Investigation of CH_3I and CH_3I-H_2O interactions by matrix-isolation FTIR spectroscopy

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Iodomethane i.e. CH_3I (^{131}I) can be found inside the containment of a pressurized water reactor (PWR) following a severe nuclear accident (Chernobyl, Fukushima…) and further it can be transported into the atmosphere in the case of a containment leakage[1]. In the atmosphere, CH_3I may interact with atmospheric species (i.e. water, aerosols and iced particles), which may influence their environmental and sanitary impacts. The investigation of interaction processes at molecular level, between CH_3I and water and between CH_3I and aerosols is a first step to better understand how CH_3I reacts or not with atmospheric species. In this context, we have studied CH_3I-CH_3I, CH_3I-H_2O and CH_3I-amorphous ice as atmospheric proxies by the matrix-isolation FTIR technique supported by DFT calculations.

Gaseous CH_3I (1000 ppm) diluted in Ar or pre-mixed samples of CH_3I/H_2O/Ar (3/6/3300) were deposited in a vacuum chamber on a NaCl window for 2 hours at 10K. Additionally, CH_3I has been deposited on amorphous ice at 25K for 2 hours. Subsequently, the deposited samples were annealed to 35 K. The gas-isolated samples were measured with an FTIR spectrometer. Moreover, to help in the identification of the formed products, the structure and vibrational spectra of $(CH_3I)_{1,2,3}$ and (1,2)CH_3I-(1,2,3)H_2O were calculated using ω B97XD/aug-cc-pVTZ method[2].

The FTIR spectrum of CH_3I in Ar matrix clearly showed peaks for both CH_3I monomer and dimer as described in the literature[3]; additional trimer forms were also identified. The FTIR spectrum of CH_3I:H_2O mixtures showed peaks for CH_3I monomer, CH_3I dimer, CH_3I trimer, and various CH_3I-H_2O complexes that may explain the formation of CH_3I-H_2O aggregates in the atmosphere. It should be noted that F.Ito[4] considered the bands observed for the complex are for 1CH_3I-1H_2O complex structure only. Similarly, the CH_3I-ice interaction showed the formation of water complexes which are fixed on the amorphous ice surface. The assignments of the observed clusters and complexes have been further confirmed by calculated wavenumbers and Gibbs energies. As expected, annealing enhanced the formation of further heavier aggregates of $(CH_3I)_{2,3}$ and CH_3I-H_2O complexes due to the diffusion of species within the matrix. The complex formation on ice has been shown to be stable as the spectra of CH_3I/Ar deposition on ice is not affected by annealing.

Therefore, when gaseous CH_3I is released in the atmosphere, complexes of water are formed as aggregates or fixed on iced aerosols that can play a significant role in the cycling life of Iodine. Marix isolation technique is well adapted for investigating such physico-chemical processes. Further work to assess the influence of water on the photo-dissociation of CH_3I in the atmosphere is scheduled.

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