

## The Dimerisation of $[I_2^+]$ to $[I_4^{2+}]$ in Fluorosulphuric Acid Solution: $^{127}I$ Mössbauer Spectroscopic Evidence

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Iodine-127 Mössbauer spectroscopic data are used to show that at low temperature, the  $[I_2^+]$  cation in fluorosulphuric acid dimerises to the  $[I_4^{2+}]$  cation; the frozen solution data are compared with those for authentic  $[I_4^{2+}]$  salts.

The paramagnetic  $[I_2][Sb_2F_{11}]$  has been characterised by a variety of techniques.<sup>1-3</sup> It had been noticed that solutions of this compound undergo a startling colour change, from an intense blue to red-brown, on cooling to low temperature.<sup>6</sup> The cause of this colour change was unknown but it was speculated that the red-brown species could be an  $[I_4^{2+}]$  cation. We here present spectroscopic evidence for the existence of this cation in solution.

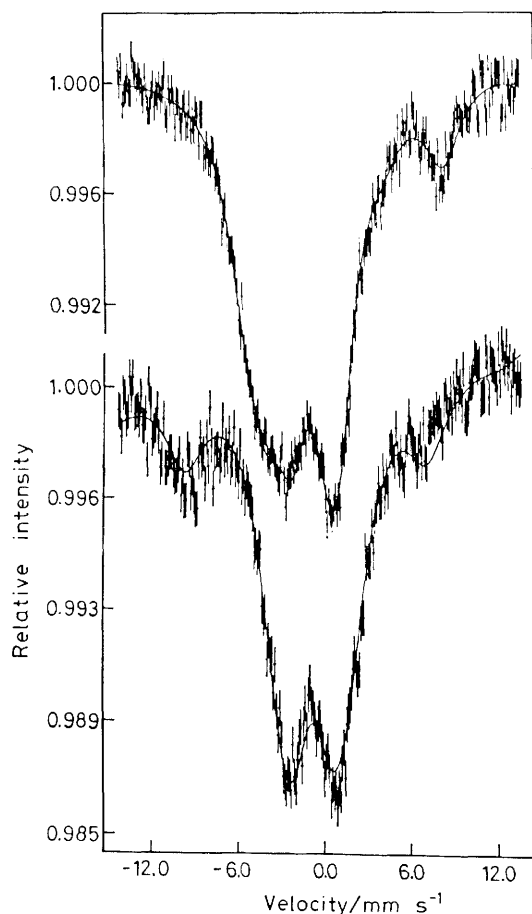
**Table 1.**  $^{127}I$  Mössbauer parameters of  $[I_2][Sb_2F_{11}]$ ,  $[I_2][Sb_2F_{11}]$  in  $HSO_3F$ , and some  $[I_4^{2+}]$  salts.

Compound	Isomer shift <sup>a</sup> /mm s <sup>-1</sup>	$e^2q^{127}Q_0/h$ /MHz	$\Gamma$ /mm s <sup>-1</sup>	$\eta$
$[I_2][Sb_2F_{11}]$	-0.68(1)	-1951(11)	1.72(7)	0.19(2)
$[I_2][Sb_2F_{11}]/HSO_3F$	-0.73(2)	1969(17)	1.99(9)	0.88(2)
$[I_4][AsF_6]_2$	-0.81(2)	2007(15)	1.78(8)	0.85(2)
$[I_4][AsF_6]_2^b$ (amorphous)	-0.71(1)	1933(20)	1.43(5)	0.84(1)
$[I_4][SbF_6][Sb_3F_{14}]$	-0.84(2)	1951(13)	2.01(5)	0.91(1)

<sup>a</sup> Isomer shifts are measured relative to KI as zero. <sup>b</sup> The reaction of  $I_2$  with  $AsF_5$  in  $SO_2$  solvent produced crystalline  $[I_4][AsF_6]_2$  while the same reaction in  $SO_2ClF$  resulted in immediate precipitation of an amorphous powder whose Mössbauer spectrum is consistent with  $[I_4^{2+}]$ .

$[I_2][Sb_2F_{11}]$  was prepared by the established procedure<sup>1</sup> and its  $^{127}I$  Mössbauer spectrum was recorded<sup>5</sup> and analysed<sup>7</sup> to yield the parameters listed in Table 1. The quality of this spectrum (see Figure 1) is superior to that reported previously and this gives more accurate parameters than the earlier analysis.<sup>5</sup> Of particular importance to the subsequent discussion is the location of the weak line (transition No. 2 in the energy level scheme)<sup>8</sup> at *ca.* +8.5 mm s<sup>-1</sup> which establishes that the iodine quadrupole coupling constant,  $e^{127}Q_0V_{zz}/h$  is negative in sign. Since  $e^{127}Q_0$  is negative,  $V_{zz}$  is therefore positive and indicative of an excess of electron density in the *xy* plane compared to the *z* direction along the I-I bond.

A solution of  $[I_2][Sb_2F_{11}]$  in pure  $HSO_3F$  was syringed into a Kel-F sample holder and cooled slowly until the intensely blue solution had become red-brown in colour. The sample was then immersed completely in liquid nitrogen, placed in the Mössbauer cryostat, and its spectrum was recorded at 4.2 K. This procedure was repeated on a second solution to ensure that the data obtained were reproducible. Fluorosulphuric acid forms a good glassy matrix and no solid appears to be precipitated during this procedure. The spectrum obtained from the frozen solution is quite different from that of the pure solid (see Figure 1) indicating that a dramatic change in the iodine environment has occurred. The spectrum is much more symmetric than that of the solid  $[I_2][Sb_2F_{11}]$  and indicates that



**Figure 1.** The  $^{127}\text{I}$  Mössbauer spectrum of  $[\text{I}_2][\text{Sb}_2\text{F}_{11}]$  (upper) and that of a frozen solution of  $[\text{I}_2][\text{Sb}_2\text{F}_{11}]$  in  $\text{HSO}_3\text{F}$  (lower) at 4.2 K.

the asymmetry parameter,  $\eta$ , is approaching unity. Computer analysis yields a value of 0.88 compared to 0.19 for the pure solid. This means that the near three-fold symmetry about the I-I bond in the  $[\text{I}_2]^+$  cation has been destroyed. Analysis of this spectrum also reveals that the sign of the quadrupole coupling constant is positive, though with an  $\eta$  value approaching 1, the sign of the coupling constant has less meaning.

These parameters are typical of an iodine atom in either a rectangular co-ordination with the non-bonded electron pairs along an axis perpendicular to the plane of the molecule, as

in  $\text{K}[\text{ICl}_4]\text{H}_2\text{O}$ <sup>8</sup> and salts of  $[\text{ICl}_2]^+$ ,<sup>9</sup> or a pentagonal bipyramidal co-ordination such as in  $\text{PhI}(\text{OAc})_2$ <sup>10</sup> where the non-bonded electron pairs are in the axial positions. Such changes could be brought about by the interaction of two  $[\text{I}_2]^+$  cations to produce an  $[\text{I}_4^{2+}]$  cation so that each iodine would have one short and one longer interaction to other iodine atoms. Additional interactions to each iodine in the same plane from the anions or solvent molecules would be necessary in order to produce the observed positive quadrupole coupling constant.

That this dimerisation in solution does occur is confirmed by a comparison (Table 1) with the Mössbauer parameters of a series of  $[\text{I}_4^{2+}]$  salts which have been prepared and characterised by Gillespie *et al.*<sup>11</sup> The frozen spectrum is virtually identical to those of the solid  $[\text{I}_4^{2+}]$  compounds which have a rectangular arrangement of iodines with additional weak interactions to the iodines from the anions. Minor differences in Mössbauer parameters between the various salts and the frozen solution sample are undoubtedly due to the interaction of the dication with the different anions or solvent molecules. In all cases there are very large asymmetry parameters and positive quadrupole coupling constants consistent with the observed geometry at iodine.

The Natural Sciences and Engineering Research Council of Canada are thanked for financial support.

Received, 2nd June 1982; Com. 620

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