

Mean Amplitudes of Vibration in Molecules with Internal Rotation

III. Dimanganese Decacarbonyl

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Spectroscopic calculations are reported for dimanganese decacarbonyl. Mean amplitudes of vibration are given for the mean amplitudes of vibration which correspond to interatomic distances being independent of the angle of internal rotation. Also given are the framework mean amplitudes for the angle-dependent distances.

The results are highly approximate and tentative, but are believed to be useful for the electron-diffraction investigation which is in progress.

The present work was initiated by the investigation of dimanganese decacarbonyl by gaseous electron diffraction.¹ In the interpretation of the electron-diffraction measurements usually some estimates of mean amplitudes, if possible from spectroscopic data, are highly appreciated, although no demand for accurate values is necessarily articulated. The present results of spectroscopic calculations for dimanganese decacarbonyl must be regarded as highly approximate because of the lack of spectral data as to the complete vibrational assignment. The adopted force field is only tentative and not reproduced in this communication. Nevertheless the calculated mean amplitudes seem to have reasonable orders of magnitude, and they are believed to be useful for the electron-diffraction investigation.

STRUCTURAL AND SPECTRAL DATA

Dimanganese decacarbonyl was assumed to possess a staggered structure (symmetry D_{4d}) with all Mn—Mn—C as right angles and Mn—C—O as linear chains in its equilibrium position. As equilibrium distances we adopted the results of Dahl and Rundle.²

$$\begin{aligned}
 R(\text{C}-\text{O } eq) &= S(\text{C}-\text{O } ax) = 1.16 \text{ \AA} \\
 D(\text{Mn}-\text{C } eq) &= 1.83 \text{ \AA}, T(\text{Mn}-\text{C } ax) = 1.79 \text{ \AA} \\
 U(\text{Mn}-\text{Mn}) &= 2.92 \text{ \AA}
 \end{aligned}$$

The available spectral data^{3,4} are fragmentary; the vibrational assignments are far from complete.

FORCE FIELD

The present calculations are based on force constants transferred from hexacarbonyls⁵ and one pentacarbonyl.⁶ It should be noted that the force fields for hexacarbonyls have been refined since the earlier publication;⁵ the computations quoted by Arnesen and Seip⁷ are based on the refined force constants. It should be understood that the present force field for manganese decacarbonyl is highly approximate. But we did not find it worth while performing refinements because of the lack of complete spectral data. In partic-

Table 1. Dimanganese decacarbonyl: Mean amplitudes of vibration (\AA units) for distances independent of the angle of rotation.

Atom pair	Type	(Equil. dist.)	Mean amplitude	
			$T=0$	298°K
11 1	C—O <i>eq</i>	(1.160)	0.035	0.035
19 9	C—O <i>ax</i>	(1.160)	0.035	0.035
21 11	Mn—C <i>eq</i>	(1.830)	0.047	0.052
21 19	Mn—C <i>ax</i>	(1.790)	0.048	0.053
21 22	Mn—Mn	(2.920)	0.039	0.048
21 1	Mn...O <i>eq</i> (lin)	(2.990)	0.047	0.052
21 9	Mn...O <i>ax</i> (lin)	(2.950)	0.047	0.053
11 13	C <i>eq</i> ...C <i>eq</i> (lin)	(3.660)	0.056	0.062
11 12	C <i>eq</i> ...C <i>eq</i>	(2.588)	0.086	0.150
11 19	C <i>eq</i> ...C <i>ax</i>	(2.560)	0.085	0.163
13 1	C <i>eq</i> ...O <i>eq</i> (lin)	(4.820)	0.057	0.062
12 1	C <i>eq</i> ...O <i>eq</i>	(3.506)	0.093	0.182
11 9	C <i>eq</i> ...O <i>ax</i>	(3.472)	0.097	0.200
19 1	C <i>ax</i> ...O <i>eq</i>	(3.485)	0.093	0.198
22 19	Mn...C <i>ax</i> (lin)	(4.710)	0.052	0.062
22 11	Mn...C <i>eq</i>	(3.446)	0.088	0.207
1 3	O <i>eq</i> ...O <i>eq</i> (lin)	(5.980)	0.057	0.063
1 2	O <i>eq</i> ...O <i>eq</i>	(4.228)	0.117	0.252
1 9	O <i>eq</i> ...O <i>ax</i>	(4.200)	0.117	0.272
19 20	C <i>ax</i> ...C <i>ax</i> (lin)	(6.500)	0.062	0.073
11 20	C <i>eq</i> ...C <i>ax</i>	(5.053)	0.101	0.232
22 9	Mn...O <i>ax</i> (lin)	(5.870)	0.052	0.062
22 1	Mn...O <i>eq</i>	(4.179)	0.107	0.282
20 9	C <i>ax</i> ...O <i>ax</i> (lin)	(7.660)	0.062	0.074
20 1	C <i>ax</i> ...O <i>eq</i>	(5.579)	0.130	0.344
11 10	C <i>eq</i> ...O <i>ax</i>	(6.149)	0.103	0.241
9 10	O <i>ax</i> ...O <i>ax</i> (lin)	(8.820)	0.062	0.074
1 10	O <i>eq</i> ...O <i>ax</i>	(6.588)	0.137	0.368

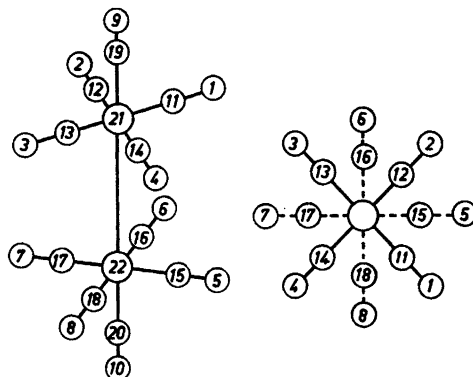


Fig. 1. Numbering of atoms in the dimanganese decacarbonyl molecule model.

ular the Mn—Mn force constant had to be assumed and is therefore rather tentative.

The possibility cannot be excluded that the electron-diffraction results in the next turn may serve as data for refinements of the force field.

MEAN AMPLITUDES OF VIBRATION

Table 1 shows the calculated mean amplitudes of vibration for the interatomic distances which are independent of the angle of rotation (θ). For the adopted numbering of atoms, see Fig. 1.

FRAMEWORK MEAN AMPLITUDES

The framework mean amplitudes were calculated according to the principles outlined in the first part of the article series.⁸

Variation of θ . Several equilibrium positions which are generated during a complete internal rotation, were assumed and identified by θ , the angle of rotation. During the variation of θ the linear equilibrium structure of all Mn—C—O chains was maintained. The molecule has the general symmetry of D_4 , possessed at any value of the angle θ . For special values of θ there exist two models with higher symmetries, *viz.* the eclipsed structure (symmetry D_{4h}), *e.g.* for $\theta=0^\circ$; and the staggered structure (D_{4d}), *e.g.* for $\theta=45^\circ$.

Assumptions about the force field. Our intention was to use the same set of force constants for all models during the variation of θ . Hence it was necessary to neglect a number of interaction force constants combining coordinates from the two movable parts of the molecule. The approximations of this kind, which seem quite reasonable to be assumed, are already introduced in the adopted force field referred to above.

Separation of the torsional modes. A complication is encountered due to the fact that there are two vibrational modes associated with the internal rotation. Firstly, one has the sum of C—Mn—Mn—C torsions representing the rotation about the Mn—Mn bond, say τ . Secondly, we have introduced a

corresponding coordinate, say τ' , involving the O—Mn—Mn—O torsions. Both these coordinates belong to the totally-symmetric species, A_1 , in the general model of D_4 symmetry. It is true that the τ' coordinate would normally not be included in the vibrational analysis; it may be expressed in terms of τ and a certain combination of linear Mn—C—O bendings. This linear-bending coordinate, however, has interaction elements in the G matrix with other totally-symmetric coordinates. This is not the case for the τ and τ' coordinates; the totally-symmetric block of the G matrix in our analysis has diagonal elements corresponding to τ and τ' , while all interaction elements involving these coordinates vanish. Our choice of the τ and τ' coordinates correspond to a partial diagonalization of the G matrix. The interaction force constants involving τ and τ' were assumed to be zero as a part of the approximations assumed for the force field (see above).

Conclusion and results. According to the principles outlined in the preceding paragraphs the vibrational modes associated with the internal rotation are completely separated from the other vibrational modes. The same feature was achieved in the analysis of ethane-type molecules.⁸

The framework mean amplitudes were calculated, neglecting both of the torsional vibrations τ and τ' . The quantities were obtained for all the distance types which depend on the angle of rotation, *i.e.* C...C, C...O, and O...O. It is referred to Table 2 for the calculated results at $T=298^\circ\text{K}$. Fig. 2 shows curves for the framework mean amplitudes as functions of θ both at absolute zero and 298°K .

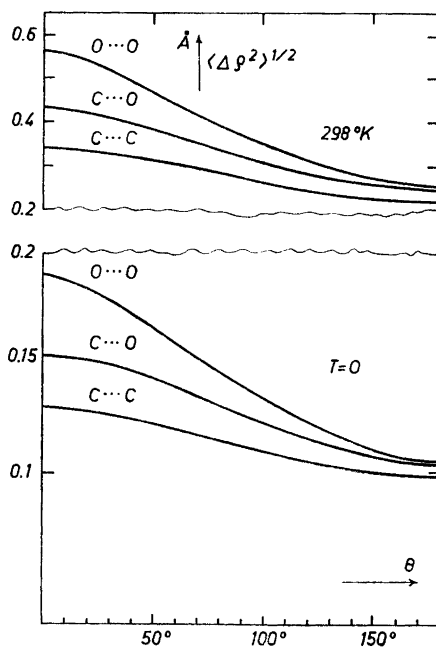


Fig. 2. Dimanganese decacarbonyl: Framework mean amplitudes as functions of the angle of rotation.

Table 2. Dimanganese decacarbonyl: Framework mean amplitudes (\AA units) at 298°K as functions of the angle of rotation, θ .

θ (°)	C...C	C...O	O...O
0	0.340	0.433	0.564
15	0.337	0.428	0.551
30	0.328	0.413	0.519
45	0.316	0.393	0.481
60	0.301	0.371	0.442
75	0.286	0.348	0.407
90	0.271	0.326	0.374
105	0.257	0.305	0.343
120	0.244	0.287	0.315
135	0.234	0.271	0.291
150	0.226	0.259	0.272
165	0.221	0.251	0.260
180	0.219	0.249	0.255

APPROXIMATE FORMULA

The functional dependence of the framework mean-square amplitudes, $\langle \Delta \rho^2 \rangle_{\text{frm}}$, may be reproduced by the formula ⁸

$$\langle \Delta \rho^2 \rangle_{\text{frm}} = (\alpha + \beta \cos \theta + \gamma \cos^2 \theta) / \rho^2$$

with almost exactness. Here ρ is the equilibrium distance of the atom pair in question, and consequently also a function of θ . The coefficients α , β , and γ on the other hand may with very good confidence be considered as independent of θ . Some comments about this apparent constancy of α , β , and γ are communicated elsewhere in this issue. For the numerical values of α , β , and γ (at $T=0$ and 298°K) for dimanganese decacarbonyl according to the present calculations, see Table 3.

Table 3. Dimanganese decacarbonyl: α , β , and γ coefficients (\AA^4 units) in the formula for framework mean-square amplitudes.

Distance		C...C	C...O	O...O
$T=0$	α	0.390	0.332	0.518
	β	-0.033	-0.054	-0.088
	γ	-0.014	-0.045	-0.123
298°K	α	1.119	2.213	3.685
	β	-0.033	-0.054	-0.088
	γ	-0.101	-0.305	-0.885

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