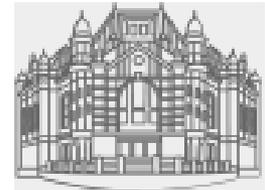


Parity nonconserving corrections to the spin-spin coupling in molecules



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J-coupling in molecules

- Tensor form of the direct dipole-dipole interaction:

$$I_1 T^{(2)} I_2$$

- Direct dipole-dipole interaction between nuclear magnetic moments is of the order of

$$\alpha^2 \left(\frac{m_e}{m_p} \right)^2 \frac{1}{R^3} \sim \text{MHz}$$

- Indirect nuclear spin-spin interaction (*J-coupling*):

$$I_1 J I_2; \quad J = J^{(0)} + J^{(1)} + J^{(2)}$$

- Indirect nuclear spin-spin interaction is of the order of

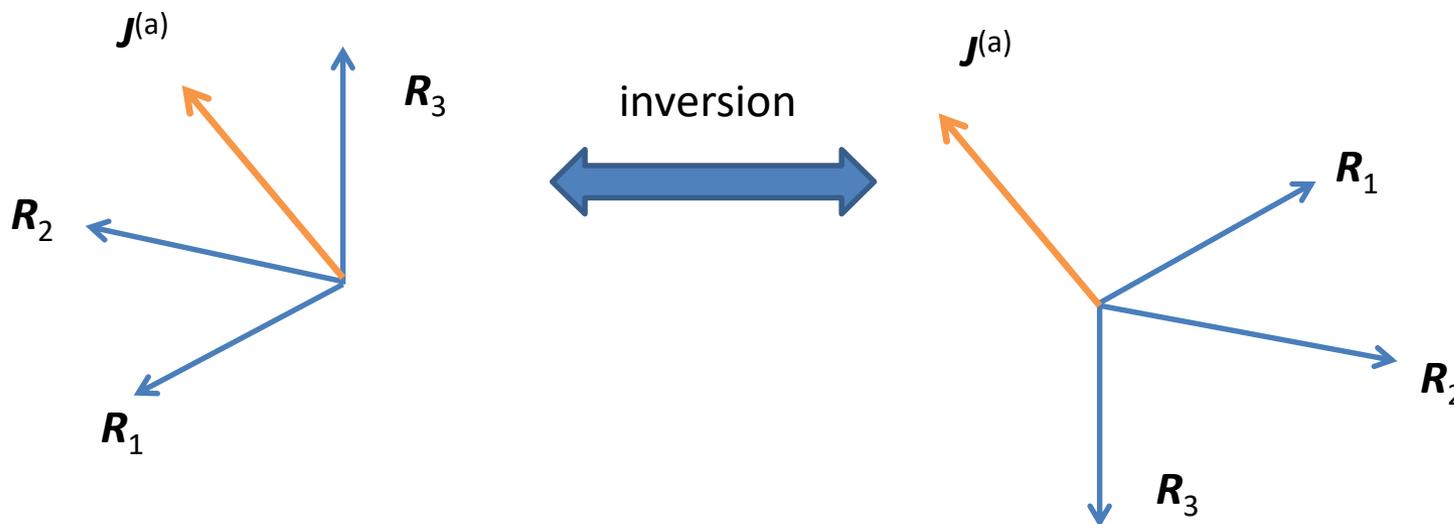
$$\alpha^4 \left(\frac{m_e}{m_p} \right)^2 Z_1 Z_2 < 100 \text{kHz}$$

- Only scalar *J*-coupling survives averaging over molecular rotation.

Vector coupling without P-odd interaction

$$I_1 J^{(1)} I_2 = I_1 \times I_2 \cdot J^{(a)}$$

If parity is conserved, then $J^{(a)}$ must be an axial vector. Non-degenerate electronic state is described only by polar vectors, such as nuclear radii R_i , therefore $J^{(a)} = 0$.

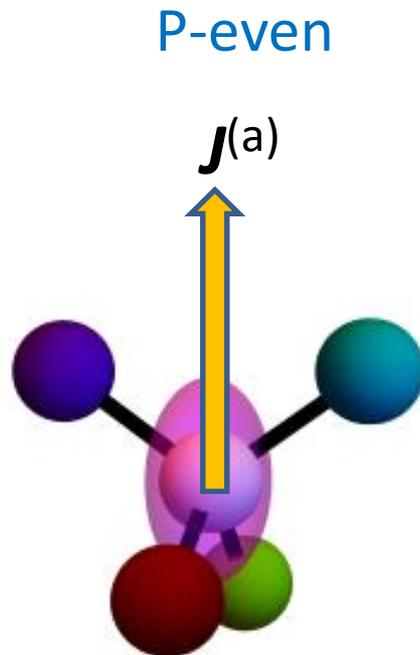


To have vector coupling $J^{(a)}$ we need chiral molecule with two degenerate states linked by inversion.

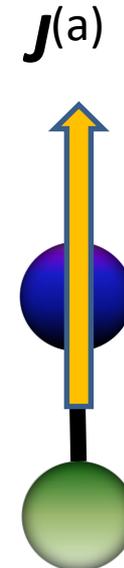
Vector coupling with P-odd interaction

$$\mathbf{I}_1 \times \mathbf{I}_2 \cdot \mathbf{J}^{(a)}$$

- If parity is not conserved, then $\mathbf{J}^{(a)}$ can be a polar vector, which is fixed in molecular frame. In this case we can have vector coupling already in diatomic molecules, where $\mathbf{J}^{(a)} \sim \mathbf{R}_{12}$.



P-odd



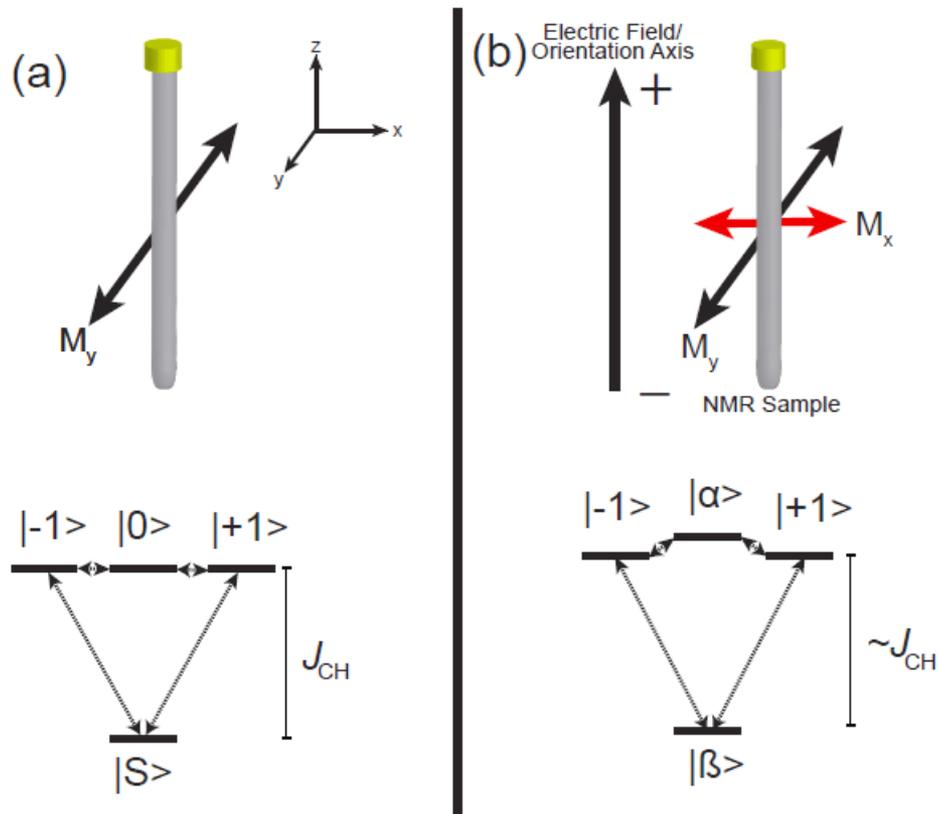
Experiment to observe vector coupling

$$\mathbf{I}_1 \times \mathbf{I}_2 \cdot \mathbf{J}^{(a)}$$

- In the molecular stationary state expectation value is zero. We need to look at the correlation signal rather than frequency shift.
- Correlation $\mathbf{I}_1 \times \mathbf{I}_2 \cdot \mathbf{J}^{(a)}$ is similar to P-odd correlation $\mathbf{I}_1 \times \mathbf{S} \cdot \mathbf{n}$, which can be observed in diatomic radicals [Yale group: S Cahn, D DeMille *et al*].
- We can polarize molecule in electric field, then $\langle \mathbf{J}^{(a)} \rangle \sim \mathbf{E}$. We also need to decouple spins from each other.

Recent proposal of NMR experiment

[JP King, TF Sjolander, & JW Blanchard,
J.Phys.Chem.Lett., **2017**, 8, 710]



PV interaction in nonrelativistic approximation

Atomic units: $\hbar = m_e = |e| = 1$

Nuclear-spin-dependent PV interaction:

$$H_{\text{PV}}^{(2)} = \frac{G\alpha}{2\sqrt{2}} \sum_{i,K} g_K^{(2)} \mathbf{I}_K [\mathbf{p}_i, \delta(\mathbf{r}_i - \mathbf{R}_K)]_+$$

In the external magnetic field

$$\mathbf{p}_i \rightarrow \boldsymbol{\pi}_i = \mathbf{p}_i + \alpha \mathbf{A}$$

$$\mathbf{A}_L = \gamma_L \frac{\mathbf{I}_L \times (\mathbf{r} - \mathbf{R}_L)}{|\mathbf{r} - \mathbf{R}_L|^3}$$

PV interaction in the magnetic field of a nucleus

$$H_{\text{PV}}^{(2)} = \frac{G\alpha}{2\sqrt{2}} \sum_{i,K} g_K^{(2)} \mathbf{I}_K [\mathbf{p}_i, \delta(\mathbf{r}_i - \mathbf{R}_K)]_+ \\ + \frac{G\alpha^2}{\sqrt{2}} \sum_{i,K,L} g_K^{(2)} \gamma_L \frac{\mathbf{I}_K \cdot \mathbf{I}_L \times (\mathbf{R}_K - \mathbf{R}_L)}{|\mathbf{R}_K - \mathbf{R}_L|^3} \delta(\mathbf{r}_i - \mathbf{R}_K)$$

Second term gives direct contribution to antisymmetric J -coupling!

[Barra & Robert, MP, 88, 875 (1996)]

PV contribution to J -coupling

$$\mathbf{J}^{(a)}(K, L) = \frac{G\alpha^2}{\sqrt{2}} \left(g_K^{(2)} \gamma_L \langle \Psi_e | \sum_i \delta(\mathbf{r}_i - \mathbf{R}_K) | \Psi_e \rangle - \gamma_K g_L^{(2)} \langle \Psi_e | \sum_i \delta(\mathbf{r}_i - \mathbf{R}_L) | \Psi_e \rangle \right) \frac{\mathbf{R}_K - \mathbf{R}_L}{|\mathbf{R}_K - \mathbf{R}_L|^3}$$

Electronic ME does not include spin, or momentum.

Therefore, the main contribution comes from 1s shell.

$$\langle \Psi_e | \sum_i \delta(\mathbf{r}_i - \mathbf{R}_K) | \Psi_e \rangle = \rho_e(\mathbf{R}_K) \approx \frac{2}{\pi} Z_K^3$$

Estimate of PV contribution to J -coupling

Typical internuclear distance R is few a.u. Assuming $R=4$ and $Z=80$ we get:

$$J^{(a)} \sim \frac{G\alpha^3}{\sqrt{2}} \frac{m_e}{m_p} g^{(2)} \frac{1}{8\pi} Z^3$$

$$\frac{1}{g^{(2)}} J^{(a)} \sim 6.8 \times 10^{-20} \text{ a.u.} = 0.45 \text{ mHz}$$

Contribution of the first term of PV interaction to J-coupling

The second-order expression for the $J^{(a)}$ has the form:

$$J^{(a)} \sim \sum_n \frac{\langle 0 | H_{\text{PV}}^{(2)} | n \rangle \langle n | H_{\text{HF}} | 0 \rangle}{E_0 - E_n}$$

$$H_{\text{PV}}^{(2)} \sim \frac{G\alpha Z^2}{2\sqrt{2}\pi} g^{(2)} \quad H_{\text{HF}} \sim \alpha^2 \frac{m_e}{m_p} Z$$

$$J^{(a)}(K, L) \sim \frac{G\alpha^3 Z_K^2 Z_L}{2\sqrt{2}\pi} \frac{m_e}{m_p} g_K^{(2)}$$

For $Z_L \ll Z_K$ this is smaller than first order term.

Relativistic operators

PV weak interaction has the form:

$$H_{\text{PV}}^{(2)} = \frac{G}{\sqrt{2}} \sum_{i,K} g_K^{(2)} \boldsymbol{\alpha}_i \mathbf{I}_K \rho_K(\mathbf{r}_i - \mathbf{R}_K)$$

There is no dependence on the second spin here and we need to consider second-order expression with H_{HF} :

$$H_{\text{HF}} = \sum_{i,K} \gamma_K \frac{\mathbf{I}_K \cdot \boldsymbol{\alpha}_i \times (\mathbf{r}_i - \mathbf{R}_K)}{(\mathbf{r}_i - \mathbf{R}_K)^3}$$

$$J^{(a)} \sim \sum_n \frac{\langle 0 | H_{\text{PV}}^{(2)} | n \rangle \langle n | H_{\text{HF}} | 0 \rangle}{E_0 - E_n}$$

Relativistic expression for $J^{(a)}$

The sum over states includes positive and negative energy spectrum, $\sum_n = \sum_{n_e} + \sum_{n_p}$. In the second sum we can substitute energy denominator by $2mc^2$ and use closure:

$$\sum_{n_p} \frac{|n_p\rangle\langle n_p|}{E_0 - E_{n_p}} \approx \frac{\alpha^2}{2} \hat{I}$$

This gives us effective operator:

$$H_{\text{PV}}^{\text{eff}} = \frac{G\alpha^2}{\sqrt{2}} \sum_{i,K,L} g_K^{(2)} \gamma_L \frac{\mathbf{I}_K \cdot \mathbf{I}_L \times (\mathbf{R}_K - \mathbf{R}_L)}{|\mathbf{R}_K - \mathbf{R}_L|^3} \rho_K(\mathbf{r}_i - \mathbf{R}_K)$$

Relativistic correction

$$\rho_e(\mathbf{R}_K) \approx \frac{2}{\pi} Z_K^3 F_{\text{rel}}$$

$$F_{\text{rel}} = \frac{2(1 + \gamma)(2ZR_{\text{nuc}})^{2\gamma-2}}{\Gamma^2(2\gamma + 1)}$$

$$\gamma = \sqrt{1 - (\alpha Z)^2}$$

$$\mathbf{J}^{(a)}(K, L) = \frac{2G\alpha^2 \mathbf{R}_{KL}}{\sqrt{2\pi} R_{KL}^3} \times \left(g_K^{(2)} \gamma_L Z_K^3 F_{\text{rel},K} - \gamma_K g_L^{(2)} Z_L^3 F_{\text{rel},L} \right)$$

Two examples

TIF

$$Z=81,$$

$$R=2.08\text{\AA}=3.9 \text{ a.u.}$$

$$\gamma_F=5.12\mu_N=2.0 \cdot 10^{-5}$$

$$F_{\text{rel}}=7.6$$

$$J^{(a)}/g^{(2)}_{\text{Tl}}=3.0 \cdot 10^{-18} \text{ a.u.}$$

$$= 20 \text{ mHz}$$

HF

$$Z=9,$$

$$R=0.92\text{\AA}=1.7 \text{ a.u.}$$

$$\gamma_H=5.58\mu_N=2.2 \cdot 10^{-5}$$

$$F_{\text{rel}}=1.0$$

$$J^{(a)}/g^{(2)}_{\text{H}}=3.0 \cdot 10^{-21} \text{ a.u.}$$

$$= 20 \mu\text{Hz}$$

Conclusions on J-couplings

- PV nuclear-spin-dependent interaction leads to antisymmetric vector coupling of nuclear spins in diamagnetic molecules.
- We can get analytical expression for this coupling. For heavy diatomic molecules it is of the order of 10 mHz.
- PV vector coupling can be observed in NMR experiment in the liquid phase in external electric field.

PNC effect in NMR spectroscopy of chiral molecules

[Eills et al PRA 96, 042119 (2017)]

Relativistic operators

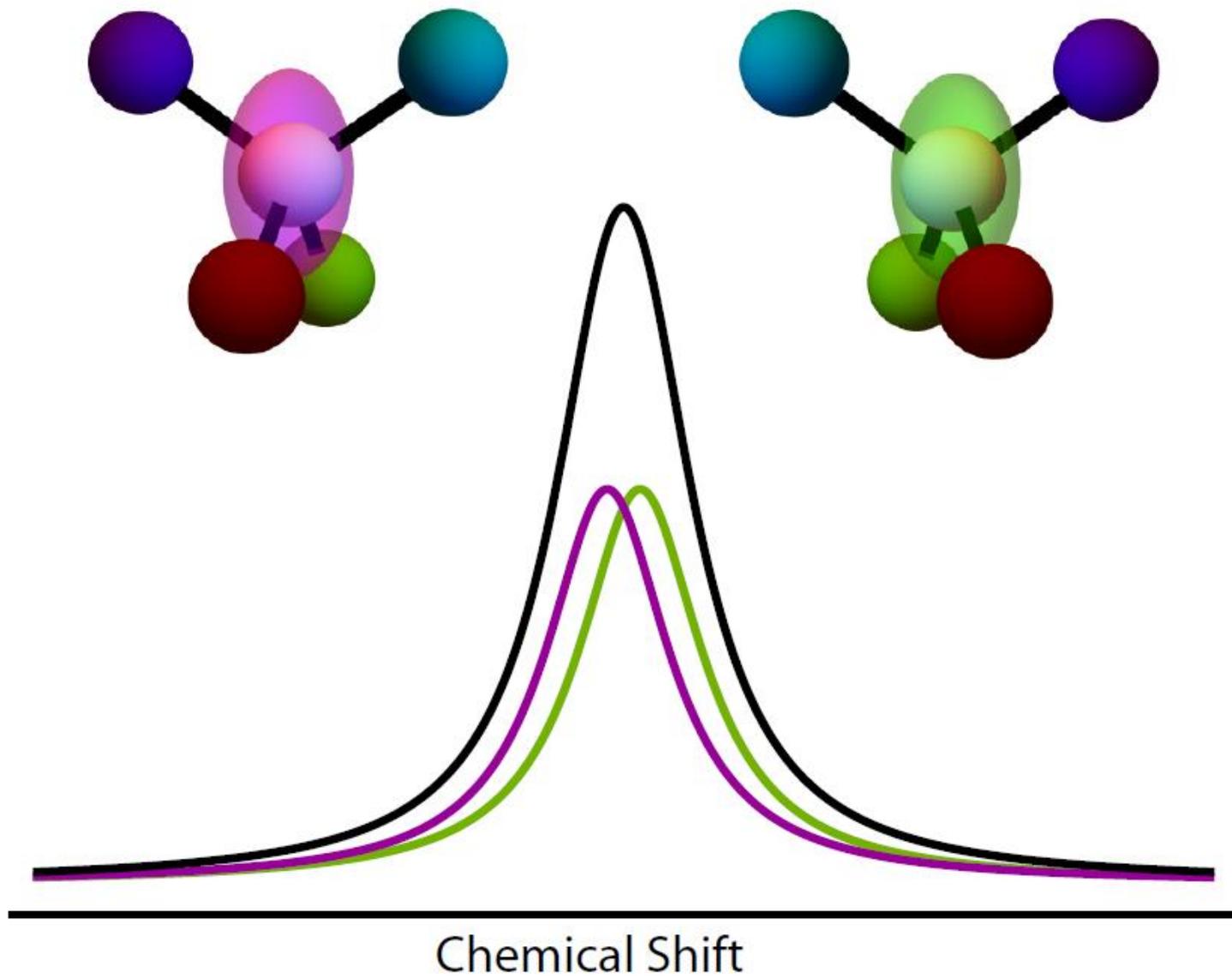
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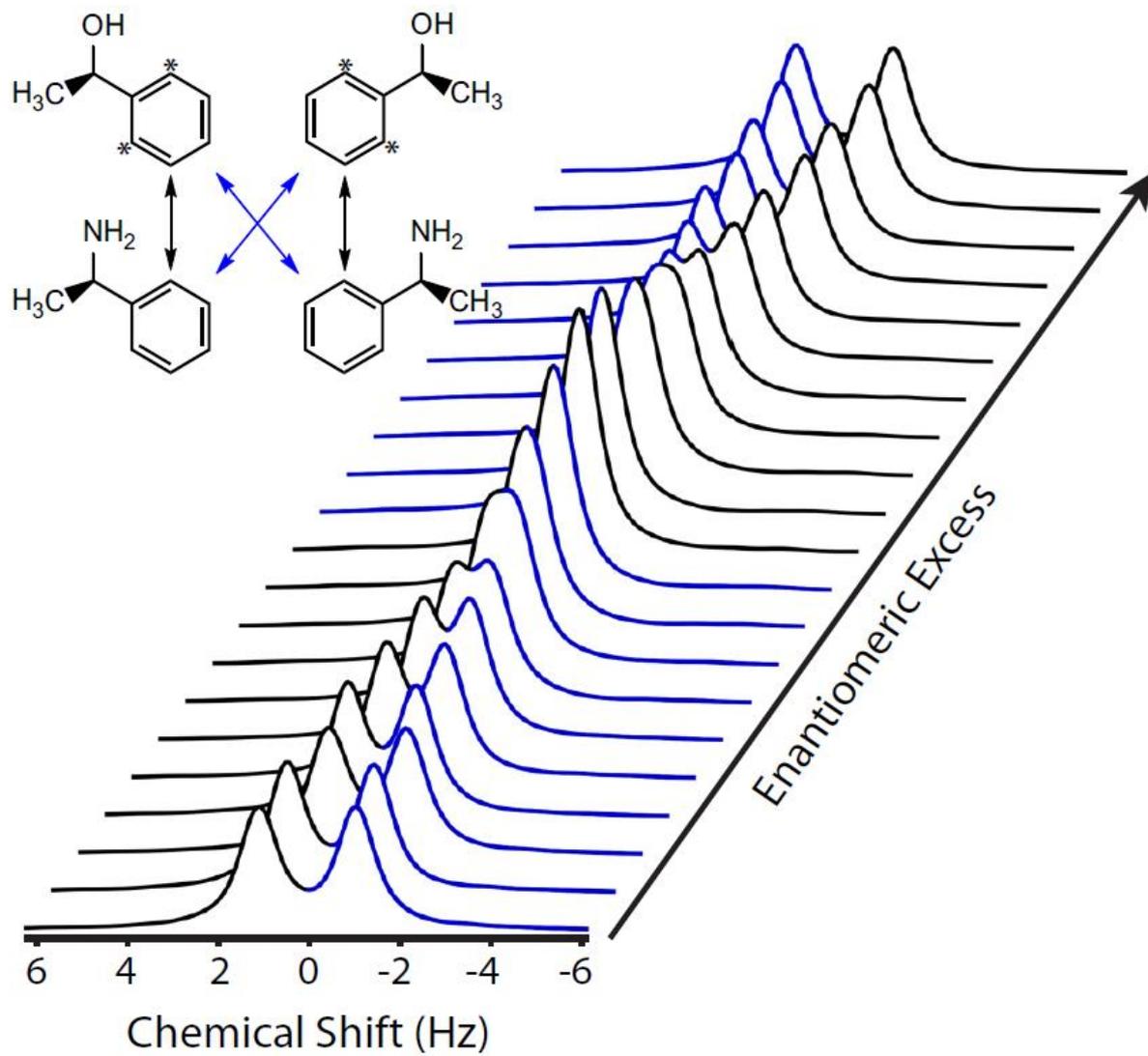
$$H_{\text{PV}}^{(2)} = \frac{G}{\sqrt{2}} \sum_{i,K} g_K^{(2)} \boldsymbol{\alpha}_i \mathbf{I}_K \rho_K(\mathbf{r}_i - \mathbf{R}_K)$$

There is no dependence on the second spin here and we need to consider second-order expression with H_{HF} :

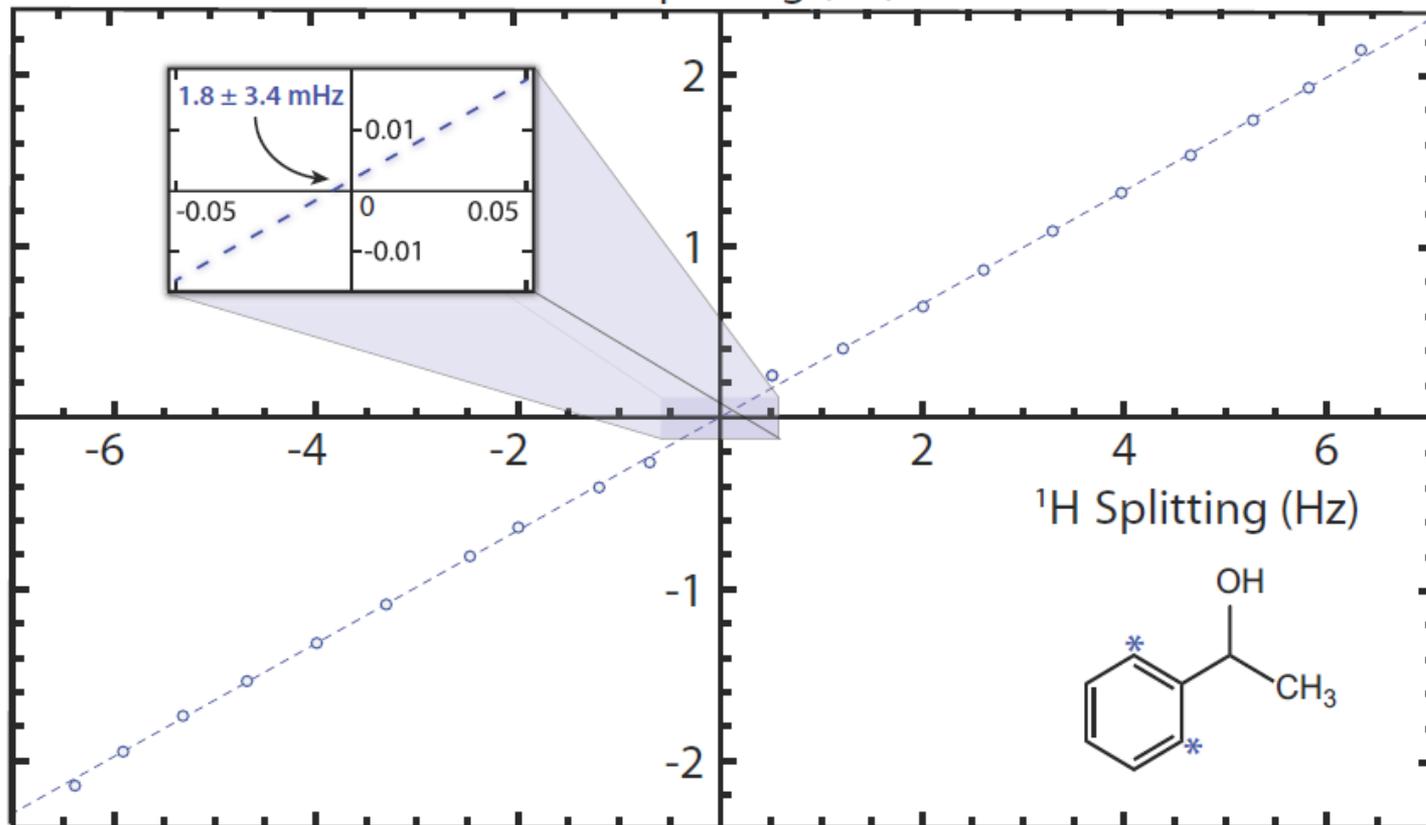
$$H_{\text{HF}} = \sum_{i,K} \gamma_K \frac{\mathbf{I}_K \cdot \boldsymbol{\alpha}_i \times (\mathbf{r}_i - \mathbf{R}_K)}{(\mathbf{r}_i - \mathbf{R}_K)^3}$$

$$J^{(a)} \sim \sum_n \frac{\langle 0 | H_{\text{PV}}^{(2)} | n \rangle \langle n | H_{\text{HF}} | 0 \rangle}{E_0 - E_n}$$





^{13}C Splitting (Hz)



Collaborators

- John Blanchard
- Dmitry Budker
- Jonathan King
- Tobias Sjolander

Thank you!