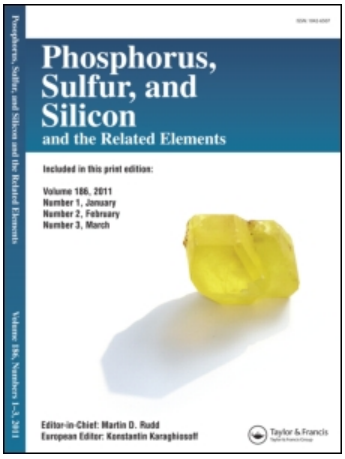


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# Solid-State and Solution FT-Raman Spectra of the Tetraiodine Dication $I_4^{2+}$

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# SOLID-STATE AND SOLUTION FT-RAMAN SPECTRA OF THE TETRAIODINE DICATION $I_4^{2+}$: IMPLICATIONS FOR THE CLAIMED EXISTANCE OF $I^+$ IN $SO_2$ SOLUTION

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Abstract $I_4^{2+}$ is the only known cyclic homopolyatomic cation or anion of iodine. It has a rectangular planar structure which may be thought of as containing two $I_2^+$ units joined by a weak $\pi^*$-$\pi^*$ 4 centre 2 electron bond.[1] In this paper we report our FT-Raman spectra of $I_4^{2+}$, which conflict with those published by Gillespie *et al.*,[1] and present evidence that the peaks attributed to a species containing iodine in the +1 oxidation state are in fact due to $I_4^{2+}$.



Early work by Arotsky et al.[2] reported the presence of an $I^+$ species in blue solutions of iodine in 65% oleum. Gillespie *et al.* disproved this by showing that the blue colour was actually due to $I_2^+$.[3] Gillespie also showed that cooling a blue solution of $I_2^+$ in $HSO_3F$ to -78 °C resulted in a red solution, which he claimed to be $I_4^{2+}$, and at the time proposed that its structure should be tetrahedral or an acyclic chain, but not square planar.[3] The crystal structure of $I_4(AsF_6)_2$ [1] was later determined to be rectangular planar, consisting of two $I_2^+$ (d = 2.575 Å) units joined by two weak $\pi^*$-$\pi^*$ bonds (d = 3.270 Å).[1]

In the course of investigating the vibrational spectra of $S_2I_4^{2+}$, we obtained very good quality FT-Raman spectra of all the known homopolyatomic cations of iodine. FT-Raman spectroscopy has been instrumental in obtaining spectra of these dark coloured salts, which were difficult, if not possible to obtain by classical laser Raman spectroscopy. Our FT-Raman spectrum of $I_2Sb_2F_{11}$ agreed with Gillespie's observation of a single peak due to the cation at 238 $cm^{-1}$.[1] However, our FT-Raman spectrum of solid $I_4(AsF_6)_2$ showed a single peak at 199 $cm^{-1}$, which differs significantly from the 232 $cm^{-1}$ observed in Gillespie's resonance Raman spectrum of $I_4(AsF_6)_2$ This led to our further investigation of the solid state and solution spectra of $I_4^{2+}$, and of Gillespie's claim that an '$I^+$' species existed in $SO_2$ solution.

Gillespie *et al.*[1] stated that they were unable to observe $I_4^{2+}$ in theirroom temperature resonance Raman solution spectra. They stated that $I_4^{2+}$ dissociated to $I_2^+$, which was unstable in $SO_2$ at r.t. and disproportionated as shown in Equation (1), implying

$$I_4^{2+} \rightleftharpoons 2\ I_2^+ \rightleftharpoons {}'I^{+}{}' + I_3^+ \qquad (1)$$

the existance of a species containing iodine in the +1 state (197 $cm^{-1}$), based on the Raman spectrum of $I(SO_3F)I$, which does contain iodine in the +1 state.[4] In contrast, our FT-Raman spectra of $I_4^{2+}$ in $SO_2$ solution show only $I_4^{2+}$ and $I_2^+$. Our FT-Raman spectra of $I_2Sb_2F_{11}$ in $SO_2$ showed essentially only $I_2^+$, with a very small peak attributable to $I_4^{2+}$. Also in contrast to Gillespie's results, we have never observed $I_3^+$ in our solid state or solution FT-Raman spectra of $I_2Sb_2F_{11}$ or $I_4(AsF_6)_2$. Based on our evidence, appears unlikely that an $'I^{+}{}'$ containing species exists in $SO_2$ solution. The identity of the peak at 232 $cm^{-1}$ in Gillespie's resonance Raman spectra remains unknown. A weighted average of 220 $cm^{-1}$ between the symmetric stretch (FT-Raman, 199 $cm^{-1}$) and the asymmetric stretch (FT-IR, 240 $cm^{-1}$) of $I_4^{2+}$ is slightly lower than one might expect (232 $cm^{-1}$) from a simple iodine-iodine stretching frequency - bond length correlation. However, the rectangular planar $I_4^{2+}$ is lattice stabilized, and the shape of the potential energy surface is probably affected by the strong electrostatic repulsion factor between the two $I_2^+$ dimers of $I_4^{2+}$(estimated to be +380 $kJ \cdot mol^{-1}$). Hence, values of the force constants would be decreased, resulting in a lowering of the observed frequency. A similar effect has been shown for $S_2O_4^{2-}$, in which the experimental vibrational spectra could only be reproduced by calculations when solid state electrostatic effects were accounted for.[5]



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