

Deuteron quadrupole coupling in benzene:  
Librational corrections using a  
temperature-dependent Einstein model, and  
summary. The symmetries of electric field  
gradients and conditions for  $\eta=1$   
(Supplementary Information)

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## 1 Derivation of eq. (12)

Consider the (time-)average of two, axially symmetrical EFG tensors whose symmetry axes lie in the directions  $z'$  and  $z''$ , respectively. Both tensors have the principal components  $(-q/2, -q/2, q)$ . The common y-axis of the three systems is directed towards the spectator.

$$X = \cos \alpha x' + \sin \alpha z' \tag{1}$$

$$Z = -\sin \alpha x' + \cos \alpha z' \tag{2}$$

$$X = \cos \alpha x'' - \sin \alpha z'' \tag{3}$$

$$Z = \sin \alpha x'' + \cos \alpha z''. \tag{4}$$

## Flips of water molecules

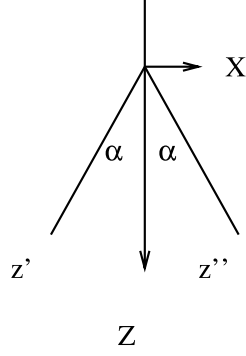


Figure 1: Two  $b$  tensors, separated by  $2\alpha$ , and their average.

The average

$$\langle Z^2 \rangle = \frac{1}{2} \langle (-\sin \alpha x' + \cos \alpha z')^2 + (\sin \alpha x'' + \cos \alpha z'')^2 \rangle \quad (5)$$

$$= \sin^2 \alpha \langle x^2 \rangle + \cos^2 \langle z^2 \rangle. \quad (6)$$

The latter expectation values are common for both subsystems. Hence

$$\langle 3Z^2/r^5 \rangle = \sin^2 \alpha \langle 3x^2/r^5 \rangle + \cos^2 \langle 3z^2/r^5 \rangle \quad (7)$$

$$\langle \frac{3Z^2 - r^2}{r^5} \rangle = \sin^2 \alpha \langle \frac{3x^2 - r^2}{r^5} \rangle + \cos^2 \alpha \langle \frac{3z^2 - r^2}{r^5} \rangle. \quad (8)$$

Requiring that the averaging halve the  $Z$  component,

$$\frac{q}{2} = \sin^2 \alpha \left(-\frac{q}{2}\right) + \cos^2 \alpha q. \quad (9)$$

$$\frac{1}{2}(1 + \sin^2 \alpha) = \cos^2 \alpha = 1 - \sin^2 \alpha, \quad (10)$$

$$\sin^2 \alpha = 1/3. \quad (11)$$

$$\alpha = \pm \arcsin 3^{-1/2} \approx 35.364^\circ. \quad (12)$$

To avoid confusion, recall that the 'magic angle' has a similar equation, but with 'arccos', instead.

For the X component of the combined EFG tensor, required to be 0, we similarly obtain

$$\langle 3X^2/r^5 \rangle = \cos^2 \alpha \langle 3x^2/r^5 \rangle + \sin^2 \alpha \langle 3z^2/r^5 \rangle \quad (13)$$

$$\langle \frac{3X^2 - r^2}{r^5} \rangle = \cos^2 \alpha \langle \frac{3x^2 - r^2}{r^5} \rangle + \sin^2 \alpha \langle \frac{3z^2 - r^2}{r^5} \rangle = 0. \quad (14)$$

$$\cos^2 \alpha \left(-\frac{q}{2}\right) + \sin^2 \alpha q = 0. \quad (15)$$

$$\tan^2 \alpha = \frac{1}{2}. \quad (16)$$

$$\alpha = \arctan \frac{1}{2} \approx 35.364^\circ. \quad (17)$$

## 2 Librational frequencies

The expansion coefficients for the librational angular frequencies,  $\omega$  (in 1/s), are given below. The last row for  $C_6D_6$  occurs twice. The momenta of inertia are for  $Cl_2$  1.148D-45 and for  $C_6D_6$  1.7845D-45 and 3.5690D-45  $kg\ m^2$ .

Table 1: Expansion coefficients for the librational frequencies.

Molecule		a	b	c
$Cl_2$		1.135445D13	-2.51012D9	-2.0072252D7
		1.567522D13	-2.019567883D9	-3.85769943D7
		1.88991354D13	-3.580952D9	-6.5439597684D7
		2.2343353D13	-1.05696845D8	-1.250827787D8
$C_6D_6$	$\omega_{w1}(T)$	1.82620423D13	-2.63179536D9	-9.613603D7
	$\omega_{w2}(T)$	1.16372969D13	-8.9589039D9	-2.585916D7
	$\omega_{w3}(T)$	1.072689D13	2.47334D9	-6.19947874D7
	$\omega_{w4}(T)$	1.698863D13	1.4717D9	-6.114946D7
	$\omega_{v1}(T)$	1.714211D13	0.D0	-5.193839D7
	$\omega_{v2}(T)$	2.3222D13	-4.76774D9	-5.440912D7
	$\omega_u(T)$	1.452753D13	-2.28965D9	-4.263463D7

## 3 The TDE program

The program is given as a separate file.

Cl\_2. Polynomial fit to frequencies.

```
1 3 2 0 0.
1.148D-45 1.148D-45
1.135445D13 -2.51012D9 -2.0072252D7
1.567522D13 -2.019567883D9 -3.85769943D7
1.88991354D13 -3.580952D9 -6.5439597684D7
2.2343353D13 -1.05696845D8 -1.250827787D8
21 54.4850
24.5 54.4827
27.9 54.4792
30.6 54.4741
35.1 54.4633
39.8 54.4490
44.7 54.4317
53.8 54.3925
61.8 54.3506
68.5 54.3096
75.0 54.2695
80.9 54.2302
88.2 54.1755
96.4 54.1111
103.6 54.0475
110.2 53.9898
115.8 53.9347
124.6 53.8428
129.2 53.7873
135.2 53.7183
140.8 53.6453
145.4 53.5816
150.7 53.5028
155.1 53.4149
159.0 53.3470
161.4 53.3015
163.0 53.2765
167.2 53.1974
0. 0.
```

Cl\_2. Polynomial fit to frequencies.

2 modes per molecule, 2 molecules per cell, 3 parameters per  
vibe.

Momenta of inertia/kg m<sup>2</sup>: Mode 1 0.11480D-44 Mode 2 0.11480D-44

Mode 1	omega(T= 100.0)=	0.10903D+14 s <sup>-1</sup> ,	57.88 cm <sup>-1</sup>
Mode 2	omega(T= 100.0)=	0.15087D+14 s <sup>-1</sup> ,	80.10 cm <sup>-1</sup>
Mode 3	omega(T= 100.0)=	0.17887D+14 s <sup>-1</sup> ,	94.96 cm <sup>-1</sup>
Mode 4	omega(T= 100.0)=	0.21082D+14 s <sup>-1</sup> ,	111.92 cm <sup>-1</sup>

All modes, zero-point vibr. corr. 0.991404D+00

NQCC (=b) data read for 28 points. Eta = 0.00000

i	T_i	B0_i	(b_stat)_i
1	21.00	0.991243D+00	54.96634
2	24.50	0.991122D+00	54.97076
3	27.90	0.990963D+00	54.97604
4	30.60	0.990808D+00	54.97945
5	35.10	0.990500D+00	54.98566
6	39.80	0.990116D+00	54.99253
7	44.70	0.989657D+00	55.00056
8	53.80	0.988671D+00	55.01575
9	61.80	0.987687D+00	55.02815
10	68.50	0.986793D+00	55.03649
11	75.00	0.985871D+00	55.04728
12	80.90	0.984992D+00	55.05651
13	88.20	0.983852D+00	55.06471
14	96.40	0.982505D+00	55.07464
15	103.60	0.981265D+00	55.07939
16	110.20	0.980082D+00	55.08701
17	115.80	0.979042D+00	55.08924
18	124.60	0.977339D+00	55.09120
19	129.20	0.976414D+00	55.08656
20	135.20	0.975170D+00	55.08610
21	140.80	0.973968D+00	55.07911
22	145.40	0.972951D+00	55.07124
23	150.70	0.971743D+00	55.05862
24	155.10	0.970709D+00	55.02667
25	159.00	0.969769D+00	55.01000
26	161.40	0.969179D+00	54.99655
27	163.00	0.968780D+00	54.99337
28	167.20	0.967714D+00	54.97221

Point-averaged b\_stat, without librations: 0.550329D+02

Extrapolated b(T=0): 0.545599D+02