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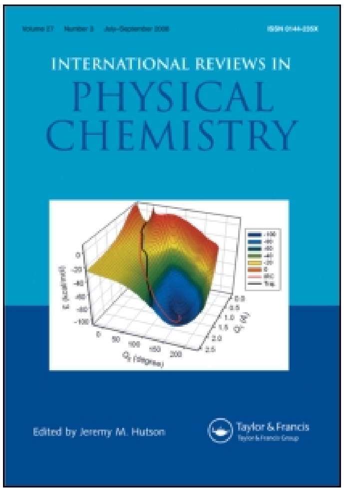

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Spectroscopy of molecular crystals and crystallographic implications

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Spectroscopy of molecular crystals and crystallographic implications

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In recent years, the correlation between crystallography and other branches of physical chemistry has received considerable attention. This interest arises from a substantial increase in the accuracy of experimental results and from very considerable advances in computing facilities and techniques. In particular, many results concerning crystallography and spectroscopy can usefully be compared, and one discipline can give substantial information to the other. For instance, the calculation of vibrational frequencies in molecular crystals, which is linked to the possibility of evaluating thermodynamic functions and temperature factors *a priori*, is becoming almost a routine operation; examples of such procedures are given.

In recent years, crystallographic measurements of high accuracy have become more frequent, and so the possibility of correlating such results with other physical-chemical procedures has become more rewarding. Among these procedures, vibrational spectroscopy seems to offer a number of interesting possibilities.

For instance, crystallography can provide the spectroscopist with unquestionable symmetry data and atomic coordinates for building a correct starting model to interpret the vibrational pattern; on the other hand, spectroscopy appears to be the best way for deriving thermal libration corrections, especially in complex cases when a rigid-body model cannot be applied. Another possibility, which does not seem to have been applied so far, might be that of deconvoluting thermal vibration effects from diffraction data for accurate electron density measurements; these possibilities are linked to the existence of a simple and reliable way of deriving temperature factors from spectroscopic data. As we shall see, if the $\mathbf{U}(\kappa)$ tensors corresponding to temperature factors are obtained with a good approximation, then there is reason to believe that also the so-called 'coupling tensors' $\mathbf{U}(\kappa\kappa') = \langle \mathbf{u}(\kappa)\mathbf{u}(\kappa')^T \rangle$ between the displacements of different atoms κ and κ', as obtained from the same spectroscopic calculations, are essentially correct, although in this case no check with the corresponding results from X-ray or neutron diffraction can be made. Together with the $\mathbf{U}(\kappa)$, such coupling tensors (which cannot be derived from Bragg diffraction) are fundamental for applying thermal libration corrections to bond lengths in the most general case.

A very promising field where both spectroscopy and crystallography can work together is the derivation of empirical potentials for interaction between the various atoms. Such potentials can be either intermolecular (Van der Waals), or intramolecular (bending, stretching, etc.); an 'effective' charge can also be derived. Although it might seem that potentials obtained from minimizing the derivatives of the lattice energy with respect to the lattice constants and the molecular position could hardly be significant for calculating frequencies, experience shows that—at least for some kinds of molecules—such potentials are very good indeed. For instance, Williams' 'IVa' functions (Williams 1967) are among the best sets for obtaining lattice frequencies of hydrocarbon crystals (see table 1). In other cases, as for instance with sulphur S_8, the

Table 1. Lattice frequencies ($\mathbf{k}=0$) for aromatic hydrocarbons (cm^{-1}). Experimental values at room temperature are by Suzuki *et al.* (1968), Wyncke *et al.* (1967) and Bree *et al.* (1972); calculated values are by Filippini *et al.* (1973) for a 'rigid-body' model using Williams' 'IVa' (1967) potential functions. These functions were derived only from fitting crystallographic data, elasticity coefficients and sublimation enthalpy; no fit to vibrational frequencies was included.

	Anthracene			Phenanthrene	
	Observed	Calculated		Observed	Calculated
A_u	48	36	B	31	27
A_g	39	40	A	33	34
B_g	45	46	A		49
B_u	63	53	B	60	50
B_g	65	61	A	62	60
A_g	70	72	B		77
A_u	104	94	A	89	82
B_g	125	122	B		97
A_g	121	128	A	112	110

Van der Waals potentials have been obtained by joint use of crystallographic and spectroscopic data. In other instances, crystal structure data were essential for calculating the effect due to packing on the molecular vibrational spectra. These calculations ended in a new set of functions which is simpler than any previous one; moreover, the agreement with experimental data is better, and transferability to similar molecules seems to be satisfactory. Further applications of these joint techniques might embrace the evaluation of reaction paths, including the activated complex, or surface chemistry.

Another important point concerns thermodynamic functions. Such functions can be evaluated in many cases from spectroscopic data via the partition function. If the vibrational frequencies for a certain crystal can be satisfactorily calculated starting from crystallographic results and empirical functions, then a reliable estimate of functions such as entropy, free energy, etc. is also obtained. Therefore, if the vibrational problem is considered, the crystal structure data can give information concerning not only a 'packing energy' depending on pressure, but also the temperature dependence of energy, and second-law functions which characterize chemical equilibrium in full (see table 2).

If such results are so important, why have only a few of these calculations been reported so far? Probably this is because lattice-dynamical calculations, which are the method of obtaining vibrational data from crystal structure and potentials, are considered to be very difficult in general, if not forbidding.

For instance, if a molecule contains N atoms, vibrational frequency calculations involve the diagonalization of a square matrix of order $3N$ (or $3N-6$), and this is a simple operation for a molecule of reasonable size; for this reason, the evaluation of thermodynamic functions for a gas by these methods has been a well-established routine for many years. For a molecular crystal, instead, a considerable number of square matrices (see below) of order $6Nz$ has to be diagonalized, where z is the number of molecules in the unit cell. Since for most molecular crystals $z=4$, this implies that the order of the dynamical matrices for a molecular crystal is usually eight times larger than for the corresponding molecule.

A still more worrying problem is the necessity of diagonalizing not only *one* matrix; it is essential to repeat the operation a considerable number of times, by scanning the Brillouin zone appropriately. In the first works of this kind, the *number* of such matrices was about 30 000 to 50 000; therefore, obtaining thermodynamic functions for a crystal was considered to be a procedure at least five orders of magnitude longer than for the corresponding molecule.

Other difficulties which are less easy to express in terms of numbers, but which are nevertheless at least as serious, concern transferability of empirical potentials, and especially the charge problem. Such a problem becomes particularly difficult to handle because charges are affected by the motion itself, and sophisticated models taking polarizability into account might be necessary to obtain reliable results. Another difficulty with charged atoms and molecules is the slowness of convergence of lattice sums, due to the Coulomb potential which decreases as $1/r$, and not, for instance, as $1/r^6$ as in most Van der Waals interactions. This slow convergence implies going over to the reciprocal lattice and modifying the routines considerably.

However, in spite of all these difficulties, a number of considerable simplifications have been worked out, so that these calculations appear to be quite feasible, at least for several interesting cases, taking the considerable development of fast computers into account.

Of these simplifications, a fundamental one considers the 'rigid-body' model: since in many cases the packing forces are much weaker than the internal forces in the molecule, only six parameters (i.e. three translational and three rotational ones) can be considered in the lattice-dynamical treatment. The equations are similar to the general case but the molecular mass and the three principal moments of inertia are taken into account instead of the mass of each single atom; the dimensions of the dynamical matrices are drastically reduced to $12z$, or 48 for the most common situation.

Such a procedure was worked out by Cochran and Pawley (1964) to calculate the diffuse scattering of hexamethylenetetramine; these authors develop ideas due to Born (1942) and Laval (1941). The rigid-body treatment of lattice vibrations is thoroughly connected with Cruickshank's (1956) or Schomaker and Trueblood's (1968) fit of molecular temperature factors. On this basis, the first attempt to derive the so-called **T** and **L** tensors is due to Pawley (1967), and the relationships between the lattice-dynamical formulation and the crystallographic procedure were exhaustively pointed out by Pawley (1967, 1968), Scheringer (1972), Willis and Pryor (1975), and other authors. In some of these works, the vibrational frequencies at the Γ-point and the phonon dispersion curves are compared with the experimental results (Pawley 1967, Pawley *et al.* 1980, Dorner *et al.* 1982); the agreement with experimental data is good to excellent. The importance of such an agreement becomes even greater on consideration that the Van der Waals functions were essentially derived from crystallographic information and only in one case (sulphur S_8) was the fit to frequencies used for final calibration (Rinaldi and Pawley 1975).

For calculating the various atomic temperature factors, the importance of a convenient sampling of the Brillouin zone was shown to be essential by Filippini *et al.* (1976). If an unevenly spaced grid is used, with a maximum thickness in the proximity of the origin (Γ-point), then the evaluation of the three acoustic branches (which determine most of the translational contribution) becomes satisfactory, even for 200–300 scanned points in the Brillouin zone. This simplification reduces the former calculations by about two orders of magnitude. Other proposals for overcoming the problem were advanced, for instance, by Kroon and Vos (1978, 1979), but the greater

Table 2. A sketch of the mathematical procedure (*a*) for molecules and (*b*) for crystals.

(*a*) Molecules

$$m(\kappa)\ddot{v}(\kappa, t) = -\sum_{\kappa'} \Phi(\kappa\kappa')\, v(\kappa', t)$$

$$v(\kappa, t) = V'_0(\kappa) \exp(-\mathrm{i}\omega t)[\exp \mathrm{i}\phi(\kappa)]$$

$$\ddot{v}(\kappa, t) = -V_0(\kappa)\, \omega^2 \exp(-\mathrm{i}\omega t)$$

$$m(\kappa)\omega^2 \exp(-\mathrm{i}\omega t)\, V_0(\kappa) = \sum_{\kappa'} \Phi(\kappa\kappa')\, V_0(\kappa') \exp(-\mathrm{i}\omega t)$$

$$m(\kappa)\omega^2 V_0(\kappa) = \sum_{\kappa'} \Phi(\kappa\kappa')\, V_0(\kappa')\omega^2 \mathbf{M}\mathbf{V}_0 = \mathbf{D}_0\mathbf{V}_0$$

($\mathbf{M}$ = diagonal mass matrix; $\mathbf{D}_0$ = force-constant matrix; $\mathbf{V}_0 = V_0(\kappa)$ vector)

$$\mathbf{M}^{-\frac{1}{2}}\omega^2 \mathbf{M}\mathbf{V}_0 = \mathbf{M}^{-\frac{1}{2}}\mathbf{D}_0\mathbf{M}^{-\frac{1}{2}}\mathbf{M}^{\frac{1}{2}}\mathbf{V}_0$$

$$\omega^2 \mathbf{M}^{\frac{1}{2}}\mathbf{V}_0 = \mathbf{D}\mathbf{M}^{\frac{1}{2}}\mathbf{V}_0$$

$$\omega^2 \xi = \mathbf{D}\xi$$

($\mathbf{D} = \mathbf{M}^{-\frac{1}{2}}\mathbf{D}_0\mathbf{M}^{-\frac{1}{2}}$ = 'reduced' dynamical matrix)

$m(\kappa)$ = mass of the κth atom
$v(\kappa, t)$ = positional coordinate of the κth atom at the time t
$\Phi(\kappa\kappa')$ = force constant relative to interaction between the atoms κ and κ'
$\phi(\kappa)$ = phase of the motion of the κth atom
ω = angular frequency of the mode

Table 2 *continued.*

(*b*) Crystals

$$m(\kappa)\ddot{v}(\kappa,t) = -\sum_{\kappa'} \Phi(\kappa\kappa')\, v(\kappa',t)$$

$$v(\kappa,t) = V_0'(\kappa)\exp(-\mathrm{i}\omega t + \mathrm{i}\mathbf{q}\mathbf{r}_\kappa)[\exp \mathrm{i}\phi(\kappa)]$$

$\mathbf{q}$ = 'wave-vector', where $|\mathbf{q}| = 2\pi/\lambda$; $V_0(\kappa) = V_0'(\kappa)\exp[\mathrm{i}\phi(\kappa)]$

$$\ddot{v}(\kappa,t) = -V_0(\kappa)\,\omega^2 \exp(-\mathrm{i}\omega t + \mathrm{i}\mathbf{q}\mathbf{r}_\kappa)$$

$$m(\kappa)\,\omega^2 \exp(-\mathrm{i}\omega t)\, V_0(\kappa) = \sum_{\kappa'} \Phi(\kappa\kappa')\, V_0(\kappa')\exp[-\mathrm{i}\omega t + i\mathbf{q}(\mathbf{r}_{\kappa'} - \mathbf{r}_\kappa)]$$

$$m(\kappa)\omega^2 V_0(\kappa) = \sum_{\kappa'} \Phi(\kappa\kappa')\exp[\mathrm{i}\mathbf{q}(\mathbf{r}_{\kappa'} - \mathbf{r}_\kappa)]\, V_0(\kappa')$$

See the 'Fourier-transform' formulation, to be compared with:

$$F(\mathbf{q}) = \int_V \rho(\mathbf{r})\exp(\mathrm{i}\mathbf{q}\mathbf{r})\,\mathrm{d}V$$

$$\omega^2 \mathbf{M}\mathbf{V}_0 = \mathbf{D}_0\mathbf{V}_0$$

....

$$\omega^2 \xi \quad = \mathbf{D}\xi$$

Average energy of the ψth mode for a certain value of $\mathbf{q}$:

$$E_\psi(\mathbf{q}) = h\nu_\psi(\mathbf{q})(\tfrac{1}{2} + \{\exp[h\nu_\psi(\mathbf{q})/kT - 1]\}^{-1})$$

Evaluation of temperature factors:

$$\mathbf{U}(\kappa) = (Nm_\kappa)^{-1} \sum_{\psi\mathbf{q}} E_\psi(\mathbf{q})\omega_\psi^{-2}(\mathbf{q})\, \xi(\kappa|\psi q)[\xi^*(\kappa|\psi q)]^T$$

Example of calculation of a thermodynamic function:

$$\text{Entropy } S = E_\mathrm{v}/T - R\sum_i g(\nu_i)\ln[1 - \exp(-h\nu_i/kT)]\Delta\nu_i$$

$$E_v = R\sum_i g(\nu_i)(h\nu_i/k)[\exp(h\nu_i/kT) - 1]^{-1}\Delta\nu_i + E_0$$

$$E_0 = R\sum_i g(\nu_i)(h\nu_i/2k)\Delta\nu_i$$

E_v = vibrational energy; E_0 = zero-point energy; $g(\nu_i)$ = density-of-states function

Table 3. Temperature factors ($\times 10^4$) for pyrene at 298 K (Gramaccioli and Filippini 1983) as functions of the internal degrees of freedom assumed in our calculations to mix with lattice modes. They are in the form: $T_i = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$, and for each line they are in sequence $B_{11}, B_{22}, B_{33}, B_{12}, B_{13}, B_{23}$. For each atom, the lines refer, in sequence, to: (1) calculated (lattice-dynamical) values for a rigid-body model, including lattice contributions only; (2) calculated values for a 'rigid-body', but including separate contributions of internal modes; (3, etc.) calculated values allowing a certain number of internal modes to mix with lattice modes: the last figures are the 'cutoff' frequency (cm^{-1}) and the number of such modes. The last lines report the observed values, taken from the literature (Hazell *et al.* 1972).

C(1)	85	201	274	15	−18	−65		
	90	216	279	21	−16	−63		
	91	214	289	13	−21	−62	200	2
	92	215	292	12	−22	−63	300	5
	91	177	234	10	23	−38	(observed)	
C(2)	70	162	320	−7	5	−55		
	74	174	325	−2	6	−54		
	75	173	336	−8	4	−55	200	2
	76	174	340	−10	3	−55	300	5
	65	149	287	−13	36	−59	(observed)	
C(3)	61	121	260	0	24	−20		
	64	129	265	2	25	−19		
	66	131	272	0	26	−21	200	2
	67	133	276	−3	26	−22	300	5
	63	104	228	−4	57	−16	(observed)	
H(2)	82	193	436	−30	10	−74		
	107	257	457	−15	15	−66		
	108	252	471	−29	11	−67	200	2
	109	251	478	−35	9	−66	300	5
	100	226	437	−60	63	−77	(observed)	
H(4)	103	168	412	−31	77	13		
	126	227	434	−18	81	21		
	130	230	445	−26	85	18	200	2
	133	230	449	−38	85	15	300	5
	121	202	462	−53	122	31	(observed)	

complexity of such procedures does not seem to give an adequate improvement of results.

A comparison of experimental temperature factors with the corresponding lattice-dynamical estimates shows remarkably good agreement (see the first line in table 3, and Filippini *et al.* 1974). This agreement is well within the limit of the presumable accuracy of **B** (about 20%) and was one of the first independent proofs of the physical meaning of anisotropic temperature factors derived from crystallography. In many cases the observed temperature factors are lower than the corresponding calculated values: this is probably due to thermal diffuse scattering (TDS). However, the best way for evaluating TDS effects on crystallographic data appears to depend on these same lattice-dynamical calculations.

Extension of this technique to non-rigid molecules can be straightforward and still comparatively simple. This is possible because in most molecules the internal degrees of freedom which correspond to low vibrational frequencies (and then can mix with the lattice modes) are comparatively few with respect to the total. Therefore, the dynamical matrices still remain relatively small. An extension of the rigid-body treatment including the lowest internal frequencies and working on the basis of normal coordinates of the isolated molecule was first proposed by Bonadeo and Burgos (1982) for diphenyl crystals; a generalized extension of such a procedure was shown by Gramaccioli and Filippini (1983), with examples concerning a series of aromatic hydrocarbons of increasing complexity and non-rigidity. The agreement with the experimental data is quite satisfactory. For 'rigid' molecules, the estimates of the **T** and **L** tensors are close—in general—to the corresponding Schomaker–Trueblood fit; the estimates of the **S** tensor do not seem, however, to agree very well (see table 4).

The introduction of the internal molecular force field in general requires a thorough calibration and selection of empirical force constants: for instance, the 'out-of-plane' vibrational frequencies in aromatic hydrocarbons were fitted directly to crystals, taking the effect of the packing forces into account. This operation yielded a five-parameter diagonal force field. Such an empirical field is simpler than any other which had been proposed, and gives the best agreement with the experimental data (see table 5) for an example, and Filippini *et al.* (1984)).

A further illustration of the transferability of force constants derived in this way, as well as of the reliability of lattice-dynamical calculations for non-rigid crystals, was obtained for two polyphenyls, i.e. *o*-terphenyl and tetraphenylmethane (Gramaccioli and Filippini 1985, Filippini and Gramaccioli 1986). The agreement with experimental data is excellent, both for the crystallographic temperature factors and for the Raman- or i.r.-active vibrational frequencies (see tables 6 and 7). In these cases it was also possible to correct the bond lengths for libration using the general formula as proposed by Busing and Levy (1964) or Scheringer (1972). This formula implies knowledge of the coupling tensors $\mathbf{U}(\kappa\kappa')$: these tensors can be obtained from the same lattice-dynamical calculations as for $\mathbf{U}(\kappa)$ (or **B**).

For tetraphenylmethane, the average of the C–C bond lengths corrected for thermal motion in the general case is 1·395 Å (excluding the bonds which are adjacent to the central C atom). This value is close to spectroscopic or theoretical results (see table 8).

A first attempt to derive thermodynamic functions for a molecular crystal via lattice dynamics and the vibrational partition function was made by Filippini *et al.* (1975). Agreement of the calculated results with experiment was satisfactory. More recently, a complete calculation was performed on crystals of sulphur S_8 (Gramaccioli and

Table 4. Estimates of Schomaker–Trueblood vibrational tensors (*a*) from fit to observed temperature factors; (*b*) from the 'rigid-body' lattice-dynamical model; (*c*) from the 'non-rigid' model (Gramaccioli and Filippini 1983, 1985).

Anthracene-d_{10} at 290 K

	T			L			λ(L) as (°)^2
(*a*)	313	163	−235	50	13	−34	31·0
		309	15		36	4	14·3
			355			67	5·1
(*b*)	387	18	−96	31	0	−5	18·1
		379	−14		24	−12	9·9
			456			50	6·3
(*c*)	420	23	104	32	0	−5	18·8
		395	12		26	−12	10·3
			484			52	6·8

Pyrene at 298 K

	T			L			λ(L) as (°)^2		S	
(*a*)	413	47	189	53	−18	4	23·0	(10)	10	−3
		354	33		47	14	17·8	9	(0)	9
			618			49	8·1	−7	−6	(−10)
(*b*)	486	78	−9	39	−13	5	19·1	1	−6	3
		439	−21		48	7	14·9	−5	0	−8
			697			42	8·5	−4	1	−10
(*c*)	504	81	−12	41	−14	5	20·0	2	−5	3
		454	−23		50	8	15·6	−6	−1	−10
			727			44	8·8	−4	1	−11

o-Terphenyl (room temperature)

	T			L			S		
(*a*)	427	−54	22	46	−15	−1	1	−12	9
		452	70		46	16	10	28	−37
			543			77	51	3	−29
(*c*)	400	−14	7	34	−14	−3	1	−21	20
		462	1		30	9	1	29	−17
			389			48	50	2	−25

Table 5. Comparison of calculated and experimental i.r. and Raman-active frequencies for h_{10}-anthracene (cm^{-1}).

	Calculated values†			Average for crystal data			
	Gas	Crystal		Exp'tal†	Calc.K‡	Cal.ES§	Calc.WC‖
B_{1u}	93	119(*A*)−109(*B*)		107	98	96	73
A_u	123	172	174	126¶	133	137	131
B_{2g}	227	240	238	243	215	235	186
B_{3g}	253	275	281	288	270	321	261
B_{1u}	383	389	395	389	378	383	310
B_{1u}	460	468	471	472	484	504	450
B_{2g}	466	475	472	479	437	466	401
A_u	475	481	484	n.d.	488	552	397
B_{3g}	565	570	571	577¶	552	617	412
A_u	701	706	706	743	774	826	710
B_{1u}	726	739	734	729	743	732	709
B_{2g}	732	749	745	747	754	739	711
B_{3g}	756	763	764	765	840	754	669
B_{3g}	845	870	870	896	858	871	799
A_u	849	874	874	860	848	876	936
B_{1u}	910	924	924	884	916	892	905
B_{2g}	920	933	933	942	949	936	967
B_{3g}	930	953	953	915	929	909	1094
B_{1u}	947	958	958	955	959	952	1008
B_{3g}	992	1002	1004	977	977	960	1333
A_u	992	1004	1006	979	975	966	1231
Δ		261			383	342	1706
$\bar{\Delta}$(%)		13·9			20·2	18·0	89·8

† For information about the sources of experimental data see Filippini *et al.* (1984), from where this table is taken.

‡ Krainov (1964).

§ Evans and Scully (1964).

‖ Whitmer *et al.* (1978).

¶ Referable to a *lattice* mode A_g.

Filippini 1984). For such a calculation, the internal molecular force field was modified to account for the effect of the Van der Waals forces; otherwise, the frequencies of the lowest branches would have been too high (see table 9). This also points out the necessity of distinguishing between a free or a packed molecule when the force field is fitted to experimental data.

The calculated values of the thermodynamic functions are reported in table 10, together with the corresponding experimental values. The agreement is remarkably good: the only flaw relates to the heat of sublimation, which is too low. This happens because in deriving the empirical Van der Waals field the zero-point energy contribution was neglected. More interesting is the effect of the revised internal force field on the entropy of the vapour: if the molecule is indeed *softer* than it appears when it

Table 6. Calculated and observed vibration frequencies (cm^{-1}), and symmetry species (first column) for tetraphenylmethane crystals at the Γ point.

	Filippini and Gramaccioli (1986)	Schlotter and Hudson (1982, 1986)	
		Observed	Calculated
B	34	39	38
E	39	40	42
A	44	48	46
A	51	—	56
E	62	54	63
E	68	67	71
A	79	—	77
E	83	83	80
A	91	—	79
B	92	84	92
E	98	104	98
B	98	—	96
B	99	105	105
B	106	—	113
A	118	—	122
E	123	121	124
B	135	132	135
A	146	135	138
E	150	143	144
B	158	154	150

is packed in the crystal, then the frequencies in the free state are lower than in the solid. This implies a considerable revision, for instance, of the reported values of entropy, which were obtained from spectroscopic data relative to the *crystal* (Guthrie *et al.* 1954).

As a whole, therefore, the effect of crystallography on other branches of physical chemistry, including thermodynamics, is far from being negligible. Although more sophisticated models might be necessary for a still better interpretation or prediction of experimental results, nevertheless the success in calculating thermodynamic functions with still simpler models, such as Einstein's or Debye's, gives us confidence in the practical validity of the above procedures. For many classes of substances, however, and especially when substantial charges are present on various atoms, a fast routine has still to be prepared: in spite of all this, there are good reasons for thinking that most difficulties will soon be overcome.

Table 7. Temperature factors (× 10^4) for two non-rigid polyphenyls (calculated values from Gramaccioli and Filippini (1985), or Filippini and Gramaccioli (1986)).

	Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
				o-Terphenyl (Brown and Levy 1979)			
C1	(cal)	33	290	65	−11	−1	−1
	(obs)	30	277	55	−10	−2	4
C2	(cal)	32	350	84	2	6	−20
	(obs)	28	324	78	−1	2	−20
C2′	(cal)	23	313	69	−1	0	−4
	(obs)	22	327	58	−6	1	3
C3′	(cal)	26	387	80	13	3	−10
	(obs)	30	398	73	28	7	14
C4′	(cal)	25	513	92	24	4	6
	(obs)	28	566	93	36	9	15
				Tetraphenylmethane (Robbins *et al.* 1975)			
C0	(obs)	51(1)	51(1)	115(3)	0	0	0
	(cal)	53	53	112	0	0	
C1	(obs)	56(1)	60(1)	111(3)	−5(1)	10(2)	0(2)
	(cal)	55	58	122	−2	0	−5
C2	(obs)	71(1)	83(2)	129(4)	−5(1)	−4(2)	−6(2)
	(cal)	62	73	134	−6	−8	−7
C3	(obs)	83(2)	111(2)	134(4)	−25(2)	1(2)	−20(2)
	(cal)	81	86	155	−19	−8	−23
C4	(obs)	111(2)	86(2)	175(4)	−26(2)	23(1)	−42(3)
	(cal)	104	77	194	−15	1	−40
C5	(obs)	107(2)	67(2)	195(4)	3(2)	23(3)	−21(2)
	(cal)	103	63	206	5	1	−31
C6	(obs)	76(2)	65(1)	144(4)	3(1)	4(2)	−11(2)
	(cal)	74	59	158	7	−2	−14

Table 8. Bond distances (Å) in tetraphenylmethane. For each bond, the columns show, in sequence: (1) the uncorrected bond length; (2) the corrected bond length according to a rigid body ST fit to the temperature factors; (3) the corrected bond length for a 'riding' motion; (4) the corrected bond length for the general case of a non-rigid molecule, using the results of lattice-dynamical estimations (from Filippini and Gramaccioli (1986)).

	(1)†	(2)	(3)	(4)
C0–C1	1·551	1·554	1·553	1·557
C1–C2	1·403	1·406	1·412	1·411
C1–C6	1·389	1·392	1·397	1·399
C2–C3	1·385	1·387	1·393	1·394
C3–C4	1·381	1·384	1·386	1·392
C4–C5	1·384	1·387	1·397	1·394
C5–C6	1·392	1·395	1·403	1·401
Average in the ring	1·3890	1·3918	1·3963	1·3985

† Data from the 'West Pa' set in Robbins *et al.* (1975).

Table 9. Internal frequencies (cm^{-1}) for the S_8 ring in crystals of orthorhombic sulphur. (1) Experimental (Raman) measurement *in the crystal* by Steudel and Mäusle (1978). The frequencies marked § were measured in CS_2 solution by i.r. spectroscopy by the same authors. The corresponding *calculated* frequencies for the vapour are reported in parentheses. (2) Calculated values for the crystal by Gramaccioli and Filippini (1984).

(1)		(2)		(1)		(2)	
E_2	82·5	B_{1u}	82	B_2	243§	B_{2u}	244
	(66·9)	B_{3u}	83		(239·6)	B_{2g}	245
		B_{3g}	86			B_{3g}	246
		B_{1g}	87			B_{3u}	247
		B_{2g}	87				
		A_g	88	B_1	411·0	B_{1u}	412
		A_u	94		(411·7)	A_g	413
		B_{2u}	98			B_{1g}	414
E_2	153·0	B_{1g}	162	E_3	439·0	B_{1g}	437
	(155·6)	B_{1u}	162		(436·8)	B_{2u}	438
		A_u	163			B_{3g}	439
		B_{2u}	164			B_{2g}	439
		A_g	165			B_{3u}	439
		B_{3g}	167			B_{1u}	439
		B_{2g}	169			A_u	440
		B_{3u}	169			A_g	441
E_1	187·0	B_{1g}	186	E_1	471§	B_{1g}	469
	(182·1)	B_{3g}	188		(472·0)	B_{1u}	469
		A_u	190	A_1	472·5	A_u	471
		B_{1u}	190		(466·9)	A_g	473
		B_{2g}	191	E_2	472·5	B_{1g}	473
		B_{3u}	191		(472·6)	B_{2u}	473
		A_g	192			B_{3u}	473
		B_{2u}	193			B_{1u}	474
						B_{2g}	474
A_1	214–218·5	B_{1u}	216			B_{3g}	474
	(212·0)	A_u	217			B_{1u}	474

Table 10. Thermodynamic functions for orthorhombic sulphur (S_8) at room temperature (25°C, 298 K) calculated by Gramaccioli and Filippini (1984); experimental data from Guthrie *et al.* (1954) and Eastman and McGavock (1937).

	Calculated	Observed
Entropy of the crystal	60·86	61·0(0·4) cal mol^{-1} K^{-1}
Heat of sublimation	23·94(24·36)	24·35(0·05) kcal mol^{-1}
C_v	41·17	40·8(0·4) cal mol^{-1} K^{-1}
C_p	43·27	43·2(0·2) cal mol^{-1} K^{-1}

Entropy of the vapour 32·23 cal mol^{-1} K^{-1}
Entropy of the vapour according to the literature 30·48 cal mol^{-1} K^{-1}

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