Carbon-13 Magnetic Shielding in Gaseous Carbon Dioxide

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Summary Studies of the ^{13}C shielding of gaseous carbon dioxide over ranges of density and temperature reveal unexpected results for the dependence of the shielding on the internal molecular motion and the intermolecular interaction.

THE nuclear magnetic shielding of a pure, imperfect gas can be expressed[1] as a power series in the molar volume V_m [equation (1)]. The coefficients σ_0, σ_1, σ_2 *etc.* are

$$\sigma = \sigma_0 + \sigma_1/V_m + \sigma_2/V_m^2 + \ldots \qquad (1)$$

temperature dependent and it has been found for most compounds that the shielding varies linearly with the density so that σ_2 and higher coefficients can be ignored. The past two years have seen the publication of more than a dozen papers reporting experimental work founded on equation (1). Early work on ^{1}H, ^{19}F, ^{31}P, and ^{129}Xe resonance in gases has been extended and several papers report the detection of a density dependence for the shielding of three nuclear species not previously studied. They are boron,[2] carbon,[2–6] and nitrogen.[3] The two principal reasons for these investigations are (a) the possibility of using accurate values of σ_0 and its temperature dependence to provide information about the variation of the shielding with the internal co-ordinates of the molecule[7] (the 'intramolecular shielding function') and (b) the hope that accurate values of σ_1 and its temperature dependence can lead to an understanding of how the shielding of a particular nucleus in a molecule depends on the distance to and the relative orientation of a perturbing molecule[1] (the 'intermolecular shielding function'). Further stimulus is provided by accurate *ab initio* calculation of the intramolecular and intermolecular shielding functions of simple systems.[8–10]

A compound for which gas phase ^{13}C n.m.r. results have proved elusive is carbon dioxide. Jameson *et al.*[3] found no detectable temperature dependence of σ_1 and obtained a temperature variation of 0·00054 p.p.m. deg^{-1} for σ_0 which is only *ca.* 10% of those obtained for the two distinct ^{15}N resonances in N_2O. A second problem concerns the composition of σ_1. This comprises a bulk susceptibility contribution $(\sigma_1)_b$ and a contribution $\sigma_1(A\text{–}A)$ which is due to interactions between pairs of A molecules. In the case of $^{13}CO_2$ gas this is expressed by equation (2). The value of

$$\sigma_1 = (\sigma_1)_b + \sigma_1(^{13}CO_2\text{–}^{13}CO_2) \qquad \cdots \quad \cdots \quad (2)$$

$(\sigma_1)_b$ for $^{13}CO_2$ gas in cylindrically shaped sample tubes with the external field transverse to the axis of the tubes is $-45{\cdot}0 \times 10^{-6}$ cm^3 mol^{-1}. Our earlier study[4] gave a value $\sigma_1 = -33(\pm 7) \times 10^{-6}$ cm^3 mol^{-1} for $^{13}CO_2$. Jameson *et al.*[3] obtained $-2{\cdot}0988 \times 10^{-3}$ p.p.m. amagat^{-1} which is $-47{\cdot}2 \times 10^{-6}$ cm^3 mol^{-1}. It is evident that the two investigations yielded values of $\sigma_1(^{13}CO_2\text{–}^{13}CO_2)$ which appear to differ in sign although that of Jameson *et al.* is, in fact, zero within experimental error. The present experimental work was undertaken to investigate these matters further.

Five gaseous samples of $^{13}CO_2$, each having a different density, were prepared and their ^{13}C nuclear shielding at −2, 22, 53, and 85 °C measured with respect to an appropriate external reference. The results are shown in the Table.† Assorted external references were necessary because of the wide temperature variation. For the two lower temperatures the results were put on the same scale, that relative to the ^{13}C shielding of Me_4Si, by using the observations σ(liq. Me_4Si, −2 °C) − σ(3% C_6H_6 in $CDCl_3$, −2 °C) = 129·224 p.p.m. and σ(liq. Me_4Si, 22 °C) −σ (3% C_6H_6 in C_6D_6, 22 °C) = 128·566 p.p.m. For the two higher temperatures the two results were placed on a scale with respect to the ^{13}C shielding of the methyl carbon nucleus of Bu^tOH by using the observations σ(Bu^tOH, 53 °C) −σ(3% C_6H_6 in C_6D_6, 53 °C) = 96·710 p.p.m. and σ(Bu^tOH, 85 °C) −σ(3% C_6H_6 in CD_3SOCD_3, 85 °C) = 98·900 p.p.m. Results converted to these references are also given in the Table. Least-squares fits were carried out to find the coefficients appropriate to equation (1) and the results are shown on the right hand side of the Table.

We first consider $\Delta\sigma_0$, the ^{13}C shielding of $^{13}CO_2$ gas at zero density with respect to Me_4Si at −2 and 22 °C and with respect to Bu^tOH at 53 and 85 °C. The first requirement is to correct for the temperature dependence of the reference shielding. Unfortunately, this cannot yet be made for Bu^tOH. However, the correction can be made for Me_4Si. For Me_4Si a careful study[11] of the temperature dependence of the ^{13}C shielding has given σ(liq, Me_4Si, *T*K) −σ(liq. Me_4Si, 300 K) = $0{\cdot}013191(T-300) + 1{\cdot}1907 \times 10^{-5}(T-300)^2$ p.p.m., from which one deduces that σ(liq. Me_4Si, 22 °C) −σ(liq. Me_4Si, −2 °C) = 0·307 p.p.m. Thus we finally obtain for $^{13}CO_2$ gas at zero density: σ(22 °C) −σ(−2 °C) = + 0·078 p.p.m. This is a rate of shielding change of +0·003 p.p.m. deg^{-1} which is of

TABLE. Shielding constant differences $\Delta\sigma$ (in p.p.m.) for $^{13}CO_2$ gas at different densities and temperatures with respect to a number of references and (at the right) the coefficients appropriate to equation (1) obtained by least squares fits. $\Delta\sigma_0$ is the shielding difference of the gas at zero density and the temperature stated from pure liquid Me_4Si or pure liquid t-butane (methyl resonance) as indicated in column 2. Shielding differences relative to Me_4Si and t-butane in columns 3—7 were obtained by applying corrections to those relative to benzene given in these columns.

		Density/g cm^{-3}						
Temp./°C	Shielding difference	0·013	0·020	0·050	0·070	0·112	$\Delta\sigma_0/10^{-6}$	$\sigma_1/10^{-6}$ cm^3 mol^{-1}
−2	$\Delta\sigma_B$[a]	5·217	5·217	5·181	5·181	5·132	—	
	$\Delta\sigma_{TMS}$[b]	−124·007	−124·007	−124·043	−124·043	−124·092	−123·993 (±0·006)	−38 (±4)
+22	$\Delta\sigma_B$[c]	4·332	4·332	4·289	4·289	4·247	—	
	$\Delta\sigma_{TMS}$[b]	−124·234	−124·234	−124·277	−124·277	−124·319	−124·222 (±0·006)	−39 (±4)
+53	$\Delta\sigma_B$[c]	4·198	4·168	4·168	4·143	4·113	—	
	$\Delta\sigma_{But}$[d]	−92·512	−92·542	−92·542	−92·567	−92·597	−92·512 (±0·009)	−34 (±6)
+85	$\Delta\sigma_B$[e]	5·193	5·145	5·145	5·145	5·108	—	
	$\Delta\sigma_{But}$[d]	−93·707	−93·755	−93·755	−93·755	−93·792	−93·719 (±0·015)	−28 (±10)

[a] With respect to 3% C_6H_6 in $CDCl_3$: [b] W.r.t. pure liq. Me_4Si: [c] W.r.t. 3% C_6H_6 in C_6H_6: [d] W.r.t. the methyl carbon of Bu^tOH. [e] W.r.t. 3% C_6H_6 in $(CD_3)_2SO$.

† ^{13}C chemical shifts were measured with a JEOL PFT 100 n.m.r. spectrometer. Gas samples were contained in sealed 5 mm o.d. sample tubes inserted in 10 mm o.d. sample tubes containing the references for −2 and +22 °C. All samples containing Me_4Si and Bu^tOH were sealed.

opposite sign and several times larger than that obtained by Jameson *et al.*[3] (see above). The result is quite unexpected since it is usual for shielding to diminish at higher temperature under the influence of increased rotational distortion. Jameson *et al.*[12] did find a similarly anomalous temperature dependence for σ_0 in the ^{31}P shielding of PH_3. However, they attributed the anomaly to the influence of HPH angle-bending which will contribute to $d\sigma/dT$ in first order. Such an explanation is not possible for a molecule as symmetric as CO_2.

At a superficial level σ_1 does appear to become less negative with increasing temperature as can be seen from the Table. However, the experimental precision is still not quite adequate enough to discern a trend of σ_1 with respect to temperature. Nevertheless the results for σ_1 are in general agreement with our earlier result[4] of $-33(\pm 7) \times 10^{-6}$ cm^3 mol^{-1} and, after correction for $(\sigma_1)_b$, lead to a value for $\sigma_1(^{13}CO_2-^{13}CO_2)$ of *ca.* $+10 \times 10^{-6}$ cm^3 mol^{-1}. Again this is a quite unexpected result since σ_1 is invariably found to be negative after correcting the susceptibility (*i.e.* intermolecular interaction decreases the shielding).

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