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Supplementary Information

Unexpected structures of the Au_{17} gold cluster: The stars are shining

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Experimental and Computational Details.

Experiment: Neutral gold clusters are produced by pulsed laser vaporization (10 Hz) in a continuous stream of He containing 1.5 % Kr at a total stagnation pressure of about 10 mbar in the source channel held at 100 K. After expansion into vacuum and passing a differential pumping stage the clusters are ionized using 7.9 eV photons emitted from an F_2 laser. The ionized distribution of bare clusters and complexes with Kr atoms is analysed by an orthogonal extraction reflectron time-of-flight mass spectrometer. Just before ionization, the clusters can be irradiated with the intense and tuneable IR radiation emitted from the "Free Electron Laser for Infrared eXperiments" (FELIX) that is scanned in this study of Au clusters between 47 cm^{-1} and 220 cm^{-1}. This range is characteristic for the vibrational modes of gold clusters. Resonant absorption of one or multiple far-IR photons by the Kr complex of an Au cluster can induce dissociation of the complex, which leads to an intensity reduction in the mass spectrum. Mass spectra with and without FEL interaction are recorded alternatingly to minimize the effect of fluctuations in the cluster signal intensity on the depletion spectra. Details on the experiment and the data evaluation procedure have been given before.[1]

Computation. Quantum chemical computations are carried out using a range of density functional (DFT)[2-11] and wavefunction (coupled-cluster) theory[12, 13] approaches. The DFT functionals employed include the PW91,[6] PBE,[7] TPSS,[8] revTPSS,[11] and M06[10] in conjunction with the correlation consistent cc-pVDZ-PP basis set,[14] which is used together with the small-core relativistic pseudopotential of Figgen *et al*.[15] with 60 electrons of Au being treated as a core. All stationary points are characterized to be true energy minima by harmonic vibrational analysis. Albeit it is quite successful in predicting the preferred structures of small gold clusters, density functional theory (DFT) still has several inherent shortcomings rendering the energy order of various isomers strongly dependent on a partuclar exchange-correlation functional employed . As for a further benchmark, calculations using the explicitly correlated local coupled cluster theory PNO-LCCSD(T)-F12[13,16, 17] are also performed for low-lying isomers using their DFT optimized geometries. This is a recently developed approximation of the conventional CCSD(T) constructed including two components. The former is using the local pair and domain approximations exploiting the short-range nature of dynamical correlation. Such a local correlation is based on pair natural orbitals and then combined with the explicit correlation F12 technique whose terms are also correct for part of the domain errors. The performance of this method for different types of

compounds was well documented.[16, 17] All computations are carried out using the Gaussian 16[18] and Molpro 2020[19-21] programs.

In the PNO-LCCSD(T)-F12b wavefunctions for the doublet state of Au_{17}, the aug-cc-pVDZ-PP (denoted as aVDZ-PP) and aug-cc-pVTZ-PP (aVTZ-PP) basis sets are used, the core orbitals defined above are frozen, the same active space is used for all isomers, and the restricted-open shell reference formalism (ROHF) is used in the correlation calculations.

For ease of comparison with the experimental data, the calculated infrared stick spectra are convoluted with a Gaussian? line-shape function with a full width at half maximum of … cm^{-1}.

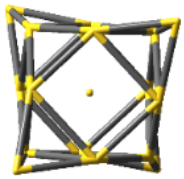
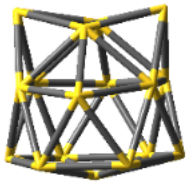
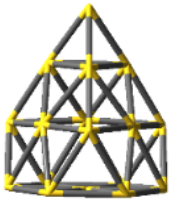
Isomer	Method/Reference
 **17_6** D_{2d}	TPSS[3]
 **17_3** C_{2v}	PBE[9, 22]
 **17_7** C_s	PW91,[4] BB95[23]

Fig. S1. Some structural motifs previously assigned as the most stable form of Au_{17}. The labeling is given according to structures displayed in Figure 1 of the main text.

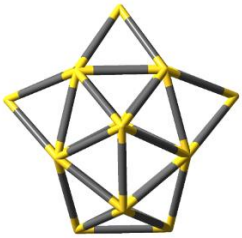
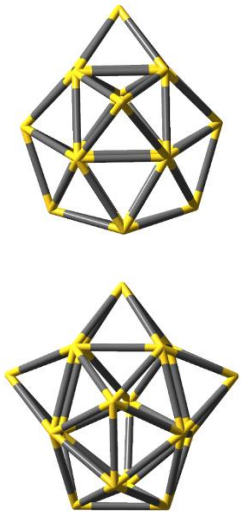
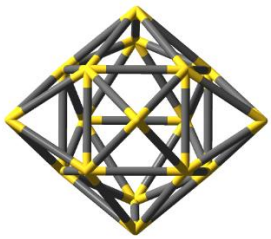
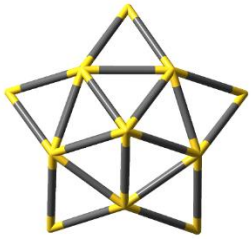
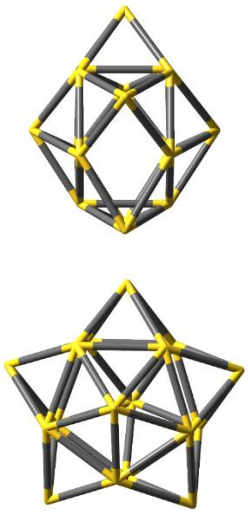
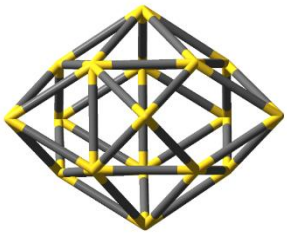
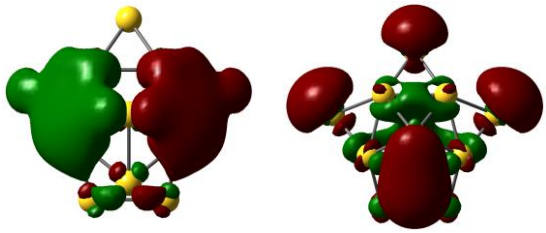
Isomer	Side view	Front view	Top view
17_1			
17_2			

Fig. S2: Star-like isomers **17_1** and **17_2** seen in different perspectives.



a_2 (SOMO) **a_1 (LUMO)**

Fig. S3. Isosurfaces (0.02 a.u.) of frontier orbitals in the **17_1** isomer.

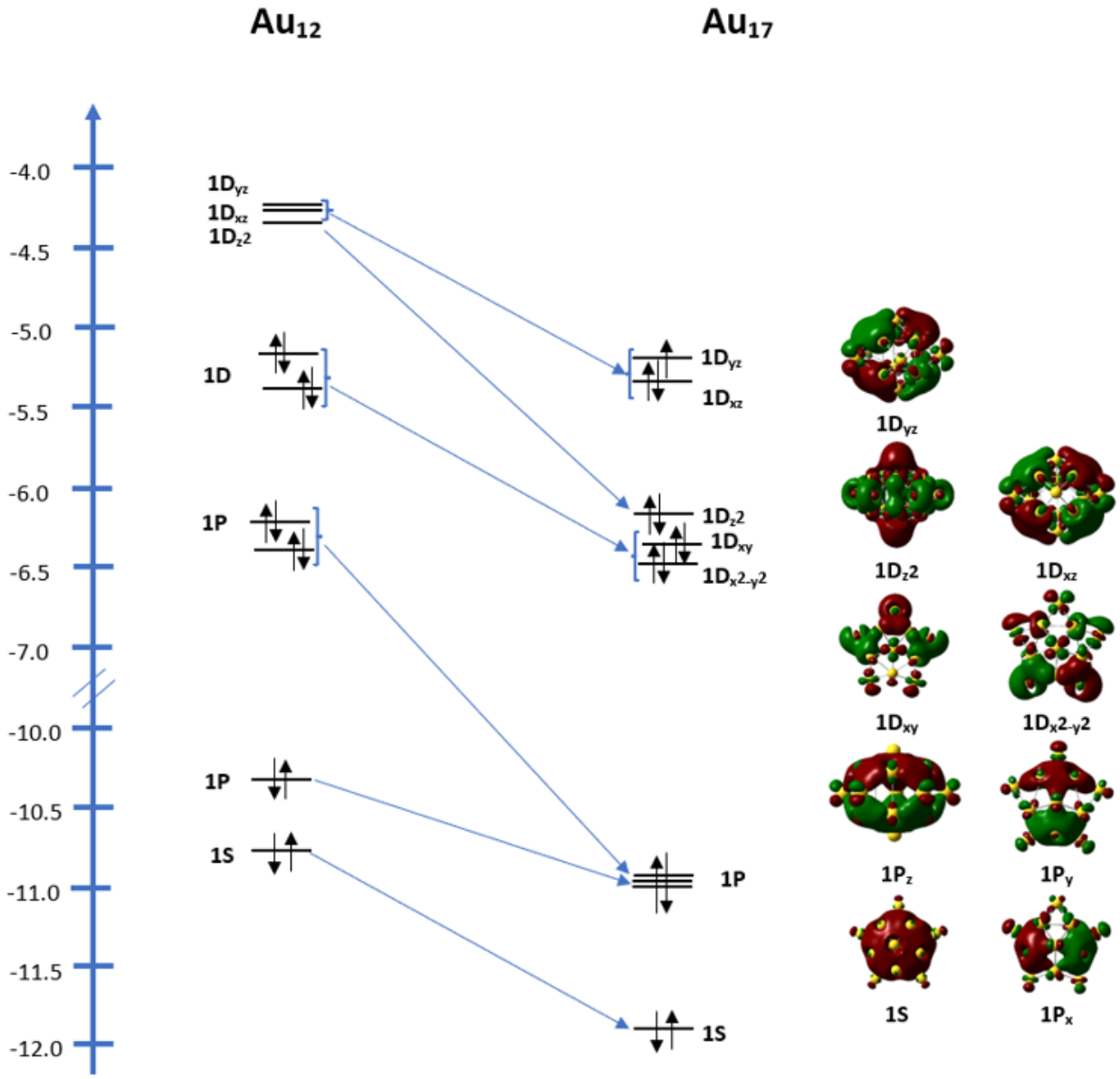
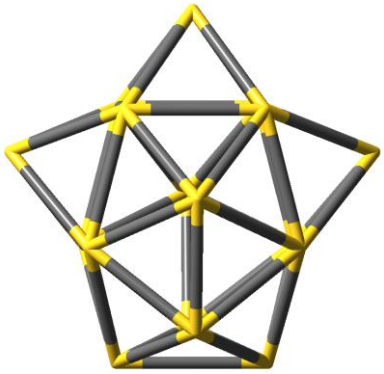
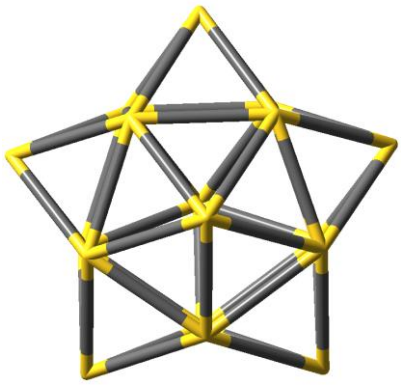
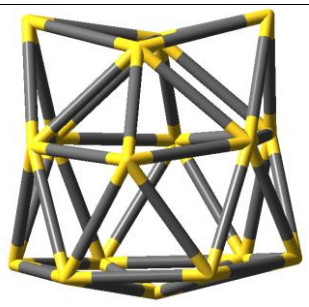
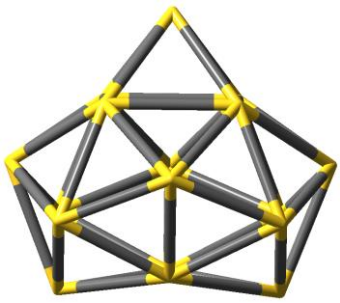
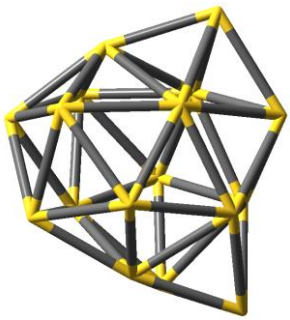
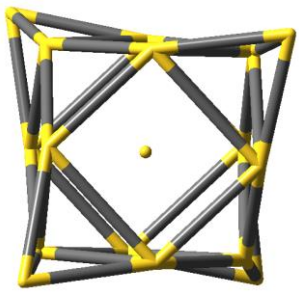
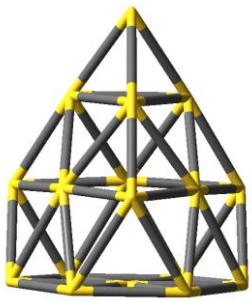
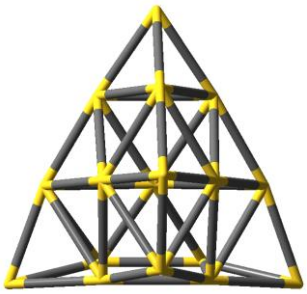
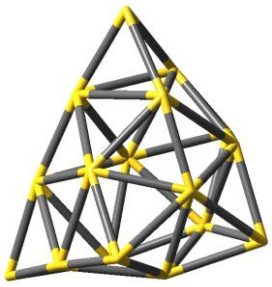


Fig. S4. An orbital correlation diagram between the Au_{12} core (a pentaprism with two Au atoms attached on both faces) and Au_{17} star cluster **17_2**. The five Au atoms string is omitted as they do not have any interaction. Shapes of the shell orbitals are given, but they are not displayed in any energy ordering.

Table S1. Low-lying isomers of the Au_{17} cluster and their Cartesian coordinates (in Å) located using TPSS/cc-pVDZ-PP geometry optimizations.

Isomer	Cartesian coordinates			
 **17_1**	79	1.377657000	1.922706000	1.425639000
	79	0.000040000	-2.417089000	-2.261997000
	79	-2.042883000	-0.772138000	-1.418461000
	79	-1.377702000	1.922665000	-1.425621000
	79	2.042896000	-0.772073000	-1.418480000
	79	1.377657000	1.922706000	-1.425639000
	79	-0.000038000	3.862791000	0.000000000
	79	-1.453776000	-3.068487000	0.000000000
	79	2.042896000	-0.772073000	1.418480000
	79	3.573572000	1.044743000	0.000000000
	79	-1.377702000	1.922665000	1.425621000
	79	-0.000013000	0.208301000	3.098493000
	79	-3.573612000	1.044639000	0.000000000
	79	-0.000013000	0.208301000	-3.098493000
	79	1.453862000	-3.068425000	0.000000000
	79	0.000040000	-2.417089000	2.261997000
	79	-2.042883000	-0.772138000	1.418461000
 **17_2**	79	0.000000000	2.945366000	0.005946000
	79	-2.190363000	-1.416743000	-0.727884000
	79	3.613550000	0.000000000	1.193858000
	79	1.362349000	1.447830000	1.911960000
	79	2.190363000	1.416743000	-0.727884000
	79	-1.362349000	-1.447830000	1.911960000
	79	-1.362349000	1.447830000	1.911960000
	79	-3.613550000	0.000000000	1.193858000
	79	0.000000000	1.484610000	-2.369677000
	79	-2.190363000	1.416743000	-0.727884000
	79	0.000000000	0.000000000	3.842980000
	79	0.000000000	-1.484610000	-2.369677000
	79	0.000000000	-2.945366000	0.005946000
	79	2.190363000	-1.416743000	-0.727884000
	79	-2.208149000	0.000000000	-3.119768000
	79	2.208149000	0.000000000	-3.119768000
	79	1.362349000	-1.447830000	1.911960000
 **17_3**	79	2.088823000	1.424793000	-0.557842000
	79	-1.387613000	-2.388575000	1.911902000
	79	-2.088823000	-1.424793000	-0.557842000
	79	0.000000000	-1.425559000	-2.401268000
	79	1.387613000	-2.388575000	1.911902000
	79	2.088823000	-1.424793000	-0.557842000
	79	2.324552000	0.000000000	-2.897643000
	79	-2.722943000	0.000000000	1.761119000
	79	1.387613000	2.388575000	1.911902000
	79	2.722943000	0.000000000	1.761119000
	79	0.000000000	1.425559000	-2.401268000
	79	0.000000000	3.254636000	-0.357066000
	79	-2.324552000	0.000000000	-2.897643000
	79	0.000000000	-3.254636000	-0.357066000
	79	0.000000000	0.000000000	2.373475000

	79	-1.387613000	2.388575000	1.911902000
	79	-2.088823000	1.424793000	-0.557842000
 **17_4**	79	0.000000000	3.298500000	0.191288000
	79	-2.354857000	-2.283310000	-0.756841000
	79	3.394608000	0.000000000	0.391376000
	79	1.407479000	1.406448000	1.698619000
	79	2.354857000	2.283310000	-0.756841000
	79	-1.407479000	-1.406448000	1.698619000
	79	-1.407479000	1.406448000	1.698619000
	79	-3.394608000	0.000000000	0.391376000
	79	0.000000000	1.405728000	-1.957562000
	79	-2.354857000	2.283310000	-0.756841000
	79	0.000000000	0.000000000	3.597245000
	79	0.000000000	-1.405728000	-1.957562000
	79	0.000000000	-3.298500000	0.191288000
	79	2.354857000	-2.283310000	-0.756841000
	79	-2.342013000	0.000000000	-2.307280000
	79	2.342013000	0.000000000	-2.307280000
	79	1.407479000	-1.406448000	1.698619000
 **17_5**	79	-0.377517000	-1.901786000	1.439588000
	79	2.339363000	-2.255494000	0.905321000
	79	1.260881000	1.122667000	-1.827211000
	79	0.457987000	-3.034573000	-0.926330000
	79	1.599954000	-0.404828000	2.807384000
	79	-1.071768000	0.298035000	3.008756000
	79	0.056541000	-1.088913000	-2.908363000
	79	2.394296000	3.046126000	-0.217609000
	79	-1.864895000	-1.633667000	-0.972946000
	79	-2.032044000	1.535442000	0.683897000
	79	2.555886000	-1.317069000	-1.710607000
	79	-1.519436000	0.983289000	-2.040007000
	79	2.830310000	0.419638000	0.433696000
	79	0.618126000	1.820338000	1.482389000
	79	-0.361780000	3.155530000	-0.763171000
	79	-3.901032000	0.209976000	-0.880316000
	79	-2.984873000	-0.954712000	1.485527000
 **17_6**	79	1.393639000	-1.541280000	1.944435000
	79	2.863019000	0.000000000	-0.009261000
	79	1.393639000	1.541280000	1.944435000
	79	-1.393639000	-1.541280000	1.944435000
	79	-1.393639000	1.541280000	1.944435000
	79	0.000000000	0.000000000	0.000000000
	79	1.541280000	1.393639000	-1.944435000
	79	0.000000000	2.863019000	0.009261000
	79	-2.863019000	0.000000000	-0.009261000
	79	-1.541280000	1.393639000	-1.944435000
	79	1.541280000	-1.393639000	-1.944435000
	79	-1.541280000	-1.393639000	-1.944435000
	79	0.000000000	-2.863019000	0.009261000
	79	0.000000000	3.527090000	-2.628629000
	79	-3.527090000	0.000000000	2.628629000
	79	0.000000000	-3.527090000	-2.628629000
	79	3.527090000	0.000000000	2.628629000

 **17_7**	79	2.483139000	-1.873888000	1.371638000
	79	0.058269000	-2.001809000	2.834342000
	79	-2.300922000	-2.205958000	1.392675000
	79	-2.300922000	-2.205958000	-1.392675000
	79	0.058269000	-2.001809000	-2.834342000
	79	2.483139000	-1.873888000	-1.371638000
	79	0.089813000	-2.056828000	0.000000000
	79	1.541688000	0.382563000	2.762618000
	79	2.008376000	0.520200000	0.000000000
	79	1.541688000	0.382563000	-2.762618000
	79	-0.951680000	0.299113000	1.612559000
	79	-3.179018000	0.090639000	0.000000000
	79	-0.951680000	0.299113000	-1.612559000
	79	0.752879000	2.579208000	-1.421024000
	79	0.752879000	2.579208000	1.421024000
	79	-1.813387000	2.431238000	0.000000000
	79	-0.272531000	4.656290000	0.000000000
 **17_8**	79	-0.049610000	-2.677579000	3.689033000
	79	-0.910830000	-0.284490000	2.800108000
	79	-1.423794000	-2.829953000	1.328969000
	79	-1.539950000	1.991533000	1.478455000
	79	-1.194598000	-0.391054000	0.000000000
	79	-2.122121000	4.181612000	0.000000000
	79	-1.423794000	-2.829953000	-1.328969000
	79	1.170538000	-1.834517000	1.359400000
	79	1.073304000	1.041393000	1.423960000
	79	-1.539950000	1.991533000	-1.478455000
	79	0.517139000	3.434429000	0.000000000
	79	-0.910830000	-0.284490000	-2.800108000
	79	1.073304000	1.041393000	-1.423960000
	79	-0.049610000	-2.677579000	-3.689033000
	79	1.170538000	-1.834517000	-1.359400000
	79	3.057467000	2.365460000	0.000000000
	79	3.102796000	-0.403221000	0.000000000
 **17_9**	79	-0.499196000	-0.941697000	-1.855659000
	79	2.179600000	-0.109778000	-1.954278000
	79	1.274617000	-2.541814000	-0.394261000
	79	-3.095412000	-0.707419000	-0.794738000
	79	-1.274612000	-2.541814000	0.394270000
	79	2.008034000	1.843203000	0.138359000
	79	-0.211937000	1.771931000	1.942304000
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	79	0.211936000	1.771920000	-1.942306000
	79	0.499197000	-0.941689000	1.855660000
	79	3.833559000	-2.217065000	-1.309545000
	79	-0.000003000	3.786446000	-0.000009000
	79	-2.008036000	1.843199000	-0.138362000
	79	-2.179599000	-0.109772000	1.954275000
	79	-3.833555000	-2.217064000	1.309553000
	79	-2.366950000	1.009406000	-2.758716000
	79	2.366948000	1.009417000	2.758715000

References

1. P. Gruene, B. Butschke, J. T. Lyon, D. M. Rayner and A. Fielicke, *Z. Phys. Chem.*, 2014, **228**, 337-350.
2. Y. Gao and X. C. Zeng, *J. Am. Chem. Soc.*, 2005, **127**, 3698-3699.
3. L. Yan, L. Cheng and J. Yang, *J. Phys. Chem. C*, 2015, **119**, 23274-23278.
4. S. Li, S. Singh, J. A. Dumesic and M. Mavrikakis, *Catal. Sci. Technol.*, 2019, **9**, 2836-2848.
5. C. Tang, W. Zhu, K. Zhang, X. He and F. Zhu, *Comput. Theor. Chem.*, 2014, **1049**, 62-66.
6. J. P. Perdew and Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244–13249.
7. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
8. J. Tao, J. P. Perdew, V. N. Staroverov and G. E. Scuseria, *Phys. Rev. Lett.*, 2003, **91**, 146401.
9. S. Bulusu and X. C. Zeng, *J. Chem. Phys.*, 2006, **125**, 154303.
10. Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.
11. J. P. Perdew, A. Ruzsinszky, G. I. Csonka, L. A. Constantin and J. Sun, *Phys. Rev. Lett.*, 2009, **103**, 026403.
12. K. A. Peterson, *J. Chem. Phys.*, 2003, **119**, 11099-11112.
13. Q. Ma and H.-J. Werner, *J. Chem. Theory Comput.*, 2018, **14**, 198-215.
14. K. A. Peterson and C. Puzzarini, *Theoretical Chemistry Accounts*, 2005, **114**, 283-296.
15. D. Figgen, G. Rauhut, M. Dolg and H. Stoll, *Chemical physics*, 2005, **311**, 227-244.
16. M. Schwilk, Q. Ma, C. Köppl and H.-J. Werner, *J. Chem. Theory Comput.*, 2017, **13**, 3650-3675.
17. Q. Ma and H. J. Werner, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, 2018, **8**, e1371.
18. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 16 Rev. B.01, Gaussian, Inc., Wallingford CT, 2016.
19. H. J. Werner, P. J. Knowles, G. Knizia, F. R. Manby and M. Schütz, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, 2012, **2**, 242-253.
20. H.-J. Werner, P. J. Knowles, F. R. Manby, J. A. Black, K. Doll, A. Heßelmann, D. Kats, A. Köhn, T. Korona and D. A. Kreplin, *J. Chem. Phys.*, 2020, **152**, 144107.
21. H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, W. Györffy, D. Kats, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, S. J. Bennie, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, S. J. R. Lee, Y. Liu, A. W. Lloyd, Q. Ma, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, T. F. M. III, M. E. Mura, A. Nicklass, D. P. O'Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang and M. Welborn, MOLPRO, version 2020.1, a package of ab initio programs, see https://www.molpro.net.
22. A. Yang, W. Fa and J. Dong, *Phys. Lett. A*, 2010, **374**, 4506-4511.
23. P. V. Nhat, N. T. Si, J. Leszczynski and M. T. Nguyen, *Chem. Phys.*, 2017, **493**, 140-148.