Raman spectroscopy of strontium tetraiododiargentate octahydrate, SrAg₂I₄·8H₂O, and its aqueous solutions

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Raman spectroscopy of SrAg₂I₄·8H₂O reveals three low frequency vibrations at 25, 65, and 105 cm⁻¹. The 25 cm⁻¹ line is extremely intense, has a narrow linewidth, and is assigned as a vibration of the Ag-I bond. This mode persists in the melt, verifying the hypothesis of Geller and Dudley that AgI entities are present in the saturated solution. Autocorrelation spectroscopy measurements on the saturated solutions do not reveal diffusion of these complexes; however, similar measurements on diluted solutions show diffusion of precipitated AgI.

INTRODUCTION

Evidence for long-range order in aqueous solutions has been presented recently for several systems. Neutron scattering experiments on highly concentrated solutions of NiCl₂ revealed unusually strong peaks in the nickel–nickel correlation function; and Raman spectroscopy of the same solutions revealed the development of a broad vibrational peak at 220 cm⁻¹ as concentrations were increased to 4 mol/l. Subsequent modeling has provided a detailed picture of the probable short-range structure in NiCl₂ aqueous solutions. However, autocorrelation spectroscopy by our group showed that Gaussian diffusion of 2 Å particles was dominant in such solutions, and that no long-range structure was present on a 10 μs time scale. We suggested that the vibrational spectra near 220 cm⁻¹ reported by Fontana might be due to Ni–Cl bonds persisting in the solutions and offered evidence that this bond is covalent. The presence of NiCl₂ molecules in aqueous solutions over long time periods was effectively proved false, however, by subsequent tracer diffusion studies. These show that the diffusion constants for chlorine and nickel are quite different in the solutions. (This does not rule out diatomic NiCl molecules, however.) There has not yet emerged a simple description of NiCl₂ solutions which explains all of these experimental results. It would appear that there is order over distances many times greater than the average Ni–Ni separation in solution, that this order is maintained over a time scale long compared with the time for one vibration at 220 cm⁻¹ (i.e., 1.5 × 10⁻¹³ s), but destroyed and randomized over time scales short compared with the response of the autocorrelation spectroscopy system (10 μs).

In the present work we have employed two of the spectroscopic tools mentioned above, Raman spectroscopy and autocorrelation techniques, to probe a second system in which long-range order in aqueous solution has been hypothesized. This system is strontium tetraiododiargentate octahydrate, SrAg₂I₄·8H₂O, which was recently the subject of structural determination by Geller and Dudley. In their work they found that the iodine ions lay at the corners of tetrahedra, with a silver ion in the center of each tetrahedron; a chain structure exists along the crystallographic c axis in which the AgI tetrahedra share edges. This structure is the same as in the red phase of mercury iodide, in regard to the AgI or Hgl tetrahedra.

The primary motivation for the examination of SrAg₂I₄ hydrates is the general interest in silver compounds as solid state electrolytes. It has been found that anhydrous compounds of strontium or barium halides with silver (or copper) halides are unobtainable at atmospheric pressure. It has been speculated that this is due to particular coordination requirements of the alkaline earth ions. Consequently, SrAg₂I₄·8H₂O has been chosen for study; although it is not itself an electrolyte, its ease of formation may provide information on the general problem of AgI double salt crystallization. Our data show that iodine–strontium bonds, through the waters of hydration, are weak, as expected, but the Ag–I bonds are very strong.

STRUCTURE

The most probable structure of SrAg₂I₄·8H₂O is given, with diagrams, in Ref. 7. Chains of AgI tetrahedra are weakly bound to Sr ions via hydrogen bonds involving the waters of hydration. By comparison, the Ag–I bonds within the tetrahedra are strong, yielding Ag–I bond lengths of 2.9 Å. This is the same as in pyridinium silver iodide, in Ag₂licable₄H₂N₂, in Ag₂licable₄H₂N₂, and in Ag₂licable₂H₂N₂. Geller and Dudley hypothesized that “it is probable that the saturated solution itself contains [Sr(H₂O)₆]²⁺ and AgI₂–chain entities.” The primary aim of the present spectroscopic work was to examine this hypothesis. As described in the following sections, our data indicate that these entities do indeed exist in the saturated solution.

EXPERIMENTAL

Our specimens were grown by S. Geller and G. F. Ruse from saturated solutions of SrI₂ which were subsequently saturated with AgI. The Raman spectra of these crystals were obtained at 514, 5 nm with an argon ion laser at typical power levels of 50 mW. Several different samples were examined, with identical results. Specimens were typically a few millimeter on a side. The spectra were obtained at room temperature (295 K), using a right-angle scattering geometry. Detection was
by means of a 0.85 double grating spectrometer, cooled RCA 31034A phototube, and rate meter. Typical spectra are shown in Fig. 1. Two broad weak scattering features are shown at about 65 and 105 cm\(^{-1}\), and a strong line is manifest at 25 cm\(^{-1}\). No spectra were found at higher energies, although a particular effort was made to search the spectral region in which water vibrations are usually found (1000–4000 cm\(^{-1}\)). The 25 cm\(^{-1}\) mode is extremely intense; the absence of other modes is largely a measure of the optical quality of the specimens. Because of the limited optical quality, polarization measurements were relatively unsuccessful, with the same three vibrational lines observed with nearly the same relative intensity for all sample geometries and polarizations.

Special attention was paid to the strong 25 cm\(^{-1}\) line. We tentatively assign it as a vibration of the Ag–I bond. This assignment is consistent with the low frequency modes seen in similar crystals. A mode at about the same frequency is present\(^6\) in red HgI\(_2\), which has the same edge-sharing iodine tetrahedral structure as SrAg\(_2\)I\(_4\)-8H\(_2\)O, and in Ag\(_{36}\)I\(_{16}\)W\(_4\)O\(_{32}\),\(^{13}\) where the observed temperature dependence allows its assignment as a vibration of silver ions against the iodine lattice. The large intensity is also compatible with that expected for silver ions, on the basis of comparisons with other silver iodide compounds.\(^{14}\)

A second possibility for the origin of the 25 cm\(^{-1}\) mode is libration of the waters of hydrogen. This is less likely to result in such narrow linewidth (compare, for example, with FeCl\(_2\)-2H\(_2\)O and its isomer\(^{15}\)), but cannot be definitely ruled out. With the assumption that the identification of the 25 cm\(^{-1}\) line as due to Ag–I vibration was correct, and that the hypothesis of Geller and Dudley concerning the existence of AgI\(_4\) chains in solution was also correct, we have analyzed the Raman spectra of saturated solutions of SrAg\(_2\)I\(_4\). These spectra were obtained exactly as the crystal spectra discussed above, with the solutions in sealed quartz containers. The results were consistent with our assumptions and are illustrated in Fig. 2. The 25 cm\(^{-1}\) mode persists in the liquid phase and becomes more highly damped. Curve fitting of the data shown in Fig. 2, and other similar data, shows that the scattering feature near 25 cm\(^{-1}\) is less than critically damped, with intensity maxima shifted down to near 20 cm\(^{-1}\) due to increased linewidth. The halfwidth at half maximum is approximately 20 cm\(^{-1}\). We believe that these spectra demonstrate the persistence of the AgI\(_4\) chains in saturated aqueous solutions. If the origin were instead due to [Sr(H\(_2\)O)\(_6\)]\(^2+\) complexes, we would expect the spectra to be broader with no maximum at finite frequencies since the bonding in these complexes is much weaker than for the AgI\(_4\) tetrahedra. Experiments with fully deuterated SrAg\(_2\)I\(_4\)-8D\(_2\)O will be reported in a subsequent paper.

In an effort to ascertain the size of the AgI\(_4\) chains in

![Image of Raman spectra of SrAg\(_2\)I\(_4\)-8H\(_2\)O and saturated solution SrAg\(_2\)I\(_4\)].
the saturated solutions at 295 K, we performed autocorrelation spectroscopy measurements on these solutions. A dilute sample was filtered through a 0.3 μm Millipore filter, then left uncapped in a dust-free cabinet to allow it to saturate. Autocorrelation spectra were taken on the resulting concentrated solution at the 514.5 nm argon line (absorption was very high for shorter wavelengths) at 45° scattering angle, using a ITT FW130 photomultiplier tube and a 64 channel Langley–Ford correlator. Two spectra are shown in Fig. 3 with sample times of 10 and 0.5 μs. Assuming a Stokes–Einstein diffusion model, these time scales correspond to particle dimensions of 30–200 and 1–30 Å, respectively. In the upper spectrum, shot noise is seen in channel one due to the finite width of the shaped pulses being processed by the correlator; otherwise both autocorrelation functions are flat.

The autocorrelation spectra shown in Fig. 3 show no evidence for diffusing particles of order 30 Å or smaller. Similar measurements at other scattering angles showed no evidence for longer chains. Thus, in disagreement with the Raman data, the autocorrelation spectroscopy experiments show no evidence for molecular structures in saturated solutions of SrAg₄I₄.

These results are identical to those reported earlier in NiCl₂ solutions, and we believe that they reflect again the basic difference in time scales for the two probes, with Raman scattering measuring response on a picosecond scale (or shorter) and autocorrelation data sampling on a microsecond (or longer) period.

As a double check that the autocorrelation apparatus was sufficiently sensitive, we diluted the saturated SrAg₄I₄ solution. This causes AgI to precipitate out (the beta phase is stable at ambient temperatures), and the diffusing microcrystals of 3-Å AgI were readily observable by our autocorrelator, as shown in Fig. 4. These data illustrate two important facts: first, the size of the nucleating AgI particles is 0.25 μm; second, the autocorrelation system shows that the Raman spectra of Fig. 2 are not due to microcrystals suspended in the saturated solution.

**SUMMARY**

Raman spectroscopy of crystalline SrAg₄I₄·8H₂O reveals an extremely intense line at 29 cm⁻¹ assigned as a vibration of the AgI tetrahedra. This line becomes heavily damped, but not diffusive, in the melt, i.e., in saturated aqueous solutions of SrAg₄I₄, confirming the hypothesis of Geller and Dudley that the AgI chains remain intact in solution. However, no evidence of such chains is manifest in the autocorrelation experiments; this indicates that the long-range ordering of the chains may not persist as long as 10 μs. In dilute solutions of SrAg₄I₄ diffusion of small particles is detected, but these are identified as 3-Å AgI precipitates.

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**FIG. 4.** Autocorrelation spectra of dilute solution of SrAg₄I₄ at 295 K, showing exponential decay due to diffusing precipitate of β-Agl, of average particulate diameter 0.25 μm.

**FIG. 3.** Autocorrelation spectra of saturated solution of SrAg₄I₄ at 295 K. (a) 0.5–33 μs; (b) 0.01–0.66 ms.


