FORCE FIELD STUDY OF NCS ION IN DIFFERENT ALKALI-HALIDE LATTICES BY PARAMETRIC REPRESENTATION METHOD

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The study of the force field of NCS ion in different alkali-halide lattices was carried out to evaluate the influence of the matrix perturbation by the parametric representation method. A linear relationship of the form $f_{CS} = (-0.224553)$ L. C. $+ 6.803822$ is found to exist between the C–S stretching force constant and the lattice constant. Other molecular constants like mean vibrational amplitudes, bond charge and path length parameters were calculated and reported.

1. Introduction

The infrared study of small ions in different lattices of ionic crystals throws light on the nature of the potential functions as well as on the interaction in different lattices. In this context, the cyanate ion has been extensively studied by Maki and Decius [1]. Bryant and Turreli [2] have calculated the contribution to the inductive, short-range and Coulombic forces to the potential energy expression in different lattices. In the present paper an attempt is made to evaluate the influence of the matrix perturbation of NCS ion by the parametric representation method.

2. Potential energy constants

The infrared spectra of NCS ion in different lattices were reported by Cundill [3], Bely [4] and recently by Smith [5]. In the present investigation spectral data of Cundill and Smith have been used. The method of Redington was employed to calculate various molecular constants like the mean amplitudes of vibration, path length and bond charge parameters in different lattices.

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TABLE I

The vibrational frequencies (cm^{-1}) and lattice constants at 100°K for NCS^- in different alkali-halide lattices

	KI	KBr	KCl
γ_{CN}	2094.9	2077.4	2091.8
γ_{CS}	767.1	763.8	770.1
δ_{NCS}	477.5	479.4	487.3
L. C.	7.06	6.60	6.28
	RbI	RbBr	RbCl
γ_{CN}	2091.8	2073.9	2088.5
γ_{CS}	762.1	758.6	763.9
δ_{NCS}	478.1	478.2	483.5
L. C.	7.34	6.90	6.58
	NaI	NaBr	NaCl [a]
γ_{CN}	2098.3	2088.8	2098.8
γ_{CS}	773.6	782.9	783.6
δ_{NCS}	473.3	477.8	—
L. C.	6.47	5.98	5.64
	CsI	CsBr	
γ_{CN}	2095.5	2074.9	—
γ_{CS}	758.9	744.7	—
δ_{NCS}	473.8	477.3	—
L. C.	4.57	4.30	4.11

[a] Predicted frequency (see text).

The method of calculating the force constants using Redington's method has been described elsewhere [6, 7]. Using this procedure and the frequency data given in Table I, the potential energy constants were calculated. These are summarised in Table II.

3. Results and discussions

In NCS ion, the normal modes are essentially bond stretches and a linear bend, the bending fundamental has the smallest force constant and the largest positive shift as we go from one lattice to another, the C–S stretch, having an intermediate force constant and an intermediate shift and the CN stretch have the largest force constant and the least positive shift as we go from the KCl to KBr and a negative shift as we go from KBr to KI. The same behaviour is also noted in the other lattices. Murchison and Overend [8] also observed the same trend in the case of ClCN isolated in argon and neon matrices.

TABLE II

Symmetrised force constants [mdyn/Å] in different alkali-halide lattices at 100 K

	KI	KBr	KCl
F_{11}	15.8307 [c]	15.5451	15.7496
F_{12}	0.7245	0.7091	0.7146
F_{22}	5.2918	5.2533	5.3438
F_{33}	0.2905	0.2928	0.3025
	RbI	RbBr	RbCl
F_{11}	15.8197	15.5213	15.7363
F_{12}	0.7327	0.7114	0.7181
F_{22}	5.2125	5.1732	5.2469
F_{33}	0.2912	0.2914	0.2979
	NaI	NaBr	NaCl [a]
F_{11}	15.8280	15.5824	15.7803
F_{12}	0.7093	0.6837	0.7067
F_{22}	5.3982	5.5624	5.5739
F_{33}	0.2855	0.2909	—
	CsI	CsBr	NaCl [b]
F_{11}	15.9004	15.6406	15.7891
F_{12}	0.7348	0.7315	0.6913
F_{22}	5.1611	4.9551	5.5767
F_{33}	0.2860	0.2903	—

[a] Predicted values from the force constant vs lattice constant plot.

[b] Calculated values using the predicted frequency.

[c] This number of significant figures is retained to secure internal consistency in calculation.

1 mdyn/Å = 10^2 N/m.

A linear relationship of the form

$$f_{CS} = (-0.224553)\ \text{L.C.} + 6.803822$$

is found to exist between the CS stretching force constant and lattice constant of the different alkali halide lattices in which the NCS ion is being embedded. The deviation of CsBr and CsI is probably due to the fact that this lattice is body centered cubic rather than face centered cubic.

As seen from the Table II, the C–S stretching force constant is perturbed much more strongly than the CN stretch and CS stretch is approximately two times weaker than the CN stretching (Bond order for CS bond = 1.5 and CN bond = 2.6 using Gordy's relation [9]). This behaviour can be explained in terms of the "loose cage", "tight cage" arguments of

Pimentel and Charles [10]. According to the argument advanced by these authors, the triatomic molecules do not fit comfortably in the substitutional site; there is a tendency for the matrix to distort the molecule to fit the available cage and the amount a given coordinate is distorted will depend on the magnitude of the force constant associated with the coordinate.

Assuming that the bond order for C≡N in CH_3CN is unity the ionicity for NCS turns out to be 12% which is in good agreement with the values obtained from Pauling's relation [11] using electronegativities. Similarly F_{CS} value suggests a reduction of 29% from the average double bond value of 7.62 reported by Wentink [12]. Accordingly, it is possible to visualise a resonance between the electronic structures.

$$N = C = S^{-} \quad \text{and} \quad N \equiv C - S^{-}.$$

The resonance between the two structures will explain the double bond character of the CS bond and the reduced bond order of C ≡ N bond correspondingly.

To check the bond orders, the bond charge parameter which is a measure of charge build up in the bond region are also calculated using the "bond charge model" proposed

TABLE III

Mean amplitudes of vibration (σ) [Å], bond charge (q) and path length (γ) [Å], parameters in different alkali-halide lattices at 100 K

	KI	KBr	KCl	RbI	RbBr
σ_{NC}	0.0356[c]	0.0357	0.0356	0.0356	0.0358
σ_{CS}	0.0417	0.0417	0.0416	0.0418	0.0419
q_{NC}	2.3760	2.3544	2.3699	2.3751	2.3526
q_{CS}	2.2174	2.2093	2.2283	2.2008	2.1924
γ_{NC}	0.6760	0.6791	0.6769	0.6761	0.6793
γ_{CS}	0.5965	0.5976	0.5951	0.5988	0.5999
	RbCl	NaI	NaBr	CsI	CsBr
σ_{NC}	0.0356	0.0356	0.0357	0.0356	0.0323
σ_{CS}	0.0418	0.0415	0.0412	0.0419	0.0423
q_{NC}	2.3689	2.3757	2.3572	2.3812	2.3617
q_{CS}	2.2080	2.2396	2.2734	2.1899	2.1457
γ_{NC}	0.6770	0.6760	0.6787	0.6753	0.6780
γ_{CS}	0.5978	0.5936	0.5891	0.6003	0.6064

[c] as in Table II.

by Borkman et al. [13] and reported in Table III together with path length parameter which represents the atomic core radii. The bond charge parameter (q) suggests that the bond order of CN bond is ~ 2.4 while that of CS is less than CN in agreement with the values calculated using Gordy's relation.

Comparing the force constants of NCO^- and NCS^-, the CN bond in NCS^- is stronger than that of NCO^- (F_{CN} = 15.4230, Ref. [14]) and is weaker than the CN bonds in other linear molecules (F_{CS} = 17.4356 – 18.1010, Ref. [15]). The CS bond in NSC^- is weaker than in CS_2 (F_{CS} = 7.62, Ref. [12]) and other linear molecules. The interaction terms are also noticeably smaller in NCS^- (F_{12ave} = 0.2928) than in NCO^- (F_{12} = 1.1526, Ref. [14]). This is because of the decreased overlap of carbon and sulfur. Since the sulfur orbitals are larger than that of oxygen, carbon and nitrogen, one can expect less interaction between the two bonds in NCS^-. The bending force constant of NCS^- is also smaller than that of NCO^- (F_α = 0.7400, Ref. [14]) which suggests that NCS^- is more ionic than NCO^- and hence it takes less energy to undergo the bending motion.

The vibrational frequencies in NaCl lattice are not available, but they have been estimated from the entrapolated line joining the points for RbCl and KCl. Using these frequencies, force constants have been calculated which are in good agreement with the values predicted from the plot of force constant vs lattice constant. These are given in Tables I and II.

These correlations can be extremely useful for suggesting reasonable values for the molecular constants and frequencies of missing members of such a series. They may also serve as an internal check within a given halide series.

REFERENCES

[1] A. Maki, J. C. Decius, *J. Chem. Phys.* **31**, 772 (1959).
[2] J. L. Bryant, G. C. Turrel, *J. Chem. Phys.* **37**, 1069 (1962).
[3] M. A. Cundill, *Ph. D. Dissertation*, Kings College, London 1968.
[4] M. U. Bely, G. I. Ermelenko, I. Y. Kushnirenke, *Ukr. Fiz. Zh.* **19**, 489 (1974).
[5] D. F. Smith, Jr., *J. Mol. Spectrosc.* **57**, 447 (1975).
[6] R. L. Redington, K. Aljibury, *J. Mol. Spectrosc.* **37**, 494 (1971).
[7] K. Ramaswamy, S. Karunanithi, *Acta Chim. Acad. Sci. Hung.* **87**, 129 (1975).
[8] C. B. Murchison, J. Overend, *Spectrochim. Acta* **27A**, 1509 (1971).
[9] W. Gordy, *J. Chem. Phys.* **14**, 305 (1946).
[10] G. C. Pimentel, S. W. Charles, *Pure Appl. Chem.* **7**, 111 (1963).
[11] L. Pauling, *The Nature of Chemical Bond*, Cornell University Press, Ithaca, New York 1960.
[12] J. Wentink, Jr., *J. Chem. Phys.* **30**, 105 (1959).
[13] R. F. Borkman, G. Simons, R. G. Parr, *J. Chem. Phys.* **50**, 58 (1969); R. F. Borkman, *J. Chem. Phys.* **51**, 5596 (1969).
[14] V. Schettino, I. C. Hisatsune, *J. Chem. Phys.* **52**, 9 (1970).
[15] K. Ramaswamy, PL. RM. Palaniappan, J. Annamalai University Science, S. India 1977.