Raman Spectra of Molten NaNO_3 - AgNO_3 Mixture

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The Raman spectra of a molten NaNO_3 - AgNO_3 mixture are investigated. The variations in frequencies of ν_1 , $2\nu_2$, ν_3 and ν_4 with the concentration of silver nitrate were shown and the splittings of ν_3 and ν_4 were also observed at the region rich in silver nitrate.

Assuming the splitting to be due to the effect of cation field around NO_3^- , the effect of cation field was estimated by using the Urey-Bradley force field method. It was found that the cation field in the region rich in silver nitrate produced a large effect on the force constants of nitrate ion and such a cation field gradually decreased with decreasing concentration of silver nitrate.

Although it is assumed that the free rotation of nitrate ion about its threefold axis is restricted microscopically in the region rich in silver nitrate as indicated by Wilmshurst, the hinderance of free rotation of NO_3^- about its threefold axis does not seem to give any effect on the transport parameters for the NaNO_3 - AgNO_3 system.

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I. Introduction

Although many Raman spectra of molten pure alkali nitrates have been published^{(1)~(12)}, only few Raman spectra of molten alkali nitrate mixtures have been obtained⁽¹³⁾.

The present paper reports the Raman spectra of molten sodium nitrate, silver nitrate and a sodium nitrate-silver nitrate mixture. In the sodium nitrate-silver nitrate system, fortunately, the various transport parameters, such as self-diffusion coefficients, interdiffusion coefficient, transference numbers and electric conductivity, and various friction coefficients have been reported previously. It is thus of interest from the microscopic point of view of the kinetic motion of entities to find the relation between vibrational spectra and various transport parameters.

II. Experimental

A melt was irradiated using a Spectra Physics Model 52 Ar laser emitting about 500 mW at 4880Å. The 90° scattered light was recorded by a Spectra Physics Model Ramalog 4 (dispersed by a double monochrometer, Model 1401, and detected using a thermoelec-

trically cooled photomultiplier, RCA Model C-31034). The melt was heated at about 350°C by a Kanthal-wound electric resistance furnace whose temperature was controlled by an on-off type controller.

Care is taken to ensure that the Raman cell is completely filled with the melt without any trapped gas bubble.

III. Results

According to many published papers, the NO_3^- is of D_{3h} symmetry in its unperturbed form with four fundamental frequencies, $\nu_1(a'_1)$ symmetric stretch near 1050 cm^{-1} , $\nu_2(a''_2)$ out-of-plane bend near 800 cm^{-1} , $\nu_3(e')$ doubly degenerated asymmetric stretch near 1350 cm^{-1} , and $\nu_4(e')$ doubly degenerated in-plane bend near 720 cm^{-1} . Since the out-of-plane bend ν_2 is a Raman forbidden fundamental, no band near 800 cm^{-1} is observed usually. In addition to the bands mentioned above, a combination band is observed. A peak located near 1650 cm^{-1} is assigned to $2\nu_2$ ⁽¹⁴⁾.

The variations of ν_1 , $2\nu_2$, ν_3 and ν_4 of NO_3^- with the concentration of silver nitrate are given in Figs. 1, 2, 3 and 4, respectively. It is obvious from Figs. 1 and 2 that the Raman lines of ν_1 and $2\nu_2$ shift from high frequency to low frequency with the increase of silver nitrate concentration. It is also evident from Figs. 3 and 4 that the lower Raman line of

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Fig. 1 Variation of ν_1 with composition at 350°C. Fig. 2 Variation of $2\nu_2$ with composition at 350°C. Fig. 3 Variation of ν_3 with composition at 350°C. Fig. 4 Variation of ν_4 with composition at 350°C.

split ν_3 is shifted to a lower frequency and higher Raman line of split ν_4 is shifted to a higher frequency with the increasing silver

nitrate concentration, whereas the higher Raman line of split ν_3 and the lower Raman line of split ν_4 remain almost constant over the whole concentration range of silver nitrate investigated.

Perhaps the most interesting aspects of the sodium nitrate-silver nitrate is the splittings of the doubly degenerated asymmetric stretch ν_3 and of the doubly degenerated in-plane bend ν_4 as shown in Figs. 3 and 4. Furthermore, it should be noted that the Raman forbidden fundamental frequency ν_2 is observed at 800 cm^{-1} in the Raman spectrum of the pure molten silver nitrate.

IV. Discussion

Although the general features of the Raman spectra have hitherto been made clear, there are still some equivocal points in the spectra which are concerned with the observed splittings of $\nu_3(e')$ and $\nu_4(e')$. The splitting can arise only if† the threefold axis of symmetry of the nitrate ion is destroyed and this may be brought about in either one of two ways, namely, by an associated species M-O-NO_2 in the melt, or by the action of cation field around the nitrate ion⁽¹⁶⁾. It was shown by Clarke⁽⁶⁾ that the observed low frequency band of 115 cm^{-1} in his report was most probably depolarized ($p=3/4$) and such depolarized property was certainly not in accord with the assignment to a metal-oxygen stretching vibration of the associated species M-O-NO_2 in the melt because the actual experience on methyl mercuric nitrate in benzene where the existence of metal-nitrate bond was well established indicated that such a Raman band could be strongly polarized⁽¹⁷⁾.

Considering the high conductivity of this system, the continuous variations of the Raman

† Since the molten silver nitrate showed spectroscopically the retention of an orthorhombic lattice structure⁽⁶⁾, it may be possible that many bands of infrared spectra of molten silver nitrate are assigned by applying a factor-group analysis to silver nitrate of the orthorhombic lattice⁽¹⁵⁾. However, it seems that the present experimental Raman spectra are assigned satisfactorily by postulating the effect of the cation field around the nitrate ion.

frequencies with the concentration of silver nitrate over the wide range from pure molten sodium nitrate to pure molten silver nitrate as shown in Figs. 1 and 2 and the failure to observe the M-O-NO_2 stretching vibration as mentioned earlier, we may conclude that the splittings of ν_3 and ν_4 must arise from the effect of the cation field around the nitrate ion. Furthermore, the continuous variation of $\Delta\nu_3$ (the difference between the splitted vibrational frequencies) with the concentration of silver nitrate as shown in Fig. 5 will also support the effect of the cation field about the nitrate ion against the postulation of an associated species since the existence of associated species should indicate the discontinuous change in Fig. 5.

The possible explanation⁽¹⁶⁾ of splittings of ν_3 and ν_4 is that the nitrate ion cannot freely rotate about its threefold axis in molten silver nitrate and must be restricted since the vibrational frequency due to the freely rotating nitrate ion would simply averaged over every available configuration and only one broad band would be observed regardless of the cation field. According to such a view, the continuous variation of $\Delta\nu_3$ with the concentration of silver nitrate for sodium nitrate-silver nitrate system as shown in Fig. 5 suggests a continuous decrease to zero of the degree of restricting rotation of the nitrate ion as the concentration of sodium ion increases. The results obtained by an infrared spectroscopy⁽¹⁸⁾ for potassium nitrate-silver nitrate system are also included in Fig. 5, indicating the same trend of variation of $\Delta\nu_3$ with composition as that for sodium nitrate-silver nitrate system.

Let us now to estimate the effect of the cation field around the nitrate ion. This can be done

Fig. 5 Variation of $\Delta\nu_3$ with composition.

Fig. 6 Changes in force constants of NO_3^- .

simply by calculating the difference of the force constants of nitrate ion from the difference between the splitted values of ν_3 . We assume the D_{3h} point-group symmetry for NO_3^- and we use a Urey-Bradley force field⁽¹⁹⁾, normalizing the value of sodium ion field around NO_3^- as zero. The changes in a stretching force constant (K), a bending force constant (H) and a non-bonded interaction constant (F) are shown in Fig. 6. The cation field in the region rich in silver nitrate produces a large effect on the force constants of nitrate ion and such a cation field gradually becomes zero with decreasing concentration of silver nitrate.

In sodium nitrate-silver nitrate system, several transport parameters, such as the self-diffusion coefficients of sodium and silver ions⁽²⁰⁾, the interdiffusion coefficient⁽²¹⁾⁽²²⁾, the transference numbers⁽²³⁾ and the electric conductivity⁽²⁴⁾⁽²⁵⁾, have been measured. The results showed that the transport parameters of sodium ion were almost identical with those of silver ion over the entire range of sodium nitrate-silver nitrate system. By comparing the results of Raman spectra with the above transport parameters, it seems likely that the hinderance of free rotation of NO_3^- about its threefold axis gives rise to no effect on the transport parameters. Alternatively, it may be assumed that such an hinderance would compensate the changes in transport parameters

† The splitting of ν_4 band is insufficiently resolved in present work, thus the differences between the splitted values of ν_4 are not used for the calculation of the effect of cation field.

caused by highly polarizable silver ion^{††}.

V. Conclusions

In order to determine the variations of vibrational spectra with composition, the Raman lines of NO_3^- such as ν_1 , $2\nu_2$, ν_3 and ν_4 are obtained over the whole range of the sodium nitrate-silver nitrate system.

The Raman lines of ν_1 and $2\nu_2$ were shifted to lower frequencies with increase in silver nitrate concentration. The lower Raman line of splitted ν_3 was shifted to a lower frequency and the higher Raman line of splitted ν_4 was shifted to a higher frequency with increase in silver nitrate concentration, while the higher Raman line of splitted ν_3 and the lower Raman line of splitted ν_4 remained almost constant over the whole range of concentration of silver nitrate. The most interesting aspects of the sodium nitrate-silver nitrate system are the splittings of the ν_3 and ν_4 and the appearance of the Raman forbidden fundamental frequency ν_2 for pure molten silver nitrate.

From the viewpoint in which the splitting is attributed to the effect of cation field around NO_3^- , we estimated the effect of cation field by using the Urey-Bradley force field method. The changes in the stretching force constant, the bending force constant and the non-bonded interaction constant are shown in Fig. 6. It is found that the cation field in the region rich in silver nitrate produces a large effect on the force constants of nitrate ion and such a cation field decreases gradually with decreasing concentration of silver nitrate. Although we assume that the free rotation of nitrate ion about its threefold axis is restricted microscopically in the region rich in silver nitrate as indicated by Wilmshurst, we may consider that the hinderance of free rotation of NO_3^- about its threefold axis gives no effect on the transport parameters for the sodium nitrate-silver nitrate system.

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REFERENCES

- (1) S. C. Wait and A. T. Ward: *J. Chem. Phys.*, **44** (1966), 448.
- (2) G. J. Janz, T. R. Kozlowski and S. C. Wait: *J. Chem. Phys.*, **39** (1963), 1809.
- (3) J. P. Devlin, G. Ritzhaupt and T. Hudson: *J. Chem. Phys.*, **58** (1973), 817.
- (4) G. E. Walrafen and D. E. Irish: *J. Chem. Phys.*, **40** (1964), 911.
- (5) M. Peleg: *J. Phys. Chem.*, **77** (1973), 2252.
- (6) J. H. R. Clarke: *Chem. Phys. Letters*, **4** (1969), 39.
- (7) J. P. Devlin and D. W. James: *J. Chem. Phys.*, **53** (1970), 4394.
- (8) D. W. James and W-H Leong: *Trans. Faraday Soc.*, No. 572 (1970), 1948.
- (9) J. H. R. Clarke, C. Solomons and K. Balasubrahmanyam: *Rev. Sci. Instrum.*, **38** (1967), 655.
- (10) W. Bues: *Z. Physik. Chem.*, **10** (1957), 1.
- (11) W. Bues: *Physico-chemical Measurements at High Temperature*, Ed. by J. O'M. Bockris, J. E. White and J. D. Mackenzie, Butterworth Pub., New York, (1959), p. 276.
- (12) S. C. Wait, Jr., A. T. Ward and G. J. Janz: *J. Chem. Phys.*, **45** (1966), 133.
- (13) G. J. Janz and D. W. James: *J. Chem. Phys.*, **35** (1961), 739.
- (14) R. E. Miller, R. R. Getty, K. L. Treuil and G. E. Leroy: *J. Chem. Phys.*, **51** (1969), 1385.
- (15) J. P. Devlin, K. Williamson and G. Austin: *J. Chem. Phys.*, **44** (1966), 1385.
- (16) J. K. Wilmshurst and S. Senderoff: *J. Chem. Phys.*, **35** (1961), 1078.
- (17) P. L. Goggin and L. A. Woodward: *Trans. Faraday Soc.*, **58** (1962), 1495.
- (18) J. K. Wilmshurst: *J. Chem. Phys.*, **39** (1963), 1779.
- (19) G. J. Janz and Y. Mikawa: *J. Mol. Spectroscopy*, **5** (1960), 92.
- (20) K. Kawamura and T. Ando: *Trans. JIM*, **14** (1973), 457.
- (21) D. Andréasson, A. Behn and C. A. Sjöblom: *Z. Naturforsch.*, **25a** (1970), 700.
- (22) A. Behn: *Dissertation*, Chalmers University of Technology, (1973), p. 73.
- (23) F. R. Duke, R. W. Laity and B. Owens: *J. Electrochem. Soc.*, **104** (1957), 299.
- (24) S. Brillant: *CEA-R-3545*, (1968), p. 68.
- (25) J. Byrne, R. Fleming and F. E. W. Wetmore: *Canad. J. Chem.*, **30** (1952), 922.

^{††} Whereas an ionic radius of silver ion is almost the same as that of sodium ion in melt, the value of polarizability of silver ion is about ten times larger than that of sodium ion.