

The general experience of the authors⁵ with the MEM is that it is ideally suited for certain classes of applications. Whenever $\rho(r)$ is close to zero (or any constant value) over a large range of r and is positive and "peaky" over a relatively smaller range of r , the restorations obtained with the MEM are very good. In particular, the *positions* and (to a lesser extent) the *strengths* of peaks are reproduced very well. On the other hand, the *shapes* of the peaks are usually not reliable. Also, if $\rho(r)$ has "plateaus" i.e., fairly extensive regions of approximately constant "height", the MEM restorations have excessive ripple on the plateaus.

It is remarkable that the weaknesses of the MEM are quite immaterial for crystallographic applications. What is important in crystal structure analysis is the ability to pinpoint the positions of the peaks, and this is precisely what the MEM is most efficient at (once the peaks have been identified, chemical information and least squares usually take over to refine the structure). This coupled with our earlier experience^{5,6} leads us to believe that the MEM is ideally suited for crystal structure analysis. Figs. 1 and 2 support this view. We should mention that reconstructions from radio astronomical data without phases have been presented by Gull and Daniell⁸ using S_2 and the method of least squares.

In the one-dimensional case, it has been noted^{2,9,5} that maximisation of S_1 is equivalent to maximising a

certain determinant built up from structure factors. This is strongly reminiscent of the maximum determinant rule^{10,11} which has been studied in connection with the phase problem. We are currently investigating this relationship.

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MOLECULAR CONSTANTS OF S_2O AND C_3 MOLECULES

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THE molecular constants of S_2O and C_3 molecules have been evaluated for the first time using the vibrational frequencies and the molecular parameters.

S_2O molecule belongs to the bent unsymmetrical XYZ type possessing C_s symmetry. It has 3 modes of vibration, all belonging to a' species. The molecule C_3 belongs to the linear symmetric XY_2 type, with D_{3h} symmetry. It has 3 modes of vibration distributed as $1\Sigma_g^+ + 1\Sigma_u^+ + 1\pi_u$.

The force constants of a molecule would offer valuable information with regard to the bond strength of the atoms in the molecule. Further, the force constants are useful to evaluate the other molecular constants like mean amplitudes of vibration, Coriolis coupling coefficients and centrifugal distortion constants. The S_2O molecule has a much lower symmetry compared to the other sulphur oxides and C_3 molecule has its bending frequency extremely low. These features

have their impact on the force constants and the other molecular constants.

The molecular parameters and the observed frequencies of S₂O and C₃ molecules have been taken from reference (1). The force constants of S₂O molecule have been calculated by Wilson's F-G matrix method using both the general valence and Urey-Bradley force fields². The values of the force constants thus obtained are given in Table I and they are found to be in good agreement. The frequencies calculated using the force constants evaluated by GVFF are 1164, 677 and 391 cm⁻¹ against the experimentally observed frequencies of 1165, 679 and 388 cm⁻¹ respectively. This close agreement records the accuracy of the force field determined in the present investigation. The force constants of C₃ molecule have been calculated using the general valence force field and Wilson's F-G matrix method². The values thus obtained are: $f_a = 10.26$, $f_{aa} = 0.444$ and $f_{\alpha} = 0.00017$ md/Å. There is no uncertainty involved in these force constants since all the three species of C₃ molecule are of first order.

Centrifugal distortion constants of S₂O molecule have been calculated following the method suggested by Kivelson and Wilson and Cyvin *et al.*^{3,4}. Since the molecule is an asymmetric top, all the six coefficients exist; $D_j = 52.88$; $D_k = 50.09$; $D_{jk} = -102.9$; $R_5 = -11.5$ $R_6 = 2.60$ and $\delta_j = -23.6$ kHz. In the case of C₃ molecule, since it is a linear symmetrical type of molecule, only three coefficients, namely, $D_j = D_k = 2953$ kHz and $D_{jk} = -5906$ KHz exist. In this case it is also observed that $D_{jk} = -2D_j$. The relatively large values of the centrifugal distortion constants may be attributed as due to the very low bending frequency and the corresponding very low force constants. In this case, R_5 , R_6 and δ_j vanish due to the symmetry of the molecule.

The mean square amplitudes of vibration⁵ of S₂O molecule calculated for 300°K are $\sigma_D = 0.00137$;

$\sigma_R = 0.00159$; $\sigma_a = 0.00188$; $\sigma_{DR} = -0.000086$; $\sigma_{Da} = -0.000332$ and $\sigma_{Ra} = -0.000366$ (in Å²).

The parallel mean square amplitudes of vibrations of C₃ molecule, calculated for 300°K, 500°K and 1000°K are given in Table II. The perpendicular mean square amplitudes, T_a and the shrinkage constant δ are presented in Table III^{5,6}.

TABLE I

General valence and Urey-Bradley force constants of S₂O molecule in md/Å

General valence force field		Urey-Bradley force field	
Force constant	Value	Force constant	Value
f_K	8.49	K_R	8.56
f_D	4.30	K_D	4.36
f_a	0.159	H	0.19
f_{RD}	-0.058	F*	-0.031

F* is the repulsive force constant between non-bonded atoms.

TABLE II

Parallel mean square amplitudes of C₃ molecule in Å²

Temp °K	σ_a	σ_{aa}	σ_{α}
300	0.001605	0.000463	0.5442
500	0.001642	0.000434	0.9026
1000	0.001951	0.000343	1.8037

TABLE III

Perpendicular mean square amplitudes and shrinkage effect of C₃ molecule

Temp. °K	T _a (Å ²)	δ (Å)
300	0.1361	0.0533
500	0.2257	0.0883
1000	0.4509	0.1765

TABLE IV

Thermodynamic functions of S₂O and C₃ molecules in cal. deg⁻¹ mol⁻¹

Temp. °K	Free energy		Heat content		Entropy		Heat capacity	
	S ₂ O	C ₃	S ₂ O	C ₃	S ₂ O	C ₃	S ₂ O	C ₃
300	56.42	53.64	8.93	10.39	65.35	64.03	10.56	11.10
400	59.08	56.91	9.46	10.61	68.54	67.52	11.44	11.50
500	61.22	60.45	9.91	10.81	71.13	71.26	12.04	11.87
600	63.22	61.52	10.30	11.03	73.52	72.55	12.47	12.29
700	64.68	63.22	10.64	11.21	75.32	74.43	12.79	12.66
800	66.09	64.49	10.91	11.38	77.00	75.87	13.00	12.98
900	67.32	65.41	11.12	11.54	78.44	77.95	13.16	13.25
1000	68.68	66.35	11.36	11.70	80.04	78.05	13.29	13.47

Applying Jahn's rule⁷ to C_2 molecule, the non-vanishing zeta values are found to be of the type ζ^u and ζ^v which arise from $\Sigma_u^+ \times \pi_u$ coupling. These values calculated⁸ are, $\zeta^u_{2,2a} = \zeta^v_{2,2a} = 1.003$. This satisfies the necessary square sum rule.

The thermodynamic functions of S_2O and C_2 molecules have been evaluated using their molecular parameters and vibrational frequencies assuming harmonic oscillator, rigid rotor approximation under one atmospheric pressure for a range of temperatures from 300°K to 1000°K. These values are given in Table IV.

The mean square amplitudes of vibration and the centrifugal distortion constants evaluated for S_2O and C_2 molecules will be useful in the electron diffraction and the microwave studies of the molecules respectively. Since it is difficult, and in some cases impossible to determine the thermodynamic functions experimentally, the values theoretically calculated will have their own significance.

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ON THE MEAN ELASTIC WAVE VELOCITIES IN SOME ORTHORHOMBIC CRYSTALS

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ABSTRACT

The elastic wave velocities in twelve orthorhombic crystals have been calculated by different methods and the results compared with computationally exact values. It is found that the values calculated by using VAA (Verma-Aggarwal approximation) are in better agreement with the exact values than those obtained by other methods.

RECENTLY the authors¹ have proposed a new scheme, viz., VAA, of averaging isotropic bulk and shear moduli obtained from single-crystal elastic coefficients and calculated the mean elastic wave velocity in a number of orthorhombic crystals. It was found that the values of the wave velocities thus calculated were much closer to computationally exact values than those obtained by other methods.

With the availability of elastic constant data for some more orthorhombic crystals, it is now possible to calculate the mean elastic wave velocities for the first time. These have been calculated by two different methods, viz., Anderson's method², using harmonic mean approximation, HMA³ and Verma-Aggarwal approximation, VAA¹ and by harmonic polynomial series expansion method⁴ with five*, with six and seven terms.

* There seems to be an error in the expression for a_0 for 5-terms in reference 4. The correct expression should be $a_0 = (7f_b - 36f_c + 16f_d + 48f_e + 25f_f)/60$.

The Debye temperature is given by the well-known relation² :

$$\theta = \left(\frac{h}{k}\right) \left(\frac{3qN\rho}{4\pi M}\right)^{1/3} v_m \quad (1)$$

and the mean velocity v_m is given by

$$v_m = \left[\frac{1}{3} \int \sum_{i=1}^3 v_i^{-3} \frac{d\Omega}{4\pi}\right]^{-1/3} \quad (2)$$

The symbols used above have their usual meanings.

Knowing v_m , it is possible to calculate the Debye temperatures of these crystals (eqn. (1)). However, the information on the value of q , the number of vibrating units per molecule, is lacking for all these crystals and hence the absolute values of the Debye temperatures could not be evaluated. In order to compare the relative accuracies of the different methods of calculating θ (and hence v_m), it will suffice if the mean velocities v_m , as obtained by different methods, are compared with the exact values. The exact