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Quantification of the gas phase methyl iodide using O_2^+ as the reagent ion in the PTR-ToF-MS technique

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Abstract

The charge-transfer-reaction between molecular oxygen ions (O_2^+) and methyl iodide (CH_3I) is studied to investigate if consistent environmental quantification of the gas phase CH_3I is possible without prior calibration. The neutral CH_3I molecule was chosen because this compound is of atmospheric chemistry and environmental importance in the field of nuclear power plant safety and nuclear energy. Molecular oxygen was used as a reagent ion source in a commercial Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS) to produce molecular oxygen ions (O_2^+). The use of O_2^+ ions allows for fast, sensitive and specific detection of gas phase CH_3I via an electron exchange reaction $O_2^+ + CH_3I \rightarrow CH_3I^+ + O_2$. The instrument response was linear in the 1-150 ppbv range and its sensitivity was humidity independent. The detection sensitivity of CH_3I normalized by the O_2^+ count rate of 10^6 cps was found to be $S = 22.6 \pm 0.3$ ncps/ppbv, independent of relative humidity. A typical O_2^+ primary ion signal was $(2.0 \pm 0.2) \times 10^6$ cps. The lowest measured CH_3I concentration was 0.23 ± 0.10 ppb. Error is $\pm \sigma$. The theoretical collision rate based on the dipole moment and molecular polarizability values is calculated using the Langevin collision rate (k_L) approximation, the average-dipole-orientation (ADO) theory and the capture rate coefficient (k_{CAP}) based on trajectory calculations. The experimental rate constant, k_{exp} , for the electron transfer reaction between O_2^+ ions and CH_3I is calculated to be $(1.72 \pm 0.22) \times 10^{-9} \text{ cm}^3\text{s}^{-1}$. Listed errors are $\pm \sigma$ and represent precision only. The experimentally determined value agrees very well with the theoretical collision rate values, $k_L = 1.24 \times 10^{-9} \text{ cm}^3\text{s}^{-1}$, $k_{ADO} = 1.73 \times 10^{-9} \text{ cm}^3\text{s}^{-1}$ and $k_{CAP} = 1.48 \times 10^{-9} \text{ cm}^3\text{s}^{-1}$. The obtained results indicate that the PTR-MS technique is an excellent analytical method to quantify gas phase CH_3I .

Introduction

First observed by Lovelock and coworkers (1973) [1], methyl iodide is a natural photochemical source of iodine in the atmosphere [2]. As first suggested by Chameides and Davis (1980) [2], iodine and its oxides play an important role in the oxidizing capacity of the troposphere [3], aerosol formation and in the ozone depleting cycles in the troposphere [4,5] and stratosphere [6]. The atmospheric photochemistry of methyl iodide is also of interest in the nuclear industry safety field 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.) [7], Chernobyl (Ukraine) [8] and Fukushima (Japan) [9] were to occur, again. It is known that iodine and methyl iodide are two of the more important fission products that are released from UO_2 fuel during a major nuclear power plant accident in pressurized water reactors due to their volatility and radiological health impact.[10] Furthermore, methyl iodide is a fission product that is difficult to retain by post-accident filtration systems [11] and is currently used in the nuclear industry field to test the organic iodine capture ability, ageing and performance of emergency charcoal filters.[12,13] Other important methyl iodide applications include agrarian control of insects, plant parasitic metabolites, soil-borne pathogens and weed seeds.[14]

To date, most gas phase environmental methyl iodide measurements are based on gas chromatographic (GC) separation equipped with a mass spectrometer (MS) or an electron capture detector (ECD). A more recent atmospheric gas phase methyl iodide measurement method is based on resonant fluorescence spectroscopy.[15] While GC-ECD (LD~10 ppt) and GC-MS (LD~100 ppt) methods are two very sensitive analytical techniques used to detect gas phase methyl iodide in various environment settings, they do not offer the time resolution and response needed to measure rapid flux or concentration changes in the gas phase. The newer resonant fluorescence technique used to detect gas phase methyl iodide in the atmosphere is fast, sensitive and selective but remains a research-grade instrument that requires advanced technical expertise and skills and may be difficult to apply in routine analyses. The chemical ionization mass spectrometric (CIMS)

50 technique has the potential for fast, sensitive, specific and real time methyl iodide measurements when rapid
51 changes in the gas phase mixing ratios need to be known or monitored continuously.

52 The proton-transfer-reaction time-of-flight mass spectrometry (PTR-ToF-MS) is a type of CIMS instrument.
53 The PTR-ToF-MS combines the concept of chemical ionization [16] with the flow-drift-tube technique.[17]
54 This technique is often used for sensitive detection of volatile organic compounds (VOCs) in the atmosphere.
55 The two more common CI reagents used in CIMS to detect atmospheric VOCs include hydronium ions (H_3O^+)
56 and molecular oxygens ions (O_2^+). While H_3O^+ are good proton sources, these CI reagent ions can be applied
57 only to gas-phase compounds with proton affinities (PA) higher than that of water, $\text{PA}(\text{H}_2\text{O})= 691.0 \text{ kJ.mol}^{-1}$.
58 ¹[18,19] Since, the proton affinity of CH_3I , $\text{PA}(\text{CH}_3\text{I}) = 691.7 \text{ kJ.mol}^{-1}$ [18,19], is only slightly higher than
59 that of water, H_3O^+ ions may not be the ideal reagent to use to detect gas phase methyl iodide. In theory, H_3O^+
60 ions may be used to ionize CH_3I , whilst this reaction is only slightly exothermic ($\Delta\text{PA}\sim 0.7 \text{ kJ.mol}^{-1}$). A recent
61 study showed that H_3O^+ ions may still be successfully used to quantify methyl iodide in the atmosphere.[20]
62 On the other hand, O_2^+ ions are often used as an alternative chemical ionization reagent in PTR-ToF-MS.
63 Contrary to H_3O^+ , which is a soft ionizer, the O_2^+ ion is observed to be a more aggressive chemical ionization
64 reagent. That is, the O_2^+ reagent ion ionization results in a mass spectrum not dissimilar to electron impact
65 albeit less fragmented. That is, the more energetic O_2^+ ions produce characteristic mass spectral "fingerprint"
66 that is less fragmented compared to electron impact and the mother ion is clearly identifiable and can be easily
67 quantified. Contrary to the proton transfer reaction between the H_3O^+ ion and CH_3I molecule, the electron
68 transfer reaction between O_2^+ ion ($\text{IE}=12.0697\pm 0.0002 \text{ eV}$) [19] and methyl iodide molecule ($\text{IE}=9.54\pm 0.02$
69 eV) [19] is highly exothermic. As a result, the use of molecular oxygen as a CI reagent the PTR-ToF-MS
70 instruments to detect CH_3I is proposed. It is shown that the proposed PTR-ToF-MS technique is an ideal tool
71 for online analyses of relatively fast changing concentrations of methyl iodide

72 Experimental

73 The charge transfer reaction between the O_2^+ reagent ion and CH_3I was studied using a commercial PTR-ToF
74 8000 mass analyzer (Ionicon Analytik GmbH, Innsbruck, Austria). The experimental details that are
75 particularly relevant to this work are given below.

76 **Generation of gas phase CH_3I .** The gas phase CH_3I concentration was generated using the gas saturation
77 method, one of the oldest and most versatile ways of studying heterogeneous equilibria involving low vapor
78 pressure compounds, first developed by Regnault in 1845.[21] The gas saturation method used in this work
79 is similar to the one described originally by Markham (1940).[22] Briefly, nitrogen carrier gas was allowed
80 to flow though the volume containing the CH_3I sample that itself was mixed with glass beads and supported
81 on a fritted glass surface. The saturator volume itself was immersed in a temperature-controlled fluid and
82 kept at a constant temperature using a temperature-controlled circulating bath with an accuracy of $\pm 0.1\text{K}$.
83 The temperature inside the saturator volume was measured using a Type-J thermocouple (Omega) with an
84 accuracy of $\pm 0.1\text{K}$. The carrier gas was allowed to enter the saturator volume, equilibrate with the sample
85 and was then allowed to exit through a capillary exit and allow to flow through a glass tube. The geometry of
86 the exiting glass tube was such that the diameter of the glass tube increased with increasing length. This was
87 done to avoid any sample condensation as the sample and the carrier gas were allowed to leave the saturator
88 system. Concentration of CH_3I at the exit of the saturation system was calculated from the given vapor
89 pressure, mass flow rates, pressure within the saturator and the total pressure. Concentration of CH_3I at the
90 exit of the saturation system was calculated using the Dalton's law of partial pressures. Assuming that the gas
91 within the saturation system is a mixture of dry nitrogen and CH_3I , the volume mixing ratio of the latter can
92 be defined as the following:

$$93 \quad [\text{CH}_3\text{I}] = \frac{p_{\text{CH}_3\text{I}}}{p_s}$$

94 where $P_{\text{CH}_3\text{I}}$ is the vapor pressure of CH_3I and P_s , the total pressure within the saturation system, was $P_s =$
95 957 Torr. The Antoine type equation used to calculate the vapor pressure of CH_3I is the following [23]:

$$96 \quad \log_{10}(p) = 4.1554 - \frac{1177.78}{\text{T}(\text{K}) - 32.058}$$

97 where the pressure p is in units of bar and the temperature T is in Kelvin and in the range from 218K to
98 315.6.[23] Under normal operating conditions, the saturator was kept at $\text{T}=274\text{K}$. At this temperature, the

99 vapor pressure of CH₃I within the saturator was calculated to be 146.37±3.40 Torr. Under typical
100 experimental conditions, the gas phase CH₃I mixing ratio within the saturation system was about 15%. This
101 vapor pressure was then further diluted using dry nitrogen carrier gas and a system of mass flow controllers
102 to obtain the desired mixing ratio in the range 1-150 ppbv. Further, the carrier gas was allowed to pass
103 through a bubbler filled with deionizer water at room temperature to evaluate the impact of relative humidity
104 (%RH) on the signal sensitivity. The relative humidity was varied between 0.3±0.2 and 76±0.5%.

105 **PTR-ToF-MS instrument.** A commercial PTR-ToF 8000 mass analyzer (Ionicon Analytik GmbH, Innsbruck,
106 Austria) was used to study the O₂⁺ reagent ion ionization process with CH₃I. The reaction chamber pressure
107 (pdrift) was 2.10 mbar, drift tube voltage was 544 V and the drift tube temperature was held constant at
108 T=333.15K. The corresponding *E/N* ratio was 127 Td. (1Td=10⁻¹⁷ Vcm²) where *E* is the electric field
109 strength applied to the drift tube and *N* is the buffer gas density.

110 **Materials.** The nitrogen carrier gases used in this study was generated using the N2LCMS 1 Nitrogen
111 Generator (Claind S.r.l., Italy). Iodomethane was purchased at Acros Organics (Belgium) and the stated
112 minimum purity was 99%. To limit any photo-catalytic or thermal decomposition during storage, CH₃I
113 original container bottles were stored under dark conditions at T=6°C. Oxygen gas was purchased at Linde
114 Gas (Linde France S.A.) and had the stated minimum purity of 99.9995%. Deionized water with a resistivity
115 greater than 18MΩ was prepared by allowing tap water to pass first through a reverse osmosis
116 demineralization filter (ATS Groupe Osmose) and then through a commercial deionizer (Milli-pore, Milli-
117 Q).

118 Results

119 Chemical ionization scheme for CH₃I

120 The electron transfer reaction between the O₂⁺ ion (IE=12.0697±0.0002) [19] and methyl iodide molecule
121 (IE=9.54±0.02) [19] is highly exothermic. As a result, molecular oxygen appears to be an ideal reagent source
122 to be used in the PTR-ToF-MS technique to quantify gas phase methyl iodide. Based on other works [24–26]
123 where molecular oxygen was used as a chemical ionization reagent to detect gas phase compounds of
124 atmospheric interest, the electron exchange reaction between the O₂⁺ ion and CH₃I may proceed as follows:



126 Although the O₂⁺ + CH₃I electron exchange reaction is highly exothermic, the reaction may result in the
127 formation of other dissociation products in addition to the mother ion as observed by Španěl and coworkers
128 [25,26] in their selected ion flow tube mass spectrometry (SIFT-MS) study of aldehydes and ketones [26]. The
129 formation of partially dissociative products is discussed below.

130 Experimental determination of $k_{(\text{O}_2^+ + \text{CH}_3\text{I})}$

131 Based on the original work of Lindinger and coworkers (1998) [27] the gas phase concentration of CH₃I may
132 be calculated using the following equation (1):

$$133 \quad [\text{CH}_3\text{I}]_{\text{cm}^{-3}} = \frac{1}{k \times t} \times \frac{I(\text{CH}_3\text{I}^+)}{I(\text{O}_2^+)} \times \frac{\text{Tr}_{\text{O}_2^+}}{\text{Tr}_{\text{CH}_3\text{I}^+}} \quad (1)$$

134 In the equation above, [CH₃I⁺] is the methyl iodide concentration in units of cm⁻³, I(CH₃I⁺) and I(O₂⁺) are the
135 observed ion count rates, *k* is the charge transfer rate constant between the molecular oxygen ion (cm³.s⁻¹), O₂⁺,
136 and the methyl iodide molecule, and *t* (μs) is the residence or reaction time of the selected ion within the drift
137 tube.[28] As shown in the equation (1) above, to correct mass dependence losses of the selected ions that are
138 allowed to travel through the transfer lens system between the drift tube and the ToF mass analyzer, the
139 detected ion count rates are normalized by their corresponding transmission factors, that is, Tr_{O₂⁺} and Tr_{CH₃I⁺}.

140 The equation (1) above may be rewritten in the following manner:

$$141 \quad [\text{CH}_3\text{I}]_{\text{ppbv}} = \frac{10^9}{N} \times \frac{1}{k \times t} \times \frac{I(\text{CH}_3\text{I}^+)}{I(\text{O}_2^+)} \times \frac{\text{Tr}_{\text{O}_2^+}}{\text{Tr}_{\text{CH}_3\text{I}^+}} \quad (2)$$

142 In the equation (2) above, $[\text{CH}_3\text{I}]_{\text{ppbv}}$ is the methyl iodide mixing ratio in units of ppbv, N is the number of
 143 molecules per cm^3 within the drift-tube volume. The reaction time, t , may be calculated using the drift tube
 144 length ($L = 9.2 \text{ cm}$) and the O_2^+ ion drift velocity (v_d).

$$145 \quad t = \frac{L}{v_d} \quad (3)$$

146 In the equation (3), the drift tube velocity (v_d) may be determined from the reduced mobility of the O_2^+ ion (μ_0
 147 $= 2.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) at given E/N ratio (equation (4)).

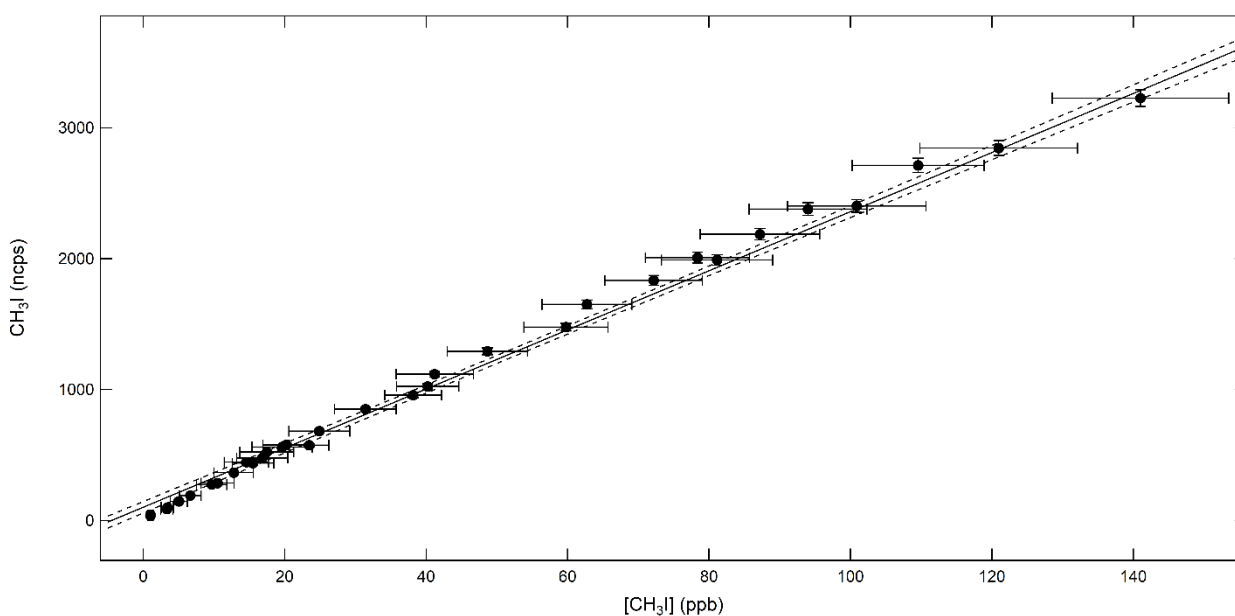
$$148 \quad v_d = \mu \cdot E = N_0 \cdot \mu_0 \cdot \left(\frac{E}{N}\right) \quad (4)$$

149 In equation (4), $N_0 = 2.68 \times 10^{19} \text{ cm}^{-3}$ and is the number of molecules per cm^3 under normal conditions of
 150 temperature and pressure.

151 If the methyl iodide mixing ratio is known, the experimental rate constant, k_{exp} , for the charge transfer reaction
 152 between the O_2^+ ion and CH_3I molecule may be calculated using the following equation (5):

$$153 \quad k_{\text{exp}} = \frac{10^9}{t \times N} \times \frac{I(\text{CH}_3\text{I}^+)}{[\text{CH}_3\text{I}]_{\text{ppbv}} \times I(\text{O}_2^+)} \times \frac{\text{Tr}_{\text{O}_2^+}}{\text{Tr}_{\text{CH}_3\text{I}^+}} \quad (5)$$

154 A typical calibration curve is shown in Figure 1. The MS signal is observed to be linear for the given methyl
 155 iodide mixing ratio.



156

157 **Figure 1. Calibration curve of the PTR-ToF-MS system used to quantify the gas phase CH_3I molecules using O_2^+ as reagent ions.**
 158 **The CH_3I signal is normalized to 1×10^6 cps of O_2^+ ions. Solid line is obtained from linear least-squares analysis and gives the**
 159 **slope that is signal sensitivity of 22.6 ± 0.3 ncps/ppbv. The lowest measured CH_3I concentration was 0.23 ± 0.10 ppb. Error is $\pm \sigma$.**
 160 **Error in the detection limit is $\pm \sigma$. Coefficient of determination (r^2) is calculated to be 0.993. The horizontal bars ($\pm \sigma$) represent**
 161 **experimental uncertainties in the generation of the gas phase methyl iodide using the saturation method followed by**
 162 **subsequent dilutions. The experimentally determined vertical error bars are $\pm 2\%$ of the measured counts.**

163 As shown in Figure 1, the measured methyl iodide PTR-ToF MS signal in counts per second (cps) was
 164 normalized using primary ion signal due to O_2^+ ions. The methyl iodide signal was normalized to aid in
 165 intercomparing of different PTR-MS techniques and to remove measured signal fluctuations in the amount of
 166 primary reagent ions and drift tube temperature and pressure.

167 As shown in Figure 1, methyl iodide signal sensitivity is obtained from linear least-squares analysis and gives
 168 $S = 22.6 \pm 0.3$ ncps/ppbv (normalized to 1×10^6 cps of O_2^+). If the solid line is forced through zero, linear
 169 least-squares analysis results in $S = 23.6 \pm 0.3$ ncps/ppbv (normalized to 1×10^6 cps of O_2^+). The lowest
 170 measured CH_3I concentration was 0.23 ± 0.10 ppb. Errors are $\pm \sigma$ and represent precision only. The count rate
 171 of O_2^+ , calculated from the count rate at m/z 34 ($^{16}\text{O}^{18}\text{O}^+$) multiplied by 250, was typically $(2.0 \pm 0.2) \times 10^6$
 172 cps. Under dry conditions, $\text{RH} = 0\%$, the hydronium ion (H_3O^+) signal is very weak (1 ± 0.2 ppm to that of
 173 O_2^+). The $\text{Tr}_{\text{O}_2^+}$ and $\text{Tr}_{\text{CH}_3\text{I}^+}$ values were measured to be 0.36 and 0.94, respectively.

174 The k_{exp} value may also be directly determined using the normalized detection sensitivity, S , as shown in the
 175 equation (6).

$$176 \quad k_{\text{exp}} = \frac{10^3}{t \times N} \times S \times \frac{\text{Tr}_{\text{O}_2^+}}{\text{Tr}_{\text{CH}_3\text{I}^+}} \quad (6)$$

177 The resulting experimental rate constant for the charge transfer reaction between the O_2^+ ion and the CH_3I
 178 neutral molecule is calculated to be $(1.72 \pm 0.22) \times 10^{-9} \text{ cm}^3\text{s}^{-1}$.

179 Theoretical determination of $k_{(\text{O}_2^+ + \text{CH}_3\text{I})}$

180 Given a large exothermicity of the electron exchange reaction between the molecular oxygen ion (O_2^+) and the
 181 neutral methyl iodide molecule (CH_3I), ion-neutral collision theories may be used to calculate the theoretical
 182 collision rate constants. Current theoretical approximations of the collision rate constants between a reagent
 183 ion and a polar neutral molecule that take place within the drift tube of a PTR-MS instrument include the
 184 Langevin collision rate k_L [29] approximation, the average-dipole-orientation (ADO) theory [30,31] and the
 185 capture rate coefficient k_{CAP} [32–34] trajectory calculation.

186 The Langevin rate constant k_L gives a first good approximation for the collision rate between a reagent ion and
 187 a non-polar molecule in the high temperature limit.[28] The following equation is the Langevin collision rate
 188 approximation [29] used to calculate k_L for the electron exchange reaction between the O_2^+ reagent ion and the
 189 polar neutral CH_3I molecule:

$$190 \quad k_L = q \sqrt{\frac{\pi\alpha}{\mu_m \epsilon_0}} \quad (7)$$

191 where α is the polarizability of the neutral molecule, q is the fundamental charge, ϵ_0 is the permittivity of the
 192 free space, μ_m is the reduced mass of the colliding partners (here, O_2^+ and CH_3I).

193 A better approximation of the rate constant between the O_2^+ reagent ion and the polar CH_3I neutral molecule
 194 is obtained using the average-dipole-orientation (ADO) theory.[30,31] That is, it has been observed that the
 195 ADO theoretical calculations of the ion-neutral molecule reaction rates are typically within 10 to 20% of the
 196 experimentally determined values.[28,30,35] The following equation was used to calculate k_{ADO} [28]:

$$197 \quad k_{\text{ADO}} = q \sqrt{\frac{\pi\alpha}{\mu_m \epsilon_0}} + C \frac{q\mu_D}{\epsilon_0} \sqrt{\frac{1}{2\pi\mu_m k_B T}} \quad (8)$$

198 where μ_D is the dipole moment, T is the temperature within the drift tube and k_B is the Boltzmann constant.
 199 Also, C is the dipole locking constant with values that range between 0 and 1 and is a function of the $\mu_D/\sqrt{\alpha}$
 200 ratio and the temperature.[36]

201 The theory most widely used to estimate the ion-molecule rate constants is based on the extensive trajectory
 202 calculations carried out by Su, Chesnavich and Bowers.[32] In their work on ion-polar molecule collision rate
 203 constants, these investigators [32,37,38] showed that the capture rate constants k_{CAP} can be parametrized using
 204 the polarizability α , permanent dipole moment μ_D , and the center-of-mass kinetic energy KE_{cm} in the following
 205 manner [39]:

$$207 \quad k_{\text{CAP}}(T, \text{KE}_{\text{cm}}) = k_L K_{\text{CAP}}(\tau, \epsilon) \quad (9a)$$

$$208 \quad \tau = \frac{\mu_D}{\sqrt{\alpha T}} \quad (9b)$$

$$209 \quad \epsilon = \frac{\mu_D}{\sqrt{\alpha \cdot \text{KE}_{\text{cm}}}} \quad (9c)$$

$$210 \quad \text{KE}_{\text{cm}} = \frac{3}{2} \cdot k_B \cdot T \cdot \left(\frac{M_R}{M_R + M_{\text{ion}}} \right) \cdot \frac{1}{2} \cdot (M_{\text{ion}} + M_{\text{buffer}}) \cdot v_d^2 \quad (9d)$$

$$211 \quad K_{\text{CAP}}(\tau, \epsilon) = 1 + c_1 \cdot \tau^{0.4} \cdot \epsilon^2 \cdot S + c_2 \cdot (1 - S) \cdot \sin[c_3 \{c_4 + \ln(\tau)\}] \cdot \tau^{0.6} \cdot \sqrt{\epsilon - 0.5} \quad (9e)$$

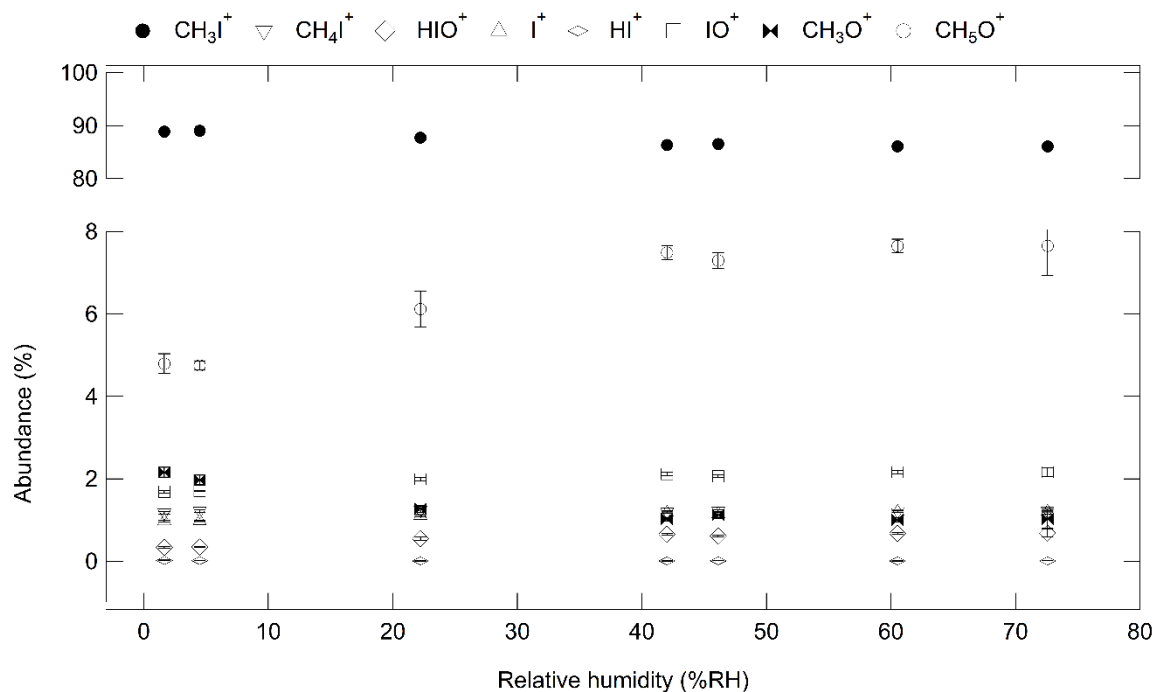
$$212 \quad c_1 = 0.727143, c_2 = 3.71823, c_3 = 0.586920, c_4 = 4.97894 \quad (9f)$$

213 $S = e^{[-2(\epsilon-1.5)]}$ if $\epsilon > 1.5$ or $S = 1$ if $\epsilon \leq 1.5$ (9g)

214 where M_{buffer} is the mass of the buffer gas (here, nitrogen + oxygen), M_{ion} is the mass of the reagent ion (here,
 215 O_2^+), M_{R} is the mass of the neutral molecule (here, CH_3I) and $v_d=930 \text{ ms}^{-1}$ and is the drift velocity of the ion
 216 The structure of methyl iodide was taken from the NIST database [19]. In this work, the dipole moment
 217 $\mu_D=1.62$ Debye and polarizability $\alpha=7.325 \text{ \AA}^3$. [19] The theoretical collision rate constants for the charge
 218 transfer reaction between the O_2^+ ion and the CH_3I molecule are calculated to be $k_L = 1.24 \times 10^{-9} \text{ cm}^3\text{s}^{-1}$,
 219 $k_{\text{ADO}} = 1.73 \times 10^{-9} \text{ cm}^3\text{s}^{-1}$ and $k_{\text{CAP}} = 1.48 \times 10^{-9} \text{ cm}^3\text{s}^{-1}$.

220 **Discussion**

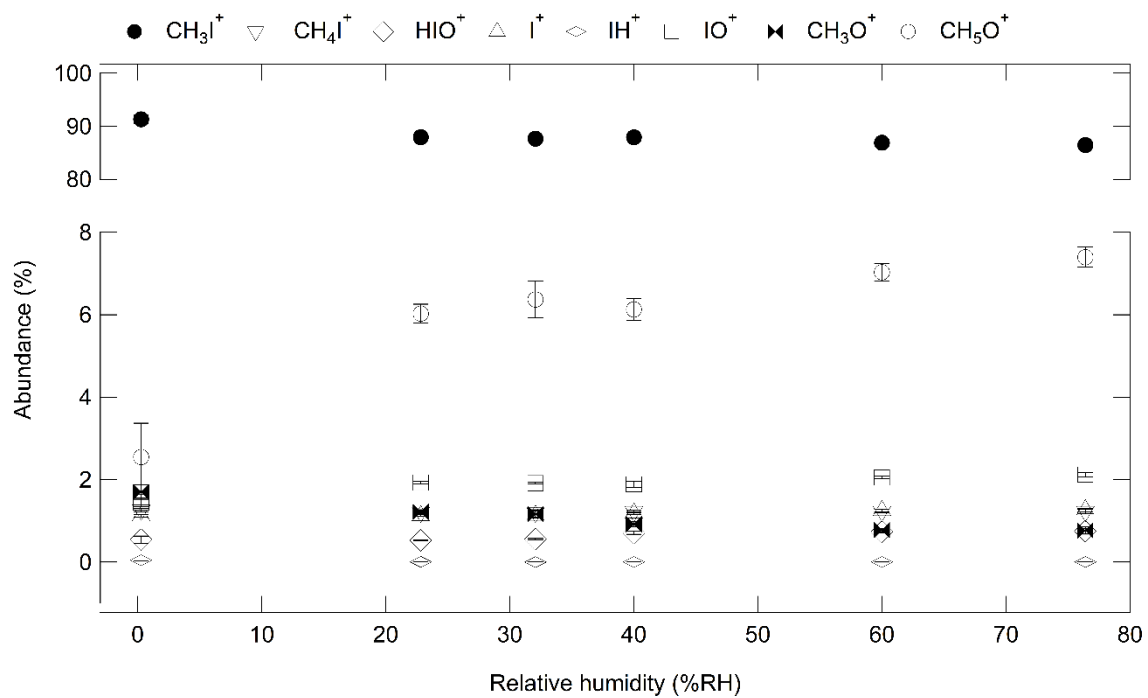
221 As stated above, the electron transfer reaction between O_2^+ ions and methyl iodide molecule is highly
 222 exothermic. While the $\text{O}_2^+ + \text{CH}_3\text{I}$ reaction proceeds via a charge transfer, the reaction may result in the
 223 formation of other dissociation products in addition to the mother ion. [25,26] Such formation of partially
 224 dissociative products was observed by Španěl and coworkers [25,26] in their selected ion flow tube mass
 225 spectrometry (SIFT-MS) reaction studies of O_2^+ ions with a series of aldehydes and ketones [26]. However, in
 226 a similar study of halogenated compounds, Španěl and coworkers observed that the reaction between the O_2^+
 227 ion and a selected short chain chloroalkanes proceeds mainly through a charge transfer, producing a single
 228 ionic product.[40] Relative abundancies of major ion signals observed when methyl iodide mix was analyzed
 229 by the PTR-ToF-MS instrument operated with O_2 gas as the reagent ion source are shown in Figure 2 and
 230 Figure 3. The ions shown in Figure 2 and Figure 3 were not present in the mass spectra when nitrogen buffer
 231 gas was allowed to flow to the PTR-MS and no methyl iodide was present in the system. Relative abundancies
 232 of major ion signals observed when methyl iodide was absent in the gas flow are shown in Figure 4 and Figure
 233 5. It should be noted that the relative abundancy profiles of major ions shown in Figure 4 and Figure 5 are
 234 independent of the presence of CH_3I in the system. That is, same mass spectrum profiles and intensities were
 235 observed whether CH_3I was present in the gas flow or not.



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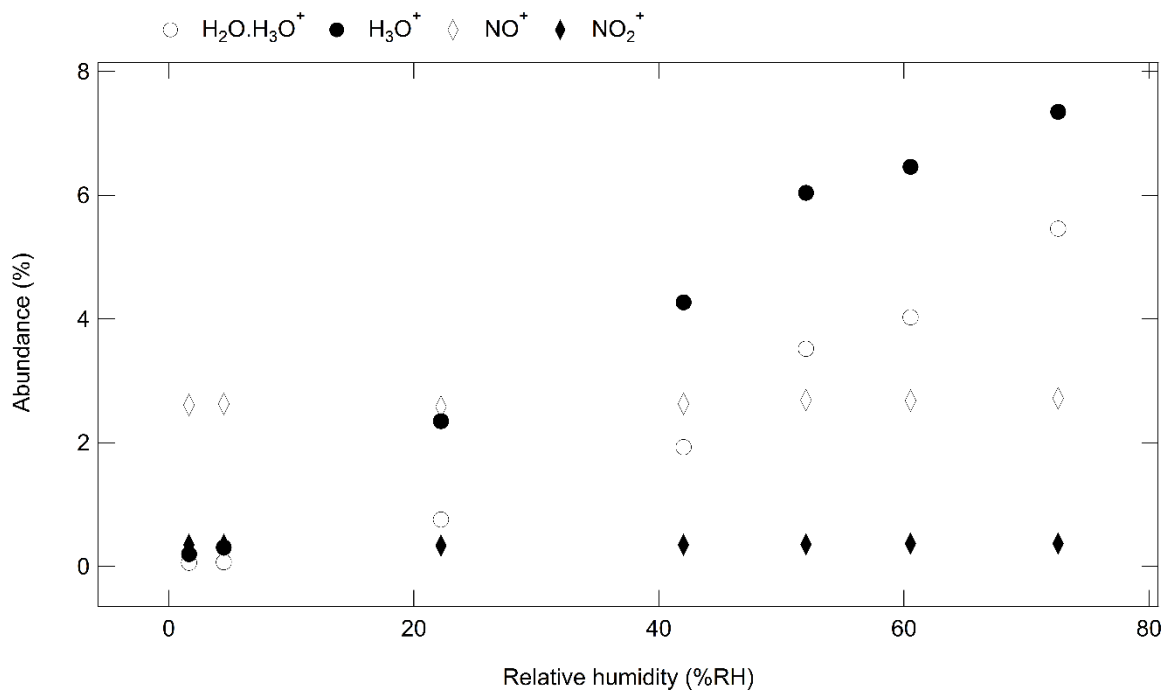
Figure 2. Plot of the signal ion abundance as a function of relative humidity. Experimental conditions: Drift T=25°C; E/N = 126 Td



238

239 **Figure 3. Plot of the signal ion abundance as a function of relative humidity. Experimental conditions: Drift T=25°C; E/N = 139 Td**

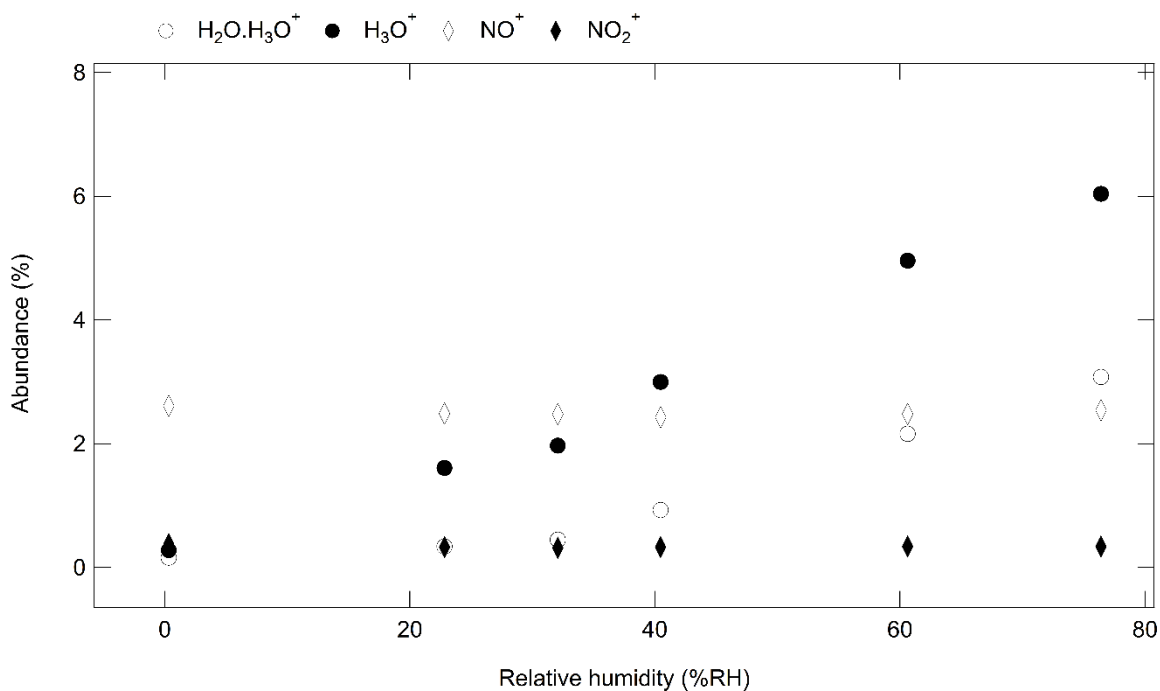
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242 **Figure 4. Plot of the signal ion abundance as a function of relative humidity. Experimental conditions: Drift T=25°C; E/N = 126 Td**

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Figure 5. Plot of the signal ion abundance as a function of relative humidity. Experimental conditions: Drift T=25°C; E/N = 139 Td

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As shown in Figure 2 to 5, the relative abundancies of H₃O⁺ (*m/Q* 19.01784), NO⁺ (*m/Q* 29.99744), NO₂⁺ (*m/Q* 45.99235) and H₃O⁺(H₂O) (*m/Q* 37.02841) were calculated relative to the molecular oxygen ion (O₂⁺) signal intensity only. On the other hand, the CH₅O⁺ (*m/Q* 33.03349), I⁺ (*m/Q* 126.90392), HI⁺ (*m/Q* 127.91175), IO⁺ (*m/Q* 142.89884), CH₄I⁺ (*m/Q* 142.93522) and HIO⁺ (*m/Q* 143.90666) ions were calculated relative to the sum of the methyl iodide mother ion (CH₃I⁺) (*m/Q* 141.92740) signal intensity and all the other fragment ions, that is, CH₃O⁺, CH₅O⁺, I⁺, HI⁺, IO⁺, CH₄I⁺ and HIO⁺. The H₃O⁺ (*m/Q* 19.01784) and O₂⁺ (*m/Q* 31.98928) ions were not counted directly. That is, to limit saturation of the electron multiplier detector of the ToF-MS system, the count rate of O₂⁺ was calculated from the count rate at *m/Q* 33.99353 (¹⁶O¹⁸O⁺) multiplied by 250. In a similar manner, the count rate of H₃O⁺ was calculated from the count rate at *m/Q* 21.02209 (H₃¹⁸O⁺) multiplied by 500. Further, the count rate of NO⁺ was calculated from the count rates at *m/Q* 30.99447 (¹⁵N¹⁶O⁺) and *m/Q* 31.00166 (¹⁴N¹⁷O⁺) multiplied by 250. All signal intensities were corrected for transmission.

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Similar to the work of Španěl and coworkers [40] on the reaction between the O₂⁺ ion and selected short chain chloroalkanes, we observe in majority a single ionic product that is CH₃I⁺. As shown in Figures 2 and 3, there is no clear dependence of the CH₃I⁺ molecular ion signal on relative humidity. However, as shown in Figures 2 to 5, the electron transfer reaction between O₂⁺ ions and the CH₃I neutral molecule results in the formation of other dissociation/association and ionization products in addition to the CH₃I⁺ mother ion. Other dissociation and ionization products include I⁺, IO⁺, HOI⁺, CH₄I⁺, CH₃O⁺, CH₅O⁺, H₃O⁺, H₃O⁺·H₂O complex, NO⁺ and NO₂⁺ ions. However, only traces (<2%) of CH₄I⁺, HIO⁺, I⁺, HI⁺, IO⁺ and CH₃O⁺ ions with no clear dependence on relative humidity are observed. The observed NO⁺ (*m/Q* 29.99744) and NO₂⁺ (*m/Q* 45.99235) ion signals are not believed to be a result of methyl iodide ionization reaction with O₂⁺ reagent ions. In a similar manner, the observed NO⁺ and NO₂⁺ ion signal counts are not believed to be a result of the electron exchange between the O₂⁺ reagent ions and background NO_x (NO_x = NO + NO₂) impurities that may be present in the nitrogen carrier gas. For example, a 1% of NO⁺ impurity within the carrier gas would correspond to a signal count rate of 10000 cps or 500 ppbv of NO (assuming 20 cps/ppb), an unrealistic value even in extremely polluted environments. On the other hand, it is known that NO⁺ and NO₂⁺ ions are produced within the ionization source of the ToF mass analyzer. That is, the nitrogen carrier gas and molecular oxygen are ionized within the ionization source as a result of a “backflush” to produce atomic N⁺ and O⁺ ions. These ions, in turn, recombine to produce NO⁺ and NO₂⁺ ions. The NO⁺ (*m/Q* 29.99744) and NO₂⁺ (*m/Q* 45.99235) ion signal abundancies do not show any humidity or *E/N* value dependence. It is possible that the observed H₃O⁺ (*m/Q* 19.01784) and H₃O⁺(H₂O) (*m/Q* 37.02841) complex ion signals are a result of ionization of H₂O by O₂⁺ reagent ions within the drift tube. However, in a similar situation listed above for the observed NO⁺ and NO₂⁺ ion

278 signals, the H_3O^+ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ ion signals are most likely a result of humidity “backflushing” into the
279 ionization source of the ToF mass analyzer to form the observed H_3O^+ (m/Q 19.01784) and $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ (m/Q
280 37.02841) ion signals. As seen in Figures 4 and 5, the H_3O^+ (m/Q 19) and $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ (m/Q 37.02841) complex
281 ion signals increase in abundance as the relative humidity is increased while other minor ion signals, namely
282 CH_4I^+ , HIO^+ , I^+ , HI^+ , IO^+ , do not show any humidity dependence. However, as shown in Figures 2 and 3, a
283 slight dependence on humidity is observed of CH_5O^+ and CH_3O^+ ions. That is, it is observed that while CH_5O^+
284 ion signal count increases with increasing humidity, the CH_3O^+ ion signal count decreases slightly with
285 increasing humidity. It should be noted that methanol is known to produce CH_3O^+ ions when the PTR-MS is
286 operated in the O_2^+ ionization mode. In turn, CH_3O^+ ions may react with H_3O^+ reagent ions to produce CH_5O^+
287 ions. However, at this point we cannot explain how (and if) methanol is produced in our system. As a result,
288 at this point we cannot explain the effect of the observed behavior of the CH_5O^+ and CH_3O^+ ion signal
289 abundance on humidity.

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291 Conclusion

292 A commercial Ionicon Analytic PTR-MS was used to study the O_2^+ reagent ion ionization process to quantify
293 gas phase methyl iodide. The electron exchange reaction between the O_2^+ reagent ion and the CH_3I molecule
294 produces a specific ion at m/Q 142 (CH_3I^+) that allows for fast and sensitive detection and quantification of
295 gas phase methyl iodide. The instrument response for CH_3I was shown to be linear in the 1 - 150 ppbV range.
296 The lowest measured CH_3I concentration was 0.23 ± 0.10 ppb. Error is $\pm \sigma$. However, this value does not
297 represent the detection limit for gas phase CH_3I . The theoretical collision rate constants are calculated based
298 on the dipole moment $\mu(\text{CH}_3\text{I}) = 1.620$ D [19] and the molecular polarizability $\alpha(\text{CH}_3\text{I}) = 7.325 \text{ \AA}^3$ [19] and
299 give $k_L = 1.24 \times 10^{-9} \text{ cm}^3\text{s}^{-1}$, $k_{\text{ADO}} = 1.73 \times 10^{-9} \text{ cm}^3\text{s}^{-1}$ and $k_{\text{CAP}} = 1.48 \times 10^{-9} \text{ cm}^3\text{s}^{-1}$. The experimental
300 collision rate, k_{exp} for the electron exchange reaction $\text{O}_2^+ + \text{CH}_3\text{I}$ is measured to be $(1.72 \pm 0.22) \times$
301 $10^{-9} \text{ cm}^3\text{s}^{-1}$. Error is $\pm \sigma$ and represents precision only. The two values agree very well with one another.
302 A good agreement between the experimentally determined rate constant for the electron exchange reaction
303 between the molecular oxygen ion and the neutral methyl iodide molecule and the theoretical values indicates
304 that the PTR-MS technique is an excellent analytical method for fast and continuous quantification of gas
305 phase CH_3I without prior calibration.
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