Weak intermolecular interactions in gas-phase NMR

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Gas-phase NMR spectra demonstrating the effect of weak intermolecular forces on the NMR shielding constants of the interacting species are reported. We analyse the interaction of the molecular hydrogen isotopomers with He, Ne, and Ar, and the interaction in the He–CO$_2$ dimer. The same effects are studied for all these systems in the ab initio calculations. The comparison of the experimental and computed shielding constants is shown to depend strongly on the treatment of the bulk susceptibility effects, which determine in practice the pressure dependence of the experimental values. Best agreement of the results is obtained when the bulk susceptibility correction in rare gas solvents is evaluated from the analysis of the He-rare gas interactions, and when the shielding of deuterium in D$_2$–rare gas systems is considered.

I. INTRODUCTION

The importance of intermolecular interactions in physics, chemistry, and biology does not need to be stressed. Intermolecular potentials determine the properties of non-ideal gases, (pure) liquids, solutions, molecular solids, and the behavior of complex molecular ensembles encountered in biological systems. They describe the so-called non-bonded contributions, as well as the special bonding terms, that are part of the force fields used in simulations of processes such as enzyme-substrate binding, drug-receptor interactions, etc. A few examples showing important applications of intermolecular potentials include the Monte Carlo and molecular dynamics simulations of biological systems, studies of processes in the earth’s atmosphere, or interstellar chemistry.

Also the NMR spectra, in particular the observed chemical shifts, depend not only on the molecular structure but also on the intermolecular forces. The changes due to the environment are difficult to interpret theoretically and make the comparison of the computed and observed spectra unreliable. The role of the intermolecular forces is undoubtedly the largest in the condensed phase, and much smaller in dilute gas-phase solutions. Moreover, it is particularly small if we analyse a system where only weak van der Waals intermolecular forces play a significant role. In this work, we describe gas-phase NMR spectra for such systems, analyse the dependence of the observed shielding constants on the intermolecular forces, and present ab initio calculations which describe this dependence.

Early NMR studies in the gas phase were reviewed by Rummens [1], another review has been written in 1991 by Jameson [2]. However, the role of the intermolecular interactions in the gas phase was almost exclusively interpreted on the basis of binary collision gas model introduced by Raynes, Buckingham, and Bernstein [3]. In this RBB model the change in the shielding constant is qualitatively described as a sum of contributions due to the bulk susceptibility, neighbor-molecule magnetic anisotropy, polar effects, and van der Waals effects. At present, by applying state-of-the-art methods of quantum chemistry we should be able to predict accurately the small changes of the shielding constants due to weak intermolecular forces. For the first time this should be possible within an ab initio approach, which is in principle more reliable than the standard methods used to describe for instance the solvent effects in liquids, such as various polarizable continuum models based on classical approximations. Therefore, a study of gas-phase model systems has a specific advantage for the comparison between experiment and theory.

Theoretical studies of the interaction-induced changes in the NMR parameters are scarce, and mostly restricted to supermolecule calculations of the interaction-induced shielding constants and spin-spin coupling constants; see, e.g. Refs. [4–11] for typical applications. To our knowledge only one paper [4] analysed (comparing the theory with the numerical results) the asymptotic long-range behavior of the shielding constant and its anisotropy in a dimer. Most of the papers reporting ab initio calculations of the NMR parameters that could directly be compared with the gas phase NMR experiment were devoted to studies of atom-atom interactions [8–12] (this is in sharp contrast with the electric properties of molecular complexes for which a general long-range theory and applications to the optical and dielectric properties of gases are available [13–15]). There are very few ab initio studies of the NMR effects of weak interactions between a molecule and an atom or two molecules. The whole property surface has been computed for the interactions in the C$_2$H$_2$–He and C$_2$H$_2$–H$^+$ complexes [6], but no Boltzmann averaging has been performed; NMR properties were also examined [5] for the optimized geometries of other binary
complexes of acetylene.

Also on the experimental side not too much has been done. The effects of weak intermolecular interactions on NMR shielding of $^1$H, $^2$H and $^3$He in gases are small and buried in the much larger bulk susceptibility correction, therefore a detailed analysis of such systems is practically impossible and the RBB model has mostly been used. We recall here that for $^3$He the effect of the weak interactions is particularly small and difficult to observe (see for instance the study of gas-to-liquid shifts [14]). For $^{21}$Ne the precision of the NMR measurements is limited because the magnetically active isotope has a large nuclear quadrupole moment; for argon the only magnetically active $^{39}$Ar isotope is radioactive. On the other hand, for $^{129}$Xe the effects are very large. They have been observed in the xenon dimer and nearly quantitative agreement of theory with experiment was reached in state-of-the-art ab initio calculations [14, 11]. Also density functional theory (DFT) calculations for Xe-rare gas dimers yield satisfactory agreement with experimental data, see Refs. [13, 14].

Most recently, the chemical shift of Xe dissolved in liquid benzene was studied in the calculations combining the DFT methods with the classical molecular dynamics [13]. However, there are no similar studies of atom-molecule systems applying well established state-of-the-art wavefunction methods and comparing the results with known experimental data.

In this paper we fill this gap and report a joint experimental and theoretical study of the gas phase shielding constants in the mixtures of atomic and molecular gases. We study the effects resulting from the weak interactions between a molecule and an atom in series of model systems: $\text{H}_2$–He, $\text{H}_2$–Ne and $\text{H}_2$–Ar dimers and their deuterium-substituted isotopomers and in $\text{He}$–$\text{CO}_2$. For the selected magnetically active nuclei—$^1$H, $^2$H, $^3$He and $^{13}$C— we observe the dependence of the NMR spectrum on the density of the solvent gas, which enables next a comparison of the ab initio and experimental results. In the analysis of the NMR spectra we take into account the bulk susceptibility correction, dependent on the magnetizability of the medium and on the shape of the NMR sample [16, 20]. In the case of the weakly interacting systems which we study this correction dominates in the density dependence of the spectrum and its proper description is essential when we extract the information on the role of the intermolecular interactions from the experimental data and compare the experimental and computed quantities.

The plan of this paper is as follows. We start with the virial expansion of the shielding constant in terms of the gas density and discuss all quantities needed on the route from the theory to a direct comparison with the experiment. This is thoroughly discussed in sec. III. The details of the computational procedures adopted in the ab initio calculations, fitting of the interaction potential and shielding surfaces, and some numerical integration procedures will be discussed in sec. IV. The experiment is described in detail in sec. V. The results of the measurements and calculations are reported and compared in sec. VI. Finally, sec. VII concludes our paper.

II. SHIELDING CONSTANTS IN THE GAS-PHASE SOLUTIONS

For a binary mixture of a gas $A$, containing the nucleus $X$ whose shielding $\sigma^A(X)$ is observed, and gas $B$ as the solvent, $\sigma^A(X)$ can be expressed as [3]:

$$\sigma^A(X) = \sigma_0^A(X) + \sigma_{1AB}^A(X)\rho_B$$

(1)

where $\rho_A$ and $\rho_B$ are the densities of $A$ and $B$, respectively, and $\sigma_0^A(X)$ is the shielding in the zero-density limit. All higher terms in Eq. (1), which represents a truncated virial expansion, can safely be neglected if the experimental dependence of the shielding on the density is linear. The coefficients $\sigma_{1AA}^A(X)$ and $\sigma_{1AB}^A(X)$ are then the only terms responsible for the medium effects. They contain the bulk susceptibility corrections, $\sigma_{1bulk}^A$, and the terms directly taking account of the intermolecular interactions during the binary collisions of the $A$–$A$ and $A$–$B$ molecules: $\sigma_{1A-A}^A(X)$ and $\sigma_{1A-B}^A(X)$, respectively. The shielding parameters in Eq. (1) are temperature dependent and for this reason all the present measurements are performed at the constant temperature of 300 K. Moreover, in the experiments the density of $A$, $\rho_A$, is always kept very low in order to eliminate the solute-solute molecular interactions and Eq. (1) can be simplified to:

$$\sigma^A(X) = \sigma_0^A(X) + \sigma_{1B}^A(X)\rho_B$$

(2)

where

$$\sigma_{1B}^A(X) = \sigma_{1bulk}^B + \sigma_{1A-B}^A(X).$$

(3)

Fig. I displays, as an example, the dependence of the helium and deuteron magnetic shielding (given with respect to the isolated systems) on the density of the rare gas solvent in gaseous solutions. The plots in Fig. I are linear, which proves that Eq. (2) is a valid approximation and allows the determination of the $\sigma_0^A(X)$ and $\sigma_{1B}^A(X)$ shielding parameters. The part of the shielding constant $\sigma^A(X)$ which is exclusively due to pair intermolecular interactions between the solute and solvent molecules is given by $\sigma_{1A-B}^A(X)$. An inspection of Eqs. (2) and (3) shows that $\sigma_{1A-B}^A(X)$ can be extracted from the experimental results once the measured shielding constant becomes linear in the gas density $\rho_B$, and if the bulk susceptibility correction, $\sigma_{1bulk}^B$, is known.

In the experiment it is not easy to measure the gas number density $\rho$, but rather the pressure $p$. Therefore, the following form of Eq. (2) was used:

$$\sigma^A(X) = \sigma_0^A(X) + \sigma_{1B}^A(X)p.$$  

(4)

For an ideal gas Eqs. (2) and (4) are equivalent, and the coefficients $\sigma_{1B}^A(X)$ and $\sigma_{1B}^A(X)$ are inter-related by the
In general Eq. (5) is not valid since the pressure depends of the power series. The gas number density appears as the variable and (2) follow from the theory, and that in the virial expansions (6) the change of the shielding constant due to binary collisions used in the experiment, while Eq. (2) describes the Eq. (6) with the characteristic coefficients of the solute to the total pressure is negligible. This means that the thermodynamics of the system is described by Eq. (3) with the characteristic coefficients of the solvent used in the experiment, while Eq. (2) describes the change of the shielding constant due to binary collisions of the NMR active molecule with the bath molecules. It is worth noting at this point that the virial expansions (6) and (2) follow from the theory, and that in the virial expansions the gas number density appears as the variable of the power series.

A precise evaluation of \( \sigma_{1\text{bulk}}^{B} \), the bulk susceptibility correction, is particularly important in the present work, because for all the nuclei the total change of the shielding due to intermolecular interactions in the gas phase is very small. We consider first the determination of \( \sigma_{B}^{1\text{bulk}} \) terms from the available \( \chi_{M} \) molar magnetic susceptibilities of gases— and applying the standard formula for an infinitely long cylindrical tube parallel to the external magnetic field \([16, 20, 21]\):

\[
\sigma_{1\text{bulk}} = -\frac{4\pi}{3} \chi_{M}
\]  

where \( \chi_{M} \) is given in ppm cgs and \( \sigma_{1\text{bulk}} \) in ppm mL/mol. The macroscopic molar magnetic susceptibility \( \chi_{M} \) is for closed shell systems proportional to the microscopic molecular magnetizability (1 ppm cgs corresponding to \( 16.60529 \times 10^{-30} \) J T\(^{-2}\)). Equation (7) may be applied for the cylindrical geometry of the sample, and assuming that the molecules of the solvent do not interact. However, this assumption is not always true, the cylinder is not infinite, and in such an approach various additional corrections are undoubtedly necessary to get realistic values of \( \sigma_{1\text{bulk}} \) (see for instance Seydoux et al. [16]). We use a different approach to determine \( \sigma_{1\text{bulk}} \); which will be discussed in detail in section III.B.

Theoretical determination of \( \sigma_{1\text{bulk}}^{A-B}(X) \) requires two steps: \textit{ab initio} calculations of the interaction potential and interaction-induced shielding constant for the binary complex \( A - B \), and the average of the latter quantity with the Boltzmann factor depending on the interaction potential. The interaction potential \( V \) is given by the standard expression:

\[
V = E_{AB} - E_{A} - E_{B},
\]  

where \( E_{AB} \), \( E_{A} \), and \( E_{B} \) are the energies of the collisional dimer \( A - B \), and of the solvent \( A \) and solute \( B \) molecules, respectively. The interaction-induced shielding constant \( \sigma_{\text{int}}^{A-B}(X) \) is given by:

\[
\sigma_{\text{int}}^{A-B}(X) = \sigma_{0}^{A-B}(X) - \sigma_{0}^{A}(X),
\]  

where \( \sigma_{0}^{A-B}(X) \) and \( \sigma_{0}^{A}(X) \) are the shielding constants of the nucleus \( X \) in the dimer \( A - B \) and in the solute molecule \( A \), respectively. Finally, \( \sigma_{1}^{A-B}(X) \) appearing in Eq. (3) is defined as:

\[
\sigma_{1}^{A-B}(X) = 
\int \int \int \sigma_{\text{int}}^{A-B}(X) \exp (-\beta V(\omega_{A}, \omega_{B}, R)) R^{2}dRd\omega_{A}d\omega_{B},
\]  

where \( \omega_{A} \) and \( \omega_{B} \) denote the two sets of the angles specifying the orientations of the monomers \( A \) and \( B \), \( R \) is the distance between the centers of mass of the monomers, \( \beta = (k_{B}T)^{-1} \), \( k_{B} \) is the Boltzmann constant, and \( T \) is the temperature in Kelvin. We note that in general the calculation of \( \sigma_{1}^{A-B}(X) \) is not an easy task. For rigid molecules \( A \) and \( B \) it requires a six-dimensional integration over five angles and one distance. For systems considered in the present paper the integral of Eq. (10) reduces to a two-dimensional integral that can easily be evaluated. The details of the computational procedures adopted in \textit{ab initio} calculations, fitting, and numerical integration will be discussed in the next section.
III. COMPUTATIONAL APPROACH

A. Ab initio calculations

In all calculations the bond lengths of the interacting subsystems were kept fixed at their experimental geometries. We report below the results for H2 obtained with the H–H distance fixed at \( r(\text{HH}) = 1.449 \text{ a}_0 \). In test calculations we have verified that practically the same results are obtained using noticeably smaller values of \( r(\text{HH}) \). Thus, we can compare the same set of \textit{ab initio} results with the experimental data for different isotopomers of the hydrogen molecule. For He–CO2, following the previous studies of the potential energy surface \( ^{28} \), we have used \( r(\text{CO}) = 2.1944 \text{ a}_0 \), an experimental value deduced from the microwave spectra.

All calculations of the energies and of the shielding constants have been performed with the coupled cluster method restricted to single, double, and noniterative triple excitations, CCSD(T). The NMR shielding constants and the magnetizabilities were obtained by applying the coupled cluster linear response theory \( ^{24, 25} \). Gauge-including atomic orbitals, GIAO’s \( ^{26, 27} \), were used in all calculations of the magnetic properties, and we have systematically corrected all the interaction-induced changes in the energies and in the shielding constants by eliminating the basis set superposition error, i.e. all calculations for the monomers were done in the full basis of the dimer. We have used the d-aug-cc-pVXZ basis sets \( ^{28} \); d-aug-cc-pVQZ for the smallest H2–He system, and the d-aug-cc-pVTZ basis set for the larger H2–Ne, H2–Ar, and He–CO2 dimers. The calculations of the energies and shielding constants were performed using the ACES II \( ^{29} \) program, while the magnetizabilities were computed using the more recent CFOUR program \( ^{30} \).

B. Interaction potentials

For two systems we used the available fitted interaction potential energy surfaces: for H2–Ar taken from Ref. \( ^{31} \) and for He–CO2 taken from Ref. \( ^{23} \). These potentials were obtained from the symmetry-adapted perturbation theory (SAPT) calculations (see Refs. \( ^{32, 33} \) for a review of the SAPT methodology and of the accuracy of the SAPT potentials). These potentials were shown to reproduce the high-resolution infrared spectra of the H2–He \( ^{34, 35} \) and the He–CO2 \( ^{23} \) van der Waals complexes. More importantly, they also reproduce very accurately the thermodynamic (pressure) virial coefficients \( ^{36} \). For other systems the interaction potential \( V(R, \theta) \) was calculated by the supermolecular method according to Eq. \( ^{38} \).

We use spherical coordinates defined with respect to the center of mass of the molecule. Calculations were performed for several angles \( \theta \) ranging from 0 to 180° and for several radial distances \( R \). For each angle \( \theta \) radial dependence of the interaction potential \( V \) was fitted with the function:

\[
V_0(R) = e^{-\alpha(\theta)R}(A_0(\theta) + A_1(\theta)R + A_2(\theta)R^2) - \frac{C_0(\theta)}{R^6} - \frac{C_8(\theta)}{R^8},
\]

where \( \alpha, A_0, A_1, A_2, C_6, \) and \( C_8 \) were adjusted to fit the computed points at a given angle \( \theta \). We note parenthetically that odd powers of \( R^{-1} \) do not appear in the long-range asymptotics of Eq. \( ^{11} \) because the H2 and CO2 molecules are centrosymmetric. Next, interpolation was used to obtain the full interaction energy surface. The points calculated for a given radial distance \( R \) from each \( V_0 \) fit were interpolated with a third-order polynomial in \( \theta \). This procedure leads to a fitted/interpolated interaction energy surface \( V(R, \theta) \), which was used in further calculations.

C. Shielding constants

The same technique was applied to obtain the \( \sigma_{\text{int}}^{A-B}(R, \theta) \) surface. For each angle the radial dependence of \( \sigma \) was fitted to the following function:

\[
S_{\theta}(R) = e^{-\alpha(\theta)R} \sum_{k=0}^{N} A_k(\theta)R^k - \sum_{m \in M} \frac{C_m(\theta)}{R^m},
\]

where all the parameters appearing on the r.h.s. of the expression above were adjusted to fit the computed values.

For the hydrogen atom in H2–He, H2–Ne, and H2–Ar a modification to the procedure described above was introduced. Since the interaction energy surface for these systems is symmetric we were allowed to use symmetrized \( \sigma \)-surface \( \bar{\sigma}(R, \theta) \) calculated as an arithmetical average of interaction-induced shifts for both H nuclei. This improved the accuracy of the further integration of the \( \sigma_{\text{int}}^{A-B} \) function with the Boltzmann factor.

D. Final integration

To obtain the final result one has to calculate for the temperature of interest the Boltzmann average of \( \sigma_{\text{int}}^{A-B}(R, \theta) \):

\[
\sigma_1^{A-B} = \int_0^{\infty} dR \int_0^\pi d\phi \int_0^{2\pi} d\varphi R^2 \sin \theta \exp(-\beta V(R, \theta)) \sigma_{\text{int}}^{A-B}(R, \theta).
\]

Due to the axial symmetry of the considered systems the integration over \( \phi \) gives 2\( \pi \). Integrations over \( R \) and \( \theta \) were done numerically with the \textsc{Mathematica} \( ^{37} \) package. First, for each angle the radial integration was performed. The integration range \([0, \infty]\) was substituted by \([R_{\text{min}}, R_{\text{max}}]\) with properly defined \( R_{\text{min}} \) and \( R_{\text{max}} \).
The $R_{\text{min}}$ value was chosen to ensure that $V(R_{\text{min}}, \theta)$ was positive and large enough to make the Boltzmann factor close to zero. The value of $R_{\text{max}}$ was chosen in such a way that $\sigma(R_{\text{max}}, \theta)$ was almost zero at $R_{\text{max}}$, independent of the angle $\theta$. This choice leads to $R_{\text{min}} = 2 \, \text{a}_0$ and $R_{\text{max}} = 300 \, \text{a}_0$ for H$_2$–He, for other systems the required integration range is smaller and within the same limits. The results obtained from the radial integration for each angle were interpolated with third-order function and this function was integrated over $\theta$.

E. Bulk susceptibilities

To estimate the bulk susceptibility correction (BSC) we first used new values of magnetizabilities obtained from CCSD(T) calculations. Using the d-aug-cc-pVQZ basis set we obtain for CO$_2$ at the experimental geometry $-22.254$ ppm cgs, with the basis set error estimated to be smaller than 0.2 ppm cgs. This value is consistent with the results of Ref. [38] and confirmed by new CCSD(T)/d-aug-cc-pCVQZ-unc calculations for the Ne and Ar atoms, which give $-7.601$ and $-20.610$ ppm cgs, also in agreement with Ref. [38]. The values of $\chi_M$ and the corresponding bulk susceptibility effects derived from Eq. (7) are given in Table I. These values may only be considered as a crude approximation to the real $\sigma^\text{B}_1^\text{bulk}$ quantities. First, because the geometric factor is unable to reproduce accurately the susceptibility corrections in nuclear shielding; this problem was frequently discussed in the literature from the early days of NMR [39, 40]. Secondly, we have used a special high-pressure tube, cf. sec. IV, which was not spinning and this may induce non-negligible unknown effects.

| TABLE I: Solvent gas (B) magnetizabilities (ppm cgs) and bulk susceptibility corrections (ppm mL/mol) |
|---------------------------------------------------|
|          | He      | Ne      | Ar      | CO$_2$  |
| $\chi_M$ | $-1.8915$ | $-7.601$ | $-20.610$ | $-22.254$ |
| $\sigma^{\text{B}}_1^\text{bulk}$ | $9.723$ | $31.839$ | $86.333$ | $93.217$ |
| $\sigma^{\text{He}^3\text{He}}_1^\text{bulk}$ | $8.29(12)$ | $28.79(6)$ | $77.36(30)$ |
| $R_{\text{He}^3\text{He}}$ | $8.62(12)$ | $29.56(6)$ | $80.26(30)$ |

$^a$For consistency with Eq. (7) we use ppm cgs units.
$^b$Calculated from Eq. (4).
$^c$Total effect observed in $^3$He–B interaction.
$^d$Determined from the total $^3$He–B interaction and the computed interaction-induced $\sigma^{^3\text{He}^3\text{He}}_1^\text{bulk}$ coefficients.

Since a precise determination of the BSC value according to Eq. (7) is impossible, we have applied our own experimental approach to estimate the bulk susceptibility corrections. It is well known that molecular interactions between the atoms of rare gases disturb the $^3$He shielding only to very small extent [16]. Moreover, a description of such interactions is available from the theoretical studies of the shielding in these gas mixtures [12]. In the present work we have measured the density dependent $^3$He shielding in helium, neon, and argon gases. It gave us the $\sigma^{\text{He}^3\text{He}}_1$, $\sigma^{\text{He}^3\text{Ne}}_1$ and $\sigma^{\text{He}^3\text{Ar}}_1$ coefficients of Eq. (2), which were used next in Eq. (3) together with the interatomic interaction coefficients, to obtain $\sigma^{\text{B}}_1^\text{bulk}$ as $\sigma^A_B(X) - \sigma^A_B(X')$. We have used the values of $\sigma^{\text{He}^3\text{He}}_1$, $\sigma^{\text{He}^3\text{Ne}}_1$ and $\sigma^{\text{He}^3\text{Ar}}_1$, based on the theoretical results of Ref. [12]: $-0.328$, $-0.776$ and $-2.901$ ppm mL/mol, respectively (another available value of $\sigma^{\text{He}^3\text{He}}_1$, derived from the full configuration interaction calculations, but with a smaller basis set, is equal to $-0.353$ ppm mL/mol [8]). In this way we determined the final values of the bulk susceptibility effects in the present NMR experiments, shown in Table II. Finally, we note that the problems related to precise determination of the bulk susceptibility effects are known, they have been recently analysed [41, 42] and discrepancies of the order of $\approx 10\%$ between the computed and experimental data have been observed [41].

IV. Experiment

The $^1$H, $^2$H, $^3$He and $^{13}$C NMR chemical shifts were measured on a Varian INOVA 500 spectrometer at 300 K operated at 500.61, 76.85, 381.36 and 125.88 MHz, respectively. $^2$H and $^{13}$C spectra were acquired with a standard two channel Varian switchable 5 mm probe, while $^3$He and $^1$H spectra in the self reconstructed helium probe [43]. Nitromethane-d$_3$ was used for a lock system when the $^1$H, $^3$He, and $^{13}$C NMR measurements were carried out. The $^2$H experiments required a high-band lock operating on the proton signal of liquid tetramethylsilane (TMS). For this purpose a special set of coaxial glass capillaries was prepared and the same set was also used for the external referencing of all the chemical shifts. The set of capillaries contained nitromethane-d$_3$ in the outer chamber and pure liquid TMS in the inner container. The capillaries were placed in a special non-spinning NMR tube which was used for all our measurements. The tube was made of zirconia and equipped with a metal valve for gas filling at high pressure (Daedalus Innovations, USA).

The described sample setup was complex, the zirconia tube with the capillaries affects the external magnetic field, and therefore we could not apply Eq. (7) in our experimental work (see also the discussion in Ref. [10]). We have bypassed the problem of bulk susceptibility corrections performing analogous measurements of $^3$He shielding in $^4$He, Ne and Ar as gaseous solvents using exactly the same setup of the sample tube with the same set of capillaries. This series of measurements was specially designed for precise determination of the bulk susceptibility effects in our experiments, according to the approach discussed in section III(A).

An efficient high-pressure system built in our laboratory permitted the NMR investigations of the hydrogen and helium gases for a wide range of densities. As indi-
We begin the discussion of the effects of intermolecular interactions on the shielding constants with a brief summary of the ab initio results. Three-dimensional plots of $\sigma_{\text{int}}^{X}(X)$ for the H$_2$–He, $^3$He–CO$_2$, and $^{13}$CO$_2$–He complexes are presented in Fig. 3. Similar plots for H$_2$–Ne and H$_2$–Ar are not reported since their $R$ and $\theta$ dependence is nearly the same as for H$_2$–He. An inspection of Fig. 3 shows that $\sigma_{\text{int}}^{H_2–H_\text{e}}(H)$ does not show any strong variations on $R$ and $\theta$. Only at very small intermolecular distances a stronger dependence shows up, but at these geometries the interaction potential is strongly repulsive, so the exponential Boltzmann factor is almost zero and these large variations of $\sigma_{\text{int}}^{H_2–H_\text{e}}(H)$ do not contribute to $\sigma_{\text{int}}^{H_2–H_\text{e}}(H)$. Slightly more pronounced is the geometry dependence of the interaction-induced shielding for both $^3$He–CO$_2$ and $^{13}$CO$_2$–He.

V. RESULTS AND DISCUSSION

We begin the discussion of the effects of intermolecular interactions on the shielding constants with a brief summary of the ab initio results. Three-dimensional plots of $\sigma_{\text{int}}^{A–B}(X)$ for the H$_2$–He, $^3$He–CO$_2$, and $^{13}$CO$_2$–He complexes are presented in Fig. 3. Similar plots for H$_2$–Ne and H$_2$–Ar are not reported since their $R$ and $\theta$ dependence is nearly the same as for H$_2$–He. An inspection of Fig. 3 shows that $\sigma_{\text{int}}^{H_2–H_\text{e}}(H)$ does not show any strong variations on $R$ and $\theta$. Only at very small intermolecular distances a stronger dependence shows up, but at these geometries the interaction potential is strongly repulsive, so the exponential Boltzmann factor is almost zero and these large variations of $\sigma_{\text{int}}^{H_2–H_\text{e}}(H)$ do not contribute to $\sigma_{\text{int}}^{H_2–H_\text{e}}(H)$. Slightly more pronounced is the geometry dependence of the interaction-induced shielding for both $^3$He–CO$_2$ and $^{13}$CO$_2$–He.

| $T$ (K) | $\sigma_{1}^{H_2–H_\text{e}}(H)$ | $\sigma_{1}^{H_2–H^3_e}(H)$ | $\sigma_{1}^{H_2–H^{13}_e}(H)$ |
|--------|-------------------------------|---------------------------|-----------------------------|
| 150    | -0.324                        | -0.230                    | -4.071                      |
| 200    | -0.352                        | -0.281                    | -4.025                      |
| 250    | -0.381                        | -0.330                    | -4.085                      |
| 280    | -0.398                        | -0.358                    | -4.144                      |
| 300    | -0.410                        | -0.377                    | -4.189                      |
| 320    | -0.422                        | -0.396                    | -4.237                      |
| 350    | -0.440                        | -0.424                    | -4.314                      |

Let us now analyse the temperature dependence of the $\sigma_{1}^{A–B}$ coefficients calculated from Eq. 13. The results for all the systems are shown in Table III. An inspection of the Table shows that the temperature effects are too small to be reliably determined from the experimental data (thus, in what follows we shall only compare theoretical results with the experiment for $T=300$ K). The dependence of the computed $\sigma_{1}^{A–B}$ on the temperature $T$ is almost linear. It is interesting to note that for H$_2$–He, H$_2$–Ne, H$_2$–Ar, and $^3$He–CO$_2$ systems $\sigma_{1}^{A–B}$ decreases with $T$, while for $^{13}$CO$_2$–He the opposite is found. The values at the lowest temperature, 150 K, do not differ

TABLE II: Calculated ab initio values of $\sigma_{1}^{A–B}$ (ppm mL/mol)

| $T$ (K) | $\sigma_{1}^{H_2–H_\text{e}}(H)$ | $\sigma_{1}^{H_2–H^3_e}(H)$ | $\sigma_{1}^{H_2–H^{13}_e}(H)$ |
|--------|-------------------------------|---------------------------|-----------------------------|
| 150    | -6.379                        | 1.3050                    |                             |
| 200    | -6.514                        | 1.2894                    |                             |
| 250    | -6.548                        | 1.2871                    |                             |
| 280    | -6.590                        | 1.2876                    |                             |
| 300    | -6.622                        | 1.2883                    |                             |
| 320    | -6.658                        | 1.2889                    |                             |
| 350    | -6.714                        | 1.2898                    |                             |
considerably from the room temperature data, suggesting that the quantum effects will start to play a noticeable role at still lower temperatures.

The temperature dependence of $\sigma^{A-B}_1$ was studied experimentally in glass samples as described earlier [43], but only for the $^{3}$He–CO$_2$ system (rare gases like He, Ne and Ar could not in practice be used as solvents in such experiments). Unfortunately, it was not possible to achieve sufficient precision to perform a quantitative analysis of the results. In addition, a most important factor required to determine $\sigma$(^3He) in $^{3}$He–CO$_2$ as a function of the temperature—the temperature dependence of CO$_2$ bulk susceptibility—is not known.

Before we consider the comparison of the *ab initio* and experimental results, we recall that for all the systems the bulk susceptibility corrections are dominant. The observed density dependence of $^2$H and $^3$He shielding in gaseous solutions is shown in Fig. 1 (the depicted range of densities corresponds to the pressure of the solvent rare gas increasing up to 300 bar). For comparison, we have shown the effect of $\sigma^B_{1\text{bulk}}$ for Ar. It is clear that for all the nuclei the total change of the shielding in the gas phase is very small, determined largely by $\sigma^B_{1\text{bulk}}$, and the precise evaluation of the bulk susceptibility corrections is crucial for the present study of weak molecular interactions. The BSC effect can be neglected in the analysis of the experimental data in two cases—when a spherical NMR sample is prepared or when the sample is fast spinning at the magic angle. Unfortunately, neither of these methods can provide accurate results for compressed gas at high density.

Our final results, obtained for 300 K, are shown in Table III. For each system, the BSC constitutes the essential part of the measured effect, thus a minor error in the evaluation of $\sigma^B_{1\text{bulk}}$ clearly leads to a very significant error in $\sigma^{A-B}_1$. In particular, the standard approximation, $\sigma^B_{1\text{bulk}} = -(4\pi/3)\chi_M$, is not sufficiently accurate. The error bars shown in Table I and Table III do not account for any systematic errors in the experiment, they represent only the errors of the linear fits to the observed density dependence of the results. We have considered systematic errors arising from a limited precision of the nominal reading of the absolute frequency, and errors in the control of the stability of the external magnetic field; they limit the precision of the measured shielding constants to ±0.015 ppm. However, let us recall that in many cases the determination of $\sigma^{A-B}_1(X)$ required two NMR experiments, one for the observed $A-B$ binary system and one for the $^3$He–$B$ solvent. Consequently, the error bars are at least doubled, to ±0.030 ppm for the $A-B$ system. Moreover, our experimental setup could slightly disturb the magnetic field as the sample was not spinning during the measurements; observing repeatedly the same samples we noticed deviations of up to 2 Hz in the measured frequencies. A complete analysis of these systematic errors, following the discussed precision of frequency measurements and possible deviations in the gas density inside the NMR tube, gives ±0.50 ppm mL/mol as an estimate of their contribution to the error bars in the $\sigma^{A-B}_1$ values. This estimate does not include the tabulated errors of the linear fitting of the results, and does not take into account the left-over errors in the analysis of the bulk susceptibility effects.

The errors in the *ab initio* calculations are also difficult to estimate. The point-wise determined shielding surface is presumably accurate for the smallest H$_2$–He system, the correlation and basis set errors becoming larger for the other systems. Although the following stages—fitting the potential and the property surfaces, followed by the
Boltzmann average—appear to be straightforward, approximations made in this part of the calculation contribute significantly to the final error bars. As shown in Fig. 3 there are regions of the shielding surface of opposite contributions to the induced shielding constant, and therefore the final result depends heavily on a significant cancellation of positive and negative contributions, which in turn depends on the potential surface. Following various test calculations we estimate that the errors of the computed $\sigma_{1}^{A-B}$ should not exceed 15-20% of the discussed above final ab initio values.

VI. CONCLUSIONS

In this paper, we reported the first measurement of the changes of the NMR shielding constants due to weak intermolecular interactions. It became possible due to a new approach for the determination of bulk susceptibility effects, which are dominant in the studied systems. The interpretation of the results is related to the corresponding ab initio calculations, and we observe qualitative agreement of the ab initio values with those derived from the experimental data. There is a series of approximations that should be analysed to improve this agreement. In particular, it is obvious that one cannot expect quantitative agreement without a better description of the bulk susceptibility effects. We have bypassed this problem transferring the necessary information from one set of the experimental data—for pairs of rare gas atoms systems—to another, that is to the studied molecule–atom systems. Such an approach appears to yield satisfactory results in our case, but in general a better theory, describing accurately the bulk susceptibility corrections, is needed. For larger systems, for instance involving molecule-molecule interactions, the experiment may be easier, but without a proper description of these effects the interpretation of the results is almost impossible. Last but not least, we note that the corresponding theoretical calculations are also demanding, high level of the ab initio theory is required to obtain a reliable description of the small changes of the shielding constants due to weak intermolecular forces. For larger systems it may be difficult to achieve satisfactory accuracy of the results, in particular when the effects due to different parts of the shielding surface partially cancel out.

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