



A FORCE FIELD CALCULATION AND VIBRATIONAL ANALYSIS OF METHYL ACETATE

Carboxylic esters present a number of difficulties in a force field calculation as the number of experimental data (fundamental frequencies) is generally insufficient to fully determine the calculated force constants. These include a large number of important interactions as the vibrational modes are strongly delocalized over the carbon-oxygen skeleton. Since little quantitative information concerning the assignments of the carbon-oxygen skeletal modes is yet available, we report in this work a force field refinement and a normal coordinates calculation for methyl acetate using previously published frequencies.

1 — INTRODUCTION

Besides the mathematical difficulties which can arise in the force constant refinement procedure and are described and discussed in [1], the calculation of force constants in large molecules (molecules for which it is not possible to accumulate as many independent experimental data as force constants included in the potential function) relies very much on (i) well known geometrical parameters; (ii) complete and secured vibrational assignments of all fundamental modes and (iii) the possibility of transferring, from chemically similar species, well established force constants.

In order to obtain a unique molecular force field, the observed frequencies of a sufficient number of isotopically labelled species have to be included in the calculation and simultaneously processed through the least squares refinement procedure. Besides increasing the computation time, this procedure has to be exercised with care for the reasons stated in [2]. In fact, the least squares force field refinement minimizes the weighted sum of the squares of the residual deviations $\delta\lambda_i = \lambda_i^{\text{calc}} - \lambda_i^{\text{obs}}$, where the vibrational eigenvalues λ_i are directly proportional to the squares of the harmonic frequencies ($\lambda_i \propto \omega_i^2$) and the summation extends over the deviations of the available experimental frequencies for the isotopically labelled species. Now, the observed values of λ_i are usually taken directly from the anharmonic experimental frequencies and include anharmonic corrections which may lead to conflicting consistent errors in the least squares refinement in so far as they are not conform to the product rule relations which are normally built in the programs. In particular, the inclusion of both CH and CD stretchings bring in large anharmonic corrections and may prevent from obtaining a converged least squares solution.

In this paper we present a calculation of a force field for the methyl acetate molecule and discuss the results on the light of existing experimental data on several deuterated species as well as of previously established assignments. Our primary objective is not to obtain a unique force field for the methyl acetate molecule but to simply present a set of force constants which can be used as a set of spectroscopically useful parameters for a quantitative assignment of the skeletal modes of the ester group in basic agreement

with previously established empirical assignments [3,4]. Starting with a previously determined force field for the ester group [5] we proceeded with a refinement for the $\text{CH}_3\text{COOCH}_3$ isotopic species. The resulting force field allows a good fitting of the ester group frequencies and conforms to the previously established assignments for methyl acetate [3,4,6]. The subsequent calculation of harmonic frequencies for the deuterated species shows a good fitting of the skeletal observed frequencies and further confirms the existence of large and conflicting anharmonic errors if CH_3 and CD_3 stretching and angular deformation frequencies are included in the refinement [2,7].

The type of approximate force field we adopt in these calculations is the simplified general valence force field. This form of the general valence force field contains a reduced number of interaction constants compatible with a good fit of the vibrational fundamental frequencies. While the arbitrariness in choosing force constants is reduced in a Urey-Bradley type of force field, the frequency fit is frequently not as good and the interaction constants often keep features of an arbitrary nature [8 and references therein]. We have decided to use the more powerful general valence force field. However, under the above mentioned conditions, the calculated force fields cannot claim uniqueness, thus losing, to some extent, the useful feature of transferability among chemically related compounds. Under these circumstances, the physical meaning of the force constants is partially lost and they restrict themselves to the role of spectroscopic parameters which simply enable us to interpret the vibrational spectra.

2 — RESULTS AND DISCUSSION

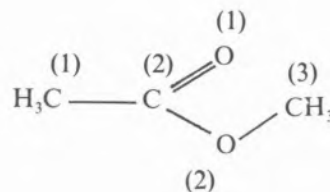
The computer programs used to perform the normal coordinates analysis were adapted to a Univac Sigma 5 computer system from [9], and consist of three programs: CART which converts molecular structural parameters to cartesian coordinates; GMAT which sets up the kinetic energy matrix and FPERT which calculates and refines the force constants using the least squares method.

The conformation chosen for methyl acetate was based on the structure of methyl formate [10] whose carbon-oxygen skeleton is planar, with the methyl

group of the methoxyl moiety *cis* with respect to the carbonyl oxygen [10,11]. Both methyl groups were assumed to have tetrahedral angles and the CH bond length was fixed at the value indicated in [10]. A list of these parameters is shown in Table 1.

Table 2 shows the definition of internal coordinates for methyl acetate. Apart from the usual changes in bond lengths and bond angles we have included three torsion coordinates around the C-C, C-O and O-C bonds and an out-of-plane wagging coordinate for C=O [12].

Before starting the calculation of force constants it is necessary to eliminate any redundant coordinates. In the case of methyl acetate, the internal coordi-



s-cis

Fig. 1

The *s-cis* conformation of methyl acetate

Table 1
Geometrical parameters for methyl acetate [10]*

Bond lengths in Å:

$\text{C}_1\text{-C}_2$	1.515
$\text{C}_2\text{-O}_1$	1.200
$\text{C}_2\text{-O}_2$	1.334
$\text{O}_2\text{-C}_3$	1.437
C-H	1.086

Bond angles in degrees:

$\angle \text{C}_1\text{C}_2\text{O}_1$	124.83
$\angle \text{C}_1\text{C}_2\text{O}_2$	110.30
$\angle \text{O}_1\text{C}_2\text{O}_2$	124.87
$\angle \text{C}_2\text{O}_2\text{C}_3$	114.78
$\angle \text{HCH} = \angle \text{HC}_1\text{C}_2 = \angle \text{HC}_3\text{O}_2$	109.47

* Nomenclature as in fig. 1.

Table 2
Definition of internal coordinates *

Skeleton:	CH ₃ -C:
$r_1 = \Delta(C_1C_2)$	$s_1 = \Delta(C_1-H_1)$
$r_2 = \Delta(C_2-O_1)$	$\alpha_1 = \Delta(\angle H_jC_1H_k) \ j, k \neq i$
$r_3 = \Delta(C_2-O_2)$	$\beta_1 = \Delta(\angle H_1C_1C_2)$
$r_4 = \Delta(O_2-C_3)$	$\tau(C_1C_2) = \text{torsion around } C_1C_2$
$\epsilon = \Delta(\angle C_1C_2O_1)$	CH ₃ -O:
$\gamma = \Delta(\angle O_1C_2X_2)$	$s'_1 = \Delta(C_3-H_1)$
$\delta = \Delta(\angle C_1C_2O_2)$	$\alpha'_1 = \Delta(\angle H_jC_3H_k) \ j, k \neq i$
$\omega = \Delta(\angle C_2O_2C_3)$	$\beta'_1 = \Delta(\angle H_1C_3X_2)$
$\tau(C_2O_2) = \text{torsion around } C_2O_2$	$\tau(O_2C_3) = \text{torsion around } O_2C_3$
$\zeta = \text{Out-of-plane of } O_1$	

* Atoms numbering as in fig. 1.

nates we have defined exceed the number of vibrational degrees of freedom ($3N-6=27$) in three. One can separate the redundant coordinates by taking linear combinations of the above mentioned bending coordinates so that three of them correspond to the sums of the bond angle changes around the atom centres where three or more bonds are coincident (these sums are identically zero). Table 3 shows the new set of internal coordinates grouped in a vector array S . In this system of coordinates, all the diagonal and off-diagonal force constants which involve any identically zero S coordinate are not included in the force field as they refer to non-existent coordinates. If any of these zero force constants were transformed back to the initial set of internal coordinates (R), one would obtain linear re-

lationships among the $F_{R_iR_j}$ force constants. Hence, by eliminating the redundant coordinates we no longer need to artificially add those constraints into the force field refinement.

Another remark about the definition of our S coordinates is necessary as we did not use the molecular symmetry group (C_s) and preferred instead the highest local symmetry coordinates consistent with the methyl group (C_{3v} symmetry). While the particular choice of any linear and orthogonal transformation among the basis coordinates is irrelevant as regards to the calculated eigenvalues and to the information contained in the final PED matrix, our seems to be justified as we are mainly fitting vibrational frequencies taken from condensed phases spectra and both methyl groups should be considered, for that purpose, to be axially symmetric around the C-C and O-C bonds. In fact, the barrier to internal rotation of the methyl group in the methoxyl moiety was found to be approximately 1.2 kcal/mole [10,4] and the value for the potential barrier around the C-methyl bond should even be smaller judging by its value in acetic acid (0.5 kcal/mole) [13] from which it should not differ much, anyway. Moreover, the primary objective of this work is to vibrationally analyse the carbon-oxygen skeleton of the molecule rather than to accurately reproduce the observed vibrational frequencies of the entire molecule, let alone the torsional motions occurring at low frequencies [14,15].

Since all the symmetrically identical elements of the

Table 3
Definition of a new set of internal coordinates and their approximate description (*)

Skeleton		CH ₃ —C		CH ₃ —O	
S ₁ =r ₁	s	S ₈ =(1/√3)(s ₁ +s ₂ +s ₃)	ss	S ₁₆ =(1/√3)(s ₁ ¹ +s ₂ ¹ +s ₃ ¹)	ss
S ₂ =r ₂	s	S ₉ =(1/√6)(2s ₁ -s ₂ -s ₃)	as	S ₁₇ =(1/√6)(2s ₁ ¹ -s ₂ ¹ -s ₃ ¹)	as
S ₃ =r ₃	s	S ₁₀ =(1/√2)(s ₂ -s ₃)	as	S ₁₈ =(1/√2)(s ₂ ¹ -s ₃ ¹)	as
S ₄ =r ₄	s	S ₁₁ =(1/√6)(α ₁ +α ₂ +α ₃ -β ₁ -β ₂ -β ₃)	sb	S ₁₉ =(1/√6)(α ₁ ¹ +α ₂ ¹ +α ₃ ¹ -β ₁ ¹ -β ₂ ¹ -β ₃ ¹)	sb
S ₅ =(1/√6)(2γ-ε-δ)	b	S ₁₂ =(1/√6)(2α ₁ -α ₂ -α ₃)	ab	S ₂₀ =(1/√6)(2α ₁ ¹ -α ₂ ¹ -α ₃ ¹)	ab
S ₆ =(1/√2)(δ-ε)	b	S ₁₃ =(1/√6)(2β ₁ -β ₂ -β ₃)	r	S ₂₁ =(1/√6)(2β ₁ ¹ -β ₂ ¹ -β ₃ ¹)	r
S ₇ =ω	b	S ₁₄ =(1/√2)(α ₂ -α ₃)	ab	S ₂₂ =(1/√2)(α ₂ ¹ -α ₃ ¹)	ab
S ₂₅ =τ(C ₂ O ₂)	t	S ₁₅ =(1/√2)(β ₂ -β ₃)	r	S ₂₃ =(1/√2)(β ₂ ¹ -β ₃ ¹)	r
S ₂₇ =ξ	ω	S ₂₄ =τ(C ₁ C ₂)	t	S ₂₆ =τ(O ₂ C ₃)	t

(*) s = stretch; b = bend; t = torsion; w = wag; r = rock; whenever two letters are used the first stands for «symmetric» (s) or «antisymmetric» (a). As the numbering of the coordinates is arbitrary, we follow the sequence set up for the computer calculation where the torsion and the out-of-plane coordinates were numbered last. However, for the purpose of this calculation, the skeletal and methyl coordinates are herein grouped under different headings.

F matrix must be changed in the same manner during the refinement, it is convenient to store the force field as a linear array of force constants ϕ and build the F matrix from the elements of ϕ by means of matrices Z , according to

$$F = \sum_i \phi_i Z^i,$$

where ϕ_i is the i th element of ϕ and Z^i is the i th Z matrix which specifies the positions of the element ϕ_i in the final F matrix [16]. Besides all the off-diagonal elements relative to the in-plane coordinates of the carbon-oxygen skeleton, we have also included the off-diagonal interactions $F_{S_1S_{11}}$ and $F_{S_4S_{19}}$. This corresponds to having ignored in [8] the off-diagonal interactions which are not consistent with the hypothesis of free internal rotations of the methyl groups. The simplicity of our force field as regards to the alkyl groups and, in particular, to the interaction elements coupling the ester and alkyl groups should not significantly affect the conclusions withdrawn for the ester group vibrations.

Table 4
Calculated valence force constants for methyl acetate

Diagonal force constants Skeleton		Off-diagonal force constants Skeleton-skeleton interactions	
(1,1)	4.0060	(1,2)	0.3875
(2,2)	11.5364	(1,3)	0.4140
(3,3)	6.2762	(1,4)	0.2137
(4,4)	5.4504	(1,5)	-0.4341
(5,5)	1.1682	(1,6)	-0.0878
(6,6)	1.0027	(1,7)	0.2183
(7,7)	0.6185	(2,3)	0.4840
(25,25)	0.6236	(2,4)	-0.0312
(27,27)	0.3589	(2,5)	0.2253
	CH ₃ -C	(2,6)	-0.3498
		(2,7)	-0.1819
(8,8)	4.9781	(3,4)	0.3885
(9,9) = (10,10)	4.7804	(3,5)	0.2859
(11,11)	0.5450	(3,6)	0.1701
(12,12) = (14,14)	0.5092	(3,7)	-0.1472
(13,13) = (15,15)	0.6727	(4,5)	-0.2461
(24,24)	0.0716	(4,6)	0.0816
		(4,7)	0.2254
	CH ₃ -O	(5,6)	0.1444
(16,16)	5.0447	(5,7)	0.0375
(17,17) = (18,18)	4.9088	(6,7)	0.1370
(19,19)	0.5690		
(20,20) = (22,22)	0.4577	Skeleton-methyl interactions	
(21,21) = (23,23)	1.1013	(1,11)	-0.1729
(26,26)	0.0029	(4,19)	-0.1667

Table 5
Observed and calculated frequencies (cm⁻¹) and approximate potential energy distribution for CH₃COOCH₃ (*)

ν_{obs} [4]	ν_{cal}	Potential energy distribution
3040	3040	S ₁₇ (73), S ₁₈ (26)
—	3040	S ₁₇ (26), S ₁₈ (73)
3000	3000	S ₉ (99)
—	2999	S ₁₀ (99)
2961	2961	S ₁₆ (100)
2940	2940	S ₈ (100)
1771	1771	S ₂ (83), S ₃ (15)
1467	1481	S ₂₃ (44), S ₂₀ (36), S ₂₁ (15)
1459	1471	S ₂₁ (43), S ₂₂ (42), S ₂₃ (14)
1446	1456	S ₁₂ (66), S ₁₄ (22)
1439	1439	S ₁₉ (89), S ₄ (19)
1439	1431	S ₁₄ (69), S ₁₂ (23)
1378	1378	S ₁₁ (98)
1275	1277	S ₂₀ (35), S ₃ (34), S ₁ (10)
1246	1220	S ₂₂ (57), S ₂₁ (30), S ₂₃ (10)
1194	1185	S ₂₀ (28), S ₂₃ (22), S ₃ (18), S ₅ (13), S ₁ (12)
1058	1058	S ₄ (65), S ₁₃ (17)
1058	1057	S ₁₅ (86)
976	978	S ₁₃ (60), S ₄ (13), S ₁ (10)
842	840	S ₁ (50), S ₃ (14), S ₅ (18)
634	633	S ₅ (51), S ₁ (14)
525	529	S ₂₇ (77), S ₂₅ (12)
427	427	S ₆ (66)
295	317	S ₂₅ (82), S ₂₇ (11)
203	202	S ₇ (86), S ₆ (18), S ₅ (11) b)
—	189	S ₂₄ (86)
40 a)	40	S ₂₆ (100)

(*) PED contributions less than 10% were ignored.

a) From [15].

b) The off-diagonal element S₆S₇ has a large negative contribution (-14%).

The calculated valence force constants are reported in Table 4 and the observed and calculated frequencies and their potential energy distribution for CH₃COOCH₃ are shown in Table 5. The conclusions from the potential energy distribution are summarised in the assignments given in Table 6 for the skeletal modes of all the isotopic labelled species. Comparison of the results reported in [5] with those of Table 5 reveals the importance of including the methyl vibrational modes for the study of the skeletal modes. In fact, there is an appreciable distribution of potential energy among the methyl and skeletal modes in a large number of vibrations despite the fact that the force constants of the methyl groups are restricted to diagonal elements with only two off-diagonal elements

Table 6
Calculated frequencies (cm^{-1}) and vibrational assignments for the skeletal modes
of $\text{CH}_3\text{COOCH}_3$ and its deuterated species

$\text{CH}_3\text{COOCH}_3$	$\text{CH}_3\text{COOCD}_3$	$\text{CD}_3\text{COOCH}_3$	$\text{CD}_3\text{COOCD}_3$	
1771	1770	1767	1766	C=O stretching
1277	1276	1276	1274	C-O stretching
1058	— a)	1040	— a)	O-CH ₃ stretching
840	809	805	791	C-C stretching
633	624	588	582	O=C-O bend
529	528	486	486	C=O out-of-plane wag
427	416	396	385	CH ₃ -C in-plane wag
317	293	309	285	Torsion around C-O
202	189	198	182	C-O-C bend
189	186	138	138	Torsion around C-C
40	30	40	29	Torsion around O-CH ₃

a) For these isotopic species a strong mixture of O-CH₃ stretching and umbrella motion (> 40%) raises these frequencies to 1225 cm^{-1} ($\text{CH}_3\text{COOCD}_3$) and 1223 cm^{-1} ($\text{CD}_3\text{COOCD}_3$).

coupling the skeleton and methyl vibrational coordinates. The assignments of Table 5 and 6 agree in general terms with those of Table 5 in [4], in particular for the skeletal modes which have a large number of force constants. However, it should be mentioned that the assignments of the CH₃-C and CH₃-O stretching in [4] should be interchanged as they do not agree either with the intensity features described in the text and shown in Tables 1-4 of the same paper or with the assignments reported in [3] and [6]. Taking this correction into consideration then the assignments shown in Table 6 show general agreement with those of [4] with the exception of the calculated frequency at 1277 cm^{-1} which deviates markedly from the observed value at 1246 cm^{-1} empirically assigned to the C-O stretching mode [3,4, 6]. Among the skeletal deformation modes, the observed bands at 295 cm^{-1} and 203 cm^{-1} [4] have been assigned to the torsion around the C-O bond and the C-O-C bend, respectively, although these assignments may still have some degree of uncertainty.

Having restricted this calculation to the methyl acetate molecule with a reduced number of interaction constants compatible with a good fit of the vibrational fundamental frequencies, the resulting force field cannot claim uniqueness, thus losing, to some extent, the feature of transferability among chemical related compounds. While this aspect of a force field calculation is not decisive on its quality, it is useful on the descriptive and chemical point of view and has been recently considered in [17] for a

series of molecules containing C=O groups, including pyruvic acid, acetone, acetic acid, methyl acetate, formic acid and methyl formate.

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RESUMO

Cálculo de constantes de força e análise vibracional do acetato de metilo.

Os ésteres carboxílicos apresentam um certo número de dificuldades no cálculo das suas constantes de força devido ao facto do número de dados experimentais (frequências fundamentais) ser geralmente insuficiente para determinar completamente as constantes de força a calcular. Estas incluem um grande número de interações importantes dado que os modos vibracionais estão fortemente deslocalizados no grupo éster. Este trabalho surge em virtude de apenas existir reduzida informação quantitativa relativa aos modos vibracionais dos ésteres carboxílicos e descreve uma optimização de constantes de força e um cálculo de coordenadas normais para a molécula de acetato de metilo partindo das frequências previamente publicadas.