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# Quantification of gas phase methyl iodide using $\text{H}_3\text{O}^+$ as the reagent ion in the PTR-MS technique

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## Abstract

In this work, the proton transfer reaction between the hydronium ion ( $\text{H}_3\text{O}^+$ ) and methyl iodide ( $\text{CH}_3\text{I}$ ) is studied to investigate if consistent quantification of the gas phase  $\text{CH}_3\text{I}$  is possible in humid air. The neutral  $\text{CH}_3\text{I}$  molecule was chosen because this compound is of environmental importance in the field of nuclear power plant safety and nuclear energy. Water was used as a reagent ion source in a conventional Innsbruck PTR-MS to produce  $\text{H}_3\text{O}^+$  reagent ions. The use of  $\text{H}_3\text{O}^+$  ions allows for fast, sensitive and specific detection of gas phase  $\text{CH}_3\text{I}$  via a proton-transfer reaction  $\text{H}_3\text{O}^+ + \text{CH}_3\text{I} \rightarrow [\text{CH}_3\text{I-H}]^+ + \text{H}_2\text{O}$ . The instrument response was linear in the tested 5 to 96 ppbV range and the PTR-MS sensitivity was observed to be humidity dependent. The observed sensitivity was in found to range between 1.6 to 3.3 cps/ppb at relative humidity between 63 and 15% at  $T = 23^\circ\text{C}$ . A typical  $\text{H}_3\text{O}^+$  primary ion signal was  $10^7$  cps and the normalized sensitivity was in the range between 0.16 and 0.33 ncps/ppb. The instrument  $\text{CH}_3\text{I-H}^+$  ion background rate was  $6.8 \pm 1.4$  cps and the dwell time was 1 second. The detection limit was calculated as 3 times the standard deviation of the background level and ranged between 1.3 and 3.8 ppb. The theoretical collision rate based on the dipole moment and molecular polarizability is calculated. The theoretical collision rate is compared with the experimentally obtained values. The results indicate that the PTR-MS technique is a good analytical method to detect and quantify gas phase  $\text{CH}_3\text{I}$  concentrations.

*Keywords:* Methyl iodide,  $\text{CH}_3\text{I}$ ,  $\text{H}_3\text{O}^+$ , PTR-MS, collision rate

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## 1. Introduction

The atmospheric importance of molecular iodine and alkyl iodides was first suggested by Chameides and Davis (1982).[1] It is now well understood that iodine and iodine containing volatile organic compounds play an important role in the oxidizing capacity of the troposphere [2], aerosol formation and in the ozone  
5 depleting cycles in the troposphere [3, 4] and stratosphere.[5] In addition to atmospheric interest, the presence of organic iodides has gained an increased interest in the field of nuclear industry safety to better understand chemical processes responsible for the formation of different fission products if a major nuclear power plant accident type Three Mile Island (U.S.A.) [6], Chernobyl (Ukraine) [7] and Fukushima (Japan) [8] were to occur, again. It is now known that iodine and methyl iodide are two of the more critical fission  
10 products that are released from  $\text{UO}_2$  fuel during a major nuclear power plant accident in light water reactors due to their volatility and radiological health impact.[9] Methyl iodide is a particularly volatile

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form of the fission product iodine ( $I_2$ ) that is difficult to retain by post-accident filtration systems.[10] Further, methyl iodide is currently used in the nuclear industry field to test the organic iodine capture ability and ageing on the performance of emergency charcoal filters.[11, 12] Methyl iodide has additional applications in the agriculture industry where it has been introduced as a fumigant pesticide used to control insects, plant parasitic metabolites, soil-borne pathogens and weed seeds.[13]

To date, most environmental  $CH_3I$  measurements are based on gas chromatographic (GC) separation equipped with a mass spectrometer (MS) or an electron capture detector (ECD). A more recent atmospheric  $CH_3I$  measurement method is based on resonant fluorescence (RF) spectroscopy.[14] While GC-ECD (LD $\sim$ 10 ppt) and GC-MS (LD $\sim$ 100 ppt) methods are two very sensitive analytical techniques used to detect gas phase  $CH_3I$  in the laboratory and field settings, they do not offer the time resolution and response needed to measure rapid flux or concentration changes in the gas phase. The newer RF technique used to detect gas phase  $CH_3I$  in the laboratory and more recently in the field is fast, sensitive and selective but remains a research-grade instrument that requires advanced technical expertise and skills. The chemical ionization mass spectrometric (CIMS) technique has the potential for fast, sensitive, specific and real time  $CH_3I$  measurements when rapid changes in the gas phase mixing ratios need to be known or monitored continuously.

The proton-transfer-reaction mass spectrometry (PTR-MS) is a type of CIMS instrument. The PTR-MS combines the concept of chemical ionization [15] with the flow-drift-tube technique.[16] While proton-transfer-reaction mass spectrometry (PTR-MS) is often used for sensitive detection of volatile organic compounds (VOCs), it can be applied only to gas-phase compounds with proton affinities (PA) higher than that of water,  $PA(H_2O) = 691.0 \pm 3 \text{ kJ mol}^{-1}$  [17, 18], and the proton transfer from  $H_3O^+$  to the analyte molecule is efficient if the difference in proton affinities is larger than  $\sim 35 \text{ kJ mol}^{-1}$ . [19] The proton affinity of  $CH_3I$ ,  $PA(CH_3I) = 691.7 \text{ kJ mol}^{-1}$ , [17, 18] is only slightly higher than that of water. Since the difference in proton affinities between water and methyl iodide is very small, the CIMS technique based on proton transfer reaction of hydronium ( $H_3O^+$ ) reagent ions with  $CH_3I$  has only been used once [20] in a laboratory setting to detect methyl iodide. Further, the one previous work has been carried out in dry helium flow only. In this work it is shown that  $H_3O^+$  ions may still be employed to detect gas phase  $CH_3I$ . The use of water ( $H_2O$ ) as a source of reagent ions in the PTR-MS instrument to detect  $CH_3I$  is proposed.  $H_3O^+$  reagent ions are used for sensitive and specific detection of gas phase  $CH_3I$  in humidified and dry air.  $H_3O^+$  ion is shown to be a good proton source and soft chemical ionization reagent. The proposed PTR-MS technique appears to be a good tool for online analyses of relatively fast changing concentrations of methyl iodide.

## 2. Experimental

The proton transfer reaction between the  $H_3O^+$  ions and  $CH_3I$  was studied using a commercial quadrupole PTR-MS mass analyzer (Ionicon Analytik GmbH, Innsbruck, Austria). The experimental details that are particularly relevant to this work are given below.

*Generation of gas phase  $CH_3I$ .* The gas phase  $CH_3I$  concentration was generated using the gas saturation method, one of the oldest and most versatile ways of studying heterogeneous equilibria involving low

vapor pressure compounds, first developed by Regnault in 1845.[21] The gas saturation method used in this work is similar to the one described originally by Markham (1940).[22] Briefly, nitrogen carrier gas was allowed to flow through the volume containing the CH<sub>3</sub>I sample that itself was mixed with glass beads and supported on a fritted glass surface. The saturator volume itself was immersed in a temperature controlled fluid and kept at a constant temperature using a thermostat with an accuracy of  $\pm 0.1$ K. The temperature inside the saturator volume was measured using a Type-J thermocouple (Omega) with an accuracy of  $\pm 0.1$ K. The carrier gas was allowed to enter the saturator volume, equilibrate with the sample and was then allowed to exit through a capillary passageway and allow to flow through a glass tube. The geometry of the exiting glass tube was such that the diameter of the glass tube increased with increasing length. This was done to avoid any sample condensation as the sample and the carrier gas were allowed to leave the saturator system. Concentration of CH<sub>3</sub>I at the exit of the saturation system was calculated from the given vapor pressure, mass flow rates, pressure within the saturator and the total pressure. The Antoine type equation used to calculate the vapor pressure of CH<sub>3</sub>I is  $\log p = -20.3718 - 1253.6/T + 13.645 \log T - 2.6955 \times 10^{-2}T + 1.6389 \times 10^{-5}T^2$  where the pressure  $p$  is in units of mmHg and the temperature  $T$  is in Kelvin and in the range from 207.7K to 528.00K.[23]. Under normal operating conditions, the saturator was kept at  $T = 268$  K. At this temperature, the vapor pressure of CH<sub>3</sub>I within the saturator was calculated to be 109.31 mmHg. This vapor pressure was then further diluted using nitrogen gas carrier gas and a system of mass flow controllers to obtain the desired concentration.

*PTR-MS instrument.* A commercial PTR-MS (Icon Analytic GmbH, Innsbruck, Austria) was used to study the H<sub>3</sub>O<sup>+</sup> reagent ion ionization process with CH<sub>3</sub>I.[24, 25] The reaction chamber pressure ( $p_{\text{drift}}$ ) was 2.11 mbar, drift tube voltage was 601V and the drift tube temperature was approximately 310K, albeit it was not controlled. The corresponding  $E/N$  ratio was 134 Td (1Td= $10^{-17}$  Vcm<sup>2</sup>) where  $E$  is the electric field strength ( $E$ ) applied to the drift tube and  $N$  is the buffer gas density. This  $E/N$  ratio value was chosen to limit clustering of the H<sub>3</sub>O<sup>+</sup> reagent ions with H<sub>2</sub>O because it is known that the resulting cluster ions ( $m/Q = 37.0501$  and  $m/Q = 55.0395$ ) may act as reagent ions, and, as a result, limit signal intensity.[24, 25] The effect of the water cluster ion formation on signal intensity [26] was assessed by changing the water content within the carrier gas. Here, nitrogen gas was allowed to pass through a bubbler filled with deionized water at room temperature. The resulting relative humidity (%RH) was measured at the inlet of the PTR-MS using a temperature-humidity mini probe (HygroClip-SC04, Rotronic International). The relative humidity was varied between 0 and 60%.

*Data analysis.* PTR-MS data files were imported using the Technical Data Management (TDM) Excel add-in for Microsoft Excel. Mass spectra were recorded up to  $m/Q$  200 and the integration rate was 1s. No specific mass calibration was performed. However, stability of the hydronium ion signal at  $m/Q$  19 was checked. The Excel raw data files were exported and analyzed using Igor Pro 6.37 commercial software.

*Materials.* The nitrogen carrier gas used in this study was generated using the N2LCMS 1 Nitrogen Generator (Claind S.r.l., Italy). Iodomethane was purchased at Acros Organics (Belgium) and the stated minimum purity was 99%. To limit any photo-catalytic or thermal decomposition during storage, CH<sub>3</sub>I

original container bottles were stored under dark conditions at  $T = 6^\circ\text{C}$ . Deionized water with a resistivity greater than 18M was prepared by allowing tap water to pass first through a reverse osmosis demineral-  
 90 ization filter (ATS Groupe Osmose) and then through a commercial deionizer (Milli-pore, Milli-Q).

### 3. Results

#### 3.1. Experimental determination of $k_{(\text{H}_3\text{O}^+ + \text{CH}_3\text{I})}$

Based on the original work of Lindinger and coworkers (1998) [25], the  $\text{CH}_3\text{I}$  gas phase concentration may be calculated using the following equation.

$$[\text{CH}_3\text{I}]_{\text{cm}^{-3}} = \frac{1}{kt} \cdot \frac{\text{CH}_3\text{I} - \text{H}^+}{\text{H}_3\text{O}^+} \cdot \frac{\text{Tr}_{\text{H}_3\text{O}^+}}{\text{Tr}_{\text{CH}_3\text{I} - \text{H}^+}} \quad (1)$$

95 In the equation (1) above,  $\text{CH}_3\text{I} - \text{H}^+$  and  $\text{H}_3\text{O}^+$  are the ion count rates,  $k$  is the rate coefficient of the proton transfer reaction of the  $\text{H}_3\text{O}^+$  reagent ion with  $\text{CH}_3\text{I}$  and  $t$  is the residence or reaction time of the ion within the drift tube ( $\sim 100 \mu\text{s}$ ). [27] The reaction time  $t$  is calculated using the length of the drift tube  $l$ , ion mobility  $\mu$ , electric field  $E$  and the electric potential applied to the drift tube  $U_{\text{drift}}$ . Given that

$$\frac{l}{t} = \mu \cdot E = \mu \cdot \frac{U_{\text{drift}}}{l} \quad (2)$$

100 therefore,

$$t = \frac{l^2}{\mu \cdot U_{\text{drift}}} \quad (3)$$

The length of the drift tube  $l = 9.3 \text{ cm}$  and  $U_{\text{drift}}$  is in units of Volts. The ion mobility  $\mu$  listed in equations 2 and 3 is calculated using the following equation 4

$$\mu = \mu_0 \cdot \frac{p_0}{p_{\text{drift}}} \cdot \frac{T_{\text{drift}}}{T_0} \quad (4)$$

where the reduced mobility  $\mu_0 = 2.8 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , pressure  $p_0 = 1013.25 \text{ mbar}$ , and temperature at standard conditions  $T_0 = 273.15 \text{ K}$ . As a result, the reaction time within the drift-tube may be calculated  
 105 using the following equation (5)

$$t = \frac{l^2}{\mu_0 \cdot U_{\text{drift}}} \cdot \frac{T_0}{T_{\text{drift}}} \cdot \frac{p_0}{p_{\text{drift}}} \quad (5)$$

where  $T_{\text{drift}}$  is the drift-tube temperature in Kelvin and  $p_{\text{drift}}$  is the drift-tube pressure in millibar. Using the ideal gas law, the number of air molecules per  $\text{cm}^3$  within the drift-tube volume may be calculated using the following equation 6

$$\text{air}_{\text{cm}^{-3}} = \frac{N_A}{22400} \cdot \frac{T_0}{T_{\text{drift}}} \cdot \frac{p_0}{p_{\text{drift}}} \quad (6)$$

where the Avogadro's number  $N_A = 6.022 \times 10^{23} \text{ mole}^{-1}$ . As a result, the mixing ration of  $\text{CH}_3\text{I}$  in the  
 110 gas phase detected by the PTR-MS may be determined using the following equation.

$$[\text{CH}_3\text{I}]_{\text{ppbv}} = \frac{10^9}{k} \cdot \frac{22400 \cdot \mu_0 \cdot U_{\text{drift}}}{N_A \cdot l^2} \cdot \frac{T_{\text{drift}}^2}{T_0^2} \cdot \frac{p_0^2}{p_{\text{drift}}^2} \cdot \frac{\text{CH}_3\text{I} - \text{H}^+}{\text{H}_3\text{O}^+} \cdot \frac{\text{Tr}_{\text{H}_3\text{O}^+}}{\text{Tr}_{\text{CH}_3\text{I} - \text{H}^+}} \quad (7)$$

The equation (7) may be simplified by including the constant factors listed above to give the following equation 8.

$$[\text{CH}_3\text{I}]_{\text{ppbv}} = 1.657 \times 10^{-11} \cdot \frac{U_{\text{drift}} \cdot T_{\text{drift}}^2}{k \cdot p_{\text{drift}}^2} \cdot \frac{\text{CH}_3\text{I} - \text{H}^+}{\text{H}_3\text{O}^+} \cdot \frac{\text{Tr}_{\text{H}_3\text{O}^+}}{\text{Tr}_{\text{CH}_3\text{I} - \text{H}^+}} \quad (8)$$

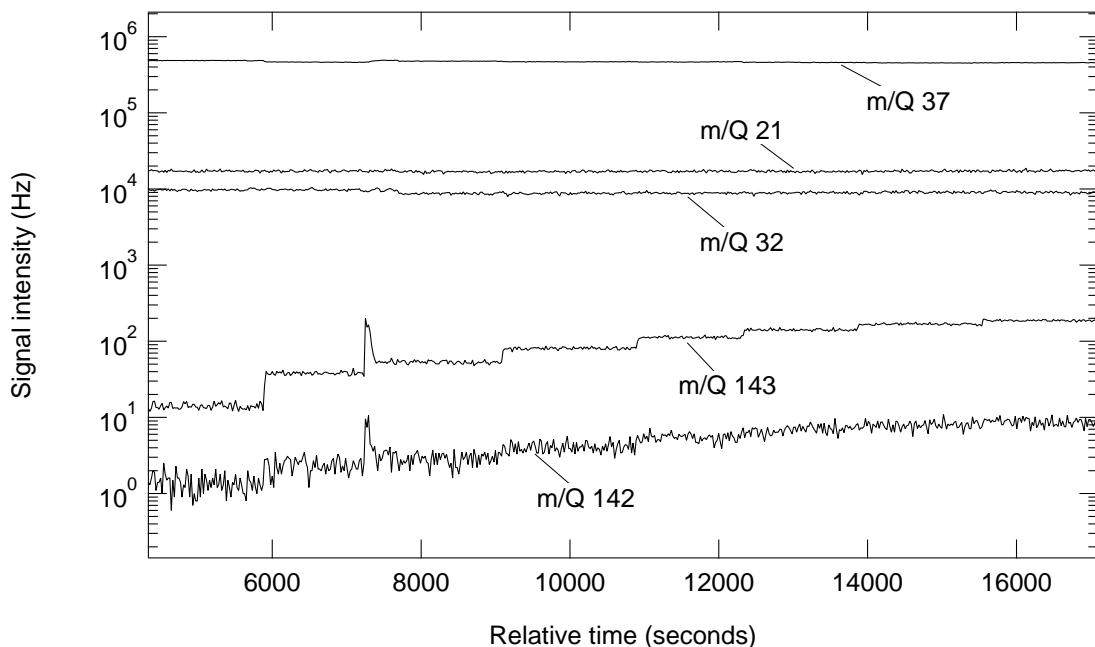


Figure 1: Typical signal ion counts (Hz) of selected ions.

If the rate coefficient for the proton transfer reaction of the  $\text{H}_3\text{O}^+$  ion with  $\text{CH}_3\text{I}$  is known, the gas phase mixing ratio of methyl iodide may be determined using the PTR-MS technique without prior calibration by simply using MS signal ion counts and given operating instrument parameters. To the best of our knowledge, there is no rate coefficient listed in the literature for the proton transfer reaction between  $\text{H}_3\text{O}^+$  ion and  $\text{CH}_3\text{I}$ . As a result, the  $k$  value has been determined experimentally and theoretically. The equation (8) above may be rewritten in the following form to give  $k_{\text{exp}}$ , that is, the experimental rate coefficient for the proton transfer  $\text{H}_3\text{O}^+ + \text{CH}_3\text{I}$  reaction.

$$k_{\text{exp}} = 1.657 \times 10^{-11} \cdot \frac{U_{\text{drift}} \cdot T_{\text{drift}}^2}{[\text{CH}_3\text{I}]_{\text{ppbV}} \cdot p_{\text{drift}}^2} \cdot \frac{\text{CH}_3\text{I} - \text{H}^+}{\text{H}_3\text{O}^+} \cdot \frac{\text{Tr}_{\text{H}_3\text{O}^+}}{\text{Tr}_{\text{CH}_3\text{I}-\text{H}^+}} \quad (9)$$

Equation (9) may then be used to determine  $k$  if  $\text{CH}_3\text{I}$  mixing ratio is known.

A typical signal intensity profile of selected ions is shown in Figure 1. As shown in Figure 1,  $m/Q$  21 refers to the hydronium ion  $\text{H}_3^{18}\text{O}^+$ ,  $m/Q$  37 refers to the water complex ion  $\text{H}_3\text{O}^+(\text{H}_2\text{O})$  (other water clusters have been ignored [28]),  $m/Q$  143 refers to the  $\text{CH}_3\text{I}-\text{H}^+$  ion and  $m/Q$  142 refers to the  $\text{CH}_3\text{I}^+$  ion. The primary ions  $\text{H}_3\text{O}^+$  at  $m/Q$  19 were not detected but were calculated based on the ion count rates of  $\text{H}_3^{18}\text{O}^+$  at  $m/Q$  21 using equation 10.

$$\text{count rate } m/Q \text{ 19} = \frac{(\text{count rate } m/Q \text{ 21}) \times 500}{\text{Transmission } \text{H}_3^{18}\text{O}^+ \text{ ion}} \quad (10)$$

In equation 10 above, the constant 500 is the isotope ratio that reflects the isotope ratio of  $\text{H}_3^{18}\text{O}^+$  to  $\text{H}_3^{16}\text{O}^+$  and the intensity of the  $\text{H}_3^{18}\text{O}^+$  ion is corrected by its transmission efficiency. Product ions of reactions caused by minor impurities, namely  $\text{NO}^+$  and  $\text{O}_2^+$ , have been shown to have negligible intensities as compared to all other product ions and were not considered.[28] The ion signal intensity at  $m/Q$  143 shown in Figure 1 is used to relate the PTR-MS response to methyl iodide mixing ratio. A typical calibration plot is shown in Figure 2. As shown in Figure 2, the MS response is linear for the given

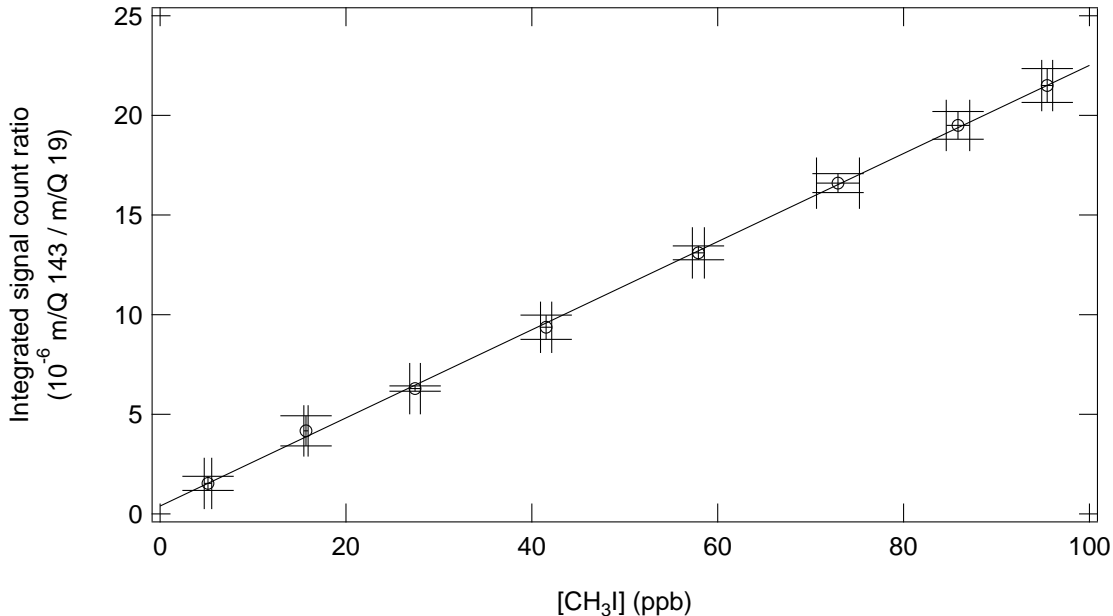


Figure 2: Plot of the methyl iodide calibration results. The  $m/Q$   $\text{CH}_3\text{I}$  signal has been normalized by  $m/Q$  19. The solid line is obtained from a linear least squares analysis; its slope is  $(2.21 \pm 0.04) \times 10^{-7}$  and the intercept is  $(3.85 \pm 2.5) \times 10^{-7}$  (Errors are  $2\sigma$ , precision only).

methyl iodide mixing ratios. Under the typical experimental conditions used, no fragmentation of the product ion was observed. That is, only the mother ion at  $m/Q$  143 that refers to the  $\text{CH}_3\text{I-H}^+$  ion was detected. The difference in proton affinities between water and methyl iodide is very small. As a result, there is no sufficient excess of energy to fragment the product ion during the proton transfer ionization process. However, as shown in Figure 1 the signal intensity of the  $m/Q$  142 that refers to the  $\text{CH}_3\text{I}^+$  ion was observed to increase slightly with increasing methyl iodide mixing ratio. It is not believed that the  $m/Q$  142 is a result of the fragmentation of the methyl iodide mother ion. It is known that a small amount of the  $\text{O}_2^+$  ion is always present within the drift tube (see Figure 1). The  $\text{O}_2^+$  reagent ion will react with methyl iodide via an electron transfer to produce  $m/Q$  142 ion signal that refers to the  $\text{CH}_3\text{I}^+$  ion. Comparison of reported measured rate coefficients for the proton transfer reaction between  $\text{H}_3\text{O}^+$  and  $\text{CH}_3\text{I}$  at different humidities is shown in Table 1. The methyl iodide mixing ratio,  $[\text{CH}_3\text{I}]_{\text{saturator}}$ , shown in Table 1 was determined at the exit of the saturation system and calculated from the given temperature, vapor pressure, mass flow rates, pressure within the saturator and total pressure.

### 3.2. Theoretical determination of $k_{(\text{H}_3\text{O}^+ + \text{CH}_3\text{I})}$

The theoretical value of the collision rate constant for the proton transfer reaction between  $\text{H}_3\text{O}^+$  and  $\text{CH}_3\text{I}$  was calculated using the average dipole orientation (ADO) theory.[29, 30] The ADO rate coefficient,  $k_{\text{ADO}}$ , is given by

$$k_{\text{ADO}} = q \sqrt{\frac{\pi \alpha}{\mu \epsilon_0}} + C \frac{q \mu_{\text{D}}}{\epsilon_0} \sqrt{\frac{1}{2\pi \mu k_{\text{B}} T}} \quad (11)$$

where  $\mu_{\text{D}}$  and  $\alpha$  are the dipole moment and polarizability of the neutral molecule, respectively,  $q$  is the fundamental charge,  $\epsilon_0$  is the permittivity of the free space,  $\mu$  is the reduced mass of the colliding partners

Table 1: Comparison of the measured rate coefficients for the proton transfer reaction between  $\text{H}_3\text{O}^+$  and  $\text{CH}_3\text{I}$  at different humidities

$[\text{CH}_3\text{I}]_{\text{sat}} \text{ range}^a$	%RH <sup>b</sup>	$k_{\text{exp}}^{a,c}$	$k_{\text{exp}}/k_{\text{ADO}}^d$
5 - 94	dry	$4.90 \pm 1.70$	0.021
75	11.4	$4.55 \pm 1.02$	0.020
75	15.5	$3.53 \pm 0.41$	0.015
5 - 96	20.1	$2.54 \pm 1.57$	0.011
5 - 95	21.5	$2.69 \pm 2.37$	0.012
5 - 96	22.6	$2.05 \pm 0.40$	0.008
75	23.3	$2.97 \pm 0.54$	0.013
75	30.5	$2.55 \pm 0.22$	0.011
75	36.5	$2.34 \pm 0.25$	0.010
75	62.8	$1.79 \pm 0.20$	0.008

<sup>a</sup> Units:  $[\text{CH}_3\text{I}]_{\text{sat}}$ : ppbV,  $k_{\text{exp}}$ :  $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ,

<sup>b</sup> Experimental uncertainty in %RH values is  $\pm 0.5\%$ RH

<sup>c</sup> Uncertainty is  $\pm 2\sigma$ , precision only

<sup>d</sup>  $k_{\text{ADO}} = 2.28 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$

(here,  $\text{H}_3\text{O}^+$  and  $\text{CH}_3\text{I}$ ),  $T$  is the temperature within the drift-tube and  $k_{\text{B}}$  is the Boltzmann constant. The dipole locking constant  $C$  is between 0 and 1 and is a function of  $\mu_{\text{D}}/\sqrt{\alpha}$  and temperature.[31]

The structure of methyl iodide was taken from NIST database.[18] In this work, the dipole moment  $\mu_{\text{D}} = 1.620$  Debye and polarizability  $\alpha = 7.325 \text{ \AA}^3$ . [18] The theoretical rate constant for the proton-transfer reaction between  $\text{H}_3\text{O}^+$  and  $\text{CH}_3\text{I}$  is calculated to be  $k_{\text{ADO}} = 2.28 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ .

## 4. Discussion

### 4.1. MS ion signal

It was observed that the ion signal sensitivity decreased as a function of relative humidity. The relationship between sensitivity and relative humidity is shown in Figure 3. As shown in Figure 3, the  $\text{CH}_3\text{IH}^+$  ion signal was normalized to the signal of  $\text{H}_3\text{O}^+$  ion ( $m/Q$  19) because the reagent ion also changes with humidity. Since the  $\text{CH}_3\text{IH}^+$  ion signal is proportional to the  $\text{H}_3\text{O}^+$  ion abundance, it needs to be taken into account to show the humidity dependence of the  $\text{CH}_3\text{IH}^+$  ion. The observed drop in sensitivity with increasing relative humidity is best explained by the water cluster formation at low drift-tube  $E/N$  ratios. For example, the plot of the fraction of the dihydrate cluster in the drift tube as a function of relative humidity and drift-tube  $E/N$  value is shown in Figure 4. It can be seen in Figure 4 that a low drift-tube  $E/N$  value promotes clustering of  $\text{H}_3\text{O}^+$  ions with  $\text{H}_2\text{O}$ . The formation of water clusters may be problematic since they may act as reagent ions. To limit cluster formation within the drift-tube, all experiments were performed at  $E/N = 140$  Td. In a similar study, Cappellin et al. (2012) [32] reported that under high electric field strength values, the protonated water cluster ion formation is strongly suppressed. Further, since the proton transfer reaction between the  $\text{H}_3\text{O}^+$  ion and  $\text{CH}_3\text{I}$  is only



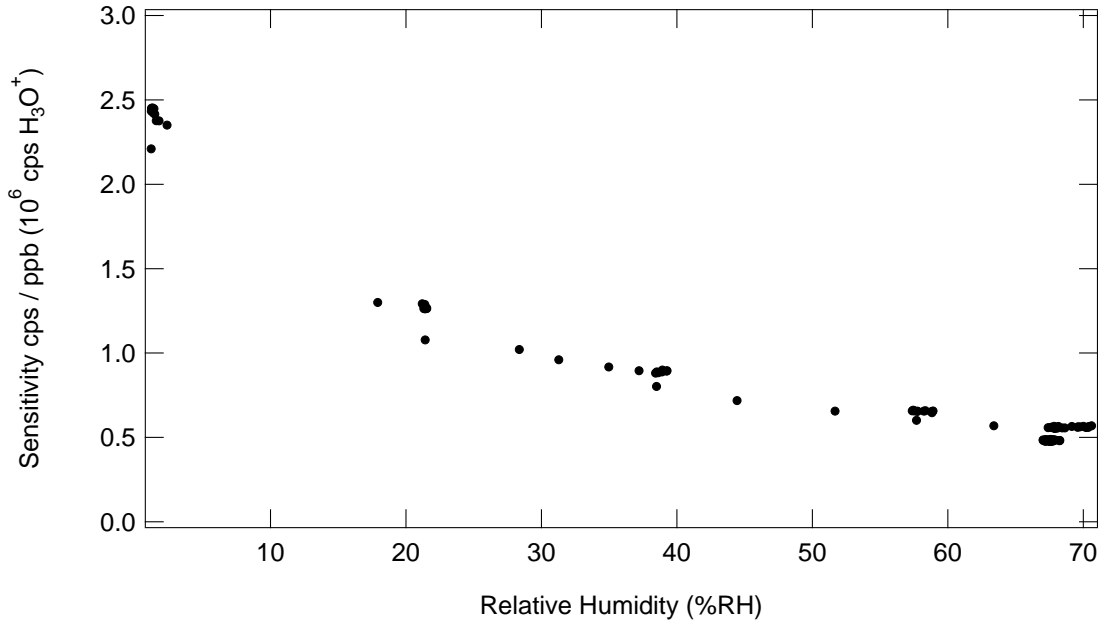


Figure 3: Plot of the signal ion sensitivity as a function of relative humidity.

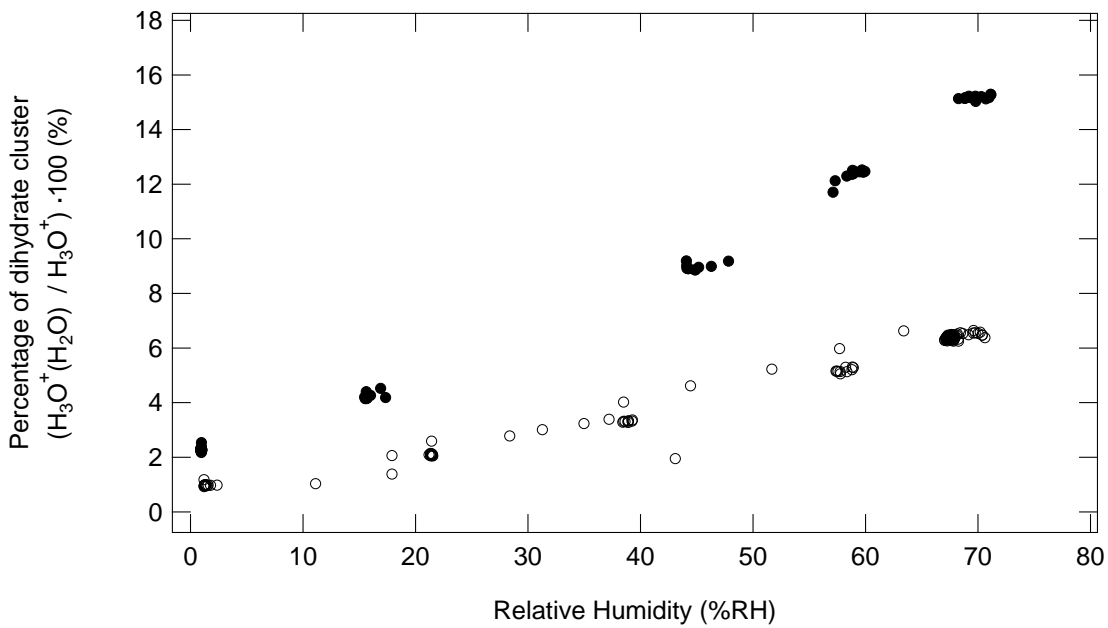


Figure 4: Plot of the fraction of the dihydrate cluster in the drift tube versus relative humidity. Experimental conditions:  $T = 298\text{K}$ ,  $E/N = 140\text{Td}$  (open circles  $\circ$ ),  $E/N = 127\text{Td}$  (closed circles  $\bullet$ ). The percentage data of dihydrate clusters were calculated using the following equation:  $\frac{[\text{H}_2\text{O}-\text{H}_3^{18}\text{O}^+] \times 250}{[\text{H}_3^{18}\text{O}^+] \times 500} \times 100$

slightly exothermic, and possibly endothermic given the uncertainties in the proton affinities, the proton transfer reaction between the water cluster and  $\text{CH}_3\text{I}$  will most likely not occur. For example, the water dimer  $(\text{H}_2\text{O})_2$ , has a proton affinity of  $808 \pm 6 \text{ kJ mol}^{-1}$ . As a result, the increased affinity of the water cluster means that some reactions that occur with  $\text{H}_3\text{O}^+$  ions will not take place with  $\text{H}_3\text{O}^+(\text{H}_2\text{O})$  ions.

#### 175 4.2. Rate constants

The agreement between the theoretical value for the rate constant for the proton-transfer reaction between  $\text{H}_3\text{O}^+$  and  $\text{CH}_3\text{I}$  ( $k_{\text{ADO}}$ ) and the experimental value ( $k_{\text{exp}}$ ) is very bad (see Table 1). This is not surprising given that the proton-transfer reaction  $\text{H}_3\text{O}^+ + \text{CH}_3\text{I}$  is only slightly exothermic ( $\Delta\text{PA} = 0.7 \text{ kJ mol}^{-1}$ ). Further, given the uncertainties in proton affinities ( $\pm 3 \text{ kJ mol}^{-1}$ ), the reaction itself  
180 may be endothermic. It has been argued that the proton-transfer from  $\text{H}_3\text{O}^+$  to the analyte molecule in the drift-tube of the PTR-MS is efficient only when the molecule has a higher proton affinity and that the difference in proton affinities is larger than  $35 \text{ kJ mol}^{-1}$ . [19] The experimental values for the proton transfer reaction between  $\text{H}_3\text{O}^+$  and  $\text{CH}_3\text{I}$  are summarized in Table 1. The experimental values range from  $1.79 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$  to  $4.90 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$  as a function of relative humidity. On the other  
185 hand  $k_{\text{ADO}} = 2.25 \times 10^{-9} \text{ cm}^3\text{s}^{-1}$ . The reaction efficiency  $k_{\text{exp}}/k_{\text{ADO}}$  is calculated to range from 0.008 (62%RH) to 0.021 in dry nitrogen flow. In this work,  $k_{\text{exp}}/k_{\text{ADO}}$  is equal to  $[\text{CH}_3\text{I}]_{\text{saturation}}/[\text{CH}_3\text{I}]_{\text{PTR-MS}}$  ratio, where  $[\text{CH}_3\text{I}]_{\text{PTR-MS}}$  is the theoretically predicted  $\text{CH}_3\text{I}$  mixing ratio estimated by the PTR-MS measurements (assuming  $k_{\text{ADO}} = 2.28 \times 10^{-9} \text{ cm}^3\text{s}^{-1}$  [33]) and  $[\text{CH}_3\text{I}]_{\text{saturation}}$  is the  $\text{CH}_3\text{I}$  mixing ratio determined at the exit of the saturation system and calculated from the given vapor pressure, mass flow  
190 rates, pressure within the saturator and total pressure.

The possible explanation for the low  $k_{\text{exp}}/k_{\text{ADO}}$  ratio is a reverse reaction of the product  $\text{CH}_3\text{I-H}^+$  ion with the molecules of  $\text{H}_2\text{O}$  even under low humidity conditions present within the drift-tube. This hypothesis is supported by the data shown in Figure 3.

The proton transfer reaction between  $\text{H}_3\text{O}^+$  and  $\text{CH}_3\text{I}$  has been studied briefly by Spanel and Smith  
195 (1999). [20] These authors calculated the  $k_{\text{exp}}/k_{\text{collision}} = 0.5$ , where  $k_{\text{collision}}$  is the collision rate constant in dry helium carrier gas calculated based on the work of Su and Chesnavich (1982). [34] In the work presented here, the  $k_{\text{exp}}/k_{\text{ADO}} = 0.02$  in dry synthetic air. At this point, we cannot determine the discrepancy between the two values. Since Spanel and Smith (1999) do not list their electric field strength (E/N) values nor which collision rate constant they calculate nor the polarizability nor the dipole moment  
200 values, it is difficult to compare the two studies. It is known that the kinetics of the ion-molecule reactions are controlled by drift-tube temperature and pressure, drift tube E/N, reactant molecule dipole moment and polarizability.

In a scenario similar to this work, Cappellin and coworkers (2014) [35] determined the rate coefficient for the reaction of ethylene with  $\text{H}_3\text{O}^+$ . Similar to the results obtained in this work, Cappellin and coworkers' theoretical value  $k_{\text{ADO}}$  for the ethylene +  $\text{H}_3\text{O}^+$  reaction does not agree with the  $k_{\text{exp}}$  value. These authors  
205 reported the experimental reaction rate coefficient between  $1.7 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$  and  $3.4 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$ , far below the collision rate ( $1.4 \times 10^{-9} \text{ cm}^3\text{s}^{-1}$ ). [35] Similar to the results observed in this work, the reaction of ethylene with  $\text{H}_3\text{O}^+$  is very inefficient. The authors attribute the observed inefficiency to the (quasi)

reaction endothermicity. The results obtained in this work for the proton-transfer reaction of  $\text{H}_3\text{O}^+$  with methyl iodide are consistent with the results obtained by Cappellin and coworkers [35].

In this work, the observed difference in  $k_{\text{exp}}$  and  $k_{\text{ADO}}$  for the  $\text{H}_3\text{O}^+ + \text{CH}_3\text{I}$  reaction does not imply that the PTR-MS technique is a poor method of choice to be used to detect gas phase  $\text{CH}_3\text{I}$ . As shown in Figures 1 and 2, with a good calibration curve, the PTR-MS technique is a perfect analytical method to detect and quantify rapid changes in the  $\text{CH}_3\text{I}$  gas phase concentrations.

## 5. Conclusion

A commercial Ionicon Analytic PTR-MS was used to study the  $\text{H}_3\text{O}^+$  reagent ion ionization process with methyl iodide. The proton transfer reaction between the  $\text{H}_3\text{O}^+$  reagent ion and  $\text{CH}_3\text{I}$  produces a specific ion at  $m/Q$  142 ( $\text{CH}_3\text{I-H}^+$ ) that allows for fast and sensitive detection of gas phase methyl iodide. The instrument response for  $\text{CH}_3\text{I}$  was shown to be linear in the 5 - 96 ppbV range. The calculated collision rate,  $k_{\text{ADO}}$  is calculated based on a dipole moment  $\mu(\text{CH}_3\text{I}) = 1.620$  D [18] and a molecular polarizability  $\alpha(\text{CH}_3\text{I}) = 7.325 \text{ \AA}^3$  [18] and gives  $k_{\text{ADO}} = 2.28 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ . The experimental collision rate,  $k_{\text{exp}}$  for the proton transfer reaction  $\text{H}_3\text{O}^+ + \text{CH}_3\text{I} \rightarrow [\text{CH}_3\text{I-H}]^+ + \text{H}_2\text{O}$  is in the range  $(1.79 - 4.90) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . The observed difference in the theoretical and experimental values of the rate constant is assumed to be the result of the fact that the proton transfer reaction between the hydronium ions and methyl iodide is only slightly exothermic and given the uncertainties in the proton affinities may be even endothermic.

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