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# $^{15}\text{N}$ , $^{13}\text{C}$ and $^1\text{H}$ nuclear magnetic shielding and spin–spin coupling constants of 1- $^{13}\text{C}$ , $^{15}\text{N}$ -enriched acetonitrile in gaseous mixtures with $\text{SF}_6$ and $\text{CO}_2$

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## Abstract

The  $^{15}\text{N}$ ,  $^{13}\text{C}$ , and  $^1\text{H}$  absolute magnetic shielding of a  $\text{CH}_3\text{}^{13}\text{C}\text{}^{15}\text{N}$  molecule has been determined from NMR measurements in the gas phase at 300 K:  $\sigma_0(\text{CN}) = -8.873(5)$  ppm,  $\sigma_0(\underline{\text{CN}}) = 74.021(3)$  ppm and  $\sigma_0(\text{CH}_3) = 29.113(1)$  ppm. It is shown that intermolecular shielding effects for the  $^{13}\text{C}$  and  $^{15}\text{N}$  nuclei in the cyano group are large and in the opposite directions. For the first time the dependence on density has also been observed for the  $^1J(\text{NC})$ ,  $^2J(\text{CH})$  and  $^3J(\text{NH})$  spin–spin coupling when the HSQC spectra of  $\text{CH}_3\text{}^{13}\text{C}\text{}^{15}\text{N}$  have been analyzed. It has permitted us to obtain the coupling constants free from intermolecular interactions:  $^1J_0(\text{NC}) = -16.20(1)$  Hz,  $^2J_0(\text{CH}) = -10.18(2)$  Hz and  $^3J_0(\text{NH}) = -1.34(2)$  Hz. The new experimental results may be useful for the verification of appropriate ab initio calculations for an acetonitrile molecule. © 2002 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Acetonitrile ( $\text{CH}_3\text{CN}$ ) is an important organic solvent because of its physical and chemical properties.  $\text{CH}_3\text{CN}$  is also frequently used as a substrate in various organic syntheses. Its molecule with a large dipole moment ( $\mu = 1.30 \times 10^{-29}$  C m [1]) can form a well-defined structure even in the liquid state, as concluded from thermodynamic, dielectric, spectroscopic, X-ray and neutron scattering studies [2,3]. Theoretical and experimental

investigations show two types of molecular association in liquid acetonitrile: the linear head-to-tail polymers and the antiparallel structures [2–7] which make up clusters of  $\text{CH}_3\text{CN}$  molecules [8].

Strong intermolecular interactions obviously change NMR spectral parameters of an acetonitrile molecule in the liquid state. It has been already shown that the condensation of  $\text{CH}_3\text{CN}$  molecules leads to the significant increase of  $^{15}\text{N}$  magnetic shielding [9] and the decrease of nuclear magnetic shielding of all the other nuclei, i.e.  $^1\text{H}$  and  $^{13}\text{C}$  [10–12]. It is worth noticing that the previous investigations of nuclear magnetic shielding of acetonitrile in the gas phase have not been complete. It seems that the  $^{15}\text{N}$  and  $^1\text{H}$  shielding of  $\text{CH}_3\text{CN}$  has been not obtained at the zero-density

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limit. Similar studies on spin–spin coupling constants of  $\text{CH}_3\text{CN}$  were never carried out and all the  $^nJ$  results of ab initio calculations [13] were compared with the measurements of constants obtained for liquid acetonitrile [14].

Modern 2D NMR techniques [15] provide spectral parameters with better precision and deliver more information than standard 1D spectra. In the present work we have used this opportunity in order to measure the spin–spin coupling and shielding constants of acetonitrile- $1\text{-}^{13}\text{C}$ ,  $^{15}\text{N}$  in the gas phase. Sulfur hexafluoride ( $\text{SF}_6$ ) and carbon dioxide ( $\text{CO}_2$ ) have been used as the gas solvents. It permitted us to observe the studied parameters at extreme low pressure of  $\text{CH}_3\text{-}^{13}\text{C}\text{-}^{15}\text{N}$  ( $\sim 19$  Torr) and as a function of solvent density. Then the measurements were extrapolated to the zero-density limit and the spectral parameters of  $\text{CH}_3\text{-}^{13}\text{C}\text{-}^{15}\text{N}$  free from intermolecular interactions with solvent molecules could successfully be determined.

## 2. Experimental

### 2.1. Preparation of samples

Gas samples were prepared by condensation of  $\text{CH}_3\text{-}^{13}\text{C}\text{-}^{15}\text{N}$  vapor and pure solvent gas ( $\text{SF}_6$  or  $\text{CO}_2$ ) from the calibrated part of vacuum line into the 4.0 mm o.d. glass tubes (approx. 5.5 cm long) which were then sealed. The volumes of sample tubes and the vacuum line were measured using mercury. Acetonitrile- $1\text{-}^{13}\text{C}\text{-}^{15}\text{N}$  (99%  $^{13}\text{C}$  and 99%  $^{15}\text{N}$ , Aldrich) from a glass container and sulfur hexafluoride (99.75%, Aldrich) or carbon dioxide (99.8%, Aldrich) from lecture bottles were used to prepare samples without further purification. In the gaseous mixtures the solute gas ( $\text{CH}_3\text{-}^{13}\text{C}\text{-}^{15}\text{N}$ ) has been used at a low constant density ( $\sim 0.001$  mol/l, pressure  $\sim 19$  Torr) and mixed with various quantities of the gaseous solvents:  $\text{SF}_6$  or  $\text{CO}_2$  (from 0.076 to 0.825 mol/l). The gas samples were fitted into the standard 5 mm o.d. thin-walled NMR tubes (Wilma 528-PP) with liquid toluene- $d_8$  in the annular space. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts were measured relative to neat liquid TMS as the external reference standard. For

this purpose the absolute frequencies of the TMS resonance was determined in the conditions of lock system tuned to the  $\text{CD}_3$  signal of external toluene- $d_8$ . The constant frequency of the lock system (76.8464 MHz) allows one to preserve the same  $B_0$  for all measurements. The absolute magnetic shielding of TMS (32.775 ppm for protons and 186.37 ppm for  $^{13}\text{C}$  nuclei in a cylindrical tube parallel to an external magnetic field) [16,17] was used to convert the NMR chemical shifts into the shielding parameters of  $\text{CH}_3\text{-}^{13}\text{C}\text{-}^{15}\text{N}$ . Liquid nitromethane ( $\text{CH}_3\text{NO}_2$ ) was used in the same way for the measurements of  $^{15}\text{N}$  nuclear magnetic shielding. Its own shielding ( $\sigma(\text{CH}_3\text{NO}_{2,\text{liq.}}, \|B_0) = -134.14$  ppm) was determined from the  $^{15}\text{N}$  chemical shift measured relative to gaseous ammonia at the zero-density limit [18] and assuming the value of  $\sigma_0(\text{NH}_3) = 264.54$  ppm [19] as the absolute  $^{15}\text{N}$  shielding of ammonia.

### 2.2. NMR spectra

All NMR spectra were acquired at 300 K on a Varian Unity Plus 500 spectrometer equipped with a Performa I z-PFG unit and a standard 5 mm ID-PFG probehead with actively shielded z-gradient coil. The PFG pulses with the duration of 2 ms and strength of 10 G/cm followed by 100  $\mu\text{s}$  recovery delay were used in HSQC experiments. 7, 12 and 27  $\mu\text{s}$  high power  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{15}\text{N}$   $\pi/2$  pulses, respectively were employed.

For the one-dimensional experiments the standard single-pulse technique was employed, with the spectrometer frequencies of 500.62, 125.89 and 50.6 MHz, for  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{15}\text{N}$ , respectively. For the acquisition of 2D spectra, necessary for the measurements of passive  $^{15}\text{N}\text{-}^1\text{H}$ ,  $^{13}\text{C}\text{-}^1\text{H}$  and  $^{15}\text{N}\text{-}^{13}\text{C}$  coupling constants, modified PFG-HSQC sequence was used. The application of commonly used standard HSQC technique with gradient echo–antiecho coherence selection e.g. [20], was not successful due to signal attenuation caused by very effective diffusion in gases. We use instead, selection of doubly longitudinal two spin  $2I_zS_z$  coherence by application of two opposite sign gradient pulses during both INEPT steps [21]. This technique enables rejecting of all unwanted transverse magnetization and is not sensitive to diffu-

sion and convection effects. In order to reduce signal losses owing to fast transverse relaxation the refocusing period before  $t_2$  data acquisition was omitted and consequently purely absorptive correlation signals appear with the active coupling in antiphase along the  $F_2$  domain. The examples of HSQC spectra obtained in this way are shown at Fig. 1a,b.

The magnitudes of passive coupling constants (involving  $^{15}\text{N}$  and  $^{13}\text{C}$  nuclei in the  $^1\text{H}$ – $^{13}\text{C}$  and

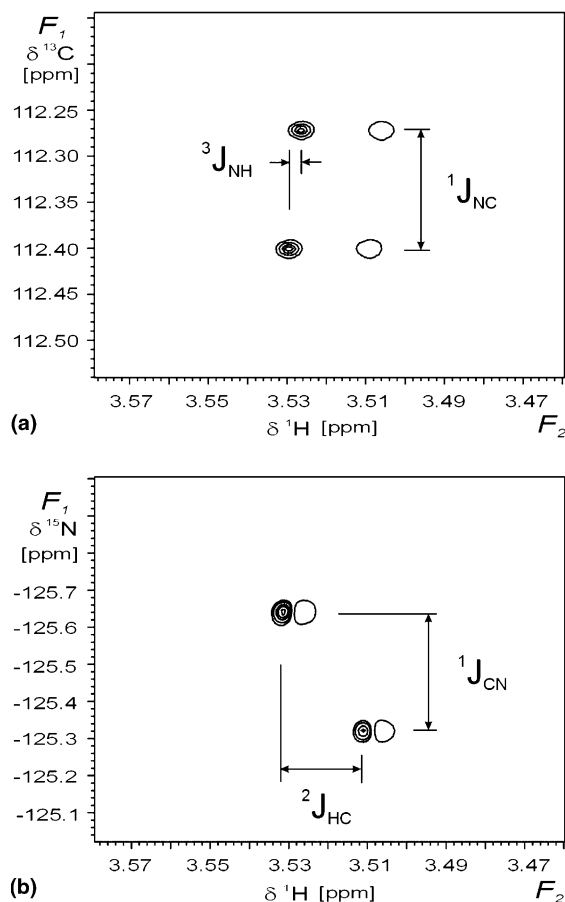


Fig. 1. The contour plot of HSQC spectra obtained for the sample of  $\text{CH}_3^{13}\text{C}^{15}\text{N}$  in  $\text{SF}_6$  (at maximum density of  $\text{SF}_6$ ). For the negative cross-peak components only one contour level is shown. The active couplings appear in antiphase along  $F_2$  domain, whereas passive ones form E.COSY cross-peak pattern. (a)  $^1\text{H}$ – $^{13}\text{C}$  experiment with polarization transfer via  $^2J(^{13}\text{C}$ – $^1\text{H})$ , (b)  $^1\text{H}$ – $^{15}\text{N}$  experiment using  $^3J(^{15}\text{N}$ – $^1\text{H})$ . The apparent cross-peak tilt reveals the same sign of all involved passive coupling constants. (Note the negative sign of  $\gamma(^{15}\text{N})$  [22].)

$^1\text{H}$ – $^{15}\text{N}$  correlation experiments, respectively), were obtained from the relevant splittings in both dimensions. In case of  $^1J(^{15}\text{N}$ – $^{13}\text{C})$  coupling constant, which was available from both 2D spectra (see Fig. 1), the values obtained from  $^1\text{H}$ – $^{15}\text{N}$  HSQC experiments appear to be more accurate due to better separation of the adequate cross-peak components in the  $F_2$  domain. The relative signs of the two pairs of coupling constants:  $^1J(^{15}\text{N}$ – $^{13}\text{C})/{}^3J(^{15}\text{N}$ – $^1\text{H})$  and  $^1J(^{15}\text{N}$ – $^{13}\text{C})/{}^2J(^{13}\text{C}$ – $^1\text{H})$  were determined from the cross-peak tilt direction, in  $^1\text{H}$ – $^{13}\text{C}$  and  $^1\text{H}$ – $^{15}\text{N}$  HSQC spectra, respectively. The results reveal the same sign of all three observed passive couplings, which agree with ab initio calculations [13]. Note, that however, acquired and processed in the standard way  $^1\text{H}$ – $^{15}\text{N}$  HSQC spectrum (Fig. 1b), reveals opposite cross-peak tilting, it should be reversed owing to negative sign of  $\gamma(^{15}\text{N})$  [22].

For all correlation experiments four scans were coherently added for each data set in the States – TPPI manner [23]. The maximum  $t_1$  times were set to 0.5 and 0.7 s for low and high density samples, respectively. The  $t_2$  times were sampled up to 0.5 s. A relaxation delay of 1.7 s was used. The initial polarization transfer was tuned to the active coupling  $^2J(^{13}\text{C}$ – $^1\text{H})$  of 10.3 Hz and  $^3J(^{15}\text{N}$ – $^1\text{H})$  of 1.8 Hz, for  $^1\text{H}$ – $^{13}\text{C}$  and  $^1\text{H}$ – $^{15}\text{N}$  HSQC experiments, respectively. The complex data matrix was multiplied by cosine function in both time domains and zero-filled to prior to Fourier transformation to achieve the digital resolution of 0.25 and 0.2 Hz/point in the  $F_1$  and  $F_2$  dimensions, respectively. Further increasing of the data matrix size did not change the evaluated coupling magnitudes.

### 3. Results and discussion

For a binary mixture of gas A, containing the nucleus X whose shielding  $\sigma(\text{X})$  is of interest, and gas B as the solvent, it can written according to the RBB approximation [24]:

$$\sigma(\text{X}) = \sigma_0(\text{X}) + \sigma_{\text{AA}}(\text{X})\rho_{\text{A}} + \sigma_{\text{AB}}(\text{X})\rho_{\text{B}} + \dots, \quad (1)$$

where  $\rho_A$  and  $\rho_B$  are the densities of A ( $\text{CH}_3^{13}\text{C}^{15}\text{N}$ ) and B ( $\text{SF}_6$  or  $\text{CO}_2$ ), respectively and  $\sigma_0(\text{X})$  is the shielding at the zero-density limit. The coefficients  $\sigma_{AA}(\text{X})$  and  $\sigma_{AB}(\text{X})$  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 ( $\sigma_{I(A-A)}(\text{X})$  and  $\sigma_{I(A-B)}(\text{X})$ ), respectively. It is worth noting that the shielding parameters in Eq. (1) are temperature dependent and for this reason all the present measurements have been performed at the constant temperature of 300 K.

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:

$$J(\text{XY}) = J_0(\text{XY}) + J_{AA}(\text{XY})\rho_A + J_{AB}(\text{XY})\rho_B + \dots, \quad (2)$$

where  $J_0(\text{XY})$  is the spin–spin coupling between X and Y nuclei at the zero-density limit and  $J_{AA}(\text{XY})$ ,  $J_{AB}(\text{XY})$  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 has been kept sufficiently low for Eqs. (1) and (2) to simplify to

$$\sigma(\text{X}) = \sigma_0(\text{X}) + \sigma_{AB}(\text{X})\rho_B, \quad (3)$$

$$J(\text{XY}) = J_0(\text{XY}) + J_{AB}(\text{XY})\rho_B. \quad (4)$$

According to Eqs. (3) and (4) the spectral NMR parameters ( $\sigma(\text{X})$  and  $J$ ) at constant temperature are expected to be linearly dependent on the density of solvent gas. Fig. 2 displays the dependence of  $^{13}\text{C}(-\text{CN})$ ,  $^1\text{H}$  and  $^{15}\text{N}$  magnetic shielding in  $\text{CH}_3^{13}\text{C}^{15}\text{N}$  on the density of solvent gases ( $\text{SF}_6$  or  $\text{CO}_2$ ) when the solute compound has been used at low and constant pressure (approx. 19 Torr). All the plots are linear and their extrapolation to the zero-density limit delivers the  $\sigma_0$  parameters for gaseous acetonitrile but the measurements for  $\text{SF}_6$  solution give slightly more precise results. The appropriate  $\sigma_0(\text{H})$ ,  $\sigma_0(\text{C})$  and  $\sigma_0(\text{N})$  values obtained in this work are shown in Table 1. The present measurement of  $\sigma_0(\underline{\text{CN}}) = 74.021(3)$  is in

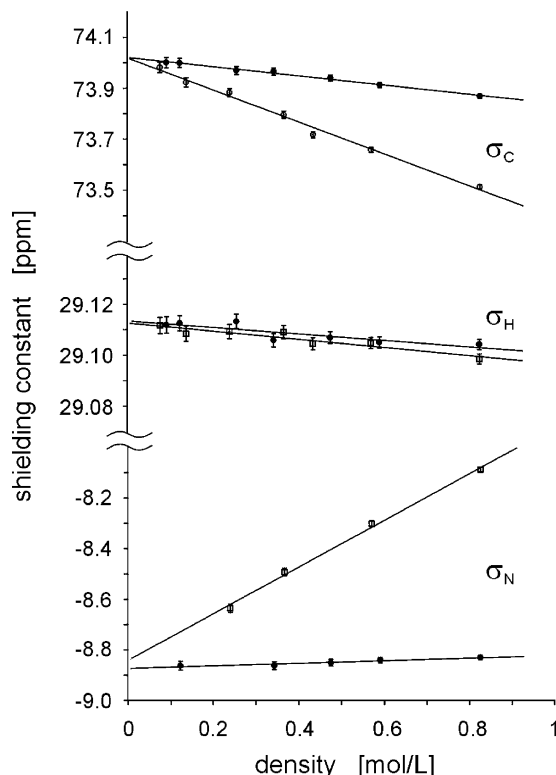


Fig. 2. The dependence of  $^{13}\text{C}(-\text{CN})$ ,  $^1\text{H}$  and  $^{15}\text{N}$  magnetic shielding in  $\text{CH}_3^{13}\text{C}^{15}\text{N}$  on the density of solvent gases (sulfur hexafluoride,  $\text{SF}_6$  (●) and carbondioxide,  $\text{CO}_2$  (□)) at 300 K. The solute compound has been observed at low and constant pressure (approx. 19 Torr). The results are corrected for bulk susceptibility effects.

good agreement with the result  $\sigma_0(\underline{\text{CN}}) = 73.8$  ppm given by Jameson and Jameson [10]. One should remember that the secondary isotope effect due to the exchange of  $^{15}\text{N}/^{14}\text{N}$  nuclei slightly increases the present result obtained for a  $\text{CH}_3^{13}\text{C}^{15}\text{N}$  molecule. It seems that the  $\sigma_0(\underline{\text{CN}})$  and  $\sigma_0(\text{H})$  shielding parameters of  $\text{CH}_3\text{CN}$  has never been obtained. However, the  $^{15}\text{N}$  NMR chemical shift of acetonitrile vapor has been measured by Litchman et al. [9] and its shielding has been estimated by Jameson et al. [19] as equal to  $-9.1$  ppm at 227.5 K. It looks like that the present measurements of  $\sigma_0(\underline{\text{CN}}) = -8.873(5)$  ppm and  $\sigma_0(\text{H}) = 29.113$  ppm are more accurate than any previous similar data and they may be used as the experimental standards.

Table 1

Nuclear magnetic shielding and spin–spin coupling of gaseous acetonitrile-1- $^{13}\text{C}$ ,  $^{15}\text{N}^{\text{a}}$  and their dependence on density in binary mixtures with sulfur hexafluoride and carbon dioxide at 300 K

Parameter	Gas solvent (B)	
	SF <sub>6</sub>	CO <sub>2</sub>
<sup>1</sup> H, <sup>13</sup> C and <sup>15</sup> N magnetic shielding		
$\sigma_0(\text{H})$ (ppm) <sup>b</sup>	29.113(1)	29.113(1)
$\sigma_0(\text{CN})$ (ppm) <sup>b</sup>	74.021(3)	74.019(12)
$\sigma_0(\text{N})$ (ppm) <sup>b</sup>	−8.873(5)	−8.843(32)
$\sigma_{(\text{A-B})}(\text{H})$ (ppm ml mol <sup>−1</sup> )	−13(3)	−16(2)
$\sigma_{(\text{A-B})}(\text{C})$ (ppm ml mol <sup>−1</sup> )	−181(7)	−627(26)
$\sigma_{(\text{A-B})}(\text{N})$ (ppm ml mol <sup>−1</sup> )	51(9)	927(39)
$\sigma_{\text{AB}}(\text{H})$ (ppm ml mol <sup>−1</sup> )	170(3)	71(2)
$\sigma_{\text{AB}}(\text{C})$ (ppm ml mol <sup>−1</sup> )	3(7)	−540(26)
$\sigma_{\text{AB}}(\text{N})$ (ppm ml mol <sup>−1</sup> )	235(9)	1014(39)
$(\sigma)_\text{b}(\text{B})$ (ppm ml mol <sup>−1</sup> ) <sup>c</sup>	184	87
<sup>1</sup> J(NC), <sup>2</sup> J(CH) and <sup>3</sup> J(NH) spin–spin coupling <sup>d</sup>		
<sup>1</sup> J <sub>0</sub> (NC) (Hz)	−16.20(1)	−16.23(2)
<sup>2</sup> J <sub>0</sub> (CH) (Hz)	−10.18(2)	−10.19(2)
<sup>3</sup> J <sub>0</sub> (NH) (Hz)	−1.34(2)	−1.43(9)
<sup>1</sup> J <sub>AB</sub> (NC) (Hz ml mol <sup>−1</sup> )	−62(14)	−191(44)
<sup>2</sup> J <sub>AB</sub> (CH) (Hz ml mol <sup>−1</sup> )	−13(37)	6(46)
<sup>3</sup> J <sub>AB</sub> (NH) (Hz ml mol <sup>−1</sup> )	−325(77)	−134(171)

<sup>a</sup> The solute (A) gas (CH<sub>3</sub><sup>13</sup>C<sup>15</sup>N) has been used at a low constant density (~0.001 mol/l, pressure ~19 Torr).

<sup>b</sup> Absolute shielding assuming:  $\sigma_0(\text{CH}_4) = 30.611(24)$  ppm [28],  $\sigma_0(\text{CO}) = 0.6(9)$  ppm [29] and  $\sigma_0(\text{NH}_3) = 264.54(5)$  ppm [19].

<sup>c</sup>  $-(4\pi/3)\chi_{\text{M}}$ , where  $\chi_{\text{M}}$  is the molar susceptibility of solvent gas [30].

<sup>d</sup> From PFG-HSQC experiments.

Fig. 2 also reveals the magnitude of intermolecular interactions between the solute and solvent molecules. For each system studied (solute–solvent–nucleus) it is described by the slope of a relevant plot in Fig. 2 and by the  $\sigma_{1(\text{A-B})}(\text{X})$  parameters in Table 1. It is seen that the carbon shielding in the cyano group is strongly decreased by the interactions with CO<sub>2</sub> molecules, similar effect for SF<sub>6</sub> is less distinguish. The shielding of protons also becomes smaller due to the interactions with solvent molecules. However, the  $\sigma_{1(\text{A-B})}(\text{H})$  effects are so small that it has been necessary to expand significantly the shielding scale for protons in Fig. 2 in order to show the plots for SF<sub>6</sub> and CO<sub>2</sub> solvents separately. Table 1 gives the  $\sigma_{1(\text{A-B})}(\text{H})$  values for the two solvents. The difference between them is really within an experimental error. In contrast to the latter results for carbons and protons the nitrogen shielding is increased due to the interactions with solvent molecules. It is consistent with some general trends

in the changes of nitrogen shielding induced by intermolecular interactions. Positive shielding effects are always observed when a nitrogen atom is doubly or triply bonded, and bears a lone pair which does not participate in the  $\pi$ -electron system. The effects are especially distinct when such a nitrogen atom acts as a hydrogen-bond acceptor. Jameson et al. [25] have qualitatively analyzed this problem assuming that the paramagnetic term of nitrogen shielding is diminished upon the hydrogen bond formation between two HCN molecules. Later, with the use of ab initio calculations it has been shown by one of us [11,12] that the nitrogen shielding constant is significantly increased when acetonitrile molecules form various association structures. Generally, the stronger molecular interactions of CH<sub>3</sub>CN give usually the larger increase of nitrogen shielding and cyano carbon deshielding. The present study reveals large difference between the influence of CO<sub>2</sub> and SF<sub>6</sub> on the nitrogen shielding of CH<sub>3</sub><sup>13</sup>C<sup>15</sup>N (cf. 927(39)

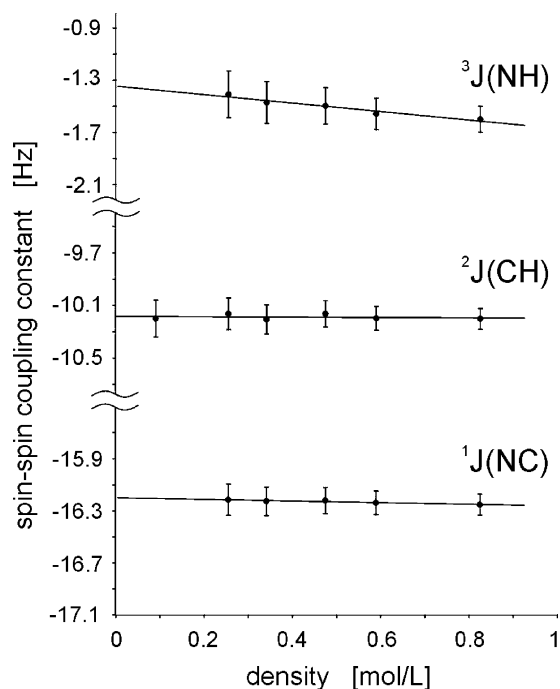


Fig. 3. The  $^1J(\text{NC})$ ,  $^2J(\text{CH})$  and  $^3J(\text{NH})$  spin-spin coupling constants in acetonitrile- $1\text{-}^{13}\text{C}$ ,  $^{15}\text{N}$  as a function of solvent density (sulfur hexafluoride) in the gas phase at 300 K.

and 51(9) ppm ml mol $^{-1}$ , respectively in Table 1). It suggests that the intermolecular interactions of acetonitrile with carbon dioxide is stronger than with sulfur hexafluoride. It also proves that the  $^{15}\text{N}$  NMR chemical shift of acetonitrile is a sensitive probe for the studies of intermolecular interactions.

For the first time Fig. 3 shows the density-dependent  $^1J(\text{NC})$ ,  $^2J(\text{CH})$  and  $^3J(\text{NH})$  coupling constants of acetonitrile in the gas phase where  $\text{SF}_6$  is used as a solvent gas. Our HSQC NMR spectra have confirmed that the  $^1J(\text{NC})$ ,  $^2J(\text{CH})$  and  $^3J(\text{NH})$  coupling constants of  $\text{CH}_3^{13}\text{C}^{15}\text{N}$  have the same sign. All the three coupling constants are negative [13,26,27] and the  $^1J(\text{NC})$  and  $^3J(\text{NH})$  parameters distinctly become less negative when the concentration of a solvent gas is decreasing. At the same conditions the  $^2J(\text{CH})$  coupling constant remains unchanged within an experimental error. It allows one to determine the  $J_0$  parameters free from solute-solvent intermolecular interactions. For

Table 2  
Spin-spin coupling constants of acetonitrile (Hz)

Coupling constant	Perera et al. [27]	This work			Sorensen et al. [31]		Diehl et al. [32]		
		Calc.	Gas phase	In $\text{C}_6\text{H}_{12}$	In acetone	Neat $\text{CH}_3\text{CN}$	In acetone- $d_6$	In $\text{C}_6\text{F}_6$	In nematic phase
$^1J(\text{CH})$	125.69	—	—	134.90(10)	136.00(10)	136.27(6)	136.25(10)	135.73(1)	135.7(2)
$^1J(\text{CC})$	—	—	—	—	56.89(8)	56.99(5)	56.94(4)	58.0(2)	57.7(3)
$^1J(\text{NC})$	—17.20	—	—16.20(2)	—16.55(8)	—17.22(6)	—17.55(5)	—17.53(10)	—	—17.8(2)
$^2J(\text{CH})$	—10.44	—	—10.15(2)	—9.96(8)	—9.92(7)	—9.97(4)	—9.94(4)	—9.94(2)	—
$^2J(\text{NC})$	3.08	—	—	3.09(7)	2.92(6)	2.81(4)	—	—	2.9(2)
$^3J(\text{NH})$	—1.33	—	—1.34(3)	—1.65(8)	—1.68(7)	—1.70(4)	—1.69(2)	—1.63(3)	—

non-polar molecules these parameters could be assigned for the isolated molecules. As it has been already mentioned an acetonitrile molecule has a large dipole moment and it is possible that some dimers of  $\text{CH}_3^{13}\text{C}^{15}\text{N}$  can still exist in the gas phase, even at the very low pressure. One should remember it using the  $\sigma_0$  and  $J_0$  values of  $(\text{CH}_3^{13}\text{C}^{15}\text{N})$  displayed in Table 1. Nevertheless, the present  $\sigma_0$  and  $J_0$  measurements are the best available approximation of spin–spin coupling and shielding constants for an isolated acetonitrile molecule and their values may be recommended for the verification of appropriate *ab initio* calculations.

Generally, spin–spin coupling constants are less affected by intermolecular interactions than nuclear shielding constants. It is also true for acetonitrile as shown in Figs. 2 and 3. Then it is more interesting to point out the tiny effects of intermolecular interactions observed in the spin–spin coupling constants. In Table 2 one can compare the spin–spin coupling constants of acetonitrile measured in various solvents with the present data obtained in the gas phase. First, it is well seen that all the coupling constants have different values in liquid solvents, e.g. the  $^1J(\text{NC})$  constant varies from  $-16.55(8)$  Hz in cyclohexane to  $-17.8(2)$  Hz in  $\text{CDCl}_3$ . It is certainly the effect of solute–solvent intermolecular interactions and it cannot be ignored when the accurate  $J_0$  parameter for an isolated molecule is required. Second, the  $^2J(\text{CH})$  constant becomes less negative due to the intermolecular interactions. In contrast, the  $^1J(\text{NC})$  and  $^3J(\text{NH})$  are more negative in liquid solvents. These data are fairly in agreement with the  $^2J_{\text{AB}}(\text{CH})$ ,  $^1J_{\text{AB}}(\text{NC})$  and  $^3J_{\text{AB}}(\text{NH})$  parameters in Table 1 though in the gas phase the dependence of  $^2J(\text{CH})$  on solvent density has been too small for the present measurements. Obviously the spin–spin coupling constants measured in various liquid solutions are not constant and the  $^nJ_o(\text{XY})$  parameters may only be used as the experimental standards.

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