AN INTERMOLECULAR FORCE FIELD FOR CHLORINATED BENZENE CRYSTALS

H. BONADEO* and E. D'ALESSIO*
Departamento de Radiaciones Atómicas y Moleculares, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina

Received 23 October 1972

Intermolecular potential parameters corresponding to atom–atom interactions of the Buckingham form are refined on the basis of static and dynamic properties of some chlorinated benzene crystals. The model reproduces well the observed properties, including $\boldsymbol{k} \neq 0$ vibrations.

The intermolecular potential model of the non-bonded atom–atom type seems to be one of the most promising empirical descriptions of intermolecular forces, being able to reproduce static as well as dynamic properties of molecular crystals.

Parameters fitted by Williams [1] on statical properties of hydrocarbon crystals for C–C, C–H, and H–H interactions have been successfully used to calculate crystal frequencies of the benzene crystal [2–4].

In the present work we extend the model to chlorinated benzenes, and refine Cl–Cl, Cl–C, and Cl–H potential parameters on the basis of observed lattice frequencies, heats of sublimation and crystal structure of C_6Cl_6, 1,3,5-$C_6H_3Cl_3$, and p-$C_6H_4Cl_2$ in its α and β phases. Williams' parameters have been preserved for the remaining interactions, thus including the benzene crystal automatically in our system.

The form of the atom–atom potential function used is

$$V_{ij} = -Ar_{ij}^{-6} + B\exp(-Cr_{ij}) ,$$

and was determined mainly by the success of the benzene calculations.

The calculation method adopted is fully described in ref. [4], and will not be presented here in detail. Basically, we start with a set of trial potential parameters, calculate the crystal properties, and set up a jacobian

$$J_{pq} = \partial X_p / \partial R_q ,$$

where the X_p's are crystal frequencies, heats of sublimation, and rigid body equilibrium conditions, and the R_q's the potential parameters, and refine these with the usual least-squares method,

$$\Delta R = (\tilde{J}\mathcal{P}J)^{-1}\tilde{J}\mathcal{P}\Delta X ,$$

where $\mathcal{P}$ is a diagonal weighting matrix.

The crystal structures of the compounds mentioned above are known [5–8] and the heats of sublimation have been measured [9–11]. We have assumed that both phases of p-$C_6H_4Cl_2$ have the same heat of sublimation. Lattice frequencies and their assignments were taken from the literature [12–15] except for β p-$C_6H_4Cl_2$, where we have used our own measurements.

The rigid-body approximation has been used throughout the refinement. We have verified that the effect of mixing with internal modes on calculated lattice frequencies is negligible.

In all, we used 54 data to determine the potential parameters. There are, in principle, nine of them, but we found that in all cases, rows of the jacobian corresponding to B and C parameters of a given interaction, are nearly proportional, i.e., B and C are not independent parameters in our system. Therefore, we have chosen to refine only on B, and are left with a two-

* Fellow of the Consejo Nacional de Investigaciones Científicas y Técnicas.

parameter function. Anyhow, B and C can be re-adjusted at any stage of the refinement, by taking into account the respective jacobian ratios, with negligible effect on calculated properties.

Given these conditions, the refined potential parameter set is unique. We have started the refinement from parameters proposed by Kitaigorodskii [16], from a set formed by averaging Cl–Cl and C–C interactions to get the C–Cl interaction, and from a refined set proposed very recently by Reynolds et al. [17], getting always the same result. This conclusion is correct only if heats of sublimation are taken into account with a significant weight in the refinement: there are many different parameter sets, with completely different shapes, that show very similar second derivatives of the potentials, as can be seen in fig. 1 for potential sets A, B, and C of table 1, which fit similarly well observed lattice frequencies. Of these, potential set A is our best refined set, and also fits observed heats of sublimation. Potential sets B and C

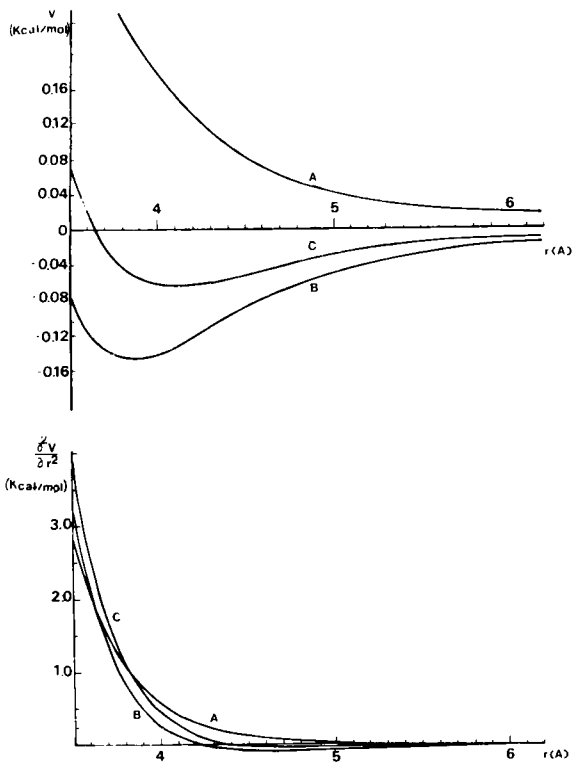

Fig. 1. Cl–C potential curve and its second derivative for parameter sets A, B, and C of table 1.

Table 1
Refined potential parameters, calculated rms errors and heats of sublimation for some chlorinated benzene crystals. Units: B (kcal/mole); C (Å^{-1}); A (kcal Å^6/mole); ΔH (kcal/mole); ν (cm^{-1})

Parameter		Parameter set A	B	C	
Cl–Cl	B	263000	243000	264000	
	C	3.51	3.51	3.51	
	A	3650	2320	3030	
Cl–C	B	44200	128000	127000	
	C	3.653	3.653	3.653	
	A	−631	808	500	
Cl–H	B	33300	15900	18600	
	C	3.623	3.623	3.623	
	A	1005	247	400	
ΔH					exp.
C_6Cl_6		21.6	23.8	28.4	21.9
1,3,5-$C_6H_3Cl_3$		16.1	17.1	19.3	14.2
β p-$C_6H_4Cl_2$		14.8	14.9	16.4	15.5
α p-$C_6H_4Cl_2$		14.8	16.7	16.7	15.5
rms error on frequencies		4.6	5.3	5.4	
rms total error		1.6	1.9	2.0	

were obtained without restrictions on the heats of sublimation, using different starting points and imposing the condition on the parameters of being positive.

The fact that the attractive parameter of the Cl–C interaction turns negative, making this potential repulsive at all distances stems, in our opinion, from the particular form chosen for the potential. It should be mentioned that we are dealing with an average potential of all atoms involved and therefore a physical interpretation of each individual interaction is not straightforward.

The final result of the calculation on lattice frequencies is shown in fig. 2. The differences between observed and calculated heats of sublimation are shown in table 1. The calculated equilibrium structures are within 1 degree and 0.01 Å difference with respect to observed ones in rigid-body rotations and translations. We feel that this result, given the roughness of the model, is extremely encouraging. Further-

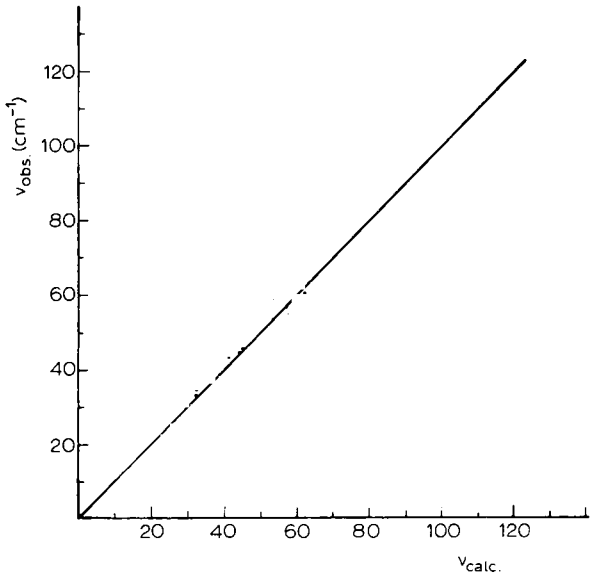

Fig. 2. Observed versus calculated frequency plot for refined potential parameters (set A of table 1).

more, the lattice frequencies of 1,2,4,5-$C_6H_2Cl_4$ calculated with potential set A show reasonable agreement with our preliminary experimental results.

Recently, Reynolds et al. [17] have presented a coherent inelastic neutron diffraction study of the β phase of deuterated paradichlorobenzene. We have calculated the dispersion curves for this crystal in the $\langle \xi\ 0\ 0 \rangle$ and $\langle 0\ \eta\ 0 \rangle$ directions in the reciprocal lattice, for which experimental data are available, and the results are shown in fig. 3. Again, the agreement is satisfactory, taking into account the spread of experimental points.

In conclusion, we have found that the atom–atom model can be extended with success to molecular crystals containing chlorine atoms; we feel that further work on the transferability of the potential parameters to other crystals should be performed, in order to establish the limitations of the model.

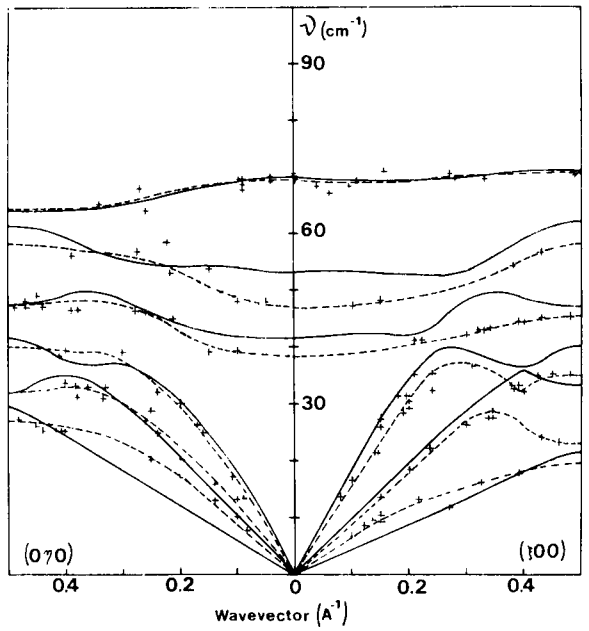

Fig. 3. Dispersion curves for β p-$C_6H_4Cl_2$ at 295°K. Crosses represent experimental points (ref. [17]); full lines are calculated with parameter set A; dotted lines represent experimental assignment (ref. [17]).

References

[1] D.E. Williams, J. Chem. Phys. 45 (1966) 3770.
[2] D.A. Oliver and S.H. Walmsley, Mol. Phys. 17 (1969) 617.
[3] E.R. Bernstein, J. Chem. Phys. 52 (1970) 4701.
[4] G. Taddei, H. Bonadeo and S. Califano, Chem. Phys. Letters 13 (1972) 136;
G. Taddei, H. Bonadeo, M.P. Marzocchi and S. Califano, J. Chem. Phys. (1973), to be published.
[5] I.N. Strel'tsova and Y.T. Struchkov, J. Struct. Chem. 2 (1961) 296.
[6] H.J. Milledge and L.M. Pant, Acta Cryst. 13 (1960) 285.
[7] E. Frasson, C. Sarbuglio and S. Bezzi, Acta Cryst. 12 (1959) 126.
[8] J. Housty and J. Clastre, Acta Cryst. 10 (1957) 695.
[9] H. Darkis, Ind. Eng. Chem. 32 (1940) 946.
[10] E. Balson, Trans. Faraday Soc. 43 (1947) 54.
[11] S. Sears and L. Hopke, J. Am. Chem. Soc. 71 (1949) 1632.
[12] J.B. Bates, D.M. Thomas, A. Bandy and E.R. Lippincott, Spectrochim. Acta 27A (1971) 637.
[13] D.E. Muller, T. Inoue, R.H. Larkin and H.D. Stidham, Spectrochim. Acta 27A (1971) 405.
[14] M. Suzuki and M. Ito, Spectrochim. Acta 25A (1969) 1017.
[15] B. Wincke, A. Hadni and X. Gerbaux, J. Phys. (Paris) 31 (1970) 893.
[16] A.I. Kitaigorodskii and V.G. Dashevsky, Tetrahedron 24 (1968) 5917.
[17] P.A. Reynolds, J.K. Kjems and J.W. White, Symposium on Neutron Inelastic Scattering, Grenoble (1972) IAEA/SM-155/B-2.