NMR Spin Relaxation Calculations

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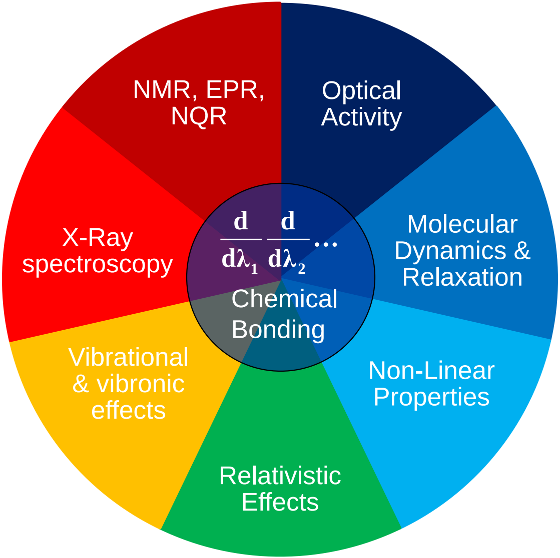


… applied to

○ organic
○ inorganic
○ lanthanide
○ actinide

systems

Codes used for developments & most applications:

NWCHEM
HIGH-PERFORMANCE COMPUTATIONAL CHEMISTRY SOFTWARE

NWChem

SCM
Software for Chemistry & Materials

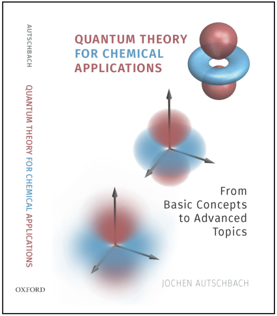
ADF Suite

CAS

OpenMolcas

and software hosted at
`https://github.com/jautschbach`
`https://github.com/exa-analytics`

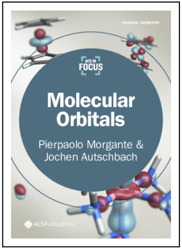
Quantum Theory for Chemical Applications (QTCA)



- MO theory front & center
- Band Structure
- Molecule–Field Interactions
- Response Theory (incl. optical activity)
- Relativistic Effects & Hamiltonians

Oxford University Press (2020). 760 pages.
Free supplementary material available on my web page.

Molecular Orbitals ACS Publications (2023)
In-Focus eBook Series



NMR Spin Relaxation

Applications to date:

Quadrupolar relaxation:

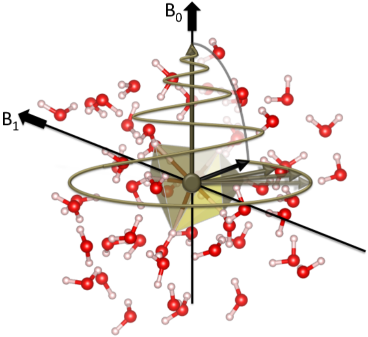
$^{7}Li^{+}$, $^{23}Na^{+}$, $^{35}Cl^{-}$, $^{81}Br^{-}$, $^{127}I^{-}$
in aqueous solution,[a,b] liquid $^{2}H_2{}^{17}O$ [b],

^{14}N relaxation of azoles in different solvents,[c]

^{17}O relaxation of uranyl carbonates[d]

$\boxed{^{23}Na^{+} \text{ vs. } ^{23}Na^{-}}$ [e]

$^{127}I^{-}$, ^{131}Xe, $^{133}Cs^{+}$: relativistic effects [f]



Dipolar & Spin-rotation relaxation:

^{1}H in water, methane, & acetonitrile[g,h]
(varying density, P, T)

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[a] S. Badu, L. A. Truflandier, JA, JCTC 9 (2013), 4074. [b] A. Philips, A. Marchenko, L. A. Truflandier, JA, JCTC 2017, 13, 4397. [c] A. Philips, A. Marchenko, L. C. Ducati, JA, JCTC 15 (2019), 509-519. [d] A. Marchenko, JA, Inorg. Chem. 56 (2017), 7384. [e] L. Abella, A. Philips, and JA, J. Phys. Chem. Lett. 11 (2020), 843 & PCCP 23 (2021), 339. [f] A. Philips, JA, JCTC 16 (2020), 5835. [g] A. Philips, JA, PCCP 21 (2019), 26621. [h] A. Philips, JA, J. Phys. Chem. B 127 (2023), 1167.

NMR Quadrupolar Relaxation from MD computations

Theory: Bloembergen & Solomon, Redfield, et al. Books: Abragam (1961), Cowan (2005), Kowalewski & Mäler (2006). We used specifically: Spiess, H. W. Rotation of Molecules and Nuclear Spin Relaxation. In *NMR Basic Principles and Progress*, Vol. 15; P. Diehl, E. Fluck, R. K., Ed.; Springer: Berlin, 1978 pages 55–214.

Quadrupolar interaction: spin vs. spatial spherical tensor operator components:

$$H_Q = \sum_{m=-2}^{2} \Gamma_{2,m} \quad ; \quad \Gamma_{2,m} = \frac{eQ}{2I(2I-1)}(-1)^m T_{2,m} R_{2,-m}$$

Spin operators

$$T_{2,0} = \frac{1}{\sqrt{6}}[3I_z^2 - I(I+1)]$$

$$T_{2,\pm1} = \sqrt{\frac{1}{2}}(I_z I_\pm + I_\pm I_z)$$

$$T_{2,\pm2} = I_\pm I_\pm$$

$$I_\pm = \mp\sqrt{\frac{1}{2}}(I_x \pm iI_y)$$

Spatial components from EFG

$$R_{2,0} = 3\sqrt{\frac{1}{6}}V_{zz}$$

$$R_{2,\pm1} = \mp V_{xz} - iV_{yz}$$

$$R_{2,\pm2} = \frac{1}{2}(V_{xx} - V_{yy}) \pm iV_{xy}$$

NMR Quadrupolar Relaxation Protocol

- Perform MD simulation (ab-initio or classical)
- Calculate EFG tensor at nucleus of interest along one or several trajectories
- Calculate EFG autocorrelation functions ($l = 2$):

$$f_{l,m}(t) = \langle R_{l,m}(t_0) R^*_{l,m}(t_0 + t) \rangle$$

  Numerically, with n MD configs: $f_{l,m}(t) = \frac{1}{n} \sum_{t_0=1}^{n-t} R_{l,m}(t_0) R^*_{l,m}(t_0 + t)$

- Form spectral densities:

$$g_{l,m}(\omega) = \int_0^\infty f_{l,m}(t) \exp(i\omega t) dt$$

- Relaxation rates from

$$\frac{1}{T_1} = \frac{e^2 Q^2 (2I + 3)}{40 I^2 (2I - 1) \hbar^2} G^Q_{2,0} \quad ; \quad \frac{1}{T_2} = \frac{e^2 Q^2 (2I + 3)}{40 I^2 (2I - 1) \hbar^2} G^Q_{2,\pm 1}$$

  with

$$G^Q_{2,0} = 4 g^Q_{2,2}(2\omega_0) + g^Q_{2,1}(\omega_0) + g^Q_{2,-1}(-\omega_0) + 4 g^Q_{2,-2}(-2\omega_0)$$
$$G^Q_{2,\pm 1} = 2 g^Q_{2,\pm 2}(\mp 2\omega_0) + 3 g^Q_{2,\pm 1}(\mp \omega_0) + 2 g^Q_{2,\pm 1}(\pm \omega_0) + 3 g^Q_{2,0}(0)$$

NMR Quadrupolar Relaxation Protocol

- Correlation times:

$$\tau_{l,m} = \int_0^\infty \frac{f_{l,m}(t)}{\langle R_{l,m}(t_0)^2 \rangle} dt$$

- 'Extreme narrowing'/fast motion regime: $\omega\tau \ll 1$
- Rotational isotropy (fast rotation in solution) and $\omega\tau \ll 1$:

$$\begin{aligned} g_{2,m}(\omega) &= g_2(0) \\ G^Q_{2,\pm 1}(\omega) &= G^Q_{2,0}(\omega) = G^Q_2(0) = 10 g_2(0) \end{aligned}$$

$$\frac{1}{T_1} = \frac{1}{T_2} := \frac{1}{T} = \frac{e^2 Q^2 (2I+3)}{40 I^2 (2I-1)\hbar^2} G^Q_2(0)$$

- Define $\langle V(0)^2 \rangle = \sum_{m=-2}^{m=2} \langle R_{l,m}(t_0)^2 \rangle$, $\quad \tau = \frac{1}{\langle V(0)^2 \rangle} \sum_{m=-2}^{m=2} g_{2,m}$

  Then: $\boxed{1/T \propto \tau \, \langle V(0)^2 \rangle \, Q^2}$

Ion Quadrupolar Relaxation (single trajectory data, 2013)

Ion	$\langle V(0)^2 \rangle$ / au	τ / ps	(1/T) / s^{-1}	$(1/T_1)$ / s^{-1} exp[a]
$^{7}Li^{+}$	$4.19{\cdot}10^{-4}$	0.508	$4.97 \cdot 10^{-2}$	$2.70 \cdot 10^{-2}$
$^{23}Na^{+}$	$3.11{\cdot}10^{-2}$	0.284	13.9	16.2
$^{35}Cl^{-}$	0.313	0.368	112	29.2
$^{81}Br^{-}$	0.610	0.397	$2.41{\cdot}10^{3}$	$1.05{\cdot}10^{3}$
$^{127}I^{-}$	1.70	0.638	$1.83{\cdot}10^{4}$	$4.60{\cdot}10^{3}$

[a] Weingärtner, H.; Hertz, H. G. *Ber. Bunsenges.* **1977,** *81,* 1204-1221.

aiMD (PBE) simulations at 300 K, PBE calculations of EFG tensors with ion + 20 water molecules + COSMO for bulk solvation. 20 ps trajectories, 4 ps at the end sampled for relaxation rates

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S. Badu, L. A. Truflandier, JA, JCTC 9 (2013), 4074. Similar agreement with experiment as in a ^{17}O and ^{2}H aiMD relaxation study of liquid D_2O by Schmidt, Hutter, Spiess, and Sebastiani, ChemPhysChem 9 (2008), 2313–2316.

Quadrupolar Relaxation Rates of Water and Aqueous Ions Improved Sampling with Multiple Trajectories

	τ_c (ps)	$\left\langle V(0)^2 \right\rangle$	$\frac{1}{T_{\text{iso}}}$ (s^{-1})	$\frac{1}{T_1}$, exp (s^{-1})
^{35}Cl$^-$(40ps)	0.43	0.19	79	29.2^a
^{35}Cl$^-$(10 × 4ps)	0.26(6)	0.21(1)	57(16)	
^{23}Na$^+$(40ps)	0.42	0.03	19	16.2^a
^{23}Na$^+$(10 × 4ps)	0.13(3)	0.028(1)	6(1)	
^{17}O(40ps)	1.11	3.54	90	140.8^b
^{17}O(10 × 10ps)	1.56(9)	3.39(3)	121(6)	
^{2}H(40ps)	1.08	0.30	1.4	1.4^c
^{2}H(10 × 10ps)	1.66(9)	0.29()	2.1(1)	

aiMD (PBE + Grimme dispersion) simulations at 350 K, PBE (water) and PBE0(ions) calculations of EFG tensors, ion clusters with 20 water molecules + COSMO for bulk solvation

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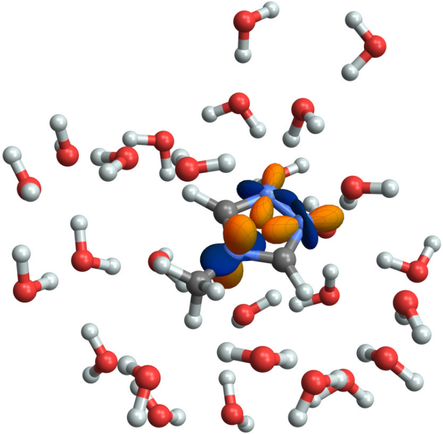
A. Philips, A. Marchenko, L. A. Truflandier, J. Autschbach, JCTC 2017, 13, 4397–4409

[a] H. Weingärtner, et. al, Ber. Bunsen-Ges. Phys. Chem., 1977, 81, 1204–1221.

[b] A. Denison, et. al, J. Phys. Chem. 1967, 71, 2606–2611

[c] J. Powles, et. al, Mol. Phys. 1966, 11, 515–523

Quadrupolar ^{14}N NMR Relaxation from Molecular Dynamics



1-methyl-3,4-triazole in water

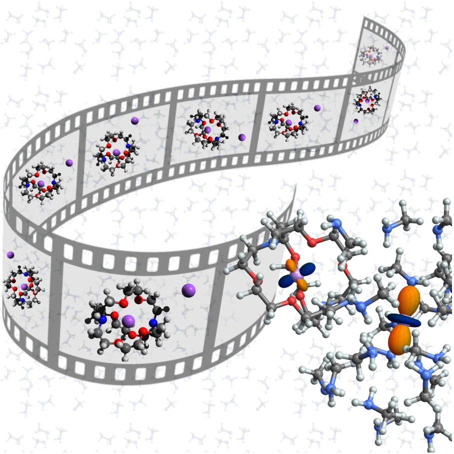
Neat acetonitrile ^{14}N relaxation

	$\frac{1}{T}$	τ_c	$\langle V(0)^2 \rangle$	$\Delta\nu$	$\Delta\nu_{\text{Expt.}}$
FFMD	230.42	0.93	1.15	73(3)	82(2)
aiMD	157.84	0.58	1.12	50(7)	82(2)

1-methyl-3,4-triazole (FFMD)

solvent	label	$\frac{1}{T}$	τ_c	$\langle V(0)^2 \rangle$	$\Delta\nu_{\text{Calc.}}$	$\Delta\nu_{\text{Expt.}}$	%dev
benzene	N^A	145.83	2.35	0.27	46 (1.00)	59 (1.00)	-21.3
	N^B	494.65	1.68	1.33	157 (3.41)	235 (3.98)	-33.0
	$N^{B'}$	501.25	1.55	1.32	160 (3.48)		-32.1
water	N^A	193.87	5.30	0.16	62 (1.00)	69 (1.00)	-10.6
	N^B	1376.65	5.39	1.07	438 (7.06)	412 (5.97)	6.4
	$N^{B'}$	1178.82	4.49	1.08	375 (6.05)		-8.9

A. Philips, A. Marchenko and JA, *J. Chem. Theory Comput.* **2019**, *15*, 509. Line width: $\Delta\nu = 1/(\pi T)$. Prior static calculations and experimental data: Jaszuński, M.; Mikkelsen, K. V.; Rizzo, A.; Witanowski, M. A Study of the Nitrogen NMR Spectra of Azoles and their Solvent Dependence. J. Phys. Chem. A 2000, 104, 1466.



The Curious Case of Sodite (Na^-)

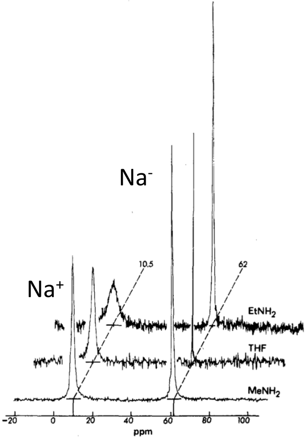
Surprisingly Small Quadrupolar Broadening of

^{23}Na NMR line widths for the
(Na^+ @ [2.2.2]cryptand) Na^- system
solvated in methylamine

	τ_c	$\langle V(0)^2 \rangle$	$\Delta\nu$ [a]	$\Delta\nu$ (Expt.)[b]
Na^-	0.75	0.44	2.8	(11)[c]
Na^+	4.49	1.22	31.6	30.8

[a] line widths from $1/(\pi T)$

[c] true quadrupolar line width is likely smaller[b]



- Na^-: ‘genuine spherical anion that interacts very weakly with its surroundings’
- Calculations and experiments are in good agreement in that the Na^- quadrupolar line widths are exceptionally small !

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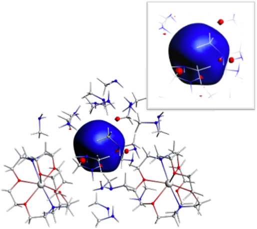
[b] J. L. Dye et al. *J. Phys. Chem.* **1975**, *79*, 3076.

Electric Field Gradient Analysis from Natural Bond Orbitals



$3s$ NBO

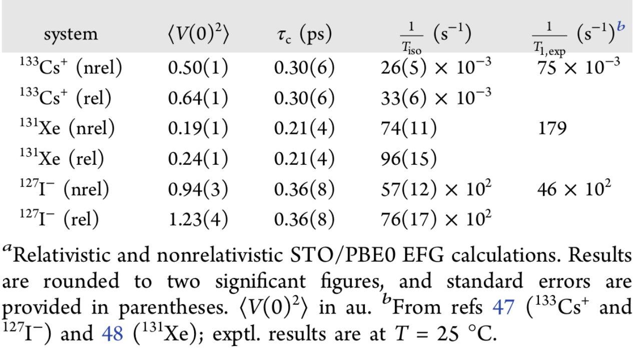
Snapshot	1	2	3	···
2p	-0.013	0.000	-0.160	
3s	-0.006	0.003	-0.049	
Σ 2p,3s	-0.019	0.003	-0.209	
Diffuse	-0.003	0.000	-0.072	
Other	0.005	0.000	-0.031	
Σ analysis	-0.017	0.006	-0.312	···
Total calcd.	-0.017	0.006	-0.293	
NBO 3s populations	1.622	1.709	1.369	···
% 3s NBO	81	85	69	···
Natural Population	11.7	11.7	11.4	···

- The 3s shell acts like a buffer between the core and the ion's surrounding
- The filled 3s shell interacts weakly with the ion's own core and nucleus

⇒ Na^- is strongly perturbed by its environment, but in NMR experiments it looks like a 'genuine spherical ion'

L. Abella, A. Philips, and JA, *J. Phys. Chem. Lett.* **2020**, *11*, 843. Follow-up study of Na chemical shifts: Abella, Philips, JA, PCCP **2021**, *23*, 339.

$^{127}I^-$, ^{131}Xe, $^{133}Cs^+$ in aq. solution: Relativistic effects:



system	$\langle V(0)^2\rangle$	τ_c (ps)	$\frac{1}{T_{\text{iso}}}$ (s^{-1})	$\frac{1}{T_{1,\text{exp}}}$ (s^{-1})[b]
$^{133}Cs^+$ (nrel)	0.50(1)	0.30(6)	$26(5) \times 10^{-3}$	75×10^{-3}
$^{133}Cs^+$ (rel)	0.64(1)	0.30(6)	$33(6) \times 10^{-3}$	
^{131}Xe (nrel)	0.19(1)	0.21(4)	74(11)	179
^{131}Xe (rel)	0.24(1)	0.21(4)	96(15)	
$^{127}I^-$ (nrel)	0.94(3)	0.36(8)	$57(12) \times 10^2$	46×10^2
$^{127}I^-$ (rel)	1.23(4)	0.36(8)	$76(17) \times 10^2$	

[a] Relativistic and nonrelativistic STO/PBE0 EFG calculations. Results are rounded to two significant figures, and standard errors are provided in parentheses. $\langle V(0)^2\rangle$ in au. [b] From refs 47 ($^{133}Cs^+$ and $^{127}I^-$) and 48 (^{131}Xe); exptl. results are at T = 25 °C.

Improvements in the calculation for $^{127}I^-$ mainly from a revision[†] of the quadrupole moment (new: –688 mb. old: –750 mb)

Sternheimer factor γ for $^{127}I^- = -162$. Used in force-field simulations[*] to scale the external EFG by $(1+\gamma)$ to account for ion polarization causing intrinsic EFG.

A. Philips, JA, JCTC 16 (2020), 5835. [*] Roberts, J. E.; Schnitker, J. Ionic quadrupolar relaxation in aqueous solution: dynamics of the hydration sphere. J. Phys. Chem. A. 1993, 97, 5410–5417. [†] P. Pyykkö, Year-2017 nuclear quadrupole moments, Mol. Phys. 2018, 116, 1328.

Dipolar and Spin-rotation Relaxation

Dipolar Relaxation from MD

$$\frac{1}{T} = \frac{\mu_0}{4\pi}^2 \gamma^4 \hbar^2 I(I+1)[g_1(0) + 4g_2(0)]$$

$$g_m(\omega) = 2Re[\int_0^\infty f_m(t) e^{-i\omega t} dt]$$

$$f_m(t) = \langle F_m^{ij}(0) F_m^{ij*}(t) \rangle$$

$$F_m^{ij}(t) = \sqrt{\frac{4\pi}{5}} Y_{2,m}[\Omega_{ij}(t)] r_{ij}^{-3}(t)$$

$Y_{2,m}[\Omega_{ij}(t)] =$ Spherical Harmonics for internuclear vector angles θ, ϕ w.r.t. z-axis

Spin-rotation Relaxation from MD

Spin-rotation Interaction: SR tensor c_{ij}, angular momentum J_j

$$H_{\mathrm{SR}} = \sum_{m=-1}^{1}(-1)^m I_m A_{-m}$$

$$A_i = \sum_{j=x,y,z} c_{ij} J_j, \;\; i = x, y, z \quad A_{\pm 1} = \mp \frac{1}{\sqrt{2}}(A_x \pm iA_y), \;\; A_0 = A_z$$

Spectral densities:

$$a_m = (-1)^m \int_0^\infty \langle A_m(t) A_{-m}(t+\tau)\rangle e^{im\omega\tau} d\tau$$

$$a_{\pm 1} = \mp \frac{1}{\sqrt{2}}(a_x \pm ia_y), \;\; a_0 = a_z$$

$$\frac{1}{T_1} = \frac{2}{3} \sum_{i,j=x,y,z} \sum c_{ij}^2 a_j(\omega_0 - \omega_J)$$

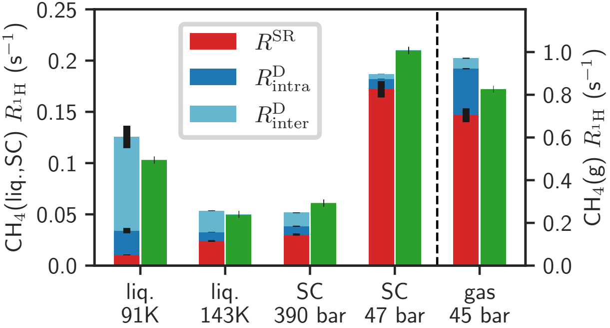
Fast motion limit, assuming rotations about different principal axes are not correlated:

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{2}{3} \sum_{i,j=x,y,z} \sum c_{ij}^2 \int_0^\infty \langle J_j(t) J_j(t+\tau)\rangle d\tau$$

$$a_0 = a_z = \sum_j c_{zj}^2 \int_0^\infty \langle J_z(t) J_z(t+\tau)\rangle \, d\tau$$

$$a_{\pm 1} = \frac{1}{2}(a_x + a_y) = \frac{1}{2} \sum_j c_{xj}^2 \int_0^\infty \langle J_x(t) J_x(t+\tau)\rangle d\tau + c_{yj}^2 \int_0^\infty \langle J_y(t) J_y(t+\tau)\rangle \, d\tau$$

Combining Dipolar and Spin Rotation Relaxation:



Methane (CH_4) in different regions of the phase diagram

Green bars: experimental data *

Calculations: NVE OPLS force-field simulations with Tinker, 20–50 ps

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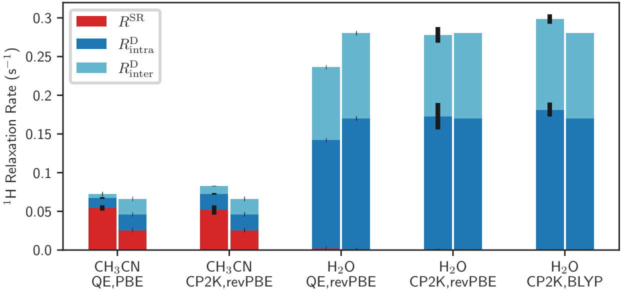
A. Philips, JA, J. Phys. Chem. B 127 (2023), 1167. * Singer, P. M.; Asthagiri, D.; Chapman, W. G.; Hirasaki, G. J. NMR spin-rotation relaxation and diffusion of methane. J. Chem. Phys. 2018, 148, 204504.

Combining Dipolar and Spin Rotation Relaxation:



Water & Acetonitrile. Neat liquids at ambient conditions.

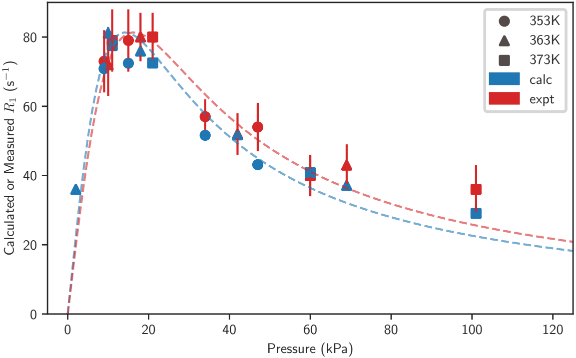
^{1}H relaxation

Right bars: experimental data*

Calculations with DFT-based forces using different codes

A. Philips, JA, J. Phys. Chem. B 127 (2023), 1167. * Woessner, D.E.; Snowden, B.S.; Strom, E. T. A Study of Molecular Re-orientation in Liquid Acetonitrile by Nuclear Spin-lattice Relaxation. Mol. Phys. 1968, 14, 265–273.

Water vapor at different densities: ^{1}H relaxation



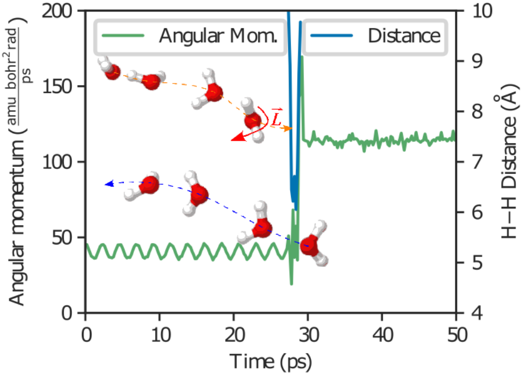
Model$^{*,\#}$ assuming mono-exponential autocorrelation functions:

$$\frac{1}{T_1} = \frac{8\pi^2 I_0 kT}{\hbar^2} C_{\mathrm{eff}}^2 \times \frac{\tau_1}{1 + (\omega_0 - \omega_J)^2 \tau_1^2}$$

In the vapor phase, only the spin-rotation mechanism is relevant. $R_1 = 1/T_1$

Simulations: TIP3P FFMD with Tinker, 20 ns

A. Philips, JA, J. Phys. Chem. B 127 (2023), 1167. * Expt. data: Mammoli, D.; Canet, E.; Buratto, R.; et al. Collisional cross-section of water molecules in vapour studied by means of ^{1}H relaxation in NMR. Sci. Rep 2016, 6, 38492–38492. # Expt. data for ω_0, ω_J from Schwenke D. W., J. Phys. Chem. A 105 (2001), 2352–2360. $\tau_1 = p_{\mathrm{max}}/[p(\omega_0 - \omega_J)]$ where p_{max} is the pressure corresponding to max. R_1. Details in Mammoli et al.* I_0 = molecular moment of inertia.



Main remaining approximations:

Molecular angular momentum – molecular orientation cross correlation is treated as de-coupled. Impacts relaxation only if SR tensor is strongly anisotropic. This is not the case for H_2O

SR tensor calculated up-front once

A. Philips, JA, J. Phys. Chem. B 127 (2023), 1167.