Structural features of the congruently melting compounds $\text{MAg(NO}_3\text{)}_2$
($\text{M} = \text{K, Rb, Cs}$) inferred from their Raman spectra

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The compounds $\text{KAg(NO}_3\text{)}_2$ and $\text{RbAg(NO}_3\text{)}_2$ exhibit similar Raman spectra which are consistent with their crystal structures determined by X-ray diffraction. Polymeric complexes are formed between silver and nitrate ions and the nitrate ions act as both unidentate and bidentate ligands. The compound $\text{CsAg(NO}_3\text{)}_2$ has a different Raman spectrum. The well separated band at 224 cm$^{-1}$ in the external vibrational region and the unique three-peak profile in the $\nu_2$ region suggest that there may exist discrete complexes of silver and nitrate ions in the crystal $\text{CsAg(NO}_3\text{)}_2$. The strong interaction which accounts for the nonequivalent sets of nitrate ions in molten $\text{AgNO}_3$ appears to exist also in the compounds $\text{KAg(NO}_3\text{)}_2$, $\text{RbAg(NO}_3\text{)}_2$ and $\text{CsAg(NO}_3\text{)}_2$.

Silver nitrate forms congruently melting compounds of the types $\text{KAg(NO}_3\text{)}_2$ and $\text{RbAg(NO}_3\text{)}_2$ with potassium nitrate and rubidium nitrate$^{1,2}$. The compounds $\text{KAg(NO}_3\text{)}_2$ and $\text{RbAg(NO}_3\text{)}_2$ can also be crystallized from the aqueous solutions$^3$. An X-ray diffraction (XRD) study$^3$ on the single crystals revealed that both $\text{KAg(NO}_3\text{)}_2$ and $\text{RbAg(NO}_3\text{)}_2$ belong to space group $P2_1/a$. In the crystal the silver ions and nitrate ions form infinite chains of the type $[\text{Ag}_2(\text{NO}_3)_4]^{2-}$ which were linked by K$^+$ or Rb$^+$. The silver ions are tetrahedrally coordinated by four nearest oxygen atoms from four different nitrate ions. Half of the nitrate ions act as unidentate ligands and the other half act as bidentate ligands.

Phase diagram studies of the $\text{AgNO}_3$-$\text{CsNO}_3$ system by thermal methods$^4$ indicated that there was an incongruently melting compound $\text{CsAg(NO}_3\text{)}_2$ and a congruently melting compound $\text{CsAg(NO}_3\text{)}_2$. It is interesting to note that in the $\text{AgNO}_3$-$\text{CsNO}_3$-$\text{H}_2\text{O}$ system$^2$, the incongruently melting compound $\text{CsAg(NO}_3\text{)}_2$ was found to crystallize readily from the aqueous solutions over a wide concentration range while the congruently melting compound $\text{CsAg(NO}_3\text{)}_2$ did not crystallize from the aqueous solutions. Chemical analysis, thermal analysis and X-ray diffraction technique were applied to confirm the identity of the compound $\text{CsAg(NO}_3\text{)}_2$ obtained from the aqueous solutions.

In this work Raman spectra of the compounds $\text{KAg(NO}_3\text{)}_2$, $\text{RbAg(NO}_3\text{)}_2$ and $\text{CsAg(NO}_3\text{)}_2$ have been measured, correlation between the structural and Raman features has been suggested, and a comparison of these features to those of the lithium compounds has been made.

Materials and Methods

The nitrates were of the analytical reagent grade and were used without further purification.

Crystals of $\text{KAg(NO}_3\text{)}_2$, $\text{RbAg(NO}_3\text{)}_2$ and $\text{CsAg(NO}_3\text{)}_2$ were prepared by slow evaporation in a desiccator of aqueous solutions of equimolar $\text{AgNO}_3$-$\text{MNO}_3$ ($\text{M} = \text{K, Rb, Cs}$). The preparation was carried out in a dark room. The crystals were transparent. The needle-shaped $\text{CsAg(NO}_3\text{)}_2$ looked different from $\text{KAg(NO}_3\text{)}_2$ and $\text{RbAg(NO}_3\text{)}_2$. When broken, the crystals of $\text{CsAg(NO}_3\text{)}_2$ tended to cleave along the axis of the needle.

Raman spectra were measured on a Spex 1403 double spectrometer with standard 90$^\circ$ scattering geometry. The 488.0 nm line of a Spectra-Physics argon ion laser (series 2000) was used as the source of excitation. The power level was 60 mW. The slits were set at 200 $\mu$m. The data were collected at 0.5 cm$^{-1}$ interval and the integral time for each point was 6 seconds. For detailed studies in the $\nu_3$ region, the slits were set at 50 $\mu$m and the data were collected at 0.2 cm$^{-1}$ interval. $\text{MoO}_3$ was used to calibrate the frequencies. The wavenumbers were accurate to 0.5 cm$^{-1}$. The compounds turned pale brown on the spot where the laser illuminated.
A 1449A Variable Temperature Assembly was used to cool the samples to 150 K.

Raman spectra of MAg(NO$_3$)$_2$ (M = K, Rb, Cs)

The most distinct Raman bands for MAg(NO$_3$)$_2$ (M=K, Rb, Cs) are summarized in Table 1. Raman spectra of AgNO$_3$, KNO$_3$, RbNO$_3$, and CsNO$_3$ were also measured for comparison.

The Raman spectra of KAg(NO$_3$)$_2$ and RbAg(NO$_3$)$_2$ are similar in both the external and internal vibrational regions (Table 1). In the external vibrational region, the strong Raman bands at 52 and 82 cm$^{-1}$ of KNO$_3$ (II) or the Raman features at 108 and 53 cm$^{-1}$ of RbNO$_3$ (IV) were not detected, suggesting the formation of the compounds. The spectral profile in this region was similar to that of AgNO$_3$ (II) [Fig. 1 (I)]; a band at about 40 cm$^{-1}$ and multi-band features between 60 and 200 cm$^{-1}$.

In the internal vibrational region, Raman bands in each of the $v_1$ to $v_2$ regions have similar frequencies with practically the same intensity patterns [Table 1 and Fig. 1 (II)]. The Raman features of AgNO$_3$ (II) and KNO$_3$ (II) or RbNO$_3$ (IV) do not appear. The observed Raman bands are due to the complex of [Ag$_2$(NO$_3$)$_3$]$_2$ in the crystals.

The band at 1042 cm$^{-1}$ in the $v_1$ region remained single at 150 K and with narrowed slits, while the band at 820 cm$^{-1}$ in the $v_1$ region was resolved into two peaks at 150 K [Fig. 2 (I)]; 824 and 818 cm$^{-1}$ for KAg(NO$_3$)$_2$ and 821 and 817 cm$^{-1}$ for RbAg(NO$_3$)$_2$. There were also two bands at 1632 and 1642 cm$^{-1}$ in the $2v_1$ region.

In the $v_2$ region, Raman features appear over a wide frequency range (160 cm$^{-1}$) and four bands can be distinguished: 1282, 1306, 1402 and 1432 cm$^{-1}$ for KAg(NO$_3$)$_2$ and 1281, 1303, 1408 and 1435 cm$^{-1}$ for RbAg(NO$_3$)$_2$. There were three bands in the $v_2$ region: 701, 714 and 724 cm$^{-1}$ for KAg(NO$_3$)$_2$ and 702, 715 and 724 cm$^{-1}$ for RbAg(NO$_3$)$_2$. The band with the highest frequency was the strongest of the three while the other two bands appeared to have the same intensity [Fig. 1 (b) and (c)].

The Raman spectrum of the crystal obtained from the aqueous solution of AgNO$_3$-CsNO$_3$ is quite different from the spectra of either the pure nitrates or KAg(NO$_3$)$_2$ and RbAg(NO$_3$)$_2$ (Table 1 and Figs 1 and 2), suggesting the formation of a compound [CsAg(NO$_3$)$_2$] with a unique structure.

Four peaks appeared in the external vibrational region at 48, 112, 132 and 224 cm$^{-1}$. The last one was well separated from the other external modes of the compound and the frequency was higher than any of the external modes in other silver compounds [Fig. 1 (I)].

The band at 1043 cm$^{-1}$ in the $v_1$ region was resolved into two bands at 1042.8 and 1044.8 cm$^{-1}$ at 150 K [Fig. 2 (II)]. Two bands at 811 and 822 cm$^{-1}$ appeared in the $v_2$ region. Unlike KAg(NO$_3$)$_2$ and RbAg(NO$_3$)$_2$, CsAg(NO$_3$)$_2$ has a three-peak profile in the $v_1$ region. Besides the two bands at 1293 and 1425 cm$^{-1}$ at both ends, there is a band at 1350 cm$^{-1}$ which is resolved into two bands at 150 K with intensities stronger than those at both ends [Fig. 2 (III)]. In the $v_2$ region only two bands are observed at 713 and 722 cm$^{-1}$ instead of three.

Discussion

According to the XRD studies, there are two crystallographically different sites for the nitrate ions in
KAg(NO₃)₂ and RbAg(NO₃)₂, and the nitrate group may act as either unidentate or bidentate ligand. As a result, the non-degenerate modes ν₁ and ν₃ of the free nitrate ion may present multi-band features and the degenerate modes ν₂ and ν₄ may split in different ways. Although the ν₂ vibration cannot be resolved into two bands (probably due to accidental coincidence), the ν₃ vibration and the 2ν₄ region exhibit a doublet structure.

Moreover, the band profiles in the ν₃ and ν₄ regions are in good agreement with the rule of thumb which identifies unidentate and bidentate nitrate ions. The splitting of the ν₂ vibration is distinctly less for unidentate nitrate ions than that for bidentate nitrate ions in the complexes of similar structures. In the Raman spectra of KAg(NO₃)₂ and RbAg(NO₃)₂, two bands of comparable intensities can be distinguished in each of the two locations: 1282, 1306 and 1402, 1432 cm⁻¹ for the former; and 1281, 1303 and 1408, 1435 cm⁻¹ for the latter. Following reference 6, the less separated bands at 1306 and 1402 cm⁻¹ (or 1303 and 1408 cm⁻¹) may be attributed to unidentate nitrate ions and the bands at 1282 and 1432 cm⁻¹ (or 1281 and 1435 cm⁻¹) may be attributed to bidentate nitrate ions. The splittings are larger in RbAg(NO₃)₂ than those in KAg(NO₃)₂ probably because the larger counterion Rb⁺ has less effect on the coordination in the Ag-ONO₂ complex than the smaller K⁺.

The three bands in the ν₄ region may also be attributed to splitting of this doubly degenerate mode due to unidentate or bidentate coordination of the nitrate ion, assuming that the much stronger band at 724 cm⁻¹ is a combination of two bands of similar energy.

Splittings were also noted in molten AgNO₃ and AgNO₃ solutions. Strong interactions between silver and the nitrate ion were believed to account for the nonequivalent sets of nitrate group in molten AgNO₃, such as ion pair and multiple ion aggregate which were suggested by Raman studies. According to the neutron diffraction study, four oxygen atoms from four nitrate groups are coordinated to a silver in molten AgNO₃. Since the ratio of silver to the nitrate ion is 1:1 in AgNO₃, the nitrate ions must be shared by the cations and thus may act as bidentate and unidentate ligands. Such a coordination state may also be present in the melts of the congruently melting compounds KAg(NO₃)₂ and RbAg(NO₃)₂. When the melts crystallize, the complex Ag-ONO₂ remains and is stabilized by the counterion K⁺ or Rb⁺, and congruently melting compounds are formed. This suggestion is supported by the similarity of the Raman spectrum of KAg(NO₃)₂ or RbAg(NO₃)₂ with the Raman spectra of the melt and the acetonitrile solution of AgNO₃ (Table 2). The similarity is striking considering the differences in state and temperature.
and then measured the Raman spectra of the C\(\text{S}_2\)Ag(\(\text{NO}_3\))\(_2\) bands. We ask components may contribute intensity at CsAg(\(\text{NO}_3\))\(_2\). readily crystallize, recrystalized a~mar systems. The Raman spectroscopic studies applied the normal methods to which were noted by most of the authors CsAg(\(\text{NO}_3\))\(_2\) a congruently melting compound were caused chiefly by the earlier report a~aly regarded as an incongruent melting compound 4. An alike. The sole difference was that the discontinuity at \(x(\text{Ag}^+) = 0.52\) for incongruently melting compound CsAg(\(\text{NO}_3\))\(_2\) shifted a little to \(x(\text{Ag}^+) = 0.50\), indicating a congruently melting compound 13. The discrepancies were caused chiefly by the non-equilibrium conditions which were noted by most of the authors 11-13 when they applied thermal methods to investigate the binary nitrate systems. The Raman spectroscopic studies in this work appear to favour the suggestion that KAg(\(\text{NO}_3\))\(_2\), and CsAg(\(\text{NO}_3\))\(_2\) are congruently melting compounds. They readily crystallize from aqueous solutions, especially CsAg(\(\text{NO}_3\))\(_2\). We have melted the three silver compounds and then measured the Raman spectra of the recrystallized samples. The Raman spectra of the compounds before and after melting were practically the same. The Raman spectrum of KAg(\(\text{NO}_3\))\(_2\) is similar to that of molten AgNO\(_3\), just as in the case of the congruently melting compounds MLi(\(\text{NO}_3\))\(_2\) (\(M = \text{K}, \text{Rb}, \text{Cs}\))\(^9\). Further work on the phase diagrams of AgNO\(_3\)-KNO\(_3\) and AgNO\(_3\)-CsNO\(_3\) is under way.

Raman studies indicated that CsAg(\(\text{NO}_3\))\(_2\) has a unique structure in the MAg(\(\text{NO}_3\))\(_2\) and MLi(\(\text{NO}_3\))\(_2\) (\(M = \text{K}, \text{Rb}, \text{Cs}\)) series. The doublet feature in the \(v_3\) region may suggest that there are crystallographically different sites for the nitrate ions in CsAg(\(\text{NO}_3\))\(_2\). However, the differently coordinated nitrate ions are not simply half unidentate and half bidentate, as is clear from the unique band profile in the \(v_3\) region [Fig. 2 (II)]. The sharper external bands and the isolated band at 224 cm\(^{-1}\) in the Raman spectrum of CsAg(\(\text{NO}_3\))\(_2\) [Fig. 1 (I)] indicate that the polymeric Ag-ONO\(_2\) complex in KAg(\(\text{NO}_3\))\(_2\) or RbAg(\(\text{NO}_3\))\(_2\) has reduced to a simpler one\(^1\). The metal-oxygen stretching vibrations in nitrate complexes were found\(^5\) to be in the range of 350 - 200 cm\(^{-1}\). Judged on the basis of its frequency and intensity, the 224 cm\(^{-1}\) band may be due to the Ag-ONO\(_2\) stretching vibration in a simple complex. This is similar to the case of KMgCl\(_4\) and CsMgCl\(_4\) (ref.16). Larger Cs\(^+\) was able to support a discrete complex MgCl\(_2\) but smaller K\(^+\) could not. In KMgCl\(_4\) there was a polymeric chain MgCl\(_4\) with bridging Cl.

### Table 2—Wavenumbers (cm\(^{-1}\)) of Raman bands in the internal vibrational region of (A) KAg(\(\text{NO}_3\))\(_2\), (B) molten AgNO\(_3\), \(^7\) and \(\bigcirc\) the acetonitrile solution of AgNO\(_3\), \(^8\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\nu_4)</th>
<th>(\nu_2)</th>
<th>(\nu_1)</th>
<th>(\nu_3)</th>
<th>(2\nu_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>701, 714, 724</td>
<td>816, 821</td>
<td>1042</td>
<td>1282, 1306, 1402, 1432</td>
<td>1632, 1642</td>
</tr>
<tr>
<td>B</td>
<td>706, 727</td>
<td>799, 813</td>
<td>1014, 1034</td>
<td>1275, * *</td>
<td>1423</td>
</tr>
<tr>
<td>C</td>
<td>709, 719-723</td>
<td>818-820</td>
<td>1031, 1038, 1042</td>
<td>1290, 1304,</td>
<td>1636, 1648, 1644</td>
</tr>
</tbody>
</table>

*Weak components may contribute intensity at 1350 and 1400 cm\(^{-1}\); a dash indicates that the 1400-1450 cm\(^{-1}\) region is masked by solvent bands.

Recent Raman studies\(^10\) indicated that the congruently melting compounds of the type MLi(\(\text{NO}_3\))\(_2\) (\(M = \text{K}, \text{Rb}, \text{Cs}\)) consist of Li-\(\text{NO}_3\) complex with a structure similar to that of RbAg(\(\text{NO}_3\))\(_2\) and KAg(\(\text{NO}_3\))\(_2\), and that the Raman spectra of the solid MLi(\(\text{NO}_3\))\(_2\) also resemble that of molten Li-\(\text{NO}_3\). Lithium ions have a coordination chemistry with the nitrate ion similar to that of silver ions because silver ions in molten AgNO\(_3\) have the same tetrahedral coordination structure with the nitrate ions as lithium ions have in molten Li-\(\text{NO}_3\) (ref. 9). The tetrahedral coordination in the molten nitrates is retained when AgNO\(_3\) or Li-\(\text{NO}_3\) forms the congruently melting compound with the heavier alkali metal nitrates.

There are discrepancies in the phase diagrams of AgNO\(_3\)-KNO\(_3\) and AgNO\(_3\)-CsNO\(_3\). The three most recent reports about AgNO\(_3\)-KNO\(_3\) presented three different pictures of phase diagrams: congruently melting compound KAg(\(\text{NO}_3\))\(_2\), incongruently melting compound KAg(\(\text{NO}_3\))\(_2\), and a eutectic 12. CsAg(\(\text{NO}_3\))\(_2\) was generally regarded as an incongruent melting compound 4. An earlier report 13 suggested that it was a congruently melting compound. The phase diagrams looked very much alike. The sole difference was that the discontinuity at \(x(\text{Ag}^+) = 0.52\) for incongruently melting compound CsAg(\(\text{NO}_3\))\(_2\) \(^4\) shifted a little to \(x(\text{Ag}^+) = 0.50\), indicating a congruently melting compound 13. The discrepancies were caused chiefly by the non-equilibrium conditions which were noted by most of the authors 11-13 when they applied thermal methods to investigate the binary nitrate systems. The Raman spectroscopic studies in this work appear to favour the suggestion that KAg(\(\text{NO}_3\))\(_2\), and CsAg(\(\text{NO}_3\))\(_2\) are congruently melting compounds. They readily crystallize from aqueous solutions, especially CsAg(\(\text{NO}_3\))\(_2\). We have melted the three silver compounds and then measured the Raman spectra of the recrystallized samples. The Raman spectra of the compounds before and after melting were practically the same. The Raman spectrum of KAg(\(\text{NO}_3\))\(_2\) is similar to that of molten AgNO\(_3\), just as in the case of the congruently melting compounds MLi(\(\text{NO}_3\))\(_2\) (\(M = \text{K}, \text{Rb}, \text{Cs}\))\(^9\). Further work on the phase diagrams of AgNO\(_3\)-KNO\(_3\) and AgNO\(_3\)-CsNO\(_3\) is under way.

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### References