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Analysis of Nuclear Magnetic Shielding in Medium-Sized Molecules

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In nuclear magnetic resonance (NMR) spectroscopy the chemical shift describes the displacement of a signal due to variations in nuclear magnetic shielding and it exactly means the difference between magnetic shielding observed in two molecules: the reference and unknown molecules, respectively. At present the absolute shielding values of numerous molecules are well-known from advanced ab initio calculations. NMR measurements in the gas phase allow the determination of chemical shifts and shielding free from intermolecular interactions. It is equivalent to the appropriate parameters of isolated molecules which are available from the quantum chemical calculations. In our laboratory we have developed many new techniques of NMR experiments in the gas phase. We found that applying an inert gas as a solvent it was possible to obtain gas-phase NMR spectra also for chemical compounds which are liquid at room temperature, e.g., for water. Next, it was shown that the simultaneous observation of resonance frequencies for 1H and another X nucleus leads to the accurate determination of the nuclear magnetic dipole moment of X what is important for nuclear physics and obviously for molecular spectroscopy. Next, we have presented a new method of the standardization of NMR spectra based on the direct measurements of magnetic shielding. All the above ideas are illustrated by our new experimental 1H, 13C, 15N and 17O NMR studies of atmospheric gases. The NMR spectra are adequately applied for dinitrogen (N2), nitrous oxide (N2O), carbon dioxide (CO2) and water (H2O) in many various gaseous mixtures, including also paramagnetic dioxygen (O2).

Introduction

Perhaps the most important discovery after the successful detection of the NMR signal has been the observation that the nuclear resonance frequencies depend on the chemical or electronic environment of the nuclei, or as Norman Ramsey states in his landmark papers of 1950: “In measurements of nuclear magnetic moments, a correction must be made for the magnetic field arising from the motions of the molecular electrons which are induced by the externally applied field.” Ramsey realized that corrections using only Lamb’s diamagnetic theory were inadequate for molecules, because in molecules there are additional shielding contributions arising from the second-order paramagnetism. To address this problem, he developed the required theoretical framework to elucidate and eventually to calculate the “chemical effect,” which might become the chemical shift commonly utilized in our day for structural elucidation. The calculation of the second-order paramagnetic contribution using perturbation theory has been a challenge to theoreticians for quite 50 years. The formal properties of the chemical shieldings are discussed below, but it important to know that although most chemists believe the chemical shift or chemical shielding as number associated with each resonant nucleus, in reality the chemical shielding is a tensor quantity. This means that the screening of the external magnetic field by the electron density of the molecule depends on the relative orientation of the external magnetic field and therefore the molecule; there- fore, the chemical shielding phenomena has got to be described by a tensor rather than a scalar number. This can be easily observed when recording the NMR spectra of solids. For single crystals, where the relative orientation of the molecules with respect to the external magnetic field can be macroscopically con-trolled by changing the orientation of the crystal with respect to the external field, the orientation dependence can be observed in the change of the position of the resonance lines of the NMR spectra as the crystal is rotated around the magnetic field. In, we present an example of this behaviour showing the large differences in the13C NMR spectra of a single crystal spectra of 1,3,5-trihydroxybenzene at different orientations. Although studies of single crystals provide complete information of the chemical shielding tensor, these experiments are quite cumbersome and have been performed using a very limited number of com-pounds. Most of the solid-state NMR studies are performed in disordered samples where the dependence of the chemical shielding with reference to the orientation of the external magnetic field results in the characteristic powder patterns shown in. These powder patterns originate within the superposition of resonances like molecules randomly oriented within the sample. A complete description of these spectra and how to extract the chemical shielding from them can be found in Orent. Note that except for the cylindrically symmetric case, top spectra in, these patterns provide only the principal values of the chemical shielding tensors; therefore, their orientation in the molecular frame has to be inferred using other methods. Calculations of the chemical shielding have become the most common method for this determination. There is considerable confusion within the literature about the utilization of the terms: “chemical shift” and “chemical shielding.” The chemical shielding is that the tensor that describes the relative change in the local magnetic field at the nucleus position relative to the external magnetic field. This change in the local magnetic field, which is originated in the interaction of the electron cloud with the external magnetic field, can produce shielding or de-shielding of the nucleus. In the first case the local magnetic field is increased with respect to the external field, whereas in the second case the local field is decreased. In general, shielding effects are associated with diamagnetic effects from spherical charge distributions, whereas de-shielding effects are associated with a non-spherical charge distribution originating from p or higher angular momentum electrons. When experiments are performed at a continuing

magnetic field, because it is generally wiped-out modern NMR spectrometers, a shielding effect results on a shift of the resonance to a higher frequency.

Differences in nuclear shielding place NMR signals in several spectral positions. Therefore, the selection of the carrier frequency is important for an honest performance of the NMR experiment. It was seen above that when the B1 field matches the Larmor frequency, there is absorption of energy. By analogy with a relays where the runners match their speed to transfer the baton, the carrier frequency should match as closely as possible the Larmor frequency of the nuclei being observed in order that excitation occurs and is best.

Sampling Bandwidth and the Nyquist Theorem- In addition to correctly choosing the B1 pulse power, length and carrier frequency to ensure that all interesting nuclei are excited, the existence of chemical shifts also forces the need to ensure that the measurement conditions are chosen so that all signals of interest are observed. NMR spectrometers record an FID that's Fourier transformed to get a spectrum. Because of this arrangement, the sampling bandwidth (usually mentioned as spectral width) observed depends on the frequency during the time of recording the FID. At current operating field intensity, the Larmor frequency is of the order of many MHz, whereas in typical solution state, biomolecular applications the chemical shifts show differences at most of the order of kHz. Therefore, the importance of correctly selecting the carrier frequency becomes apparent. The most favourable condition occurs when the carrier frequency can be placed in the centre of the spectrum because of the following: (1) The excitation profile of the B1 pulse extends symmetrically from the carrier frequency covering a range inversely proportional to the pulse length. Therefore, at the centre of the spectrum we've rock bottom demands on pulse duration and power. (2) Also, this is often the condition where the minimum sampling is important, because the difference between the carrier frequency and any signal within the spectrum is, at most, half of the spectral width. The consequence is the minimisation of the experimental time. This is a consequence of the entire experimental time, being the number of samplings made, multiplied by the sampling interval. Until now, we've seen that NMR provides information on the amount and relative abundance of chemically distinguishable nuclei within the sample. It also provides information on the transverse relaxation rate that is related with the molecular size. If there is need to perform multiple scans to improve the signal to noise of the spectrum, the T1 must be determined in order to know how long one must wait until the magnetisation has returned to the z direction. T1, unlike T2, cannot be directly estimated from the spectrum, and its measurement requires that a specially designed experiment is performed.

Ramsey's theory for nuclear shielding in diamagnetic NMR is predicated on orbital interactions. Expanding the nonrelativistic (NR) kinetic energy expression $\pi 2/2me$ in the presence of the magnetic vector potential contributions (from both the external field and nuclear magnetic dipole field) to the momentum, $\pi = p + A0 + AK$, leads to, on the one hand, orbital Zeeman and orbital hyperfine (paramagnetic nuclear spin-electron orbit) interactions that are linear in the magnetic field B0 and nuclear magnetic moment $\mu K = \gamma K \hbar IK$, respectively. Here, IK is that the dimensionless nuclear spin and γK is that the gyromagnetic ratio. As detailed in chapter 2 of this volume, these interactions produce to the paramagnetic a part of the shielding tensor σK, during a second-order perturbation theory expression. On the other hand, the quadratic terms of the Hamiltonian include an operator bilinear in B0 and IK and, hence, a first-order (expectation value), diamagnetic contribution to σK.

An important ingredient within the analysis of pNMR shift has been the concept of pseudo contact shift (PCS), an isotropic contribution resulting from the long-range dipolar interaction of the nuclear and electronic spins as mediated by the anisotropy of the electronic g-tensor, which parameterizes the electronic Zeeman interaction with B0 in ESR. In turn, this quantity is proportional to the spin magnetizability of the molecule. In particular, this shift contribution encodes in itself the distance from the unpaired electron (assumed localized, e.g., at a metal centre) and the NMR nucleus. Hence, PCS provides a handle on the molecular structure and has been used in structural determination of, for example, metalloproteins. To extract the PCS contribution from experimental chemical shift data, it's necessary to eliminate both the orbital shift (by using the same diamagnetic compound) and therefore the contact shift, the latter often by ESR experiments or empirically scaled or corrected quantum-chemical calculations.