CHAPTER 9

LASER RAMAN STUDY OF INTERACTION BETWEEN MICROCLUSTERS OF
AgI AND HgI₂

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9.1 Introduction

A problem of great fundamental interest in the science of microclusters is the study of the nature and extent of interaction between clusters of different materials (1-10). The interactions involving clusters may be characterised as surface chemisorption or bulk reaction. Different techniques have been used to extensively investigate chemisorptive type of reactions while much results have not been reported on bulk reactions. The study of the feasibility of bulk interaction between small particles of different materials using electron diffraction, X-ray diffraction and EDAX is described in chapter 6. It seems that laser Raman spectroscopy could be efficiently used to investigate the possibility of bulk interaction between small particles of different materials. IR and LRS have been extensively made use of in studying the special vibrational properties of highly dispersed particles (11-24). This chapter consists of a report of the study of interaction between microclusters of AgI and HgI₂ using LRS. In this study the laser Raman spectrum of the product of interaction between nanoparticles of AgI and HgI₂ was found to exhibit most of the characteristic lines of the Raman spectrum of the crystalline superionic conductor Ag₂HgI₄, but in a frequency shifted manner. This indicated that the clusters of AgI and HgI₂ could enter into interaction.
resulting in the breaking or rearrangement of existing chemical bonds and the establishment of new ones.

9.2 Experiment and Observation

The microclusters used in the present study were prepared at room temperature and allowed to interact by directly mixing the suspensions (as discussed in section 2 of chapter 6). The suspensions of AgI, HgI₂ and the product of interaction were subjected to TEM and electron diffraction studies. Laser Raman spectra of the product of interaction was recorded at room temperature using computer controlled DILOR Z24 Raman spectrometer in the stokes region from 20 to 300 cm⁻¹ and using the 647.1 nm line from a Kr⁺ at a power of 50 mw as the exciting radiation (Fig. 9.1).

9.3 Discussion

The room temperature Raman spectrum of crystalline Ag₂HgI₄ has been reported to consist of seven sharp bands at 25, 30, 35, 38, 82, 104 and 122 cm⁻¹ in the stokes region above 20 cm⁻¹ (25, 26). The intense band at 122cm⁻¹ has been assigned to the A₁ symmetric stretch of (HgI₄)⁻² species. The two bands in the 80 to 100 cm⁻¹ region are most likely composed of silver iodide stretching modes. The bands at 25 and 30cm⁻¹ are due to Ag-I deformation type bands. The laser Raman spectrum of the product of interaction between AgI and
Fig. 9.1. LRS of the product of interaction between AgI and HgI$_2$ culsters.
HgI₂ clusters (Fig. 9.1) showed three somewhat broad lines at 24.1, 34.7 and 121.1 cm⁻¹ and two weak bands at 80.1 and 102.4 cm⁻¹ compared to the seven characteristic lines in the spectrum of crystalline Ag₂HgI₄. The close resemblance of the spectrum of the product of interaction between small particles of AgI and HgI₂ with that of the crystalline Ag₂HgI₄ reported in the literature suggests that the nanoparticles of AgI and HgI₂ might have entered into interaction resulting in a rearrangement of chemical bonds so that in the resulting mass the species (HgI₄)²⁻ and AgI which give rise to characteristic Raman lines of crystalline Ag₂HgI₄ are present. The two weak bands at 30 and 38 cm⁻¹ and the strong band at 35 cm⁻¹ of the crystalline Ag₂HgI₄ appear to have merged into a single strong band at 34.7 cm⁻¹ in the spectrum of the product of interaction. The band corresponding to (HgI₄)²⁻ symmetric stretch appear as a very strong band at 121.1 cm⁻¹. The presence of this strong line shows that the interaction between AgI and HgI₂ has actually led to the formation of the (HgI₄)²⁻ species. The strong bands at 24.1 cm⁻¹ corresponds to the deformation type motions of iodide lattice relative to the Ag ions confirms the presence of bond between iodine atom and Ag atoms. The LRS of nanoparticles of HgI₂ show sharp lines at 30.7 and 112.6 cm⁻¹ and a shoulder at 140 cm⁻¹ (see Fig. 8.2 of chapter 8). None of these lines are observed in the LRS of the product of interaction. The LRS of nanoparticles of AgI show three lines at 33, 81.4 and 103.4 cm⁻¹ (see Fig. 8.1 of
chapter 8) which are close to the lines at 34.7, 80.1 and 112.4 cm\(^{-1}\) in the LRS of the product of interaction. But the very strong line at 121.1 cm\(^{-1}\) is a conspicuous feature of the spectrum of the product of interaction and this line confirms the presence of the species \((\text{HgI}_4)^{-2}\) and indicates that interaction between \(\text{AgI}\) and \(\text{HgI}_2\) has actually taken place. The small change in the frequencies of the spectral lines of the product of interaction compared to those of crystalline \(\text{Ag}_2\text{HgI}_4\) may be due to the formation of the product of interaction in a highly dispersed state and the consequent vibrational size effect (11-24).

9.4 Conclusion

The laser Raman spectrum of the product of interaction between nanoparticles of \(\text{AgI}\) and \(\text{HgI}_2\) has been studied. The close resemblance of this spectrum with that of the LRS of crystalline \(\text{Ag}_2\text{HgI}_4\) indicates that interaction has taken place between nanoparticles of \(\text{AgI}\) and \(\text{HgI}_2\). The slight shift in the observed frequencies of the product of interaction compared to the frequencies of crystalline \(\text{Ag}_2\text{HgI}_4\) may be due to the formation of the product of interaction in a highly dispersed state and the consequent vibrational size effect.
References