

# The third virial coefficients for argon from the first principles

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## Motivation:

➤To calculate bulk properties without any experimental parameters, but Planck's constant, charge of electron, etc.

➤The third virial coefficient

The simplest thermodynamic quantity where the three-body intermolecular interactions play role.

$$C = C_{add} + C_{nadd}$$

$$C_{add} = -16\pi N^2 r_m^6 \int_0^\infty \int_r^\infty \int_s^{r+s} f(r)f(s)f(t)t dt s ds r dr$$

$$C_{nadd} = 16\pi N^2 r_m^6 \int_0^\infty \int_r^\infty \int_s^{r+s} e(r)e(s)e(t)[\exp(-\beta u_3) - 1] t dt s ds r dr$$

where  $f(r) = e(r) - 1 = \exp[-\beta u(r)] - 1$ ,  $u(r)$  is the pair potential,  $u_3 \equiv u_3(r, s, t)$  is the three-body potential, and  $\beta = 1/k_B T$ .

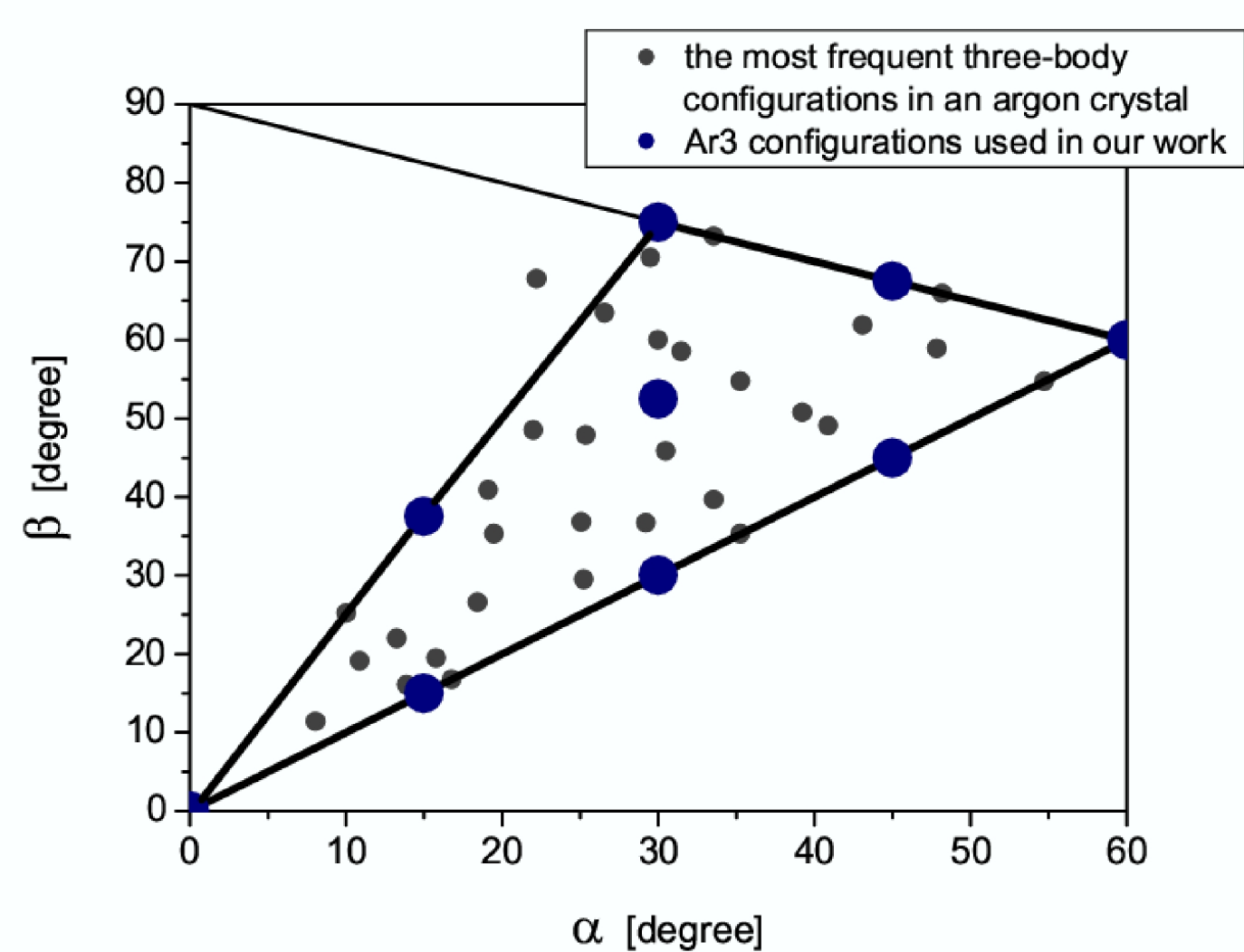
➤Argon

Since the molecule is monoatomic, nonpolar and spherically symmetric, argon is generally used as a reference fluid to test molecular approaches.

## New ab initio three-body potential:

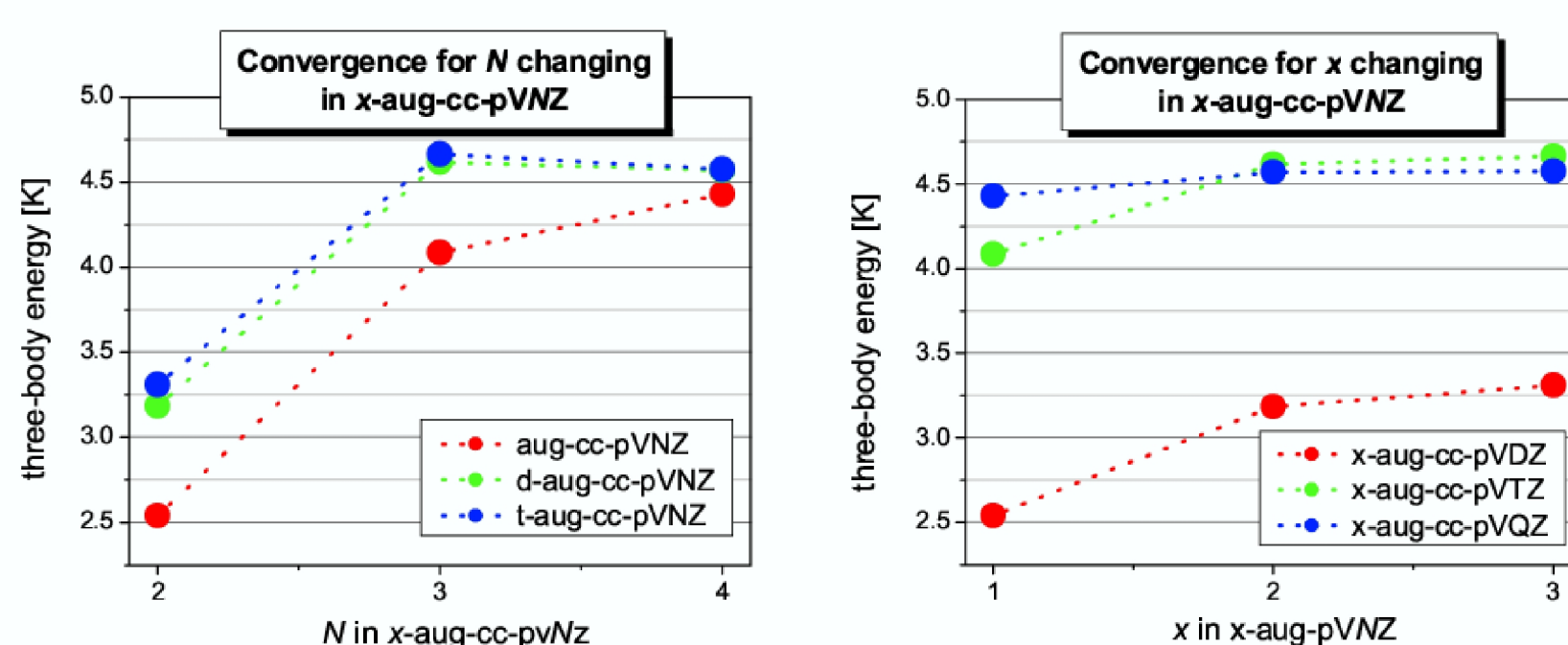
### Choice of points

➤The geometry of Ar<sub>3</sub> has been described by the perimeter of the Ar<sub>3</sub> triangle,  $\rho$ , and by the two smaller angles in this triangle,  $\alpha$  and  $\beta$ .  
➤Angles  $\alpha$  and  $\beta$  used in our *ab initio* calculations have been chosen so that they spread over all the relevant three-body geometries in both an fcc and an hcp argon crystal.

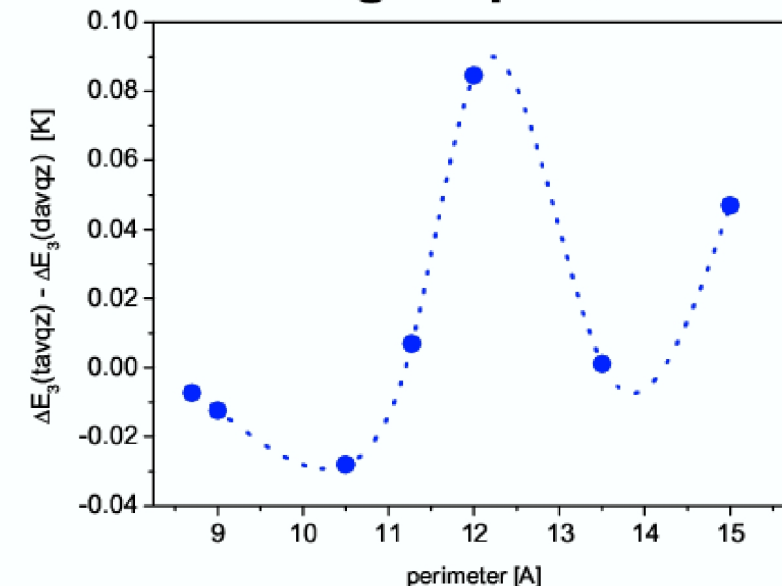


### Analysis of convergence

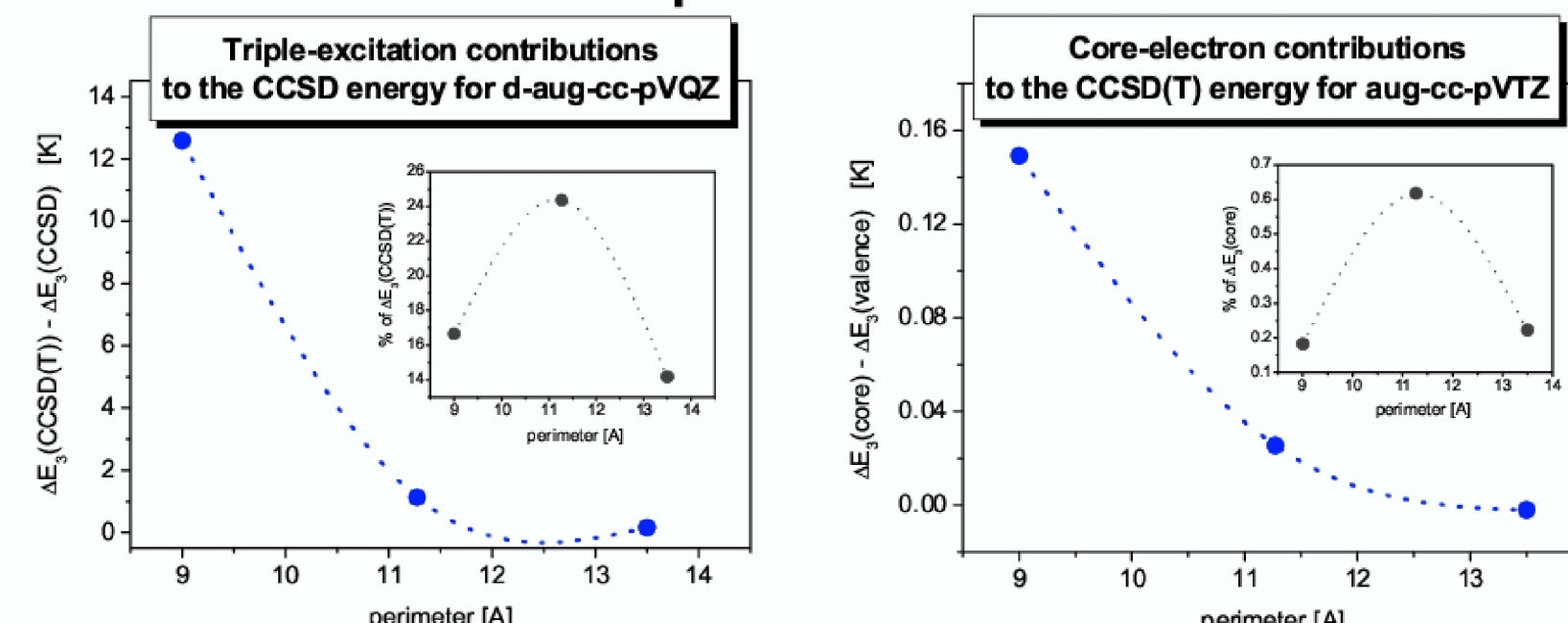
Three-body energies for D<sub>3h</sub> geometry and perimeter = 3 x 3.757 Å.



Differences between t-aug-cc-pVQZ and d-aug-cc-pVQZ.



Contributions due to triple-excitations and core correlations.

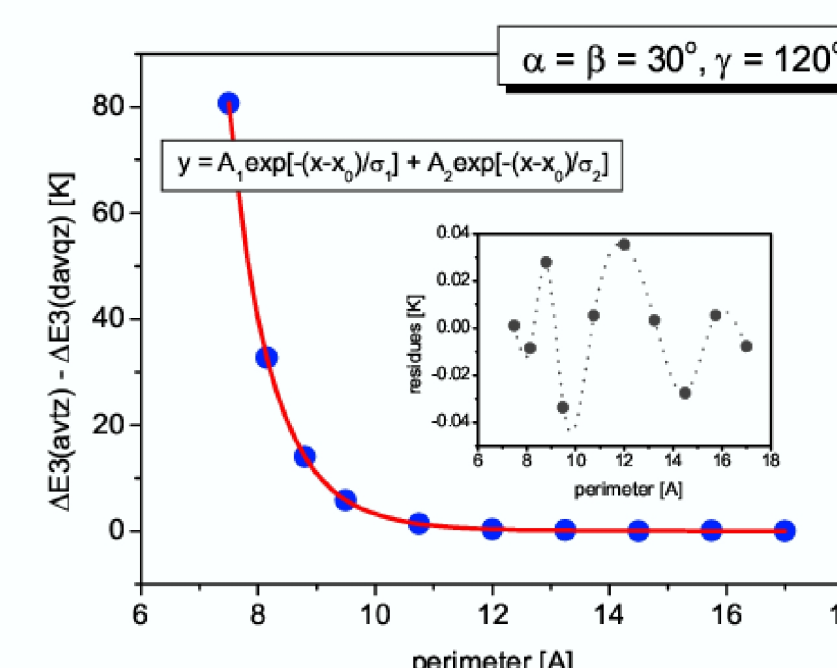


### Calculations

For each choice of Ar<sub>3</sub> geometry, three-body energies have been calculated at the CCSD(T) + d-aug-cc-pVQZ level for a sufficiently broad range of perimeters. The calculations seem to be converged within about several tenths of K at this level.

To save computer time, the following procedure has been adopted:

- A small set of energies has been calculated for a small number of perimeters, at both the aug-cc-pVTZ and the d-aug-cc-pVQZ level. This has usually taken 7 – 10 days of computer time.
- Differences between the aug-cc-pVTZ and the d-aug-cc-pVQZ energies have been fitted to an analytical formula.
- A much larger set of energies has been calculated (20 – 40) at the aug-cc-pVTZ level (about one hour of computation).
- Finally, the aug-cc-pVTZ energies have been corrected.

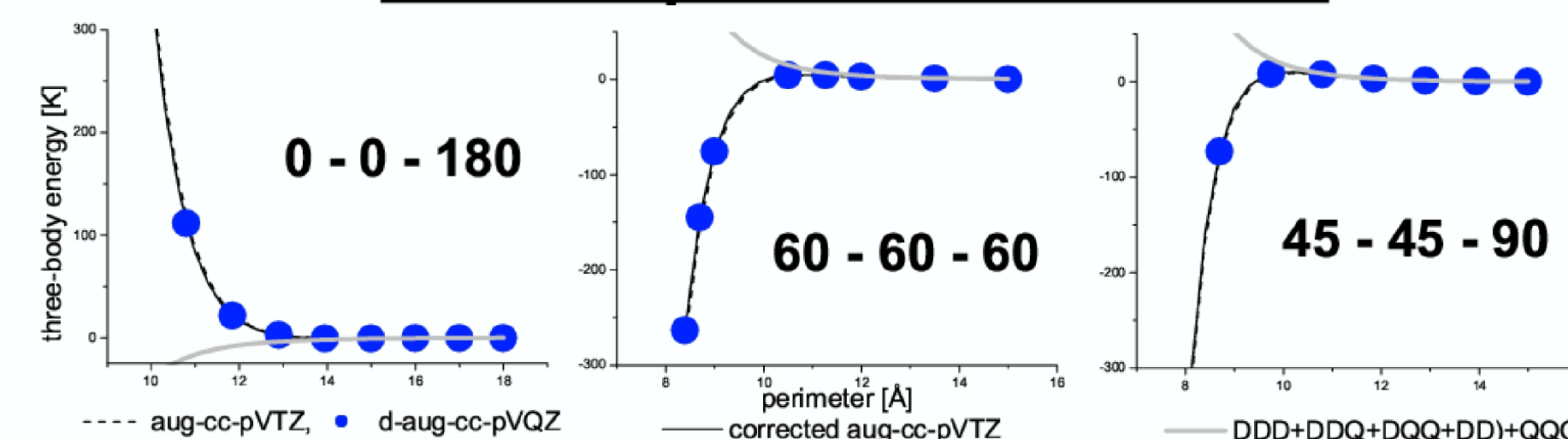


Differences between the aug-cc-pVTZ and d-aug-cc-pVQZ energies for a selected C<sub>2v</sub> geometry, and the corresponding least-square fit.

### Methods and basis sets

- correlation method – CCSD(T)
- only valence electrons have been correlated
- basis sets – x-aug-cc-pvNz with N = D, T, Q and x = s, d, t
- MOLPRO 2002 suite of *ab initio* programs
- computer – PIV 2.3 GHz, 2 GB RAM, and about 10 GB HDD requested

### Examples of results



## Pair potentials used:

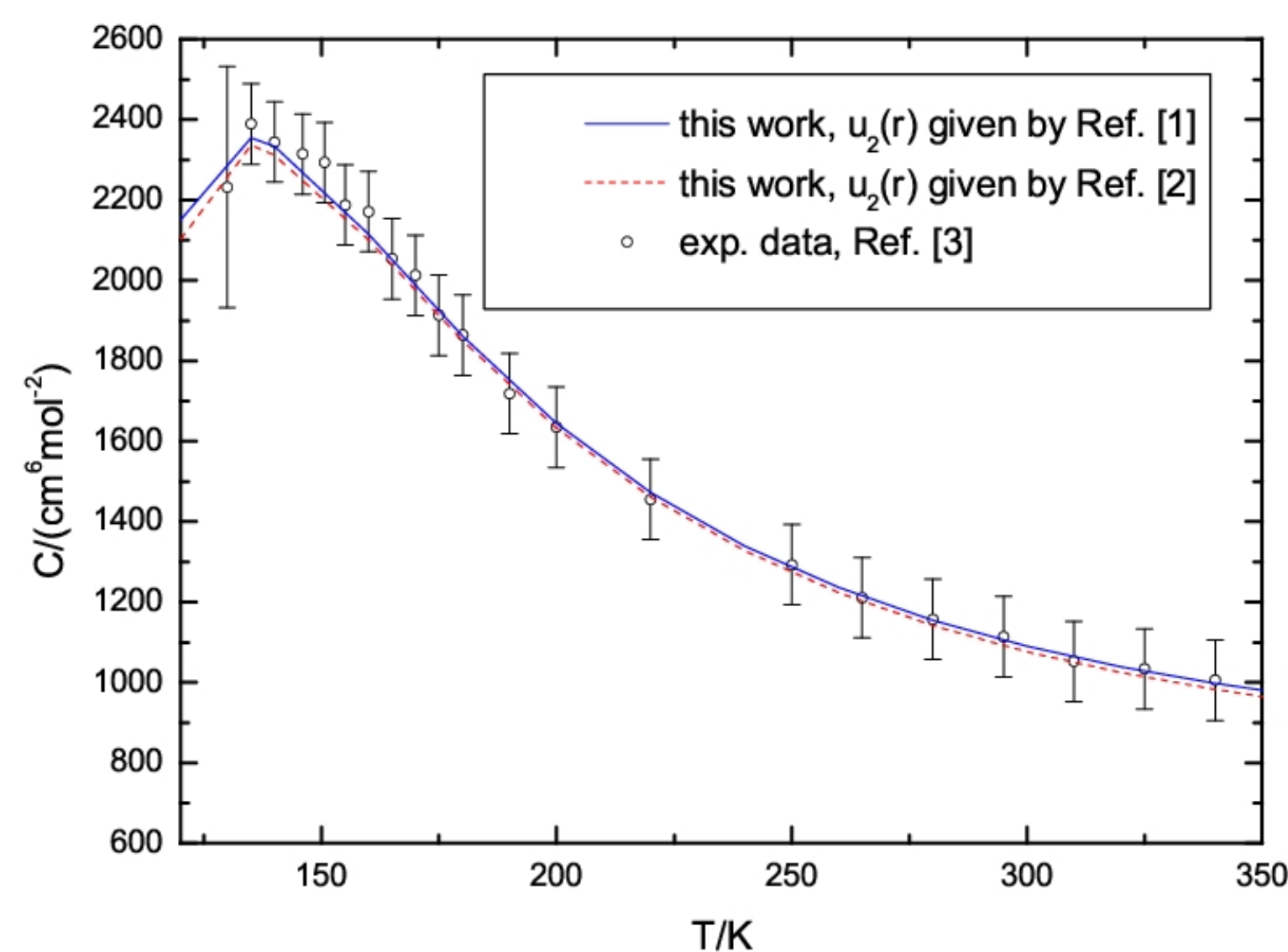
➤*Ab initio* potential of Slaviček et al., Ref. [1].

All-electron CCSD(T) and CCSDT correlation methods, extended basis sets: aug-cc-pVXZ, X=D, T, Q, 5, 6 combined with spd and spdfig bond functions.

➤Semi-empirical HFD-B potential of Aziz, Ref. [2].

Parameters fitted to experimental data.

## Results:



## Conclusions:

- The theoretical results for the third virial coefficient are in a perfect agreement with the state-of-art experimental data within their estimated uncertainties. The results obtained using the semi-empirical Aziz's pair potential and the present three-body contribution are similar.
- New three-body potential will be used to calculate vibration spectra of argon trimers, crystal structure and their binding energies.
- Works on the heavier rare gases (krypton and xenon) are also in progress.
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## References:

- [1] P. Slaviček, R. Kalus, P. Paška, I. Odvárková, P. Hobza, and A. Malijevský: State-of-the-art correlated *ab initio* potential curves for heavy rare gas dimers: Ar<sub>2</sub>, Kr<sub>2</sub>, and Xe<sub>2</sub>. *J. Chem. Phys.*, **119**, 2102 (2003).
- [2] R. A. Aziz: A highly accurate interatomic potential for argon. *J. Chem. Phys.*, **99**, 4518 (1993).
- [3] Ch. Tegeler, R. Span, and W. Wagner: A new Equation of State for Argon Covering the Fluid Region for Temperatures from the Melting Line to 700 K at Pressures up to 1000 MPa. *J. Phys. Chem. Ref. Data*, **28**, 779 (1999).

## Acknowledgements:

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