

DIPOLE DERIVATIVES AND INFRARED INTENSITIES OF THE ESTER GROUP. AN AB INITIO AND FORCE FIELD STUDY OF METHYL ACETATE

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ABSTRACT

Dipole derivatives have been obtained (using both 3-21G and 6-31G basis sets) for methyl acetate. Using a force field refined from experimental data on methyl acetate and its deuterated derivatives, infrared intensities have been calculated. The good frequency and intensity agreement indicate that these force constants and dipole derivatives can serve as satisfactory transferable parameters for the ester group.

INTRODUCTION

Dipole derivatives provide important insights into interactions between similar groups on adjacent molecules, which determine band splittings in vibrational spectra, and permit calculation of infrared (IR) intensities, which can serve as an independent test of force fields. Such ab initio derivatives for the peptide group [1, 2] have validated the proposal that transition dipole coupling accounts for amide mode band splittings in spectra of polypeptides [3, 4], and the corresponding IR intensities have provided support for our empirically refined force field for polyglycine I [2].

This paper presents dipole derivatives and IR intensities for the ester group. We have used methyl acetate (MA) as a model, and have tried to derive a set of transferable parameters that will yield reliable frequencies and IR intensities for this group. In the process, we have refined an alternative intramolecular valence force field for this molecule. The transferability of the force field and group moment derivatives will be tested in future work on poly(methyl methacrylate) and polydepsipeptides.

Infrared and Raman spectra have been reported for MA [5, 6] and its deu-

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terated derivatives [6], and tentative band assignments have been given. Force field refinements for MA have been done in a methyl-group point-mass approximation [7], as part of a transferable force field for a series of molecules containing C=O groups [8], and on the individual molecule [9]. Our force field refinement was based only on experimental vibrational data for MA and its deuterated derivatives. The analysis of IR band intensities followed previous procedures [2], calculating *ab initio* dipole moment derivatives with respect to local symmetry coordinates. Intensities were determined using both our own and the Hollenstein and Günthard [8] force fields. Comparison of the results with experiments shows that the observed IR intensities can be very well reproduced.

CALCULATIONS

In the normal mode and *ab initio* calculations, we used the equilibrium geometrical structure of the MA molecule obtained by a Hartree-Fock optimization with the 4-21G basis set [10]. The local symmetry internal coordinates \tilde{S} , constructed from the internal coordinates defined in the standard way, are listed in Table 1 with the numbering of atoms shown in Fig. 1. The out-of-plane angle bends, $\Delta\omega$, and the torsions, $\Delta\tau$, are defined as before [11]. The vibrational band frequencies of $\text{CH}_3\text{COOCH}_3$, $\text{CH}_3\text{COOCD}_3$, $\text{CD}_3\text{COOCH}_3$, and $\text{CD}_3\text{COOCD}_3$ [6] were used in the refinement of the intramolecular valence force field. Since the force field is intended to be transferred to polymers, it was refined with respect to band frequencies measured in the spectra of MA in the condensed phase.

A combined valence force field of acetic acid [12] and of methyl formate [13] was used to derive an initial set of MA force constants. The refinement was started with a diagonal force field, since we wished to keep the number of parameters of the force field to a minimum. The most relevant interaction force constants were included in the force field in the next steps of the refinement, but in such a way that the least-squares method could be applied to the entire force field in one run. Calculations showed that some changes in the proposed band assignments [6] were necessary, most of the alterations having already been proposed [8]. The fit between observed and calculated frequencies was improved iteratively until the sum of the squared residuals became stationary.

Dipole moments of MA were calculated by the *ab initio* Hartree-Fock method. We used a version of the Gaussian 76 program system [14] that was modified to run on a VAX computer [2]. The dipole moments were computed using both the 3-21G and the 6-31G basis sets. The dipole moment derivatives, $\partial\vec{\mu}/\partial S_i$, with respect to the local symmetry coordinates \tilde{S} were evaluated by numerical differentiation. Bonds were distorted by ± 0.01 Å and angles by ± 0.025 rad.

TABLE 1

Local symmetry coordinates of methyl acetate

Species	Symmetry coordinate	Description
A'	$S_1 = \Delta(2r_{49} - r_{4,10} - r_{4,11})/\sqrt{6}$	(C)CH ₃ as
	$S_2 = \Delta(2r_{56} - r_{58} - r_{57})/\sqrt{6}$	(O)CH ₃ as
	$S_3 = \Delta(r_{56} + r_{57} + r_{58})/\sqrt{3}$	(O)CH ₃ ss
	$S_4 = \Delta(r_{49} + r_{4,10} + r_{4,11})/\sqrt{3}$	(C)CH ₃ ss
	$S_5 = \Delta r_{23}$	C=O s
	$S_6 = \Delta(2\alpha_{758} - \alpha_{658} - \alpha_{657})/\sqrt{6}$	(O)CH ₃ ab
	$S_7 = \Delta(2\alpha_{10,4,11} - \alpha_{94,11} - \alpha_{94,10})/\sqrt{6}$	(C)CH ₃ ab
	$S_8 = \Delta(\alpha_{657} + \alpha_{658} + \alpha_{758} - \alpha_{156} - \alpha_{157} - \alpha_{158})/\sqrt{6}$	(O)CH ₃ sb
	$S_9 = \Delta(\alpha_{94,10} + \alpha_{94,11} + \alpha_{10,4,11} - \alpha_{249} - \alpha_{24,10} - \alpha_{24,11})/\sqrt{6}$	(C)CH ₃ sb
	$S_{10} = \Delta r_{12}$	C ₂ -O s
	$S_{11} = \Delta(2\alpha_{156} - \alpha_{157} - \alpha_{158})/\sqrt{6}$	(O)CH ₃ ip rock
	$S_{12} = \Delta r_{24}$	CC s
	$S_{13} = \Delta(2\alpha_{249} - \alpha_{24,10} - \alpha_{24,11})/\sqrt{6}$	(C)CH ₃ ip rock
	$S_{14} = \Delta r_{15}$	O-C s
	$S_{15} = \Delta(\alpha_{324} - \alpha_{123})/\sqrt{2}$	C=O ib
	$S_{16} = \Delta(2\alpha_{124} - \alpha_{324} - \alpha_{123})/\sqrt{6}$	OCC d
	$S_{17} = \Delta\alpha_{215}$	COC d
A''	$S_{18} = \Delta(r_{4,10} - r_{4,11})/\sqrt{2}$	(C)CH ₃ as
	$S_{19} = \Delta(r_{57} - r_{58})/\sqrt{2}$	(O)CH ₃ as
	$S_{20} = \Delta(\alpha_{658} - \alpha_{657})/\sqrt{2}$	(O)CH ₃ ab
	$S_{21} = \Delta(\alpha_{94,11} - \alpha_{94,10})/\sqrt{2}$	(C)CH ₃ ab
	$S_{22} = \Delta(\alpha_{157} - \alpha_{158})/\sqrt{2}$	(O)CH ₃ op rock
	$S_{23} = \Delta(\alpha_{24,10} - \alpha_{24,11})/\sqrt{2}$	(C)CH ₃ op rock
	$S_{24} = \Delta\omega$	C=O ob
	$S_{25} = \Delta(\tau_{3215} + \tau_{4215})/\sqrt{2}$	C ₂ -O tor
	$S_{26} = \Delta(\tau_{2156} + \tau_{2157} + \tau_{2158})/\sqrt{3}$	O-C tor
	$S_{27} = \Delta(\tau_{1249} + \tau_{124,10} + \tau_{124,11} + \tau_{3249} + \tau_{324,10} + \tau_{324,11})/\sqrt{6}$	CC tor

^as = stretch, as = antisymmetric stretch, ss = symmetric stretch, ab = antisymmetric bend, sb = symmetric bend, ib = in-plane bend, ob = out-of-plane bend, op = out-of-plane, d = deformation, tor = torsion.

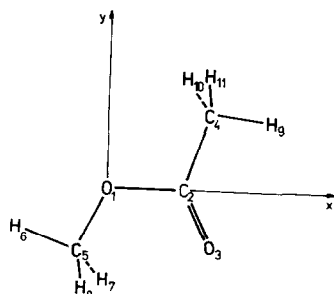


Fig. 1. Methyl acetate molecule, with coordinate system and atom numbering.

Cartesian displacements corresponding to each internal coordinate distortion were obtained from $\vec{X} = \mathbf{M}^{-1}\mathbf{B}(\mathbf{B}\mathbf{M}^{-1})^{-1}\vec{S}$, where \mathbf{M} is the matrix of atomic masses and $\vec{S} = \mathbf{B}\vec{X}$. The transformation of the dipole moment derivatives into the normal coordinate basis \vec{Q} was performed using the relation

$$\frac{\partial \vec{\mu}}{\partial Q_\alpha} = \sum_i \mathbf{L}_{i\alpha} \frac{\partial \vec{\mu}}{\partial S_i} \quad (1)$$

The eigenvector matrix \mathbf{L} , defined by $\vec{S} = \mathbf{L}\vec{Q}$, was obtained from the normal mode calculations. The integrated infrared intensity of the α th mode is then given by

$$A_\alpha = \frac{N\pi}{3c^2} \left(\frac{\partial \vec{\mu}}{\partial Q_\alpha} \right)^2 \quad (2)$$

where N is Avogadro's number and c is the velocity of light.

RESULTS AND DISCUSSION

Our final set of valence force constants for MA is given in Table 2. The force field was refined in the non-redundant local symmetry coordinates of Table 1.

TABLE 2

Valence force constants for methyl acetate^a

No.	Coordinates	Value	No.	Coordinates	Value
1	1,1	4.852(0.029)	19	19,19	4.789(0.029)
2	2,2	4.859(0.029)	20	20,20	0.518(0.006)
3	3,3	5.050(0.029)	21	21,21	0.517(0.006)
4	4,4	5.009(0.029)	22	22,22	0.835(0.012)
5	5,5	11.009(0.109)	23	23,23	0.567(0.026)
6	6,6	0.485(0.007)	24	24,24	0.734(0.038)
7	7,7	0.507(0.007)	25	25,25	0.210(0.023)
8	8,8	0.661(0.009)	26	26,26	0.032
9	9,9	0.563(0.009)	27	27,27	0.024
10	10,10	5.031(0.223)	28	5,10	0.971(0.055)
11	11,11	0.868(0.021)	29	5,12	0.971
12	12,12	4.046(0.176)	30	8,14	-0.639(0.050)
13	13,13	0.685(0.019)	31	9,12	-0.537(0.022)
14	14,14	5.062(0.132)	32	9,16	-0.162(0.042)
15	15,15	1.259(0.042)	33	10,14	0.731(0.222)
16	16,16	1.129	34	10,15	-0.219(0.023)
17	17,17	1.729(0.133)	35	12,15	0.219
18	18,18	4.785(0.029)	36	23,24	-0.112(0.014)

^aNumbers in parentheses are dispersions for refined force constants.

TABLE 3

Observed and calculated frequencies (in cm^{-1}) of methyl acetate

	Obs.	Calc.	No.	Potential energy distribution ^a
<i>CH₃COOCH₃</i>				
A'	3028	3030	1	(O)CH ₃ as(99)
	3028	3023	2	(C)CH ₃ as(99)
	2955	2956	3	(O)CH ₃ ss(100)
	2940	2947	4	(C)CH ₃ ss(100)
	1747	1747	5	C=O s(83), OCC d(10)
	1455	1458	6	(O)CH ₃ ab(75), (O)CH ₃ r(23)
	1438	1440	7	(C)CH ₃ ab(88)
	1438	1433	8	(O)CH ₃ sb(99)
	1372	1374	9	(C)CH ₃ sb(68)
	1249	1251	10	(C)CH ₃ sb(31), CC s(25), C ₂ -O s(23), C=O ib(19)
	1190	1195	11	(O)CH ₃ r(56), (O)CH ₃ ab(18), COC d(11)
	1051	1054	12	O-C s(66), (C)CH ₃ r(18)
	982	998	13	(C)CH ₃ r(56), O-C s(20), CC s(13)
	846	852	14	C ₂ -O s(37), CC s(22), COC d(10)
	638	633	15	C=O ib(43), CC s(34), COC d(10)
	433	434	16	OCC d(46), COC d(14), C ₂ -O s(13), C=O ib(12)
	302	299	17	COC d(47), OCC d(39), C=O ib(10)
A''	3002	3001	18	(O)CH ₃ as(99)
	3002	3000	19	(C)CH ₃ as(99)
	1462	1467	20	(O)CH ₃ ab(88), (O)CH ₃ r(12)
	1445	1444	21	(C)CH ₃ ab(94)
	1161	1163	22	(O)CH ₃ r(85), (O)CH ₃ ab(11)
	1051	1060	23	(C)CH ₃ r(64), C=O ob(17)
	609	615	24	C=O ob(66), (C)CH ₃ r(26)
	203	211	25	C ₂ -O tor(80), O-C tor(10)
	-	131	26	O-C tor(85), C ₂ -O tor(12)
	-	116	27	CC tor(96)
<i>CH₃COOCD₃</i>				
A'	3023	3023		(C)CH ₃ as(99)
	2950	2947		(C)CH ₃ ss(100)
	2259	2267		(O)CD ₃ as(97)
	2085	2124		(O)CD ₃ ss(98)
	1746	1745		C=O s(83), OCC d(10)
	1438	1438		(C)CH ₃ ab(90)
	1372	1377		(C)CH ₃ sb(65), C ₂ -O s(12), C=O ib(10)
	1265	1259		(C)CH ₃ sb(33), CC s(24), C ₂ -O s(23), C=O ib(18)
	1093	1096		O-C s(44), (O)CD ₃ sb(43)
	1065	1061		(O)CD ₃ sb(65), (O)CD ₃ r(13)
	1038	1039		(O)CD ₃ ab(69), (O)CD ₃ r(19)
	1017	1008		(C)CH ₃ r(73), C ₂ -O s(10)
	957	956		O-C s(42), CC s(21), (O)CD ₃ r(15)
	778	778		(O)CD ₃ r(37), C ₂ -O s(24), CC s(20)
	616	617		C=O ib(46), CC s(26)
	419	422		OCC d(50), C ₂ -O s(12), CC s(12), COC d(12)
	278	277		COC d(51), OCC d(33), C=O ib(10)

TABLE 3 (continued)

	Obs.	Calc.	No.	Potential energy distribution ^a
A''	2992	3000		(C)CH ₃ as(99)
	2277	2238		(O)CD ₃ as(98)
	1446	1444		(C)CH ₃ ab(94)
	1065	1064		(C)CH ₃ r(62), C=O ob(18)
	1055	1051		(O)CD ₃ ab(93)
	900	900		(O)CD ₃ r(90)
	605	611		C=O ab(68), (C)CH ₃ r(27)
	200	196		C ₂ -O tor(82)
	-	117		CC tor(96)
	-	95		O-C tor(90)
<i>CD₃COOCH₃</i>				
A'	3030	3030		(O)CH ₃ as(99)
	2956	2956		(O)CH ₃ ss(100)
	2250	2259		(C)CD ₃ as(97)
	2119	2119		(C)CD ₃ ss(99)
	1742	1741		C=O s(84)
	1453	1458		(O)CH ₃ ab(76), (O)CH ₃ r(23)
	1435	1434		(O)CH ₃ sb(100)
	1263	1276		C ₂ -O s(41), C=O ib(30), CC s(22)
	1190	1195		(O)CH ₃ r(52), (O)CH ₃ ab(16), COC d(11)
	1080	1066		O-C s(53), (C)CD ₃ sb(19), (O)CH ₃ r(11)
	1032	1033		(C)CD ₃ ab(84), O-C s(10)
	995	997		(C)CD ₃ sb(62), CC s(19), O-C s(17)
	864	847		C ₂ -O s(20), CC s(14), (C)CD ₃ r(10)
	780	781		(C)CD ₃ r(66), C ₂ -O s(18)
596	594		C=O ib(36), CC s(35)	
401	411		OCC d(34), COC d(20), C=O ib(17), C ₂ -O s(13)	
290	289		OCC d(47), COC d(41)	
A''	2998	3001		(O)CH ₃ as(99)
	2250	2238		(C)CD ₃ as(98)
	1460	1467		(O)CH ₃ ab(88), (O)CH ₃ r(12)
	1158	1162		(O)CH ₃ r(86), (O)CH ₃ ab(11)
	1032	1039		(C)CD ₃ ab(96)
	918	920		(C)CD ₃ r(43), C=O ob(39)
	529	532		(C)CD ₃ r(46), C=O ob(45)
	208	204		C ₂ -O tor(76), O-C tor(11)
	-	130		O-C tor(87), C ₂ -O tor(13)
	-	85		CC tor(99)
<i>CD₃COOCD₃</i>				
A'	2258	2267		(O)CD ₃ as(97)
	2258	2259		(C)CD ₃ as(96)
	2125	2124		(O)CD ₃ ss(98)
	2125	2119		(C)CD ₃ ss(99)
	1738	1740		C=O s(84)
	1283	1286		C ₂ -O s(43), C=O ib(31), CC s(24)

TABLE 3 (continued)

Obs.	Calc.	No.	Potential energy distribution ^a
1096	1105		O-C s(52), (O)CD ₃ sb(21), COC d(11), (O)CD ₃ r(10)
1061	1066		(O)CD ₃ sb(85)
1035	1039		(O)CD ₃ ab(79), (O)CD ₃ r(13)
1035	1032		(C)CD ₃ ab(86)
992	996		(C)CD ₃ sb(87), CC s(16)
968	959		O-C s(42), (O)CD ₃ r(20), CC s(13), (O)CD ₃ ab(10)
829	814		(C)CD ₃ r(47), CC s(11)
745	740		(O)CD ₃ r(29), (C)CD ₃ r(29), C ₂ -O s(28)
586	583		C=O ib(41), CC s(30)
387	397		OCC d(40), COC d(17), C=O ib(12), C ₂ -O s(11)
270	269		COCd(46), OCCd(41)
A''	2270	2239	(O)CD ₃ as(98)
	2270	2238	(C)CD ₃ as(98)
	1053	1052	(O)CD ₃ ab(94)
	1035	1039	(C)CD ₃ ab(96)
	922	936	C=O ob(31), (C)CD ₃ r(27), (O)CD ₃ r(25)
	896	884	(O)CD ₃ r(66), (C)CD ₃ r(16)
	527	529	(C)CD ₃ r(46), C=O ob(46)
	200	188	C ₂ -O tor(80)
	-	97	O-C tor(80), CC tor(10)
	-	83	CC tor(89), O-C tor(11)

^aPotential energy distribution, diagonal elements $\geq 10\%$. Abbreviations: s = stretch, as = anti-symmetric stretch, ss = symmetric stretch, ab = antisymmetric bend, sb = symmetric bend, ib = in-plane bend, ob = out-of-plane bend, d = deformation, r = rock, tor = torsion.

The force constants for methyl torsions (O-CH₃ and C-CH₃) were kept fixed at the values transferred from methyl formate [13] and acetic acid [12], because corresponding bands were not observed in the spectra of MA [5, 6]. Force constant No. 16 (OCC deformation) was not refined from its initial value, because it showed very large uncertainties in the course of least-squares fitting of the calculated frequencies. For the same reason, only one parameter was used for the pairs of correlated force constants 28, 29 and 34, 35 in the refinement of the force field. Since the CD₃ stretching region (2100–2300 cm⁻¹) is very complex in the recorded spectra of MA [6] (due to effects such as Fermi resonance), the methyl stretch force constants were fitted only to the band frequencies corresponding to the vibrations of the undeuterated methyl groups.

As can be seen from Table 3, most of the discrepancies between the observed and calculated frequencies are less than 10 cm⁻¹ for all four isotopic species. Several larger differences probably arise from the anharmonicities not included in the calculations. The normal mode calculations indicate that the bands in the 2250–2260 cm⁻¹ region correspond to the CD₃ antisymmetric stretch modes in the A' block (modes Nos. 1 and 2). Changes in the assignments given in [6] are proposed also for some bands in the 900–1100 cm⁻¹ region of the spectra of CH₃COOCD₃ and CD₃COOCD₃ (see Table 3).

Dipole moment derivatives, $\partial \vec{\mu} / \partial S_i$, were calculated using the 3-21G and 6-

TABLE 4

Dipole moment derivatives (in D/A or D/rad) of methyl acetate (6-31G basis)

Coordinate ^a	$\frac{\partial \mu_x}{\partial S_i}$	$\frac{\partial \mu_y}{\partial S_i}$	$\frac{\partial \mu_z}{\partial S_i}$	$\left \frac{\partial \vec{\mu}}{\partial S_i} \right $	θ^b
(C)CH ₃ as	-0.449	0.049	0.0	0.452	-6.2
(O)CH ₃ as	0.400	0.225	0.0	0.459	29.3
(O)CH ₃ ss	0.468	-0.433	0.0	0.637	-42.8
(C)CH ₃ ss	-0.116	0.283	0.0	0.306	-67.8
C=O s	-4.030	-4.275	0.0	5.875	46.7
(O)CH ₃ ab	-0.348	-0.111	0.0	0.365	17.7
(C)CH ₃ ab	0.412	0.221	0.0	0.467	28.2
(O)CH ₃ sb	-0.140	-0.126	0.0	0.189	41.8
(C)CH ₃ sb	-0.150	0.457	0.0	0.481	-71.8
C ₂ -O s	5.110	-0.765	0.0	5.167	-8.5
(O)CH ₃ ip rock	0.036	0.144	0.0	0.148	76.0
CC s	0.000	0.165	0.0	0.165	90.0
(C)CH ₃ ip rock	-0.261	0.049	0.0	0.266	-10.6
O-C s	-2.260	3.145	0.0	3.873	-54.3
C=O ib	2.486	-2.059	0.0	3.228	-39.6
OCC d	1.806	-0.340	0.0	1.838	-10.7
COC d	-2.728	-0.292	0.0	2.744	6.1
(C)CH ₃ as	0.0	0.0	-0.350	0.350	
(O)CH ₃ as	0.0	0.0	-0.612	0.612	
(O)CH ₃ ab	0.0	0.0	0.379	0.379	
(C)CH ₃ ab	0.0	0.0	0.438	0.438	
(O)CH ₃ op rock	0.0	0.0	-0.017	0.017	
(C)CH ₃ op rock	0.0	0.0	-0.181	0.181	
C=O ob	0.0	0.0	0.460	0.460	
C ₂ -O tor	0.0	0.0	-2.040	2.040	
O-C tor	0.0	0.0	0.008	0.008	
CC tor	0.0	0.0	-0.044	0.044	

^as = stretch, as = antisymmetric stretch, ss = symmetric stretch, ab = antisymmetric bend, sb = symmetric bend, ib = in-plane bend, ob = out-of-plane bend, op = out-of-plane, d = deformation, tor = torsion.

^b $\tan \theta = (\partial \mu_y / \partial S_i) / (\partial \mu_x / \partial S_i)$.

31G basis sets; the 6-31G values are given in Table 4. Both sets of ab initio derivatives were used in the calculations of the IR band intensities. The eigenvector matrix **L** in (1) was obtained from normal mode calculations using two different force fields: the force field from [8] (Set I) and the force field refined in this paper (Set II). Calculated IR band intensities are listed in Table 5 together with the experimental values. The absolute value of the IR intensity of the C=O stretch normal mode (No. 5) was taken from ref. 15. The relative IR intensities of the other modes listed in Table 5 were determined by numerical integration of the band areas in the spectrum of liquid CH₃COOCH₃ (the

TABLE 5

Comparison of experimental and calculated IR band intensities of methyl acetate

Mode No.	IR intensity (km mol^{-1})				
	Experimental	Calculated			
		Force field I ^a		Force field II ^b	
		3-21G	6-31G	3-21G	6-31G
1,2 ^c	18.0	23.1	25.9	19.8	19.9
3	35.8	23.7	25.0	28.1	30.5
4	4.6	0.1	1.5	0.6	2.3
5	281.3	236.0	279.9	248.7	311.7
6,7,8,20,21 ^d	97.6	55.1	63.0	67.6	76.3
9	69.9	111.4	93.0	51.6	53.8
10	355.8	325.5	323.4	430.3	405.9
11	<3.0	0.5	0.7	1.5	2.4
12,23 ^c	112.3	85.4	76.2	62.8	69.2
13	7.6	40.8	47.5	2.6	5.8
14	38.2	31.5	36.1	33.7	38.3
15	10.4	6.6	6.6	7.5	8.1
18,19 ^c	27.4	26.5	26.2	26.7	26.3
22	<3.0	1.6	2.5	1.7	2.5
24	17.6	11.9	14.8	14.8	18.4

^aForce field from ref. 8. ^bForce field from Table 2. ^cTwo overlapping bands in IR spectrum. ^dBands corresponding to methyl bend modes except (C)CH₃ sb.

spectrum was measured on a Bomem DA3 FTIR spectrometer). Relative intensities were then normalized with respect to the published carbonyl band intensity [15]. Overlapping bands in the spectrum were separated by a least-squares procedure using Lorentzian type functions as the band shapes. In cases of close overlap of bands, such that the separation of the bands could not be carried out reliably, the sum of the IR band intensities is given in Table 5. Only upper limits could be determined from the IR spectrum for the intensities of the very weak bands corresponding to normal modes No. 11 and No. 22 ((O)CH₃ in-plane and out-of-plane rock).

It can be seen from Table 5 that there is a good qualitative agreement between the experimental and calculated IR band intensities. This result supports the proposed assignments of the bands. A detailed comparison of the 3-21G and 6-31G results given in Table 5 indicates that the observed band intensities are better reproduced using the dipole derivatives calculated with the 6-31G basis, and this is true for both sets of force constants. In the amide group analysis [2] the best results were obtained using the 3-21G basis set.

Both force field sets I and II give fairly good agreement between observed

and calculated frequencies of MA, with set II being somewhat better for the CH₃ modes. From the point of view of predicted IR intensities (Table 5), the set I force field provides a better prediction of the absolute intensities of the two strongest bands (No. 5, C=O stretch, and No. 10, C₂-O stretch), although not of their ratio, but it is somewhat poorer for the other bands. Its worst predictions, compared to set II, are for the weak bands, such as No. 4, No. 11, and particularly No. 13, (C)CH₃ in-plane rock. These results demonstrate the very strong dependence of band intensities on the eigenvectors, and show that intensities can provide a sensitive test of a force field.

It is concluded that our force field and ab initio dipole derivatives provide a good reproduction of the observed vibrational frequencies and IR intensities of MA, and therefore can serve as satisfactory transferable parameters for the ester group.

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