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Chemical Characterization of Sulphur-Iodine Thermochemical Cycle Flowstreams by Raman Spectroscopy

Raffaele Liberatore, Mauro Falconieri, Michela Lanchi, Annarita Spadoni, ENEA CR Casaccia, Italy

Abstract

The Sulphur–Iodine (S-I) thermochemical cycle for hydrogen production from water is one of the widest investigated cycles in the world. Considered the complexity of the S-I process scheme, the focus on chemical characterization of the flowstreams in the loop plant is crucial in order to fully understand chemical equilibriums involved at varying hydriodic acid: ($HI:I_2$) ratio in the mixtures and to determine HI and I_2 contents as well. Raman spectroscopy has been widely used to investigate iodine solutions, however few works deals with I_2 in HI aqueous mixtures. The aim of the present study is to use Raman spectroscopy for a rapid qualitative and quantitative characterization of the $HI–H_2O–I_2$ mixtures involved in the S-I process. At this purpose, Raman spectra of solutions with known HI and I_2 concentration have been recorded at varying I_2 and HI compositions. It has been found that the chemistry of these solutions is highly dependant on $HI:I_2$ molar ratio. For ratio up to 1:1, the dominant iodine compounds are I_3^- and its corresponding ion pair HI_3. At higher values, close to those of the hydriodic phase HIx of the Bunsen reaction, there is experimental evidence of the formation of higher polyiodine and polyiodides compounds.

1 Introduction

The Sulphur–Iodine (S-I) thermochemical cycle for hydrogen production from water is one of the widest investigated cycles in the world [1]. As it is known, the S-I cycle is based on three main sections: the Bunsen reaction, the hydriodic acid decomposition and the sulphuric acid decomposition. A very crucial step in this process concerns the optimization of the phases separation occurring in the Bunsen section and the consequent hydriodic phase HIx purification. Up until now, the improvement of operative parameters in those steps have been attained mainly by experimental tests, but the relationship between the chemico-physical behaviour of these solutions and the chemical structures of the iodine compounds involved are not yet fully understood.

The literature have earned a wide attention [2] over iodine chemistry. Despite this, few works were dedicated to the experimental determination of the chemical species contained in aqueous solutions of iodine I_2 and hydriodic acid HI. Improving this understanding is the basis for the present experimental investigations and Raman scattering is a proper probe of structure over aqueous solutions because it is sensitive to both local and long-range chemical order, so it is an effective diagnostic mean for short and long iodine compounds. One of the major controversy regarding $HI-I_2$ aqueous solutions is about the existence or not of I5- or heavier polyiodide and the presence of polyiodine forms. Calabrese [3] suggested the formation of triiodide ions I_3^- and other polyiodine species, designated as I2x, where x=2,3 etc, stabilized by H^+ ions in the solution and does not support the formation of polyiodide ions such as I_5^- and I_7^-. Milne [4] findings were consistent with Calabrese. Raman spectroscopy was used to identify the various iodine species present in aqueous solutions of I_2 in HI (1:1 mole ratio). It has been shown that the changing of Raman spectra with changing concentration is a result of ion-pairing $H^+I_3^-$ caused by interaction between H^+ and I_3^- and not from vibrational modes of I_2 or I_5^-. However, Ramos-Sànchez [5] was in contrast and suggested that the major iodine containing species were the triiodide anion I_3^-, and two other compounds such as I-(I_2), and I-(I_2)$_2$.

The aim of the present work is to understand chemical equilibriums existing in HI-I_2 aqueous solutions and whether I_3^- or higher polyiodide and polyiodine species are present. At this purpose, Raman spectra of HI-I_2-H_2O solutions with known HI and I_2 concentration were recorded over a range of HI concentrations c(HI) from 1 to 7.6 M varying I_2 content c(I2) from 0.2 to 15 M. Since, in this case, the peak intensity ratio is proportional to the concentration of the species that originates the peak, the course of the peak intensity ratio obtained experimentally was compared to the calculated concentration ratio of polyiodides and polyiodines species hypothesised. This comparison has furnished the evidence of the existing species in solution.

2 Experimental

HI aqueous solutions and I_2 in pellets were purchased from Sigma–Aldrich. Ultra pure water (oxygen free) were used. Standardized sodium thiosulfate ($Na_2S_2O_3$) solution and standardized sodium hydroxide (NaOH) solution were supplied by Carlo Erba Reagents Company in order to determine by titration I_2 and HI content respectively. Raman measurements were carried out using an He-Ne: 633 nm laser radiation (incident laser power at the sample ~5 mW) which was directed onto the samples through an optical microscope objective and collected along the same optical pathway in a backscattering mode. Raman spectra were obtained using a Notch holographic filter to attenuate the laser Raylight scattering. The remaining light was focused through the entrance slit of a 500 mm single monochromator and the spectrum was measured by a charge-coupled device (CCD) detector. Overlapping peaks has been deconvoluted assuming Gaussian line shapes.

3 Results and Discussion

Peak assignment for aqueous solutions containing iodine compounds is still not completely understood. This is mostly due to the fact that Raman vibrational modes of possible iodine species are quite close and tend to overlap: each band can't be assigned univocally to each compound. In general, for a linear I_3^- ion the bands obtained in a Raman spectrum derive from the v1 (symmetric stretching), v2 (deformation) and v3 (asymmetric stretching) modes and can be expected at approximately 110, 50-70 and 130-140 cm-1 respectively [2]. Theoretically, v2 and v3 are formally forbidden Raman modes and arise from selection rules departures according to symmetry lowering. In table 1 are summarized the Raman vibrational frequencies observed experimentally with the relatives peak assignments for I_3^- and I_5^- in various solutions at varying concentrations[6-9].

Table 1: Raman vibrational frequencies observed experimentally for I_3^- and I_5^-.

compound	wavenumber (cm-1)	mode designation	remarks
	70-80	v2, bending deformed linear I3-	various solutions
	103-114	v1, symmetric stretching linear I3-	various solutions
I3-	125 145 143-152 150	v3, asymmetric stretching linear I3- v3, asymmetric stretching linear I3- v3, asymmetric stretching linear I3- 2v2, Fermi Resonance	(dbcr)I3 in the solid state1 (R3S)I3 solid2 various solutions HI-I2 solutions (1:1) in water
	170-172	v I-I stretching ion-pair HI3	HI-I2 solutions (1:1) in water
	164	v1, linear I5-	
I5-	140 155	v2, bent I5- v1, linear I5-	Polyvinylalcool thin film (iodine doped PVA)
	170	I2 v1 mode I-.2I2 or I3- I2	(R3S)I3 liquid2
	168	I2 v1 mode L-shaped I5-	(dbcr)I51

1,(dbcr)= dibenzo-18-crown-6
2,(R3S)I3= alkylsulfur triiodide

Extra spectral features in the Raman spectra were found at 150 and 172 cm-1 by Milne [4] investigations over HI/I_2 solutions (1:1 mole ratio) ranged from 0.1 M up to 3,3 M. The 150 cm-1 band was assigned to Fermi resonance between v1 and 2v2, while the 172 cm-1 band was attributed to the I-I stretch of the ion-pair $H^+I_3^-$, designated as HI_3. Milne envisioned the change in I-I bonding in triiodide in terms of strengthening of one of I-I bonds (D1) lying at 172 cm-1 and weakening of the other (D2) which would be shifted to 84 cm-1, according to the scheme 1.

Scheme 1: ion pair formation I-I-I + H+ → I-I------I- H+ , where I-I =D1; I------I- =D2

The Raman spectra of HI-I_2-H_2O solutions were measured over a range of HI concentrations c(HI) from 1 to 7.6 M (1-2.3-3.6-4.9-6.2-7.5 M) at I_2 fixed concentration of 0.2 M and varying I_2 content c(I_2) from 0.2 to 15 M (0.2-1.68-4.47-6.7-8.3-10-11.5-13-15.8-30 M) at HI fixed concentration of 7.6 M.

The spectra of the HI-H_2O solutions for HI concentrations c(HI) from 1 to 7.5 M, shown in figure 1A, are representative of the spectra as observed. These solutions contain a very small concentration of I_2, determined by titration, arising from the photocatalysed oxidation of HI solutions: $2HI+1/2O_2=I_2+H_2O$. The spectra consist of a strong peak at 114 cm-1, a shoulder at 140 cm-1, a peak at 162 cm-1 and a weak line at 220 cm-1. In figure 1B are reported the normalized intensities on the basis of the peak at 114 cm-1: it can be noted that as the concentration c(HI) increases, the peak intensity at 162 cm-1 grows into the spectrum. According to previous findings, it can be seen that the peak at ca. 114 cm-1 is attributable to triiodide I_3^- symmetric v1 stretch. The peak at 140 cm-1 has been variously attributed to linear I3- asymmetric stretching, v3 or to Fermi resonance between v1 and 2v2; but in any case this peak is not diagnostic to discriminate between I_5^- and I_3^-. The peak at 162 cm-1 could be assigned to the νI_2 mode in a I_5^- configuration or to the νI_2 mode in a triiodide ion-paired HI_3, as it is shown in scheme 1.

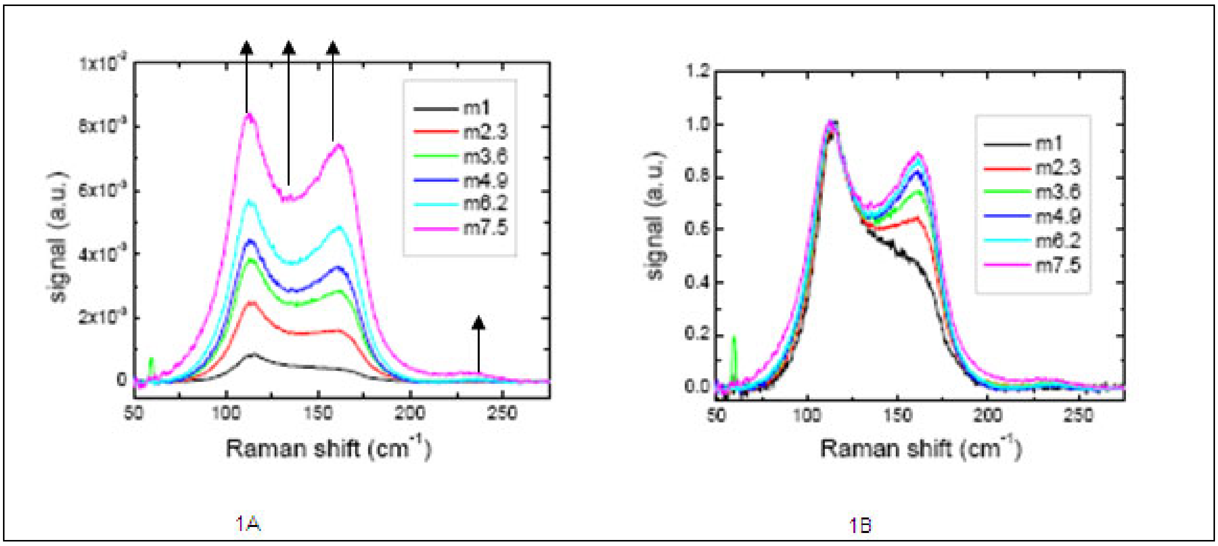

Figure 1: **Raman spectra of HI-H_2O solutions at varying HI concentrations and fixed I_2 content of 0.2 M.**

As it is known the area of a band is correlated to the concentration of the species that generates the peak. In this case, the concentration of the chemical species in the solution has been related to the intensity of the peaks, because it has been seen by the deconvolution of the bands obtained that the forbidden mode at 140 cm-1 is not very intense and does not interfere significantly with the area of the peaks at 114 cm-1 and 162 cm-1. For the calculation of the concentration of the existing species in solution, the following equilibrium existing in the solutions have been considered [10,11]

Polyiodide In- formation reactions: $I^- + I_2 \rightarrow I_3^-$ (1)
$I_3^- + I_2 \rightarrow I_5^-$ (2)
$2I_3^- \rightarrow I^- + I_5^-$ (3)
Ion pair HIn dissociation: $HI \rightarrow H^+ + I^-$ (4)
$HI_3 \rightarrow H^+ + I_3^-$ (5)
$HI_5 \rightarrow H^+ + I_5-$ (6)
Polyiodine I2x formation: $2I_3^- \rightarrow I_6^-$ (7)
I2x +H+→ I2xH+ x=2,3 (8)
Charge transfer complex: $I_2 + H_2O \rightarrow$ I2…H_2O (9)
HI dissociation: $5H_2O + HI \rightarrow (5H_2O,H+)$ +I- (10)

An estimate of the concentration of major species arising from the above equilibriums has been made using the charge and mass balance equations according to Milne's assumptions [4]. Species such as I-, I_3^-, I_5^- and their respective H^+In^- ion pairs, designated as HIn and I_{2x}

species have been taken into account. The ratio of the concentrations of these compounds has been compared to the change in I162/I114 ratio observed in Raman Spectra.

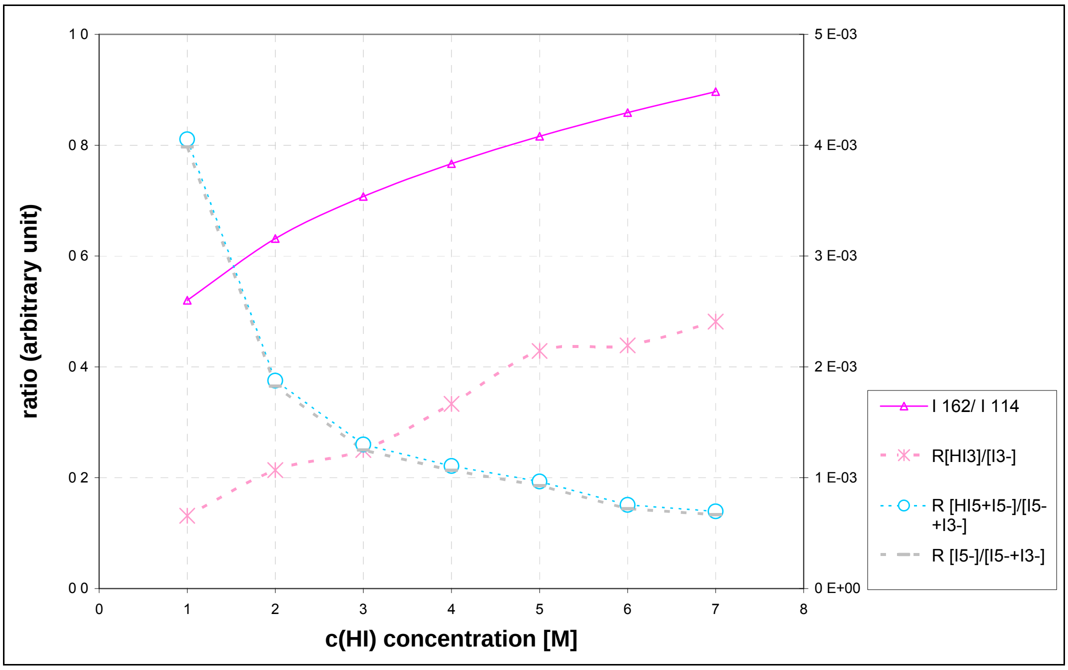

Figure 2: Experimental I162/I114 ratio and calculated iodine species concentrations ratio against cHI concentration.

In figure 2 are shown the trends of “I_5” and “I_3” species, designated as R[HI5]+[I5]/[I5-]+[I3-] and the ratio of [HI3] to [I3-], R[HI3]/[I3-] as a function of c(HI) concentration. It could be noted that its trend reflects the change of R[HI3]/[I3-] with c(HI) concentration: the increase of I162/I114 ratio suggests that the intensity of the bands attributed to I_3- (114 cm-1) decrease at the expense of that assigned to the vI_2 mode from triiodide ion-paired HI_3. It could be concluded that at low iodine concentration the peak at 162 cm-1 stems for triiodide ion-paired HI_3. Further evidence for these conclusions comes from ion to ion interaction’s considerations: the more c(HI) is high, the less the I^- and I_3^- are rounded by H_2O molecules for solvatation and the more triiodides in solution tends to form the corresponding ion-pair. The weak broad peak at 220 cm-1 is ascribed to 2v1 Fermi Resonance [2].

The spectra of the HI-H_2O-I_2 solutions for I_2 concentrations c(I2) ranging from 0 to 10M with I_2:HI ratio corresponding to 0:1, 0.2:1, 0.6:1, 1:1, 1.3:1 to 15 M at HI fixed concentration c(HI) of 7,5 M, are shown in figure 3. If I2:HI molar ratio is lower than 1:1, the spectra obtained are similar to those obtained for HI-H_2O solutions, showed in figure 1. In figure 4 the course of I162/I114 ratio is shown against I2:HI ratio: it could be noted that the line that best reflects this behaviour is the one corresponding to the ratio R[HI3]/[I3]. It can be concluded that in the range of HI:I_2 concentration up to 1:1 no polyiodine higher than I_3^- and HI_3 are formed. These findings were consistent with Calabrese to the extent that species such as I_5^- or I_7^- are not formed in this range of iodine concentration. Additionally, these results agree with Milne’s observation which showed that the existing iodine species in aqueous solutions of I_2 in HI

(1:1 mole ratio) are mainly I_3^- and the HI_3 ion pair neglecting higher polyiodides such as I_5^- or polyiodines such as I_6^-.

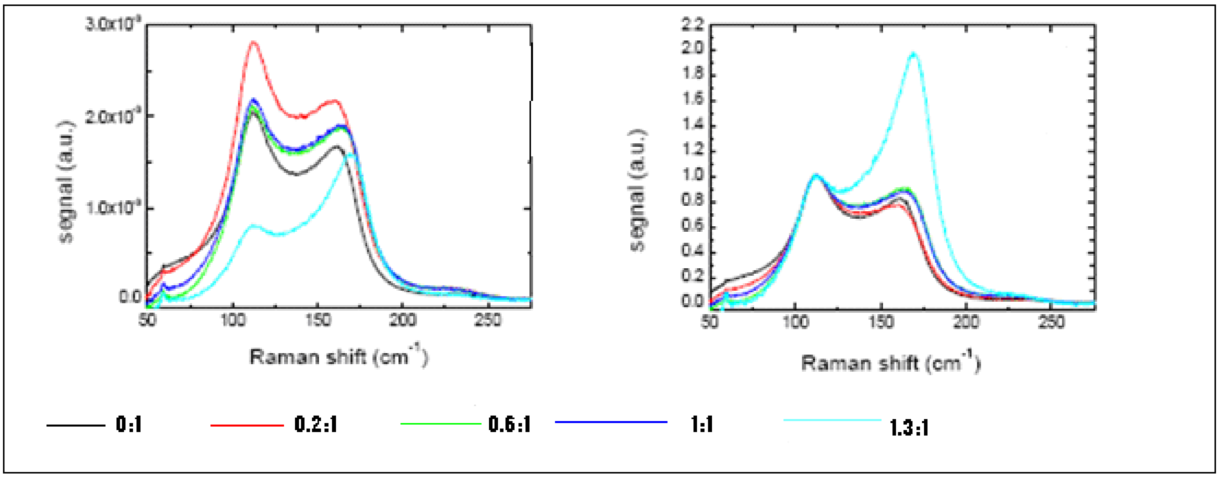

Figure 3: **Raman spectra of HI-I_2-H_2O solutions at varying I_2 concentrations and fixed HI content of 7,6 M.**

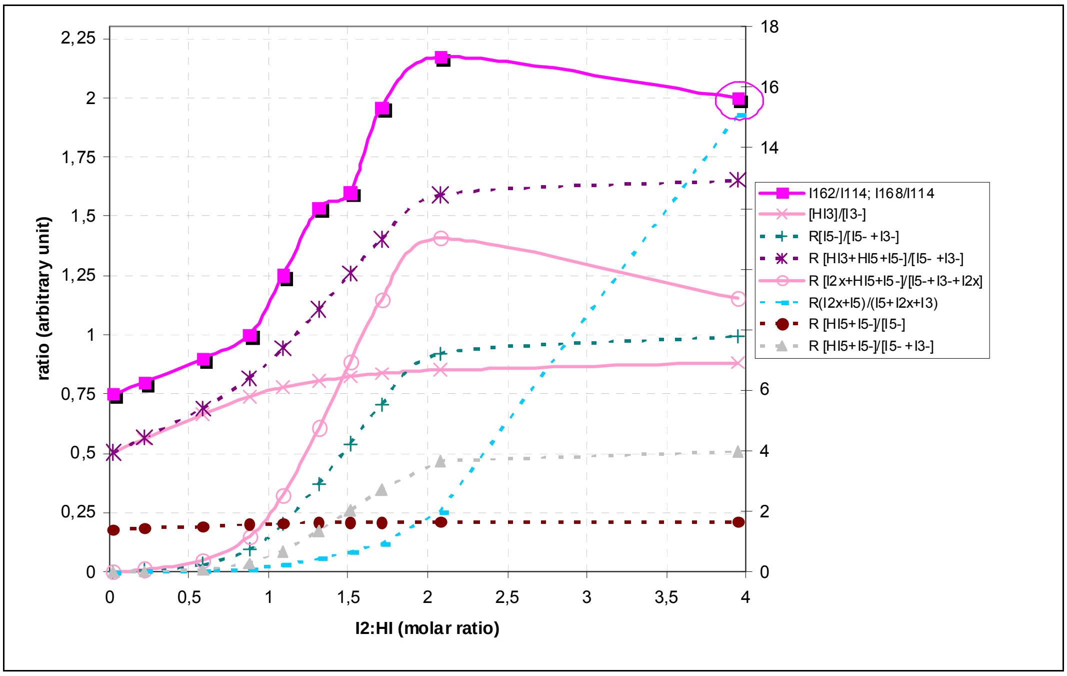

Figure 4: **Experimental I162/I114 ratio and calculated iodine species concentrations ratio against I_2:HI molar ratio.**

However, for I_2:HI ratios higher than 1:1, it can be observed (figure 3) that the band at 162 cm-1 is shifted to higher wavelength at 168 cm-1 and peak registered at 220 cm-1 becomes weaker/disappear. In figure 3 are reported the normalized intensities on the basis of the peak at 114 cm-1: as the concentration c(I2) increases, the peak intensity at 162 and 168 cm-1 grows into the spectrum. In figure 4 have been reported I168/I114 ratios as a function of I_2:HI ratios. The value corresponding to the I_2:HI ratio of 4:1 has been obtained from Sanchez determinations [5]. It could be seen that the course of R [HI3]/[I3-] no longer matches the experimental I168/I114 trend as it happened for lower I_2:HI ratios: other chemical species than I_3^- and HI_3 must be taken into account. The peak assignment has been attempted from the comparison of experimental I168/I114 ratio with the ratio of the concentrations of chemical species deriving from equilibriums 1 to 5 , designed as “I5”, “I3” and “I2x” species. Several hypothesis have been proposed, as depicted in figure 4. It could be noted from figure 4 that the line that best reflects the experimental behaviour of I168/I114 ratio is the one corresponding to the ratio R[I2x+HI5+I5]/[I5-+I3-+I2x] for which I2x, I_5^- and HI_5 species must be considered.

4 Conclusions

It has been found that the chemistry of these solutions is highly dependant on I_2:HI molar ratio. For ratio up to 1:1, the dominant iodine compounds are I_3^- and its corresponding ion pair HI_3. However, in the range of I_2:HI concentrations higher than 1:1, polyiodine and polyiodide species must be taken into account: I_5^- and the corresponding HI_5 ion pair are formed while the HI_3 ion pair could be neglected. Additionally, the formation of polyiodine species such as I2x has been evidenced: at higher iodine concentration the cluster formation among the I_2 molecules becomes more favoured. Furthermore, since a correlation between I_2:HI ratio content and intensity peak ratio has been found, it is theoretically possible to determine HI concentration by comparing the experimental peak area value with the value in a matrix of data based over standardized solution with known concentration. This will be the object of further investigations.

References

[1] A. Le Duigou et al. An EC funded search for a long term massive hydrogen production route using solar and nuclear technologies. Int J Hydrogen Energy 2007;32:1516–29.

[2] Per H.Svensson et al. Synthesis, Structure, and Bonding in Polyiodide and Metal Iodine-Iodine Systems, Chemical Reviews, 2003, Vol. 103, No. 5

[3] V. T. Calabrese and A. Khan, Polyiodine and Polyiodide Species in an Aqueous Solution of Iodine +KI: Theoretical and Experimental Studies, 2000, J.Phys. Chem. A, Vol. 104 No.6, pp1287-1292

[4] J.Milne, A Raman spectroscopic study of the effect of ion pairing on the structure of the triiodide and tribromide ions, Spectrochimica Acta, 1992, Vol. 48A, No. 4, pp 533-542

[5] Ramos-Sanchez et al. Chemistry of the Bunsen section of the sulphur-iodine thermochemical cycle: in situ Raman characterization of the HIx and H2SO4 phases. 17 th WHEC 2008, Brisbane

[6] H.Sato, F.Hirata, A.B.Myers, Theoretical study of the solvent effect on triiodide ion in solutions, J.Phys.Chem.A, 1998,102,2065-2071

[7] J.H Z. dos Santos et al. High Pressure Fourier Transform micro-Raman Spectroscopic investigation of diiodine-heterocyclic thioamide adducts Spectrochimica Acta Part A, 58 (2002) 2725-2735

[8] F.W. Parret and N.J Taylor , J.Inorg.Nucl.Chem 32 2458 (1970)

[9] W. Kaya, N.Mikami, Y.Udagawa, M.Ito, Resonance Raman effect of I3- ion by ultraviolet laser excitation, Chem Phys Letters 16,151,(1972)

[10] R. Liberatore, A. Ceroli, M. Lanchi, A. Spadoni, P. Tarquini, Experimental vapour–liquid equilibrium data of HI–H2O–I2 mixtures for hydrogen production by Sulphur–Iodine thermochemical cycle, Int. J of Hydrogen Energy, 2008, 33: 4283 – 4290

[11] M. Lanchi, A. Ceroli, R. Liberatore, L. Marrelli, M. Maschietti, A. Spadoni, P. Tarquini, S–I thermochemical cycle: A thermodynamic analysis of the HI–H2O–I2 system and design of the HIx decomposition section , Int. J of Hydrogen Energy, 2009, 34: 2121–2132.