NMR of Partially Aligned Liquids: Magnetic Susceptibility Anisotropies and Dielectric Properties

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In this Account recently developed aspects of the NMR of "partially oriented" molecules will be discussed. The partial orientation is dynamic in nature, not static, since it is observed in pure liquids and liquid solutions. This means that anisotropic properties can be measured while the advantages of high-resolution NMR are preserved. Partial orientation occurs, for example, in liquid crystals by applying an electric or magnetic field of moderate strength, but it may also be induced by a strong external electric or magnetic field in a normal liquid. Several reviews on NMR in liquid crystals have appeared in the literature;[1] here only NMR studies on normal liquids will be considered.

The use of NMR for studying orientation effects in liquids is relatively new, partly because very strong fields of sufficient homogeneity are required. Kerr- and Cotton–Mouton effect measurements, by which the double refraction of a liquid partially aligned by an electric or magnetic field is studied, are less demanding in this respect. NMR and double refraction measurements have their own characteristics, but both are useful tools for studying anisotropic properties of molecules in liquids. The experiments to be described are the NMR analogues of the Kerr- and the Cotton–Mouton effect.

The influence of alignment on NMR spectra has been described in a number of classic papers[2] and review articles.[3] Early experiments to detect effects of external electric fields on NMR spectra can be found in ref 4 and 5.

A prerequisite for inducing partial alignment, as well as for detecting its effects by NMR, is anisotropy of the molecular properties involved. An obvious example is the alignment of polar molecules by an electric field. Here the electric field interacts with a vector quantity: the electric dipole moment, and so the interaction is directionally dependent. Apolar molecules with an anisotropic polarizability tensor (α) also give rise to partial alignment, though not detected by NMR so far. Analogously, molecules with an anisotropic magnetic susceptibility (χ) are partially aligned by a magnetic field.

The alignment of an axially symmetric molecule can conveniently be expressed by the average $\langle^{3}/_{2} \cos^{2} \theta - ^{1}/_{2}\rangle$ in which θ is the angle between the principal molecular axis and the applied field. The latter usually is a magnetic field for NMR studies in liquid crystals

Table I
Orders of Magnitude of the Alignment $\langle^{3}/_{2} \cos^{2} \theta - ^{1}/_{2}\rangle$ Attainable in Liquids and Liquid Crystals

alignment mechanism	$|\langle^{3}/_{2} \cos^{2} \theta - ^{1}/_{2}\rangle|$
electric field	
polar molecules	10^{-5}–$10^{-4\,a}$
apolar molecules	$10^{-6\,a,b}$
magnetic field, molecules with anisotropic susceptibility	10^{-6}–$10^{-5\,c}$
thermotropic liquid crystals	10^{-1}–1
lyotropic liquid crystals	10^{-2}

^{a} Field strength about 5×10^6 V/m. ^{b} Estimated for aromatic molecules like naphthalene, anthracene, triphenylene; not yet detected. ^{c} Magnetic field of 10 tesla.

and also in normal liquids if the molecules are to be aligned by their anisotropic magnetic susceptibility. It is an electric field in dielectric alignment studies.

To give an idea of the value of $\langle^{3}/_{2} \cos^{2} \theta - ^{1}/_{2}\rangle$, henceforth referred to as the alignment, that can be attained in specific cases, some values are collected in Table I. As mentioned already, the alignment brought about by a strong electric field acting on an anisotropic polarizability has not been detected by NMR as yet. Neither has the NMR analogue of flow birefringence. The alignment of molecular quadrupoles in an external electric field gradient is too small to be detected by NMR with the present techniques.

The alignment of the molecules of a liquid may become apparent in the NMR spectrum through an anisotropic interaction of the nuclear spins. In our work, two interactions of this type have been studied extensively, i.e., the anisotropic dipole–dipole interaction between nuclear spins and the interaction of a nuclear quadrupole with the local electric field gradient. A specific example is the ^{2}H spectrum of perdeuterio-

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(3) (a) A. D. Buckingham and K. A. McLauchlan, "Progress in NMR Spectroscopy", Pergamon, Oxford, 1967, Vol. 2; (b) A. Saupe, Angew. Chem., Int. Ed. Engl., 7, 107 (1968); (c) G. R. Luckhurst, Q. Rev., 22, 179 (1968); (d) S. Meiboom and L. C. Snyder, Science, 162, 1337 (1968); (e) P. Diehl and C. L. Khetrapal, "NMR, Basic Principles and Progress", Springer, Berlin, 1969, Vol. 1.

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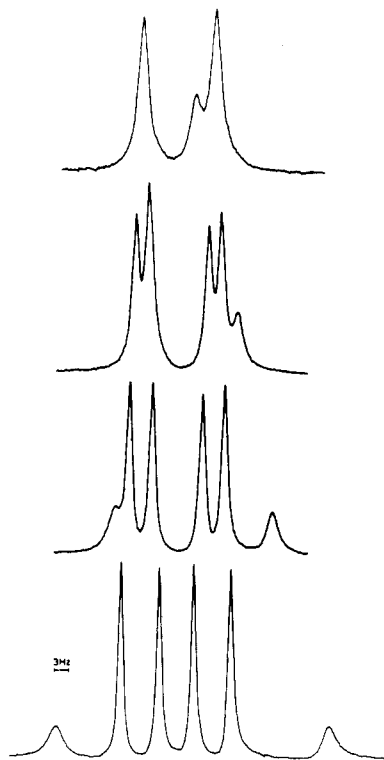(5) C. W. Hilbers and C. MacLean, "NMR, Basic Principles and Progress", Springer, Berlin, 1972, Vol. 7.

Figure 1. ^{2}H EFNMR spectra of nitrobenzene-d_5, measured in a sample cell with a 5-mm electrode distance. From top to bottom, the Voltage over the cell amounts to 0, 17, 23, and 31 kV, respectively.

nitrobenzene: the three chemically shifted ^{2}H resonances are split into doublets when an electric field is applied over the liquid (see Figure 1). The line splittings depend on the angles between the respective C–D bonds and the molecular dipole and are proportional to the quadrupole coupling constants (qcc's) of the deuterons, to the square of the electric field strength, and to the square of the electric dipole moment.

NMR studies of molecules aligned by a magnetic field provide a simple and efficient method to measure susceptibility anisotropies. Combining these with Cotton–Mouton studies leads to information about the so-called temperature-independent term in the Cotton–Mouton effect.[6] Furthermore, alignment effects in strong magnetic fields may introduce an apparent field dependence of indirect spin–spin couplings, e.g., J_{CH} and J_{HH}, through contributions from dipolar couplings.

Electric alignment studies provide a variety of data, which complement conventional studies of dielectric liquids, e.g., dipole moment measurements, the internal field problem, saturation phenomena, etc. Moreover, other possibilities arise in the study of quadrupolar coupling, by virtue of the fact that an electric field NMR (EFNMR) experiment provides the component of the quadrupole coupling tensor parallel to the molecular dipole moment. This allows the assignment of the major component of the former to a specific molecular axis. Analogously, the orientation of the dipole moment in a molecule can be determined. Finally, EFNMR measurements provide the well-defined quantity $\langle 3/2 \cos^2 \theta - 1/2 \rangle_E$, which complements $\langle \cos \theta \rangle_E$ from polarization studies.

(6) A. D. Buckingham, W. H. Prichard, and D. H. Whiffen, *Trans. Faraday Soc.*, *63*, 1057 (1967).

Experimental Techniques

To induce alignment effects with an external magnetic field, no specific precautions are necessary. Standard high field/high resolution equipment can be used. Splittings in spectra of protons and deuterons of 0.35 Hz or larger are readily detectable. As an example, for coronene at 11.7 tesla, the ^{2}H quadrupolar splitting is 2.45 Hz and the H–H and ^{13}C–H dipolar couplings are −0.13 and −0.37 Hz, respectively.

Alignment studies in external electric fields are more difficult to perform, one problem being electric conduction. To obtain a strong and homogeneous electric field, conduction should be as low as possible. Satisfactory experiments can be done with currents lower than about 500 nA. This can be achieved by carefully purifying the samples and by applying electrodialytic membranes to the electrodes of the sample cell. Teflon was chosen as the material for the cell in view of its good insulating properties and because it can easily be machined. Technical difficulties have prevented the use of spinning cells so far. This, together with the material and the construction of the cell, limits the attainable magnetic field homogeneity. To give an idea: ^{2}H line widths are a few hertz compared to a few tenths of 1 Hz in normal sample tubes. To accommodate the sample cell and the necessary wiring for the high voltage supply, a wide-bore/wide-gap magnet is convenient. Most experiments described here were performed on a Bruker WH 180 wide-bore spectrometer. For details concerning cell construction and sample purification, the reader is referred to the original papers.[7]

Theory

The Hamiltonian of a spin system in a magnetic field is often written as a sum of several contributions

$$H = H_Z + H_\sigma + H_J + H_Q + H_D \qquad (1)$$

H_Z, the Zeeman interaction, is the dominating term in the magnetic fields normally used in NMR. The remaining terms, if convenient, may be treated as first-order perturbations. H_σ is the chemical shielding term, H_J corresponds with the scalar couplings, H_Q with the quadrupolar interactions, and H_D with the dipole–dipole couplings.

H_Q and H_D vanish in an isotropic medium since they are described by traceless tensors. These two types of interaction are mainly responsible for the modification of the NMR spectrum upon alignment of the molecules. They assume their simplest mathematical form when described in a suitable molecular or a local frame of reference. In case of a quadrupolar interaction, the z axis of a local frame may be chosen along the major principal component of the electric field gradient tensor. The expressions in a laboratory frame, in which the spins are quantized and the interactions are measured, are obtained by straightforward transformation of axes.[8] The molecular axes are denoted by (x, y, z), the laboratory axes are indicated by primes (x', y', z'), and the local axes, if distinct from the molecular ones, by double primes (x'', y'', z'').

To first order the quadrupolar Hamiltonian of a nuclear spin is[8,9]

(7) (a) T. M. Plantenga, B. H. Ruessink, and C. MacLean, *Chem. Phys.*, *48*, 359 (1980); (b) T. M. Plantenga, Thesis, Free University, Amsterdam, 1981.

$$H_Q = \frac{3}{2} \frac{eQ}{6I(2I-1)} V_{z'z'} [3I_{z'}^2 - I^2] \qquad (2)$$

I is the spin quantum number, eQ is the nuclear quadrupole moment, and $V_{z'z'}$ is the field gradient at the nucleus, generated by the electrons and the other nuclei. The z' axis is chosen along the magnetic field B_0. If $I = 1$ (e.g., ^2H, ^{14}N) eq 2 leads to a line splitting (in hertz)

$$\Delta\nu = \tfrac{3}{2}(eQ/h)V_{z'z'} \qquad (3)$$

To relate line splittings to molecular properties, $V_{z'z'}$ has to be expressed in molecular field gradients $V_{\alpha\beta}$.[5,7] Using polar angles θ and ϕ (θ is the angle between z and z')

$$V_{z'z'} = V_{zz}\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right) +$$
$$\frac{1}{2}(V_{xx} - V_{yy})\sin^2\theta \cos 2\phi + V_{xy}\sin^2\theta \sin 2\phi +$$
$$V_{xz}\sin 2\theta \cos\phi + V_{yz}\sin 2\theta \sin\phi \qquad (4)$$

In a liquid the angular functions have to be averaged over the Brownian motion. For symmetric molecules and by a judicious choice of axes, most of the averages in eq 4 disappear. For the cases presently reviewed, only the first two terms need to be considered.

The molecular and local frames do not in general coincide. If the local frame of reference is chosen to coincide with the principal axes of the electric field gradient tensor, an additional transformation is necessary to relate V_{zz} and $(V_{xx} - V_{yy})$ in eq 4 to the components in the local frame. Denoting the direction cosines of the molecular α axis in the local frame by l, $V_{z''z''}$ by eq, and $(V_{x''x''} - V_{y''y''})V_{z''z''}$, the so-called asymmetry parameter of the electric field gradient, by η, $V_{\alpha\alpha}$ may be written as

$$V_{\alpha\alpha} = eq\left\{\left[\frac{3}{2}(l_{z''\alpha})^2 - \frac{1}{2}\right] + \frac{1}{2}\eta[(l_{x''\alpha})^2 - (l_{y''\alpha})^2]\right\} \qquad (5)$$

The averaged dipolar interaction between spins S and I is to first order given by[9]

$$H_D = D\left[S_{z'}I_{z'} - \frac{1}{4}(S_+I_- + S_-I_+)\right] \qquad (6)$$

in which

$$D = -\gamma_S\gamma_I\hbar^2\left\langle\frac{3z'^2 - r^2}{r^5}\right\rangle \qquad (7)$$

γ_S and γ_I denote the magnetogyric ratios of spins S and I, r is the internuclear distance, and z' is the component of $\vec{r}$ along the magnetic field. The average is taken over the molecular tumbling and the intramolecular motions, e.g., vibrations, which for most applications may be assumed independent.

Alignment by an Electric Field

In an EFNMR experiment on a polar molecule it is convenient to choose the molecular z axis along the dipole moment. In the experiments to be discussed, the

electric field is applied parallel to the magnetic field. Then, since all values of ϕ are equally probable, only the first term on the right-hand side of eq 4 is retained. As an example, the quadrupolar splitting for the para-deuteron in nitrobenzene-d_5 can readily be obtained by combining eq 3 and 4

$$\Delta\nu(\text{Hz}) = \frac{3}{2}\frac{e^2qQ}{h}\left\langle\frac{3}{2}\cos^2\theta - \frac{1}{2}\right\rangle_E \qquad (8)$$

If the phenyl group is assumed to be rigid and hexagonal, the C–D bonds of the ortho and meta deuterons make angles of 60° and 120°, respectively, with the dipole moment. The quadrupolar splitting for the ortho and meta deuterons is expected to be one-eighth of that for the para deuteron. This is borne out experimentally (see figure 1).

For an aromatic molecule a reasonable value of the deuterium quadrupole coupling constant is 186 ± 6 kHz.[10] Substituting this, the alignment can be obtained from the measured splittings. Applying Boltzmann statistics, the alignment can be related to the effective dipole moment and the directing field[5]

$$\left\langle\frac{3}{2}\cos^2\theta - \frac{1}{2}\right\rangle_E = \frac{1}{15}\left[\frac{pE_d}{kT}\right]^2 \qquad (9)$$

p is the effective dipole moment of the molecule in the liquid and E_d is the electric field in the liquid that is effective in orienting the dipole. This directing field contains contributions from the applied electric field and the fields of the surrounding dipoles and will be affected by intermolecular interactions. Thus, electric field NMR can be used to study models for the internal field.

Alignment by a Magnetic Field

Here the orienting mechanism is due to a tensorial property, not a vector property as above. Therefore effective axial symmetry does not apply in general, in contrast to electric dipole orientation. The principal axes of the molecular magnetic susceptibility tensor χ, are in many cases apparent from symmetry. In an aromatic molecule it is obvious to choose the z axis, which corresponds to the largest (absolute) principal value of χ, perpendicular to the molecular plane. If the molecule is assumed planar and rigid, and if the asymmetry parameter η for deuterium may be neglected, the quadrupolar line splitting is (eq 3–5)

$$\Delta\nu_i =$$
$$-\frac{3}{4}\left(\frac{e^2qQ}{h}\right)_i\left\{\left\langle\frac{3}{2}\cos^2\theta - \frac{1}{2}\right\rangle_B + c_i\langle\sin^2\theta\cos 2\phi\rangle_B\right\} \qquad (10)$$

The subscript B indicates averaging in the applied magnetic field and c_i accounts for the transformation of molecular axes to local axes x'', y'', and z'', which coincide with the principal axes of the quadrupole tensor of nucleus i (see eq 5).

The averages over the molecular tumbling can again be calculated from Boltzmann statistics[11]

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$$\left\langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right\rangle_B = \frac{1}{15} \frac{\Delta \chi B^2}{kT} \qquad (11)$$

$$\langle \sin^2 \theta \cos 2\phi \rangle_B = \frac{1}{15} \frac{\delta \chi B^2}{kT} \qquad (12)$$

B is the magnetic induction; $\Delta \chi = \chi_{zz} - {}^1/_2 (\chi_{xx} + \chi_{yy})$ is the anisotropy in the diamagnetic susceptibility and $\delta \chi = \chi_{xx} - \chi_{yy}$ its asymmetry. The χ's should be replaced by effective susceptibilities to account for intermolecular interactions. For instance, for nitrobenzene solutions $\Delta \chi$ is strongly concentration dependent,[12] so one has to extrapolate to infinite dilution in an inert solvent to obtain the molecular value.

From eq 10 it follows that the averages of the angular functions or "motional constants", and thus $\Delta \chi$ and $\delta \chi$ according to eq 11 and 12, can be obtained by measuring the quadrupolar line splitting for two ^{2}H nuclei with different but known c_i. Since the sign of the line splitting cannot be obtained from the spectrum, in principle four possibilities arise, depending on the relative signs of the line splittings. In most cases the correct assignment can readily be made using physical arguments.

Alignment Experiments in Magnetic Fields

Magnetic field alignment effects can modify the NMR spectra of molecules in the liquid phase. For diamagnetic molecules, such effects are small. They were detected for the first time in 1978 by Lohman and MacLean[11] in the ^{2}H spectra of triphenylene-d_{12} and phenanthrene-d_{10} in a field of 9.3 tesla. Quadrupolar line splittings in ^{2}H spectra have since been observed for many diamagnetic compounds.[12-16] Domaille[17] first measured quadrupolar splittings in a paramagnetic system. Recently, Bothner-By et al. reported dipolar couplings in paramagnetic[18] as well as diamagnetic[19] species. In this review, we restrict ourselves to diamagnetic compounds.

The observed splittings can be related to the anisotropy ($\Delta \chi$) and the asymmetry ($\delta \chi$) in the magnetic susceptibility (eq 11 and 12). The number of motional constants in the formula for the line splitting depends on molecular symmetry. For molecules with at least a threefold symmetry axis, only the anisotropy term differs from zero ($\delta \chi = 0$). So, for molecules like benzene, coronene, and triphenylene a single line splitting is sufficient to determine $\Delta \chi$. In cases of lower symmetry at least two splittings, corresponding to nuclei with different directional positions in the molecule, have to be available. The magnitude of a line splitting due to alignment effects depends mainly on the magnetic field strength and the type of interaction for the nucleus studied. Dipolar couplings between
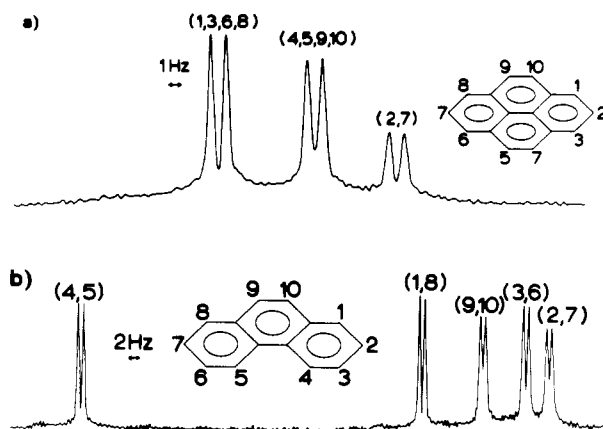
(12) T. M. Plantenga, H. Bulsink, and C. MacLean, *Chem. Phys.*, *61*, 271 (1981).

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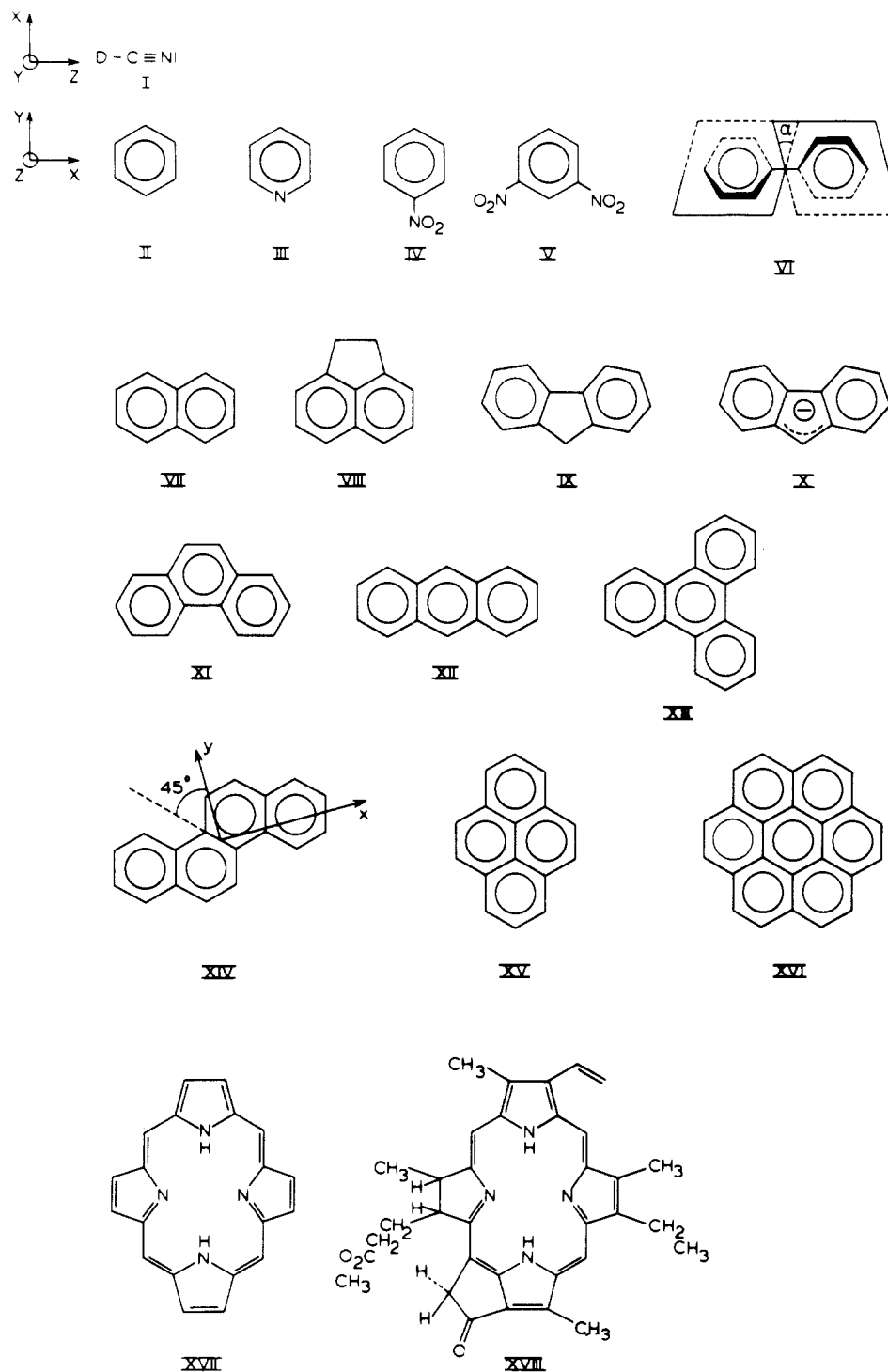(19) C. Gayathri, A. A. Bothner-By, P. C. M. van Zijl, and C. MacLean, *Chem. Phys. Lett.*, *87*, 192 (1982).

Figure 2. Resolution enhanced ^{2}H NMR spectra of pyrene-d_{10} (a) and phenanthrene-d_{10} (b) in a field of 11.7 tesla.

inequivalent protons or between ^{13}C and ^{1}H nuclei may become visible as an apparent magnetic field dependence of the scalar coupling constant.[18,19] Here, the accuracy of the measured splitting is only determined by the line width, since the resonances are already separated by a scalar coupling. If, as a consequence of alignment effects, a resonance line is split into two overlapping lines, the smallest splitting that can still be detected with reasonable accuracy (depending on line width) is about 0.35 Hz. For most molecules studied, the ^{2}H quadrupolar couplings are well above this limit. Dipolar couplings between equivalent protons can only be directly observed in larger molecules, as for instance porphyrins.

A method capable of revealing line splittings even smaller than about 0.35 Hz is the measurement of the field dependence of the amplitude of the NMR line. For a doublet of two identical overlapping Lorentzian lines, the amplitude at the center of the resulting line, as a function of the line splitting $\Delta \nu$, is

$$A(\Delta \nu) = cT_2^*(1 + \pi^2 \Delta \nu \, {}^2 T_2^{*2})^{-1} \qquad (13)$$

in which T_2^* is the effective transverse relaxation time and c is a constant. The amplitude ratio of the resonance lines of the molecule under investigation and a nonaligning reference compound ($\Delta \nu = 0$) is then measured at different magnetic fields. The ratio of the line splittings at two fields is known from their proportionality to B^2, so $\Delta \nu$ can be calculated if the amplitude and T_2^* of the probe molecule and of the internal standard are determined experimentally. It should be noted, however, that this method is only suitable if there is one coupling. For instance, in benzene-d_6, this method leads to erroneous results[14] as was demonstrated recently.[15]

With the availability of high-field spectrometers (up to 14.1 tesla) and of advanced resolution enhancement techniques, fully resolved ^{2}H NMR spectra of many deuterated compounds have been obtained. This is illustrated in Figure 2 for two compounds in a field of 11.7 tesla. In view of the improved experimental conditions, some of the previously measured NMR values for the magnetic susceptibility anisotropy have been redetermined. Together with more recent results, they are given in Table II.

As the splittings can be measured within a few percent, the accuracy of the calculated quantities mainly depends on the assumptions underlying the formulae

Figure 3. Structural formulae and molecular frames for the compounds mentioned in Table II. For biphenyl (VI), the y axis is the bisector of the dihedral angle α.

and on the constants used. So the main sources of error in a quadrupolar experiment are the chosen quadrupole coupling constant and the assumption $\eta = 0$, whereas in the dipolar case the error in the internuclear distance dominates. However, most of these values are known well and the accuracy of $\Delta\chi$ is estimated to be 5–10%. This is illustrated in Table II, where the values obtained in different ways can be compared. It is striking, although not wholly unexpected, that for compounds with an equal number of π-electrons, e.g., anthracene, phenanthrene, and the fluorenyl anion, the same $\Delta\chi$ is found. It should be noted that for all deuterated compounds, except DCN, a quadrupole coupling constant

of 186 kHz has been used.[10] The structure of the measured compounds is given in Figure 3.

Concentration and Solvent Effects

As already mentioned in the introduction, $\Delta\chi$ is to be regarded as an effective susceptibility anisotropy if intermolecular interactions play a role. Since NMR traces molecular rather than bulk properties, it is particularly suitable to measure the concentration dependence of $\Delta\chi$ of solute molecules.

Recently, nitrobenzene, m-dinitrobenzene, naphthalene,[12] and benzene[14,15] were studied in different solvents. For nitrobenzene and m-dinitrobenzene a strong

Table II
Listing of $\Delta\chi$'s and $\delta\chi$'s Measured by the NMR Method and Comparison with Literature Values[a]

compound	solvent	$10^{28}\Delta\chi$, emu	$10^{28}\delta\chi$, emu	ref	$10^{28}\Delta\chi_{lit.}$, emu
DCN (I)	Et_2O/CD_2Cl_2	−0.08		b	−0.07[c]
benzene-d_1 (II)	Me_2CO-d_6 (80 mol %)	−0.93		d	
	(1 mol %)	−1.11		d	−1.06,[e] −1.05,[f] −1.04[c,g]
pyridine (III)		−1.1	−0.1	h	−0.95[c]
nitrobenzene (IV)		−3.4		h	
	Me_2CO/Me_2CO-d_6	−1.5	−0.1	h	−1.45[i]
m-dinitrobenzene (V)	Me_2CO/Me_2CO-d_6	−1.9	−0.1	h	−1.2[j]
biphenyl (VI)	Et_2O	−1.73	0.29	k	−1.98[c,l]
naphthalene (VII)	Me_2CO-d_6	−2.0	0.0	h	−1.99[c]
acenaphthene (VIII)	Et_2O	−2.2	0.0	m	−1.90[c]
fluorene (IX)	Et_2O	−2.6	0.0	n	−2.01[c]
fluorenylcarbanion (X)	Et_2O	−3.1	+0.18	n	
phenanthrene (XI)	Et_2O	−3.1	+0.05	m	−2.75[o]
anthracene (XII)	Et_2O	−3.2	+0.15		−3.03[c]
triphenylene (XIII)	Et_2O	−3.9	−0.09		−3.92[p]
chrysene (XIV)	CH_2Cl_2	−4.4	−0.12	m	−3.70[o]
pyrene (XV)	Et_2O	−4.0	−0.09		−3.69[q]
coronene (XVI)	CH_2Cl_2	−7.9		m	−6.5[o]
	CS_2/Me_2CO-d_6	−7.8		m	
(^{13}CH)	CD_2Cl_2	−7.2		q	
(HH)	CD_2Cl_2	−7.4		q	
porphine (XVII)	CH_2Cl_2	−12.4		q	
methylpyropheophorbide (HH) (XVIII)	CD_2Cl_2	−8.0		q	

[a] The NMR values are from ^{2}H measurements on fully deuterated compounds, unless specified otherwise. Roman numerals refer to Figure 3. [b] P. R. Luyten, J. Bulthuis, and C. MacLean, *Chem. Phys. Lett.*, **89**, 287 (1982). [c] W. H. Flygare, *Chem. Rev.*, **74**, 653 (1974). [d] A. A. Bothner-By, C. Gayathri, P. C. M. van Zijl, and C. MacLean, *J. Magn. Reson.*, **56**, 456 (1984). [e] M. R. Battaglia and G. L. D. Ritchie, *J. Chem. Soc., Faraday Trans. 2*, **73**, 209 (1977) (at infinite dilution in tetra). [f] D. Sutter, *Z. Naturforsch., Teil A*, **26**, 1644 (1971) (gas phase). [g] H. Geschka, S. Pferrer, H. Haüssler, and W. Hüttner, *Ber. Bunsenges. Phys. Chem.*, **86**, 790 (1982) (gas phase). [h] T. M. Plantenga, H. Bulsink, and C. MacLean, *Chem. Phys.*, **61**, 271 (1981). [i] R. J. W. Le Fevre, P. H. Williams, and J. M. Eckert, *Aust. J. Chem.*, **18**, 1133 (1965). [j] M. A. Lasheen, *Acta Crystallogr., Sect. A*, **A24**, 289 (1968). [k] C. Gayathri and A. A. Bothner-By, unpublished results (14.1 tesla magnet); the result leads to $\alpha = 33°$. [l] Planar structure assumed. [m] This Account. [n] P. C. M. van Zijl, N. H. Velthorst, and C. MacLean, *Mol. Phys.*, **49**, 315 (1983). [o] A. A. Bothner-By and J. A. Pople, *Ann. Rev. Phys. Chem.*, **16**, 43 (1965). [p] R. J. W. Le Fevre and D. S. N. Murthy, *Austr. J. Chem.*, **22**, 1415 (1969). [q] C. Gayathri, A. A. Bothner-By, P. C. M. van Zijl, and C. MacLean, *Chem. Phys. Lett.*, **87**, 192 (1982).

concentration effect was found. For pure nitrobenzene $\Delta\chi = -3.4 \times 10^{-28}$ emu, whereas, extrapolated to infinite dilution, $\Delta\chi = -1.5 \times 10^{-28}$ emu. For naphthalene, no significant concentration or solvent effect was found. It seems plausible that for the large aromatic compounds in Table II, where the concentrations are below 1 mol %, the $\Delta\chi$ values found correspond to the molecular values.

Benzene, dissolved in acetone-d_6, shows a concentration dependence too, but it is an anomalous one: $|\Delta\chi|$ increases with decreasing concentration and becomes constant at about 60 mol %.[15] This will probably correspond to a change in the relative orientation of the benzene molecules upon dilution; a detailed discussion can be found in ref 15.

Comparison with Other Methods

As is clear from Table II, most $\Delta\chi$ values agree with the literature data within a few percent. Some NMR values are somewhat higher than those obtained from the Cotton–Mouton effect. The remaining small differences for some molecules can perhaps be attributed to inaccuracies in the assumed values of the quadrupole coupling constant and asymmetry parameter in the NMR method or to inavailability of accurate values for the temperature independent term and polarizability anisotropies used in the Cotton–Mouton experiments.[20]

Summarizing, it can be stated that the NMR method forms a new, but established, method to determine $\Delta\chi$. Compared with the other techniques, it is simple and

provides some additional advantages: (i) Apart from the anisotropy $\Delta\chi$, the asymmetry $\delta\chi$ can be obtained. (ii) The different compounds in a mixture can be studied separately. (iii) Unlike microwave spectroscopy, the method is applicable to polar as well as nonpolar compounds and large aromatic systems can be studied.

Alignment by an Electric Field

The alignment of a polar liquid by an external electric field can be expressed in terms of the dipole moment p and the directing field E_d by Boltzmann statistics (eq 9). In polar liquids the molecular dipole moment is usually larger than in the gas phase by virtue of the "reaction" field. This field is generated by a polar molecule but is ineffective in orienting the dipole. Simple reaction field theory predicts that the effective dipole moment in the liquid is given by

$$p = \mu \left[\frac{2\epsilon + 1}{2\epsilon + n^2} \frac{n^2 + 2}{3} \right] \quad (14)$$

μ is the gas-phase dipole moment, ϵ the permittivity of the liquid, and n its index of refraction.

The alignment and thus the NMR line splittings are expected to be proportional to the square of E_d, which, in turn, is proportional to the applied field, the Maxwell field E_M. The proportionality between the line splittings and E_M^2 is illustrated in Figure 4 for nitrobenzene. The figure also gives the behavior expected from the models of Lorentz[21] and Onsager.[22] Strongly associ-

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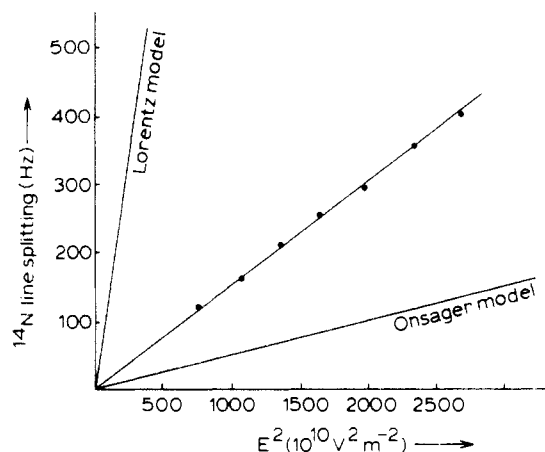(21) H. A. Lorentz, "The Theory of Electrons", Teubner, Leipzig, 1909.

Figure 4. The proportionality between the ^{14}N line splitting and the square of the electric field strength for nitrobenzene. The behavior predicted by the models of Lorentz and Onsager is also indicated.

ating liquids like nitrobenzene deviate from both; liquids that do not associate are best described by Onsager's model.[5] Statistical calculations of the alignment can be found in ref 23 and 24.

Saturation Effects

As stated in the previous section, the directing field E_d is proportional to the Maxwell field E_M. The form of the proportionality factor depends on the model used; if E_d equals the cavity field, then

$$\vec{E}_d = \frac{3\epsilon}{2\epsilon + 1}\vec{E}_M \qquad (15)$$

The permittivity ϵ depends slightly on the applied field. In general ϵ is found to decrease with increasing field strength; this is called "normal saturation".[25] The alignment will also show a saturation effect: when the alignment approaches its limiting value, it will increase less than proportional with $E_M{}^2$. Even if this type of saturation would be absent, substitution of eq 14 and 15 in the expression for the alignment, (eq 9) suggests that whenever ϵ shows normal saturation, the alignment will follow this tendency.

It is therefore of interest to see how the alignment behaves in the particular case of nitrobenzene, where a reverse effect has been reported,[26] i.e., ϵ increases with increasing field strength ("anomalous saturation"). To establish the NMR analogue of this effect, ^{14}N and ^{2}H quadrupolar line splittings in pure perdeuterionitrobenzene were measured as a function of the electric field strength.[27] A plot of the measured line splitting vs. $E_M{}^2$ did not give a straight line. The deviation from linearity, however, corresponds with normal saturation: the alignment increases less than proportional with $E_M{}^2$. To

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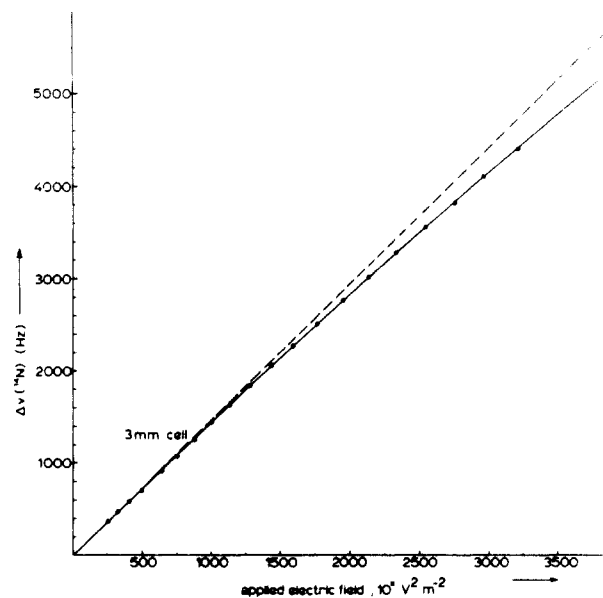
Figure 5. ^{14}N line splittings for perdeuterionitrobenzene as a function of the square of the external electric field E_M. The dashed line is a linear fit to the points up to $E_M = 6.3 \times 10^6$ V m^{-1}. The lower line is the polynomial fit given in eq 16b.

fit the curve (Figure 5), a term in $E_M{}^4$ was added (odd powers of E_M do not contribute to the series expansion of the alignment). The best fits were obtained with

$$\Delta\nu(^2\mathrm{H}_{para}) =$$
$$\frac{3}{2}\frac{e^2qQ(^2\mathrm{H})}{h}[(6.25 \times 10^{-18})E_M{}^2 - (1.43 \times 10^{-33})E_M{}^4] \qquad (16a)$$

and

$$\Delta\nu(^{14}\mathrm{N}) =$$
$$\frac{3}{2}\frac{e^2qQ(^{14}\mathrm{N})}{h}[(6.40 \times 10^{-18})E_M{}^2 - (1.32 \times 10^{-33})E_M{}^4] \qquad (16b)$$

Application of Boltzmann statistics, assuming that the Onsager model is valid, leads to[2a]

$$\Delta\nu = \frac{3}{2}\frac{e^2qQ}{h}[(3.55 \times 10^{-18})E_M{}^2 - (1.80 \times 10^{-35})E_M{}^4]$$

In view of the assumptions underlying the Onsager model, the agreement for the coefficient of $E_M{}^2$ is reasonable, but the model fails to reproduce the coefficient of $E_M{}^4$. The experimental value for the $E_M{}^2$ coefficient is in agreement with other results.[28]

The reported anomalous saturation of the electric permittivity of nitrobenzene was believed to be caused by antiparallel coupling of molecular dipoles.[29] Of course, such a mechanism does not necessarily lead to anomalous saturation of the alignment, which is not found experimentally. In addition, it should be noted that the statistic–mechanical approach leads to different expressions for ϵ and the alignment as a function of the electric field; so also from this point of view the two quantities need not follow the same tendency.

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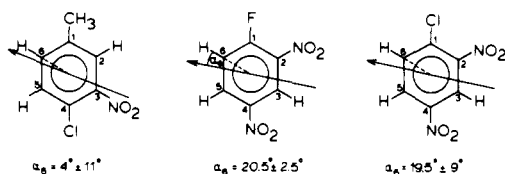
Figure 6. Orientation of the dipole moment in 4-chloro-3-nitrotoluene, 1-fluoro-2,4-dinitrobenzene, and 1-chloro-2,4-dinitrobenzene. The different margins of error in α_6 reflect the accuracies in the ratios of the dipolar couplings.

Dipole Moment Orientation

The magnitude of the dipole moment of a molecule can be obtained from permittivity measurements. Its orientation relative to molecular axes is usually estimated by vectorial addition of partial dipole moments of bonds and groups.[30] For small polar molecules in the gas phase, both magnitude and orientation of the dipole moment can be obtained from the Stark effect in the microwave spectrum.[31]

The orientation of the dipole moment of a molecule in a liquid can also be determined by EFNMR. This possibility has been demonstrated for three substituted nitrobenzenes, recording natural-abundance ^{13}C NMR spectra.[7,32] Assuming rigid molecules, the ^{13}C–H dipolar couplings can be written (in hertz) as (cf. eq 7)

$$D_{CH} = -\gamma_C \gamma_H \hbar r_{CH}^{-3} \pi^{-1} \left(\frac{3}{2} \cos^2 \alpha - \frac{1}{2} \right) \left\langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right\rangle_E \quad (17)$$

α is the angle between the C–H bond and the dipole moment. Only dipolar couplings between carbons and directly bonded protons are large enough to be measured. Assuming equal C–H bond lengths, the ratio of two couplings, D_i and D_j, only depends on the angles α_i and α_j

$$D_i/D_j = \left(\frac{3}{2} \cos^2 \alpha_i - \frac{1}{2} \right) \Big/ \left(\frac{3}{2} \cos^2 \alpha_j - \frac{1}{2} \right) \quad (18)$$

Since the α's can be expressed in one another in any adopted molecular structure, there is only one unknown. Because of the cosine-square terms, two solutions are possible in principle, corresponding to two orientations of the dipole moment. In the molecules studied, one of these could always be rejected on physical grounds. The results, given in Figure 6, were obtained assuming a regular hexagonal arrangement of the C–C bonds. The agreement between the EFNMR result and the estimate from partial moments is satisfactory.[32]

Determination of the Principal Components of ^{14}N Quadrupole Coupling Tensors

In electric field experiments the quadrupolar splitting is given by (eq 3 and 4)

$$\Delta \nu = \frac{3}{2} \frac{eQ}{h} V_{zz} \left\langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right\rangle \quad (19)$$

V_{zz}, the field gradient along the dipole moment, can be expressed in the three principal components of the electric field gradient tensor by means of eq 5. If two

different quadrupolar nuclei (e.g., ^{14}N, ^{2}H) are studied in the same molecule, the ratio of the two splittings is

$$\frac{\Delta \nu (^{14}N)}{\Delta \nu (^2H)} = \frac{(eQ/h) V_{zz} (^{14}N)}{(eQ/h) V_{zz} (^2H)} \quad (20)$$

Let us first consider deuterated nitrobenzene. For the para deuteron eQV_{zz}/h is the well-known ^{2}H quadrupole coupling constant. The numerator on the right-hand side of eq 20 can thus be obtained from the line splittings (note that it is not necessarily the major principal component of the ^{14}N quadrupole coupling). Its value has been studied for nitrobenzene in benzene and acetonitrile at concentrations between 25 and 100 mol %.[28] Within the limits of error, neither solvent nor concentration dependence was found, the mean value being 1.52 MHz. As discussed in ref 33, environmental effects may affect quadrupole coupling constants. Lucken[34] states that they decrease by some 5% when going from the gas phase to the liquid. The conclusion from the EFNMR work is that intermolecular interactions in the solutions studied do not lead to detectable changes in the component of the ^{14}N quadrupole coupling parallel to the dipole moment.

To determine all three principal components, ^{2}H and ^{14}N splittings in deuterated *m*-dinitrobenzene were measured. For the deuteron in meta–meta position, the denominator in eq 20 is taken the same as in nitrobenzene. Assuming equivalent ^{14}N quadrupole couplings in the nitro groups in the two molecules, the field gradient at the nitrogen parallel to the dipole moment can be expressed in the two principal in-plane components: $V_{zz} = \frac{1}{4} V_{z''z''} + \frac{3}{4} V_{x''x''}$ (eq 5). From the measured splittings,[35] taking into account the traceless character of the quadrupole coupling tensor, one obtains

$$(eQ/h) V_{z''z''} = \pm (1.52 \pm 0.06) \text{ MHz}$$
$$(eQ/h) V_{y''y''} = \mp (1.18 \pm 0.10) \text{ MHZ}$$
$$(eQ/h) V_{x''x''} = \mp (0.34 \pm 0.04) \text{ MHz}$$

The major principal component is along the C–N bond, as also found in the solid state from single-crystal work by Cheng and Brown.[36] The second largest component is perpendicular to the plane of the nitro group, a finding in contradiction with results based on relaxation studies.[37] Also literature values for the quadrupole coupling constants of ^{14}N in nitrobenzene vary strongly: 2.6 MHz from relaxation,[38] 1.08 MHz from NMR line widths,[39] and 1.76 MHz from liquid crystal NMR.[40] The solid-state value is reported to be 1.43 MHz.[41]

Final Remarks

Our studies of alignment effects in magnetic fields constitute a simple method to measure anisotropies and asymmetries of diamagnetic susceptibilities of molecules. We are now extending our work to other systems,

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e.g., molecules of biochemical interest, in cooperation with Professor A. A. Bothner-By (Pittsburgh). Attention is also being paid to small molecules to study the correspondence with $\Delta\chi$ determinations using microwave spectroscopy.[42]

EFNMR studies are at the moment focused on binary mixtures. The addition of a second component to the solution affects the alignment which thus provides information about intermolecular interactions.[43,44] In a recent study,[44] the change of the alignment upon dilution is interpreted in possible changes of the quadrupole

coupling constant, the asymmetry parameter, and the molecular geometry. At the moment, charge-transfer interactions between suitable donor and acceptor molecules are being studied. Furthermore, the feasibility to study zero-quantum transitions in proton spectra, to overcome the problems connected with the broad single-quantum lines, is being explored. Also pretransitional phenomena in the isotropic phase of liquid crystals, just above the transition temperature, are being successfully studied by EFNMR.

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Organic Radical Ions in Rigid Systems

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Radical ions are important chemical entities occurring in one-electron oxidation or reduction of closed-shell molecules. They are produced in chemical reactions as well as upon electrolysis, photolysis, and radiolysis.

Having an odd electron, radical ions are, in general, reactive, and their systematic generation and unambiguous spectroscopic characterization is not necessarily straightforward. This is particularly true for radical ions in fluid solutions. In rigid media, however, such species can be produced in situ by radiolysis or photolysis, and the observation of potentially reactive species can be carried out at leisure.

Tadamasa Shida, born in 1935, received his B.Sc. and Ph.D. from the University of Tokyo. From 1958 to 1974 he was a research fellow at the Institute of Physical and Chemical Research, Wako, Japan, where he worked mainly under Dr. Masashi Imamura. In 1974 he joined the faculty of Kyoto University, and he is now Professor of Chemistry. Professor Shida was a Fulbright research fellow to the University of Notre Dame (1964–1966), where he was associated with Professor William H. Hamill. He earned the Chemical Society of Japan Award for Young Chemists in 1970.

Edwin Haselbach was born in 1940 in Zurich, Switzerland. He received his university education from the Federal Institute of Technology (ETH) of Zurich where he completed a Ph.D. in physical–organic chemistry with Professor Edgar Heilbronner. After postdoctoral work with Professor Michael Dewar at the University of Texas at Austin (1967–1969), he returned to Switzerland where he became Professor of physical chemistry at the University of Basel. Since 1980 he is director of the Institute of Physical Chemistry of the University of Fribourg (Switzerland). He was recipient of the Association of Swiss Chemists Award in 1971 and the 1976 Werner Award of the Swiss Chemical Society.

Thomas Bally was born in 1948 in Geneva, Switzerland. After obtaining his Ph.D. at the University of Basel, he joined the group of Professor Satoru Masamune at MIT where he became acquainted with the technique of matrix isolation. In 1981 he returned to Switzerland and joined the institute of Professor Haselbach at the University of Fribourg where he is currently working on the spectroscopy and photochemistry of radical ions in matrices.

Generation of Radical Ions by Photolysis

Recent developments in cryogenic technology have led to the widespread use of matrix isolation spectroscopy.[1] In particular, vacuum-UV excitation of molecules embedded in rare gas matrices[2] or argon resonance photoionization during sample deposition[3] have enabled detailed vibronic analyses of elusive polyatomic radical cations. Interestingly, the spectra obtained in neon matrices at 4 K are comparable to those of the rotationally cooled gaseous ions.[2] Recent progress in the spectroscopy, photophysics, and photochemistry of ions and other transient species embedded in low-temperature rare-gas matrices has been reviewed by Bondybey.[2] Somewhat earlier optical studies of matrix-isolated charged species were reviewed by Andrews[3] and by Jacox,[4] emphasizing mostly IR spectroscopic results.

Finally, two recent innovations in this field should be mentioned. Firstly, Knight and Steadman[5] have launched the ESR study of simple radical cations such as $CO^+\cdot$, $NO_3^+\cdot$, and $H_2O^+\cdot$ generated by neon-discharge photolysis. Secondly, Andrews has begun to explore the technique of biphotonic UV/vis resonance photoionization in the presence of electron traps to generate relatively complex organic radical cations, such as those

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