多核NMR①: 測定しやすい核としにくい核

多核NMR:

(核の種類による)検出感度(同じ濃度の時)

\[ S = I(I+1)v_0^3N \]

\( I \): 核スピン
\( v_0 \): 共鳴周波数
\( N \): 核スピン濃度

相対感度(\(^{13}\text{C} \)核を基準)

\[
R' = \left[ \frac{I(I+1)}{2} \left( \frac{1}{2} \right) + 1 \right] \times \left[ \frac{v_0}{v_{13\text{C}}} \right]^3
\]

総合相対感度
(天然存在比も考慮して\(^{13}\text{C} \)核を基準)

\[
R' = \left[ \frac{I(I+1)}{2} \left( \frac{1}{2} \right) + 1 \right] \times \left[ \frac{v_0}{v_{13\text{C}}} \right]^3 \times \left[ \frac{\alpha_0}{\alpha_{13\text{C}}} \right]
\]

線幅因子 (line width factor)

\[
LW = \frac{(2I+3)Q^2}{P(2I-1)} \]

\( I \): 核スピン
\( Q \): 核四極子モーメント

よく利用される\( I = 1/2 \)の核

\(^{15}\text{N} \) (0.37%), \(^{19}\text{F} \) (100%), \(^{29}\text{Si} \) (4.7%), \(^{31}\text{P} \) (100%)

\(^{77}\text{Se} \) (7.58%), \(^{111}\text{Cd} \) (12.75%), \(^{119}\text{Sn} \) (8.58%)

\(^{125}\text{Te} \) (6.99%), \(^{195}\text{Pt} \) (33.8%), \(^{207}\text{Pb} \) (22.6%)

よく利用される\( I = 1/2 \)以外の核

\(^2\text{H} \) (\( I = 1, 0.015\%)\), \(^7\text{Li} \) (\( I = 3/2, 92.6\%)\)

\(^{11}\text{B} \) (\( I = 3/2, 81.2\%)\), \(^{14}\text{N} \) (\( I = 1, 99.6\%)\)

\(^{17}\text{O} \) (\( I = 5/2, 0.037\%)\)

他の核とのカップリングがよく利用される核

\(^{103}\text{Rh} \) (\( I = -1/2, 100\%)\)

\(^{107}\text{Ag} \) (\( I = -1/2, 51.82\%)\), \(^{109}\text{Ag} \) (\( I = -1/2, 48.18\%)\)

三共出版「多核種の溶液および固体NMR」
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核スピンや感度、それぞれの核の基準物質などのデータが多数掲載
共鳴周波数は核ごとに決まっている

電磁波のエネルギー\( \Delta E = h \nu \) とすると

\[
\nu = \frac{\gamma \cdot B_0}{2\pi}
\]

測定前に行うオートチューニングは
この共鳴周波数を調整する作業

それぞれの核における共鳴周波数(\(^1\text{H}\)を100 MHzとしたとき)

http://www.chem.wisc.edu/areas/reich/nmr/notes-7-multi.pdf

通常は高周波数の核を\(^1\text{H}\)に固定して測定
低周波数側をいろいろ設定することが多い
(=\(^1\text{H}\)測定の後はチューニングを\(^1\text{H}\)に戻す)

共鳴周波数の高い核
\(= \) high frequency核
共鳴周波数の低い核
\(= \) low frequency核

化学シフト幅は核ごとに異なる

\(^1\text{H} \sim 15 \text{ ppm}\)
\(^1\text{3C} \sim 200 \text{ ppm}\)
\(^1\text{1B} \sim 210 \text{ ppm}\)
\(^3\text{1P} \sim 450 \text{ ppm}\)
\(^7\text{7Se} \sim 3000 \text{ ppm}\)
\(^1\text{9Pt} \sim 6700 \text{ ppm}\)
\(^5\text{9Co} \sim 18000 \text{ ppm}\)
多核NMR各論: $^2$H NMRスペクトル

$^2$H、核スピン$I = 1$、天然存在比0.015%、磁気回転比$\gamma = 4.1066$
四極子モーメント = $2.8 \times 10^{-3}$、相対総合感度 = $1.45 \times 10^{-6}$

化学シフト基準はSi(CD$_3$)$_4 = 0$

例：部分重水素化された化合物8のスペクトル

$^1$H NMR spectrum (C$_6$D$_6$)

$^2$H NMR spectrum (C$_6$D$_6$)

応用例：styrene-$d_8$のMeReO$_3$を用いた触媒的ジヒドロキシ化反応速度測定

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Solvent</th>
<th>$k_{obs}/[Re]_{T/7}/\text{M}^{-1}\text{s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[EtPy]BF$_4$</td>
<td>0.20 ± 0.02</td>
<td></td>
</tr>
</tbody>
</table>

$J.\text{Mol. Cat. B: Enzymatic}\ 2011,73,17.$

多核NMR各論：\(^7\)Li, \(^6\)Li NMRスペクトル

\(^7\)Li, 核スピン\(I = 3/2\), 天然存在比92.6%, 磁気回転比\(\gamma = 10.396\)
四極子モーメント = \(-4 \times 10^{-2}\), 相対総合感度 = \(1.54 \times 10^3\)

\(^6\)Li, 核スピン\(I = 1\), 天然存在比7.4%, 磁気回転比\(\gamma = 3.937\)
四極子モーメント = \(-8 \times 10^{-4}\), 相対総合感度 = 3.58

\(^7\)Li応用例：Me\(_3\)Siアセチレンの脱プロトン化をRl(rapid injection)NMR法で迅速モニター

\(^6\)Li応用例：(Ph\(^6\)Li)\(_2\)と(Ph\(^6\)Li)\(_4\)の平衡をEt\(_2\)O溶媒中低温の\(^6\)Liおよび\(^{13}\)C NMRスペクトルで観測

化学シフト基準はLiCl/D\(_2\)O = 0
範囲は約-10~5 ppm


Prof. Hans J. Reich@U Wisconsin

the CO ligand, exhibiting extraordinarily strong

Preparation of diborene PhB₂–diborene complex [(Et₂B)₂]

ΔE = 1.510(14), Pt1–B2 164.2(8). The torsion angle B2–C4–B3–B2 is identical to that calculated for the free B2–C4–B3–B2 structure.

The coupling constant (J) of 1,726 Hz is significantly higher than those of the B–B interaction in AB (typically 5–10 mmol) and in some cases contained co-crystallized solvents. The coupling constant is associated in a new hybrid phase with 1 : 1 stoichiometry.

The first term, C26–B2–C4, is the backbonding interaction between the transition metal and the B–B unit, which is characterized by a confident assignment of this resonance to the phosphorus coupling constant of 1,726 Hz, higher than those of the B–B interaction in AB (typically 5–10 mmol) and in some cases contained co-crystallized solvents.

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多核NMR各論: $^{15}$N NMRスペクトル

$^{15}$N、核スピン$I = -1/2$、天然存在比0.37%、磁気回転比$\gamma = -2.716$
四極子モーメント = なし、相対総合感度 = $2.19 \times 10^{-2}$
化学シフト基準は$\text{CH}_3\text{NO}_2 = 0$
範囲は約600~600 ppm

最近の応用例: 窒素分子錯体の同定

$^{1}H$-$^{15}N$ HSQC

$N$-terminals
$Lysine 43$
$C$-terminals
$Lysine 48$

ubiquitin (76 amino acids, 8.5 kDa)

$^3$D HNCA

$\delta_N = -29.0$
(dt, $^1J_{NN} & ^2J_{PN} = 6.1 & 2.4$ Hz, terminal $N\alpha$)
$\delta_N = -16.5$
(d, $^1J_{NN} = 6.1$ Hz, terminal $N\beta$)
$\delta_N = 8.5$
(s, bridging $N$)

$P = P_i\text{Pr}_2$

$\text{Nat. Chem. 2011, 3, 120.}$
使用例: 含フッ素ポリマーの構造解析
http://www.cerij.or.jp/

最近の応用例: ネズミの腫瘍にF-cytosineを注射、そのままF-uracilを検出

二次元^{19}F NMR:
http://www.toray-research.co.jp/new_bunseki/index.html

多核NMR各論：$^{29}$Si NMRスペクトル

$^{29}$Si, 核スピン$I = -1/2$, 天然存在比4.7%, 磁気回転比$\gamma = -5.3190$
四極子モーメント = なし, 相対総合感度 = $4.95 \times 10^{-1}$

化学シフト基準は$\mathrm{SiMe}_4 = 0$
範囲は約-200~100 ppm

使用例：固体$^{29}$Si NMRによる
Al, Si含有ゼオライトの分析


使用例：ビーズ表面に形成した
シロキサンの状態分析


最近の例：特殊な環境の$^{29}$Si核を含む化合物

$\delta_{\mathrm{Si}} = 90$

*Science* 2004, 305, 1755.

$\delta_{\mathrm{Si}} = -52, -50, 300, 308$

*Science* 2011, 331, 1306.
多核NMR各論: $^{31}$P NMRスペクトル

$^{31}$P, 核スピン$I = 1/2$, 天然存在比100%, 磁気回転比$\gamma = 10.8394$
四極子モーメント = なし, 相対総合感度 = $1.44 \times 10^2$

利用例:

(a) 1 + xantphos (1 eq), 80 °C, 15 min, in CD$_2$Cl$_2$ under H$_2$/CO (1/1, 0.1 MPa)
(b) 1 + xantphos (1 eq), 120 °C, 15 min, in DMA; under H$_2$/CO (1/1, 0.1 MPa)
(c) Rh(acac)(CO)$_2$ + xantphos (1 eq) + 1 (2.5 eq), 120 °C, 15 min, in DMA, under H$_2$/CO (1/1, 0.1 MPa)
(d) Rh(acac)(CO)$_2$ + xantphos (1 eq), 120 °C, 15 min, in DMA; under H$_2$/CO (1/1, 0.1 MPa)
(e) Rh(acac)(CO)$_2$ + xantphos (1 eq), 120 °C, 15 min, in DMA; under CO (0.1 MPa)
(f) Rh(acac)(CO)$_2$ + xantphos (1 eq), 80 °C, 15 min, in CD$_2$Cl$_2$ under H$_2$/CO (1/1, 0.1 MPa)
(g) Rh(acac)(CO)$_2$ + xantphos (1 eq), 120 °C, 15 min, in DMA; under Ar (0.1 MPa)