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Force field calculation for inplane vibrations of ethylene using CNDO/Force method

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Abstract. CNDO/Force method is used to evaluate redundancy-free internal valence force field (RFIVFF) for inplane vibrations of ethylene. The bending force constants, the stretch-bend and bend-bend interaction force constants are predicted reasonably well in magnitude and sign by this method; whereas stretching force constants and stretch-stretch interactions are overestimated. Initial force field is set up by transferring stretching force constants from structurally-related molecules and including the rest of the force constants from CNDO force field. The force field so constructed is subjected to refinement by the least square method. A total of 64 vibrational frequencies of C_2H_4, C_2D_4, $C_2H_2D_2$ and their ^{13}C isotopic modifications are used to determine force field containing 15 parameters. The final force field is found to be reasonable on the basis of frequency fits, potential energy distribution and band assignments.

Keywords. Force field; normal coordinate analysis; ethylene; inplane vibrations; CNDO/Force method.

1. Introduction

Several attempts have been made to study the IR and Raman spectra of ethylene. Duncan *et al* (1972, 1973), Duncan and Hamilton (1981), Lambean *et al* (1980), Hirota *et al* (1981 and the references therein) made an extensive study to determine the structural and other spectroscopic constants. Dewar and Komornicki (1977) carried out MINDO/3 calculations on the force field of ethylene. Bock *et al* (1979) calculated the cubic and quartic force constants by *ab initio* method and then evaluated the theoretical vibrational frequencies of ethylene. Pulay and Meyer (1971) determined the force field of ethylene by FORCE method using SCF MO wave functions. Fletcher and Thomson (1968) carried out the hybrid orbital force field calculations for isotopic ethylenes. Novikov and Malyshev (1981) reported a general valence force field for ethylene, using their program for refinement.

For the determination of the harmonic force field the least square method is generally employed for the refinement of force constants using vibrational frequencies and other spectroscopic data. For a satisfactory refinement the number of force constants to be evaluated should be lesser than the number of vibrational frequencies used. It is a normal practice to include vibrational frequencies of several isotopic species of the molecule. The initial force field is set up by transferring the force constants from structurally-related molecules. The final force field resulting from these calculations often depends on the initial force field and leads to the possibility of more than one solution. In the case of ethylene, for example, two sets of physically realistic force constants, predicting very different normal coordinates have been obtained. One such solution gives C=C stretching force constant in the range of ~11 mdyn Å^{-1}, while the other is in the range of ~9·0 mdyn Å^{-1}. The discrepancy arises because of different initial force fields considered. While it is quite justified to transfer diagonal force constants from chemically-related molecules, transfer of off-diagonal force constant is not reasonable as the sign as well as magnitude of these force constants, very much depend upon the geometry of the molecules considered. It is of course clear that the final force field depends largely on the set of force constants and their signs selected for the initial force field and therefore a reasonable initial set of interaction force constants is very important. Pulay (1969), Kanakavel *et al* (1976) and Annamalai and Singh (1982a, b) have demonstrated that the sign and magnitude of bend-bend and stretch-bend interaction ,constants, as well as bending force constants predicted by CNDO/Force method are reasonable whereas stretching force constants and stretch-stretch interaction constants are overestimated by 2 to 2·5 times and ~ 1·5 times respectively. In the present calculations for ethylene initial force field is set up by transferring diagonal force constants from chemically-related molecules, off diagonal stretch-bend and bend-bend interaction constants from CNDO force field and scaled CNDO/Force values (Annamalai and Singh 1982a) for stretch-stretch interaction force constants. As suggested by IUPAC (1977) redundancy-free internal valence force field is evaluated. Vibrational frequencies of 10 isotopically substituted species are considered for force field refinement.

2. Mode of computation

A semi-empirical gradient method called CNDO/Force method is employed to optimise the geometry. Details of the calculations are given by Kanakavel *et al* (1976) and Annamalai and Singh (1982a,b). The molecular geometry is optimised by the steepest descend method proposed by Pulay and Torok (1973). The forces acting on each atom in a molecule are computed by analytical differentiation of total energy with reference to nuclear coordinates making use of the CNDO wave functions and the initial geometry. All the atoms are moved in the direction of the forces through a small distance, say 0·01 Å and the forces are calculated in the new configuration. They are then allowed to relax towards the equilibrium until the net force on the atoms reaches a preset minimum value. This process is repeated till the consistency in geometry is obtained. A modified form (Kanakavel *et al* 1976) of the original program CNINDO given by Pople and Beveridge (1970) is used.

To evaluate the theoretical force field the cartesian forces for the equilibrium geometry are calculated. The molecule is then deformed by an amount $\pm \triangle R_i$, where R_i is the ith internal coordinate. For different normal modes, the cartesian forces F_i are computed using suitable transformations and then the cartesian forces are transformed into internal forces ϕ_i. The force constants are then calculated using the numerical differentiation of internal forces with reference to internal coordinates given by

$$F_{ij} = - \triangle\phi_i / \triangle R_j,$$

and $$F_{ji} = -\Delta\phi_j/\Delta R_i.$$

The insignificant difference observed in F_{ij} and F_{ji} values is overcome by averaging, thus establishing the symmetry of the force field matrix.

3. Results and discussion

Ethylene belongs to the D_{2h} symmetry and its nine inplane vibrations are distributed as follows. $3A_{1g} + 2B_{1g} + 2B_{2u} + 2B_{3u}$. The 15 force constants for the inplane vibrations are refined using 64 vibrational frequencies. The harmonic frequencies reported by Duncan and Hamilton (1981) for the molecules H_2CCH_2, $H_2C^{13}CH_2$, $H_2^{13}C^{13}C\,H_2$, H_2CCD_2, $H_2C^{13}CD_2$, $H_2^{13}CCD_2$, D_2CCD_2, $D_2C^{13}CD_2$, $D_2^{13}C^{13}CD_2$, $HDCCH_2$ are used for refinements. Schachtschneider's (1964) FPERT program with damped least squares improvement is used to refine the force fields employing the familiar Wilson's FG matrix method. The redundancy-free internal coordinates are given in table 1 and the internal coordinates are shown in figure 1.

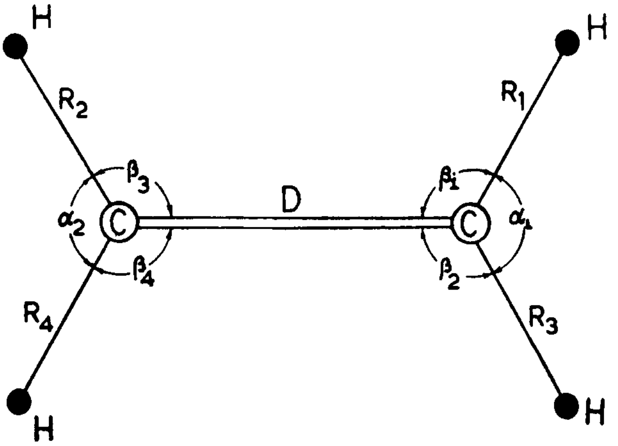

Figure 1. Internal coordinates of ethylene.

Table 1. Redundancy-free internal coordinates of ethylene (inplane)

		Coordinate	Description
1	$\nu_{C=C}$	$= D$	C = C stretch
2	ν_{C-H}	$= R_1$	C − H stretch
3	ν_{C-H}	$= R_2$	,,
4	ν_{C-H}	$= R_3$	,,
5	ν_{C-H}	$= R_4$	,,
6	δ_{HCH}	$= 6^{-1/2}(2\alpha_1 - \beta_1 - \beta_2)$	HCH deformation
7	δ_{HCH}	$= 6^{-1/2}(2\alpha_2 - \beta_3 - \beta_4)$	,,
8	ρ_{CH_2}	$= 2^{-1/2}(\beta_1 - \beta_2)$	CH_2 rock
9	ρ_{CH_2}	$= 2^{-1/2}(\beta_3 - \beta_4)$	,,

The theoretical and experimental structural parameters of ethylene are reported in table 2. Flood and Skanche (1978) optimised the geometry of ethylene by using the *ab initio*/Force method. Duncan *et al* (1972) reported the ground state structure from the set of rotational constants of isotopic ethylene. Hirota *et al* (1981) observed the pure rotational spectra of ethylenes H_2CCD_2, H_2CCHD and HDCCHD (*cis*) by microwave spectroscopy and calculated the structure. For comparison these experimental and *ab initio* geometrical parameters are also given in table 2. The CNDO optimised C=C bond length is lower than the experimental value but agrees well with the *ab initio* value. The C-H bond length is slightly lower than the experimental value but is closer to the *ab initio* value. Not much difference exists between the theoretical and experimental values of the angle considered.

Two types of force fields are considered. Since the signs of the interaction constants predicted by the CNDO/Force method are reliable, we have refined the force field keeping the signs unaltered during iteration in the first attempt. The signs of the interaction constants are then allowed to vary for a better frequency fit. The two force fields are called FF_1 and FF_2 respectively. In both the calculations Overend and Scherer's (1960) absolute weighting factor is used. The theoretical CNDO force constants, the final force fields FF_1 and FF_2 along with literature values are given in table 3. Pulay and Meyer (1971) calculated the C=C stretching force constant as

Table 2. Calculated and experimental geometry of ethylene (distance in Å and angle in degrees).

		Theoretical		Experimental	
		CNDO/FORCE	*Ab initio*/Force Flood and Skancke (1978)	Hirota *et al* (1981)	Duncan *et al* (1972)
1	$R_{C=C}$	1·3108	1·315	1·3391	1·339
2	R_{C-H}	1·0796	1·073	1·0869	1·089
3	<HCH	116·52	116·2	117·07	117·08

Table 3. Force field of ethylene.

Force constant	Theoretical CNDO	FF_1	FF_2	Duncan and Hamilton (1981)	Pulay and Meyer (1971)
1. F1, 1	25·1064	9·4285	9·4139	9·418	9·939
2. F1, 2	0·4935	0·1470	0·2090	0·080	0.096
3. F1, 6	− 0·4142	− 0·2226	− 0·2131	− 0·264	− 0·273
4. F2, 2	14·2071	5·5466	5·5559	5·562	5·911
5. F2, 3	− 0·0015	− 0·0009	− 0·0039	0·016	0·016
6. F2, 4	0·1989	0·0273	0·0178	0·042	0·032
7. F2, 5	0·0265	0·0113	− 0·135	0·010	− 0·009
8. F2, 6	0·0916	0·0127	− 0·041	0·094	0·103
9. F2, 7	− 0·0173	− 0·0010	− 0·0620	− 0·006	− 0·021
10. F2, 8	0·0521	0·0061	− 0·0848	0·052	0·148
11. F2, 9	− 0·0471	− 0·1485	− 0·0637	− 0·168	− 0·060
12. F6, 6	0·4887	0·4599	0·4615	0·599	0·715
13. F6, 7	0·0265	0·0151	0·0173	0·023	0·031
14. F8, 8	0·4501	0·5526	0·5474	0·481	0·534
15. F8, 9	− 0·1502	− 0·0756	− 0·0814	− 0·070	− 0·089

Units for force constant; stretch, stretch-stretch mdyn Å^{-1}
Stretch bend in mdyn rad^{-1} and bend-bend in mdyn Å rad^{-2}

9·939 from *ab initio* and Bock *et al* (1979) calculated it to be still larger (10·23), and stated that the C=C force constants in hydrocarbons are generally overestimated in the *ab initio* results using small basis sets.

The present calculation shows a value closer to the experimental value of Duncan and Hamilton (1981). Novikov and Malyshev (1981) obtained a value of 8·91 for $f_{C=C}$. Similar deviations in the C-H stretching force constant are also noticed. The interaction constants $f_{C=C}/f_{C-H}$ and $f_{C=C}/f_{CH_2\ def}$ are found to have a significant magnitude. The signs of all the interaction constants predicted by CNDO agree satisfactorily with experimental and *ab initio* values. The observed and calculated frequencies for various isotopic species together with their potential energy distribution are given in table 4. The error $\Delta\omega$ using harmonic frequencies is less than 1.5% in the present study. The frequencies calculated from *ab initio* using

Table 4. Observed (harmonised) and calculated frequencies (in cm^{-1}) and P. E. D. for ethylene and its isotopes

Observed frequency	Calculated frequency	$\Delta\omega$	Calculated frequency	$\Delta\omega$	P. E. D. for FF_1 (in %)
H_2CCH_2					
3139·0	3145·3	− 6·1	3141·4	− 2·2	F2, 2 (99)
1650·8*	1655·5	− 4·7	1658·3	− 7·5	F1, 1(69), F1, 6(− 17), F6, 6(45)
1369·4*	1372·3	− 2·9	1371·4	− 2·0	F1, 1(31), F1, 6(12), F6, 6(54)
3211·0	3211·8	− 0·5	3212·1	− 0·8	F2, 2(101)
1244·8	1249·0	− 4·2	1249·8	− 5·0	F8, 8(89), F8, 9(12)
3234.3	3235·5	− 1·2	3236·4	− 2·1	F2, 2(99)
842·8	843·4	− 0·7	842·9	− 0·1	F8, 8(117), F8, 9(− 16)
3137·8	3132·9	4·9	3136·9	0·9	F2, 2(100)
1473·0	1475·6	− 2·6	1474·6	− 1·6	F6, 6(103)
$H_2C^{13}CH_2$					
3135·7	3142·3	− 6·6	3139·4	− 3·7	F2, 2(99)
1632·3	1633·5	− 1·2	1636·6	− 4·3	F1, 1(65), F6, 6(49), F1, 6 (− 17)
1364·4	1365·7	− 1·3	1364·6	− 0·2	F1, 1(36), F1, 6(13), F6, 6(50)
3205·0	3203·8	1·2	3204·2	0·8	F2, 2(101)
—	1240·0	—	1240·9	—	F8, 8(89), F8, 9(12)
3227·2	3230·3	− 3·1	3231·4	− 4·2	F2, 2(100)
842·3	842·9	− 0·6	842·3	0·0	F8, 8(117), F8, 9(− 16)
3134·9	3129·3	5·6	3132·3	2·7	F2, 2(100)
1469·9	1472·7	− 2·8	1471·6	− 1·7	F6, 6(103)
$H_2{}^{13}C^{13}CH_2$					
3131·5	3137·6	− 6·1	3133·4	− 1·9	F2, 2(99)
1611·1	1611·5	− 0·5	1614·9	− 3·8	F1, 1(61), F1, 6(− 17), F6, 6(54)
1356·5	1358·2	− 1·7	1356·9	− 0·4	F1, 1(40), F1, 6(13), F6, 6(45)
3199·5	3199·3	0·2	3199·5	0·0	F2, 2(101)
—	1230·9	—	1231·8	—	F8, 8(89), F8, 9(12)
3221·2	3221·5	− 0·3	3223·0	− 1·8	F2, 2(100)
841·8	842·4	− 0·6	841·7	0·1	F8, 8(117), F8, 9(− 16)
3132·8	3127·4	5·4	3131·7	1·1	F2, 2(100)
1467·0	1470·1	− 3·1	1469·0	− 1·9	F6, 6(103)

Table 4. *Contd.*

Observed frequency	Calculated frequency	Δω	Calculated frequency	Δω	P. E. D. for FF$_1$ (in %)
D_2CCD_2					
2331·9	2325·7	6·2	2325·8	6·1	F1, 1(11), F_2, 2(91)
1542·9*	1538·6	4·3	1537·0	5·9	F1, 1(84), F1, 6(− 11), F6, 6(15)
999·2	999·3	—0·1	1000·1	− 0·9	F1, 1(9), F6, 6(82)
2387·1	2392·1	− 5·0	2393·3	− 6·2	F2, 2(101)
1016·7	1018·9	− 2·2	1019·2	− 2·5	F8, 8(87), F8, 9(12)
2414·6	2414·5	0·1	2409·9	4·7	F2, 2(99)
603·7	604·8	—1·1	605·8	− 2·1	F8, 8(117), F8, 9(−16)
2267·3	2268·2	− 0·9	2267·8	− 0·5	F2, 2(99)
1094·3	1090·7	3·6	1091·6	2·7	F6, 6(102)
$D_2C^{13}CD_2$					
2322·1	2316·5	5·6	2316·3	5·8	F1, 1(10), F2,2(92)
1516·8	1516·3	0·5	1515·0	1·8	F1, 1(85), F1, 6(− 11), F6, 6(16)
—	998·7	—	999·5	—	F6, 6(82)
—	2379·3	—	2379·8	—	F2, 2(101)
—	1010·2	—	1010·5	—	F8, 8(87), F8, 9(12)
2408·2	2408·5	− 0·3	2405·0	3·2	F2, 2(100)
—	604·3	—	605·1	—	F8, 8(117), F8, 9(− 16)
2263·2	2263·5	− 0·3	2263·4	—0·2	F2, 2(99)
1090·5	1087·2	3·3	1087·9	2·6	F6, 6(102)
$D_2{}^{13}C^{13}CD_2$					
—	2306·9	—	2305·9	—	F2, 2(93)
—	989·0	—	1491·9	—	F1, 1(85), F1, 6 (− 11), F6, 6(17)
					F6, 6(81)
—	2373·3	—	2374·4	—	F2, 2(102)
—	1001·4	—	1001·8	—	F8, 8(87), F8, 9(12)
—	2395·7	—	2391·9	—	F2, 2(99)
—	603·7	—	604·5	—	F8, 8(117), F8, 9(− 16)
2259·9	2260·1	− 0·2	2260·2	− 0·3	F2, 2(99)
1087·6	1084·1	3·5	1084·7	2·9	F6, 6(103)
H_2CCD_2					
3134·4	3139·2	− 4·8	3138·6	− 4·2	F2, 2(99)
1608·5	1609·7	− 1·2	1606·2	2·3	F1, 1(65), F1, 6(− 14), F6, 6(43)
1048·1*	1044·0	4·1	1043·5	4·6	F6, 6(91)
2407·9	2403·3	4·6	2401·5	6·4	F2, 2(100)
1164·2	1163·7	0·5	1162·6	8·6	F8, 8(90), F8, 9(11)
3222·6	3223·3	− 0·7	3224·4	− 1·8	F2, 2(101)
698·8	696·8	2·0	698·1	0·7	F8, 8(115), F8, 9(− 14)
2297·8	2297·9	− 0·1	2299·3	− 1·5	F2, 2(95)
1411·1	1411·7	− 0·6	1415·4	− 1·3	F1, 1(25), F6, 6(68)
$H_2C^{13}CD_2$					
—	3139·1	—	3138·5	—	F2, 2(99)
1594·3	1596·2	− 1·9	1593·1	1·2	F1, 1(61), F1, 6(− 14), F6, 6(49)
—	1043·6	—	1043·1	—	F6, 6(91)
2388·8	2384·6	4·2	2383·0	5·8	F2, 2(100)
—	1157·1	—	1156·3	—	F8, 8(90), F8, 9(10)

Table 4. *Contd.*

Observed frequency	Calculated frequency	$\Delta\omega$	Calculated frequency	$\Delta\omega$	P. E. D. for FF_1 (in %)
—	3223·3	—	3224·4	—	F2, 2(101)
—	694·4	—	695·4	—	F8, 8(115), F8, 9(− 14)
2285·1	2284·5	0·6	2286·0	− 0·9	F8, 8(96)
	1399·4	—	1402·7	—	F1, 1(32), F6, 6(62)
$H_2{}^{13}CCD_2$					
3127·9	3132·6	− 4·7	3132·1	− 4·2	F2, 2(99)
1582·3	1583·6	− 1·3	1580·2	2·1	F1, 1(62), F1, 6(− 14), F6, 6(47)
—	1040·4	—	1039·8	—	F6, 6(90)
—	2403·3	—	2401·5	—	F2, 2 (100)
—	1153·7	—	1152·6	—	F8, 8(90), F8, 9 (10)
3208·9	3210·1	− 1·2	3211·4	− 2·5	F2, 2(100)
—	696·8	—	698·0	—	F8, 8(115), F8, 9(− 14)
—	2297·1	—	2298·3	—	F2, 2(94)
—	1410·0	—	1413·9	—	F1, 1(28), F6, 6(65)
$HDCCH_2$					
3141·9	3138·8	3·8	3138·8	3·1	F2, 2(99)
1633·8*	1628·0	5·8	1628·0	5·8	F1, 1(70), F1, 6(−15), F6, 6(40)
1319·0*	1313·1	5·9	1312·6	6·4	F1, 1(12), F6, 6(49), F8, 8(29)
3190·1	3182·5	7·6	3182·5	7·6	F2, 2(100)
1153·4	1146·1	7·3	1146·0	7·4	F8, 8(65), F6, 6(24)
3225·5	3225·3	0·2	3226·3	− 0·8	F2, 2(100)
746·9	746·3	0·6	746·5	0·4	F8, 8(110), F8, 9(− 14)
2344·6	2348·3	− 3·7	2347·8	− 3·2	F2, 2(97)
1430·2	1430·5	− 0·3	1431·9	− 1·7	F1, 1(14), F6, 6(83)

*The vibrational frequencies reported by Cvistas *et al* (1979) were harmonised and included here instead of those reported by Duncan and Hamilton (1981) which are slightly different.

harmonic frequencies give an error of 6·6%. The MINDO/3 systematically overestimates the C–H stretching frequency by 500 cm^{-1} and the overall agreement is ± 10%.

To conclude, the present method of combining CNDO/FORCE calculated with least square refinement of force field employing experimental vibrational frequencies results in a physically acceptable solution agreeing with both experimental and theoretical values. Further studies are being carried out on substituted ethylenes and other vinyl compounds.

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