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Nuclear Magnetic Shielding and Spin−Spin Coupling of 1,2-^{13}C-Enriched Acetylene in Gaseous Mixtures with Xenon and Carbon Dioxide

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^{13}C and ^{1}H NMR spectra have been measured for 1,2-^{13}C-acetylene at low density in binary mixtures with xenon and carbon dioxide gases as the solvents. It was found that both the chemical shifts and the ^{1}J(CC) coupling constant of $^{13}C_2H_2$ were linearly dependent on the solvent density. The appropriate NMR parameters for an isolated $^{13}C_2H_2$ molecule were determined, together with the coefficients responsible for the solute−solvent molecular interactions. The ^{13}C NMR measurements were extended to solutions of 1,2-^{13}C-acetylene in liquid solvents. All of the ^{13}C gas-to-solution shifts were found to be positive (deshielding effects), and the ^{1}J(CC) coupling constant in liquid acetone was diminished by more than 5% in comparison with the value of 174.78 Hz observed in the gas phase.

Introduction

Acetylene (C_2H_2) is an interesting compound mostly because of its role as a reactant in numerous organic syntheses. Since 1962, the ^{1}H and ^{13}C NMR spectra of various isotopomers of acetylene have been investigated. Previous studies have provided information on chemical shifts, spin−spin coupling constants, and isotope effects.[1−6] For ^{13}C-enriched acetylene, it is possible to observe four coupling constants: ^{1}J(CC), ^{1}J(CH), ^{2}J(CH), and ^{3}J(HH).

Unfortunately, acetylene is an explosive gas when compressed, and the earlier experimental work has been mostly limited to liquid solutions. In one case, the NMR spectra were observed for liquid acetylene at low temperature (−70 °C),[2] and one result for ^{13}C magnetic shielding of gaseous acetylene was reported.[5] It seems that the existing NMR data on acetylene are still not sufficiently accurate. On the other hand, acetylene as a small molecular system is attractive for ab initio calculations,[6−19] among which are those intended to test new computational methods for determining nuclear shielding and spin−spin coupling constants.[8,20,21] The latter data should be compared with the NMR measurements for an isolated C_2H_2 molecule, and such results can be obtained only in the gas phase.[22,23] Also, the attempted theoretical estimations of environmental effects on acetylene NMR parameters[19] creates a demand for such measurements as reported in this work.

In this paper, we present gas-phase measurements of the ^{1}H and ^{13}C NMR chemical shifts and spin−spin coupling constants for 1,2-^{13}C-enriched acetylene ($^{13}C_2H_2$) at very low density. 1,2-^{13}C-acetylene gives an AA′XX′ NMR spectrum[24] of which the AA′ and XX′ parts can be separately monitored by the ^{1}H and ^{13}C NMR methods. Xenon and carbon dioxide have been used as the gaseous solvents. This enabled us to observe the ^{1}H and ^{13}C NMR spectra of $^{13}C_2H_2$ as a function of xenon (or carbon dioxide) density, and after extrapolation to zero density, it was possible to determine the shielding and spin−spin coupling constants independent of the gaseous solvent. The latter values were corrected for acetylene−acetylene intermolecular interactions, and in this way, we could determine reliable NMR parameters for an isolated $^{13}C_2H_2$ molecule. In addition, we have also investigated the NMR spectra when acetylene was diluted in some liquid solvents. The appropriate gas-to-solution effects were determined, and they confirmed the medium influence on all of the monitored NMR parameters of 1,2-^{13}C-acetylene.

Experimental Section

NMR spectra were obtained on a Varian UNITYplus-500 FT spectrometer (at 125.88 MHz for ^{13}C and at 500.60 MHz for ^{1}H) under following conditions: temperature, 300 K; spectral width, 520 Hz; 32 K data points with double precision and digital resolution of 0.02 Hz/point. Both the ^{1}H and the ^{13}C NMR spectra were jointly used for the measurements of the spin−spin coupling constants. The chemical shifts were observed using a relatively larger spectral width: 7500 Hz for ^{13}C NMR experiments and 2000 Hz for ^{1}H NMR experiments. Gas samples were prepared by the condensation of pure gases from the calibrated part of the vacuum line into 4-mm o.d. glass tubes (approximately 5 cm long), which were sealed. The glass tubes were slightly longer (up to 7 cm) for liquid solvents, for which the level of liquid phase was 5 cm high. The volumes of the sample tubes and the vacuum line were measured using mercury. 1,2-^{13}C-acetylene (ABCR Karlsruhe, Germany), xenon (99.9%, Messer Duisburg, Germany), and carbon dioxide (99.8%, Aldrich) from lecture bottles were used to prepare samples without further purification. The solute gas ($^{13}C_2H_2$) was used at low pressure (∼0.7 atm) and mixed with various quantities of the gaseous solvents (approximately 7−49 atm). The liquid solvents were carefully dehydrated and degassed before $^{13}C_2H_2$ was added. The sealed 4-mm o.d. gas samples were fit into standard 5-mm o.d. thin-walled NMR tubes (Wilmad 528-PP) with liquid benzene-d_6 in the annular space. Benzene-d_6 was used for the lock system and as the external reference standard. Later, the chemical shifts were expressed relative to external liquid TMS. Three to five spectra were recorded for each sample in order to avoid accidental errors and increase the precision of measurements.

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TABLE 1: ^{13}C and ^{1}H Magnetic Shielding and ^{13}C−^{13}C Spin−Spin Coupling of 1,2-^{13}C-acetylene and Their Dependence on Density in Binary Mixtures with Xenon and Carbon Dioxide at 300 K

	gas solvent (B)	
parameter	Xe	CO$_2$
^{13}C and ^{1}H Magnetic Shielding		
σ_o(C) (ppm)[a]	116.58 ± 0.9	116.58 ± 0.9
σ_o(H) (ppm)[a]	29.278 ± 0.024	29.276 ± 0.024
$(\sigma_A)_b$ (ppm mL mol^{-1})[b,c]	87.1	87.1
$(\sigma_B)_b$ (ppm mL mol^{-1})[b]	190.8	87.1
σ_{AA}(C) (ppm mL mol^{-1})[c,d]	−122	−122
σ_{AB} (C) (ppm mL mol^{-1})	−76 ± 5	−93 ± 5
$\sigma_{1(A-B)}$(C) (ppm mL mol^{-1})	−267 ± 5	−180 ± 5
σ_{AA}(H) (ppm mL mol^{-1})[c,d]	76	76
σ_{AB}(H) (ppm mL mol^{-1})	162 ± 3	60 ± 3
$\sigma_{1(A-B)}$(H) (ppm mL mol^{-1})	−29 ± 3	−27 ± 3
Spin−Spin Coupling between ^{13}C Nuclei		
J_o(CC) (Hz)	174.77 ± 0.02	174.78 ± 0.02
J_{AB}(CC) (Hz mL mol^{-1})	−30 ± 20	−301 ± 20

[a] Absolute shielding assuming $\sigma_o(\underline{C}O) = 0.6 \pm 0.9$ ppm[27] and $\sigma_o(C\underline{H}_4) = 30.611 \pm 0.024$ ppm.[28] [b] $-(4\pi/3)\chi_M$, where χ_M is the molar susceptibility of solvent gas.[31] [c] Specified only by the properties of acetylene. [d] Estimated from the σ_1(C) and σ_1(H) parameters of ethylene[26,22] and the molar susceptibility of acetylene.[31]

Results and Discussion

In the present study, we have found that the AA′ and XX′ parts of an AA′XX′ spectrum for gaseous 1,2-^{13}C-acetylene are well resolved in ^{1}H and ^{13}C NMR spectra if the pressure of gas components exceeds 6 atm. This could not be safely done with pure acetylene, so we used xenon (Xe) and carbon dioxide (CO$_2$) as the gaseous solvents. For a binary mixture of gas A, containing the nucleus X whose shielding σ(X) is of interest, and gas B as the solvent, the shielding of nucleus X can be written as[22]

$$\sigma(X) = \sigma_o(X) + \sigma_{AA}(X)\rho_A + \sigma_{AB}(X)\rho_B + ... \qquad (1)$$

where ρ_A and ρ_B are the densities of A and B, respectively, and σ_o(X) is the shielding for an isolated molecule. The coefficients σ_{AA}(X) and σ_{AB}(X) contain the bulk susceptibility corrections [$(\sigma_A)_b$ and $(\sigma_B)_b$], and the terms taking account of intermolecular interactions during the binary collisions of A−A and A−B molecules are $\sigma_{1(A-A)}$(X) and $\sigma_{1(A-B)}$(X), respectively.[25] It is worth noting that the shielding parameters in eq 1 are temperature-dependent, and for this reason, all of the present measurements have been performed at the constant temperature of 300 K. Figure 1a and b shows plots of the ^{13}C and ^{1}H NMR chemical shifts of 1,2-^{13}C-acetylene as a function of density for xenon and carbon dioxide. The density dependence is linear in every case, and it allows one to determine the quantities $\sigma_o + \sigma_{AA}\rho_A$ and σ_{AB}. The first term is almost equal to the shielding in an isolated molecule (σ_o), as the acetylene density (ρ_A) is constant and very small. We have assumed that the intermolecular interactions in the gas phase are of the same order of magnitude for acetylene and ethylene because such an approximation is sufficiently good for all other molecules of light hydrocarbons.[22,26] Then, we could use the σ_1 parameters for ethylene[22,26] and the susceptibility of acetylene[31] in order to estimate the $\sigma_{AA}\rho_A$ terms in eq 1. The value of −0.007 ppm has been obtained from the ^{13}C-shielding and +0.004 ppm from the ^{1}H-shielding. The small $\sigma_{AA}\rho_A$ terms are nevertheless included in the final results, which are shown in Table 1. The absolute shielding constants have been determined using an improved carbon-13 scale [$\sigma_o(CO) = 0.6 \pm 0.9$ ppm],[27] the proton shielding of methane [$\sigma_o(CH_4) = 30.611 \pm 0.024$ ppm],[28] and our measurements of the latter parameters at 300 K: $\sigma_o(^{13}C_2H_2) - \sigma_o(CO) = 115.98$ ppm and $\sigma_o(^{13}C_2H_2) - \sigma_o(CH_4) = -1.334 \pm 0.002$ ppm or σ(liq TMS) − $\sigma_o(CO) = 186.07$ ppm and σ(liq TMS) − $\sigma_o(CH_4) = 2.874$ ppm (for liquid TMS sealed in a cylindrical tube and a parallel external magnetic field). Our final result for the ^{13}C-shielding of 1,2-^{13}C-acetylene is very close to the value given by Jameson et al.[5] [$\sigma_o(C_2H_2) = 116.8$ ppm at 300 K, if corrected for the same scale of carbon-13 shielding[27]]. Intermolecular interactions between acetylene and solvent molecules lead to the deshielding effects in both the ^{13}C and the ^{1}H NMR spectra, as described by the $\sigma_{1(A-B)}$ parameters in Table 1. The intermolecular effect is quite modest for protons, and the direct observation of ^{1}H NMR spectra reveals mostly the influence of magnetic susceptibility, cf. the apparent increase of proton shielding in Figure 1b.

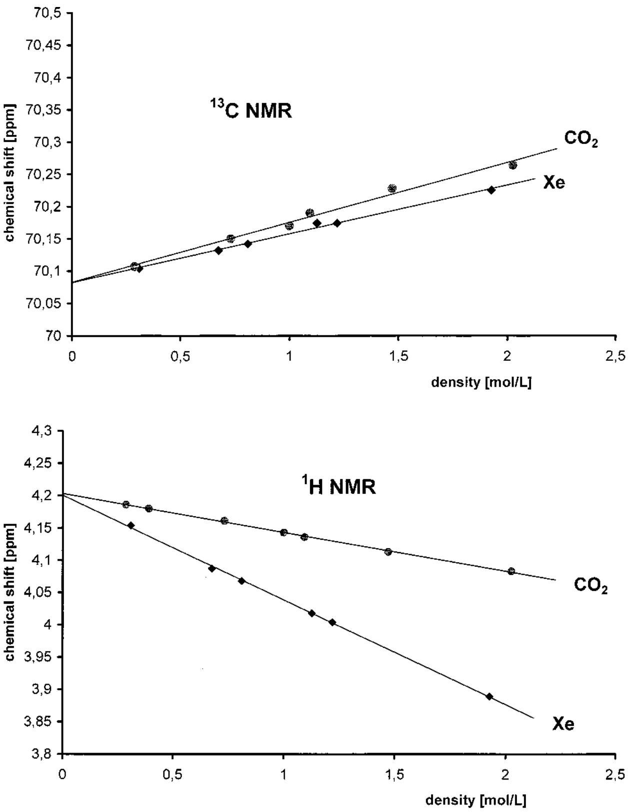

Figure 1. Density dependence of the (a) ^{13}C and (b) ^{1}H chemical shifts of 1,2-^{13}C-acetylene in binary mixtures with xenon and carbon dioxide with respect to the shielding of pure liquid TMS at 300 K [$\delta(i) = \sigma(TMS) - \sigma(i)$]. The absolute shielding of liquid TMS: $\sigma[Si(CH_3)_4] = 186.67$ ppm and $\sigma[Si(CH_3)_4] = 33.485$ ppm, as described in the text.

In the gas phase, nuclear spin−spin coupling is also modified by interactions between pairs of molecules and multiple interactions; the appropriate equation for the binary mixtures of gases (A and B) is similar to eq 1 at constant temperature

$$J = J_o + J_{AA}\rho_A + J_{AB}\rho_B + ... \qquad (2)$$

where J_o is the spin−spin coupling for an isolated molecule and J_{AA} and J_{AB} are solely due to intermolecular effects in the binary collisions of A−A and A−B molecules, respectively. In the present work, the density of A ($^{13}C_2H_2$) has been kept sufficiently low for eq 2 to simplify to

$$J = J_o + J_{AB}\rho_B \qquad (3)$$

TABLE 2: Spin-Spin Coupling Constants (Hz)[a] and Carbon Gas-to-Solution Shifts (ppm) for 1,2-^{13}C-acetylene

C_2H_2 sample	NMR method	^1J(CC)	^1J(CH)	^2J(CH)	^3J(HH)	$\Delta\delta$(C)[b]	ref
dissolved in CCl_4	^{1}H	171.5 ± 0.2	248.4 ± 0.3	49.4 ± 0.2	9.5		1
liquid at −70 °C	^{1}H	171.6, 170.6	249.0,248.7	49.3, 49.7	9.55, 9.8		2
dissolved in C_6H_6[c]	^{1}H, ^{13}C		249.0	49.6	9.5		3
in $(CD_3)_2CO$[c]	^{13}C		248.29 ± 0.03	49.74 ± 0.03			4
in LC solutions[d]	^{1}H, ^{13}C	169.63−169.82	248.12−248.29	49.20−49.26	9.41−9.50		6
in $(CH_3)_2CO$	^{13}C	165.8	248.3	49.9	9.6	+6.23	this work
in CH_3CN	^{13}C	166.4	248.8	49.9	9.6	+6.04	this work
in CH_2I_2	^{13}C	169.2	249.4	49.1	9.5	+8.23	this work
in $(CH_3)_3COH$	^{13}C	169.3	248.1	49.7	9.6	+5.84	this work
in C_6H_6	^{13}C	170.6	248.4	49.6	9.5	+4.71	this work
in $CHCl_3$	^{13}C	170.7	248.9	49.6	9.5	+5.55	this work
in $(CH_3)_3SiCCH$	^{13}C	171.4	248.5	49.7	9.5	+5.09	this work
in c−C_6H_{12}	^{13}C	173.6	248.1	49.7	9.5	+3.96	this work
isolated molecule	^{1}H, ^{13}C	174.78 ± 0.02	247.56 ± 0.05	50.14 ± 0.05	9.62 ± 0.05	0.00	this work

[a] ±0.1 Hz or as described. [b] The positive value means deshielding of carbon nuclei. [c] Measured for 1-^{13}C-acetylene. [d] Liquid-crystalline solution.

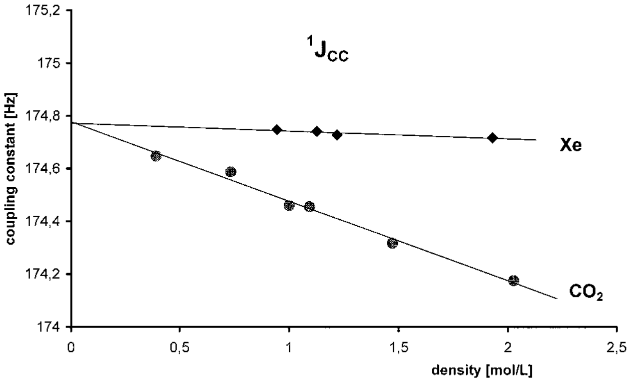

Figure 2. ^{13}C−^{13}C spin−spin coupling in 1,2-^{13}C-acetylene as a function of density for gaseous solvents xenon and carbon dioxide at 300 K.

We have monitored all four spin−spin couplings for 1,2-^{13}C-acetylene in gaseous mixtures with xenon and carbon dioxide. Figure 2 shows the distinct density dependence that has been found for the ^{13}C−^{13}C coupling in $^{13}C_2H_2$. This is the first observation of such an effect between carbon nuclei. For the $^{13}C_2H_2$/Xe mixture, the dependence is quite modest [cf. $J_{AB}(CC) = -30 \pm 20$ Hz mL mol^{-1} in Table 1], but for the $^{13}C_2H_2/CO_2$ solutions, intermolecular interactions diminish the J(CC) coupling much more strongly [$J_{AB}(CC) = -301 \pm 20$ Hz mL mol^{-1} in Table 1). The latter result is even more pronounced than the density dependence of $^1J(^{29}Si^{19}F)$ in SF_6 and of $^1J(^{11}B^{19}F)$ in BF_3, as reported by Jameson et al.[29,30] It is interesting that the density dependence of carbon−carbon coupling permits one to determine the ^1J(CC) constant with greater accuracy than would be possible without the dependence. The value of 174.78 ± 0.02 Hz can be safely accepted as the reliable value of ^1J(CC) for an isolated $^{13}C_2H_2$ molecule at 300 K. The other coupling constants [^1J(CH), ^2J(CH), and ^3J(HH)] have been measured in the same experiments, but each of their density dependences has been within experimental error. The final results are given in Table 2, together with previous measurements carried out in different experimental conditions[1−4,6] and our observations in liquid solvents. Table 2 confirms once again that the ^1J(CC) coupling in $^{13}C_2H_2$ is the most sensitive to intermolecular interactions; it varies from 174.78 Hz for an isolated molecule to 165.8 Hz for the solution in acetone, i.e., more than 5%. It is interesting to admit that intermolecular interactions diminish the ^1J(CC) coupling constant, whereas the smaller effects on ^1J(CH) have the opposite sign. Table 2 also gives the ^{13}C gas-to-solution shifts, which reveal deshielding effects for 1,2-^{13}C-acetylene in the liquid solutions.

Conclusions

The present study yields experimental results for the ^{13}C and ^{1}H magnetic shielding and spin−spin coupling constants of 1,2-^{13}C-acetylene in the gas phase. We have found distinct density dependences of nuclear magnetic shielding and ^{13}C−^{13}C coupling for the $^{13}C_2H_2$/Xe and $^{13}C_2H_2/CO_2$ binary mixtures. The appropriate parameters for an isolated $^{13}C_2H_2$ molecule have been determined with high accuracy. Our new results permit us to judge the quality of numerous ab initio calculations of NMR parameters for acetylene; the calculations themselves have been carefully discussed in a few recent papers.[6,13,18] The present study also shows that intermolecular interactions cannot be neglected a priori if precise measurements of spin−spin coupling constants are required.

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