

# Analysis of HAN data

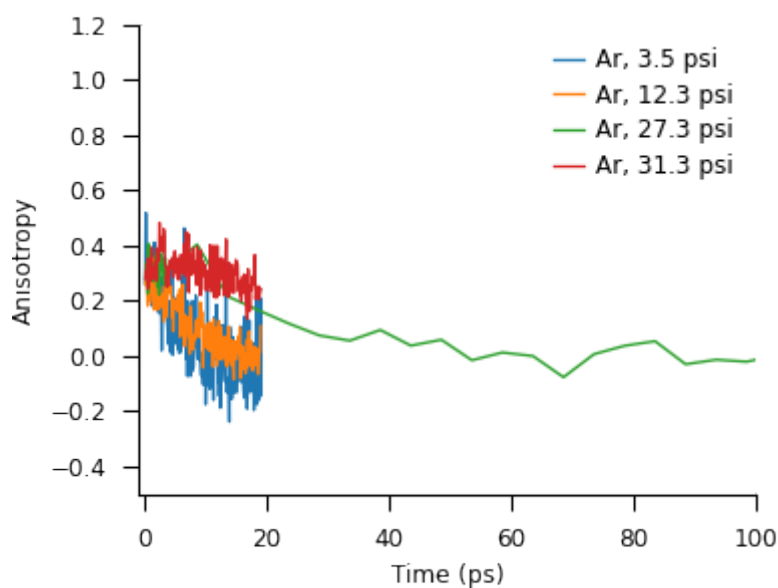
January 29, 2021

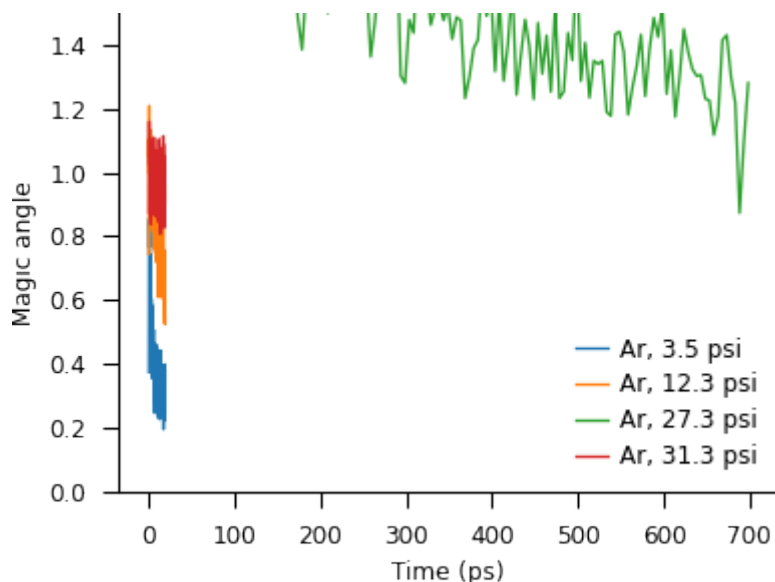
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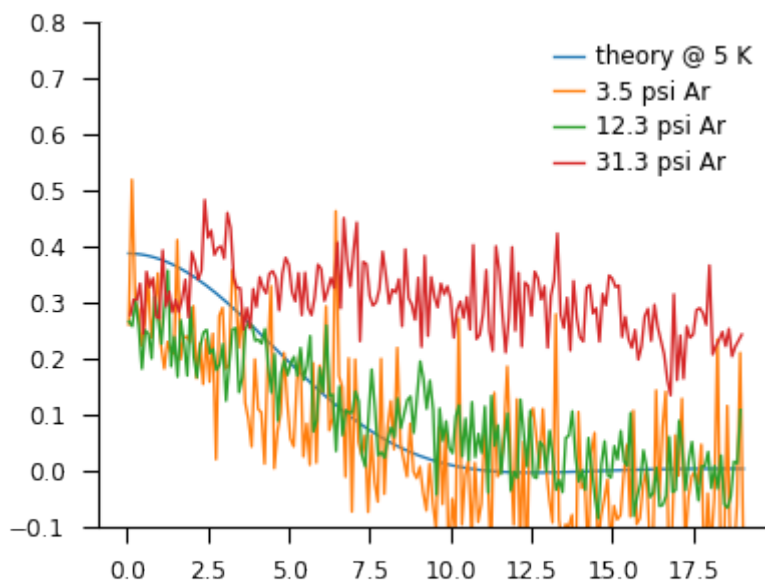
## 1. SA measurements

Plot anisotropy and fake magic angle data for SA.





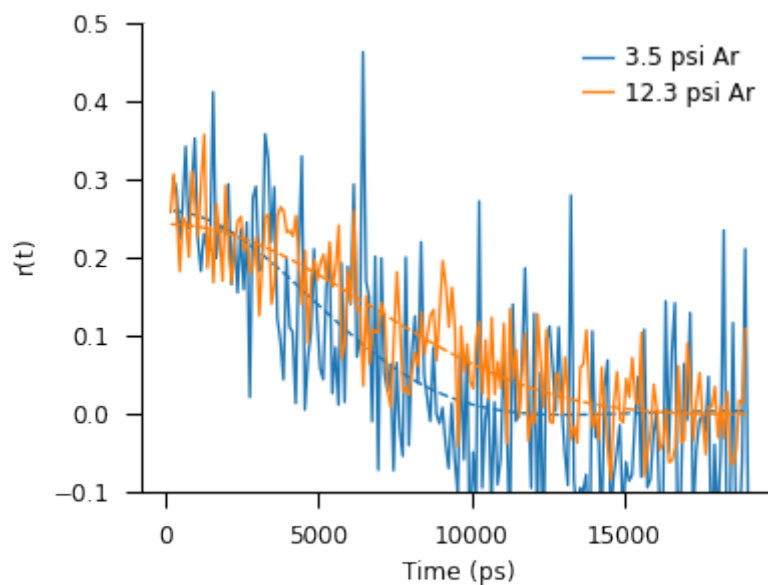
Taking optimized planar SA geometry from [1] and calculating rotational constants with Psi4, we get  $A = 0.106$ ,  $B = 0.040$  and  $C = 0.029 \text{ cm}^{-1}$ . Using these constants, we need to go as low as  $T=5 \text{ K}$  to obtain agreement with experimental anisotropy.



Signals have quite similar shape both for data which is supposed to only show rotational coherence and for data which is supposed to show everything but rotational coherence. We cannot make any conclusions about rotational coherence based on SA data.

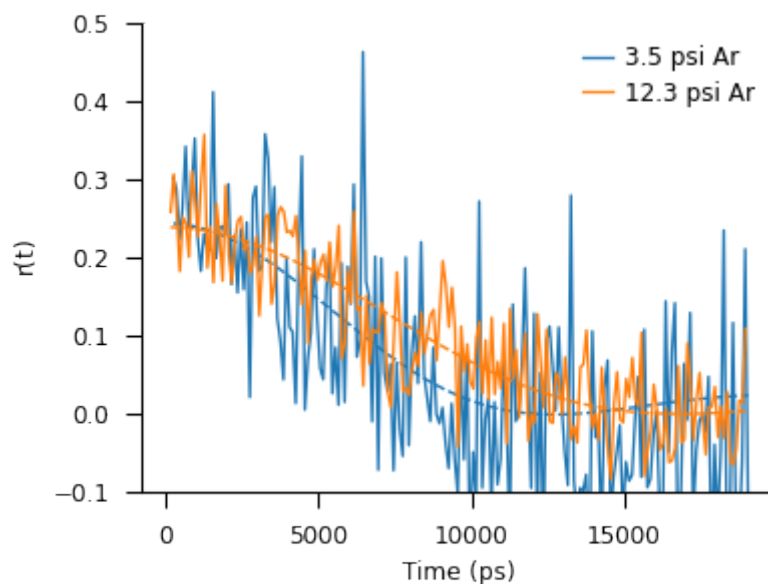
## 1.1. Temperature fits

Let's try fitting temperature at two lowest pressures. This is for planar geometry.



This gives 4.57 K for 3.5 psi and 2.32 K for 12.3 psi.

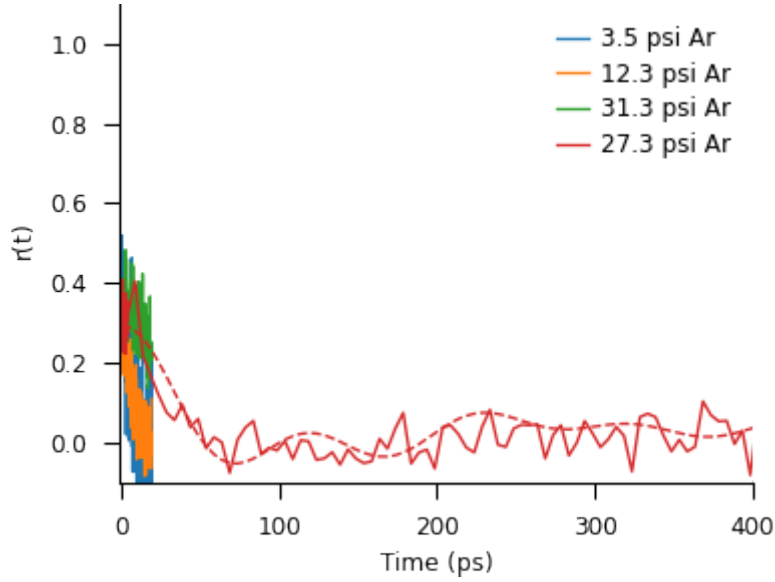
For twisted geometry the rotational constants much smaller and the molecule's geometry is quite close to a symmetric top,  $A = 0.0664$ ,  $B = 0.00909$  and  $C = 0.00822 \text{ cm}^{-1}$ .



We get  $T=17 \text{ K}$  for 3.5 psi and  $T=9.8 \text{ K}$  for 12.3 psi.

## 1.2. High pressure data

Fits of rotational constant for  $T=17 \text{ K}$ .



We get for 12.3 psi  $B = 0.666B_0 = 0.00576 \text{ cm}^{-1}$ , for 27.3 psi (long)  $B = 0.141B_0 = 0.00122 \text{ cm}^{-1}$ , for 31.3 psi  $B = 0.178B_0 = 0.00154 \text{ cm}^{-1}$ .

## 2. On clusters

According to [2] the size of an Ar cluster is:

$$R_n = \left( \frac{3mn}{4\pi\rho} \right)^{1/3} = n^{1/3}R_1, \quad (1)$$

where:

- $m$ , mass of an atom,
- $\rho$ , density of the solid,
- $n$ , number of atoms in the cluster.

For Ar cluster  $R_1 = 2.08 \text{ \AA}$ , so density in  $\text{kg/m}^3$  is:

1759.8969940542645

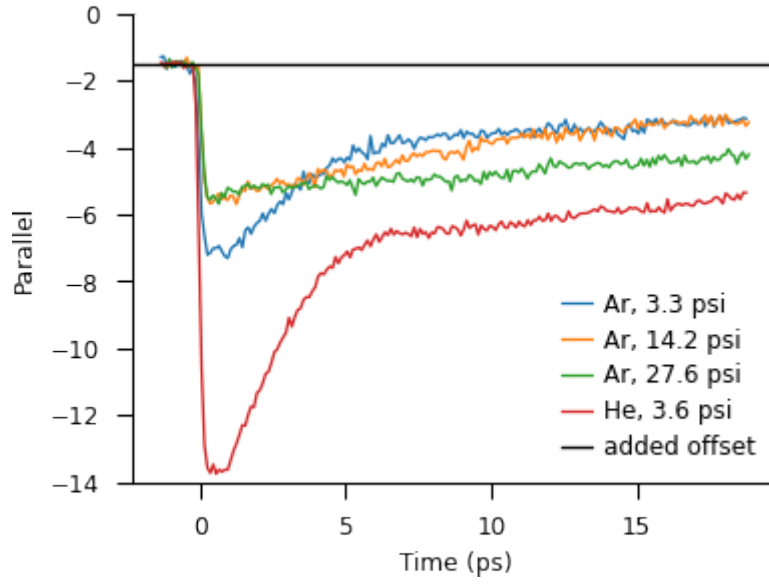
Moment of inertia of a solid sphere of Ar atoms is  $I = \frac{2}{5}MR^2 = \frac{2}{5}n^{5/3}m_{\text{Ar}}R_1^2$ . Combining this with the standard equation for the rotational constant (in  $\text{cm}^{-1}$ )  $I = \frac{h}{100c8\pi^2B_{\text{cm}}}$  gives as **24 Ar atoms** from  $B = 0.00122 \text{ cm}^{-1}$ .

## 3. HAN measurements

HAN measurements were all shifted by  $\Delta OD = 1.5 \times 10^{-8}$ .

### 3.1. Parallel

Plot parallel polarization,

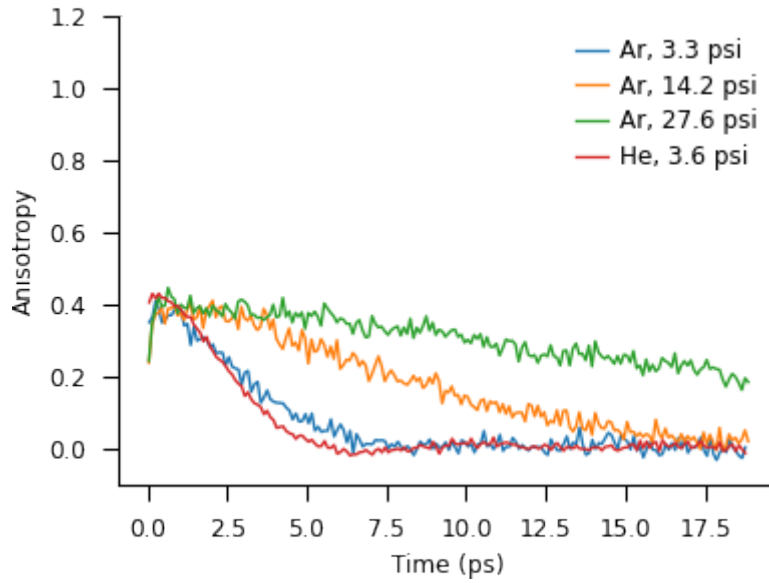


### 3.2. Anisotropy

Plot anisotropy,

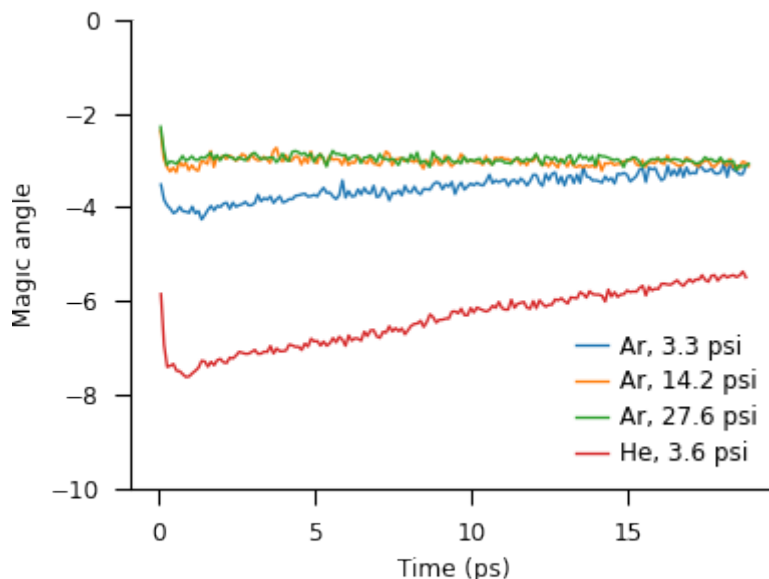
$$r(t) \equiv \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)} \quad (2)$$

of HAN in He and Ar. The denominator is proportional to magic-angle data.



### 3.3. Magic angle

Magic angle data is  $(I_{\parallel}(t) + 2I_{\perp}(t))/3$ .

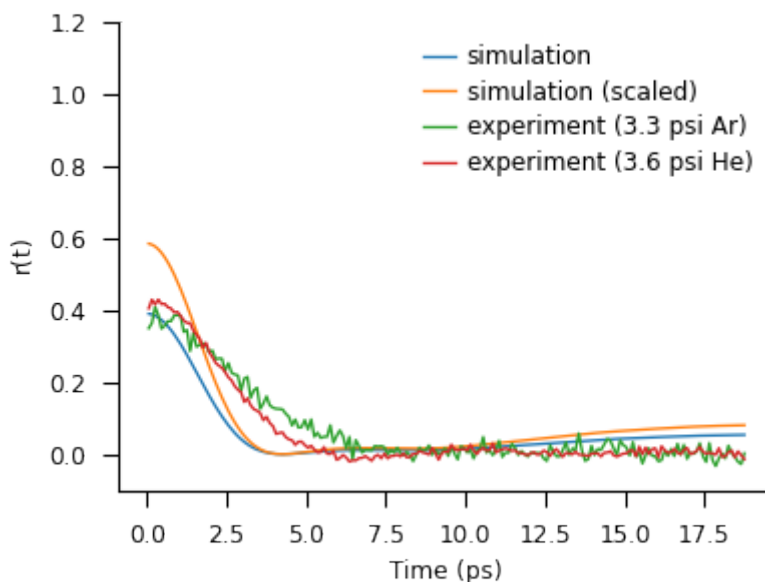


So the signal we see does come from rotational coherence.

## 4. HAN rotational coherence

HAN rotational constants are:  $A = 0.05570$ ,  $B = 0.01603$  and  $C = 0.01248 \text{ cm}^{-1}$ . This is an asymmetric rotor. Modeling rotational coherence of an asymmetric top requires obtaining the rotor's wavefunctions in the basis of symmetric top wavefunctions. As a simpler alternative, one can pretend that the asymmetric rotor is a symmetric rotor and take  $B' = (B + C)/2$ . This is what I do.

Let's assume  $T = 100 \text{ K}$  and let's assume that the lowest pressure data has no clusters. We are also assuming that the transition dipole is along the molecular axis and not perpendicular to it.



It is difficult to see why the anisotropy would be larger in reality than from theory. From RCS theory,  $r(0)$  is 0.4 for parallel absorption and emission dipoles and it is  $-0.2$  for perpendicular configuration. This is also true for asymmetric tops [3].

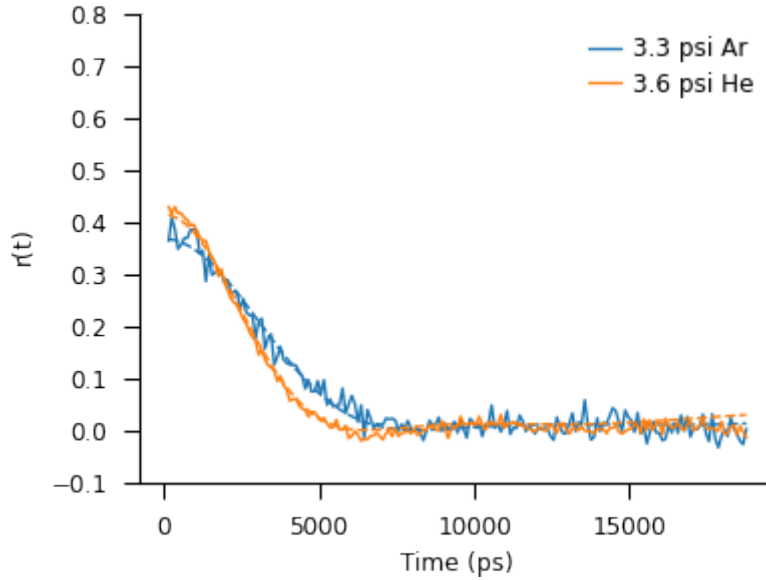
Regarding the difference in decay time, the coherence decay time for symmetric tops with parallel transition dipole is the longest. For perpendicular dipole it is shorter and for asymmetric tops it may be shorter still, because the states of asymmetric top are less mutually coherent and they do not rephase as well as symmetric ones.

The width of the transient scales as [3],

$$\Delta t \sim \frac{1}{\sqrt{BT}} \quad (3)$$

so we can try to retrieve temperature from this data.

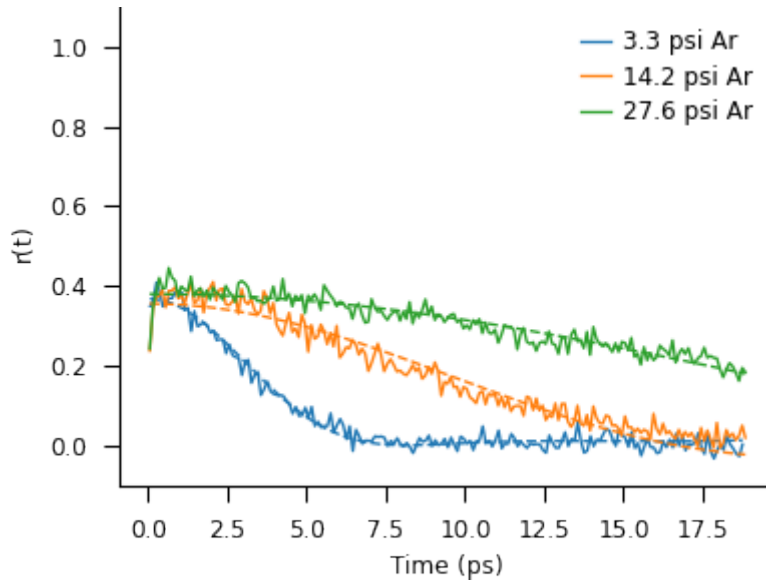
#### 4.1. Temperature fits



From these fits we get  $T = 26$  K for Ar and  $T = 42$  K for He.

#### 4.2. High pressure data

Let's fit the rotational constant assuming that  $T = 26$  K.



As a result we have at 14.2 psi  $B = 0.22B_0 = 0.031 \text{ cm}^{-1}$  and at 27.6 psi we have  $B = 0.11B_0 = 0.017 \text{ cm}^{-1}$ .

### 5. TODO

- fluorescence yield of HAN,
- 20% fluorescence surviving each pulse,
- long fluorescence decay of HAN,

## References

- [1] Shiela Pijeu, Donneille Foster, and Edward G. Hohenstein. Effect of nonplanarity on excited-state proton transfer and internal conversion in salicylideneaniline. *The Journal of Physical Chemistry A*, 122(25):5555–5562, 2018.
- [2] Udo Buck and Reinhard Krohne. Cluster size determination from diffractive he atom scattering. *The Journal of Chemical Physics*, 105(13):5408–5415, 1996.
- [3] Peter M. Felker and Ahmed H. Zewail. Purely rotational coherence effect and time-resolved sub-doppler spectroscopy of large molecules. i. theoretical. *J. Chem. Phys.*, 86(5):2460–2482, 1987.