Calculations on the r_z-Structure of Dimethylsulfoxide

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On the basis of three different force fields the zero point average structure of dimethylsulfoxide has been calculated. Three different types of calculation were performed. It is found that the different force fields virtually do not affect the resulting parameters while the results from different types of calculation agree within three times the standard errors. The asymmetry of the methyl groups found with the calculation scheme of the r_s-structure is also present in the average structure.

Dimethylsulfoxide (DMSO) has been the subject of an extensive investigation on the molecular structure by means of microwave spectroscopy [1]. Several r_0-structures and the complete r_s-structure have been obtained. It seemed to be worthwhile to calculate also the zero point average structure (r_z-structure) [2, 3] for several reasons: 1) The r_z-structure still has been obtained for a small number of molecules. DMSO gives the opportunity to increase experience with this type of structure calculations. 2) The r_s-structure of Ref. [1] resulted in a methyl group with a high degree of asymmetry. Though one H-atom could not be reliably located the difference of 0.04 Å in the C–H bond length of that particular H-atom seemed to be too large to be solely due to this fact. Therefore one aim of the present paper is to investigate to which extent the structural parameters of Ref. [1] are influenced by vibrational effects. 3) The calculation of the r_z-structure requires the calculation of the harmonic contributions to the rotational constants and the estimation of isotopic differences in bond lengths from the harmonic force field. However three different force fields — essentially due to different assignments and constraints on nondiagonal force constants — are given for DMSO in the literature [4, 5, 6]. Thus the harmonic contributions can be calculated on the basis of different force fields and one is able to study the effects of uncertainties of this kind on the resulting structure.

Recently Iijima and Tsuchiya [7] developed a method to calculate the r_z-structure for molecules containing one symmetric internal rotor. This method was not applied in the present investigation because a generalization for molecules with two not necessarily symmetric rotors is not available. In addition a detailed analysis of the internal rotation in DMSO by Dreizler and Dendl [8] yielded a hindering potential of about 2900 cal/mol, and very few rotational transitions of the ground state have observable splittings. Therefore the contributions of internal rotation to the harmonic vibrational part of the ground state rotational constants were approximated by calculations with harmonic torsional oscillations.

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Internal Coordinates and Force Fields

Throughout this paper the calculations of vibration-rotation interaction constants were based on the r_{0III}-structure of Ref. [1]. The vibrational symmetry coordinates defined by Horrocks and Cotton [4] were used with the exception of the torsional coordinates: here the coordinates described by Hilderbrandt [9] were used. The two redundancies were removed with the method described in [10].

The force fields given in Refs. [4], [5], and [6] were used directly in the calculations. In addition the torsional force constants were adjusted to fit the frequencies 231 cm^{-1} (A′) and 207 cm^{-1} (A″) in accordance with Tranquille et al. [5]. The values $f_{13,13} = 0.0964$ mdyn Å and $f_{24,24} = 0.0812$ mdyn Å were found. These values correspond to a hindering potential of 2840 cal/mol in good agreement with the experimental values 2915 cal/mol [8] and 2923 cal/mol [1], respectively.

An attempt was made to test the different force fields independent of the assignment of vibrational frequencies by comparing calculated centrifugal distortion constants with experimental values. The agreement is moderate for all force fields, though a slight preference may be given to the results of Horrocks and Cotton [4].

Table 1. Harmonic corrections of rotational constants (in MHz) of DMSO from different force fields and rms deviation from mean value. Note that in DMSO-O18 the a- and b-axis are interchanged with respect to the normal species. For designation of isotopic species see Ref. [1]. HC: Horrocks, Cotton [4]; TLFF: Tranquille, Labarbe, Fouassier, Forel [5]; GH: Geiseler, Hanschmann [6].

DMSO-		-N	-S34	-O18	-C13	-D1I	-D1II	-D1III	-D3	-D6
HC	ΔA	− 3.208	− 3.150	− 6.723	− 3.696	− 2.551	− 4.447	− 2.845	− 1.419	+ 0.072
	ΔB	− 6.700	− 6.600	− 3.314	− 6.115	− 5.662	− 4.435	− 5.653	− 4.379	− 3.233
	ΔC	− 1.360	− 1.378	− 1.295	− 1.338	− 1.170	− 1.105	− 1.398	− 0.976	− 0.665
TLFF	ΔA	− 2.670	− 2.632	− 6.092	− 3.147	− 2.078	− 3.875	− 2.281	− 0.880	+ 0.575
	ΔB	− 6.076	− 5.969	− 2.806	− 5.549	− 5.086	− 3.702	− 5.252	− 3.864	− 2.775
	ΔC	− 1.255	− 1.272	− 1.195	− 1.242	− 1.046	− 0.982	− 1.303	− 0.842	− 0.516
GH	ΔA	− 3.634	− 3.581	− 7.139	− 4.124	− 2.966	− 4.847	− 3.231	− 1.800	− 0.266
	ΔB	− 7.125	− 7.020	− 3.678	− 6.528	− 6.039	− 4.781	− 6.088	− 4.699	− 3.484
	ΔC	− 1.330	− 1.349	− 1.262	− 1.311	− 1.153	− 1.082	− 1.335	− 0.939	− 0.624
$\sigma(\Delta A)$		0.483	0.475	0.527	0.490	0.444	0.489	0.478	0.462	0.423
$\sigma(\Delta B)$		0.528	0.529	0.438	0.491	0.480	0.551	0.418	0.421	0.360
$\sigma(\Delta C)$		0.054	0.055	0.051	0.050	0.067	0.065	0.048	0.069	0.077

Vibrational Corrections

As was shown by a number of authors [11—14] the average rotational constants $B_z^{(\alpha)}$ are related to the effective rotational constants $B_0^{(\alpha)}$ of the ground vibrational state by the well known relation:

$$B_z^{(\alpha)} = B_0^{(\alpha)} - \sum_s \frac{(B^{(\alpha)})^2}{\omega_s} \cdot \left[3A_{ss}^{(\alpha\alpha)} + 4 \sum_t{}' (\zeta_{st}^{(\alpha)})^2 \frac{{\omega_t}^2}{{\omega_s}^2 - {\omega_t}^2} \right] + B_{\text{cent}}^{(\alpha)} . \quad (1)$$

The calculation of the centrifugal correction $B_{\text{cent}}^{(\alpha)}$ showed that this contribution is less than 25% of the uncertainty assigned to the vibrational correction and hence was neglected. The calculated harmonic corrections from different force fields are listed in Table 1.

In Table 1 it is observed that the corrections from different force fields differ by up to 1 MHz. The last rows of this table give the rms deviations σ of the calculated corrections from their respective mean value. It is seen that σ is of the order 10% of the harmonic corrections, a value which is frequently used as the estimate for the uncertainty of the vibrational corrections. For the subsequent calculations it was assumed that the σ-values of Table 1 give a realistic estimate of the uncertainty of the vibrational contributions and hence of the average rotational constants. Therefore these values were used directly to calculate the weights in the evaluation of the r_z-structure.

Isotopic Differences in Bond Lengths

As was shown by Kuchitsu et al. [2] it is important to include small isotopic differences in bond lengths into the calculation of the r_z-structure. Following these authors the isotopic shifts were estimated by

$$\delta r_{ij} = \tfrac{3}{2} a_3 \, \delta \langle \Delta z_{ij}^2 \rangle_0 - \tfrac{1}{2} \delta \langle \Delta \varrho_{ij}^2 \rangle_0 / r_{ij} . \quad (2)$$

The parallel and perpendicular mean square amplitudes $\langle \Delta z_{ij}^2 \rangle_0$ and $\langle \Delta \varrho_{ij}^2 \rangle_0$ entering Eq. (2) were calculated from the force fields. The Morse anharmonicity parameters a_3 were taken from [15] to be 1.981 Å^{-1}, 1.945 Å^{-1}, and 2.072 Å^{-1} for CH, CS, and SO, respectively. Following Kuchitsu and Oyanagi [16] also secondary isotopic differences were taken into account. The calculated isotopic shifts are summarized in Table 2.

It is interesting to note in Table 2 that in any case the substitution H → D causes a lengthening of the C–H bond distance due to large changes in the perpendicular mean square amplitudes. It is also observed that the isotopic differences on monodeuteration are about half those on perdeuteration of a methyl group. Moreover Table 2 shows a remarkable consistency of the estimates δr_z obtained from different force fields. This consistency is found although the mean square amplitudes are noticeably different. This gives confidence to use the estimated values of Table 2, especially the small values of the skeletal isotopic shifts.

Table 2. Estimated isotopic differences in bond lengths (subst.-normal) in DMSO from different force fields (in 10^{-4} Å).

DMSO-		S–C	S–C′	S–O	C–H_I	C–H_{II}	C–H_{III}	C′–H'_I	C′–H'_{II}	C′–H'_{III}
	HC	− 0.4	− 0.4	− 0.2	0.0	0.0	0.0	0.0	0.0	0.0
-S34	TLFF	− 0.4	− 0.4	− 0.2	0.0	0.0	0.0	0.0	0.0	0.0
	GH	− 0.5	− 0.5	− 0.2	0.0	0.0	0.0	0.0	0.0	0.0
	HC	− 0.3	− 0.3	− 0.5	− 0.2	− 0.5	− 0.4	− 0.2	− 0.5	− 0.4
-O18	TLFF	− 0.3	− 0.3	− 0.4	− 0.3	− 0.6	− 0.4	− 0.3	− 0.6	− 0.4
	GH	− 0.3	− 0.3	− 0.4	− 0.3	− 0.5	− 0.4	− 0.3	− 0.5	− 0.4
	HC	− 1.3	− 0.2	− 0.2	− 0.2	− 0.2	− 0.3	− 0.4	− 0.2	− 0.3
-C13	TLFF	− 1.4	− 0.1	− 0.1	− 0.2	− 0.1	− 0.2	− 0.4	− 0.2	− 0.3
	GH	− 1.4	− 0.2	− 0.2	− 0.2	− 0.2	− 0.2	− 0.4	− 0.2	− 0.3
	HC	− 0.1	− 0.7	− 0.3	+10.2	+ 9.8	+10.1	− 0.5	− 0.3	− 0.4
-D1I	TLFF	0.0	− 0.7	− 0.4	+11.6	+10.2	+10.5	− 0.5	− 0.2	− 0.5
	GH	− 0.1	− 0.7	− 0.3	+ 9.5	+ 9.9	+10.2	− 0.5	− 0.2	− 0.4
	HC	− 0.1	− 0.4	− 0.6	+10.0	+11.5	+10.0	− 0.8	− 0.8	− 0.7
-D1II	TLFF	+ 0.1	− 0.4	− 0.7	+10.2	+12.1	+10.3	− 0.8	− 0.8	− 0.8
	GH	− 0.1	− 0.4	− 0.6	+10.0	+ 9.5	+ 9.9	− 0.8	− 0.8	− 0.7
	HC	0.0	− 0.5	− 0.4	+ 9.9	+10.0	+11.1	− 0.7	− 0.5	− 0.7
-D1III	TLFF	+ 0.2	− 0.5	− 0.4	+10.4	+10.3	+10.9	− 0.7	− 0.6	− 0.8
	GH	0.0	− 0.5	− 0.4	+10.0	+ 9.9	+ 9.3	− 0.7	− 0.5	− 0.7
	HC	− 0.1	− 1.4	− 1.3	+23.3	+24.6	+24.6	− 1.7	− 1.4	− 1.6
-D3	TLFF	+ 0.3	− 1.6	− 1.4	+25.2	+25.6	+26.1	− 1.8	− 1.5	− 1.9
	GH	− 0.1	− 1.5	− 1.3	+22.6	+22.5	+22.6	− 1.6	− 1.4	− 1.7
	HC	− 1.2	− 1.2	− 2.3	+21.4	+23.0	+22.7	+21.4	+23.0	+22.7
-D6	TLFF	− 1.0	− 1.0	− 2.5	+23.1	+24.0	+24.0	+23.1	+24.0	+24.0
	GH	− 1.3	− 1.3	− 2.3	+20.7	+20.9	+20.8	+20.7	+20.9	+20.8

Additional confidence comes from a comparison of the sums of weighted squared residuals from the fit of the structural parameters including primary isotopic differences only and from a fit with inclusion of primary and secondary shifts. The improvement of the variance of about 48% seems to be significant.

A further check is possible with the substitution of atoms lying in a principal plane: here the planar moment of inertia P perpendicular to this plane cannot change with substitution provided the average positions of all other atoms are unchanged with this substitution. In DMSO the sulfur and the oxygen atom lie in the b-c-plane and therefore the planar moment $P_a = \sum m_i \cdot a_i^2$ should not change with the substitutions $^{32}S \rightarrow {}^{34}S$ and $^{16}O \rightarrow {}^{18}O$. This condition is not met for the experimental values of the planar moments of inertia. In consequence from Kraitchman's equations an imaginary coordinate a is obtained for the sulphur atom and $|a| = 0.011$ Å for the oxygen atom. However the inclusion of the isotopic differences of Table 2 results in almost perfect agreement of the planar moments P_a of the normal species with those of the substituted species. Note that for the substitution $^{16}O \rightarrow {}^{18}O$ this agreement is achieved only by the inclusion of secondary isotopic differences.

One comment should be made to the value $a_3 = 1.981$ Å^{-1} for CH. Some authors (e.g. [17], [18], [19]) use the value $a_3 = 2.5$ Å^{-1}. This value would give primary isotopic differences for the C–H bond distance which are shorter by 0.0013 Å, while leaving the secondary differences unchanged. It can be shown that the complete effects of this change in δr_z is a lengthening of all average C–H bond distances by 0.0026 Å. Thus structural parameters obtained on the basis $a_3 = 2.5$ Å^{-1} are not listed separately.

Structure Calculations

Three different types of structure calculations have been performed: 1) Fitting of internal parameters (bond lengths, bond angles, dihedral angles) by weighted least squares to average rotational constants B_z. 2) Fitting of internal parameters to differences ΔB_z (subst.-normal) of average rotational constants as suggested by Nösberger et al.

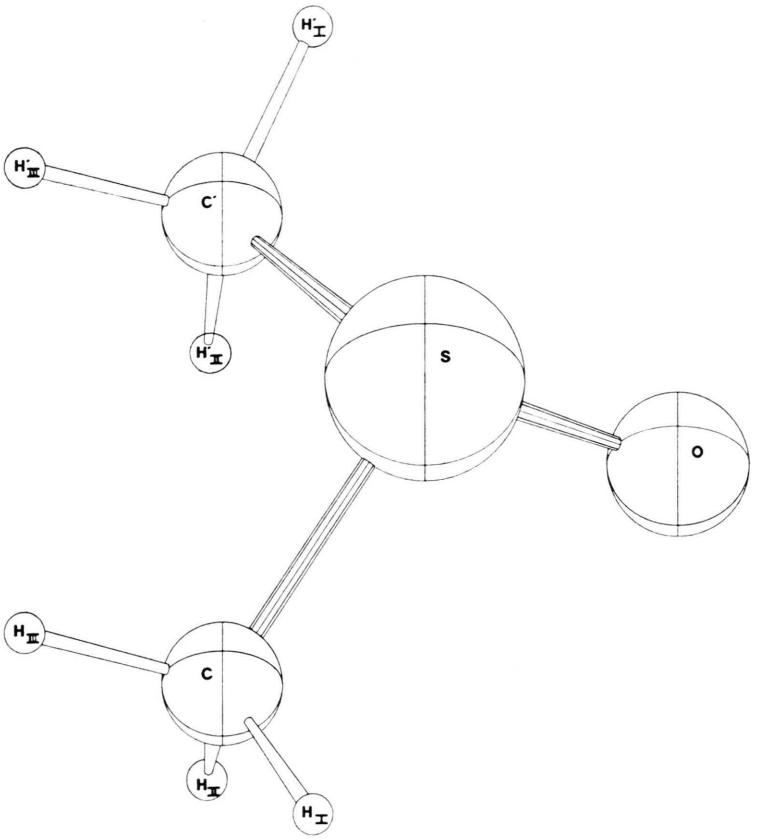

Fig. 1. View of dimethylsulfoxide with designation of atoms.

[20] and by Schwendeman [21]. 3) Fitting of Cartesian coordinates by Kraitchman's method modified as to allow for isotopic differences [22]. Since the first two methods include automatically the principal axis and center of mass condition these constraints have been added explicitly also in the Kraitchman-type calculations. In all cases the average rotational constants obtained by substracting the harmonic corrections of Table 1 from the ground state rotational constants of Ref. [1] were used. The weights have been chosen inversely proportional to the squares of the relative errors of the average rotational constants, i.e.

$$w \sim (B_z/\sigma(B_z))^2$$

with $\sigma(B_z)$ taken from Table 1.

In the course of the calculations of type 3 it became apparent that some inconsistency is present in the rotational constants affecting the structure of the methyl groups. Therefore in a first attempt to locate this inconsistency the assignment of the rotational transitions and the rotational constants of the species DMSO-C13, -D1I, -D1II, -D1III, and -D3 [23] have been checked critically. In any case at least ten additional lines were found in the recordings which confirmed unambiguously the values of the rotational constants of Ref. [1]. Therefore in a second step use was made of the fact that the modification [22] of Kraitchman's method allows the calculation of the substitution structure with different sets of isotopic species. Table 3 gives the C–H bond distances obtained with different sets of deuterated species. In the latter calculations weights and the principal axis and center of mass condition have not been employed. From Table 3 it is apparent that the inconsistency is introduced by the inclusion of the D3-species. Since at the present stage no explanation for this anomalous behaviour can be given the rotational constants of this isotope have been omitted for the final calculations of the r_z-structure.

The most prominent feature of the structure calculations is the observation that the different vibrational corrections from the three force fields

Table 3. r_z-substitution bond distances C–H in DMSO calculated with different sets of deuterated species. In addition to the isotopic species of skeletal substitutions the following species were included: 1) D1I, D1II, D1III; 2) D1I, D1II, D6; 3) D1I, D1III, D6; 4) D1II, D1III, D6; 5) D1I, D1II, D3; 6) D1I, D1III, D3; 7) D1II, D1III, D3; 8) D1I, D1II, D1III, D3, D6.

	1	2	3	4	5	6	7	8
$C–H_I$	1.0586	1.0568	1.0568	1.0565	1.0570	1.0569	1.0870	1.0840
$C–H_{II}$	1.0935	1.0935	1.0926	1.0935	1.0935	1.1298	1.0935	1.0930
$C–H_{III}$	1.0705	1.0673	1.0705	1.0705	1.0971	1.0705	1.0705	1.0784

Table 4. Average geometrical parameters of DMSO by calculations of type 1. $\tau(H)$ is the dihedral angle C′–S–C–H, θ is the angle between the plane C′–S–C and the bond S–O. For errors see text.

	HC	TLFF	GH	mean
S–C	1.8086 (14)	1.8088 (16)	1.8087 (15)	1.8087 (1)
S–O	1.4827 (13)	1.4823 (14)	1.4825 (13)	1.4825 (2)
$C–H_I$	1.0244 (368)	1.0205 (395)	1.0235 (367)	1.0228 (23)
$C–H_{II}$	1.0976 (87)	1.0973 (95)	1.0983 (88)	1.0977 (6)
$C–H_{III}$	1.0667 (77)	1.0659 (79)	1.0670 (73)	1.0665 (6)
C′–S–C	96.58 (7)	96.58 (8)	96.57 (8)	96.58 (1)
$S–C–H_I$	110.12 (392)	110.39 (433)	110.24 (402)	110.25 (14)
$S–C–H_{II}$	107.63 (13)	107.60 (14)	107.63 (13)	107.62 (2)
$S–C–H_{III}$	110.66 (52)	110.65 (53)	110.64 (49)	110.65 (1)
$\tau(H_I)$	2.18 (704)	2.15 (790)	2.42 (737)	2.25 (17)
$\tau(H_{II})$	123.00 (68)	123.02 (71)	123.05 (65)	123.02 (3)
$\tau(H_{III})$	243.79 (72)	243.93 (74)	243.87 (68)	243.86 (7)
θ	115.40 (12)	115.41 (14)	115.40 (13)	115.40 (1)
$\sum w_i(\Delta B_i)^2$	4.4909-7	4.7741-7	4.1042-7	

virtually do not affect the resulting geometrical parameters within each type of calculation. This is demonstrated in Table 4 with the results of the calculation of type 1. In this table the geometrical parameters are given with the single standard errors of the fit. The last column contains the mean value of column 1, 2, and 3 with the largest deviation of the parameters from the mean value in brackets. Obviously the deviations are much smaller than the single standard errors. The same behaviour is observed for calculations of type 2 and 3. Therefore only the mean values of the geometrical parameters are given as final results for each type of calculation in Table 5. The errors given in Table 5 are the single standard errors of the HC-fit. The errors of the type 3 calculation have been obtained from the standard errors of the r_z-substitution-coordinates with inclusion of the correlation matrix. Of course these errors indicate only the relative reliability of the parameters within one method.

In Table 4 the small deviations of the individual geometrical parameters from their mean value are partly due to the larger weight given to the rotational constants C_z. However different weighting schemes (e.g. unit weights for all observations) produce changes of the structural parameters within twice the standard errors of Table 4. These changes are not significant.

In Table 5 it is seen that the structural parameters generally agree within three times the assigned single standard errors. Therefore at the present stage it seems the best to estimate the r_z-structure by the weighted mean of the three types of calculation given in column 4 of Table 5. The range of the individual parameters given in the last column is then believed to give an estimate for the uncertainty of the r_z-structure.

Discussion

Examining the structural parameters of Table 5 it is obvious that the asymmetry of the methyl groups is not reduced by taking vibrational contributions into account. In fact all parameters compare well with the previously reported r_s-structure [1]. The only exceptions are the S–C bond distance and the position of the atom H_{III}. For the S–C bond length the assigned error limits

Table 5. Mean values of average geometrical parameters of DMSO obtained by different types of calculation. Column 4 contains the weighted mean of columns 1, 2, and 3, and column 5 contains the range of the calculated parameters. For designations see Table 4. The last column gives the r_s-structure from Ref. [1] for comparison.

Calculation of type	1	2	3	Weighted mean	Range	r_s
S–C	1.8087 (14)	1.8090 (4)	1.8049 (6)	1.8076	0.0041	1.799 (5)
S–O	1.4825 (13)	1.4871 (5)	1.4820 (10)	1.4848	0.0051	1.485 (6)
C–H_I	1.0228 (368)	1.0621 (91)	1.0506 (51)	1.0521	0.0393	1.054 (12)
C–H_{II}	1.0977 (87)	1.0998 (14)	1.0967 (13)	1.0982	0.0031	1.097 (8)
C–H_{III}	1.0665 (77)	1.0749 (26)	1.0692 (18)	1.0709	0.0084	1.093 (8)
C′–S–C	96.58 (7)	96.65 (2)	96.49 (6)	96.60	0.16	96.57 (3)
S–C–H_I	110.25 (392)	107.82 (73)	108.42 (43)	108.33	2.43	108.27 (10)
S–C–H_{II}	107.62 (13)	107.82 (4)	107.79 (5)	107.78	0.20	108.17 (3)
S–C–H_{III}	110.65 (52)	110.53 (19)	110.71 (14)	110.64	0.18	109.55 (5)
$\tau(H_I)$	2.25 (704)	1.35 (96)	1.63 (68)	1.55	0.90	1.00 (18)
$\tau(H_{II})$	123.02 (68)	123.42 (17)	123.11 (18)	123.24	0.40	122.47 (10)
$\tau(H_{III})$	243.86 (12)	243.52 (28)	243.56 (15)	243.58	0.34	243.13 (18)
θ	115.40 (12)	115.38 (5)	115.44 (11)	115.40	0.06	115.50 (5)

overlap and this difference seems not to be significant. However the difference 0.02 Å in the bond distance C–H_{III} is significant and is at least partly due to vibrational effects. Unfortunately this conclusion cannot be completely ascertained since the small increase in the S–C bond distance which seemed insignificant could have induced the large decrease in the bond distance C–H_{III}. Therefore, to determine more precisely the bond lengths S–C and S–O and to eliminate their numerical influence on the positions of the hydrogen atoms we started to collect data from gas phase electron diffraction and to calculate the r_{av}-structure.

It is interesting to find C–H bond distances of 1.05, 1.07, and 1.10 Å, respectively, also in a X-ray study on the crystal structure of DMSO [24]. However the effects of the condensed phase do not allow a direct comparison.

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Note added in proof: The computer programs used in this investigation are: GMAT (author: Schachtschneider; calculation of B-matrix), TAUZET (author: Typke; calculation of vibrational corrections and mean square amplitudes), and MWSTR and RSDELR (author: Typke; structure calculations).

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