

Tensor-decomposed vibrational coupled-cluster theory

Niels Kristian Madsen, Ian H. Godtlielsen, and Ove Christiansen
nielskm@chem.au.dk, ian@chem.au.dk, ove@chem.au.dk

VCC theory

Vibrational coupled-cluster theory is a **highly accurate** method for calculating vibrational spectra and properties of small to medium-sized molecules at **reasonable cost** [1,2].

$$H|\Psi\rangle = E|\Psi\rangle, \quad |\text{VCC}\rangle = \exp(T)|\Phi_i\rangle$$

↓

$$E_{\text{VCC}} = \langle\Phi_i|H\exp(T)|\Phi_i\rangle$$

$$e_{\mu^m}^m \equiv \langle\mu^m|\exp(-T)H\exp(T)|\Phi_i\rangle = 0$$

Obtaining the VCC energy requires the solution of the set of non-linear amplitude equations.

Computational bottlenecks

The bottleneck of VCC calculations is evaluating the error vector for a given set of amplitudes. This involves:

- Tensor contractions:

$$e_{a^{m_1}a^{m_2}b^{m_3}}^{\{m_1m_2m_3\}} \leftarrow \sum_{a^{m_3}} h_{b^{m_3}a^{m_3}}^{m_3} t_{a^{m_1}a^{m_2}a^{m_3}}^{\{m_1m_2m_3\}}$$

- Direct products:

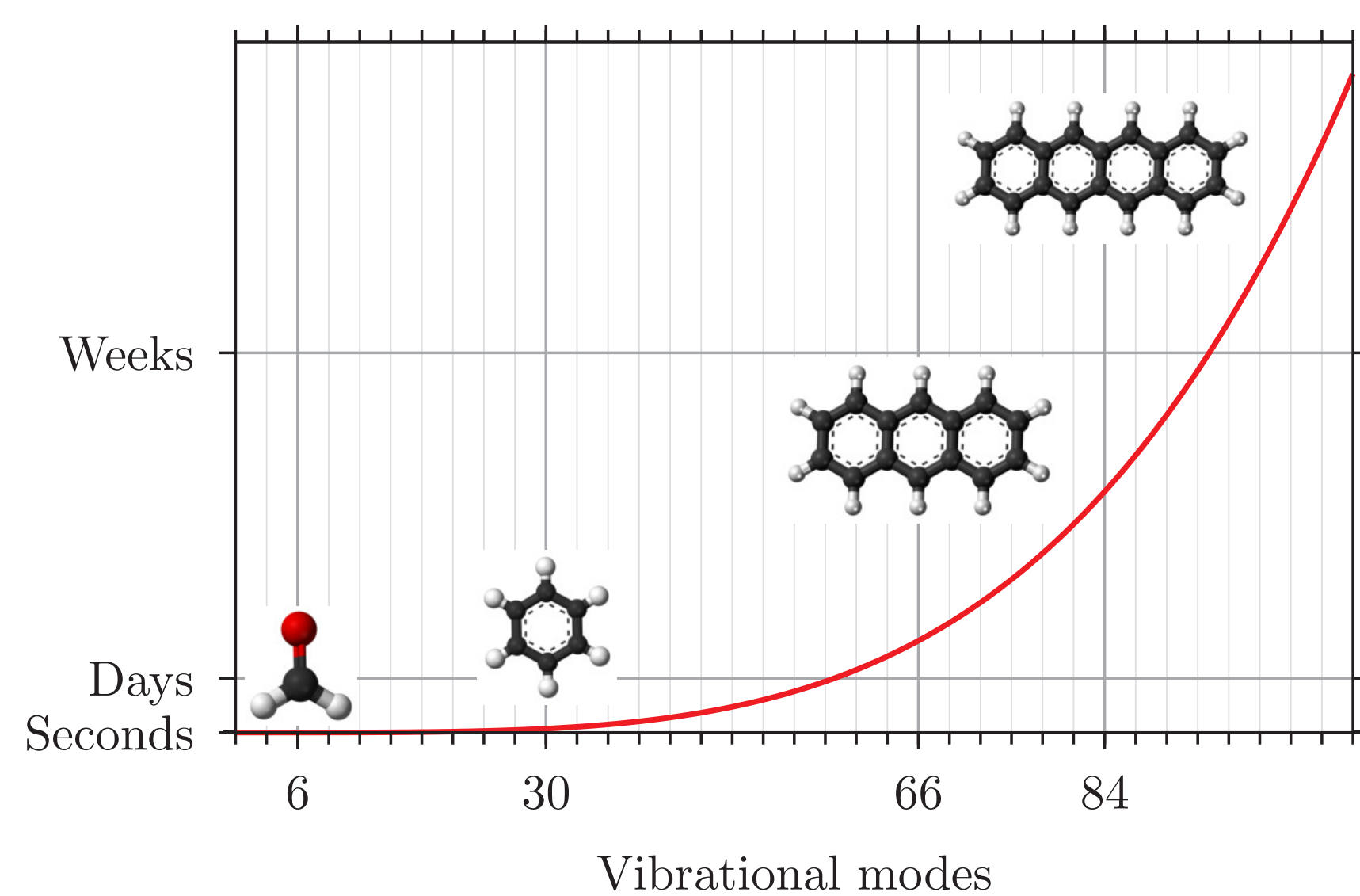
$$e^{\{m_1m_2m_3\}} \leftarrow \mathbf{t}^{m_1} \otimes \mathbf{t}^{m_2m_3}$$

- Storage of intermediates:

$$\mathbf{I}_{m_1m_2} = \sum_{m_3} c_{m_1m_2m_3} \mathbf{t}^{m_3}$$

The polynomial scaling w.r.t. the number of vibrational modes M , operator terms O , and one-mode basis functions N increases when including higher-order excitations in the VCC wave function.

Illustration of M^4 scaling (VCC[3] or VCC[3pt4])



VCC response theory

Vibrational spectra can be calculated from VCC response theory, where excitation energies are obtained as eigenvalues of the VCC Jacobian matrix [8,9],

$$A_{\mu^m\nu^m'} = \langle\mu^m|\exp(-T)[H, \tau_{\nu^m}^{\prime}] \exp(T)|\Phi_i\rangle,$$

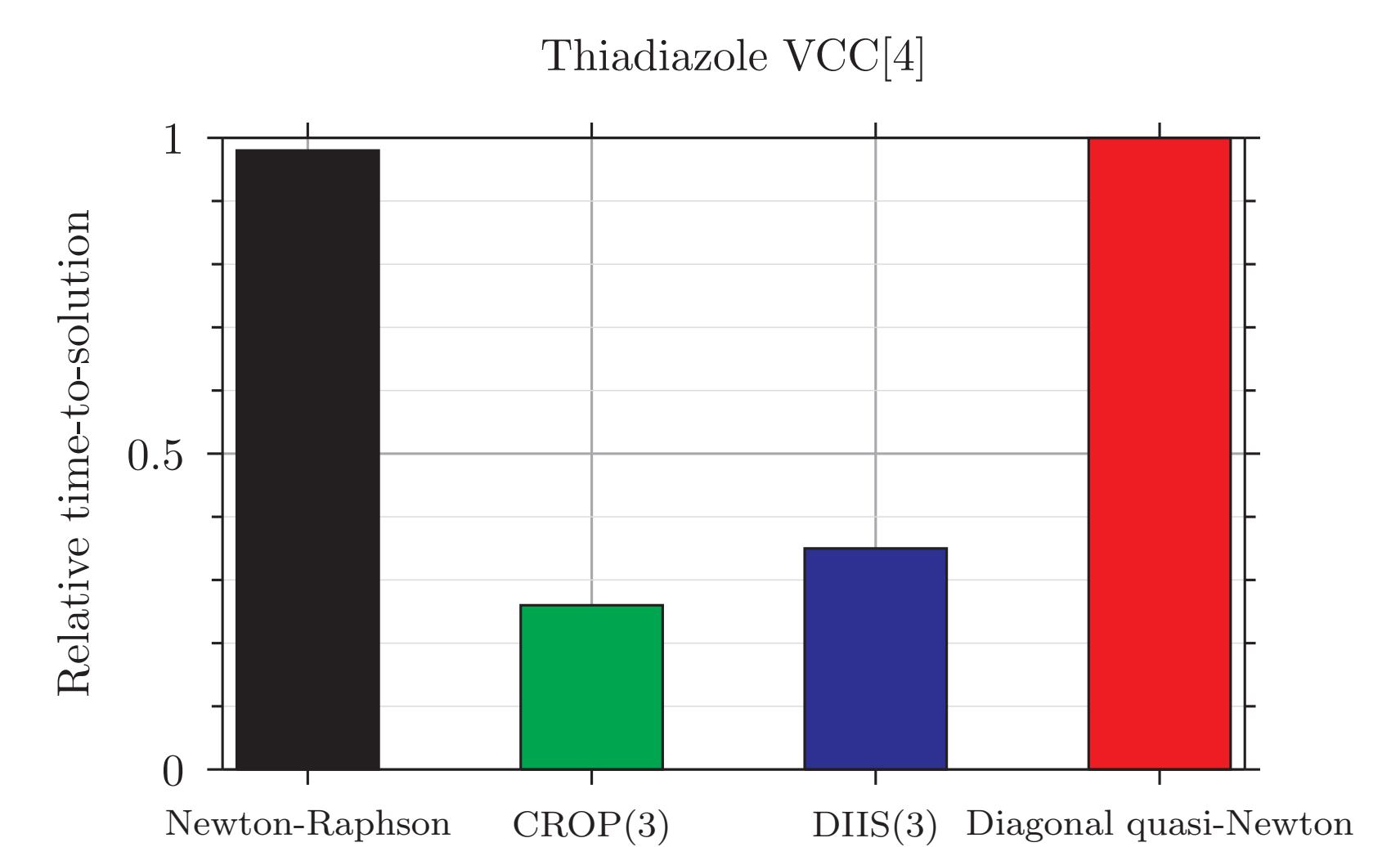
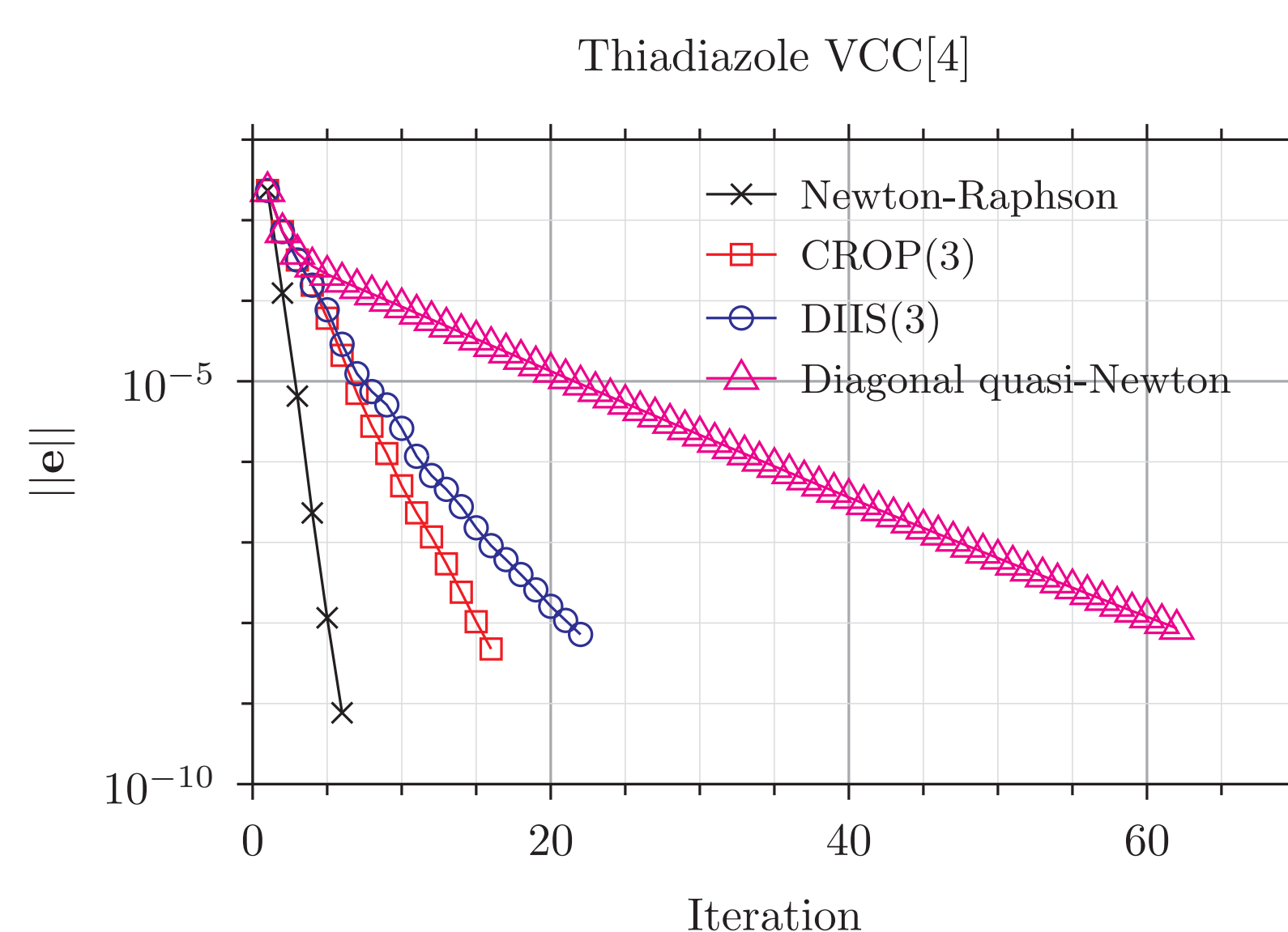
$$\mathbf{LAR} = \mathbf{\Omega}, \quad \Omega_{ij} = \omega_i \delta_{ij}.$$

It has been shown in previous studies from our group that the eigenvalue equations can be solved with all trial vectors decomposed to the CP format [10].

In this work we focus on reducing the computational cost by keeping all tensors in CP format during all stages of the calculation.

Solving the non-linear VCC amplitude equations

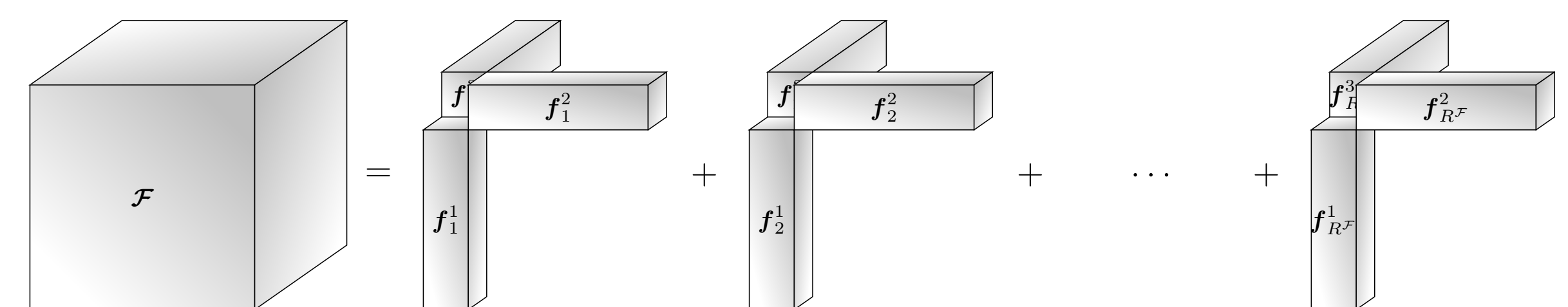
We have tested an array of non-linear-equation solvers ranging from a full Newton-Raphson algorithm to diagonal quasi-Newton methods using different types of convergence acceleration [3]. We find that the *conjugate residual with optimal trial vectors* (CROP) algorithm [4,5] using three subspace vectors offers the best balance between computational cost and convergence rate.



Tensor decomposition and the CP-VCC algorithm

The VCC amplitudes and error vectors can be viewed as sets of individual tensors with a dimensionality or order corresponding to the excitation level: $\mathbf{t} = \{\mathbf{t}^m\}$ and $\mathbf{e} = \{\mathbf{e}^m\}$ [3,6]. The computational cost and memory requirements of VCC calculations can be reduced by decomposing all tensors to the *canonical polyadic* (CP) format [7].

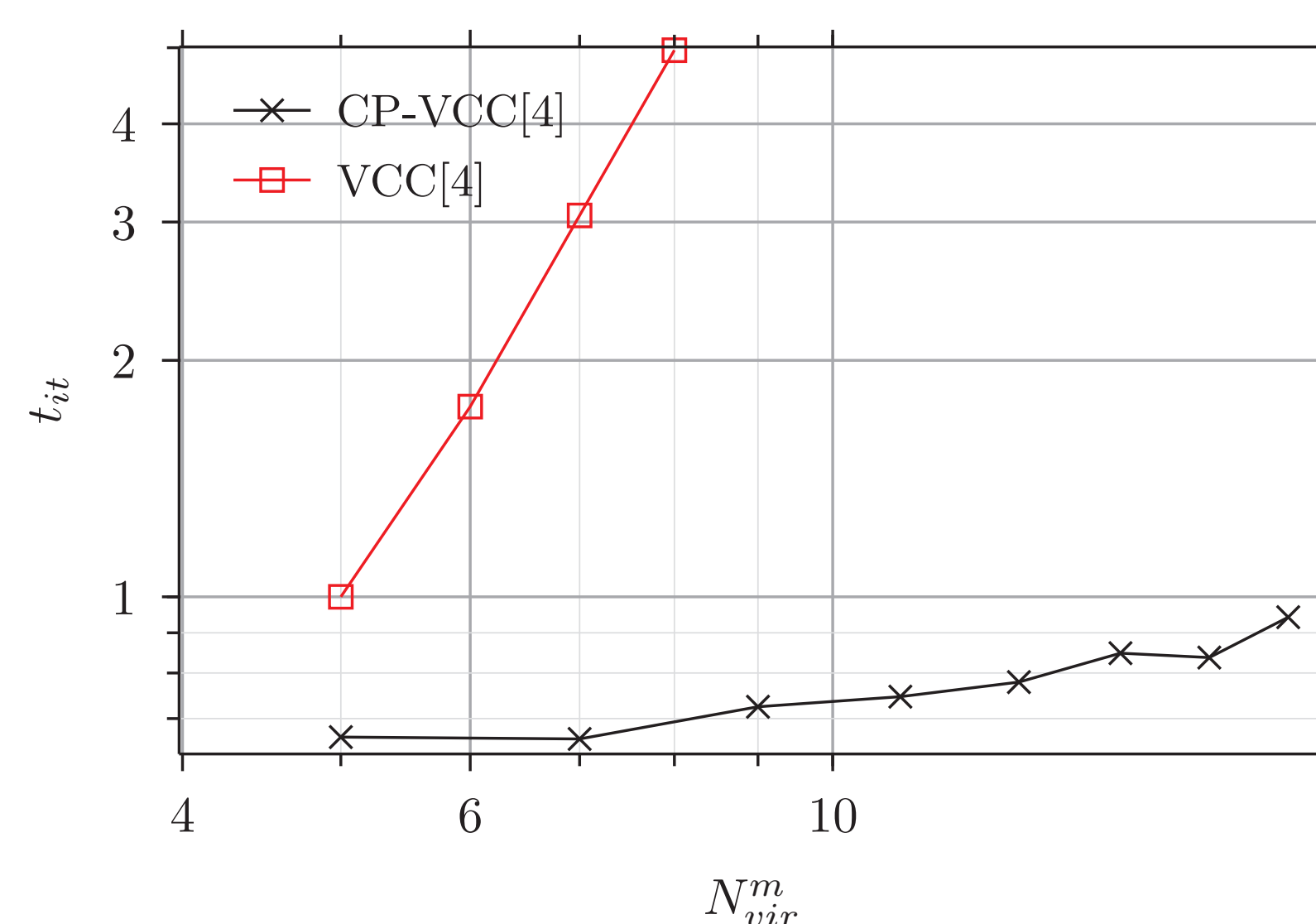
$$\mathcal{F} \approx \sum_{r=1}^{R^{\mathcal{F}}} \mathbf{f}_r^1 \otimes \mathbf{f}_r^2 \otimes \dots \otimes \mathbf{f}_r^{D^{\mathcal{F}}},$$



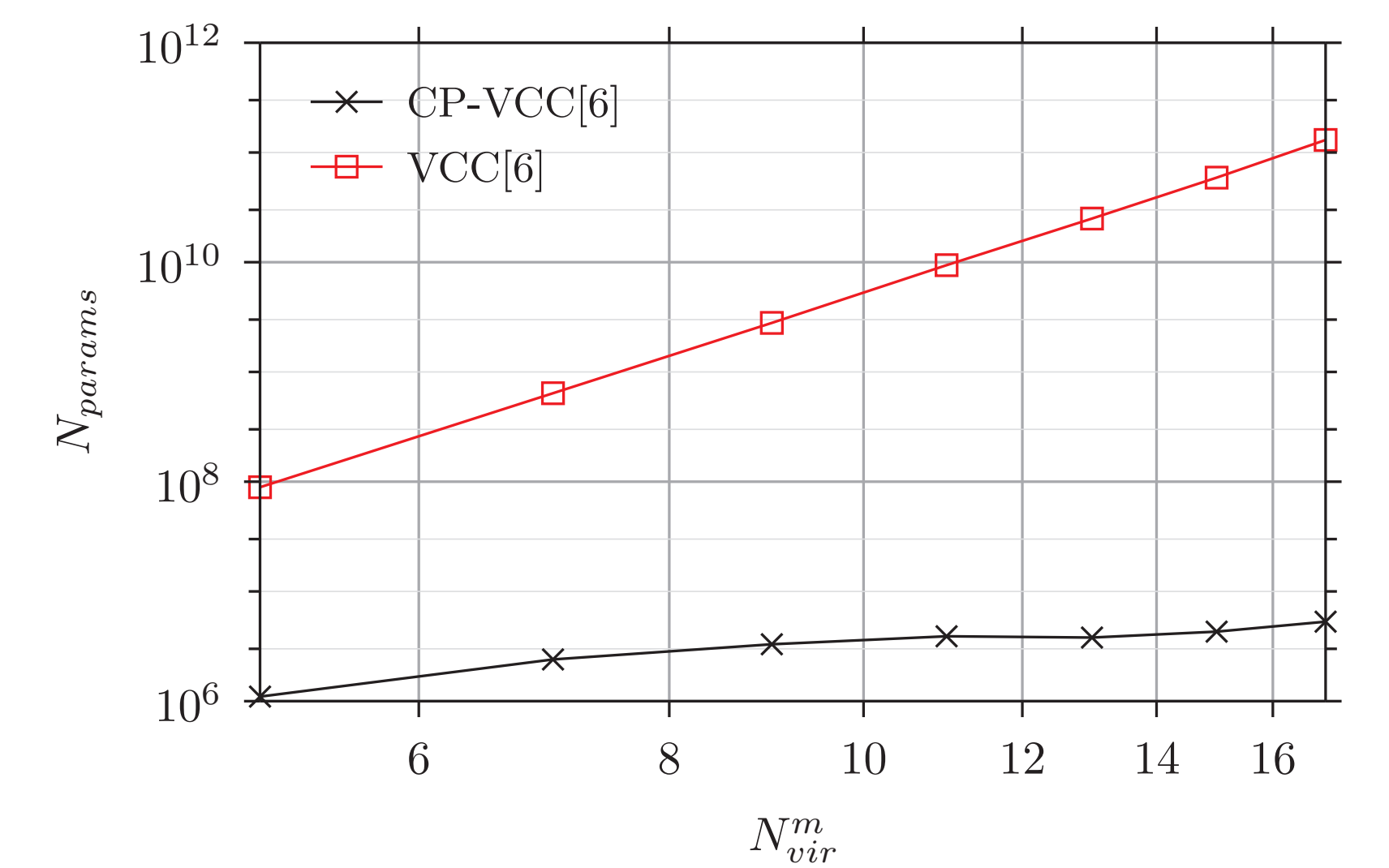
The CP-VCC algorithm

- Solves the VCC equations to the same accuracy as the conventional, full-tensor VCC algorithm.
- Error control is obtained by decomposing all tensors to a given accuracy instead of choosing a pre-defined representation rank.
- The ranks are small for tensors describing weak interactions. Thereby, the computational cost is adapted to the strength of the physical interactions in the molecule.
- The computational cost of tensor contractions and direct products is reduced significantly. Instead, the bottleneck of the CP-VCC algorithm is recompression of the sum of terms during the error-vector calculation.
- The memory requirements of amplitudes, error-vectors, and intermediates are reduced significantly.

Naphthalene VCC[4] N scaling



Thiadiazole CP-VCC[6]



References

- [1] O. Christiansen. *J. Chem. Phys.*, 120(5):2149, 2004.
- [2] P. Seidler and O. Christiansen. *J. Chem. Phys.*, 131(23):234109, 2009.
- [3] N. K. Madsen, I. H. Godtlielsen, and O. Christiansen. *J. Chem. Phys.*, 146(13):134110, 2017.
- [4] M. Ziólkowski, V. Weijo, P. Jørgensen, and J. Olsen. *J. Chem. Phys.*, 128(20):204105, 2008.
- [5] P. Etenhuber and P. Jørgensen. *J. Chem. Theory Comput.*, 11(4):1518–1524, 2015.
- [6] I. H. Godtlielsen, B. Thomsen, and O. Christiansen. *J. Phys. Chem. A*, 117:7267–7279, 2013.
- [7] T. G. Kolda and B. W. Bader. *SIAM Review*, 51(3):455–500, 2009.
- [8] P. Seidler and O. Christiansen. *J. Chem. Phys.*, 126(20):204101, 2007.
- [9] P. Seidler, M. Sparta, and O. Christiansen. *J. Chem. Phys.*, 134(5):054119, 2011.
- [10] I. H. Godtlielsen, M. B. Hansen, and O. Christiansen. *J. Chem. Phys.*, 142(2):024105, 2015.