

## GAS-PHASE $^{13}\text{C}$ CHEMICAL SHIFTS IN THE ZERO-PRESSURE LIMIT: REFINEMENTS TO THE ABSOLUTE SHIELDING SCALE FOR $^{13}\text{C}$

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$^{13}\text{C}$  chemical shifts have been measured relative to  $^{13}\text{CO}$  in the zero-pressure limit for over twenty molecules for which theoretical calculations of  $^{13}\text{C}$  nuclear shielding have recently been reported. Rovibrational averaging effects on the spin-rotation constant in  $^{13}\text{C}^{16}\text{O}$  have been used to find  $\sigma_c(^{13}\text{C} \text{ in } ^{13}\text{C}^{16}\text{O}) = 3.0 \pm 1.2$  ppm and  $\sigma_o(^{13}\text{C} \text{ in } ^{13}\text{C}^{16}\text{O}) = 1.0 \pm 1.2$  ppm. With the latter, the  $\sigma_o$  values for the  $^{13}\text{C}$  nuclei in this work have been determined absolutely and compared with calculated values. Agreement is generally good in most cases except where low-lying  $n \rightarrow \pi^*$  transitions contribute significantly to the paramagnetic shielding.

### 1. Introduction

Theoretical calculations of  $^{13}\text{C}$  shielding in small molecules have reached a level of accuracy such that the calculated chemical shifts for  $\text{CH}_3\text{CH}_3$ ,  $\text{CH}_2=\text{CH}_2$ , and  $\text{HCCH}$  relative to  $\text{CH}_4$  are within experimental error. At this stage it becomes necessary to have better experimental values with which to compare. Little gas-phase data are available for  $^{13}\text{C}$  shifts [1-4]. There are  $^{13}\text{C}$  spin-rotation constants from molecular beam experiments on  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{OCS}$ ,  $\text{HCN}$ , and  $\text{CH}_3\text{CN}$ . The last yields only  $\sigma_P$ , so that only four nuclear shielding values may be considered "known" in an absolute sense, after computed diamagnetic shielding values have been added to the SR-derived paramagnetic terms. The remainder of the  $^{13}\text{C}$  shielding information for these small molecules is in the form of chemical shift tensor components measured in the solid state (at 20 K in an argon matrix or in the pure solid) or in the neat liquid. The individual shielding tensor elements from solid state data provide a more stringent test of theory than do the isotropic shifts and are thus better indicators of any theoretical deficiencies. The extent to which the-

ory reproduces the observed shielding anisotropy has improved dramatically. Agreement is better than  $\pm 10$  ppm for many molecules [5]. Nevertheless, there still remain some problems in utilizing experimentally determined values with which to compare various calculations. First, there may be a referencing problem in that external references of liquid benzene, liquid  $\text{CS}_2$  or  $\text{Me}_4\text{Si}$  (TMS) have been used and it is usually not stated whether the reference was in a cylindrical sample with axis perpendicular or parallel to  $B_0$ , or corrected to a spherical sample. Secondly, solid-state data do not refer to isolated molecules at the equilibrium geometry, whereas theoretical calculations do. The intermolecular effects present in the solid state may be estimated and corrections can be made prior to comparison with theory. However, it is desirable to take measurements under conditions as close as possible to the isolated molecule, i.e. in the gas phase in the zero-pressure limit. Under these conditions bulk susceptibility and medium effects are not present.

We choose  $^{13}\text{C}^{16}\text{O}$  as the primary reference molecule in which the absolute shielding is defined by molecular beam measurements, which enables the

measured differences  $\sigma_0(300\text{ K}) - \sigma_0(\text{CO}, 300\text{ K})$  to be converted to shielding on an absolute scale. We report measurements for twenty-three nuclear environments. We also report the absolute shielding of three reference liquids (TMS, benzene, and  $\text{CS}_2$ ), corrected to a spherical geometry (to remove bulk susceptibility effects).

## 2. Experimental

$^{13}\text{C}$  spectra in natural abundance were obtained at 50.33 MHz in an IBM WP 200SY FT NMR spectrometer in sealed samples containing mixtures of gases at low densities (0.1 to 1.5 amagat of each gas). The molecules were observed in groups of three or four per sample tube, with overlap between samples so that many molecules are observed in at least two different spectra. Since the CO signal is broader than other signals, a small amount of  $^{13}\text{C}$ -labeled  $\text{CO}_2$  in each sample served as the practical reference peak. The chemical shifts are subsequently expressed relative to CO. The repeatability of our shift measurements was better than  $\pm 0.1$  ppm. The temperature was regulated to  $\pm 0.1$  K at 300 K. This is not critical for  $^{13}\text{C}$  shifts, which are relatively insensitive to small variations in temperature in low-density gas samples. On the other hand, the reference liquids have temperature-dependent shifts due to changes in liquid density. Under the conditions of these experiments, intermolecular effects (including bulk susceptibility effects, which are 0.003–0.014 ppm/amagat) are less than 0.05 ppm. We estimate that our reported values of  $\sigma_0 - \sigma_0(\text{CO})$  at 300 K are good to  $\pm 0.1$  ppm. The chemical shifts of the neat reference liquids TMS, benzene, and  $\text{CS}_2$  were each observed in the annular region surrounding a sealed gas sample.

The appropriate procedure for establishing the  $^{13}\text{C}$  shielding scale is that used by Hindermann and Cornwell for  $^{19}\text{F}$  [6], in which the molecular beam value of the spin-rotation tensor,  $C$ , for the primary reference is corrected to the value at the equilibrium structure so that the exact relation between  $C_e$  and  $\sigma_e^p$  may be used. The resulting  $\sigma_e$  is then corrected to  $\sigma_0(300\text{ K})$  and the measured  $\sigma_0$  differences can then be converted to absolute  $\sigma_0(300\text{ K})$  values by adding this precise amount to each. This has not previ-

ously been done for CO. The accepted value of 3.20 ppm comprises a diamagnetic term evaluated at the equilibrium structure added to a paramagnetic term which is evaluated from a vibrationally averaged ( $v=0, J=1$ ) value of  $C$  [7]. In effect the value  $3.2 \pm 1.2$  ppm is somewhere between  $\sigma_e$  and  $\sigma_0(300\text{ K})$ . (The original error estimate,  $\pm 0.27$  ppm was smaller than was appropriate for the error in  $C$ .) As long as theoretical values differed from experimental chemical shifts by more than 10 ppm, the vibrational corrections for the primary reference value could be neglected, and 3.20 ppm has been widely used as a value for both  $\sigma_0$  and  $\sigma_e$  in  $^{13}\text{C}^{16}\text{O}$ . We make the appropriate corrections below.

The experimentally measured SR constant  $\langle C \rangle_{v,J}$  is corrected by means of the following equations to obtain the value  $C_e$  for the equilibrium internuclear distance [8],

$$\langle C \rangle_{v,J} = C_e + C_e' \langle \xi \rangle_{v,J} + \frac{1}{2} C_e'' \langle \xi^2 \rangle_{v,J}, \quad (1)$$

where  $\xi = (R - R_e)/R_e$  and the averages are

$$\begin{aligned} \langle \xi \rangle_{v,J} &= -3(v+1/2)a_1(B_e/\omega_e) \\ &\quad + 4J(J+1)(B_e/\omega_e)^2, \end{aligned} \quad (2)$$

$$\langle \xi^2 \rangle_{v,J} = 2(v+1/2)(B_e/\omega_e). \quad (3)$$

The experimental value reported by Meerts et al. [9] for  $^{13}\text{C}$  in  $^{13}\text{C}^{16}\text{O}$  in the  $v=0, J=1$  state is  $\langle C \rangle_{0,1} = 32.70 \pm 0.12$  kHz, in good agreement with the previous value  $32.59 \pm 0.15$  kHz obtained by Ozier et al. [10]. The relativistic correction arising from the nuclear acceleration is small enough to be neglected and vanishes at  $R_e$ . Values of  $C$  for  $^{13}\text{C}$  in  $^{13}\text{C}^{16}\text{O}$  have been calculated at four bond lengths by Stevens and Karplus [11] with the coupled Hartree-Fock method, from which values one obtains  $C_e' = -3.97$  kHz and  $\frac{1}{2}C_e'' = 52.30$  kHz. Using average values  $\langle \xi \rangle_{0,1}$  and  $\langle \xi^2 \rangle_{0,1}$  calculated in eqs. (2) and (3), we find  $C_e = (32.70 \pm 0.12) + 3.15 \times 10^{-2}$  kHz.

The correction is well within the experimental error. With  $C_e = 32.73 \pm 0.12$  kHz we can obtain the paramagnetic contribution to  $^{13}\text{C}$  shielding by

$$\sigma_e^p(\text{origin at } ^{13}\text{C}) = \frac{m_p C_e}{3mgB_e} - \frac{e^2}{3mc^2} \frac{Z_{N'}}{R_e},$$

where  $N'$  is oxygen and the rotational constant  $B_e$  is

Table 1  
 $\sigma_0(300\text{ K})$  for  $^{13}\text{C}$ , in ppm. To the  $\sigma_0 - \sigma_0(\text{CO})$  measured at 300 K in the zero-pressure limit  $\sigma_0(\text{CO}) = 1.00 \pm 1.2$  ppm has been added

Molecule	$\sigma_0(300\text{ K})$		Calculated $\sigma_e$									
	this work <sup>a)</sup>	other <sup>b)</sup>	ref. [16]	ref. [17]	ref. [18]	ref. [19]	ref. [20]	ref. [21]	other			
free C atom	(260.74) <sup>c)</sup>											
$\text{CH}_4$	195.1	195.15	196	193	196.7	199.2		215				
TMS	188.1				212.3							
$\text{CH}_3\text{CN}$	187.7											
$\text{CH}_3\text{CH}_3$	180.9	180.9	184	181.2	183.5	191.1	186.2					
$\text{CH}_3\text{NH}_2$	158.3			162.5		171.2						
$(\text{CH}_3)_2\text{CO}$	158.0											
$\text{CH}_3\text{CHO}$	157.2		166		176.5	173.8						
$\text{CH}_3\text{OH}$	136.6		145	134.6	157.2	152.5						
$\text{HC}\equiv\text{CH}$	117.2		122	118.3	116.4	132.7	119.1					
$\text{CH}_3\text{F}$	116.8	116.3		128.1	139.8	133.7		136				
$\text{CH}_2=\text{C}=\text{CH}_2$	115.2				116.7	126.1						
HCN	82.1		78	74.8	72.9	92.1						
MeCN	73.8											
$\text{CH}_2=\text{CH}_2$	64.5	64.6	63	62.2	61.6	76.7	60.4	82	78.6 <sup>d)</sup>			
$\text{CF}_4$	64.5	64.5			101	105.4						
$\text{CO}_2$	58.8	58.8	58		50.7							
$\text{C}_6\text{H}_6$	57.2				81.6							
OCS	30.0							47				
CO	(1.0)			-21.3	-23.8			-6	65.9(C), 56.1(cm) <sup>e)</sup>			
MeCHO	-6.7		-8		5.4	5.9		8				
$\text{CS}_2$	-8.0											
$\text{Me}_2\text{C}=\text{O}$	-13.1											
$\text{CH}_2=\text{C}=\text{CH}_2$	-29.3				-37.8	-87		-15				

<sup>a)</sup> Errors in  $\sigma_0 - \sigma_0(\text{CO})$  at 300 K are estimated to be  $\pm 0.1$  ppm.

<sup>b)</sup> Gas phase measurements by Jackowski and Raynes [1] of which  $\text{CH}_4$ ,  $\text{CH}_3\text{CH}_3$ ,  $\text{CH}_2=\text{CH}_2$  and  $\text{CO}_2$  are extrapolated to zero pressure.

<sup>c)</sup> Ref. [22]. <sup>d)</sup> Ref. [23]. <sup>e)</sup> Ref. [24].

Table 2  
 Comparison with absolute shielding obtained from spin-rotation constants<sup>a)</sup>

Molecule	$ C $ (kHz)	$\sigma_1^z$	$\sigma^p$	$\sigma_1^x$	$\sigma_1^y$	$\sigma_1^z$	$\sigma_1^x$	$\sigma_1^y$	$\Delta\sigma$	$\sigma$	$\sigma_0$ this work
$^{13}\text{CH}_4$	$15.94 \pm 2.37$ <sup>b)</sup>		$-100.66 \pm 9.9$						0	$195.8 \pm 9.9$	195.1
$\text{D}^{13}\text{C}^{14}\text{N}$	$15.0 \pm 1.0$ <sup>c)</sup>	$-374.3 \pm 12$	$-249.5 \pm 8$							$77.2 \pm 8$ <sup>c)</sup>	82.1
				345	287				$316.3 \pm 12$	$77.1 \pm 8$	
$^{16}\text{O}^{13}\text{CS}$	$3.1 \pm 0.2$ <sup>d)</sup>	$-579 \pm 14$	$-386 \pm 9$	483	299				$395 \pm 14$ <sup>d)</sup>	$35 \pm 9$ <sup>d)</sup>	30.0
$\text{CH}_3^{13}\text{CN}$	$3.6 \pm 0.2$ <sup>e)</sup>	$-418 \pm 14$	$< -279$	407	289				$< 88$		73.8

<sup>a)</sup> Quoted error estimates include only error in the spin rotation constant, not in the calculation of  $\sigma^d$ .

<sup>b)</sup> Ref. [25]. <sup>c)</sup> Ref. [26]. <sup>d)</sup> Ref. [27]. <sup>e)</sup> Ref. [28]. <sup>f)</sup> Ref. [29]. <sup>g)</sup> Ref. [30]. <sup>h)</sup> Ref. [31].

calculated from  $R_e = 1.1282 \text{ \AA}$ . The second term is  $-66.6 \text{ ppm}$  and  $\sigma_e^p(^{13}\text{C}) = -324.2 \pm 0.9 \text{ ppm}$ . Using the best theoretical value,  $\sigma_e^d(^{13}\text{C}) = 327.16 \text{ ppm}$  [12], we get  $\sigma_e = 3.0 \pm 0.9 \text{ ppm}$ , which is not significantly different from the originally accepted value [7]. The thermal average shielding is [8]

$$\sigma_0(300 \text{ K}) = \sigma_e + \sigma' \langle \xi \rangle^{300 \text{ K}} + \frac{1}{2} \sigma'' \langle \xi^2 \rangle^{300 \text{ K}}.$$

Using the derivatives from the calculations of Stevens and Karplus [11,13] ( $\sigma' = -466.5 \text{ ppm}$  and  $\sigma'' = -525 \text{ ppm}$ ) and  $\langle \xi \rangle^{300 \text{ K}} = 3.86 \times 10^{-3}$  and  $\langle \xi^2 \rangle^{300 \text{ K}} = 8.70 \times 10^{-4}$ , leads to a rovibrational correction for  $^{13}\text{C}^{16}\text{O}$  of  $-2.0 \text{ ppm}$  at  $300 \text{ K}$ , which is in good agreement with earlier estimates [13,14]. Other experimental measurements of the change in  $\sigma(^{13}\text{C})$  as a function of the CO bond length, such as the  $^{18}\text{O}$ -induced  $^{13}\text{C}$  isotope shift and the temperature dependence of the  $^{13}\text{C}$  shift, are consistent with a rovibrational correction of  $-2.0 \pm 0.3 \text{ ppm}$  [14,15]. Thus, for  $^{13}\text{C}$  in  $^{13}\text{C}^{16}\text{O}$ ,  $\sigma_0(300 \text{ K}) = 1.0 \pm 1.2 \text{ ppm}$ . The measured differences  $\sigma_0 - \sigma_0(\text{CO})$  can be converted to the absolute  $\sigma_0$  scale by adding  $1.0 \text{ ppm}$  as shown in table 1.

$^{13}\text{C}$  spin-rotation constants have been measured for a few molecules and independent values of the absolute shielding ( $\approx \sigma_e$  or  $\sigma_0$ ) can be derived from these (see table 2). Comparison with our data shows very good agreement. The differences are not only smaller than the experimental errors of the spin-rotation constants but also within the magnitudes of typical rovibrational corrections.

Intermolecular effects on  $^{13}\text{C}$  shielding are obtained by comparison of the measured  $\sigma_0(300 \text{ K})$  and  $\sigma(\ell, \text{sph}, 300 \text{ K})$  values for TMS, benzene, and  $\text{CS}_2$ . These effects are deshielding and are respectively  $-4.0$ ,  $-1.5$ , and  $-0.2 \text{ ppm}$ . The magnitude of the uncertainty due to unspecified reference geometry can thus be estimated. Older data were likely to be referenced to  $(\ell, \text{cyl} \perp B_0)$  whereas more recent data are referenced to  $(\ell, \text{cyl} \parallel B_0)$  or  $(\ell, \text{sph})$ . We provide these corrections in table 3. The solid state  $^{13}\text{C}$  chemical shift data of Pines, Gibby, and Waugh [33], and of Grant et al. [21,34,35] can be converted to  $\sigma(s, 20 \text{ K})$  on an absolute scale by using  $\sigma(\ell, \parallel B_0, 300 \text{ K}) = 58.3 \text{ ppm}$  for benzene and  $\sigma(\ell, \parallel B_0, 300 \text{ K}) = 186.4 \text{ ppm}$  for TMS. The earlier value of  $\sigma(\text{TMS}, \ell, \text{sph})$  was  $185.4 \text{ ppm}$  [36], which was based on  $\sigma_0(\text{CO}) = 3.20 \text{ ppm}$ . When the chemical

Table 3

Shielding values for  $^{13}\text{C}$  nuclei in neat reference liquids at  $300 \text{ K}$ , based on  $\sigma_0(\text{CO}, 300 \text{ K}) = 1.0 \pm 1.2 \text{ ppm}$

Reference	$\sigma(\ell, \text{cyl} \parallel B_0)$	$\sigma(\ell, \text{sph})^a$	$\sigma(\ell, \text{cyl} \perp B_0)$
TMS	186.4	184.1	183.0
$\text{C}_6\text{H}_6$	58.3	55.7	54.5
$\text{CS}_2$	-5.4	-8.3	-9.8

<sup>a)</sup> Bulk susceptibility correction used  $\chi_m$  and liquid densities from the compilation in ref. [32].

shift data in the condensed phases are converted to the absolute scale,  $^{13}\text{C}$  nuclei are found to be *least* shielded in the solid, followed by the liquid, compared to the gas at the zero-pressure limit. Intermolecular effects on  $^{13}\text{C}$  shielding in the solid for the molecules in table 1 range from  $-1$  to  $-10 \text{ ppm}$  (and  $-0.1$  to  $-9 \text{ ppm}$  in the liquid). The most affected nuclear environments are the  $\text{C}=\text{O}$  carbons in  $\text{MeCHO}$  and  $\text{Me}_2\text{C}=\text{O}$  in the solid.

Ideally, the  $\sigma_0(300 \text{ K})$  values in table 1 should be corrected to  $\sigma_e$  values before comparison with theory. This can only be done accurately by using anharmonic force fields for each molecule and only if derivatives  $(\partial\sigma/\partial r)_e$ ,  $(\partial^2\sigma/\partial r^2)_e$ , etc. are known. Since this is not the case, we consider estimates of these corrections.

One method of estimation follows from the use of observed isotope shifts, since the mass dependence of the shielding is a measure of the rovibrational corrections [37]. For the shielding of the A nucleus in a symmetrical  $\text{AX}_n$  molecule, it has been shown that

$$\sigma_0^A(300 \text{ K}) - \sigma_e \approx n^1 \Delta^R(\text{AX}),$$

where the *reduced* isotope shift is

$$^1\Delta^R(\text{AX}) = \left( \frac{m' - m}{m'} \frac{1}{2} \frac{m_A}{m_A + m} \right)^{-1} ^1\Delta_A(m'/m\text{X}),$$

where  $^1\Delta_A(m'/m\text{X})$  is the isotope shift observed in nucleus A per substitution of  $m\text{X}$  by  $m'\text{X}$ . For a *rough* estimate of the rovibrational corrections to C shielding in less symmetrical environments, let

$$\sigma_0^C(300 \text{ K}) - \sigma_e \approx \sum_i^{\text{bonds CX}_i} ^1\Delta^R(\text{CX}_i).$$

Each direct bond to the resonant  $^{13}\text{C}$  nucleus is included in the sum. Using the D-induced  $^{13}\text{C}$  isotope shifts observed in these molecules [38-40], we

Table 4  
Rovibrational corrections to  $^{13}\text{C}$  shielding

Molecule	$\sigma_0(300\text{ K}) - \sigma_e(\text{ppm})^a)$	$\sigma_e(\text{ppm})$
$\text{CH}_4$	$-3.3 (-3.56)^b)$	198.7
$\text{CO}$	$-2.0$ (see text)	$3.0 \pm 0.9$
$\text{CO}_2$	$-1.5$	60.3
$\text{CS}_2$	$-2.1$	$-5.9$

<sup>a)</sup> Estimated from ref. [14]

<sup>b)</sup> Zero-point vibrational corrections reported by Fowler et al. [41].

calculate  $^1\Delta^R(\text{CH})$ . These contributions to the rovibrational corrections range from  $-0.65$  ppm per CH bond in  $\text{CH}_3\text{CN}$  to  $-1.26$  ppm in  $\text{C}_6\text{H}_6$ . Contributions from CC and CO bonds can be estimated from isotope shift data in other molecules [39], leading to rovibrational corrections of the order of  $-0.5$  to  $-1.5$  ppm for each CC bond,  $-0.5$  to  $-2$  ppm for C–O and  $-1.5$  to  $-3$  ppm for C=O bonds. Using these reduced isotope shifts, the rovibrational corrections are estimated to be  $-1.5$  to  $-4.5$  ppm for  $^{13}\text{C}$  in these molecules, of which a few are shown in table 4.

The theoretical  $\sigma_e$  values in table 1 can thus be corrected by the addition of  $-1.5$  to  $-4.5$  ppm in order to make a direct comparison with our  $\sigma_0(300\text{ K})$  data. Even with these corrections, there remain discrepancies between theoretical and experimental numbers:  $-25$  ppm in CO to  $14$  ppm in  $\text{CS}_2$ . (The theoretical value for TMS was calculated using a double-zeta basis set and is somewhat poorer.) We note that errors are worse for carbons which are not  $\text{sp}^3$  hybridized and which are attached to heteroatoms (i.e. not C or H). It is anticipated that larger basis sets and electron correlation corrections will eliminate these differences. Nevertheless, the agreement with experimental absolute shielding is generally good. We can therefore say that  $^{13}\text{C}$  shielding calculations have reached a point where we can believe the results to  $\pm 5$  ppm for most molecules. We can also see in which cases there is still room for improvement, namely in C=O environments. Photoelectron spectra reveal that  $n \rightarrow \pi^*$  excitations are relatively low-lying, giving rise to large  $\sigma^p$  contributions so that small relative errors in these terms can give rise to large errors in absolute shielding.

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