interactions between atmospherically relevant molecules. Even if working at low temperature and pressure does not mimic atmospheric conditions, it brings insights at molecular level. However, working in these conditions allows the study of the ground energy potential of those atmospheric complexes and aggregates. Dimers and trimers of CH<sub>3</sub>I are observed despite the high water amount in the initial mixture: this may be explained by the low affinity of CH<sub>3</sub>I with water. Monomer of CH<sub>3</sub>I perturbing water dimer and trimer are observed rather than hetero complexes that would suggest hetero aggregation process. Finally, considering the concentration of iodomethane used in our experiments and the poor ability of CH<sub>3</sub>I to diffuse into the matrix, we state that the aggregates are rather originally formed in the gas phase and not in the matrix cage. The other complexes such as 2:1 and 2:2 cannot be completely excluded but appear as minor species. Thus, the inter molecular behavior between CH<sub>3</sub>I and H<sub>2</sub>O molecules determined for the first time experimentally and supported by DFT calculation highlights that, in the atmosphere, gaseous iodomethane and water will likely form hetero aggregates of water and iodomethane clusters instead of (CH<sub>3</sub>I)<sub>n</sub>-(H<sub>2</sub>O)<sub>m</sub> complexes. This result is consistent with recent theoretical studies, which have predicted the



incomplete hydration of iodine species [27, 29]. In principle, the abundant low-volatility condensing vapors other than iodine are required in the atmosphere for the growth of iodine clusters to CCN. Our results suggest that the CH<sub>3</sub>I would be partially condensed with water on aerosols during the CCN process rather than serves as CCN it-self. The Henry constant value ( $H^{CP}$  (at 298 K) = 2-3.5 10<sup>-3</sup> mol.m<sup>-3</sup>.Pa<sup>-1</sup> [36]) predicts that CH<sub>3</sub>I will remain in the gaseous phase and thus, will be subject to the oxidative photolysis to form in term iodine oxide particles (IOPs) [37]. The atmospheric gas-to-particle conversion mechanism requires initial clustering steps, which are driven by I<sub>x</sub>O<sub>y</sub> in both dry and humid conditions. However, the IR and UV photolysis of hetero aggregates in gaseous phase has not been considered until now. In the future, the photochemical behavior of such CH<sub>3</sub>I-water aggregates will be investigated. Finally, in the context of the NNP's severe accident, our work is contributing to better understand the fate of nuclear species in the atmosphere and thus, the **radionuclide** dispersion.

#### **Author statement**

Sophie Sobanska: Oversight and leadership responsibility for the research activity planning and execution, acquisition of the financial support for the project leading to this publication, writing, reviewing and editing the paper.

Hanaa Houjeij: Performing the experiments and theoretical calculations

Stephane Coussan: Participating to the interpretation of the experimental and theoretical results and to the manuscript writing and reviewing.

Christian Aupetit: Providing experimental services

Sonia Taamali: Providing training and support for theoretical calculations

Florent Louis: Providing a part of theoretical discussion and of computational section writing.

Laurent Cantrel: Participating to the acquisition of the financial support.

Anne Cécile Gregoire: Acquisition of the financial support, reviewing of the paper.

Joëlle Mascetti: Formulation and evolution of overarching research goal and aims, performing the experiments.

#### **Declaration of competing interest**

No potential conflict of interest is reported by the authors

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**Figure captions:**

Fig. 1: IR spectra in  $\nu_2$  [bending CH),  $\nu_6$  (rocking CH<sub>3</sub>) regions of pure iodomethane matrix (trace (a)) (CH<sub>3</sub>I/Ar = 1/1000), recorded at 10 K, and of mixed CH<sub>3</sub>I/H<sub>2</sub>O/Ar = 1/25/1500, recorded at 10 K (trace (b)).

Fig. 2: IR spectra in  $\nu_1$  (antisymmetric stretching) region of pure water cluster matrix (trace (a)) (H<sub>2</sub>O/Ar = 7/1000), recorded at 4 K, and of mixed CH<sub>3</sub>I/H<sub>2</sub>O/Ar = 1/25/1500, recorded at 10 K (trace (b)).

Fig. 3: Calculated structures of the unambiguously identified (CH<sub>3</sub>I)<sub>n</sub>-(H<sub>2</sub>O)<sub>m</sub> isomers at the  $\omega$ B97X-D/ aug-cc-pVTZ-PP level of theory observed experimentally

**Table captions:**

Table 1: Table 1: Experimental IR band positions for  $\nu_1$ ,  $\nu_2$  and  $\nu_6$  (in cm<sup>-1</sup>) for CH<sub>3</sub>I (1000 ppm) in Ar matrix, observed and calculated shift from the monomer and tentative assignment (in bold the most intense IR bands) – Experimental IR band positions for  $\nu_1$ ,  $\nu_2$  and  $\nu_6$  (in cm<sup>-1</sup>) for CH<sub>3</sub>I (1000 ppm) in Ar matrix from (18) and (31) and CH<sub>3</sub>I in gas phase from (31).

Table 2: Experimental IR band positions for  $\nu_1$ ,  $\nu_2$ , and  $\nu_6$  (in cm<sup>-1</sup>) in CH<sub>3</sub>I spectral range for mixed CH<sub>3</sub>I/H<sub>2</sub>O/Ar = 1/25/1500, recorded at 10 K, calculated spectral shifts ( $\Delta\nu$ ) to experimental spectrum of CH<sub>3</sub>I monomer and tentative assignment.

Table 3: Experimental IR band positions for  $\nu_1$ , and  $\nu_3$  (in cm<sup>-1</sup>) in H<sub>2</sub>O spectral range for reference spectra of monomer and dimer, mixed CH<sub>3</sub>I/H<sub>2</sub>O/Ar = 1/25/1500, recorded at 10 K, for H<sub>2</sub>O (4:1000) at 4K, calculated spectral shift ( $\Delta\nu$ ) to experimental spectrum for H<sub>2</sub>O monomer and tentative assignment.

## Tables

Table 1: Experimental IR band positions for  $\nu_1$ ,  $\nu_2$  and  $\nu_6$  (in  $\text{cm}^{-1}$ ) for  $\text{CH}_3\text{I}$  (1000 ppm) in Ar matrix, observed and calculated shift from the monomer and tentative assignment (in bold the most intense IR bands) – Experimental IR band positions for  $\nu_1$ ,  $\nu_2$  and  $\nu_6$  (in  $\text{cm}^{-1}$ ) for  $\text{CH}_3\text{I}$  (1000 ppm) in Ar matrix from [18] and [31] and  $\text{CH}_3\text{I}$  in gas phase from [31].

Vibrational modes		$\nu$ experimental $\text{cm}^{-1}$	$\Delta\nu$ from monomer		$\nu$ $\text{cm}^{-1}$ [18]	$\nu$ $\text{cm}^{-1}$ [31]	$\nu_{\text{gas phase}}$ $\text{cm}^{-1}$ [31]	tentative assignment
			obs	cal				
$\nu_1$	$\text{CH}_3$ stretch	2976	11	-				-
		2967	2	2				dimer HT
		<b>2965</b>	0	0	2965	2965	2953	monomer / trimer $\text{THT}_1$
		2960	-5	2 / -2 / -4				dimer HT / dimer HH / trimer $\text{THT}_1$
$\nu_2$	Sym $\text{CH}_3$ deformation	1248	3	3				dimer HT / trimer $\text{THT}_1$
		1246	1	0				dimer HT / trimer $\text{THT}_1$
		<b>1245</b>	0	0	1245	1245	1251	monomer / dimer HT
		1244	-1	-1				dimer HH
		1243	-2	-2				trimer $\text{THT}_1$
		1240	-5	-				-
$\nu_6$	$\text{CH}_3$ rocking	886	4	5 / 3				dimer HT / dimer HH / trimer $\text{THT}_1$
		<b>882</b>	0	0	882		882	monomer / dimer HH
		881	-1	-1	880	880		monomer/ dimer HH
		878	-4	-2				dimer HH

Table 2: Experimental IR band positions for  $\nu_1$ ,  $\nu_2$ , and  $\nu_6$  (in  $\text{cm}^{-1}$ ) in  $\text{CH}_3\text{I}$  spectral range for mixed  $\text{CH}_3\text{I}/\text{H}_2\text{O}/\text{Ar} = 1/25/1500$ , recorded at 10 K, calculated spectral shifts ( $\Delta\nu$ ) to experimental spectrum of  $\text{CH}_3\text{I}$  monomer and tentative assignments.

Vibrational Mode	$\text{CH}_3\text{I}$ monomer	$\text{CH}_3\text{I}-\text{H}_2\text{O}$	$\Delta\nu$	tentative assignments
$\nu_1 \text{CH}_3\text{I}$		2976	11	$\text{CH}_3\text{I}$
		2968	3	dimer HT
	2965	2965	0	monomer / trimer $\text{THT}_1$
		2961	-4	dimer HT / dimer HH / trimer $\text{THT}_1$
		<b>2925</b>		n.c.
		<b>2868</b>		n.c.
		<b>2855</b>		n.c.
		<b>2846</b>		n.c.
		<b>2825</b>		n.c.
		<b>2819</b>		n.c.
$\nu_2 \text{CH}_3\text{I}$		<b>1257</b>	<b>12</b>	$\text{CH}_3\text{I}-3\text{H}_2\text{O}$ (1 :3a)
		<b>1256</b>	<b>11</b>	$\text{CH}_3\text{I}-3\text{H}_2\text{O}$ (1 :3a)
		<b>1254</b>	<b>9</b>	see text
		<b>1250</b>	<b>5</b>	$\text{CH}_3\text{I}-2\text{H}_2\text{O}$ (1 :2a)
		<b>1248</b>	<b>3</b>	dimer HT / trimer $\text{THT}_1$ / $\text{CH}_3\text{I}-\text{H}_2\text{O}$ (1:1a)
		1246	1	dimer HT / trimer $\text{THT}_1$
	1245	1245	0	monomer / dimer HT /
		1243	-2	dimer HH/ trimer $\text{THT}_1$
		1240	-5	$\text{CH}_3\text{I}$
$\nu_6 \text{CH}_3\text{I}$		<b>909</b>	<b>27</b>	$\text{CH}_3\text{I}-2\text{H}_2\text{O}$ (1:2a) / $\text{CH}_3\text{I}-3\text{H}_2\text{O}$ (1:3c)
		<b>903</b>	<b>21</b>	$\text{CH}_3\text{I}-\text{H}_2\text{O}$ (1 :1a)
		<b>899</b>	<b>17</b>	$\text{CH}_3\text{I}-2\text{H}_2\text{O}$ (1:2a) / $\text{CH}_3\text{I}-3\text{H}_2\text{O}$ (1:3a)
		<b>896</b>	<b>14</b>	$\text{CH}_3\text{I}-3\text{H}_2\text{O}$ (1:3a)
		<b>891</b>	<b>11</b>	$\text{CH}_3\text{I}-\text{H}_2\text{O}$ (1 :1a)
		<b>888</b>	<b>6</b>	see text
		<b>886</b>	<b>4</b>	dimer HT / dimer HH / trimer $\text{THT}_1$ / $\text{CH}_3\text{I}-3\text{H}_2\text{O}$ (1:3a)
	882	882	0	monomer / dimer HH
	881	881	-1	monomer/ dimer HH
		879	-2	dimer HH

674 Table 3: Experimental IR band positions for  $\nu_1$ , and  $\nu_3$  (in  $\text{cm}^{-1}$ ) in  $\text{H}_2\text{O}$  spectral range for  
675 reference spectra of monomer and dimer, mixed  $\text{CH}_3\text{I}/\text{H}_2\text{O}/\text{Ar} = 1/25/1500$ , recorded at 10 K,  
676 for  $\text{H}_2\text{O}$  (4:1000) at 4K, calculated spectral shifts ( $\Delta\nu$ ) to experimental spectrum for  $\text{H}_2\text{O}$   
677 monomer and tentative assignments.

<b><math>\text{H}_2\text{O}</math> monomer and dimer[29]</b>	<b><math>\text{H}_2\text{O}</math> 4:1000</b>	<b><math>\text{CH}_3\text{I}-\text{H}_2\text{O}</math></b>	<b><math>\Delta\nu</math></b>	<b>tentative assignments</b>
3776	3777	3777		$\text{H}_2\text{O}$ rovibrational band $\nu_3$
3757	3756	3756		$\text{H}_2\text{O}$ rovibrational band $\nu_3$
	3753	3753		$\text{H}_2\text{O}$ rovibrational band $\nu_3$
		<b>3752</b>	<b>16</b>	<b>see text</b>
		<b>3749</b>	<b>13</b>	<b>see text</b>
3739				$\text{H}_2\text{O}$ rovibrational band $\nu_3$
3738	3738	3738		$\text{H}_2\text{O}$ dimer PA
3736	3736	3736		$\text{H}_2\text{O}$ $\nu_3$ [nrm)
	3731	3731		$\text{H}_2\text{O}$ rovibrational band $\nu_3$
3725	3721	3721		$\text{H}_2\text{O}$ rovibrational band $\nu_3$
		<b>3720</b>	<b>-16</b>	<b><math>\text{CH}_3\text{I}-3\text{H}_2\text{O}</math> [1 :3c)</b>
3716	3716	3716		$\text{H}_2\text{O}$ dimer PD
3711	3711	3711		$\text{H}_2\text{O}$ rovibrational band $\nu_3$
		<b>3713</b>	<b>-23</b>	<b><math>\text{CH}_3\text{I}-\text{H}_2\text{O}</math> [1 :1a) / <math>\text{CH}_3\text{I}-3\text{H}_2\text{O}</math> [1:3c)</b>
3708	3708			$\text{H}_2\text{O}$ dimer PD
3670	3670	3670		$\text{H}_2\text{O}$ dimer PD / $\text{H}_2\text{O}$ rovibrational band $\nu_1$
	3662	3662		$\text{H}_2\text{O}$ dimer PD
3654	3654	3654		$\text{H}_2\text{O}$ dimer PD / $\text{H}_2\text{O}$ rovibrational band $\nu_1$
	3648	3648		$\text{H}_2\text{O}$ dimer PD
	3647	3647		$\text{H}_2\text{O}$ dimer PD
		<b>3642</b>	<b>4</b>	<b>see text</b>
	3640	3640		$\text{H}_2\text{O}$ dimer PD
3638	3638	3638		$\text{H}_2\text{O}$ $\nu_1$ [nrm)
3633	3633	3633		$\text{H}_2\text{O}$ dimer PA
	3630	3630		$\text{H}_2\text{O}$ dimer PD
	3628	3628		$\text{H}_2\text{O}$ dimer PD
3623				$\text{H}_2\text{O}$ rovibrational band $\nu_1$
	3617	3617		$\text{H}_2\text{O}$ dimer PD
	3612	3612		$\text{H}_2\text{O}$ dimer PD
		<b>3609</b>	<b>-29</b>	<b><math>\text{CH}_3\text{I}-\text{H}_2\text{O}</math> [1 :1a)</b>
3607	3607	<b>3607</b>	-31	$\text{H}_2\text{O}$ rovibrational band $\nu_1$ / <b>see text</b>
		<b>3603</b>	<b>-35</b>	<b>see text</b>
		<b>3582</b>	<b>-56</b>	<b>see text</b>
3574	3576	3574		$\text{H}_2\text{O}$ dimer PD
	3567	3567		$\text{H}_2\text{O}$ trimer
	3564	3564		$\text{H}_2\text{O}$ trimer
		<b>3553</b>	<b>-85</b>	<b><math>\text{CH}_3\text{I}-2\text{H}_2\text{O}</math> [1:2a) / <math>\text{CH}_3\text{I}-3\text{H}_2\text{O}</math> [1:3c)</b>
	3549	3549		$\text{H}_2\text{O}$ trimer
	3543	3543		$\text{H}_2\text{O}$ trimer
	3528	3528		$\text{H}_2\text{O}$ trimer
	3515	3515		$\text{H}_2\text{O}$ trimer



		<b>3463</b>	<b>-175</b>	<b>CH<sub>3</sub>I-3H<sub>2</sub>O [1 :3a)</b>
	3445	3445		H <sub>2</sub> O tetramer
	3402	3402		H <sub>2</sub> O tetramer
	3392	3392		H <sub>2</sub> O tetramer
	3373	3373		H <sub>2</sub> O tetramer
	3332	3332		H <sub>2</sub> O pentamer
	3325	3325		H <sub>2</sub> O pentamer
	3209	3209		H <sub>2</sub> O High polymer / 2v <sub>2</sub> harmonic

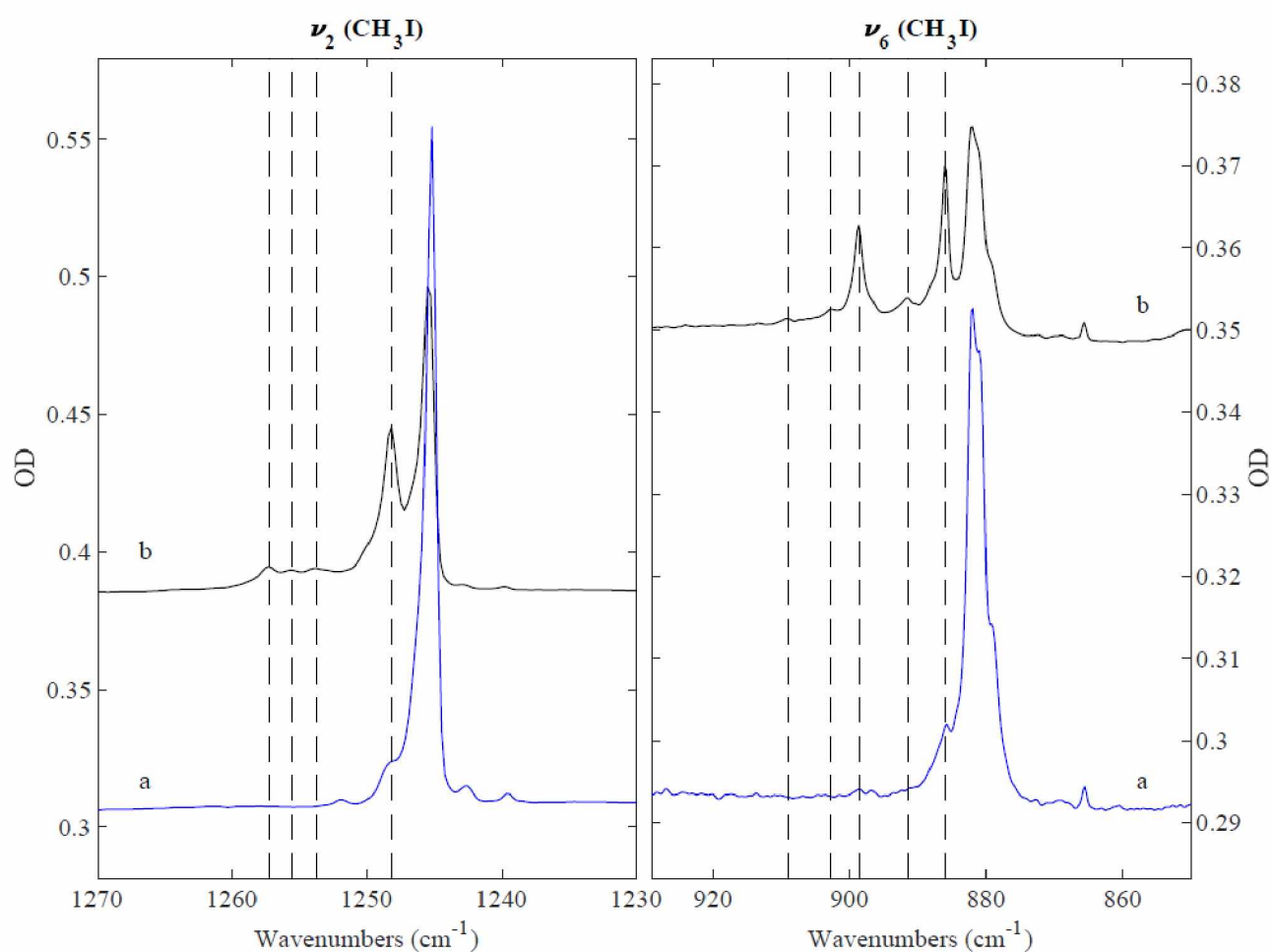
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681 **Figures**

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684 Fig. 1 : IR spectra in  $\nu_2$  (bending CH),  $\nu_6$  (rocking  $\text{CH}_3$ ) regions of pure iodomethane matrix  
 685 (trace [a]) ( $\text{CH}_3\text{I}/\text{Ar} = 1/1000$ ), recorded at 10 K, and of mixed  $\text{CH}_3\text{I}/\text{H}_2\text{O}/\text{Ar} = 1/25/1500$ ,  
 686 recorded at 10 K (trace (b)).

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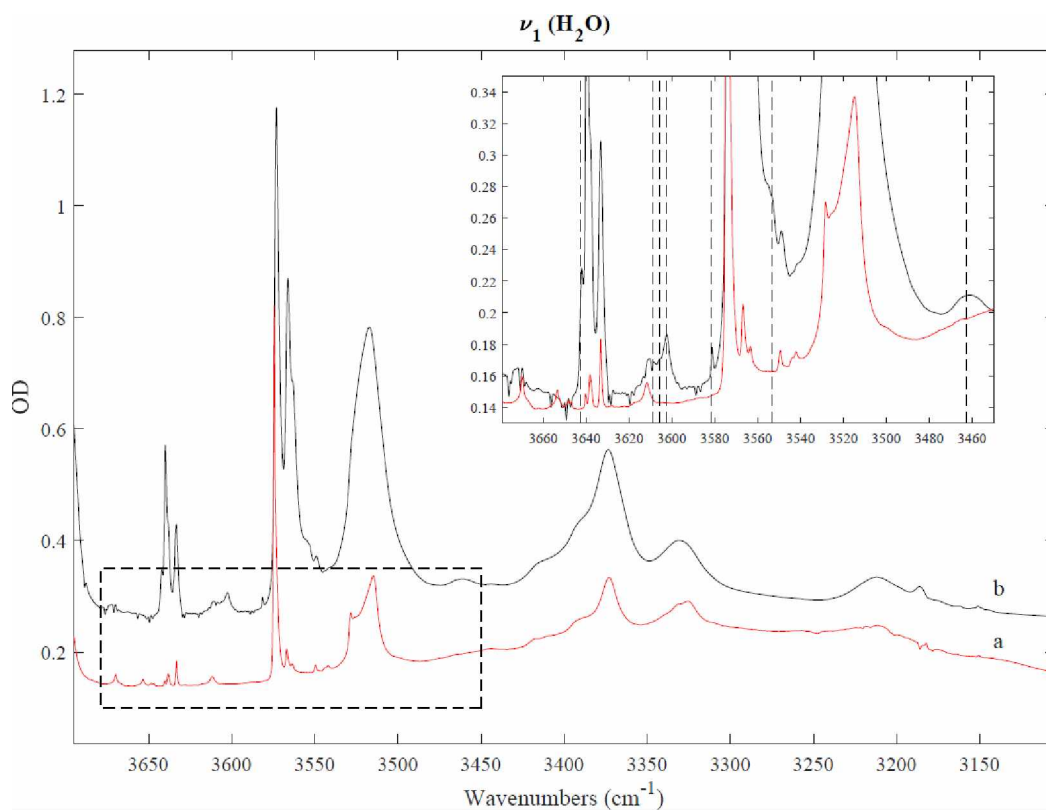


Fig. 2: IR spectra in the  $\nu_1$  (antisymmetric stretching) regions of pure water cluster matrix [trace (a)] ( $\text{H}_2\text{O}/\text{Ar} = 7/1000$ ), recorded at 4 K, and of mixed  $\text{CH}_3\text{I}/\text{H}_2\text{O}/\text{Ar} = 1/25/1500$ , recorded at 10 K (trace (b)).

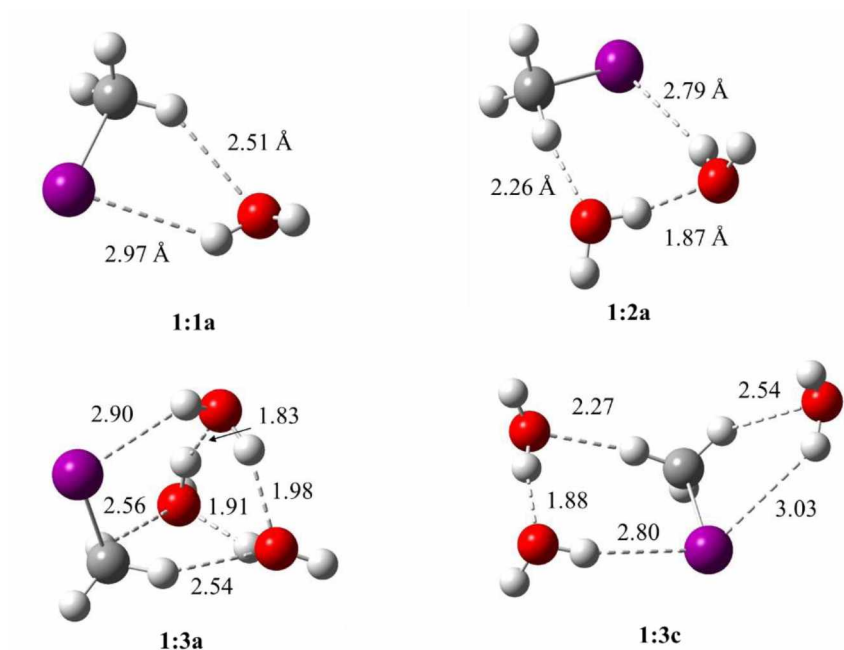


Fig. 3: Calculated structures of the unambiguously identified (CH<sub>3</sub>I)<sub>n</sub>-(H<sub>2</sub>O)<sub>m</sub> isomers at the ωB97X-D/ aug-cc-pVTZ-PP level of theory observed experimentally

## **Infrared matrix-isolation and theoretical studies of interactions between CH<sub>3</sub>I and water**

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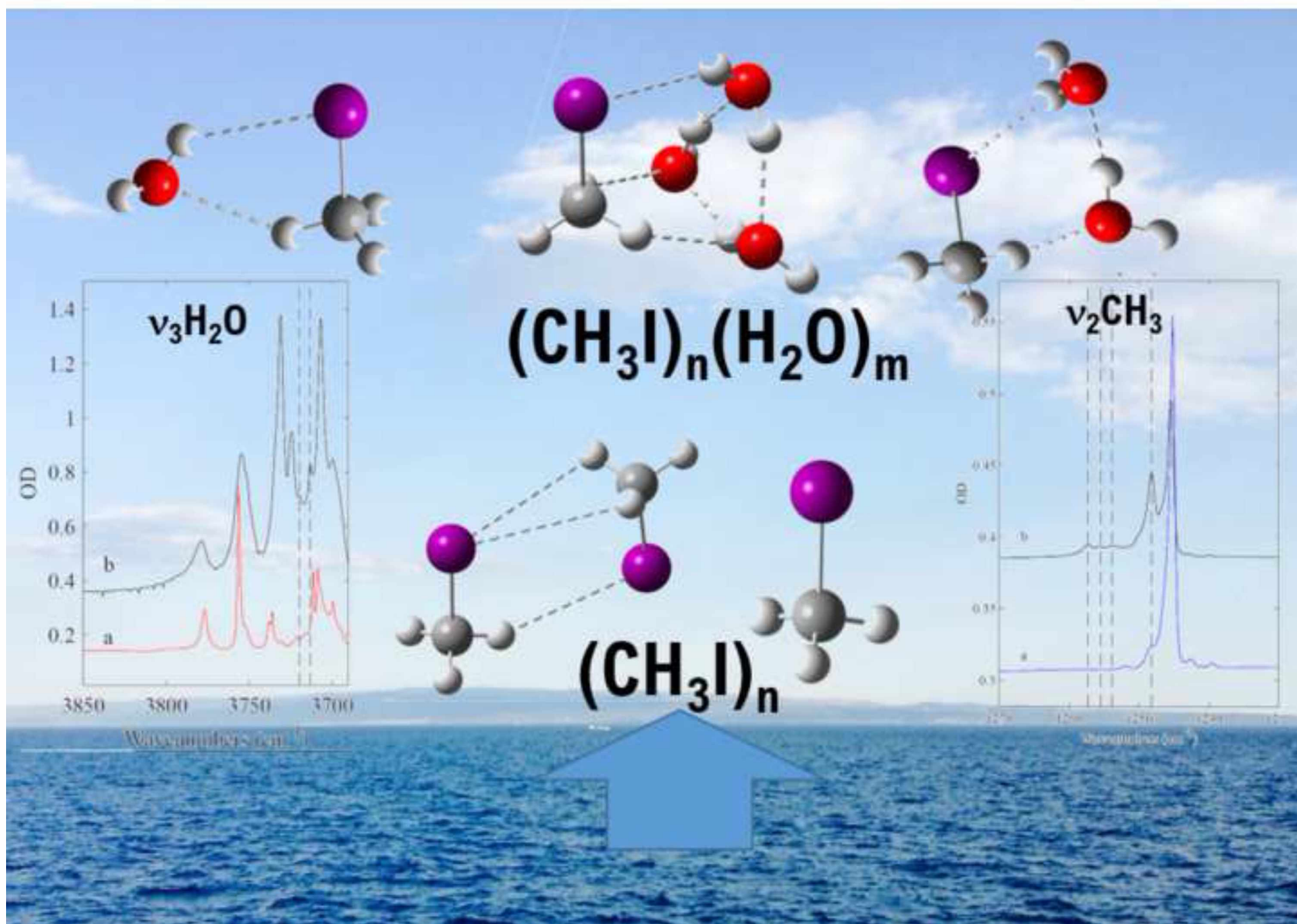
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### **Highlights:**

- Microhydration of iodomethane is explored by matrix isolation infrared spectroscopy
- Microhydration with a large excess of water is investigated
- Hetero-aggregates between CH<sub>3</sub>I and H<sub>2</sub>O are formed with dimers and trimers of CH<sub>3</sub>I
- Interaction between CH<sub>3</sub>I and H<sub>2</sub>O is not favored in the atmosphere





# Infrared matrix-isolation and theoretical studies of interactions between CH<sub>3</sub>I and water

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## Supporting information

### Figure list:

Fig. S1:  $\omega$ B97X-D/aug-cc-pVTZ-PP-predicted geometry (distance in Å) and Gibb free energy ( $\Delta G$  in kJ.mol<sup>-1</sup>) of CH<sub>3</sub>I dimers (a) and trimers (b).

Fig. S2: IR spectra of CH<sub>3</sub>I/Ar sample at 10 K in the 3100-2750 cm<sup>-1</sup> and 1350-750 cm<sup>-1</sup> spectral range corresponding to the CH<sub>3</sub> stretching and CH<sub>3</sub> deformation and rocking regions, respectively.

Fig. S3: IR spectra of the annealing of CH<sub>3</sub>I/Ar sample until 35 K in the spectral range (a) 3080-2944 cm<sup>-1</sup>(b) 1270-1237 cm<sup>-1</sup>(c) 905-870 cm<sup>-1</sup>. Bands denoted in green, pink and orange are assigned to CH<sub>3</sub>I monomer, CH<sub>3</sub>I dimer, and CH<sub>3</sub>I trimer, respectively.

Fig. S4:  $\omega$ B97X-D/aug-cc-pVTZ-PP-predicted geometry (distances in Å) and Gibbs free energy ( $\Delta G$  in kJ mol<sup>-1</sup>) of CH<sub>3</sub>I.H<sub>2</sub>O isomers.

Fig. S5:  $\omega$ B97X-D/aug-cc-pVTZ-PP-predicted geometry (distances in Å) and Gibbs free energy ( $\Delta G$  in kJ mol<sup>-1</sup>) of CH<sub>3</sub>I.(H<sub>2</sub>O)<sub>2</sub> isomers.

Fig. S6:  $\omega$ B97X-D/aug-cc-pVTZ-PP-predicted geometry (distances in Å) and Gibbs free energy ( $\Delta G$  in kJ mol<sup>-1</sup>) of CH<sub>3</sub>I.(H<sub>2</sub>O)<sub>3</sub> isomers.

Fig. S7:  $\omega$ B97X-D/aug-cc-pVTZ-PP-predicted geometry (distances in Å) and Gibbs free energy ( $\Delta G$  in kJ mol<sup>-1</sup>) of (CH<sub>3</sub>I)<sub>2</sub>.(H<sub>2</sub>O) isomers.

Fig. S8:  $\omega$ B97X-D/aug-cc-pVTZ-PP-predicted geometry (distances in Å) and Gibbs free energy ( $\Delta G$  in kJ mol<sup>-1</sup>) of (CH<sub>3</sub>I)<sub>2</sub>.(H<sub>2</sub>O)<sub>2</sub> isomers.

Fig. S9: Distribution of NBO charges calculated at  $\omega$ B97X-D/aug-cc-pVTZ level of theory for CH<sub>3</sub>I, H<sub>2</sub>O monomers and 1:1a and 1:1b complexes.

Fig. S10: IR spectra in the  $\nu_3$  (symmetric stretching) and  $\nu_2$  (bending mode) regions of pure water cluster in matrix (trace (a)) (H<sub>2</sub>O/Ar = 7/1000), recorded at 4 K, and of mixed CH<sub>3</sub>I/H<sub>2</sub>O/Ar = 1/25/1500, recorded at 10 K (trace (b) new bands are marked with dashed lines).

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Table S4. Optimized Cartesian Coordinates of CH<sub>3</sub>I.(H<sub>2</sub>O)<sub>2</sub> at the  $\omega$ B97X-D/aug-cc-pVTZ level of theory

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Table S8. Calculated wavenumbers (cm<sup>-1</sup>) and intensities (I in km/mol) of CH<sub>3</sub>I monomer, HH and HT dimers and THT<sub>1</sub> and THT<sub>2</sub> trimers. The IR bands are predicted at the  $\omega$ B97X-D/aug-cc-pVTZ-PP level of theory. The frequency shifts are calculated with respect to the monomer position ( $\Delta\nu = \nu - \nu_{\text{monomer}}$ ).

Table S9. Calculated wavenumbers (cm<sup>-1</sup>) and intensities (I in km/mol) of CH<sub>3</sub>I.H<sub>2</sub>O complexes compared to the calculated wavenumber (cm<sup>-1</sup>) and intensities (I) of CH<sub>3</sub>I monomer and H<sub>2</sub>O monomer and dimer. The IR bands are predicted at the  $\omega$ B97X-D/aug-cc-pVTZ-PP level of theory. The frequency shifts are calculated with respect to the monomer position ( $\Delta\nu = \nu - \nu_{\text{monomer}}$ ).

Table S10. Calculated wavenumbers (cm<sup>-1</sup>) and intensities (I in km/mol) of CH<sub>3</sub>I.(H<sub>2</sub>O)<sub>2</sub> complexes compared to the calculated wavenumber (cm<sup>-1</sup>) and intensities (I) of CH<sub>3</sub>I monomer and H<sub>2</sub>O monomer and dimer. The IR bands are predicted at the  $\omega$ B97X-D/aug-cc-pVTZ-PP level of theory. The frequency shifts are calculated with respect to the monomer position ( $\Delta\nu = \nu - \nu_{\text{monomer}}$ ).

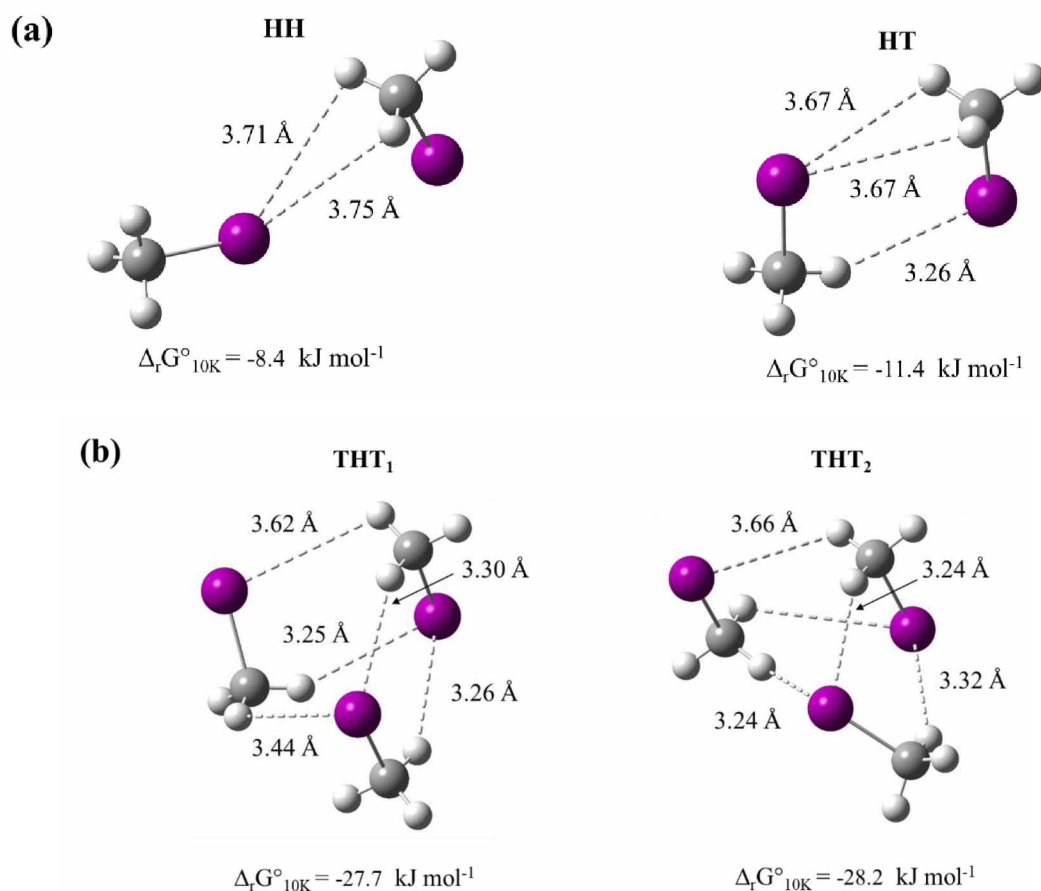
Table S11. Calculated wavenumbers (cm<sup>-1</sup>) and intensities (I in km/mol) of CH<sub>3</sub>I.(H<sub>2</sub>O)<sub>3</sub> complexes compared to the calculated wavenumber (cm<sup>-1</sup>) and intensities (I) of CH<sub>3</sub>I monomer and H<sub>2</sub>O monomer and dimer. The IR bands are predicted at the  $\omega$ B97X-D/aug-cc-pVTZ-PP level of theory. The frequency shifts are calculated with respect to the monomer position ( $\Delta\nu = \nu - \nu_{\text{monomer}}$ ).

Table S12. Calculated wavenumbers (cm<sup>-1</sup>) and intensities (I in km/mol) of (CH<sub>3</sub>I)<sub>2</sub>.(H<sub>2</sub>O) complexes compared to the calculated wavenumber (cm<sup>-1</sup>) and intensities (I) of CH<sub>3</sub>I monomer and H<sub>2</sub>O monomer and dimer. The IR bands are predicted at the  $\omega$ B97X-D/aug-cc-pVTZ-PP level of theory. The frequency shifts are calculated with respect to the monomer position ( $\Delta\nu = \nu - \nu_{\text{monomer}}$ ).

Table S13. Calculated wavenumbers (cm<sup>-1</sup>) and intensities (I in km/mol) of (CH<sub>3</sub>I)<sub>2</sub>.(H<sub>2</sub>O)<sub>2</sub> complexes compared to the calculated wavenumber (cm<sup>-1</sup>) and intensities (I) of CH<sub>3</sub>I monomer and H<sub>2</sub>O monomer and dimer. The IR bands are predicted at the  $\omega$ B97X-D/aug-cc-pVTZ-PP level of theory. The frequency shifts are calculated with respect to the monomer position ( $\Delta\nu = \nu - \nu_{\text{monomer}}$ ).



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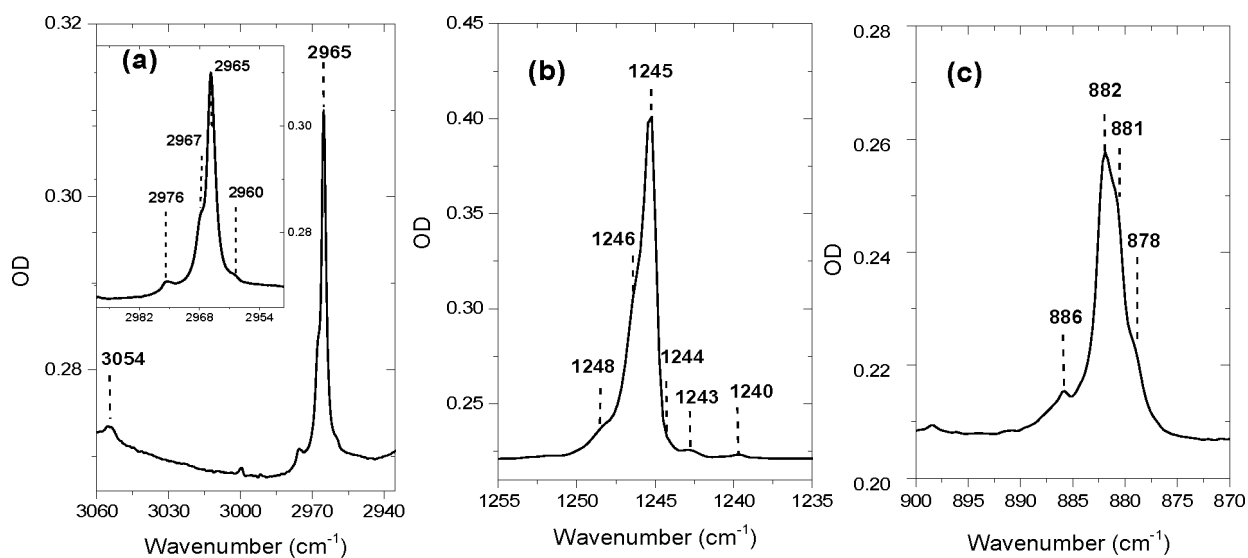


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Fig. S1:  $\omega$ B97X-D/ aug-cc-pVTZ-PP-predicted geometries (distances in Å) and Gibbs free energies ( $\Delta G$  in kJ/mol) of  $\text{CH}_3\text{I}$  dimers (a) and trimers (b).

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Fig. S2: IR spectra of  $\text{CH}_3\text{I}/\text{Ar}$  sample at 10 K in the  $3100\text{--}2750 \text{ cm}^{-1}$  and  $1350\text{--}750 \text{ cm}^{-1}$  spectral range corresponding to (a) the  $\text{CH}_3$  stretching ( $\nu_1$ ), (b)  $\text{CH}_3$  deformation ( $\nu_2$ ) and (c) rocking ( $\nu_6$ ) regions, respectively.

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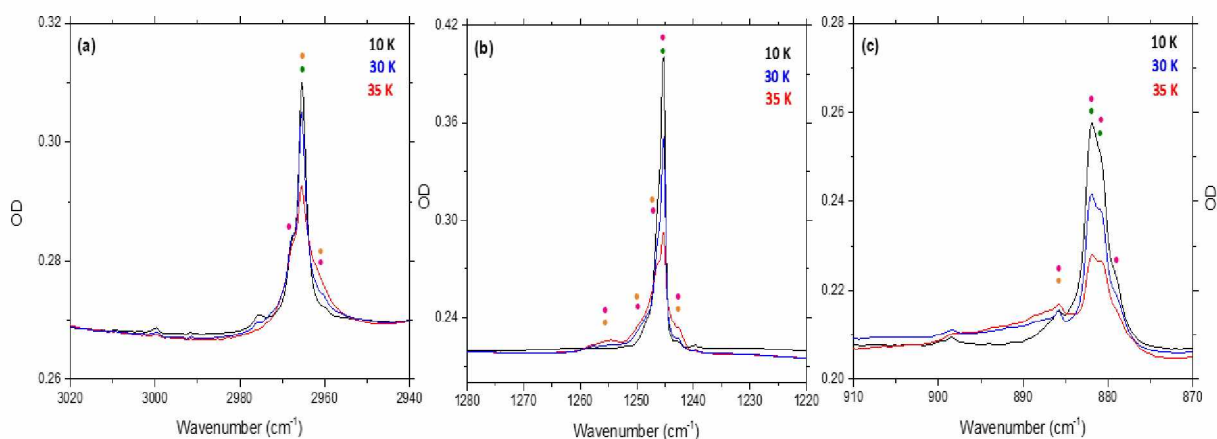


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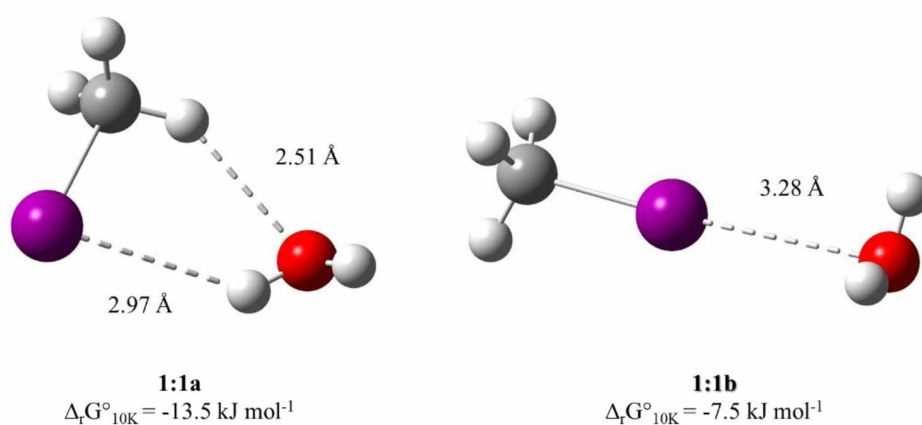


Fig. S4:  $\omega\text{B97X-D/aug-cc-pVTZ-PP}$ -predicted geometry (distances in Å) and Gibbs free energy ( $\Delta G$  in  $\text{kJ mol}^{-1}$ ) of  $\text{CH}_3\text{I}.\text{H}_2\text{O}$  isomers.



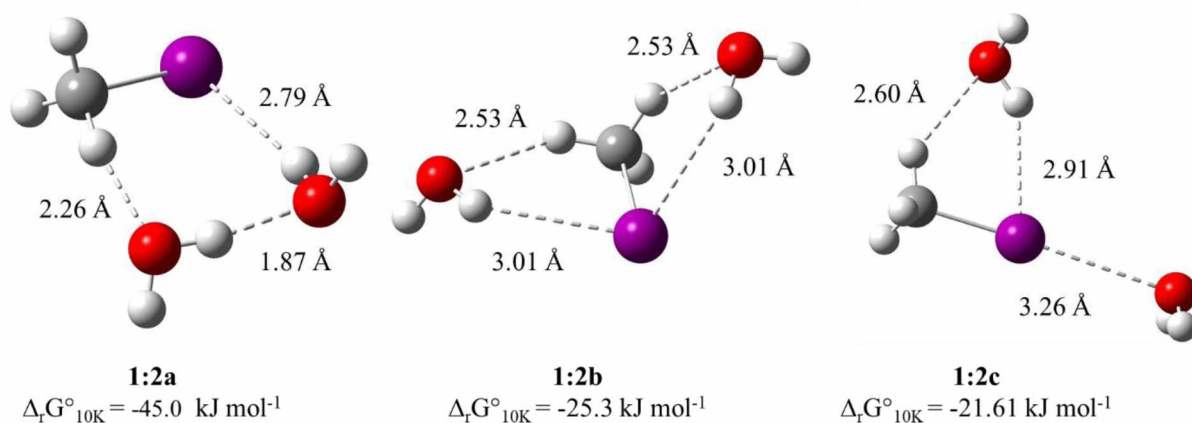


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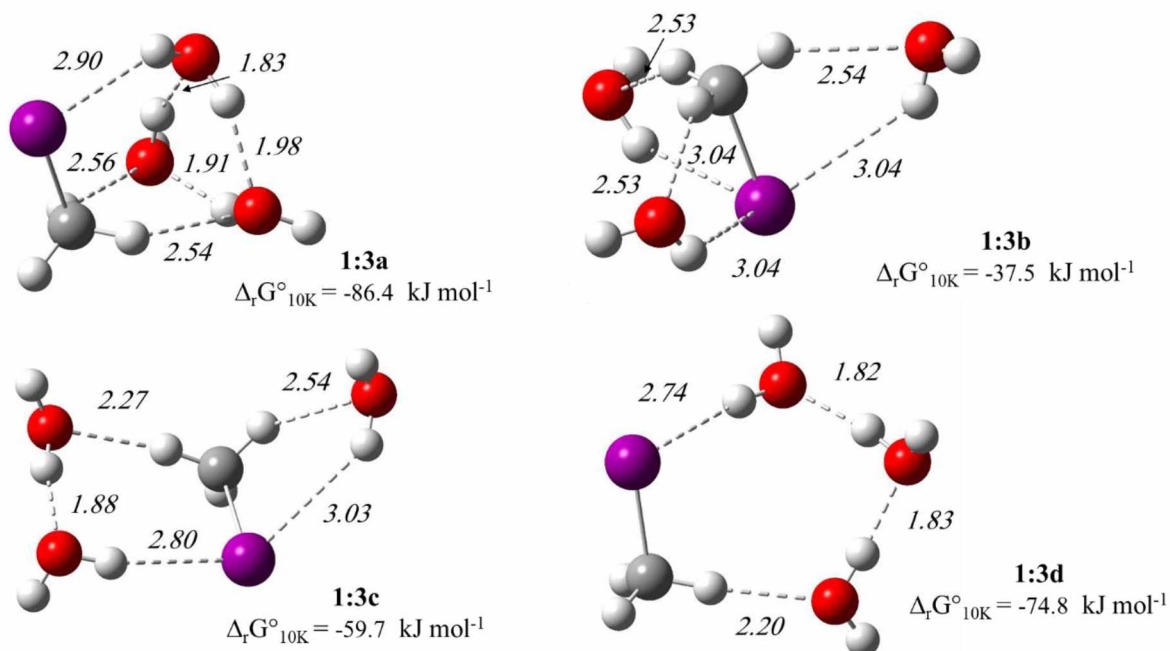


Fig. S6:  $\omega$ B97X-D/ aug-cc-pVTZ-PP-predicted geometry (distances in Å) and Gibbs free energy ( $\Delta G$  in  $\text{kJ mol}^{-1}$ ) of  $\text{CH}_3\text{I}(\text{H}_2\text{O})_3$  isomers.

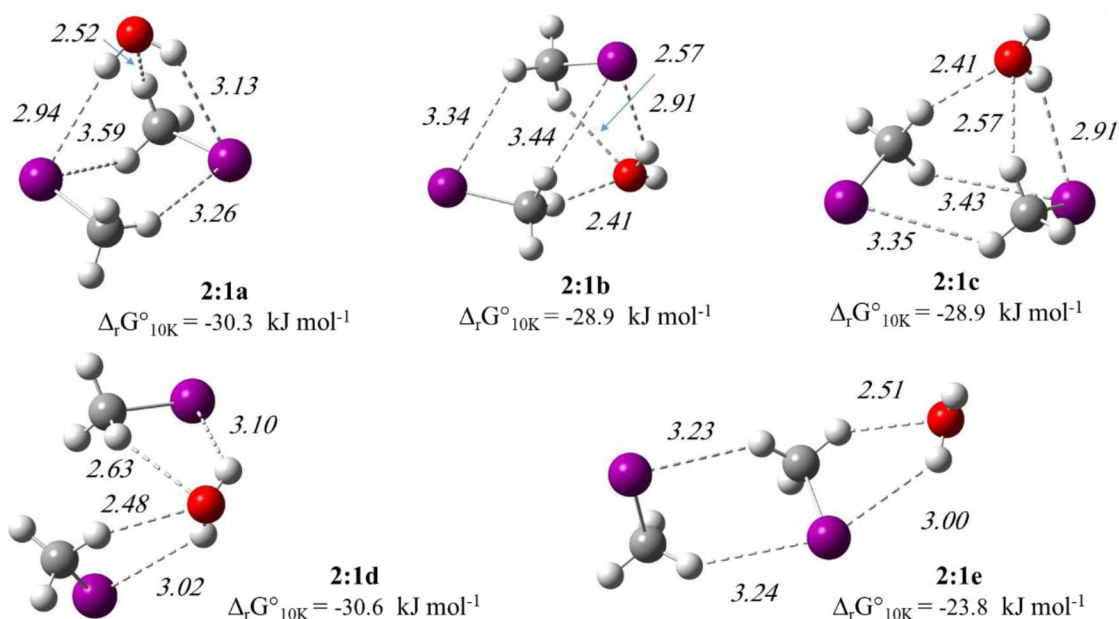


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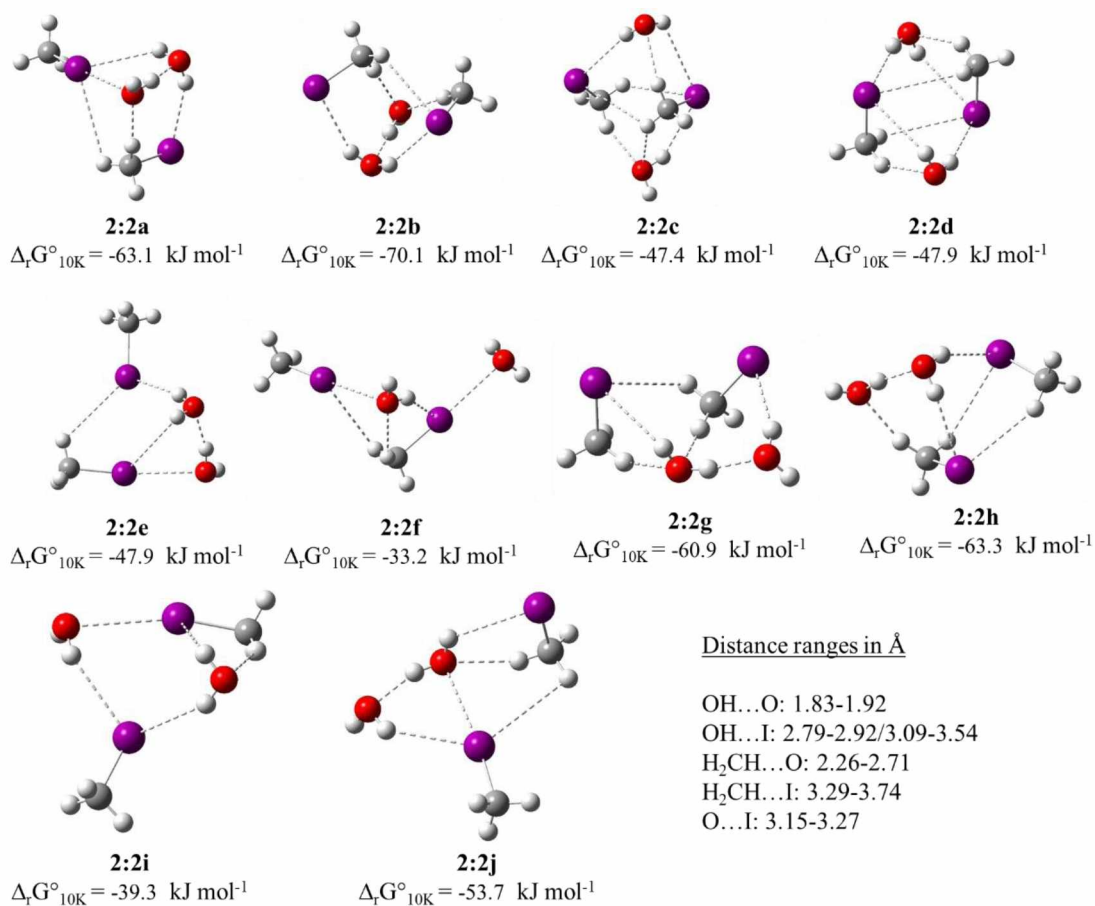


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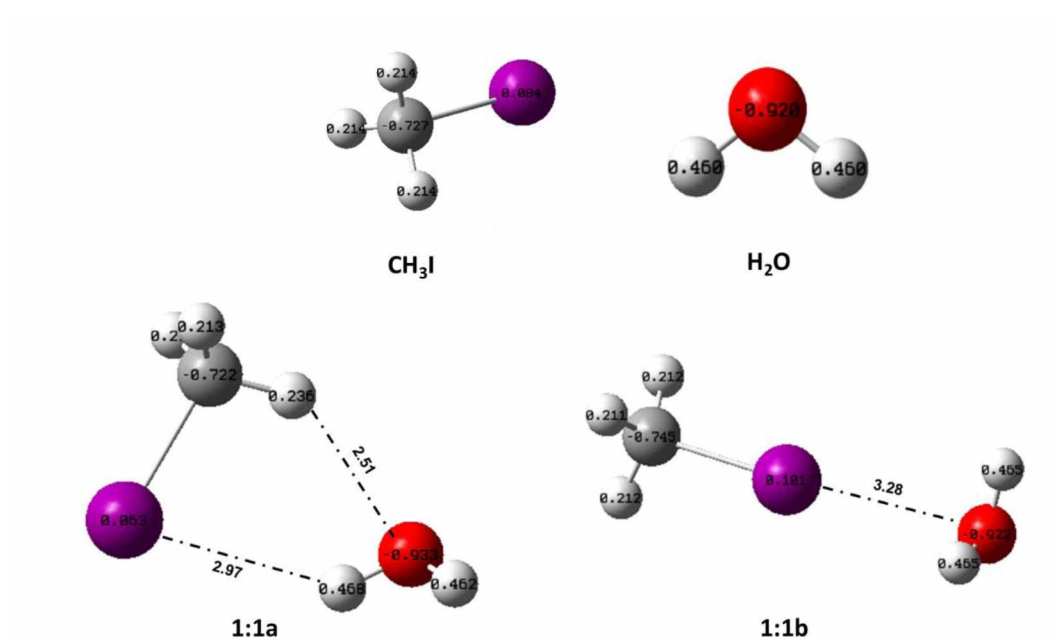


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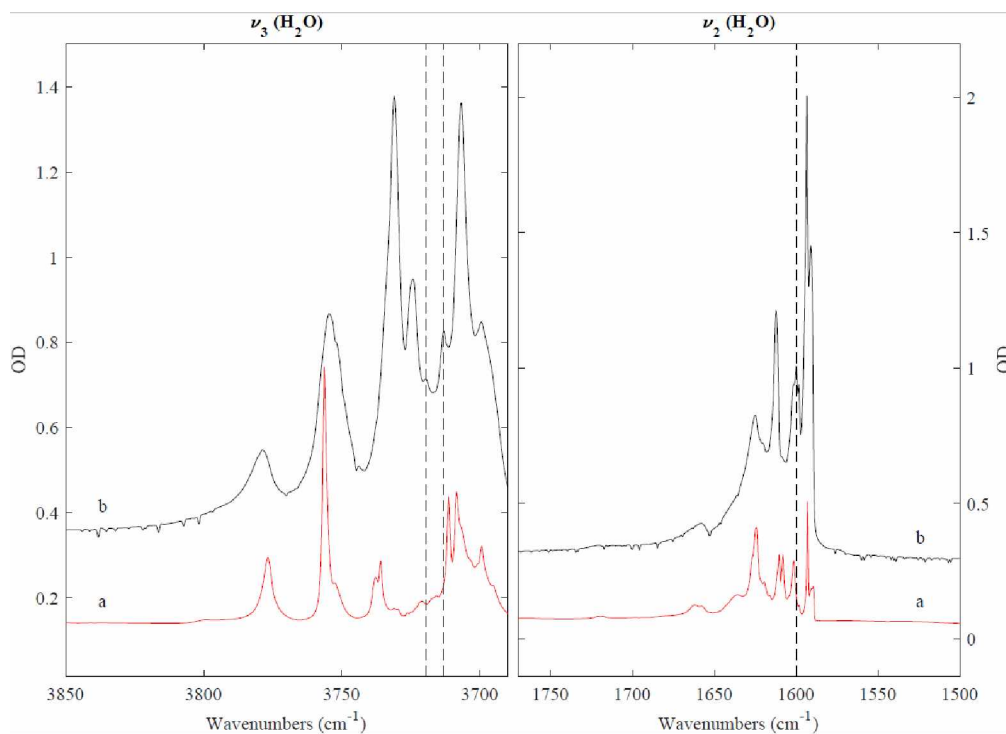


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153 **Table S1.** Optimized Cartesian Coordinates of (H<sub>2</sub>O)<sub>n</sub> at the ωB97X-D/aug-cc-pVTZ level of theory

154 **(H<sub>2</sub>O)**

155	O	-0.000000	0.000000	0.116383
156	H	0.000000	0.760161	-0.465533
157	H	-0.000000	-0.760161	-0.465533

159 **(H<sub>2</sub>O)<sub>2</sub>**

160	O	1.501446	-0.000598	-0.120598
161	H	1.916104	0.003574	0.741310
162	H	0.551378	-0.000064	0.053544
163	O	-1.385260	0.000411	0.114636
164	H	-1.699478	-0.763555	-0.370726
165	H	-1.697491	0.761544	-0.376434

167 **Table S2.** Optimized Cartesian Coordinates of (CH<sub>3</sub>I)<sub>n</sub> at the ωB97X-D/aug-cc-pVTZ level of theory

168 **(CH<sub>3</sub>I)**

169	C	0.000000	0.000000	-1.811644
170	I	0.000000	0.000000	0.326414
171	H	0.000000	1.031350	-2.143367
172	H	0.893175	-0.515675	-2.143367
173	H	-0.893175	-0.515675	-2.143367

175 **(CH<sub>3</sub>I)<sub>2</sub> HH**

176	C	-3.907754	0.390987	-0.004362
177	I	-1.838951	-0.154458	0.001166
178	H	-3.969591	1.472138	-0.040989
179	H	-4.366730	-0.053585	-0.879470
180	H	-4.355098	0.007545	0.905010
181	C	1.665941	1.816332	0.000879
182	I	2.243080	-0.243018	-0.000569
183	H	2.569710	2.413619	-0.019023
184	H	1.058971	1.986833	-0.880054
185	H	1.094765	1.995721	0.903781

187 **(CH<sub>3</sub>I)<sub>2</sub> HT**

188	C	1.622437	1.814822	0.000071
189	I	2.278767	-0.220718	-0.000015
190	H	0.538611	1.804962	-0.001982
191	H	2.011550	2.285114	0.895105
192	H	2.014959	2.286406	-0.892798
193	C	-1.482055	-1.763383	0.000070
194	I	-2.304184	0.211418	-0.000015
195	H	-2.309355	-2.463006	-0.000137
196	H	-0.875177	-1.864681	-0.891350
197	H	-0.875788	-1.864529	0.891907

199 **(CH<sub>3</sub>I)<sub>3</sub> THT<sub>1</sub>**

200	C	-2.611265	-0.156029	1.535612
201	H	-3.674467	-0.082235	1.730068
202	I	-2.354844	-1.202688	-0.311660
203	H	-2.160561	0.822633	1.418122
204	H	-2.111858	-0.726937	2.309631
205	C	1.103445	-1.240263	1.647369
206	H	1.753062	-1.322161	2.510703
207	I	2.308466	-1.482244	-0.100793
208	H	0.355746	-2.024739	1.636964
209	H	0.645072	-0.259067	1.589717



210	C	0.423170	1.700963	-1.762384
211	H	0.003244	2.380145	-2.494538
212	I	0.241593	2.630053	0.156476
213	H	-0.126321	0.767960	-1.720854
214	H	1.477570	1.524966	-1.936626

215

216 **(CH<sub>3</sub>I)<sub>3</sub>-THT<sub>2</sub>**

217

218	C	2.145148	2.734239	0.397215
219	H	2.178470	3.194791	1.377319
220	I	0.092032	2.376726	-0.085539
221	H	2.552316	3.394720	-0.358936
222	H	2.649296	1.774587	0.395383
223	C	0.925720	-1.532791	-1.411356
224	H	0.273384	-2.375321	-1.214532
225	I	2.454356	-1.524893	0.085833
226	H	1.410959	-1.630193	-2.374967
227	H	0.386654	-0.595555	-1.332725
228	C	-1.378208	-1.217054	1.430838
229	H	-1.875731	-1.182816	2.392580
230	I	-2.851214	-0.849020	-0.075398
231	H	-0.625893	-0.440256	1.348768
232	H	-0.949663	-2.195364	1.247436

233

234 **Table S3. Optimized Cartesian Coordinates of CH<sub>3</sub>I.H<sub>2</sub>O at the ωB97X-D/aug-cc-pVTZ level of theory**

235 **CH<sub>3</sub>I\_ (1:1a)**

236	C	-0.324666	1.691645	-0.008427
237	I	0.637281	-0.222031	-0.001147
238	H	-1.392797	1.509590	-0.046959
239	H	-0.039582	2.202525	0.903298
240	H	0.022906	2.227418	-0.883518
241	O	-3.082563	-0.345960	0.081432
242	H	-2.262422	-0.835751	0.185006
243	H	-3.495515	-0.718337	-0.697934

244

245 **CH<sub>3</sub>I (1:1b)**

246	C	2.307237	-0.003551	-0.166295
247	I	0.178576	0.001026	0.049239
248	H	2.667308	0.999157	0.032560
249	H	2.715483	-0.707898	0.549203
250	H	2.543533	-0.303803	-1.180597
251	O	-3.102335	-0.000221	0.013228
252	H	-3.205324	0.751192	-0.572008
253	H	-3.210251	-0.769953	-0.546874

254

255

256 **Table S4. Optimized Cartesian Coordinates of CH<sub>3</sub>I.(H<sub>2</sub>O)<sub>2</sub> at the ωB97X-D/aug-cc-pVTZ level of theory**

257 **CH<sub>3</sub>I (1:2a)**

258	C	0.116256	1.741200	0.280616
259	H	-0.948043	1.638711	0.092753
260	H	0.319186	2.018187	1.308074
261	I	1.018017	-0.176580	-0.046812
262	H	0.583949	2.431321	-0.411423
263	O	-3.126561	1.052353	-0.116378
264	H	-3.710066	1.199234	-0.859808
265	H	-2.996516	0.092444	-0.074015
266	O	-2.372825	-1.667010	0.089172
267	H	-2.480960	-2.032587	0.967911

268	H	-1.424912	-1.518494	-0.008498
269				
270	<b>CH<sub>3</sub>I (1:2b)</b>			
271	C	0.000343	0.997859	1.240818
272	H	-0.900298	1.556198	1.011883
273	H	0.000288	0.636026	2.261971
274	I	-0.000078	-0.724250	-0.039093
275	H	0.901257	1.555763	1.011877
276	O	-2.946397	1.544332	-0.472769
277	H	-3.768260	1.150397	-0.179493
278	H	-2.452615	0.821528	-0.867688
279	O	2.946091	1.543875	-0.472455
280	H	3.770948	1.152828	-0.183775
281	H	2.453218	0.819674	-0.865956

282				
283	<b>CH<sub>3</sub>I (1:2c)</b>			
284	C	-1.682986	-1.368027	-0.060041
285	I	0.195580	-0.341787	0.019537
286	O	-2.695047	1.976821	-0.081435
287	H	-2.462800	-0.615086	-0.028316
288	H	-1.716504	-1.930080	-0.985919
289	H	-1.737091	-2.029032	0.797035
290	H	-1.751392	1.811066	-0.161677
291	H	-2.788982	2.456539	0.741744
292	O	3.092707	1.148174	0.009620
293	H	3.335933	1.102866	-0.915775
294	H	3.671701	0.526608	0.452207

295  
296 **Table S5.** Optimized Cartesian Coordinates of CH<sub>3</sub>I.(H<sub>2</sub>O)<sub>3</sub> at the ωB97X-D/aug-cc-pVTZ Level of Theory  
297 **CH<sub>3</sub>I (1:3a)**

298	C	0.010512	-1.464690	0.213293
299	H	-0.612854	-1.208631	1.061957
300	H	-0.575667	-1.497340	-0.697415
301	I	1.470805	0.086950	-0.012056
302	H	0.548915	-2.390457	0.376729
303	O	-2.917972	-0.155402	1.427486
304	H	-3.582123	0.109208	2.062601
305	H	-2.532802	0.666126	1.068307
306	O	-1.856114	1.740086	-0.254743
307	H	-2.115655	1.094109	-0.928451
308	H	-0.894684	1.741489	-0.263691
309	O	-2.901353	-0.680713	-1.314662
310	H	-3.707041	-0.823556	-1.809960
311	H	-3.140314	-0.742902	-0.375521

312				
313	<b>CH<sub>3</sub>I (1:3b)</b>			
314	C	-0.005267	0.001934	1.442340
315	H	1.032388	-0.030912	1.754539
316	H	-0.498362	0.919908	1.741535
317	I	0.009429	-0.003160	-0.706516
318	H	-0.556495	-0.881057	1.745340
319	O	3.408414	-0.202132	0.883067
320	H	2.949832	-0.137947	0.042091
321	H	3.769426	-1.088828	0.901001
322	O	-1.911022	-2.829204	0.862906
323	H	-2.854128	-2.664211	0.878937
324	H	-1.611164	-2.471901	0.023828

325	O	-1.544158	3.042614	0.855416
326	H	-1.361723	2.616753	0.014597
327	H	-0.963766	3.803873	0.878346
328				
329	<b>CH<sub>3</sub>I (1:3c)</b>			
330	C	-0.288616	1.063986	1.180678
331	H	-1.090712	1.708947	0.839708
332	H	-0.382344	0.825398	2.233199
333	I	-0.511068	-0.782496	0.105452
334	H	0.693083	1.459272	0.939261
335	O	-2.962766	1.894174	-0.861011
336	H	-2.729856	0.972004	-0.991932
337	H	-2.702561	2.331617	-1.672028
338	O	2.831352	1.929167	0.325530
339	H	3.153499	2.649977	-0.214208
340	H	3.023054	1.122057	-0.175804
341	O	3.035139	-0.567788	-0.995759
342	H	2.105906	-0.801911	-0.889804
343	H	3.518433	-1.223400	-0.491497

344				
345	<b>CH<sub>3</sub>I (1:3d)</b>			
346	C	0.724463	-1.626333	0.798241
347	H	1.390783	-2.407409	0.451906
348	H	0.833210	-1.461186	1.863477
349	I	1.330811	0.180462	-0.184809
350	H	-0.307395	-1.817155	0.517780
351	O	-3.599594	0.454128	-0.513019
352	H	-3.582593	0.704562	-1.436333
353	H	-3.011245	1.080383	-0.058692
354	O	-2.413831	-2.040049	-0.067579
355	H	-3.057099	-2.583321	0.385726
356	H	-2.865405	-1.194571	-0.234134
357	O	-1.716973	2.000965	0.836722
358	H	-1.576828	2.947628	0.829704
359	H	-0.859993	1.604241	0.637010

360  
361 **Table S6.** Optimized Cartesian Coordinates of (CH<sub>3</sub>I)<sub>2</sub>.H<sub>2</sub>O at the ωB97X-D/aug-cc-pVTZ level of theory  
362 **2 CH<sub>3</sub>I (2:1a)**

363	C	-1.575315	0.977955	1.456682
364	I	-2.262936	-0.364071	-0.064336
365	8	-0.197901	2.590166	-1.248997
366	H	-1.190055	1.855777	0.949939
367	H	-2.423576	1.213604	2.088018
368	H	-0.796625	0.466645	2.009733
369	H	-0.836154	1.964730	-1.598248
370	H	0.558742	2.048659	-1.007545
371	C	1.668714	-1.620225	-1.017960
372	H	2.119107	-2.521154	-0.619153
373	I	2.281513	0.009132	0.225408
374	H	2.020281	-1.417040	-2.022285
375	H	0.586517	-1.667193	-0.977615

376				
377	<b>2 CH<sub>3</sub>I (2:1b)</b>			
378	C	1.114383	-0.416188	1.418991
379	I	2.532677	-0.393328	-0.186788
380	O	0.990773	2.894500	0.406319
381	H	0.724805	0.591081	1.514019

382	H	0.332060	-1.117573	1.154882
383	H	1.641221	-0.727223	2.312972
384	H	1.693452	2.389679	-0.012888
385	H	1.420559	3.654417	0.798844
386	C	-1.336739	0.913093	-1.110691
387	H	-1.902725	1.370256	-1.913501
388	I	-2.702943	-0.251959	0.054882
389	H	-0.581666	0.239949	-1.500442
390	H	-0.895615	1.662207	-0.463247
391				
392	<b>2 CH<sub>3</sub>I (2:1c)</b>			
393	C	1.101742	-0.433871	1.395182
394	I	2.551156	-0.386601	-0.181899
395	O	0.974577	2.887192	0.404833
396	H	0.697171	0.567854	1.486407
397	H	0.333887	-1.144454	1.113696
398	H	1.614564	-0.741685	2.298382
399	H	1.685426	2.387834	-0.007053
400	H	1.398516	3.633078	0.829335
401	C	-1.329928	0.885948	-1.115426
402	H	-0.896740	1.648015	-0.477799
403	I	-2.717338	-0.249051	0.054642
404	H	-1.881829	1.326529	-1.937093
405	H	-0.570805	0.202390	-1.478472
406				
407	<b>2 CH<sub>3</sub>I (2:1d)</b>			
408	C	2.411190	1.212758	1.149612
409	I	2.311909	-0.457949	-0.185928
410	O	0.011015	2.384778	-0.973575
411	H	1.712084	1.956599	0.783797
412	H	2.137140	0.859098	2.136602
413	H	3.429219	1.582844	1.136632
414	H	0.424145	1.603317	-1.350322
415	H	-0.928898	2.233724	-1.095605
416	C	-1.236576	0.254033	1.538528
417	H	-1.866087	0.481385	2.390492
418	I	-2.515476	-0.242118	-0.102814
419	H	-0.649901	1.112877	1.232491
420	H	-0.604421	-0.605273	1.728977
421				
422	<b>2 CH<sub>3</sub>I (2:1e)</b>			
423	C	1.982056	-1.143374	1.168453
424	I	2.618939	0.365834	-0.206205
425	H	1.835033	-0.671597	2.132800
426	H	1.055835	-1.561256	0.790385
427	H	2.760794	-1.894890	1.218089
428	C	-1.297628	0.888439	1.084621
429	I	-1.912271	-0.710726	-0.201186
430	H	-2.076099	1.642061	1.044678
431	H	-1.190142	0.479736	2.082326
432	H	-0.352840	1.260972	0.704926
433	O	-4.363495	2.092095	0.120870
434	H	-4.450018	2.622727	-0.671386
435	H	-4.234609	1.194386	-0.195520
436				
437	<b>Table S7. Optimized Cartesian Coordinates of (CH<sub>3</sub>I)<sub>2</sub>.(H<sub>2</sub>O)<sub>2</sub> at the ωB97X-D/aug-cc-pVTZ level of theory</b>			
438	<b>2 CH<sub>3</sub>I (2:2a)</b>			
439	C	3.081757	-1.899383	0.573459
440	I	2.186556	-0.088214	-0.131107

441	H	3.781850	-1.646030	1.360920
442	H	2.292403	-2.540078	0.948874
443	H	3.592992	-2.365730	-0.260634
444	C	-1.543864	0.047054	-1.716193
445	I	-2.501840	-0.446960	0.136091
446	H	-2.325735	0.160615	-2.457626
447	H	-0.990122	0.967665	-1.566115
448	H	-0.880539	-0.773985	-1.959882
449	O	-0.268159	2.020701	1.813847
450	H	0.439033	1.383295	1.946965
451	H	-1.041157	1.477300	1.623846
452	O	0.468182	2.577566	-0.830998
453	H	0.201208	2.577418	0.103395
454	H	0.812560	3.451574	-1.010321
455				
456	<b>2 CH<sub>3</sub>I (2:2b)</b>			
457	C	-2.524571	0.921063	-1.292330
458	I	-2.283772	-0.642602	0.153657
459	H	-3.538010	1.292139	-1.197452
460	H	-1.792814	1.691085	-1.070181
461	H	-2.360696	0.480533	-2.268750
462	C	1.299805	0.246935	-1.603239
463	I	2.500446	-0.433548	0.034409
464	H	1.937258	0.269928	-2.479123
465	H	0.491495	-0.465656	-1.720633
466	H	0.929720	1.234744	-1.348314
467	O	0.105059	1.581876	2.025227
468	H	0.875145	1.037911	1.825614
469	H	-0.640282	0.981596	1.921561
470	O	-0.112062	3.029100	-0.344552
471	H	-0.020382	2.649547	0.546927
472	H	0.039502	3.968343	-0.249154
473				
474	<b>2 CH<sub>3</sub>I (2:2c)</b>			
475	C	-1.395242	-0.386223	1.631930
476	I	-2.316589	-0.088136	-0.281590
477	H	-2.185821	-0.375265	2.372565
478	H	-0.894045	-1.346413	1.583388
479	H	-0.697731	0.430656	1.777365
480	C	1.514736	1.323279	-1.252202
481	I	2.428441	-0.087425	0.073748
482	H	2.291389	1.700864	-1.906434
483	H	0.749727	0.796074	-1.809971
484	H	1.083432	2.107222	-0.640349
485	O	0.038000	-3.077137	0.113373
486	H	0.725288	-2.426543	-0.059202
487	H	-0.613213	-2.927790	-0.573795
488	O	-0.628466	3.005650	0.715742
489	H	-1.051796	3.779950	1.086562
490	H	-1.328587	2.515563	0.274196
491				
492	<b>2 CH<sub>3</sub>I (2:2d)</b>			
493	C	1.661247	0.828440	1.608611
494	I	2.227108	-0.154645	-0.208699
495	H	2.536557	0.859352	2.246013
496	H	1.318568	1.819313	1.332110
497	H	0.863950	0.246068	2.055005
498	C	-1.659685	-0.854195	-1.605328
499	I	-2.227386	0.154637	0.197262
500	H	-2.535122	-0.896560	-2.241900



501	H	-0.863609	-0.276917	-2.060336
502	H	-1.315054	-1.840294	-1.314448
503	O	0.181839	3.101143	-0.412147
504	H	-0.568556	2.507934	-0.313831
505	H	0.730712	2.687795	-1.080565
506	O	-0.182278	-3.080201	0.475843
507	H	-0.733752	-2.616985	1.108713
508	H	0.575213	-2.502256	0.346095
509				
510	<b>2 CH<sub>3</sub>I (2:2e)</b>			
511	C	-4.058086	-0.129304	0.097990
512	I	-1.933695	-0.228816	-0.151890
513	H	-4.421201	0.714972	-0.475828
514	H	-4.476995	-1.058302	-0.270287
515	H	-4.264833	-0.000939	1.153758
516	C	1.830716	-2.375832	0.587534
517	I	1.998716	-0.342122	-0.060119
518	H	2.514283	-2.525747	1.415235
519	H	0.805807	-2.546122	0.897922
520	H	2.090624	-3.017233	-0.246623
521	O	1.929789	2.719045	-0.800768
522	H	1.600115	2.990630	-1.656703
523	H	1.205952	2.879918	-0.176670
524	O	-0.047681	2.723993	1.259234
525	H	-0.692854	2.081861	0.944410
526	H	0.500328	2.227199	1.870403
527				
528	<b>2 CH<sub>3</sub>I (2:2f)</b>			
529	C	-3.833642	1.047303	-1.195959
530	I	-2.449162	0.128178	0.152330
531	H	-3.273725	1.674606	-1.879900
532	H	-4.354911	0.262890	-1.732354
533	H	-4.528561	1.640434	-0.612826
534	C	0.947089	-1.788523	-1.027733
535	I	2.221732	-0.232840	-0.291313
536	H	1.568427	-2.513269	-1.540633
537	H	0.444540	-2.230925	-0.175195
538	H	0.229044	-1.335010	-1.700423
539	O	4.113312	2.245794	0.685052
540	H	3.730172	2.934681	0.140729
541	H	4.952419	2.037625	0.272674
542	O	-0.288164	-1.127528	2.188496
543	H	0.485734	-0.640239	1.887285
544	H	-0.481208	-0.782533	3.060503
545				
546	<b>2 CH<sub>3</sub>I (2:2g)</b>			
547	C	-2.601810	0.742400	1.487567
548	I	-2.513396	-0.342873	-0.356218
549	H	-2.406729	0.040126	2.289572
550	H	-1.843957	1.516442	1.438407
551	H	-3.596782	1.162551	1.572402
552	C	1.003333	-0.251107	1.525499
553	I	2.331883	-0.772027	-0.070663
554	H	1.593971	-0.177210	2.430850
555	H	0.544087	0.695111	1.256433
556	H	0.268364	-1.044644	1.594193
557	O	-0.189304	2.598415	0.126178
558	H	0.713328	2.816875	-0.151207
559	H	-0.606207	2.232354	-0.655671
560	O	2.518261	2.859726	-0.682463

561	H	2.748410	1.924341	-0.639240
562	H	3.164909	3.310825	-0.139160
563				
564	<b>2 CH<sub>3</sub>I (2:2h)</b>			
565	C	1.941760	-1.802726	0.798900
566	I	2.373788	0.021359	-0.232776
567	H	2.477977	-2.597155	0.293986
568	H	2.279594	-1.690087	1.821998
569	H	0.869725	-1.955338	0.749506
570	C	-1.641265	0.417592	-1.619113
571	I	-2.133358	-0.782851	0.088551
572	H	-2.353801	0.167172	-2.395911
573	H	-1.716053	1.456945	-1.315400
574	H	-0.629827	0.158066	-1.908520
575	O	-0.216884	1.932432	1.783529
576	H	0.624748	1.634716	1.424105
577	H	-0.795386	1.168178	1.689988
578	O	-1.344665	3.452697	-0.316925
579	H	-0.947970	3.054199	0.473961
580	H	-1.862379	4.192168	-0.001332
581				
582	<b>2 CH<sub>3</sub>I (2:2i)</b>			
583	C	-4.033673	-0.180420	0.015353
584	I	-1.910671	-0.043831	-0.226804
585	H	-4.474475	0.707770	-0.421343
586	H	-4.367442	-1.073627	-0.499145
587	H	-4.244132	-0.239590	1.076456
588	C	2.688375	-1.587228	-0.861775
589	I	2.056453	0.296860	-0.063986
590	H	2.513839	-1.569589	-1.931096
591	H	3.743272	-1.703090	-0.642370
592	H	2.095135	-2.353213	-0.374089
593	O	0.255945	2.965542	0.954840
594	H	-0.503782	2.378535	0.928786
595	H	0.234393	3.428417	0.116486
596	O	0.366945	-2.722840	1.464830
597	H	-0.419859	-2.376039	1.037779
598	H	0.785246	-1.945801	1.841573
599				
600	<b>2 CH<sub>3</sub>I (2:2j)</b>			
601	C	3.296608	-2.031918	-0.402920
602	I	1.934437	-0.449623	0.068795
603	H	4.132718	-1.976172	0.284289
604	H	2.766874	-2.970606	-0.289493
605	H	3.626854	-1.898921	-1.426475
606	C	-1.808918	-0.399049	1.619179
607	I	-2.717930	-0.127822	-0.300441
608	H	-1.100880	0.410749	1.753334
609	H	-2.598529	-0.372333	2.360523
610	H	-1.309238	-1.360217	1.607438
611	O	0.086782	2.148846	0.585116
612	H	-0.588640	2.106092	-0.094790
613	H	0.806468	2.676086	0.209649
614	O	2.529644	3.188402	-0.469390
615	H	2.848524	2.283797	-0.549461
616	H	3.083421	3.593947	0.198826
617				
618				
619				



Table S8. Calculated wavenumbers ( $\text{cm}^{-1}$ ) and intensities ( $I$  in  $\text{km/mol}$ ) of  $\text{CH}_3\text{I}$  monomer, HH and HT dimers and THT and TTH trimers. The IR bands are predicted at the  $\omega\text{B97X-D/aug-cc-pVTZ-PP}$  level of theory. The frequency shifts are calculated with respect to the monomer position ( $\Delta\nu = \nu - \nu_{\text{monomer}}$ ).

Vibrational Modes		$\text{CH}_3\text{I}$	$(\text{CH}_3\text{I})_2$ dimers				$(\text{CH}_3\text{I})_3$ trimers			
		monomer	HT	$\Delta\nu$	HH	$\Delta\nu$	THT	$\Delta\nu$	TTH	$\Delta\nu$
v4	C-H stretching degenerated	3214 (0)	3221 (0)	7	3214 (0)	0	3221 (0)	7	3215 (1)	1
			3217 (1)	3	3214 (1)	0	3216 (1)	2	3214 (0)	0
			3215 (0)	1	3211 (1)	-3	3214 (1)	0	3213 (2)	-1
			3214 (1)	0	3211 (1)	-3	3213 (1)	-1	3211 (0)	-3
							3210 (1)	-4	3210 (2)	-4
							3206 (1)	-8	3206 (1)	-8
v1	Sym $\text{CH}_3$ stretching	3101 (11)	3103 (8)	2	3100 (9)	-1	3101 (8)	0	3097 (10)	-4
			3099 (13)	-2	3100 (14)	-1	3097 (10)	-4	3096 (10)	-5
							3094 (14)	-7	3093 (11)	-8
v5	$\text{CH}_3$ deformation degenerated	1477 (6)	1485 (14)	8	1477 (8)	0	1482 (3)	6	1486 (7)	9
			1480 (7)	3	1477 (6)	0	1479 (12)	2	1485 (3)	8
			1477 (5)	0	1474 (10)	-3	1477 (8)	0	1478 (7)	1
			1474 (2)	-3	1473 (12)	-4	1474 (2)	-3	1477 (7)	0
							1473 (12)	-4	1474 (3)	-3
							1470 (2)	-7	1470 (9)	-7
v2	Sym $\text{CH}_3$ deformation	1297 (23)	1300 (41)	3	1297 (12)	0	1300 (39)	3	1305 (2)	8
			1297 (1)	0	1296 (40)	-1	1297 (10)	0	1296 (46)	-1
							1295 (16)	-2	1294 (27)	-3
v6	$\text{CH}_3$ rocking degenerated	903 (5)	913 (15)	10	906 (7)	3	921 (8)	18	914 (7)	11
			910 (4)	7	905 (7)	2	917 (15)	14	911 (10)	7
			909 (4)	6	902 (3)	-1	911 (7)	8	909 (15)	6
			908 (5)	5	901 (4)	-2	910 (7)	7	907 (3)	4
							906 (10)	3	906 (7)	3
							904 (2)	1	905 (4)	2

627 Table S9. Calculated wavenumbers (cm<sup>-1</sup>) and intensities (I in km/mol) of CH<sub>3</sub>I.H<sub>2</sub>O complexes  
628 compared to the calculated wavenumber (cm<sup>-1</sup>) and intensities (I) of CH<sub>3</sub>I monomer and H<sub>2</sub>O monomer  
629 and dimer. The IR bands are predicted at the ωB97X-D/aug-cc-pVTZ-PP level of theory. The frequency  
630 shifts are calculated with respect to the monomer position ( $\Delta\nu = \nu - \nu_{\text{monomer}}$ ).

Vibrational Mode		H <sub>2</sub> O monomer	H <sub>2</sub> O dimer	CH <sub>3</sub> I monomer	CH <sub>3</sub> I-H <sub>2</sub> O (1 :1a)	Δv	CH <sub>3</sub> I-H <sub>2</sub> O (1 :1b)	Δv
ν <sub>3</sub> H <sub>2</sub> O	anti sym stretching	3986 (63)	3974 (85)		3958 (106)	-28	3975 (63)	-11
			3954 (86)					
ν <sub>1</sub> H <sub>2</sub> O	sym stretching	3879(5)	3871 (11)		3838 (48)	-41	3869 (11)	-10
			3751 (339)					
ν <sub>2</sub> H <sub>2</sub> O	bending	1637 (63)	1658 (39)		1642 (49)	5	1636 (67)	-1
			1637 (94)					
ν <sub>4</sub>	C-H stretching			3214 (0)	3215 (0)	1	3207 (1)	-7
					3213 (5)	-1	3207 (1)	-7
ν <sub>1</sub>	Sym CH <sub>3</sub> stretching			3101 (11)	3096 (12)	-5	3097 (15)	-4
ν <sub>5</sub>	CH <sub>3</sub> deformation			1477 (6)	1484 (5)	7	1478 (6)	1
					1474 (4)	-3	1478 (6)	1
ν <sub>2</sub>	Sym CH <sub>3</sub> deformation			1297 (23)	1301 (22)	4	1296 (23)	-1
ν <sub>6</sub>	CH <sub>3</sub> rocking			903 (5)	925 (7)	22	900 (5)	-3
					909 (5)	6	899 (5)	-4

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633 Table S10. Calculated wavenumbers (cm<sup>-1</sup>) and intensities (I) of CH<sub>3</sub>I.(H<sub>2</sub>O)<sub>2</sub> complexes compared to the calculated wavenumber (cm<sup>-1</sup>) and intensities (I in  
634 km/mol) of CH<sub>3</sub>I monomer and H<sub>2</sub>O monomer and dimer. The IR bands are predicted at the ωB97X-D/aug-cc-pVTZ-PP level of theory. The frequency shifts  
635 are calculated with respect to the monomer position ( $\Delta\nu = \nu - \nu_{\text{monomer}}$ )

Vibrational Mode		H <sub>2</sub> O monomer	H <sub>2</sub> O dimer	CH <sub>3</sub> I monomer	CH <sub>3</sub> I-2H <sub>2</sub> O 1:2a	$\Delta\nu$	$\nu$ CH <sub>3</sub> I-2H <sub>2</sub> O 1:2b	$\Delta\nu$	CH <sub>3</sub> I-2H <sub>2</sub> O 1:2c	$\Delta\nu$
$\nu_3$ H <sub>2</sub> O	anti sym stretching	3986 (63)	3974 (85)		3950 (74)	-36	3960 (18)	-26	3978 (66)	-8
			3954 (86)		3940 (131)	-46	3960 (188)	-26	3955 (107)	-31
$\nu_1$ H <sub>2</sub> O	sym stretching	3879(5)	3871 (11)		3782 (256)	-97	3845 (35)	-34	3872 (13)	-7
			3751 (339)		3674 (358)	-205	3845 (35)	-34	3828 (77)	-51
$\nu_2$ H <sub>2</sub> O	bending	1637 (63)	1658 (39)		1662 (40)	25	1639 (92)	2	1642 (45)	5
			1637 (94)		1638 (61)	1	1638 (9)	1	1636 (73)	-1
$\nu_4$	C-H stretching			3214 (0)	3215 (1)	1	3216 (1)	2	3210 (1)	-4
					3205 (34)	-9	3215 (14)	1	3209 (2)	-5
$\nu_1$	C-H stretching			3101 (11)	3087 (28)	-14	3093 (9)	-8	3095 (14)	-6
$\nu_5$				1477 (6)	1491 (4)	14	1484 (3)	7	1484 (4)	7
	Sym CH <sub>3</sub> stretching				1475 (4)	-2	1478 (2)	4	1476 (4)	-1
$\nu_2$	CH <sub>3</sub> deformation			1297 (23)	1312 (27)	5	1303 (20)	6	1300 (21)	3
$\nu_6$				903 (5)	935 (4)	31	937 (9)	33	921 (6)	18
					917 (5)	14	925 (5)	22	905 (4)	2

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641 Table S11. Calculated wavenumbers (cm<sup>-1</sup>) and intensities (I in km/mol) of CH<sub>3</sub>I.(H<sub>2</sub>O)<sub>3</sub> complexes compared to the calculated wavenumber (cm<sup>-1</sup>) and  
642 intensities (I) of CH<sub>3</sub>I monomer and H<sub>2</sub>O monomer and dimer. The IR bands are predicted at the ωB97X-D/aug-cc-pVTZ-PP level of theory. The frequency  
643 shifts are calculated with respect to the monomer position ( $\Delta\nu = \nu - \nu_{\text{monomer}}$ ).

Vibrational modes	H <sub>2</sub> O monomer	H <sub>2</sub> O Dimer	CH <sub>3</sub> I monomer	CH <sub>3</sub> I-3H <sub>2</sub> O 1 :3a	Δν	CH <sub>3</sub> I-3H <sub>2</sub> O 1 :3b	Δν	CH <sub>3</sub> I-3H <sub>2</sub> O 1 :3c	Δν	CH <sub>3</sub> I-3H <sub>2</sub> O 1 :3d	Δν
ν <sub>3</sub> H <sub>2</sub> O	3986 (63)	3974 (85)		3950 (60)	-36	3962 (54)	-24	3961 (94)	-25	3949 (74)	-37
		3954 (86)		3948 (99)	-38	3961 (124)	-25	3951 (71)	-35	3948 (132)	-38
				3861 (205)	-125	3960 (119)	-26	3941 (140)	-45	3943 (78)	-43
ν <sub>1</sub> H <sub>2</sub> O	3879(5)	3871 (11)		3716 (294)	-63	3849 (19)	-30	3848 (29)	-31	3761 (354)	-118
		3751 (339)		3663 (358)	-216	3848 (32)	-31	3788 (246)	-91	3660 (499)	-219
				3557 (276)	-322	3848 (32)	-31	3680 (342)	-199	3606 (545)	-273
ν <sub>2</sub> H <sub>2</sub> O	1637 (63)	1658 (39)		1669 (27)	32	1640 (27)	3	1661 (40)	24	1677 (36)	40
		1637 (94)		1653 (138)	16	1640 (27)	3	1640 (74)	3	1662 (32)	25
				1647 (58)	10	1638 (94)	1	1639 (37)	2	1636 (76)	-1
ν <sub>4</sub> CH <sub>3</sub> I			3214 (0)	3219 (2)	5	3216 (12)	2	3216 (2)	2	3215 (0)	1
3218 (2)				4	3213 (13)	-1	3206 44)	-8	3199 (50)	-15	
ν <sub>1</sub> CH <sub>3</sub> I			3101 (11)	3101 (6)	0	3088 (2)	-13	3085 (18)	-16	3079 (47)	-25
ν <sub>5</sub> CH <sub>3</sub> I			1477 (6)	1485 (21)	8	1484 (1)	7	1493 (3)	16	1491 (5)	14
				1475 (7)	-2	1484 (2)	7	1476 (3)	-1	1474 (4)	-3
ν <sub>2</sub> CH <sub>3</sub> I			1297 (23)	1310 (27)	13	1305 (20)	8	1314 (26)	17	1316 (28)	19
ν <sub>6</sub> CH <sub>3</sub> I			903 (5)	918 (5)	15	946 (7)	44	951 (5)	48	940 (3)	37
				916 (11)	13	945 (7)	43	929 (5)	26	919 (5)	16

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645 Table S12. Calculated wavenumbers ( $\text{cm}^{-1}$ ) and intensities (I in  $\text{km/mol}$ ) of  $(\text{CH}_3\text{I})_2(\text{H}_2\text{O})$  complexes compared to the calculated wavenumber ( $\text{cm}^{-1}$ ) and  
646 intensities (I) of  $\text{CH}_3\text{I}$  monomer and  $\text{H}_2\text{O}$  monomer and dimer. The IR bands are predicted at the  $\omega\text{B97X-D/ aug-cc-pVTZ-PP}$  level of theory. The frequency  
647 shifts are calculated with respect to the monomer position ( $\Delta\nu = \nu - \nu_{\text{monomer}}$ ).

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Vibrational modes	H <sub>2</sub> O monomer	H <sub>2</sub> O dimer	CH <sub>3</sub> I monomer	2CH <sub>3</sub> I-H <sub>2</sub> O 2 :1a	Δν	2CH <sub>3</sub> I-H <sub>2</sub> O 2 :1b	Δν	2CH <sub>3</sub> I-H <sub>2</sub> O 2 :1c	Δν	2CH <sub>3</sub> I-H <sub>2</sub> O 2 :1d	Δν	2CH <sub>3</sub> I-H <sub>2</sub> O 2 :1d	Δν
ν <sub>3</sub> H <sub>2</sub> O	3986 (63)	3974 (85)		3925 (106)	-61	3957 (114)	-29	3957 (114)	-29	3925 (106)	-61	3959 (103)	-27
		3954 (86)											
ν <sub>1</sub> H <sub>2</sub> O	3879(5)	3871 (11)		3825 (84)	-54	3825 (65)	-54	3825 (66)	-54	3833 (28)	-46	3842 (40)	-32
		3751 (339)											
ν <sub>2</sub> H <sub>2</sub> O	1637 (63)	1658 (39)		1643 (70)	6	1634 (63)	-3	1633 (61)	-4	1646 (71)	9	1640 (49)	3
		1637 (94)											
ν <sub>4</sub> CH <sub>3</sub> I			3214 (0)	3217 (1)	3	3218 (0)	4	3218 (0)	3	3214 (2)	0	3213 (3)	-1
				3216 (0)	2	3217 (8)	3	3216 (9)	2	3214 (0)	0	3213 (1)	-1
				3212 (4)	-2	3215 (2)	1	3214 (1)	0	3212 (2)	-2	3210 (1)	-4
				3211 (2)	-3	3209 (1)	-5	3209 (2)	-5	3211 (2)	-1	3208 (7)	-6
ν <sub>1</sub> CH <sub>3</sub> I			3101 (11)	3097 (11)	-4	3099 (4)	-2	3098 (4)	-3	3097 (16)	-4	3098 (9)	-3
				3095 (11)	-6	3096 (7)	-5	3096 (7)	-5	3096 (3)	-5	3091 (7)	-10
ν <sub>5</sub> CH <sub>3</sub> I			1477 (6)	1483 (11)	6	1496 (7)	19	1495 (6)	18	1488 (3)	11	1484 (5)	7
				1477 (3)	0	1483 (25)	6	1482 (28)	4	1481 (19)	4	1481 (3)	4
				1473 (2)	-4	1477 (8)	0	1478 (8)	1	1475 (10)	-2	1478 (9)	1
				1469 (8)	-8	1472 (12)	-5	1474 (9)	-2	1470 (7)	-7	1472 (9)	-5
ν <sub>2</sub> CH <sub>3</sub> I			1297 (23)	1302 (35)	5	1308 (10)	11	1307 (8)	10	1302 (16)	5	1302 (27)	5
				1297 (5)	0	1301 (45)	0	1301 (48)	4	1298 (28)	1	1297 (21)	0
ν <sub>6</sub> CH <sub>3</sub> I			903 (5)	926 (6)	23	924 (8)	21	925 (8)	22	925 (8)	22	930 (12)	27
				916 (11)	13	914 (2)	11	913 (5)	10	921 (6)	18	915 (4)	12
				913 (7)	10	913 (5)	10	913 (3)	10	910 (8)	7	911 (8)	7
				908 (4)	5	910 (7)	7	908 (7)	5	907 (5)	4	904 (6)	1

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650 Table S13. Calculated wavenumbers (cm<sup>-1</sup>) and intensities (I in km/mol) of (CH<sub>3</sub>I)<sub>2</sub>·(H<sub>2</sub>O)<sub>2</sub> complexes compared to the calculated wavenumber (cm<sup>-1</sup>) and  
651 intensities (I) of CH<sub>3</sub>I monomer and H<sub>2</sub>O monomer and dimer. The IR bands are predicted at the ωB97X-D/aug-cc-pVTZ-PP level of theory. The frequency  
652 shifts are calculated with respect to the monomer position ( $\Delta\nu = \nu - \nu_{\text{monomer}}$ ).

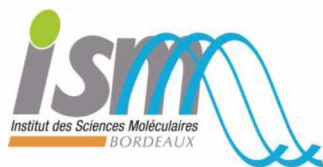
Vibrational modes	H <sub>2</sub> O monomer	H <sub>2</sub> O dimer	CH <sub>3</sub> I monomer	2CH <sub>3</sub> I-2H <sub>2</sub> O 2 :2a	Δν	2CH <sub>3</sub> I-2H <sub>2</sub> O 2 :2b	Δν	2CH <sub>3</sub> I-2H <sub>2</sub> O 2 :2c	Δν	2CH <sub>3</sub> I-2H <sub>2</sub> O 2 :2d	Δν	2CH <sub>3</sub> I-2H <sub>2</sub> O 2 :2e	Δν
ν <sub>3</sub> H <sub>2</sub> O	3986 (63)	3974 (85)		3949 (77)	-37	3950 (74)	-36	3954 (126)	-28	3937 (146)	-49	3948 (74)	-38
		3954 (86)		3888 (164)	-98	3864 (235)	-122	3937 (94)	-39	3934 (29)	-52	3922 (111)	-64
ν <sub>1</sub> H <sub>2</sub> O	3879(5)	3871 (11)		3793 (152)	-86	3787 (142)	-92	3818 (151)	-61	3823 (159)	-56	3803 (156)	-76
		3751 (339)		3631 (310)	-248	3607 (370)	-266	3814 (58)	-65	3822 (18)	-57	3685 (318)	-194
ν <sub>2</sub> H <sub>2</sub> O	1637 (63)	1658 (39)		1655 (49)	18	1665 (42)	28	1643 (42)	6	1642 (3)	5	1665 (39)	32
		1637 (94)		1645 (81)	8	1646 (82)	9	1631 (57)	-6	1642 (136)	5	1649 (82)	12
ν <sub>4</sub> CH <sub>3</sub> I			3214 (0)	3217 (3)	3	3213 (3)	-1	3216 (1)	2	3219 (1)	5	3213 (0)	1
3213 (17)				-1	3211 (4)	-3	3215 (10)	1	3218 (1)	4	3213 (0)	-1	
3208 (1)				-6	3209 (24)	-5	3214 (11)	0	3216 (8)	2	3206 (1)	-8	
3208 (1)				-6	3206 (13)	-8	3213 (1)	-1	3213 (7)	-1	3203 (1)	-11	
ν <sub>1</sub> CH <sub>3</sub> I			3101 (11)	3098 (13)	-3	3091 (26)	-10	3096 (10)	-5	3097 (11)	-4	3100 (12)	-1
				3095 (15)	-6	3088 (10)	-13	3092 (9)	-9	3095 (12)	-6	3095 (16)	-6
ν <sub>5</sub> CH <sub>3</sub> I			1477 (6)	1492 (13)	15	1496 (4)	19	1486 (20)	9	1488 (16)	11	1478 (4)	1
				1478 (5)	1	1486 (13)	9	1482 (7)	5	1486 (4)	9	1478 (3)	1
				1477 (6)	0	1476 (7)	-1	1473 (14)	-4	1471 (9)	-6	1476 (7)	-1
				1475 (8)	-2	1473 (9)	-4	1472 (2)	-5	1470 (2)	-7	1476 (7)	-1
ν <sub>2</sub> CH <sub>3</sub> I			1297 (23)	1312 (28)	15	1312 (17)	15	1304 (36)	7	1303 (37)	6	1296 (29)	-1
				1296 (21)	-1	1307 (34)	10	1304 (12)	7	1300 (0)	3	1296 (22)	-1
ν <sub>6</sub> CH <sub>3</sub> I			903 (5)	931 (5)	28	932 (5)	29	937 (7)	34	932 (2)	29	902 (4)	-1
				917 (6)	14	932 (5)	29	922 (4)	19	931 (10)	28	901 (5)	-2
				901 (3)	-2	916 (9)	13	921 (7)	18	913 (9)	10	900 (6)	-3
				900 (6)	-3	914 (4)	11	914 (9)	11	913 (6)	10	898 (3)	-5

654 Table S13. (continued)

Vibrational modes	H <sub>2</sub> O monomer	H <sub>2</sub> O dimer	CH <sub>3</sub> I monomer	2CH <sub>3</sub> I-2H <sub>2</sub> O 2 :2f	Δv	2CH <sub>3</sub> I-2H <sub>2</sub> O 2 :2g	Δv	2CH <sub>3</sub> I-2H <sub>2</sub> O 2 :2h	Δv	2CH <sub>3</sub> I-2H <sub>2</sub> O 2 :2i	Δv	2CH <sub>3</sub> I-2H <sub>2</sub> O 2 :2j	Δv
ν <sub>3</sub> H <sub>2</sub> O	3986 (63)	3974 (85)		3977 (64)	-19	3945 (132)	-41	3951 (77)	-35	3955 (102)	-31	3946 (129)	-40
		3954 (86)		3950 (122)	-36	3911 (106)	-75	3870 (200)	-116	3935 (83)	-51	3901 (173)	-85
ν <sub>1</sub> H <sub>2</sub> O	3879(5)	3871 (11)		3871 (12)	-8	3782 (236)	-97	3794 (134)	-85	3844 (44)	5	3817 (112)	-62
		3751 (339)		3803 (132)	-76	3683 (360)	-196	3659 (411)	-200	3843 (46)	4	3710 (288)	-169
ν <sub>2</sub> H <sub>2</sub> O	1637 (63)	1658 (39)		1638 (67)	1	1672 (59)	35	1663 (37)	26	1646 (100)	9	1653 (60)	16
		1637 (94)		1636 (65)	-1	1635 (36)	-2	1646 (120)	9	1639 (63)	2	1638 (45)	1
ν <sub>4</sub> CH <sub>3</sub> I			3214 (0)	3217 (2)	3	3214 (5)	0	3218 (0)	4	3215 (0)	1	3221 (4)	7
				3210 (1)	-4	3212 (1)	-2	3216 (0)	2	3214 (0)	0	3216 (2)	2
				3206 (1)	-8	3210 (5)	-4	3209 (30)	-5	3210 (0)	-4	3209 (1)	-5
				3205 (1)	-9	3201 (16)	-13	3206 (3)	-8	3207 (3)	-7	3208 (1)	-7
ν <sub>1</sub> CH <sub>3</sub> I			3101 (11)	3099 (10)	-2	3094 (17)	-7	3094 (11)	-7	3101 (10)	0	3100 (11)	-1
				3096 (16)	-5	3084 (15)	-9	3091 (24)	-10	3093 (15)	-8	3098 (13)	-3
ν <sub>5</sub> CH <sub>3</sub> I			1477 (6)	1482 (16)	5	1490 (6)	13	1491 (7)	14	1487 (4)	10	1506 (8)	29
				1478 (6)	1	1483 (16)	6	1477 (4)	0	1476 (6)	-1	1478 (7)	1
				1478 (5)	1	1475 (6)	-2	1474 (3)	-3	1476 (7)	-1	1478 (11)	1
				1474 (7)	-3	1469 (10)	-8	1471 (4)	-6	1474 (4)	-3	1477 (0)	0
ν <sub>2</sub> CH <sub>3</sub> I			1297 (23)	1302 (23)	5	1306 (26)	9	1310 (27)	13	1298 (14)	1	1304 (26)	7
				1295 (26)	-2	1301 (25)	4	1298 (13)	2	1296 (41)	-1	1296 (26)	-1
ν <sub>6</sub> CH <sub>3</sub> I			903 (5)	921 (5)	18	937 (5)	34	934 (4)	31	920 (7)	17	935 (8)	32
				907 (7)	4	926 (9)	23	920 (10)	17	907 (5)	5	914 (5)	11
				899 (7)	-4	915 (7)	12	912 (9)	9	904 (3)	1	901 (5)	-2
				897 (4)	-6	908 (5)	5	909 (4)	6	902 (4)	-1	898 (4)	-5

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### Credit author statement

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Title “**Infrared matrix-isolation and theoretical studies of interactions between CH<sub>3</sub>I and water.**” as a regular research paper in **Journal of Molecular Structure.**

Authors: Sophie Sobanska, Hanaa Houjeij, Stéphane Coussan, Christian Aupetit, Sonia Taamalli, Florent Louis, Laurent Cantrel, Anne Cécile Gregoire, Joëlle Mascetti

We declare that the work was carried out by all the authors associated with the manuscript. The tasks were distributed as follows:

**S. Sobanska** is the PI of the project and the corresponding authors. She participates to the interpretation of the experimental results and writing of the manuscript.

**S. Coussan and J. Mascetti** conducted the matrix experiments, help in the interpretation of the experimental and theoretical results and writing of the manuscript.

**H. Houjeij, C. Aupetit** did the matrix experiments

**S. Taamalli and F. Louis** did the theoretical calculations

**AC Gregoire and L. Cantrel** participates to the global project and read the final manuscript version

**Declaration of interests**

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:



Sophie Sobanska