

**The Vibrationally Averaged Structures  
of Ethylene, Ethylene-1-13C and Ethylene-1,2-13C  
as determined by NMR of Partially Oriented Molecules**

Diehl P., Sykora S., Wullschleger E.

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Abstract:

This Communication is an example of the application of vibrational correction in HR-NMR spectra of oriented molecules.

The vibrationally averaged structures of ethylene, ethylene-1- $^{13}\text{C}$  and ethylene -1,2- $^{13}\text{C}$  as determined by NMR of partially oriented molecules.

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by P. Diehl and S. Šýkora, Department of Physics, University of  
Basel, CH-4056 Basel, Switzerland

and

E. Wullschleger, Department of Physical Chemistry, University of  
Basel, CH-4056 Basel, Switzerland

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In discussions of molecular structure ( $r_d$ ) as determined by NMR of oriented molecules Lucas [1] suggested to use an average structure ( $r_z$ ) which is corrected for harmonic vibrational motion. Unlike the  $r_d$ -structure, the  $r_z$ -structure is geometrically consistent.

In this communication we present the  $r_d$  and  $r_z$ -structures of ethylene and determine the influence of  $^{13}\text{C}$ -substitution on the molecular vibration and the corresponding corrections. A computer program developed for this study will be described in a future publication.

The ethylene samples enriched to 65 atom % of  $^{13}\text{C}$  were prepared with 6 atm pressure at equilibrium with the liquid crystal Merck Licristal Phase V. The Varian HA 100 spectrometer was operated in the HR mode and the spectrum was analysed by means of the programs LEQUOR and SHAPE [2].

The results are presented in Table 1 and compared with IR data [3].

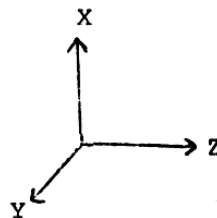
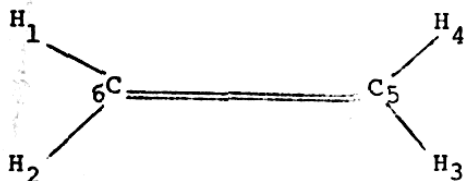


Table 1. Distance ratios and bond angles in ethylene as determined from NMR spectra of oriented molecules. Both the  $r_d$ - and  $r_z$ -structure values are given and the latter are compared with IR data. The vibrational corrections  $\Delta_{\text{vib}}$  were calculated using the force field given in reference [4].

Distance ratio	Isotope	IR [3] <sup>a</sup> ( $r_z$ )	NMR		$\Delta_{\text{vib}} =$ ( $r_z$ )-( $r_d$ )
			( $r_d$ )	( $r_z$ )	
$r_{14}/r_{12}$	$^{13}\text{C}-^{13}\text{C}$		1.3197(51)	1.3259(51)	+0.0062
	$^{13}\text{C}-^{12}\text{C}$		1.3175(21)	1.3261(21)	+0.0086
	$^{12}\text{C}-^{12}\text{C}$	1.3290(42)	1.3150(17)	1.3232(17)	+0.0082
$r_{16}/r_{12}$	$^{13}\text{C}-^{13}\text{C}$		0.5844(09)	0.5844(09)	0.0000
	$^{13}\text{C}-^{12}\text{C}$	0.5853(08)	0.5849(14)	0.5845(14)	-0.0004
$r_{56}/r_{12}$	$^{13}\text{C}-^{13}\text{C}$	0.7206(17)	0.7146(17)	0.7210(17)	+0.0064
$\angle \text{HCC}$	$^{13}\text{C}-^{13}\text{C}$	$121^\circ 19' \pm$ 7.5'	$121^\circ 10.5' \pm$ 6.6'	$121^\circ 10.5' \pm$ 6.6'	0.0'

<sup>a</sup> The IR data regard the  $^{12}\text{C}-^{12}\text{C}$  isotope; the differences between the individual isotopes are however much smaller than the experimental errors [3].

We found close agreement between NMR and IR data and generally small vibrational corrections (less than 1%). It is interesting to notice that the vibrational corrections in the ratio  $r_{14}/r_{12}$  are practically the same for ethylene and ethylene-1- $^{13}\text{C}$  whereas there is a significant deviation for ethylene-1,2- $^{13}\text{C}$ .

In the computer fit performed with program SHAPE we noticed that all the couplings were well fitted except  $D_{56}$  in ethylene-1,2- $^{13}\text{C}$ . For this  $^{13}\text{C}-^{13}\text{C}$  direct coupling there remained a residual error of  $\sim 3$  Hz. If this deviation is attributed to an anisotropic con-

tribution of the indirect  $^{13}\text{C}$ - $^{13}\text{C}$  coupling to the D-value, a relation for the J-coupling anisotropy may be obtained. Taking into account the values of the order parameters (in our case roughly  $S_{zz}=0.053$ ,  $S_{xx}=-0.027$ , and  $S_{yy}=-0.026$ , the exact values varying somewhat from sample to sample), the relation becomes  $J_{zz} - \frac{1}{2} (J_{xx} + J_{yy}) \approx 90$  Hz. This order of magnitude agrees well with earlier theoretical predictions [5].

### References

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