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FORCE CONSTANT CALCULATIONS FOR DIMETHYLMERCURY

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Summary

Force constants of dimethylmercury are calculated using the vibrational frequencies of gaseous $(CH_3)_2Hg$ and $(CD_3)_2Hg$. A force constant calculation utilizing the generalised inverse matrix procedure is discussed briefly. Assuming a free rotational model, the force field is introduced as a trigonometrical function of the torsional angle γ; the time variant corrections of vibrational frequencies and normal coordinate vectors which this involves are investigated.

Introduction

Vibrational spectra of dimethylmercury [1–11] and perdeuteriodimethylmercury [9–11] have been studied from time to time. Structural studies by electron diffraction [12,13] and high resolution pure rotational Raman spectroscopy [14] suggest a linear C—Hg—C structure, and from the vibrational spectroscopic behaviour free internal rotation is assumed to occur [4,9–11,15].

Calculation of force constants for dimethylmercury was first reported by Gutowsky [4], using a simplified potential energy function. A modified Urey—Bradley potential function was employed by Kittila [16] to carry out a least squares fit of the calculated to the observed frequencies. A similar calculation was carried out by Miles et al. [17], who also discussed the variation of the force constants. Quite recently Bribes and Gaufres [18], and Bakke [19] also used the frequencies of perdeuteriated dimethylmercury in a further study with a relatively simplified force field.

We were particularly interested in further investigating vibrational coupling across the heavy atom and the consequences of the very low barrier to internal rotation of the methyl groups. In the calculations presented here we have tried to determine a more complete force field, using a modified force constants refinement procedure, and we have investigated the effects of a slight dependence of the force constants on the torsional angle γ.

TABLE 1

INTERNAL VALENCE SYMMETRY COORDINATES OF DIMETHYLMERCURY

Species	Coordinate
A_{1g}	$S_1 = (\frac{1}{6})^{\frac{1}{2}}(\Sigma_t r_i + \Sigma_f r_j)^a$
	$S_2 = (\frac{1}{12})^{\frac{1}{2}}[(P-Q)(\Sigma_t \alpha_i + \Sigma_f \alpha_j) - (P+Q)(\Sigma_t \beta_i + \Sigma_f \beta_j)]^b$
	$S_3 = (\frac{1}{2})^{\frac{1}{2}}(R_1 + R_2)$
A_{2u}	$S_4 = (\frac{1}{6})^{\frac{1}{2}}(\Sigma_t r_i - \Sigma_f r_j)$
	$S_5 = (\frac{1}{12})^{\frac{1}{2}}[(P-Q)(\Sigma_t \alpha_i - \Sigma_f \alpha_j) - (P+Q)(\Sigma_t \beta_i - \Sigma_f \beta_j)]$
	$S_6 = (\frac{1}{2})^{\frac{1}{2}}(R_1 - R_2)$
E_u	$S_{7a} = (\frac{1}{12})^{\frac{1}{2}}(2r_1 - r_2 - r_3 + 2r_4 - r_5 - r_6)$
	$S_{7b} = \frac{1}{2}(r_2 - r_3 + r_5 - r_6)$
	$S_{8a} = (\frac{1}{12})^{\frac{1}{2}}(2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6)$
	$S_{8b} = \frac{1}{2}(\alpha_2 - \alpha_3 + \alpha_5 - \alpha_6)$
	$S_{9a} = (\frac{1}{12})^{\frac{1}{2}}(2\beta_1 - \beta_2 - \beta_3 + 2\beta_4 - \beta_5 - \beta_6)$
	$S_{9b} = \frac{1}{2}(\beta_2 - \beta_3 + \beta_5 - \beta_6)$
	$S_{10a} = \epsilon$
	$S_{10b} = \epsilon'$
E_g	$S_{11a} = (\frac{1}{12})^{\frac{1}{2}}(2r_1 - r_2 - r_3 - 2r_4 + r_5 + r_6)$
	$S_{11b} = \frac{1}{2}(r_2 - r_3 - r_5 + r_6)$
	$S_{12a} = (\frac{1}{12})^{\frac{1}{2}}(2\alpha_1 - \alpha_2 - \alpha_3 - 2\alpha_4 + \alpha_5 + \alpha_6)$
	$S_{12b} = \frac{1}{2}(\alpha_2 - \alpha_3 - \alpha_5 + \alpha_6)$
	$S_{13a} = (\frac{1}{12})^{\frac{1}{2}}(2\beta_1 - \beta_2 - \beta_3 - 2\beta_4 + \beta_5 + \beta_6)$
	$S_{13b} = \frac{1}{2}(\beta_2 - \beta_3 - \beta_5 + \beta_6)$

[a] Σ_t denotes $\Sigma_{i=1}^{3}$, i.e. over coordinates in the top; Σ_f denotes $\Sigma_{j=4}^{6}$, i.e. over coordinates in the frame. [b] In all terms relating to the coordinates S_2 and S_6 extra factors $(P+Q)$ and $(P-Q)$ were included: these arise in removing the redundancy for slightly distorted tetrahedral angles, where: $P = \frac{1+K}{(2+2K^2)^{1/2}}$, $Q = \frac{1-K}{(2+2K^2)^{1/2}}$, and $K = \frac{\sin\beta \times \cos\beta}{\sin\alpha}$ [25,26].

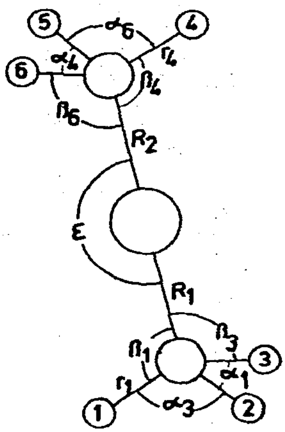

Fig. 1. The internal coordinates of dimethylmercury.

Calculation of force constants

The correct symmetry group for freely rotating $Hg(CH_3)_2$ and $Hg(CD_3)_2$ is the G_{36} group, introduced by Longuet-Higgins [20] in the form of the double group G_{36}^{+}, which was later proposed by Hougen [21,22] and Bunker [23] for dimethylacetylene. The nearly free internal rotation means that the normal coordinates are functions of the torsional angle γ, and this introduces some difficulties into the calculations. Although the symmetry coordinates can be chosen in such a way that the elements of the G matrix are completely independent of γ and the elements of the F matrix depend but slightly on it [24], the solution of the inverse vibrational problem, which involves time-variant force constants, is not convenient from the computational point of view. We shall therefore first determine the force field for the $Hg(CH_3)_2$ molecule on the assumption that the force constants are not dependent on the torsional angle.

It is not difficult to demonstrate that the force fields for the various equilibrium geometries D_{3d}, D_{3h}, D'_{3h} or G_{36}^{+} are effectively equivalent and, conversely, that the calculated frequencies are practically independent of the chosen configuration. For this reason the D_{3d} point group and the internal valence symmetry coordinates presented in Table 1 were adopted; these internal coordinates are also shown in Fig. 1. Exact molecular geometry (slightly distorted tetrahedral angles) was considered throughout the calculations. The equilibrium interatomic distances and valence angles are summarised in Table 2. The kinetic energy matrix was found with a computer program described elsewhere [27].

TABLE 2

MOLECULAR GEOMETRY[a]

$r_e(CH) = 1.09$ Å	∠ (HCH) = 109°18′
$r_e(CHg) = 2.094$ Å	∠ (HCHg) = 109°38′
	∠ (CHgC) = 180°

[a]Ref. [14].

TABLE 3

FORCE CONSTANTS OF DIMETHYLMERCURY COMPUTED BY LEAST SQUARES FIT IN TERMS OF SYMMETRY COORDINATES (UNITS ARE mdyn/Å)

Species	Force constant	Bribes and Gaufres [18]	Bakke [19]	This work, Final set.
A_{1g}	F_{11}	4.971	4.870	4.771
	F_{12}	−0.172	0	−0.293
	F_{13}	0	0	−0.131
	F_{22}	0.351	0.322	0.382
	F_{23}	0	0	−0.175
	F_{33}	2.380	2.460	2.409
A_{2u}	F_{44}	4.971	4.840	4.771
	F_{45}	− 0.172	0	−0.293
	F_{46}	0	0	−0.131
	F_{55}	0.363	0.330	0.382
	F_{56}	0	0	−0.097
	F_{66}	2.243	2.550	2.348
E_u	F_{77}	4.747	4.600	4.723
	F_{78}	0	0	−0.006
	F_{79}	0	0	0.055
	F_{88}	0.438	0.481	0.433
	F_{89}	0	−0.025	0.041
	F_{99}	0.366	0.354	0.388
	F_{1010}	0.405	0.377	0.382
E_g	F_{1111}	4.747	4.600	4.723
	F_{1112}	0	0	−0.006
	F_{1113}	0	0	0.005
	F_{1212}	0.438	0.462	0.433
	F_{1213}	0	−0.025	0.041
	F_{1313}	0.284	0.283	0.285

For dimethylmercury 26 experimental frequencies are available for the two isotopic species, but no more than 16 force constants could be accurately fixed. All the infrared active fundamental frequencies except ν_{10}, (which was taken from the literature [8,10]) were measured in the high-resolution infrared spectra of gaseous samples [11] while some of the infrared inactive frequencies (viz. ν_2, ν_3, ν_{12} and ν_{13}) were calculated from combination tones and overtones observed in the infrared spectra of gaseous samples [11]; the remaining ν_1 and ν_{11} fundamentals were assumed equal to ν_4 and ν_7 respectively. Very good agreements were found between theoretical and experimental values of the Teller—Redlich products. The initial force field was constructed using the results of Bribes and Gaufres [18] and Bakke [19], but the final set was practically independent of the initial force field. The force constant calculation method is discussed below.

The converged values of force constants are given in terms of symmetry coordinates in Table 3, where they are compared with the results of earlier calculations [18,19]. The agreement is quite good. The observed and calculated frequencies, with their deviations (in %), and in the transposed L matrices for $Hg(CH_3)_2$ and $Hg(CD_3)_2$ are collected in Tables 4 and 5 respectively. Because of the weak vibrational coupling of two methyl groups, L' matrices show close similarity for the A_{1g}, A_{2u} and E_g, E_u pairs of symmetry blocks.

The transformation equations between symmetry coordinate and internal coordinate force constants are presented in Table 6. The internal valence force

(continued on p. 7)

TABLE 4

OBSERVED[a] AND CALCULATED FREQUENCIES AND TRANSPOSED L MATRIX ELEMENTS FOR SCALED SYMMETRY COORDINATES OF DIMETHYL-MERCURY

Species		Observed	Calcd.	$(\Delta\nu/\nu)\times 100$	L'				Assignment
					S_1	S_2	S_3		
A_{1g}	ν_1	2920.6	2921.7	0.04	0.98	−0.48	−0.08		CH stretching
	ν_2	(1180)[b]	1180.2	0.04	0.24	1.48	0.12		CH_3 bending
	ν_3	(520)[b]	520.6	0.04	−0.01	−0.11	0.25		CHg stretching
					S_4	S_5	S_6		
A_{2u}	ν_4	2920.6	2922.7	0.07	0.98	−0.49	−0.08		CH stretching
	ν_5	1200.1	1207.9	0.65	0.25	1.47	0.14		CH_3 bending
	ν_6	546.3	549.2	0.53	−0.02	−0.20	0.26		CHg stretching
					S_7	S_8	S_9	S_{10}	
E_u	ν_7	2978.5	2976.8	0.06	1.02	0.49	0.07	0.07	CH stretching
	ν_8	1465.1	1447.8	1.17	−0.25	1.36	0.69	−0.03	CH_3 deformation
	ν_9	791.9	794.7	0.35	0.03	−0.77	0.78	−0.10	CH_3 rocking
	ν_{10}	153.0	155.5	0.16	0.01	−0.02	0.02	0.19	CHgC bending
					S_{11}	S_{12}	S_{13}		
E_g	ν_{11}	2978.5	2976.1	0.08	1.02	0.48	0.07		CH stretching
	ν_{12}	(1446)[b]	1438.1	0.60	−0.25	1.42	0.62		CH_3 deformation
	ν_{13}	(693)[b]	679.7	1.88	−0.02	−0.67	0.83		CH_3 rocking

[a] Average error: 0.44%. [b] Calculated frequencies from combination tones and overtones of the infrared spectra of gaseous sample.

TABLE 5

OBSERVED[a] AND CALCULATED FREQUENCIES AND TRANSPOSED L MATRIX ELEMENTS FOR SCALED SYMMETRY COORDINATES OF PERDEUTERODIMETHYLMERCURY

Species		Observed	Calcd.	$(\Delta\nu/\nu)\times 100$	L'				Assignment
					S_1	S_2	S_3		
A_{1g}	ν_1	2124.3	2123.5	0.04	0.71	−0.34	−0.10		CD stretching
	ν_2	(902)[b]	901.2	0.04	0.12	1.15	0.16		CD_3 bending
	ν_3	(470)[b]	469.4	0.04	0.01	−0.10	0.22		CHg stretching
					S_4	S_5	S_6		
A_{2u}	ν_4	2124.3	2125.7	0.07	0.71	−0.35	−0.10		CD stretching
	ν_5	938.9	934.1	0.52	0.12	1.14	0.17		CD_3 bending
	ν_6	496.7	495.0	0.55	0.003	−0.17	0.23		CHg stretching
					S_7	S_8	S_9	S_{10}	
E_u	ν_7	2231.3	2215.2	0.72	0.78	0.31	−0.12	0.10	CD stretching
	ν_8	1041.8	1040.7	0.11	−0.06	1.05	0.44	0.02	CD_3 deformation
	ν_9	604.9	598.2	1.08	0.03	−0.51	0.62	−0.11	CD_3 rocking
	ν_{10}	141.0	138.5	1.81	0.00	−0.02	0.02	0.17	CHgC bending
					S_{11}	S_{12}	S_{13}		
	ν_{11}	2231.3	2213.3	0.81	0.78	0.31	−0.12		CD stretching
	ν_{12}	(1021)[b]	1035.6	1.37	−0.07	1.08	0.39		CD_3 deformation
	ν_{13}	(519)[b]	507.1	2.02	0.03	−0.43	0.65		CD_3 rocking

[a]Average error: 0.63%. [b]Note see Table 4.

TABLE 6

RELATION[a] BETWEEN SYMMETRY COORDINATE AND INTERNAL COORDINATE FORCE CONSTANTS FOR THE $Hg(CH_3)_2$ AND $Hg(CD_3)_2$

Species		
A_{1g}	F_{11}	$= f_r + 2f_{rr}$
	F_{12}	$= 1/\sqrt{2}[(P-Q)(f_{r\alpha'}+2f_{r\alpha})-(P+Q)(f_{r\beta}+2f_{r\beta'})]$ [b]
	F_{13}	$= \sqrt{3}f_{rR}$
	F_{22}	$= \frac{1}{2}[(P-Q)^2(f_\alpha+2f_{\alpha\alpha})+(P+Q)^2(f_\beta+2f_{\beta\beta})-2(P^2-Q^2)(f_{\alpha\beta'}+2f_{\alpha\beta})]$
	F_{23}	$= \sqrt{3}/\sqrt{2}[(P-Q)f_{R\alpha}-(P+Q)f_{R\beta}-(P+Q)f'_{R\beta}]$
	F_{33}	$= f_R + f'_{RR}$
A_{2u}	F_{44}	$= F_{11}$
	F_{45}	$= F_{12}$
	F_{46}	$= F_{13}$
	F_{55}	$= F_{22}$
	F_{56}	$= \sqrt{3}/\sqrt{2}[(P-Q)f_{R\alpha}-(P+Q)f_{R\beta}+(P+Q)f'_{R\beta}]$
	F_{66}	$= f_R - f'_{RR}$
E_u	F_{77}	$= f_r - f_{rr}$
	F_{78}	$= f_{r\alpha'} - f_{r\alpha}$
	F_{79}	$= f_{r\beta} - f_{r\beta'}$
	F_{710}	$= F_{810} = F_{910} = 0$
	F_{88}	$= f_\alpha - f_{\alpha\alpha}$
	F_{89}	$= f_{\alpha\beta'} - f_{\alpha\beta}$
	F_{99}	$= f_\beta - f_{\beta\beta} + f'_{\beta\beta}$
	F_{1010}	$= f_\epsilon$
E_g	F_{1111}	$= F_{77}$
	F_{1112}	$= F_{78}$
	F_{1113}	$= F_{79}$
	F_{1212}	$= F_{88}$
	F_{1213}	$= F_{89}$
	F_{1313}	$= f_\beta - f_{\beta\beta} - f'_{\beta\beta}$

[a]Notes: all symbols refer to Mills [25] and Duncan [26] notations; f' interaction force constants relating the two methyl groups. [b]P and Q see Table 2.

constants determined using these expressions are given in Table 7. On the analogy of the work of Mills [25] and Duncan [26] on CH_3X molecules, some of the valence force constants (viz. $f_{r\alpha}$, $f_{R\alpha}$, $f_{\alpha\alpha}$ and $f_{\alpha\beta}$) were assumed equal to zero. The value of 2.379 mdyn/Å obtained for the CHg stretching force constant falls in the range of previously calculated values (mdyn/Å): 2.311 [18], 2.45 [8,16], 2.50 [19] and 2.58 [17].

Force constant refinement procedure

The basic problem faced in force constant calculations is the need to determine an adjustment vector Δf which minimizes the sum of the weighted squares of residuals $\tilde{r}Wr$, where $r = \Delta\nu - J\Delta f$ (J is the Jacobian matrix and $\Delta\nu$ is the difference between the experimental and calculated frequencies). In the "classical" procedure [29] Δf is obtained from a linearised set of normal equations:

$$(\tilde{J}WJ)\,\Delta f = \tilde{J}W\Delta\nu \qquad (1)$$

If the matrix $\tilde{J}WJ$ is nearly singular, however, a stable solution cannot be expected.

The method applied in this paper, which was described in detail in a previous paper [28], removes the singularity difficulties by applying the generalized inverse [30] of the Jacobian matrix J and takes into account its rank. The $m \times n$ $(m > n)$ matrix $J_W = W^{1/2} J$ is written in the following decomposition form [31]:

$$J_W = U\Sigma_n \tilde{V} \quad (2)$$

where Σ_n is an $n \times n$ diagonal matrix the elements σ_i of which are the non-negative square roots of the eigenvalues of $\tilde{J}_W J_W = \tilde{J}WJ$ and are called the singular values of J_W. The matrices U and V, both of which satisfy equation(3), are the eigenvector matrices of the eigenvalue problems of matrices $J_W \tilde{J}_W$ and

$$\tilde{U}U = \tilde{V}V = V\tilde{V} = E_n \quad (3)$$

$\tilde{J}_W J_W$, respectively, and can be obtained [31] without solving the eigenvalue problems.

If the matrix $\tilde{J}_W J_W$ is ill-conditioned, then one or more σ_i will be very small in comparison with the others. Assuming that the σ_i values are arranged in descending order and replacing the relatively small σ_{p+1}, σ_{p+2} ···, ···, $\sigma_n (p < n)$ by zero, which is equivalent to perturbing J_W by a matrix whose Frobenius norm [32] is $(\Sigma_{i=p+1}^{r} \sigma_i^2)^{1/2}$, we obtain the matrix:

$$\hat{J}_W = U\Sigma_p \tilde{V} \quad (4)$$

$(\tilde{U}U = \tilde{V}V = E_p)$ the condition of which is sufficiently good to make convergence certain. In this case an approximation of the generalised inverse [32] of J_W is:

$$\hat{J}_W^+ = V\Sigma_p^+ \tilde{U} \quad (5)$$

with $\Sigma_p^+ = \text{diag}\,(\sigma_1^{-1}, \cdots, \sigma_p^{-1})$, and the minimal least squares solution [33] of the sum of $\tilde{r}Wr$ is:

$$\Delta f = \hat{J}_W^+ \Delta\nu_W \quad (6)$$

where $\Delta\nu_W = W^{1/2} \Delta\nu$.

The following notations are used: u, v for vectors u and v; A, B for matrices A and B; and $\tilde{A}$, $\tilde{B}$ for the transposes of matrices A and B.

Investigation of the effect of γ-dependent force field

The set of force constants of dimethylmercury determined above was obtained for the point group D_{3d}. In order to satisfy the experimentally observed frequency splittings between in-phase (A_{1g} and E_g) and out-of-phase (A_{2u} and E_u) methyl species, viz. between the pairs of modes (ν_2, ν_5), (ν_8, ν_{12}) and (ν_9, ν_{13}), the small interaction force constants $f'_{RR} = 0.031$, $f'_{R\beta} = 0.032$ and $f'_{\beta\beta} = 0.051$ (all mdyn/Å) were introduced, the values of which were found in terms of internal coordinates (see Table 7). The first two of

TABLE 7

THE FORCE CONSTANTS[a] OF DIMETHYLMERCURY IN INTERNAL COORDINATE REPRESENTATION

f_r	4.739
f_{rr}	0.016
f'_{RR}	2.379
f_{RR}	0.031
f_{rR}	−0.075
$f_{r\alpha}$	0.006
$f_{r\alpha'}$	0
$f_{r\beta}$	0.179
$f_{r\beta'}$	0.124
$f_{R\alpha}$	0
$f_{R\beta}$	0.111
$f'_{R\beta}$	0.032
f_{α}	0.433
$f_{\alpha\alpha}$	0
f_{β}	0.280
$f_{\beta\beta}$	−0.057
$f_{\alpha\beta}$	−0.041
$f_{\alpha\beta'}$	0
f_{ϵ}	0.382
$f'_{\beta\beta}$	0.051

[a]Notes: see Table 6.

these constants (which were included in the species A_{1g} and A_{2u}) only are not, from symmetry considerations, greatly dependent on the torsional angle γ, but the third, which is the top frame rock—rock interaction force constant, can exhibit fluctuations as γ is varied. Since the very strong splitting of the two degenerate rocking vibrations (about 90 cm^{-1}) shows that rock—rock coupling between two methyl groups must be the strongest, and as the hydrogen displacements in this vibrational mode are directed against each other the γ-dependence of the ν_9, ν_{13} pair seems reasonable on physical grounds. We shall investigate in detail only this interaction force constant.

Let us express the force field of the rock—rock interaction in terms of the internal coordinate representation:

	β_4	β_5	β_6
β_1	d_1	d_2	d_3
β_2	d_3	d_1	d_2
β_3	d_2	d_3	d_1

where d_1, d_2 and d_3 are functions of γ and are interconvertible during the rotation of methyl groups. After the symmetry transformation, we have for the symmetry species:

$$\begin{aligned} A_{1g}(A_{1s}) &: F'_{22} = F_{22} + \tfrac{1}{2}(d_1 + d_2 + d_3) \\ A_{2u}(A_{4s}) &: F'_{55} = F_{55} - \tfrac{1}{2}(d_1 + d_2 + d_3) \end{aligned} \quad (7a)$$

$$\begin{aligned} E_u(E_{1d}) &: F'_{99} = f_\beta - f_{\beta\beta} + [d_1 - \tfrac{1}{2}(d_2 + d_3)] \\ E_g(E_{2d}) &: F'_{1313} = f_\beta - f_{\beta\beta} - [d_1 - \tfrac{1}{2}(d_2 + d_3)] \end{aligned} \quad (7b)$$

the bracketed species of point groups G^{+}_{36} and F_{22} and F_{55} are taken from Table 6. When the γ-dependence of d_i elements, in accordance with Howard's determination [34] has the form:

$$\begin{aligned} d_1 &= k \cos 6\gamma \\ d_2 &= -k \cos (6\gamma - \pi/3) \\ d_3 &= -k \cos (6\gamma + \pi/3) \end{aligned} \tag{8}$$

we find that

$$\sum_{i=1}^{3} d_i = 0 \tag{9}$$

while the $f'_{\beta\beta}$ force constants of rock—rock interactions in degenerate species have the form (see Table 6):

$$f'_{\beta\beta} = d_1 - \tfrac{1}{2}(d_2 + d_3) \tag{10}$$

This means that we may consider the interaction force constants d_i to exhibit fluctuations as γ is varied in time but their sum remains equal to zero. We can therefore treat the γ-dependent corrections to F'_{99} and F'_{1313} as a non-vanishing interaction term in the degenerate symmetry species only. Equation (7b) then becomes:

$$\begin{aligned} F'_{99} &= F^{\circ}_{99} + \tfrac{3}{2}k \cos 6\gamma \\ F_{1313} &= F^{\circ}_{1313} - \tfrac{3}{2}k \cos 6\gamma \end{aligned} \tag{11}$$

where $F^{\circ}_{99} = F^{\circ}_{1313} = f_{\beta} - f_{\beta\beta}$

This γ-dependence of the F'_{99} and F'_{1313} force constants for the degenerate symmetry species has the same form as that proposed by Howard [34] and is very similar to the dependence obtained by Bunker and Hougen [24] in their hypothetical force field for dimethylacetylene.

Using the results of our force field calculation, we can express functions (8) and (11) in numerical form. For the fixed staggered configuration, when $\gamma = 30°$, we have:

$$f'_{\beta\beta} = \tfrac{3}{2}k \cos 6\gamma = 0.051$$

The d_i are given by:

$$\begin{aligned} d_1 &= 0.034 \cos 6\gamma \\ d_2 &= -0.034 \cos (6\gamma - \pi/3) \\ d_3 &= -0.034 \cos (6\gamma + \pi/3) \end{aligned} \tag{12}$$

and F_{99} and F_{1313} by:

$$\begin{aligned} F_{99} &= 0.337 + 0.051 \cos 6\gamma \\ F_{1313} &= 0.337 - 0.051 \cos 6\gamma \text{ (all in mdyn/Å)} \end{aligned} \tag{13}$$

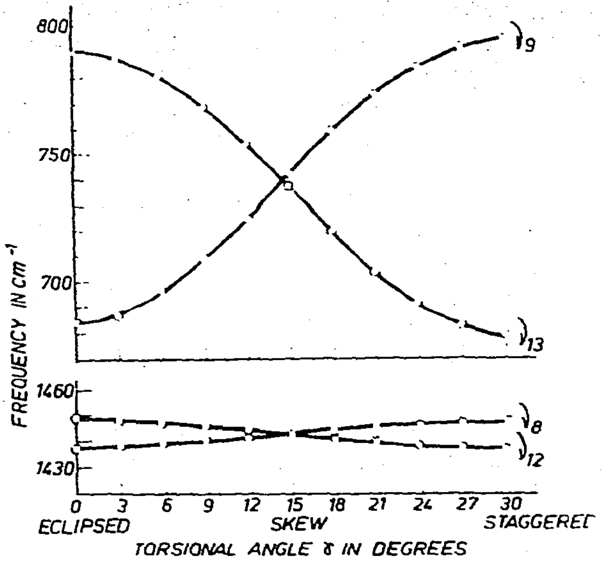

Fig. 2. The γ-dependence of methyl rocking (ν_9, ν_{13}) and methyl deformation (ν_8, ν_{12}) degenerate frequency pairs using the force field given by eqn. (13).

Normal coordinate calculations were performed with the set of force constants given in Table 3, in which the γ-dependent terms are added to the elements F_{99} and F_{1313} given by eqn. (13).

From diagonalizing the FG matrix for many values of γ (from 0 to 30° in 3° steps), we can determine how the Λ and L matrices vary with torsion. It was observed that not only do the ν_9 and ν_{13} normal modes vary greatly with γ but the methyl deformation frequency pair ν_8 and ν_{12} as well, although the remaining frequencies of degenerate modes are only very slightly sensitive to the γ-dependent force field. The way in which these frequency pairs depend on the torsional angle is presented in Fig. 2. Intersection of vibrational frequencies near $\gamma = 15°$ is observed for every frequency pair of two degenerate species.

On the analogy of dimethylacetylene [24] another set of force constants was investigated:

$$
\begin{aligned}
F_{93} &= 0.337 + 0.051 \cos 6\gamma \\
F_{913} &= 0.025 \sin 6\gamma \qquad (14) \\
F_{1313} &= 0.337 - 0.051 \cos 6\gamma \text{ (all in mdyn/Å)}
\end{aligned}
$$

Here a γ-dependent cross term F_{913} is added to the force field; when this term is present, the frequency pairs ν_9, ν_{13} and ν_8, ν_{12} do not show the above cosinusoidal dependence on the torsional angle γ; the actual dependence is plotted in Fig. 3. The influence exerted by the small force constant F_{913} clearly prevents intersection of the curves for the calculated frequency pairs in the region where this would be expected (viz. where the pairs of vibrational frequencies are very close to each other). The extremum of the curves, however, is found to occur near $\gamma = 15°$; the frequency difference between ν_9 and

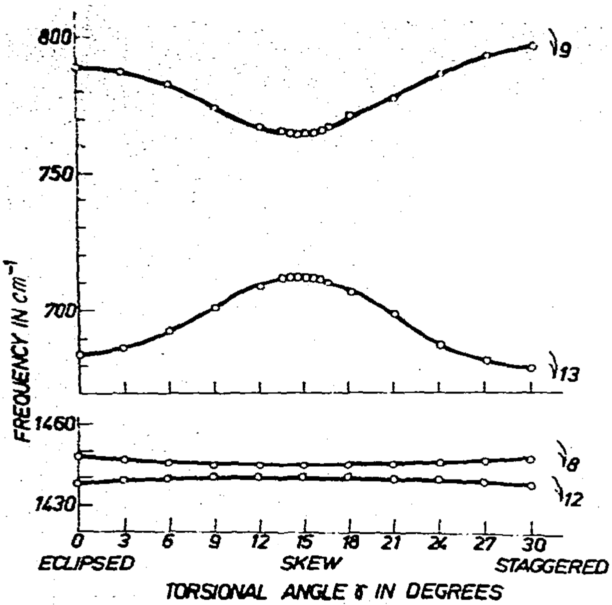

Fig. 3. The γ-dependence of methyl rocking (ν_9, ν_{13}) and methyl deformation (ν_8, ν_{12}) degenerate frequency pairs using the force field given by eqn. (14).

ν_{13} was established as about 53.5 cm^{-1} and that between ν_8 and ν_{12} as 4.5 cm^{-1}. With values of the coefficient of sin 6γ smaller than 0.025 the maximum and minimum of ν_9 and ν_{13} would be nearly equal.

The variation of the L matrix with torsional angle was investigated by determining the eigenvectors of the FG matrix for the hypothetical force fields established by eqns. (13) and (14). Using the force field of eqn. (13) in the L

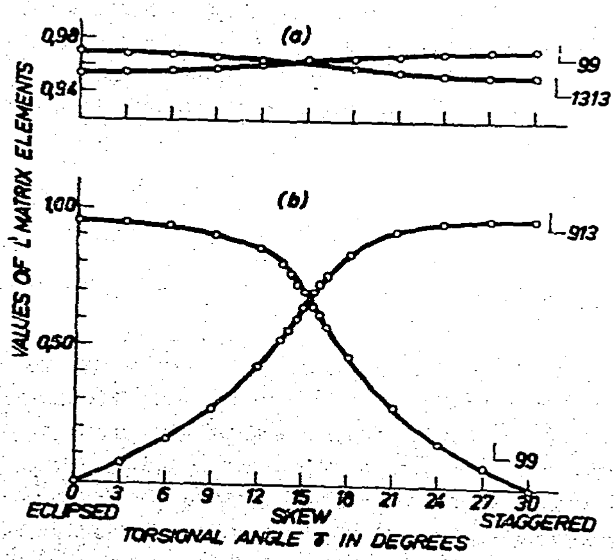

Fig. 4. Characteristic functions of eigenvector matrix elements from the torsional angle γ using the force field given, (a) by eqn. (13), and (b) by eqn. (14).

matrix, about ten matrix elements were found which vary strongly with γ. The nature of this dependence, which is very similar to that found for the vibrational frequency pairs, can be seen for L_{99} and L_{1313} matrix elements in Fig. 4a. From this it can be concluded that when $F_{913} = 0$, the normal coordinates remain pure *trans*-type (E_{1d}) or pure *cis*-type (E_{2d}) vibrations for all values of γ.

The eigenvector matrix exhibits a more complicated behaviour if the force field of eqn. (14) is considered; all the out-of-block diagonal matrix elements show a considerable dependence on the torsional angle. In the plotted dependences for the L_{99} and L_{913} matrix elements (Fig. 4b), the curves intersect near $\gamma = 15°$. Evidently, when the molecule is near to the eclipsed or staggered position the normal coordinates involve largely *cis*-type (E_{1d}) and *trans*-type (E_{2d}) vibrational coordinates, respectively, whereas in the crossover region they involve mixed E_{1d} and E_{2d} symmetry coordinates.

From these results the following conclusions may be drawn. Equations (13) and (14) require a considerably stronger γ-dependence of the force field for dimethylmercury than that used for dimethylacetylene; the observed effects are, in fact, similar to those for CH_3—C=C—CH_3 by Bunker and Hougen [24]. The γ-dependent force constants can be introduced using a rock—rock interaction force constant obtained by force constant calculation.

As would be expected from the very strong coupling of rocking modes with the other methyl vibrations, the observed perturbing effect of the γ-dependent force field is not restricted to the vibrational pair ν_9, ν_{13} alone; other frequencies and normal coordinates also exhibit a considerable sensitivity to γ. The introduction of the F_{913} cross-interaction force constant [eqn. (14)] has a fairly strong perturbing effect on the frequencies and normal coordinates within the two degenerate symmetry species.

The introduction of a γ-dependent force field requires time-variant corrections of L and Λ. It would be particularly interesting to establish how the magnitudes of Coriolis coupling the mean square amplitudes and the calculated vibrational intensities are influenced by the application of time-variant force fields.

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