MOA Calculations of CH Stretching Frequencies and Dissociation Energies in Hydrocarbons

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A relation between CH stretching frequencies and s characters of the corresponding bonds is obtained, using the data of CH, CHD and CHD_2 groups in hydrocarbons and the maximum overlap approximation [MOA] method. A relationship between dissociation energies and overlap integrals of CH bonds is also found. A new formula for calculating bond energies in hydrocarbons is proposed.

The idea that CH stretching frequencies should be proportional to the s character of the corresponding hybrid orbitals was put forward by Walsh[1]. This idea was recently examined and confirmed in more quantitative terms. Thus Galabov and Simov[2] have shown, using a five-atom model, that the observed increase of CH stretching frequencies in cycloalkanes is due to stronger force constants. The latter was rationalized by the increased s character of the exocyclic bonds in these molecules. On the other hand, we have found a good correlation between CH stretching frequencies and hybridization for a number of hydrocarbons[3]. The s character of the ψ_{CH} hybrids were calculated using the MOA (maximum overlap approximation) approach[4]. It turned out that the hybridization contribution to $\bar{\nu}_{CH}$ is less than one fifth of the total value. Other contributions were, however, roughly constant for all examined hydrocarbons, so that the changes in hybridization did account for the variation in CH stretching frequencies.

It is well known, that the symmetrical and antisymmetrical modes in CH_2 and CH_3 groups are coupled, giving two, or even three, different $\bar{\nu}_{CH}$ values. This obstacle can be avoided by the partial deuteration of the methylene and methyl group, leaving only one H atom in a group. By means of this technique, McKean et al.[5] obtained "pure" CH stretching frequencies. For some molecules they averaged frequencies so that CH, CH_2 and CH_3 values could be plotted on the same graph. We correlate here the experimental $\bar{\nu}_{CH}$ values of McKean et al. with our MOA hybridization parameters. We consider also the relation between CH dissociation energies and the corresponding overlap integrals, S_{CH}.

Firstly, we shall give a brief account on the MOA method. The local response of atomic orbitals on the molecular formation is their polarization. They form the so called hybrid orbitals

$$\psi_A = a(2s)_A + (1-a^2)^{1/2}(2p)_A$$

which are orthogonal if placed on the same atom A. The hybridization parameters "a" are determined by maximizing the suitably scaled bond overlaps:

$$E = k_{CC}\sum_{CC} S_{CC} + k_{CH}\sum_{CH} S_{CH} \qquad (1)$$

where $k_{CC} = 121$ kcal/mole and $k_{CH} = 136$ kcal/mole, if a Clementi double zeta[6] basis set is employed. The sums in Eq. (1) are extended over all CC and CH bonds in a molecule. The s characters of the so obtained hybrids, $(s\%)_{CH} = 100\, a_{CH}^2$, are correlated with experimental CH frequencies of McKean et alias[5]. The least squares fit gives the following relationship:

$$\bar{\nu}_{CH} = 20.8\,(s\%)_{CH} + 2411.6\ \text{cm}^{-1}. \qquad (2)$$

The results presented in Table 1 reveal a good overall agreement between the calculated and experimental frequencies. If we exclude cyclopropane, cyclobutane and methane from the correlation, a standard deviation of $10\ \text{cm}^{-1}$ is obtained. While the too low value of the calculated $\bar{\nu}_{CH}$ in cyclopropane is expected, because MOA underestimates s characters of ψ_{CH} hybrids[7], the dicrepancies for cyclobutane and particularly for methane are somewhat surprising. Nevertheless, the above relationship is satisfactory.

Table 1. Comparison between calculated and experimental CH stretching frequencies (in cm^{-1}).

Molecule	$(s\%)_{CH}$	$\bar{\nu}_{CH}$ (exp.)[a]	$\bar{\nu}_{CH}$ (calcd.)	$\Delta\bar{\nu}$
$CH_3-C\equiv C-H^*$	44.6	3334	3341	− 7
$H-C\equiv C-H$	43.6	3336	3320	16
C_2H_4	31.6	3060	3070	−10
C_6H_6	31.5	3065	3068	− 3
$H_2C=C=CH_2$	31.2	3049	3062	−13
Cyclopropane	28.6	3056	3008	48[b]
Cyclobutane	27.4	2956	2983	−27[b]
$CH_3^*-C\equiv C-H$	25.9	2958	2951	7
$C_6H_5\cdot CH_3^*$	25.5	2953	2943	10
C_2H_6	25.4	2950	2941	9
CH_4	25.0	2992	2932	59[b]
$(CH_3)_4C$	25.0	2934	2933	1

[a] From Ref.[5]. [b] Excluded from the correlation.

The CH dissociation energies are closely related to the stretching frequencies in the simple and intuitive picture of chemical bonding. McKean et al. found a good linear relationship for most molecules

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Table 2. Comparison between experimental and calculated CH bond dissociation energies (in kcal/mole).

Molecule	S_{CH}	D^0_{298} (exp.)	D^0_{298}(calcd.)	McKean et al. [a]	ΔD^0
$H-C\equiv C-H$	0.769	128	127.3	132.9	0.7
C_6H_6	0.741	110.5	110.4	109.5	0.1
C_2H_4	0.7403	108	109.8	109.1	− 1.8
$H_2C=C=CH_2$	0.739		109.3	108.1	
Cyclopropane	0.733	100.4	105.2	108.7	− 4.8 [b]
$CH_3^*-C\equiv C-H$	0.730		103.2	100.3	
Cyclobutane	0.729	96.8	102.6	100.1	− 5.8 [b]
$C_6H_5\cdot CH_3^*$	0.725	88.3	101.1	99.1	−12.8 [b]
$(CH_3)_4C$	0.723	99.3	99.3	98.2	0
CH_4	0.722	104	98.8	103.2	5.2 [b]
C_2H_6	0.720	98	97.0	99.6	1

[a] Based on the correlation $\bar{\nu}_{CH}$ stretching frequency and bond energy; Reference [5]. [b] Excluded from the correlation.

which dissociate into sigma radicals possessing very low stabilization energies. We correlated their D^0_{298} values with the corresponding S_{CH}'s, since it is well documented that the bond overlap integrals provide a reliable measure of the bond strength in hydrocarbons [4, 8, 9]. The linear least squares method gives the correlation:

$$D^0_{298} = 617.8\, S_{CH} - 347.5 \text{ kcal/mole}. \tag{3}$$

We compare the estimates of the CH bond dissociation energies obtained by Eq. (3) with the results of McKean et al. [5] and the available experimental data in Table 2. Our values are in better agreement with the bond energies predicted by McKean et al. than with the experimental ones. It seems that some of the experimental data should be reinvesigated. This is apparently necessary for bond energies in cyclopropane, the CH energy of the methyl group in toluene and perhaps that in cyclobutane. The agreement with experiment for the rest of the molecules is pretty good.

Equation (3) in conjunction with Eq. (5) of the Ref. [9]

$$D^\circ(C-C) = 372.3\, S_{CC} - 143.7 \tag{4}$$

might lead to a better version of the MOA method. Instead of Eq. (1) one should maximize the overall bond energy of a molecule:

$$E_b = 372.3 \sum_{CC} S_{CC} + 617.8 \sum_{CH} S_{CH} - (143.7\, n_C + 347.5\, n_H) \tag{5}$$

where n_C and n_H is the number of carbon and hydrogen atoms, respectively. Such an endeavour is in progress.

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