A UNIQUE FORCE FIELD FOR FORMALDEHYDE

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Using the Parametric Representation Method to solve (3×3) order vibrational problems, an attempt has been made to fix the unique force field for formaldehyde. The isotopic shifts, rotational distortion parameters and interaction Zeta constants were used to obtain unambiguous solutions for the angle parameters. The proper set of the Eulerian angles representing the suitable force field for H_2CO was found to be $\chi = 69°11'$, $\theta = 66°5'$ and $\phi = 4°46'$ for the a_1 species of vibration and the single parameter $\phi = 41°3'$ was found to represent the b_1 species.

1. Introduction

A determination of the unique force field for polyatomic molecules has been attempted by the parametric representation method used by many workers [1–3]. Recently an attempt was made to extend the parametric method to XY_3Z type molecules with (3×3) order cases [4]. It was shown that it is possible to fix the molecular force field unambiguously using the Eulerian angles and with additional data like the Coriolis coupling constants, isotopic shifts and rotational distortion constants. The present paper discusses the extension of the above method to the case of XY_2Z type molecules, a typical example of this group being formaldehyde.

2. Theoretical considerations

Planar XY_2Z type molecules belong to the point group C_{2v} with the normal modes coming under $\Gamma = 3a_1 + 2b_1 + b_2$. Of these the b_2 species can be exactly solved while the b_1 species involving the (2×2) order can be represented by means of a single parameter ϕ and can be uniquely fixed with isotopic data and or the Coriolis coupling constants. The complete methodology is given in reference [5]. To solve the (3×3) a_1 species, three such angle parameters χ, θ and ϕ are required and simultaneous use of isotopic shifts [4] and rotational distortion parameters makes it possible to solve the relevent equations.

To solve the 2×2 equation in b_1 species of formaldehyde, experimentally observed isotope shifts, interaction ξ constant and rotational distortion parameter τ_{abab} were used. For (3×3) a_1 species isotope shifts along with the rotation distortion parameters τ_{aaaa}, τ_{bbbb} and τ_{aabb} were used.

The details of procedure involved in solving the inverse vibrational problem of formaldehyde are briefly given below.

The force constant matrix F is given by

$$F = \widetilde{L_0}^{-1} A\Lambda\tilde{A} L_0^{-1}, \tag{1}$$

where L_0 satisfies the normalizing condition $L_0 \widetilde{L^0} = G$, the inverse kinetic energy matrix and A is a proper orthogonal parameter matrix. For the (2×2) case A is chosen as

$$A = \begin{bmatrix} C_\phi & S_\phi \\ -S_\phi & C_\phi \end{bmatrix}, \tag{2}$$

while for the (3×3) case it is represented (4) through the three independent Eulerian angles χ, θ and ϕ as

$$\begin{bmatrix} C_\chi & S_\chi & 0 \\ -S_\chi & C_\chi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & C_\theta & C_\theta \\ 0 & -S_\theta & C_\theta \end{bmatrix} \begin{bmatrix} C_\phi & S_\phi & 0 \\ -S_\phi & C_\phi & 0 \\ 0 & 0 & 1 \end{bmatrix}, \tag{3}$$

where C and S refer to the cosine and sine of the respective angles. The relation between the isotopic shifts and A can be expressed [4] through the equation

$$\frac{K}{\Lambda} = \tilde{A} B A, \tag{4}$$

where K is known as the "Kinematic term" in the differential form [2] of Wilson's [6] secular equation and $B = L_0^{-1} \Delta G \widetilde{L_0}^{-1}$. Here ΔG is the change in the G matrix between the two isotopic molecules considered.

For the (2×2) b_1 species, the single parameter ϕ can be directly calculated using the relations given earlier [5]. They are:

$$\tan \phi_1 = \frac{B_{45} \pm \sqrt{B_{45}^2 - \left(B_{44} - \dfrac{K_{44}}{\Lambda_4}\right)\left(B_{55} - \dfrac{K_{44}}{\Lambda_4}\right)}}{\left(B_{55} - \dfrac{K_{44}}{\Lambda_4}\right)} \tag{5}$$

and

$$\tan \phi_2 = \frac{-B_{45} \pm \sqrt{B_{45}^2 - \left(B_{44} - \dfrac{K_{55}}{\Lambda_5}\right)\left(B_{55} - \dfrac{K_{55}}{\Lambda_5}\right)}}{\left(B_{44} - \dfrac{K_{55}}{\Lambda_5}\right)}. \tag{6}$$

Here B_{ik}'s are the elements of B matrix and $\dfrac{K_{44}}{\Lambda_4} + \dfrac{K_{55}}{\Lambda_5} = B_{44} + B_{55}$. Similarly τ_{abab}, which depends upon the (2×2) species alone [7], can be used to fix ϕ. For this, a graph can be drawn between ϕ and τ_{abab} in the interval $-90°$ to $90°$ and the intersection of the experimental value with the curve gives the proper solution for ϕ. The proper ϕ can also be fixed [5] with the use of the interaction ξ_{56}^a constant between ν_5 and ν_6 (out of plane). For various values of ϕ, ξ_{56}^a can be calculated and a graphical solution may be obtained.

For the (3×3) a_1 species, the expansion of equation (4) in terms of the B and A matrix elements leads to the following set of relations:

$$\frac{K_{11}}{\Lambda_1} = pC_\phi^2 + qS_\phi^2 + 2rS_\phi C_\phi, \tag{7}$$

$$\frac{K_{22}}{\Lambda_2} = pS_\phi^2 + qC_\phi^2 - 2rS_\phi C_\phi, \tag{8}$$

$$\frac{K_{33}}{\Lambda_3} = [B_{11}S_\chi^2 + B_{22}C_\chi^2 + 2B_{12}S_\chi C_\chi]S_\theta^2 + B_{33}C_\theta^2 + 2[B_{13}S_\chi + B_{23}C_\chi]S_\theta C_\theta, \tag{9}$$

where

$$p = [B_{11}C_\chi^2 + B_{22}S_\chi^2 - 2B_{12}S_\chi C_\chi]$$

$$q = [B_{11}S_\chi^2 + B_{22}C_\chi^2 + 2B_{12}S_\chi C_\chi]C_\theta^2 + B_{33}S_\theta^2 - 2[B_{13}S_\chi + B_{23}C_\chi]S_\theta C_\theta$$

and

$$r = [B_{12}(S_\chi^2 - C_\chi^2) + (B_{22} - B_{11})S_\chi C_\chi]C_\theta + (B_{13}C_\chi - B_{23}S_\chi)S_\theta.$$

Here

$$\frac{K_{11}}{\Lambda_1} + \frac{K_{22}}{\Lambda_2} + \frac{K_{33}}{\Lambda_3} = B_{11} + B_{22} + B_{33}.$$

From the above, it is seen that of the three parameters, χ is independent and the other angles θ and ϕ are constrained through equations (7), (8) and (9). The value of χ in the interval $-90°$ to $90°$ generates four sets of A matrices with angle combinations $A_1(\chi, \theta_1, \phi_1)$, $A_2(\chi, \theta_1, \phi_2)$, $A_3(\chi, \theta_2, \phi_3)$ and $A_4(\chi, \theta_2, \phi_4)$. For each set of combinations the rotational distortion parameters $\tau_{\alpha\beta r\delta}$ are calculated [8] and the set which reproduces the experimental value can be taken as an acceptable solution for force field calculations.

3. Results and discussion

The spectral data and other molecular parameters used in the present calculations are given in Table I. Anharmonic corrected frequencies of Curtis [9] were used.

For the (2×2) b_1 species, the use of $\dfrac{K_{44}}{\Lambda_4}$ in equation (5) gives two solutions for ϕ

TABLE I

Observed vibrational wave numbers (cm^{-1}), harmonic wave numbers (cm^{-1}), bond distances (Å), Coriolis coupling constant, rotational distortion parameters ($\times 10^{-6}$ cm^{-1}) and (C = O) shift (cm^{-1}) for the ^{12}C$-^{13}$C isotopes for formaldehyde

	H$_2$CO			D$_2$CO		
1.	2766.4	3009		2056.4	2189	
2.	1746.07	1773		1700	1716	
3.	1500.6	1634		1106	1199	Ref. [9]
4.	2843.4	3084		2160.3	2314	
5.	1247.4	1359		990.2	1067	
6.	1163.5	—		938	—	Ref. [7]

D (C = O) = 1.203 $\tau^a_{aaaa} = -3396.72$

d (C − H) = 1.101   Ref. [9] $\tau_{bbbb} = -13.453 \ (-12.8)$

α (H C H) = 116°31′

$\xi^a_{56} = 0.54$ Ref. [10] $\tau_{aabb} = 47.037 \ (60)$

(^{12}C = O$-^{13}$C = O) = 37.95   Ref. [11] $\tau_{abab} = -109.809$

$S_1 = CH_2$ Str. $S_4 = CH_2$ Str.

$S_2 = C = O$ Str. $S_5 = HCO$ Def.

$S_3 = CH_2$ Def. $S_6 = (C = O)$ out of plane.

[a] The axes a, b, c are essentially those of Ref. [7]. The $\tau_{\alpha\beta r\varrho}$ values are from Ref. [13] as quoted in Ref. [12]. The values if paranthesis are from Ref. [12].

[42°58′ and −69°38′] and $\dfrac{K_{55}}{\Lambda_5}$ in equation (6) gives two other solutions [39°8′ and −65°48′]. This discrepancy in the ϕ solutions is due to a slight disagreement in the sum rule $B_{44} + B_{55} = \dfrac{K_{44}}{\Lambda_4} + \dfrac{K_{55}}{\Lambda_5}$. The average values of $\phi_1 = 41°3′$ and $\phi_2 = -67°43′$ were considered for force field calculations. The use of ξ^a_{56} (= 0.54) yields a solution of ϕ (= 46°54′) as seen from Fig. 1 and the experimental value of τ_{abab}(= 109.809 × 10^{-6} cm^{-1}) as seen from Fig. 2 gives two more solutions of ϕ (35°44′ and −7°19′).

The calculated values of symmetrized force constants and other molecular constants for all these solutions are presented in Table II, from which it is clear that the two solutions $\phi = -67°43′$ and 7°19′ which correspond to inverse assignments can be neglected. Of the remaining three solutions, $\phi = 35°44′$ is also to be discarded as this solution yields a value of ξ^a_{56}(= 0.367) which is inconsistent with the observed value. This suggests that the observed value of τ_{abab} is slightly on the higher side. For the solution $\phi = 41°3′$, the calculated values of τ_{abab} (= −102.96 × 10^{-6} cm^{-1}) and ξ^a_{56}(= 0.45) are in good agreement with the observed values while the solution $\phi = 46°54′$ is unable to reproduce τ_{abab}. Incidentally it is found that the solution $\phi = 41°3′$ is the mean value of the other two solutions obtained using ξ^a_{56} and τ_{abab} and hence it is taken to represent the best fit solution for the b_2 species.
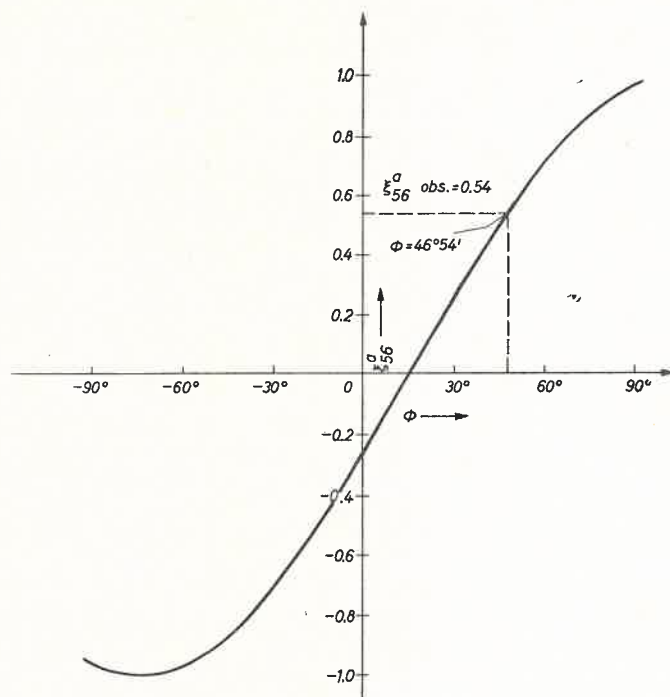
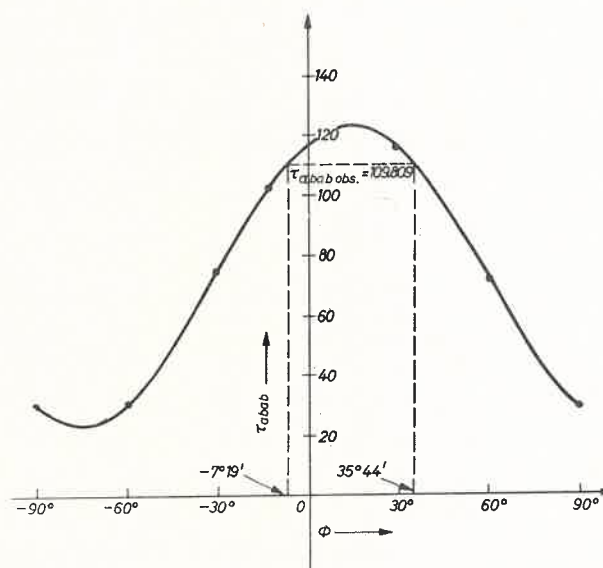Fig. 1. Plot of ξ_{56}^a versus ϕ for the b_1 species of vibration for H_2CO

Fig. 2. Plot of τ_{abab} ($\times 10^{-6}$cm^{-1}) versus ϕ for the b_1 species of vibration for H_2CO

TABLE II

The various angle parameters, the symmetrized force constants[a] (m. dyn/Å), τ_{abab} parameter ($\times 10^{-6}$ cm^{-1}), interaction Coriolis Coupling Constants and isotopic frequencies (cm^{-1}) as calculated using various molecular constants for the (2×2) b_1 species of formaldehyde

Molecular constants	Using ξ^a_{56}	Using $\dfrac{K_{ii}}{\varLambda_i}$		Using τ_{abab}	
ϕ	46°54′	41°3′	−67°43′	35°44′	−7°19′
F_{44}	5.0786[b]	4.9126	2.2535	4.6956	1.8750
F_{55}	0.7747	0.8002	3.4590	0.8804	2.8516
F_{45}	0.1864	−0.1763	1.9735	−0.4837	−1.2028
τ_{abab}	−94.2439	−102.9626	−25.8751	−109.8360	−109.813
ξ^a_{46}	0.8417	0.8922	0.1403	0.9302	0.9302
ξ^a_{56}	0.5400	0.4516	0.9900	0.3670	−0.3670
ω^*_4	2296	2323	2323	2349	2514
ω^*_5	1083	1071	1071	1060	989

[a] Force constants are calculated using d as the scaling factor 1 m. dyn/Å $= 10^2$ N/m.
[b] This number of significant figures is retained to secure internal consistency in calculations.

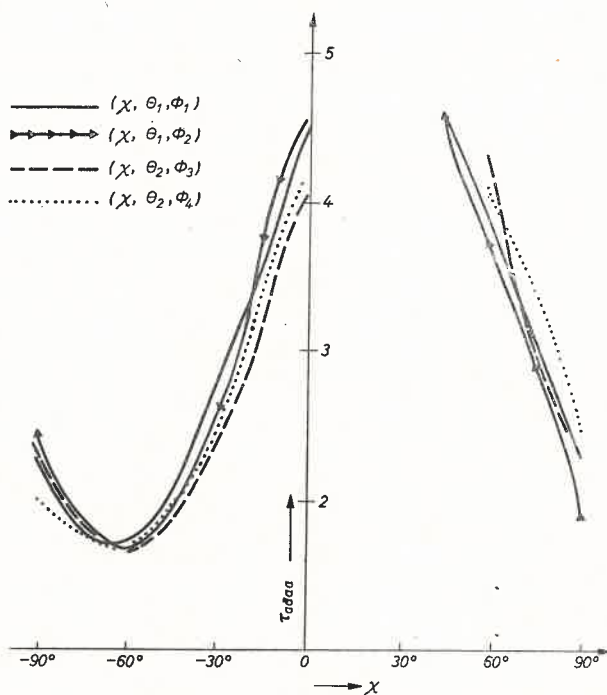Fig. 3. Plot of four sets of τ_{aaaa} ($\times 10^{-3}$ cm^{-1}) versus χ for various angle combinations obtained by using $\dfrac{K_{11}}{\varLambda_1}$ and $\dfrac{K_{33}}{\varLambda_3}$ for the a_1 species of vibration for H_2CO

For the (3×3) a_1 species, for each value of the variable parameter in the interval $-90°$ to $90°$ the four sets of τ_{aaaa} were calculated using $\dfrac{K_{33}}{\Lambda_3}$ and $\dfrac{K_{11}}{\Lambda_1}$ and their behaviour with χ are shown graphically in Fig. 3. It is found that the ϕ values become imaginary in the intervals $0°$ to $30°$ for (χ, θ_1, ϕ_1) and (χ, θ_1, ϕ_2) and $0°$ to $45°$ for (χ, θ_2, ϕ_3) and (χ, θ_2, ϕ_4) and the curves in Fig. 3 show discontinuities. The experimental value τ_{aaaa} $(= -3396.72 \times 10^{-6} \text{ cm}^{-1})$ intersects the four curves respectively at $69°11'$, $65°58'$, $-11°42'$ and $-15°6'$ for the angle combinations (χ, θ_1, ϕ_1), (χ, θ_1, ϕ_2), (χ, θ_2, ϕ_3) and (χ, θ_2, ϕ_4). The other intersection solutions in the interval $-15°$ to $-30°$ for (χ, θ_1, ϕ_1) and (χ, θ_1, ϕ_2) and $60°$ to $75°$ for (χ, θ_2, ϕ_3) and (χ, θ_2, ϕ_4) are to be discorded as in these regions they vary asymptotically. The symmetrized force constants, isotopic frequencies and $\tau_{\alpha\beta r\delta}$ parameters calculated for the four sets of angles are presented in Table III from which it is seen that the solutions $\chi = -11°42'$ and $-15°6'$ correspond to inverse assignments and hence need not be considered. Of the remaining two sets, the solution $\chi = 65°58'$ of (χ, θ_1, ϕ_2) combination yields values of 16.78 m. dyn/Å for the $(C = 0)$ force constant

TABLE III

The various angle parameters, symmetrised force constants[a] (m. dyn/Å), rotational distortion parameters $(\times 10^{-6} \text{ cm}^{-1})$ and isotopic frequencies (cm^{-1}) as calculated using $\dfrac{K_{ii}\text{'s}}{\Lambda_i}$ and τ_{aaaa} for the (3×3) a_1 species of formaldehyde

Molecular constants	Using $\dfrac{K_{11}}{\Lambda_1}$ and $\dfrac{K_{33}}{\Lambda_3}$ for the combinations of				Using $\dfrac{K_{22}}{\Lambda^2}$ and $\dfrac{K_{33}}{\Lambda_3}$ for the combination of
	(χ, θ_1, ϕ_1)	(χ, θ_1, ϕ_2)	(χ, θ_3, ϕ_3)	(χ, θ_2, ϕ_4)	$(\chi. \theta_1, \phi_1)$
χ	$69°11'$	$65°58'$	$-11°42'$	$-15°6'$	$72°16'$
θ	$66°5$	$66°21'$	$-65°14'$	$-65°3'$	$65°54'$
ϕ	$4°46'$	$24°4'$	$-23°5'$	$-3°49'$	$-4°18'$
F_{11}	4.9654[b]	4.9778	1.7898	1.7898	4.7967
F_{22}	13.5760	16.7586	16.7119	13.5779	13.7223
F_{33}	0.5637	0.4823	1.6235	1.6280	0.5499
F_{12}	1.2806	4.0239	-0.3657	0.3374	-0.0169
F_{13}	-0.4123	-0.3938	0.5223	0.5068	-0.3462
F_{23}	-0.5870	-0.9213	-2.4695	-0.9270	-0.4264
τ_{aaaa}	-3396.58	-3396.81	-3396.71	-3396.13	-3396.71
τ_{bbbb}	-11.4374	-10.0632	-8.6013	-11.4468	-11.7416
τ_{aabb}	34.3927	62.7261	62.7869	-34.5223	19.6895
ω_1^*	2189	2189	2189	2189	2241
ω_2^*	1743	1743	1743	1743	1716
ω_3^*	1199	1199	1199	1199	1199

[a],[b] as given in Table II.

and a very high value of 4.02 m. dyn/Å for the F_{12} interaction constant and hence can be neglected. Thus the remaining solution $\chi = 69°11'$ of (χ, θ, ϕ_1) combination alone reproduces acceptable values of force constants and other constants and is taken to represent the true force field for H_2CO. Graphical representation of the variation of τ_{aabb} for (χ, θ_1, ϕ_1) combination showed that the experimental values did not intersect the curves in any region. The experimentally observed values appear to be quite high compared to the theoretically calculated values. The calculated values of τ_{bbbb} $(= -11.43 \times 10^{-6} \text{ cm}^{-1})$ agree well with the experimental values $-12.8 \times 10^{-6} \text{ cm}^{-1}$ and $47.03 \times 10^{-6} \text{ cm}^{-1}$, respectively. It may be pointed out here that there is a wide variation in the values of τ_{aabb} reported by Oka et al. [13] and Toth [12].

The use of $\dfrac{K_{33}}{\Lambda_3}$ and $\dfrac{K_{22}}{\Lambda_2}$ for the set (χ, θ_1, ϕ_1) yields a solution of $\chi = 72°16'$.

The discrepancy found in the values of χ obtained by using $\dfrac{K_{11}}{\Lambda_1}$ and $\dfrac{K_{22}}{\Lambda_2}$ is due to disagreement in the sum rule. The calculated values of molecular constants for this solution are also presented in Table III. This solution also reproduces the symmetrized force constants reasonably but fails to reproduce τ_{aabb} and ω_1^*. The calculated values of $\tau_{aabb}(= 19.69 \times 10^{-6} \text{ cm}^{-1})$ and ω_1^* $(= 2241 \text{ cm}^{-1})$ show large deviations from the observed values and so this solution is discarded. Hence the solution $\chi = 69°11'$, $\theta = 66°5'$ and $\phi_1 = 4°46'$

TABLE IV

Symmetrised force constants[a] (m. dyn/Å) and $(^{12}C = O - ^{13}C = O)$ isotopic shift (cm^{-1}) for the best fit angle parameters

Molecular constants	Present study	Shimanouchi et al. Ref. [14]	Becher et al. Ref. [11]
F_{11}	4.9654[b]	4.4026	4.43
F_{22}	13.5760	12.7632	12.8
F_{33}	0.5637	0.5600	0.444
F_{12}	1.2806	0.9587	0.45
F_{13}	−0.4123	−0.1782	0.23
F_{23}	−0.5870	−0.4070	−0.40
F_{44}	4.9126	4.3268	4.40
F_{55}	0.8002	0.8520	0.673
F_{45}	−0.1763	−0.0620	0.26
F_{66}	0.3184	—	—
$\Delta \nu$	37	—	37.95

[a, b] as given in Table II.

which reproduces all the molecular constants is taken as the unique solution for the a_1 species.

The best fit values of symmetrized force constants are reported in Table IV along with those of Shimanouchi et al. [14] and Becher et al. [11]. It is seen that the force con-

stants are in general agreement with those of earlier reporters. Mills [15] and Fletcher and Thompson [16] have discussed the stretch bend interactions in CH_2X type molecules on the basis of H. O. F. F. Mills predicted a negative value for F_{23} and stressed the negative sign in order to fit the vibrational frequencies. This fact is consistent with the present calculations. However, positive value of F_{13} and F_{45} as expected by Mills do not obey the present values. The (C = O) frequency shift for the ^{12}C and ^{13}C isotopes was also calculated for the best fit angles and the calculated value of $\Delta\nu(37 \text{ cm}^{-1})$ is in good agreement with the observed value of 37.95 cm^{-1} reported by Becher et al. [11].

4. Inertia defect and mean vibrational amplitudes

Oka and Morino [7] have reported the nonvanishing interaction constants and the necessary equations to calculate the inertia defect in the case of XY_2Z planar molecules. The G matrix element for the out of plane vibration in H_2CO is taken from reference [17]. Using the relations of Meal and Polo [18], the various ξ constants were calculated for the best fit angles and used in the computation of Δ_{vib}, the vibrational contribution to the

TABLE V

The inertia defect (a. m. u. Å^2) and the mean vibrational amplitudes (Å) for various bonded and non-bonded atoms as calculated using the best fit angle parameters

Constants	Present study	Ref[a].
Δ_{vib}	0.0564	0.0597
Δ_{elec}	−0.0051	−0.0052
Δ_{cent}	0.0019	0.0016
Δ_0	0.0532	0.0561
		(0.0574)
$\sigma_{(C-H)}$	0.0783	0.0801
$\sigma_{(C=O)}$	0.0371	0.0372
$\sigma_{(H..H)}$	0.1261	0.1170
$\sigma_{(H..O)}$	0.0890	0.0912

[a] The inertia defect terms are from Ref. [7]. The value in paranthesis refers to observed value given in Ref. [7]. The mean amplitudes of vibration are from Ref. [20].

inertia defect. Similarly the electronic contribution, Δ_{elec} and the centrifugal contribution Δ_{cent} were also calculated and the intertia defect Δ_0 in the ground state was obtained. The Δ values are reported in Table V.

The calculated Δ_0(0.0532 a. m. u. Å^2) is in good agreement with the observed value (0.0574 a. m. u. Å^2). Using the procedure given by Ramaswamy et al. [19] mean amplitudes of vibration for various bonded and non-bonded atoms were calculated at 298.16°K for the best fit angles and are also reported in Table V. The calculated mean vibrational amplitudes are in good agreement with those reported by Cyvin [20].

TABLE VI

Valence force constants[a] (m. dyn/Å) in internal co-ordinate system for formaldehyde

Constants	Present study	Ref. [21]	Constants	Present study	Rer. [21]
f_d	4.9390[b]	4.38	$f_{d\alpha}$	-0.2380	0.19
f_D	13.5760	13.2	$f_{d\beta}$	0.0308	0.01
f_α	0.3758	0.32	$f'_{d\beta}$	0.2071	—
f_β	0.4940	0.705	$f_{D\alpha}$	-0.4793	-0.49
			$f_{D\beta}$	0.2396	—
f_{dd}	0.0264	0.01	$f_{d\beta}$	-0.1879	—
f_{dD}	0.9055	0.23	$f_{\beta\beta}$	-0.3061	—

[a], [b] as given in Table II.

The valence force constants in the internal co-ordinate system are also calculated and given in Table VI along with those of Beckmann et al. [21].

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