Force field of acetic acid: use of CNDO/force calculations

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The redundancy-free internal valence force field of monomeric acetic acid is evaluated using CNDO/force calculations and least-squares refinement. The initial force field is set up by taking the interaction and bending force constants from CNDO force field and transferring the stretching force constants from the force fields of chemically related molecules. Vibrational frequencies of monomeric CH_3COOH, CH_3COOD, CD_3COOH, and CD_3COOD are used to refine the force constants. The experimental force field thus obtained is found to be reasonable when compared to the force fields of related molecules as well as on the basis of the frequency fits and potential energy distributions.

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Utilisant des calculs de force/CNDO et des ajustements par la méthode des moindres carrés, on a évalué le champ de force de valence interne sans répétition de l'acide acétique sous forme monomère. On a établi le champ de force initial en prenant l'interaction et les constantes de force de courbure du champ de force CNDO et en transferrant les constantes de force de tension à partir des champs de force de molécules chimiquement apparentées. On a utilisé les préférences de vibration des acides monomères: CH_3COOH, CH_3COOD, CD_3COOH et CD_3COOD pour ajuster les constantes de force. On a trouvé que le champ de force expérimental ainsi obtenu est raisonnable quand lon le compare aux champs de force des molécules apparentées ainsi que sur la base des agréments des fréquences et des distributions d'énergie potentielle.

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Introduction

A number of papers (1–7) deal with the ir and Raman spectroscopic studies of acetic acid monomer and its deuterated derivatives. Considering point mass models, force field calculations were carried out by Thomas (8), and Nakamoto and Kishida (9). Other force field calculations for acetic acid were carried out by Fukushima and Zwolinski (10) using a modified Urey–Bradley force field, and by Brooks and Haas (11), Alfheim and Cyvin (12), and Meyer *et al.* (5) using valence force fields. In the widely used least-squares method of force field refinement, an initial force field matrix ($\mathbf{F}_0$) is set up by transferring the force constants from chemically related molecules, and then refined using experimental data such as vibrational frequencies. The diagonal force constants can reasonably be transferred among chemically related molecules but in the case of interaction force constants, such a transfer is not justified as it very much depends on the geometry of the molecule. In the previous studies (13–17) it is found that the CNDO/force MO calculations predict reasonably well the signs of interaction force constants. The magnitudes of bending as well as stretch–bend and bend–bend interaction force constants are also reasonably estimated by these calculations. The stretch–stretch interaction constants are about 50% higher than the experimental values and the stretching force constants are overestimated by a factor of 2 to 3.5. CNDO/force calculations provide us with a reasonable way of choosing the bending and interaction force constants for the $\mathbf{F}_0$ matrix in order to perform least-squares refinement. It was pointed out by IUPAC (18) that the force constants corresponding to the coordinates expressed by redundancy conditions are indeterminate and recommendations were made that redundancy-free coordinates should be used in order to have meaningful force fields. In the present work, initial force field is set up by taking interaction and bending force constants from CNDO force field and trans-

ferring stretching force constants from the force fields of chemically related molecules from literature. Redundancy-free internal valence force field (RFIVFF) is then calculated by refining this force field using vibrational frequency data on various isotopic species of acetic acid.

Computational details and results

The CNDO/force calculations are carried out using a modified form (15) of Pople's computer program CNINDO (19). The molecular geometry is optimised as described earlier (13, 15) using the steepest descent method. The forces are then calculated by distorting the molecule from the optimised reference geometry in the positive and negative directions of redundancy-free internal coordinates. The distortions considered are 1 pm, 1°, and 2° respectively for stretching, bending, and torsional coordinates. The CNDO force constants are then derived from the forces using the relationships given earlier (15). The redundancy-free internal coordinates[2] are expressed below in terms of the internal coordinates given in Fig. 1. The CNDO/force field is given in Table 1.

In-plane:

1. $\nu_{C=O} = R$
2. $\nu_{C-C} = D$
3. $\nu_s(CH_3) = (1/\sqrt{3})(r_1 + r_2 + r_3)$
4. $\nu'_s(CH_3) = (1/\sqrt{6})(2r_1 - r_2 - r_3)$
5. $\nu_{C-O} = L$
6. $\nu_{O-H} = d$
7. $\delta_{C-C-O} = (1/\sqrt{6})(2\delta_1 - \delta_2 - \delta_3)$
8. $\rho_{C=O} = (1/\sqrt{2})(\delta_2 - \delta_3)$
9. $\delta_s(CH_3) = [3(1 + b^2)]^{-1/2}[b(\alpha_1 + \alpha_2 + \alpha_3) - (\beta_1 + \beta_2 + \beta_3)]$
   $(b = -3 \sin \beta \cos \beta/\sin \alpha)$

[2]The corresponding redundancy coordinates are $(1/\sqrt{3})(\delta_1 + \delta_2 + \delta_3)$ and $[3(1 + b^2)]^{-1/2}[(\alpha_1 + \alpha_2 + \alpha_3) + b(\beta_1 + \beta_2 + \beta_3)]$, where $b = -3\sin \beta \cos \beta/\sin \alpha$.

10. $\delta_s'(CH_3) = (1/\sqrt{6})\,(2\alpha_1 - \alpha_2 - \alpha_3)$
11. $\rho_{\parallel}(CH_3) = (1/\sqrt{6})\,(2\beta_1 - \beta_2 - \beta_3)$
12. $\delta_{C-O-H} = \theta$

Out-of-plane:
13. $\nu_a(CH_3) = (1/\sqrt{2})\,(r_2 - r_3)$
14. $\delta_a(CH_3) = (1/\sqrt{2})\,(\alpha_2 - \alpha_3)$
15. $\rho_{\perp}(CH_3) = (1/\sqrt{2})\,(\beta_2 - \beta_3)$
16. $\gamma_{C=O} = \phi$
17. $\tau(CH_3) = (1/\sqrt{6})\,(\tau_1 + \tau_2 + \tau_3 + \tau_1' + \tau_2' + \tau_3')$
18. $\tau(OH) = (1/\sqrt{2})\,(\tau_4 + \tau_5)$

The initial force field is constructed according to the procedure given above. The stretch–stretch interaction force constants of the CNDO force field are scaled down by a factor of 0.65 (17) before being included in the F_0 matrix. Schachtschneider's FPERT program (20) is used to carry out the refinement after including the damped least-squares subroutines. The force field is refined using absolute weighting factors (21) for the frequency parameters. All the calculations were performed on an IBM 370/155 computer. The vibrational frequencies of CH_3COOH, CH_3COOD, CD_3COOH, and CD_3COOD listed by Meyer *et al.* (5) with the revised assignments for a few bands are employed in the calculations. Since the CH and OH stretching frequencies were not given by Meyer *et al.*, they are taken from ref. 4. The **G** matrices are calculated on the basis of the geometry obtained by Derissen (22) from the electron diffraction data. The bond angles around the methyl C atom are assumed to be 109.47°. Based on C_s symmetry of acetic acid the 18 fundamental modes can be distributed as $12A' + 6A''$ vibrations. Calculations for A' and A'' vibrations were carried out separately. Since the number of independent force constants of acetic acid exceeds the number of available vibrational frequencies, some reasonable constraints on the force field are imposed. For the experimental force fields 38 significant parameters were considered for A' species whereas 9 force constants were considered for A'' species. The force constants are refined using 46 frequencies for A' species and 19 frequencies for A'' species. In the case of A' vibrations, the parameters *F8,9* and *F8,11* corresponding to the interactions $\rho_{C=O}/\delta_s(CH_3)$ and $\rho_{C=O}/\rho_{\parallel}(CH_3)$ respectively are constrained to zero, since the trial calculations carried out indicate negligibly small values for these constants. The force constant *F17,17* corresponding to the methyl group torsional mode is kept fixed at 0.004×10^{-18} N m rad^{-2} based on similar values obtained for acetaldehyde and acetone (17). The experimental force field obtained is also included in Table 1. In Table 2 the calculated and observed frequencies are given along with the potential energy distributions (PED).

Discussion

The force field reported in this work is rather too elaborate and includes all the diagonal and off-diagonal force constants. Meyer *et al.* (5) reported a value of 8.048×10^2 N m^{-1} for the carbonyl stretching force constant ($F_{C=O}$) of acetic acid which is considerably different from the present value (12.692×10^2 N m^{-1}). In a redundancy valence force field obtained by Ha, Meyer, and Gunthard (23) employing the *ab initio* results as the initial force constants and refining the force field using vibrational frequency data, the $F_{C=O}$ of formic acid was found to be 13.05×10^2 N m^{-1}. The estimate of Meyer *et al.* for acetic acid makes a difference of 5×10^2 N m^{-1} between the $F_{C=O}$ values of formic acid and acetic acid. For these two acids, the
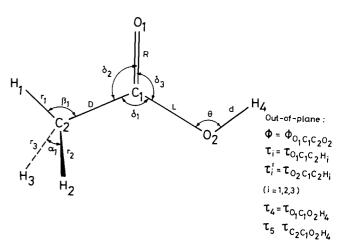

FIG. 1. Internal coordinates of acetic acid.

TABLE 1. Force fields of acetic acid[a]

Force constant	Theoretical CNDO/force	Exp.	Force constant	Theoretical CNDO/force	Exp.
F1,1	30.305	12.692	F 5,12	0.504	0.441
F1,2	1.312	0.778	F 6,6	16.472	7.225
F1,5	2.282	1.327	F 6,7	0.029	—
F1,7	−0.534	−0.533	F 6,8	−0.023	—
F1,8	−0.115	−0.149	F 6,12	0.341	0.201
F1,9	−0.066	−0.182	F 7,7	0.865	1.129
F1,10	0.022	—	F 7,8	0.148	0.087
F1,11	−0.098	−0.067	F 7,10	0.011	—
F1,12	0.075	0.117	F 7,11	0.125	0.001
F2,2	16.058	4.525	F 7,12	0.097	0.295
F2,3	0.566	0.396	F 8,8	1.060	1.085
F2,5	0.896	0.444	F 8,9	−0.047	—
F2,7	0.195	0.350	F 8,11	−0.054	—
F2,8	0.436	0.460	F 9,9	0.720	0.583
F2,9	−0.398	−0.413	F 9,10	−0.015	—
F2,10	−0.034	—	F 9,11	−0.042	−0.073
F2,11	0.099	0.128	F10,10	0.730	0.516
F2,12	0.083	0.076	F10,11	−0.048	—
F3,3	12.273	5.061	F11,11	0.752	0.716
F3,8	0.035	—	F11,12	0.025	—
F3,9	0.179	0.108	F12,12	0.818	0.729
F4,4	11.803	4.955	F13,13	11.771	4.798
F4,7	0.054	—	F13,14	−0.255	−0.014
F4,8	−0.024	—	F13,15	0.281	0.114
F4,10	−0.252	−0.059	F13,16	−0.032	—
F4,11	0.286	0.037	F14,14	0.757	0.533
F5,5	21.742	6.065	F14,15	−0.035	—
F5,6	0.628	0.188	F15,15	0.501	0.522
F5,7	0.086	0.199	F15,16	−0.128	−0.118
F5,8	−0.548	−0.189	F16,16	0.619	0.669
F5,9	−0.051	—	F17,17	0.0003	0.004[b]
F5,11	0.049	—	F18,18	0.0562	0.0805

[a]Units: stretch–stretch, 10^2 N m^{-1} (mdyn Å^{-1}), stretch–bend, 10^{-8} N rad^{-1} (mdyn rad^{-1}), and bend–bend, 10^{-18} N m rad^{-2} (mdyn Å rad^{-2}).
[b]Constrained force constant values.

$F_{C=O}$ values obtained using CNDO/force calculations are found to differ only by about 1.6×10^2 N m^{-1} (24). Hence, it is felt that the value of $F_{C=O}$ reported in the present work for acetic acid is more reasonable. The almost insignificant decrease in $F_{C=O}$ value ($\sim 0.04 \times 10^2$ N m^{-1}) from formic acid to acetic acid due to the substituent CH_3 is parallel to the similar observations made when the $F_{C=O}$ values of formaldehyde,

TABLE 2. Observed and calculated frequencies (in cm^{-1}) and PED for acetic acid[a]

ν				ν			
Obs.	Calcd.	$\Delta\nu$	PED	Obs.	Calcd.	$\Delta\nu$	PED
CH₃COOH				CD₃COOH			
A' 3583	3594	−11	F6,6(100)	A' 3582	3594	−12	F6,6(100)
3051	3047	4	F4,4(100)	2285	2278	7	F4,4(99)
2944	2949	−5	F3,3(101)	2118	2116	2	F3,3(101)
1779	1779	0	F1,1(93)	1774	1777	−3	F1,1(94) F5,5(26) F11,11(15)
1439	1466	−7	F10,10(56) F9,9(17) F11,11(12)	1332	1326	6	F5,5(37) F12,12(28) F8,8(19)
1380	1381	−1	F9,9(48) F10,10(35)				F2,2(13) F5,12(13)
(1280)	1293	−13	F9,9(40) F5,5(27) F2,2(22)	(1182)	1178	4	F12,12(55) F5,5(33) F5,12(−18)
			F12,12(20) F8,8(12) F2,9(−15)	1070	1067	3	F9,9(93) F2,2(28) F2,9(−26)
1181	1194	−13	F12,12(54) F5,5(22) F11,11(11)	1034	1027	7	F10,10(93)
			F5,12(−14)	817	820	−3	F2,2(39)
987	986	1	F11,11(72) F5,5(22)	(774)	774	0	F11,11(66) F2,2(20) F7,7(11)
847	855	−8	F2,2(80) F5,5(13)	563	560	3	F8,8(70)
581	576	5	F8,8(75)	408	399	9	F7,7(92) F12,12(18) F7,12(−26)
428	434	−6	F7,7(100) F12,12(21) F7,12(−30)	A" 2230	2235	−5	F13,13(99)
A" 2996	2996	0	F13,13(100)	1034	1035	−1	F14,14(97)
1434	1431	3	F14,14(95)	919	920	−1	F16,16(41) F15,15(40) F15,16(16)
1044	1047	−3	F15,15(62) F16,16(20) F15,16(19)	610	613	−3	F18,18(82) F15,15(16)
639	648	−9	F18,18(55) F16,16(34) F15,15(20)	479	474	5	F16,16(57) F15,15(46) F18,18(16)
			F15,16(−10)				F15,16(−20)
535	528	7	F16,16(50) F18,18(45) F15,15(18)	—	85	—	F17,17(100)
			F15,16(−11)	CD₃COOD			
—	116	—	F17,17(100)	A' 2642	2626	16	F6,6(100)
CH₃COOD				2275	2277	−2	F4,4(99)
A' 3039	3047	−8	F4,4(100)	2116	2116	0	F3,3(101)
2952	2949	3	F3,3(101)	1766	1766	0	F1,1(98)
2642	2626	16	F6,6(100)	(1282)	1278	4	F5,5(61) F8,8(25) F2,2(24)
1770	1768	2	F1,1(97)				F2,8(−10)
1436	1441	−5	F10,10(65) F9,9(14) F11,11(12)	1073	1068	5	F9,9(93) F2,2(27) F2,9(−25)
1377	1375	2	F9,9(64) F10,10(27)	1035	1033	2	F10,10(80)
1267	1265	2	F5,5(49) F2,2(32) F9,9(28)	1001	988	13	F12,12(55) F10,10(12) F5,5(10)
			F8,8(19) F2,8(−10) F2,9(−15)				F7,12(10) F5,12(−10)
—	1031	—	F11,11(44) F12,12(26)	818	809	9	F11,11(41) F5,5(22) F2,2(20)
956	958	−2	F12,12(35) F5,5(32) F11,11(32)	(747)	750	−3	F11,11(38) F2,2(36) F12,12(17)
			F5,12(−14)	535	536	−1	F8,8(73)
835	826	9	F2,2(72) F12,12(15)	—	386	—	F7,7(96) F12,12(26) F7,12(−33)
545	551	−6	F8,8(78)	A" 2240	2235·	5	F13,13(99)
418	416	2	F7,7(103) F12,12(32) F7,12(−37)	—	1035	—	F14,14(97)
CH₃COOD				919	919	0	F15,15(41) F16,16(41) F15,16(16)
A" 2996	2996	0	F13,13(100)	531	534	−3	F15,15(48) F16,16(39) F18,18(28)
1429	1431	−2	F14,14(95)				F15,16(−17)
1051	1047	4	F15,15(62) F16,16(20) F15,16(14)	409	403	6	F18,18(71) F16,16(23) F15,15(13)
604	608	−4	F16,16(70) F15,15(33) F18,18(14)	—	85	—	F17,17(100)
			F15,16(−19)				
422	417	5	F18,18(86) F16,16(14)				
—	116	—	F17,17(100)				

[a]Values in parentheses are estimated by Meyer et al. (5).

acetaldehyde, and acetone are considered (17). Force constants of C—O and O—H stretching, and COH bending modes of acetic acid are very close to the corresponding force constants of formic acid (23). The C=O/C—O interaction force constant obtained in this work (1.327 × 10² N m^{-1}) is in good agreement with the *ab initio* value reported by Ha *et al.* (23) for formic acid (1.3 × 10² N m^{-1}). The C—O stretching force constant of acetic acid (6.065 × 10² N m^{-1}) is greater than the corresponding force constants of methyl alcohol (5.4 × 10² N m^{-1}) (25) and diethyl ether (5.04 × 10² N m^{-1}) (26). In both the studies (25, 26), the initial force fields were transferred from chemically related molecules and not obtained from MO calculations and whereas the force field obtained for methanol was redundancy free, the force field for ether had redundant force constants. However, a greater C—O stretching force constant in acetic acid in comparison to methyl alcohol and ether, to some extent, may be in order because of π electron delocalisation in acetic acid. This is also reflected in the C=O/C—O interaction force constant which has a very high positive value in the case of acetic acid. The force constants corresponding to the methyl group vibrations do not differ significantly from those obtained for acetaldehyde and acetone in similar calculations (17). The observed frequencies are well reproduced by the calculated force field. The potential energy

distributions in the present work are found to be in general similar to those reported by Meyer *et al.* (5).

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