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Coulombic Nonbonded Interatomic Potential Functions Derived from Crystal-Lattice Vibrational Frequencies in Hydrocarbons

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The method of calculation of crystal-lattice normal-mode frequencies of hydrocarbons was sharpened to include bond foreshortening of C–H bonds, dynamic derivatives, and atomic point charges. A test of the method was made with 118 observed structural parameters from 18 aromatic and saturated hydrocarbon crystal structures, and 58 observed crystal frequencies from five aromatic hydrocarbon crystal structures. The use of dynamic derivatives significantly improved the fit to the observed frequencies. The use of atomic point charges also significantly improved the fit to the observed frequencies; the optimum values found for the point charges were essentially identical to the optimum values obtained from structural data alone. The direct parameter-fit method, although giving reasonable results for the structural parameters, was found not to transfer well to the calculation of lattice frequencies. The force-fit method gave significantly better results for the lattice frequencies. The final optimum (exp$-6-1$) nonbonded interatomic potential functions derived from the combined structural and vibrational data were very similar to the functions derived from the structural data alone.

Introduction

The calculation of crystal lattice vibration frequencies has been the subject of much study since the initial formulation by Born & Huang (1954). Extension to molecular crystals was performed by Pawley (1967, 1972) using the rigid-molecule and atom–atom potential approximations. With this method the complete phonon dispersion curves can be calculated with relatively few adjustable parameters. These results can then be compared directly with experimental results from neutron inelastic scattering or Raman and IR spectroscopy. Other properties such as elastic constants, thermal diffuse scattering of X-rays, Debye–Waller factors and the Debye temperature can be calculated from the dispersion curves and compared with experiment. The use of such calculations to predict solid-state properties is the general aim of such investigations.

The error in the calculated frequencies introduced because of the rigid-molecule assumption has been investigated by several authors. For benzene, the errors are quite small (Taddei, Bonadeo, Marzocchi & Califano, 1973) and for a more flexible molecule such as naphthalene, the shifts are only about 10% (Pawley & Cyvin, 1970). Even for durene which includes the relatively low-frequency oscillations of methyl groups, the rigid-molecule approximation gives results within 10% of an extended treatment (Sanquer & Messager, 1975). Thus, the rigid-molecule approximation seems to be quite satisfactory, at least for fused-ring systems. Since the internal degrees of freedom systematically lower the lattice frequencies, this knowledge can be used implicitly when comparing calculated frequencies with experiment.

The critical problem in these calculations is an accurate description of the intermolecular potential. The atom–atom method has already proven quite successful for the calculation of heats of sublimation and crystal structures (Williams & Starr, 1977). A physically meaningful potential that gives good values for these static crystal properties should also give good results for the lattice dynamics. This is a fairly stringent test for a set of potential parameters but is critical to further applications of the potential. It is important that the potential be used consistently in both the static and dynamic calculations. Some authors have made small modifications in the structure-derived potentials for calculating the lattice frequencies. It should be noted that such modifications will, in general, worsen the fit to the heats of sublimation and crystal structure.

In the atom–atom method the intermolecular potential is given as the sum of atom–atom potentials. In principle, a whole class of molecules can be treated using only a few interactions. Rather than obtain potential parameters to give the best results for one particular molecule, we desire potential parameters that give reasonably good results for a wide range of systems. This will ensure the usefulness of the potentials for future applications.

Lattice dynamics

In the harmonic approximation to crystal-lattice dynamics, the crystal energy is expanded in a Taylor series in small displacements from the equilibrium position, neglecting terms to third order and higher. The first-order terms drop out since they correspond to the forces and torques on the molecule, which at equilibrium are zero. The solution to the equations of motion of the molecule in the crystal reduces to an eigenvalue problem. The eigenvalues of the dynamical matrix give the vibration frequencies while the eigenvectors give the normal modes. The dynamical matrix can be obtained from the atom–atom intermolecular potentials as shown by Pawley (1972).

On physical grounds, the dynamical matrix is required to be Hermitian. As noted by Scheringer (1974) and by actual calculations in this laboratory, Pawley's method does not strictly obey this constraint. Since the difference is small, the dynamical matrix is symmetrized by simply averaging the cross-diagonal terms. This has only a slight effect on the calculated frequencies.

For any particular set of potential parameters, the observed crystal structure will not exactly obey the equilibrium conditions of zero force and torque. Thus, small displacements from the observed structure must be made to reach the energy minimum required for the lattice dynamics calculation. Although the shifts in position may be quite small, this can have a relatively large effect on the frequencies.

The harmonic approximation for lattice dynamics and the atom–atom model contain no information about temperature. For crystal structures, this is not serious since thermal effects are rather small. For lattice frequencies this is not the case and the temperature variation is considerably larger. Some method of fixing the calculated frequencies to a particular temperature is desired. In the quasi-harmonic approximation the frequencies depend only on the volume (Leibfried & Ludwig, 1961) and the temperature variation is the indirect result of thermal expansion. Using this we set the lattice constants for a particular temperature from experiment. The calculated frequencies are then compared with experimental frequencies at the same temperature.

Previous work on hydrocarbons

The intermolecular potential for hydrocarbons can be obtained in the atom–atom model from interatomic potentials for C–C, H–H, and C–H. The interatomic potential can be written as a Buckingham potential (exp – 6)

$$V(r) = -Ar^{-6} + B\exp(-Cr)$$

or including Coulombic interactions (exp – 6 – 1)

$$V(r) = -Ar^{-6} + B\exp(-Cr) + q_1q_2r^{-1}\,.$$

A, B and C are adjustable parameters and q_1 and q_2 are the point charges on atoms 1 and 2. Certain assumptions are usually made about the distribution of charges to reduce the number of independent parameters (Williams, 1974).

Using non-Coulombic potential parameters from Kitaigorodsky, Pawley (1967) calculated the lattice frequencies for naphthalene and anthracene. His results are consistently high compared with the Raman results (Suzuki, Yokayama & Ito, 1968) with an r.m.s. error of about 17 cm^{-1}. More recently, Filippini, Gramaccioli, Simonetta & Suffritti (1973) have calculated frequencies for nine hydrocarbons using a non-Coulombic potential from this laboratory. Their results are generally low with an r.m.s. error of about 11 cm^{-1}. Although this could be considered good agreement there are two problems. First, the inclusion of non-rigid motion in the calculation is expected to lower the frequencies somewhat. Since the calculated frequencies are already generally too low, the agreement will become worse. The second problem is with the use of Williams's potential parameters. In deriving the parameters from crystal data, Williams has assumed a foreshortened C–H bond distance of 1·027 Å for aromatics (Williams, 1965). Consistent application of these potentials requires the use of this foreshortened bond length in the lattice-dynamics calculation.

Table 1 shows the effect of foreshortening on the lattice frequencies of naphthalene with the same potentials used by Filippinni *et al.* (1973). All the frequencies decrease significantly when foreshortening is used, resulting in a poorer fit to experiment. Thus, this potential is not as good for the calculation of lattice dynamics as it first appears.

Table 1. *Naphthalene lattice frequencies* (cm^{-1})

Mode	Experimental value[a]	C–H = 1·09 Å	1·027 Å
A_g	109	114·3	104·1
B_g	125	114·2	105·8
A_u	98	89·2	85·0
A_g	74	81·0	73·8
B_g	71	68·5	60·0
B_u	73	53·4	50·3
A_g	51	51·7	46·6
B_g	46	43·6	41·4
A_u	39	42·3	39·3
	R.m.s. error	9	12

References: (*a*) Suzuki, Yokayama & Ito (1968); Bazhulin & Rakhinov (1967).

Taddei, Bonadeo, Marzocchi & Califano (1973) have also used this potential in calculating the lattice dynamics of benzene. In addition to the neglect of foreshortening, these workers did not shift the molecule to the energy minimum prior to the lattice-dynamics calculation. The effect of this is shown in Table 2. Both foreshortening the C–H bonds and relaxing the forces have a great effect on the frequencies and, in general, result in a worsening of the fit to experimental values. Thus, this hydrocarbon potential does not give good results for the lattice dynamics when consistently applied.

More recent parameter sets

More recent potential parameter sets have been derived from crystal structure data with two different methods. The force method has been used previously by Williams (1970) and is based on minimizing the

Table 2. *Comparison of lattice-dynamics models*

Lattice frequencies (cm)$^{-1}$ of benzene at 138 K

Mode	Experimental value[a]	Observed structure CH = 1·090 Å	Observed structure 1·027 Å	Minimized structure 1·090 Å	Minimized structure 1·027 Å
A_g	93	91·9	83·9	92·6	80·0
	78	69·6	65·8	75·6	66·9
	57	46·3	42·9	36·7	27·2
B_{1g}	128	125·9	116·0	137·3	118·8
	84	84·3	74·9	87·0	73·0
	61	60·3	51·4	69·6	57·9
B_{2g}	90	98·1	89·2	103·0	85·9
	–	88·9	78·0	91·3	76·9
	79	78·9	73·1	80·2	69·3
B_{3g}	128	128·0	117·3	139·0	119·1
	100	91·7	82·8	97·7	82·9
	57	52·8	48·6	47·5	40·5
A_u	–	97·8	90·8	103·2	88·8
	–	66·0	59·5	71·6	62·3
	–	56·5	53·0	59·1	52·1
B_{1u}	98	98·5	92·0	97·4	83·7
	65·5	53·1	50·5	57·1	49·7
B_{2u}	100	101·4	94·8	108·9	95·1
	56	58·6	54·8	56·6	49·3
B_{3u}	88·5	86·7	80·5	90·5	78·6
	73	72·4	66·7	74·3	65·5
R.m.s. error		6	10	8	13

Reference: (*a*) Taddei, Bonadeo, Marzocchi & Califano (1973).

forces at the observed crystal structures. The direct parameter-fit method was proposed by Hagler & Lifson (1974), and minimizes the estimated shifts from the observed structure with a Taylor series expansion. The details of these schemes and the derived potentials are given in another paper (Williams & Starr, 1977). Potential I uses the force method and has no point charges. Potential II also uses the force method but includes Coulombic effects. Potential III is a Coulombic potential derived with the direct parameter-fit method. A comparison of these potentials for the calculation of crystal structure shows the two Coulombic potentials to be about equally good and much better than the non-Coulombic. The values for the potential parameters are given in Table 3.

Table 3. *Hydrocarbon potential parameters derived from crystal data* (kJ mol^{-1}, Å, *electrons*)

Parameter	Force method Set I non-Coulombic	Force method Set II Coulombic	Direct parameter fit Set III Coulombic
A_{HH}	102	136	153
B_{HH}	9080	11677	14662
C_{HH}	3·74	3·74	3·74
A_{HC}	467	574	642
B_{HC}	35600	65485	84788
C_{HC}	3·67	3·67	3·67
A_{CC}	2140	2414	2695
B_{CC}	300000	367250	490290
C_{CC}	3·60	3·60	3·60
q_H(CH)	0·000	0·153	0·167

These potentials are used to calculate the Raman and IR frequencies for five aromatic hydrocarbons for which experimental values are available. Convergence acceleration is used for the Coulombic potentials (Williams & Starr, 1977). Fixing the lattice constants at the experimental values, the molecules are shifted slightly to the energy minimum with the computer program *PCK6* (Williams, 1972), before calculating the frequencies. For benzene, the low-temperature extrapolated lattice constants are used. The calculated frequencies are compared with experiment in Table 4. Potential II gives the best fit to experiment with an r.m.s. error of 14 cm^{-1}. Potential I gives an r.m.s. error of 20 cm^{-1} and potential III gives 27 cm^{-1}. Although potentials II and III give similar results for the crystal structure, potential II is clearly superior for the crystal dynamics. The Coulombic potential II is again shown superior to the non-Coulombic potential I. Inclusion of internal degrees of freedom should result in a general improvement in the results for potentials II and III and a worsening for potential I. Overall, the best fit to both structure and dynamics is obtained with the Coulombic potential derived using the force method.

Table 4. *Observed and calculated frequencies* (cm^{-1})

The potential sets are given in Table 3.

Crystal	Mode	Experimental value	Force non-Coulombic	Force Coulombic	Direct parameter fit Coulombic
Benzene[a] 77 K	A_g	97·5	79·2	105·0	121·3
		83·0	65·7	92·3	104·8
		61·0	27·3	47·0	48·0
	B_{1g}	132·0	118·4	163·7	189·9
		87·0	72·9	98·2	112·7
		67·0	56·4	67·4	79·4
	B_{2g}	–	85·5	129·7	148·4
		94·0	77·4	106·5	121·8
		83·0	69·4	95·2	111·0
	B_{3g}	132·0	118·3	163·7	188·7
		105·0	82·8	123·5	143·3
		65·0	42·5	60·3	68·0
	A_u	–	89·6	124·2	144·4
		–	62·5	77·7	92·5
		–	52·9	70·0	82·5
	B_{1u}	102·0	85·0	122·3	142·5
		71·0	50·4	67·6	78·7
	B_{2u}	105·0	96·6	131·2	155·1
		59·0	49·9	69·6	80·7
	B_{3u}	91·5	79·5	105·2	123·9
		76·0	66·1	89·0	106·3
Naphthalene[b] 298 K	A_g	109	99·8	135·7	158·9
		74	67·5	91·8	108·3
		51	41·6	53·8	62·4
	B_g	125	100·7	140·2	164·9
		71	54·2	77·6	91·7
		46	37·7	53·8	55·8
	A_u	98	79·7	110·8	133·2
		39	34·2	46·8	55·6
	B_u	73	45·4	69·1	80·3
Anthracene[c] 293 K	A_g	121	113·2	149·7	180·5
		70	61·7	90·0	114·9
		39	29·4	39·4	45·8
	B_g	125	108·7	148·9	184·4
		65	49·6	71·2	89·1
		45	37·3	47·5	59·1
	A_u	–	83·8	115·9	146·9
		–	28·2	40·8	50·6
	B_u	–	45·2	70·0	83·4

Table 4 (*cont.*)

Crystal	Mode	Experimental value	Force non-Coulombic	Force Coulombic	Direct parameter fit Coulombic
Phenanthrene[d]	A	127	97·9	133·3	158·0
298 K		108	71·0	97·7	116·5
		89	48·1	69·6	82·0
		62	42·8	54·8	64·2
		33	28·2	40·7	47·7
	B	109	87·0	121·7	145·9
		99	65·2	94·6	112·4
		60	43·5	63·9	74·8
		31	21·7	30·0	36·2
Pyrene[e]	A_g	127	86·0	108·9	127·4
298 K		92	75·6	98·3	116·3
		76	51·6	72·7	87·1
		56	38·4	45·7	57·7
		46	31·2	41·8	49·8
		17*	16·0	20·7	24·1
	B_g	126	87·7	112·8	132·5
		93	76·4	100·8	120·3
		67	56·5	78·7	95·4
		56	35·4	46·7	55·7
		41	30·5	45·4	53·3
		30	22·0	30·5	36·8
	A_u	102	91·4	119·4	139·9
		71	69·8	87·9	101·6
		–	41·2	61·8	75·8
		–	36·6	52·1	61·0
		–	19·1	28·6	34·4
	B_u	105	91·5	120·5	141·0
		89	72·4	94·5	112·9
		70	43·0	62·7	74·2
		–	25·1	35·0	40·7
R.m.s. error			19·6	13·6	26·8

References: (*a*) Structure: Bacon, Curry & Wilson (1964). Frequencies: Sataty & Ron (1976), Sataty, Ron & Brith (1973). (*b*) Structure: Cruickshank (1957). Frequencies: Suzuki, Yokayama & Ito (1968), Bazhulin & Rakhinov (1967). (*c*) Structure: Mason (1964). Frequencies: Suzuki, Yokayama & Ito (1968). (*d*) Structure: Trotter (1963). Frequencies: Bree, Solven & Vilkos (1972). (*e*) Structure: Camerman & Trotter (1965). Frequencies: Bree, Kydd, Misra & Vilkos (1971). * Zallen, Griffiths, Slade, Hayek & Brafman (1976).

Derivation of parameters using lattice frequencies

Since the direct parameter-fit method more directly fits the crystal parameters, a modification of this method was made to include the fit to lattice vibrations. This was done by including the frequencies directly in the least-squares fitting scheme to obtain potential parameters.

Examples of the derivation of potential parameters using lattice frequencies are quite limited. Taddei, Bonadeo, Marzocchi & Califano (1973) used a least-squares procedure to improve the fit to the frequencies of benzene. This work is subject to the problems discussed earlier: they do not relax the forces before calculating the frequencies and they do not use the proper foreshortened bond lengths. Bonadeo & D'Alessio (1975) refined the potential parameters for a series of chlorobenzenes and their work has the same problems as the benzene study.

The only completely satisfactory studies of molecular crystals are Rinaldi & Pawley (1975) for orthorhombic sulfur and Huler & Zunger (1975) for solid nitrogen. The latter work goes beyond a simple intermolecular potential model to include entropy effects. The method of Rinaldi & Pawley is equivalent to that described in this paper. Orthorhombic sulfur is a particularly simple case since it contains only one type of atom and one crystal structure. A unified refinement involving a broad range of hydrocarbons and using heats of sublimation, crystal structure parameters, and lattice frequencies has not been performed previously.

In general, a particular crystal lattice frequency is a function of the potential parameters (q) and the structural parameters (p) at the equilibrium position. The position of equilibrium is also a function of the potential parameters so that the frequency is affected both directly and indirectly by the potential parameters.

$$\omega = \omega[q, p(q)]\,.$$

For a least-squares fitting, the derivative of the frequency with respect to each potential parameter is needed. This is given by

$$\mathrm{d}\omega/\mathrm{d}q_i = \partial\omega/\partial q_i + \sum_j \partial\omega/\partial p_j\ \partial p_j/\partial q_i\,. \qquad (1)$$

The first term corresponds to holding the structure constant while varying the potential parameters. This derivative, which we will call the static derivative, can be obtained analytically as outlined by Pawley (1972). The squared frequencies in the lattice-dynamics calculations are obtained as eigenvalues of the dynamical matrix, M. That is, the matrix R, of eigenvectors, diagonalizes the dynamical matrix giving the squared frequencies, $\Omega = \omega^2$ as the diagonal elements:

$$\mathsf{R}\mathsf{M}\mathsf{R}^{-1} = \mathsf{R}\mathsf{M}\mathsf{R}^{T} = \Omega \text{ since R is orthogonal}\,.$$

For a small change Δq in a potential parameter

$$\Delta\Omega = \mathsf{R}'(\partial\mathsf{M}/\partial q_i \Delta q_i)\mathsf{R}'^{T}\,.$$

Dividing by Δq and taking the limit, we obtain

$$\partial\omega/\partial q_i = \mathsf{R}\,\partial\mathsf{M}/\partial q_i \mathsf{R}^{T}\,.$$

The diagonal elements of this matrix will give the necessary derivatives:

$$\partial\omega/\partial q_i = (\partial\Omega/\partial q_i)/2\omega\,.$$

The dynamical matrix can be written as a sum of terms, each involving only one potential type, with the potential parameters A, B, and q factored out of the lattice sums

$$\mathsf{M} = A_{\mathrm{HH}}\mathsf{M}_6(\mathrm{HH}) + A_{\mathrm{HC}}\mathsf{M}_6(\mathrm{HC})\ldots + B_{\mathrm{CC}}\mathsf{M}_R(\mathrm{CC})\ldots + q^2\mathsf{M}_1$$

where $\mathsf{M}_6(\mathrm{HH})$ is a summation over the crystal involving only r^{-6} terms between two hydrogens. M_R and M_1 have similar meanings for the repulsive and Coulombic terms. The exponents C_{HH}, C_{HC} and C_{CC}

cannot be factored out of the expression. The derivatives are then taken directly.

$$\partial\Omega/\partial A_{\mathrm{HH}} = \mathrm{RM}_6(HH)\mathrm{R}^T, \textit{ etc.}$$

Obtaining these derivatives takes only slightly longer than obtaining the frequencies alone.

As a first approximation, the other terms in (1) are neglected and the derivatives obtained are used in a least-squares fitting scheme. It is convenient to refine the parameters a_{H}, b_{H}, a_{C}, b_{C} and q where $a_{\mathrm{H}}^2 = A_{\mathrm{HH}}$, $a_{\mathrm{C}}^2 = A_{\mathrm{CC}}$, $b_{\mathrm{C}}^2 = B_{\mathrm{CC}}$ and the parameter q is the partial charge in electrons on an aromatic hydrogen. Assuming the geometric-mean combining law,

$$a_{\mathrm{H}}a_{\mathrm{C}} = A_{\mathrm{HC}}, \quad b_{\mathrm{H}}b_{\mathrm{C}} = B_{\mathrm{HC}}$$

and

$$\begin{aligned}
\partial\omega/\partial a_{\mathrm{H}} &= 2a_{\mathrm{H}}\partial\omega/\partial A_{\mathrm{HH}} + a_{\mathrm{C}}\partial\omega/\partial A_{\mathrm{HC}} \\
\partial\omega/\partial b_{\mathrm{H}} &= 2b_{\mathrm{H}}\partial\omega/\partial B_{\mathrm{HH}} + b_{\mathrm{C}}\partial\omega/\partial A_{\mathrm{CC}} \\
\partial\omega/\partial a_{\mathrm{C}} &= 2a_{\mathrm{C}}\partial\omega/\partial A_{\mathrm{CC}} + a_{\mathrm{H}}\partial\omega/\partial A_{\mathrm{HC}} \\
\partial\omega/\partial b_{\mathrm{C}} &= 2b_{\mathrm{C}}\partial\omega/\partial B_{\mathrm{CC}} + b_{\mathrm{H}}\partial\omega/\partial A_{\mathrm{HC}}\,.
\end{aligned}$$

The structural data for 18 aromatic and saturated hydrocarbons yield 118 observational equations. The five aromatic hydrocarbons yield 58 observed crystal frequencies. Heats of sublimation for benzene and *n*-hexane are included to scale the potential. These compounds were selected as representative aromatic and saturated hydrocarbons. Their heats of sublimation have been determined calorimetrically to good accuracy.

Weighting scheme

In any non-linear least-squares procedure the choice of weights is important, particularly when fitting such a wide variety of data. Ideally the weight is the reciprocal of the square of the standard deviation of the observation. Using this relation we obtain weights from estimates of error for each type of data. These estimates are: unit-cell edge 1%, cell angles and molecular rotations 0·02 rad, molecular translations 0·05 Å, lattice frequencies 4·5 cm^{-1}, heats of sublimation 0·2 kJ mol^{-1}.

Results – static derivatives

After an initial improvement of the frequency fit at the expense of the structure fit, subsequent cycles showed no improvement. Indeed, the overall fit worsened in some cycles, indicating that the shifts chosen were not correct. This suggests that the derivatives for the crystal frequencies are not correct and that the last terms in (1) cannot be neglected.

Comparison of static and dynamic derivatives

Calculation of the additional terms in (1) cannot be done analytically. The correct derivatives, which we will call dynamic derivatives, can be calculated numerically by making a small change in a potential parameter, minimizing the energy and recalculating the frequencies. The derivative is evaluated from:

$$\partial\omega/\partial q_i = [\omega(q_i + \Delta q_i) - \omega(q_i)]/\Delta q_i$$

where q_i is a particular parameter. This procedure requires considerable computer time but is possible with the available facilities. A comparison of static and dynamic derivatives for benzene illustrates the failure of the static-derivative approximation. The difference between the derivatives is largest for b_{C} and q with several derivatives that change sign. The lowest A_g mode, which caused a great deal of difficulty in the first fitting attempt, shows particularly large changes in the derivatives.

Results – dynamic derivatives

Using dynamic derivatives the least-squares fit proceeded smoothly with each cycle resulting in a better fit than the previous. Convergence was obtained after five cycles resulting in the parameter set given in Table 5. Comparison with Table 3 indicates a striking similarity between this parameter set and that derived with the force method and structure data only. The frequencies calculated from the two sets are practically identical. This result strongly supports the force method as yielding the 'best' set of parameters consistent with both structure and dynamics.

Table 5. *Potential parameters from unified refinement* (kJ mol^{-1} *and* Å)

A_{HH}	126	C_{HC}	3·67
B_{HH}	9816	A_{CC}	2420
C_{HH}	3·74	B_{CC}	409600
A_{HC}	552	C_{CC}	3·60
B_{HC}	63410	q	0·159

Conclusion

The Coulombic potential II which is derived from structural data with the force method is successful in the calculation of both crystal structure and crystal-lattice dynamics. The non-Coulombic potential does not compare well in either calculation. The potential derived using the direct parameter-fit method fails for the lattice-frequency calculation. These results support the Coulombic model for hydrocarbons and the force method for the derivation of the potential parameters. Inclusion of internal vibrations in the calculation will generally give an improvement in the fit to experiment. Further work toward improving the potential model will be needed to include the temperature variations of the frequencies and cell constants.

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An X-ray Diffraction Study of NaF

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NaF gives rise to very weak odd-index reflexions in X-ray diffraction. These reflexions have been studied to determine the best models for electron distribution in the NaF crystal. Data were obtained from a single crystal at room temperature for Ag $K\alpha$, Mo $K\alpha$, Cu $K\alpha$ and Co $K\alpha$ radiations. Least-squares analyses were made on the Ag $K\alpha$ and Mo $K\alpha$ data. Scattering factors for Hartree–Fock singly charged free ions allowed a good fit to the data, and there was a marginal improvement of the fit with similar scattering factors modified for effects of crystalline environment. The mean thermal parameter for the ions was $\bar{B}=0{\cdot}905\pm0{\cdot}025$ Å^2. An attempt to account for the wavelength dependence of intensities of the strong reflexions, with current theories of extinction, was unsuccessful.

1. Introduction

The structure of NaF was established early in the history of X-ray crystallography. There are nevertheless a number of pertinent questions which might be answered from a careful study of the intensities of the various reflexions. These questions include:

1. How can the data be processed to yield structure factors on the correct scale?
2. What are the values of the thermal parameters B_{Na} and B_{F}?
3. How are the intensities affected by extinction in any particular crystal?
4. To what extent are the tabulated atomic/ionic scattering factors adequate for describing the diffraction? This question relates to the suitability of various models for the electron distribution in NaF.

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