

## INFRARED SPECTRA OF THE $\text{NO}_3^-$ ANION IN $\text{NaClO}_4$ , $\text{Na}_2\text{SO}_4$ , $\text{NaClO}_3$ , AND $\text{NaIO}_3$ HOST STRUCTURES

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The planar  $\text{NO}_3^-$  ion (own symmetry  $D_{3h}$ ) was embedded in  $\text{NaClO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaClO}_3$  and  $\text{NaIO}_3$  host structures containing tetrahedral ( $T_d$ ) or pyramidal ( $C_{3v}$ ) anions, and its infrared spectra were interpreted in terms of group analysis of the crystal symmetry. Where the correlation is satisfied, *viz.* in  $\text{NaClO}_4$ ,  $\text{NaClO}_3$  and  $\text{NaIO}_3$ , the  $\text{NO}_3^-$  anion possesses the site symmetry of the host structure ( $C_{2v}$ ,  $C_3$  and  $C_s$ , respectively), whereas in  $\text{Na}_2\text{SO}_4$  an additional symmetry lowering takes place ( $D_2 \rightarrow C_2$ ).

The study of the site symmetry of an anion requires elimination of the mutual vibrational influencing of this species in the elementary cell. This can be achieved by embedding a small amount of a substance with this anion in a host structure with a different crystal structure. Spectral changes indicating symmetry lowering to the site symmetry of the host structure have been observed for substances where anions with the same own symmetries were substituted<sup>1</sup>. In the present work, changes in the infrared spectra are examined for the  $\text{NO}_3^-$  anion (own symmetry  $D_{3h}$ ) on its embedding in host structures containing anions with own symmetries  $T_d$  or  $C_{3v}$ .

### EXPERIMENTAL

The salts used were of reagent grade purity. Mixtures of  $\text{NaClO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaClO}_3$ , and  $\text{NaIO}_3$ , respectively, with 5–10 mole %  $\text{NaNO}_3$  were dissolved in distilled water and concentrated for crystallization, and the crystals obtained were filtered out and dried at room temperature. Samples of the  $\text{NaClO}_4$ – $\text{NaNO}_3$  system were heated at 150°C for approximately 3 h.

Infrared spectra of the samples in KBr disks (13 mm in diameter) were measured over the region of 4 000–200  $\text{cm}^{-1}$  on a Perkin–Elmer 325 spectrophotometer.

### RESULTS AND DISCUSSION

The basic crystallographic data of the starting substances used as the host structures were taken from refs<sup>2–5</sup>; these substances possess the orthorhombic  $D_{2h}^{16}$  ( $\text{NaIO}_3$ ),  $D_{2h}^{17}$  ( $\text{NaClO}_4$ ) and  $D_{2h}^{24}$  ( $\text{Na}_2\text{SO}_4$ ) and the cubic  $T^4$  ( $\text{NaClO}_3$ ) structures. The own symmetries and site symmetries of the anions and the numbers of formula units in the elementary cells are given in Table I.

The  $\text{NO}_3^-$  anion was introduced in the form of  $\text{NaNO}_3$  which crystallizes<sup>2</sup> at room temperature in the space group  $D_{3d}^6$ :  $C_1(12)$ ,  $D_3(2)$ ,  $C_{3i}(2)$ ,  $C_3(4)$ ,  $C_i(6)$ ,  $C_2(6)$ . The number of formula units in the trigonal elementary cell is  $Z = 2$ . The own symmetry of the anion is  $D_{3h}$ , its site symmetry in the salt is  $D_3$ .

The six normal vibrations of the  $\text{NO}_3^-$  anion are distributed into the representations  $A_1' + A_2'' + 2E'$ , the two last species being infrared-active. In the site group and factor group approximation, *i.e.*, in the correlation  $D_{3h} \rightarrow D_3 \rightarrow D_{3d}$ , the number of infrared-active vibrations remains unaltered ( $A_2'' \rightarrow A_2 \rightarrow A_{2u}$ ,  $E' \rightarrow E \rightarrow E_u$ ).

The infrared spectrum of  $\text{NaNO}_3$  exhibits the  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$  and  $\nu_4$  vibrations<sup>6</sup> at 1 068, 838, 1 395 and 727  $\text{cm}^{-1}$ , respectively. The activity of the  $\nu_1$  vibration disagrees with the theoretical group analysis; this can be explained in terms of a lowering of the site symmetry  $D_3$  to the effective site symmetry  $C_3$  caused by the  $T(E)$  and  $R(E)$  vibrations contained in the  $2A + 2E(D_3)$  lattice vibrations of the anion. It should be noted that the site symmetry  $D_3$  has been found<sup>7</sup> at room temperature (and  $C_{3v}$  at  $-196^\circ\text{C}$ ) for the  $\text{NO}_3^-$  anion embedded in  $\text{RbCl}$ ,  $\text{RbBr}$ , and  $\text{RbI}$ .

### The Infrared Spectra of the Mixed Systems

*The  $\text{NaClO}_4$ - $\text{NaNO}_3$  system.* The  $\text{NO}_3^-$  anion in  $\text{NaClO}_4$  with the site symmetry  $C_{2v}$  exhibits vibrations  $\nu_2 \sim 835$  and  $\nu_3 \sim 1\,380, 1\,365 \text{ cm}^{-1}$ . The  $\nu_1$  vibration is obscured by the very strong  $\nu_3$  vibration of the  $\text{ClO}_4^-$  anion. The  $\nu_4$  vibration of the  $\text{NO}_3^-$  anion is generally very little marked, particularly at a high dilution of the substance (Fig. 1).

The observed splitting of the  $\nu_3$  vibration disagrees with the  $D_{3h} \rightarrow D_3 \rightarrow D_{3d}$  correlation. In view of the theoretically feasible relations between the  $D_{3h}$  symmetry of the anion, the site symmetry of the  $\text{NaClO}_4$  host lattice<sup>3,4</sup>, *viz.*  $D_{2h}^{17}$ :  $C_1(16)$ ,

TABLE I

Crystallographic data of the host structures and the experimentally found site symmetries of the guest  $\text{NO}_3^-$  anion

| Compound                 | Space group          | Z | Own symmetry of anion | Site symmetry of anion | Site symmetry of $\text{NO}_3^-$ anion |
|--------------------------|----------------------|---|-----------------------|------------------------|----------------------------------------|
| $\text{NaNO}_3$          | $D_{3d}^6-R\bar{3}C$ | 2 | $D_{3h}$              | $D_3$                  | $D_3$                                  |
| $\text{NaClO}_4$         | $D_{2h}^{17}-Cmcm$   | 4 | $T_d$                 | $C_{2v}$               | $C_{2v}$                               |
| $\text{Na}_2\text{SO}_4$ | $D_{2h}^{24}-Fddd$   | 8 | $T_d$                 | $D_2$                  | $C_2$                                  |
| $\text{NaClO}_3$         | $T^4-P2_13$          | 4 | $C_{3v}$              | $C_3$                  | $C_3$                                  |
| $\text{NaIO}_3$          | $D_{2h}^{16}-Pnma$   | 4 | $C_{3v}$              | $C_s$                  | $C_s$                                  |

$2C_{2h}(4)$ ,  $C_{2v}(4)$ ,  $C_i(8)$ ,  $C_2(8)$ ,  $2C_3(8)$ , and the observed vibrations, the infrared spectrum can be interpreted as exhibiting the  $C_{2v}$  symmetry of the  $\text{NO}_3^-$  anion, in agreement with the group correlations (Table II); this symmetry is identical with the site

TABLE II

Correlation of the own symmetry of the  $\text{NO}_3^-$  anion ( $D_{3h}$ ) and the corresponding site-group

| $D_{3h} \longrightarrow D_3 \longrightarrow C_3$                        |                                     |                                 |                  |
|-------------------------------------------------------------------------|-------------------------------------|---------------------------------|------------------|
| $A'_1$                                                                  | $A_1$                               | $A(\text{IR})$                  |                  |
| $A''_2(\text{IR})$                                                      | $A_2(\text{IR})$                    | $A(\text{IR})$                  |                  |
| $2E'(\text{IR})$                                                        | $2E(\text{IR})$                     | $2E(\text{IR})$                 |                  |
| $D_{3h} \longrightarrow C_{2v} \longrightarrow C_2 \longrightarrow C_s$ |                                     |                                 |                  |
| $A'_1$                                                                  | $A_1(\text{IR})$                    | $A(\text{IR})$                  | $A'(\text{IR})$  |
| $A''_2(\text{IR})$                                                      | $B_1(\text{IR})$                    | $B(\text{IR})$                  | $A''(\text{IR})$ |
| $2E'(\text{IR})$                                                        | $2A_1(\text{IR}) + 2B_2(\text{IR})$ | $2A(\text{IR}) + 2B(\text{IR})$ | $4A'(\text{IR})$ |

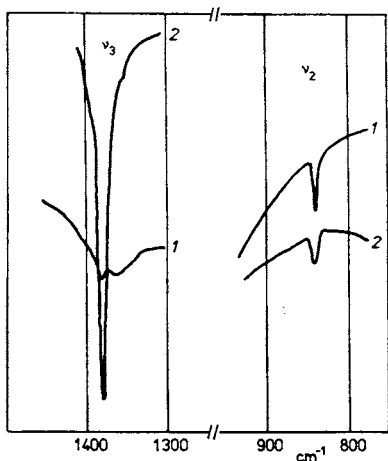


FIG. 1

$\nu_2$  and  $\nu_3$  vibrations of the  $\text{NO}_3^-$  anion in host structures of 1  $\text{NaClO}_4$  and 2  $\text{Na}_2\text{SO}_4$

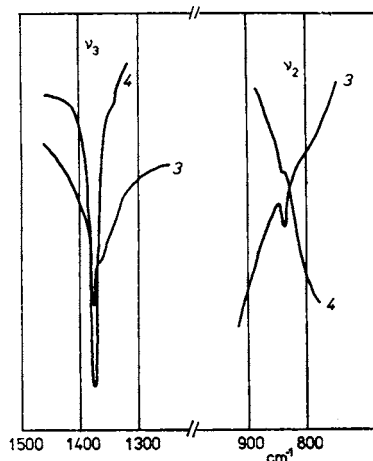


FIG. 2

$\nu_2$  and  $\nu_3$  vibrations of the  $\text{NO}_3^-$  anion in host structures of 3  $\text{NaClO}_3$  and 4  $\text{NaIO}_3$

symmetry of the  $\text{ClO}_4^-$  anion in the host structure (Table I). All of the  $A_1$ ,  $B_1$ , and  $B_2$  vibrations are infrared-active.

*The  $\text{Na}_2\text{SO}_4$ - $\text{NaNO}_3$  system.* In the host structure<sup>3,5</sup> of  $\text{Na}_2\text{SO}_4$ , with the symmetry  $D_{2h}^{16}$ :  $C_1(32)$ ,  $2D_2(8)$ ,  $2C_2(16)$ ,  $3C_2(8)$ , the site symmetry of the anion is  $D_2$ . This group is not allowed by group theory for the  $\text{NO}_3^-$  anion in this lattice.

The infrared spectrum of the  $\text{NO}_3^-$  anion exhibits the active vibration  $\nu_2 \sim 840 \text{ cm}^{-1}$  and the split degenerate vibration  $\nu_3 \sim 1385, 1355 \text{ sh cm}^{-1}$  (Fig. 1). Based on the correlation table, the spectrum of the  $\text{NO}_3^-$  anion can be interpreted in terms of symmetry lowering to  $C_2$ , i.e., the  $\text{NO}_3^-$  anion occupies the  $C_2$  site.

*The  $\text{NaClO}_3$ - $\text{NaNO}_3$  system.* Substitution of the  $\text{ClO}_3^-$  anion in the host structure by the  $\text{NO}_3^-$  anion manifests itself in the spectrum by vibrations  $\nu_1 \sim 1050 \text{ sh}$ ,  $\nu_2 \sim 835$ ,  $\nu_3 \sim 1385, 1370 \text{ sh cm}^{-1}$ ; the  $\nu_4$  vibrations are overlapped (Fig. 2). The  $\text{ClO}_3^-$  anion in the  $\text{NaClO}_3$  structure<sup>2</sup> ( $T^4$ :  $C_1(12)$ ,  $C_3(4)$ ) exhibits the site symmetry  $C_3$ . The spectral patterns of the guest  $\text{NO}_3^-$  anion give evidence of the  $C_3$  symmetry for this anion, i.e., the site symmetry of the host structure.

*The  $\text{NaIO}_3$ - $\text{NaNO}_3$  system.* The  $\text{NO}_3^-$  anion in  $\text{NaIO}_3$  exhibits vibrations  $\nu_1 \sim 1065$ ,  $\nu_2 \sim 845$ , and  $\nu_3 \sim 1385, 1355 \text{ sh cm}^{-1}$ . The  $\text{NaIO}_3$  host structure with the symmetry  $D_{2h}^{16}$ :  $C_1(8)$ ,  $2C_2(4)$ ,  $C_2(4)$  displays the site symmetry of the anion  $C_s$ . This site symmetry also satisfies the group correlations of the  $\text{NO}_3^-$  anion. The infrared spectrum (Fig. 2) confirms the theoretical assumption that the  $\text{NO}_3^-$  anion in this host structure possesses the site symmetry  $C_s$ ; hence, anion exchange is involved.

The observed site symmetries of the  $\text{NO}_3^-$  anion in the four host structures are summarized in Table I.

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