

04.5-10 ENERGY ANALYSES FOR THE ALKALINE-EARTH FORMATES. By M. Matsui and T. Watanabé*, Chemical Laboratory, Kanazawa Medical University, Uchinada, Ishikawa-ken. *Osaka University, Yamada, Suita, Japan.

The structures of the alkaline-earth formates have been investigated in terms of lattice energy calculations. The lattice energy was approximated to be the sum of electrostatic and repulsive terms, where the repulsive potential used was in the form: $(1/12)f(R_{\alpha}+R_{\beta})^{13}r^{-12}$ (r ; interatomic distance, f ; arbitrarily chosen standard force, R_{α} ; repulsive radius of an atom α). The formate ions were treated as rigid bodies. The repulsive radii of atoms concerned and the net charge on each atom of the formate ion were derived using the three known crystal structures, α -Ca(HCOO)₂, α -Sr(HCOO)₂ and Ba(HCOO)₂, by a least-square fit. The results are as follows: $R_{Ca}(A) = 1.591$, $R_{Sr} = 1.802$, $R_{Ba} = 2.025$, $R_O = 1.870$ for $f = 1 \text{ kJ} \cdot \text{A}^{-1} \cdot \text{mol}^{-1}$, $q_O(|e|) = -0.86$, $q_C = +0.87$, $q_H = -0.15$. R_H was fixed at 1.337 A, and R_C was assumed to be equal to R_O . The reliability of these potential parameters were tested by the calculations of energy minimized structures for the above three structures and for the structure of β -Ca(HCOO)₂, with the results that the observed structures were all well reproduced. The potential and potential parameters proposed were successfully used for the determination of the structure of β -Sr(HCOO)₂, for the differentiation of the structures of α -Sr(HCOO)₂ and Ba(HCOO)₂, and for the interpretation of the large anisotropy of thermal vibrations in β -Ca(HCOO)₂.

04.5-11 POTENTIAL-ENERGY CALCULATIONS IN CRYSTALS: CARBON DIOXIDE, CO₂, AND 9,10-ANTHRAQUINONE, C₁₄H₈O₂.

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In 1970, carbon...oxygen and oxygen...oxygen potentials of the Buckingham 6-exp type were derived from crystal and molecular data for carbon dioxide (Kitaigorodsky, Mirskaya, Nauchitel, Soviet Physics-Crystallography(1970) 14,769). The lattice energy of CO₂ was represented as a sum of the van der Waals (vdW) and electrostatic terms. The C...C empirical parameters were transferred to CO₂ from hydrocarbons. Later, the C...C parameters were refined (Mirskaya, Kozlova, Bereznitskaya, Phys.Stat.Sol. (1974)62b,291) and the electrostatic term, which provides most of the calculated lattice energy of carbon dioxide, was reexamined (Hirshfeld, Mirsky, Acta Cryst.(1979)A35, 366). We have recently revised the O...O parameter values.

We are now making crystal-structure and energy calculations for another oxygen-containing compound, 9,10-anthraquinone, using the same O...O potential in combination with the C...C and H...H ones. The electrostatic-energy contributions, due to the interactions of the C=O groups, are not expected to be as significant here as in CO₂, but they might be responsible for the pseudoorthorhombic molecular arrangement and the negative thermal expansion coefficient along the c axis (Lonsdale, Milledge, El Sayed, Acta Cryst.(1966)20,1). We consider this calculation a further test of the assumption of transferability of the vdW potential functions, one of the basic assumptions of the atom-atom potential approach to the investigation of non-bonded intra- and intermolecular interactions.

The computations are made using the WMIN computer program (Busing, Acta Cryst.(1972)A28,S252). The research is supported by NSF grants CHE77-18748 and CHE80-22526.

04.5-12 INTERMOLECULAR POTENTIAL FUNCTION FOR CRYSTALLINE HALOGENS. By G. B. Carpenter, Department of Chemistry, Brown University, Providence, RI 02912 and W. R. Busing, Chemistry Division, Oak Ridge National Laboratory, P. O. Box X, Oak Ridge, TN 37830, U.S.A.

Many potential energy functions have been suggested for the crystalline halogens, and it is widely agreed that intermolecular bonding must be included to stabilize the observed structure (see, for example, Hsu & Williams, Inorg. Chem. (1979) 18, 79). The directional nature of this bonding has usually been omitted as unimportant or too complicated for reasonable calculation. Instead, Hsu & Williams have included a bonding term arbitrarily assigned to the shortest intermolecular contact only. Although their model B+Q+M reproduced the observed structure, the calculated frequencies for the 7 optical external-mode vibrations are not in good agreement with the observed frequencies: values calculated by the program WMIN (Busing, Acta Cryst. (1972) A28, S 252; "WMIN, a computer program to model molecules and crystals in terms of potential energy functions", ORNL-5747, Oak Ridge National Laboratory, in press) are listed as $\nu(I)$ in the table.

Mode	B _{3g}	A _g	B _{2u}	B _{2g}	B _{1u}	B _{1g}	A _u
$\nu(\text{obs})/\text{cm}^{-1}$	113	96	89	81	62	--	--
$\nu(I)/\text{cm}^{-1}$	80	50	99	27	75	27	-7
$\nu(II)/\text{cm}^{-1}$	100	96	101	82	77	67	22

We have tested a model that is composed of Buckingham terms of the form $B_R \exp[(A_R-r)/B_R] - P_L/r^6$ and anisotropic intermolecular bonding terms R_B^Y/B_B where

$$R_B = -B_B \exp[(A_B-r)/B_B]$$

and

$$Y_B = \exp \{ -[(A-\phi_i)^2 + (180-\phi_j)^2]/2\sigma^2 \} \\ + \exp \{ -[(A-\phi_j)^2 + (180-\phi_i)^2]/2\sigma^2 \}$$

The angle-dependent factor Y_B describes the conditions for formation of bonding molecular orbitals between adjacent molecules, namely, that one angle be near 180° and the other be near Δ , which we have determined empirically to be 108.2° for Cl₂, Br₂, and I₂.

The current choices of other parameters in kcal mol⁻¹, A, and degrees) are tabulated.

	A _R /2	B _R /2	P _L ^{1/2}	A _B /2	B _B /2	σ
Cl	1.940	0.1424	42.058	1.959	0.2062	32.68
Br	2.069	0.1524	51.821	2.208	0.2242	33.50
I	2.248	0.1650	74.900	2.446	0.2500	30.69

These parameters reproduce the correct unit cell dimensions to better than 1%, and the orientation of the molecule in the layers to better than 0.4°. For chlorine the calculated frequencies are tabulated above as $\nu(II)$, and it is apparent that they agree much better with observed values than do the frequencies calculated for isotropic bonding.

Research sponsored by the Division of Materials Sciences, U. S. Department of Energy, under contract W-7405-eng-26 with Union Carbide Corporation.