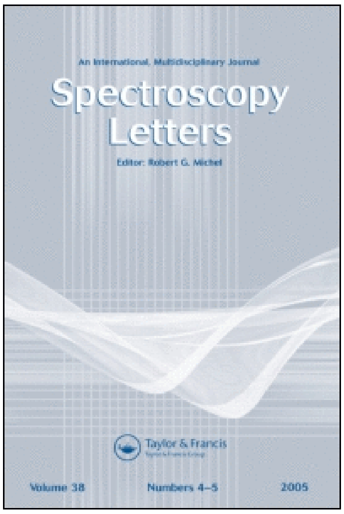

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The General Valence Force Field of Ethylene

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THE GENERAL VALENCE FORCE FIELD OF ETHYLENE

KEY WORDS: Ethylene, force constants, infrared spectra, Raman spectra.

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During the course of studies of the vibrational spectra of olefinic-type molecules, it was found that differences in the results of force constant calculations were obtained by various workers[3-7]. This diversity in results can be attributed not only to differences in frequency assignments and in assumed force fields, but also in choice of coordinates. The present note deals with the two different sets of symmetry coordinates in common use by various authors for ethylene-type molecules.

Both sets of symmetry coordinates shown in Table 1 are based on the same internal coordinates (Fig. 1). Since the two sets differ only in the bending coordinates, S_3 in the A_g symmetry species and S_9 in the B_{3u} species, the force constants obtained for the vibrations in the B_{1g} and B_{2u} species are not affected by the differences in these bending coordinates. Thus the vibrations in the B_{1g} and B_{2u} symmetry species will not be considered in this note.

TABLE 1

Symmetry Coordinates for Ethylene

Symmetry Type	Set I	Set II
A_g	$S_1 = 1/2(r_1+r_2+r_3+r_4)$	$S_1 = 1/2(r_1+r_2+r_3+r_4)$
	$S_2 = R$	$S_2 = R$
	$S_3 = 1/2(a_1+a_2+a_3+a_4)$	$S_3 = \frac{1}{2\sqrt{3}}(2b_1-a_1-a_2+2b_2-a_3-a_4)$
B_{1g}	$S_4 = 1/2(r_1-r_2-r_3+r_4)$	
	$S_5 = 1/2(a_1-a_2-a_3+a_4)$	
B_{2u}	$S_6 = 1/2(r_1-r_2+r_3-r_4)$	
	$S_7 = 1/2(a_1-a_2+a_3-a_4)$	
B_{3u}	$S_8 = 1/2(r_1+r_2-r_3-r_4)$	$S_8 = 1/2(r_1+r_2-r_3-r_4)$
	$S_9 = 1/2(a_1+a_2-a_3-a_4)$	$S_9 = \frac{1}{2\sqrt{3}}(2b_1-a_1-a_2-2b_2+a_3+a_4)$

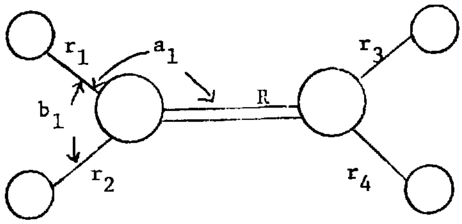

FIG. 1

Internal Coordinates for ethylene.

Sufficient frequency data (Table 2) were available in the literature[5,8] for employing the General Valence Force Field. The results of the normal coordinate calculations for the two sets of symmetry coordinates are shown in Table 3. Both sets yielded calculated frequencies which were in good agreement with the observed frequencies. However, the following considerations

TABLE 2

Fundamental Vibrations of Ethylene (cm^{-1})

Vib. No.	C_2H_4 [5]	C_2D_4 [5]	$C_2H_2D_2$ [8]
	A_{-} Species		A_1 Species
1	3026.4	2260	3019
2	1622.6	1518	1585
3	1342.2	987	1031
	B_{3u} Species		
8	2989.5	2200.2	2231
9	1443.5	1077.9	1384

suggest that set I contains the physically meaningful symmetry coordinates.

Firstly, the value of 12.77 mdyne/A obtained from set II for the C=C stretching force constant is too high (Table 3). Previous studies of ethylene

TABLE 3

The General Valence Force Constants for Ethylene (mdynes/A)

		Sym. Coord. Set I		Sym. Coord. Set II	
Description	No.	F		F	(F)
CH str.	1	5.090	0.158	4.517	0.261
C=C str.	2	10.754	0.230	12.772	1.093
CH_2 bend	3	1.377	0.160	0.544	0.089
CH str.	8	4.682	0.133	4.787	0.144
CH_2 bend	9	1.346	0.064	0.441	0.023
	1-2	0.857	0.521	3.632	0.556
	1-3	0.825	0.369	0.748	0.192
	2-3	1.610	0.209	0.343	0.124
	8-9	0.757	0.109	-0.413	0.073

and halogenated ethylenes using different assumed force fields have yielded values of between 7 and 11 mdyne/A[3-7,9]. If ethylene is considered as a diatomic system and the harmonic oscillator approximation is employed, a value of $F_{C=C}$ = 10.95 mdynes/A is obtained. Furthermore Snyder[10] has developed a method for estimating multiple bond force constants from thermochemical data. This method yields a value of 10.86 mdyne/A for the C=C stretching force constant in good agreement with the value obtained from set I (Table 3).

Secondly, examination of the potential energy distributions of the A_g symmetry species (Table 4) shows that, from the calculations using set II, the vibrational frequency at 1622.6 cm^{-1} (assigned to the C=C stretching vibration) has almost equal contributions from the C-H stretching constant (24%) and the C=C stretching constant (28%). On the other hand, in set I the frequency at 1622.6 cm^{-1} is essentially a C=C stretching mode with a very small contribution from the CH_2 bending constant.

TABLE 4

Potential Energy Distributions for the A_g Species of Ethylene for the Two Sets of Symmetry Coordinates

No.	Frequency	Principle Force Constants CH Str.	C=C Str.	CH_2 Bend
		Set I		
1	3026.4	84.27	1.93	1.75
2	1622.6	1.02	75.96	4.38
3	1342.2	6.27	13.80	46.07
		Set II		
1	3026.4	56.79	3.68	6.35
2	1622.6	24.23	28.50	6.56
3	1342.2	8.33	8.61	50.06

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