Structural assignments of NMR chemical shifts in $Ge_xSe_{\{1-x\}}$ glasses through first principles calculations for $GeSe_2$, Ge_4Se_9, and GeSe crystals

Mikhail Kibalchenko, TCM Group, Cambridge University

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Introduction: $Ge_xSe_{\{1-x\}}$ glasses

- sensitive to the absorption of electromagnetic radiation[1]
- applications in passive and active optics[2]

[1] A. Zakery and S. R. Elliott, J. Non-Cryst. Solids 330, 1 (2003)
[2] K. Shimakawa, A. Kolobov, and S. R. Elliott, Adv. Phys. 44, 475 (1995)

Introduction: $Ge_xSe_{\{1-x\}}$ glasses

- corner-sharing and edge-sharing tetrahedral arrangements[1]

- under-coordinated and over-coordinated atoms[2]

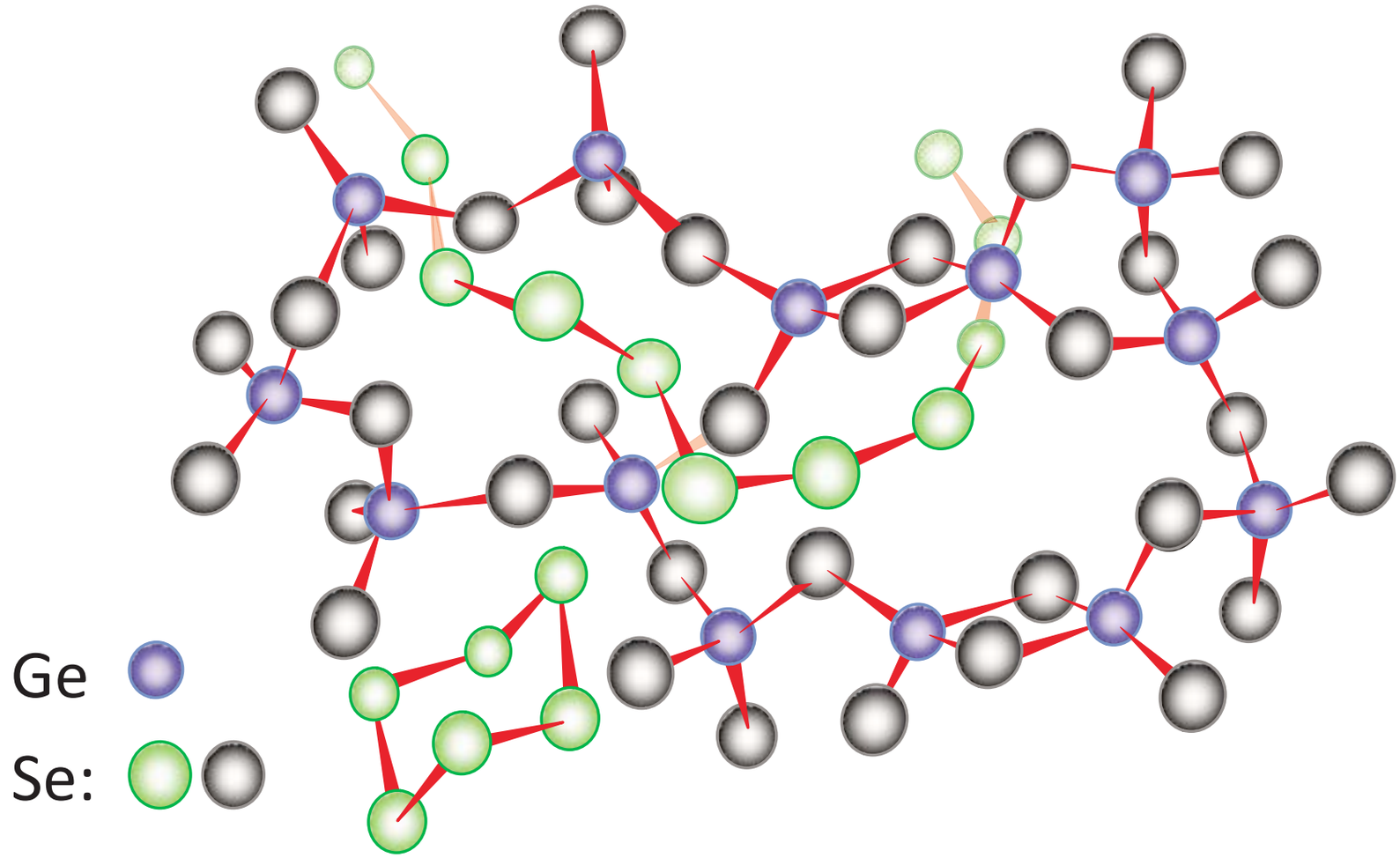
- homopolar bonds[1]

[1] I. Petri, P. S. Salmon, and H. E. Fischer, Phys. Rev. Lett. 84, 2413 (2000)
[2] C. Massobrio, M. Celino, P. S. Salmon, R. A. Martin, M. Micoulaut, and A. Pasquarello, Phys. Rev. B 79, 174201 (2009)
C. Massobrio and A. Pasquarello, Phys. Rev. B 77, 144207 (2008)

Introduction: $Ge_xSe_{\{1-x\}}$ glasses

1. bimodal phase: Se-Se-Se bonds and Ge-Se-Ge bonds only[1]

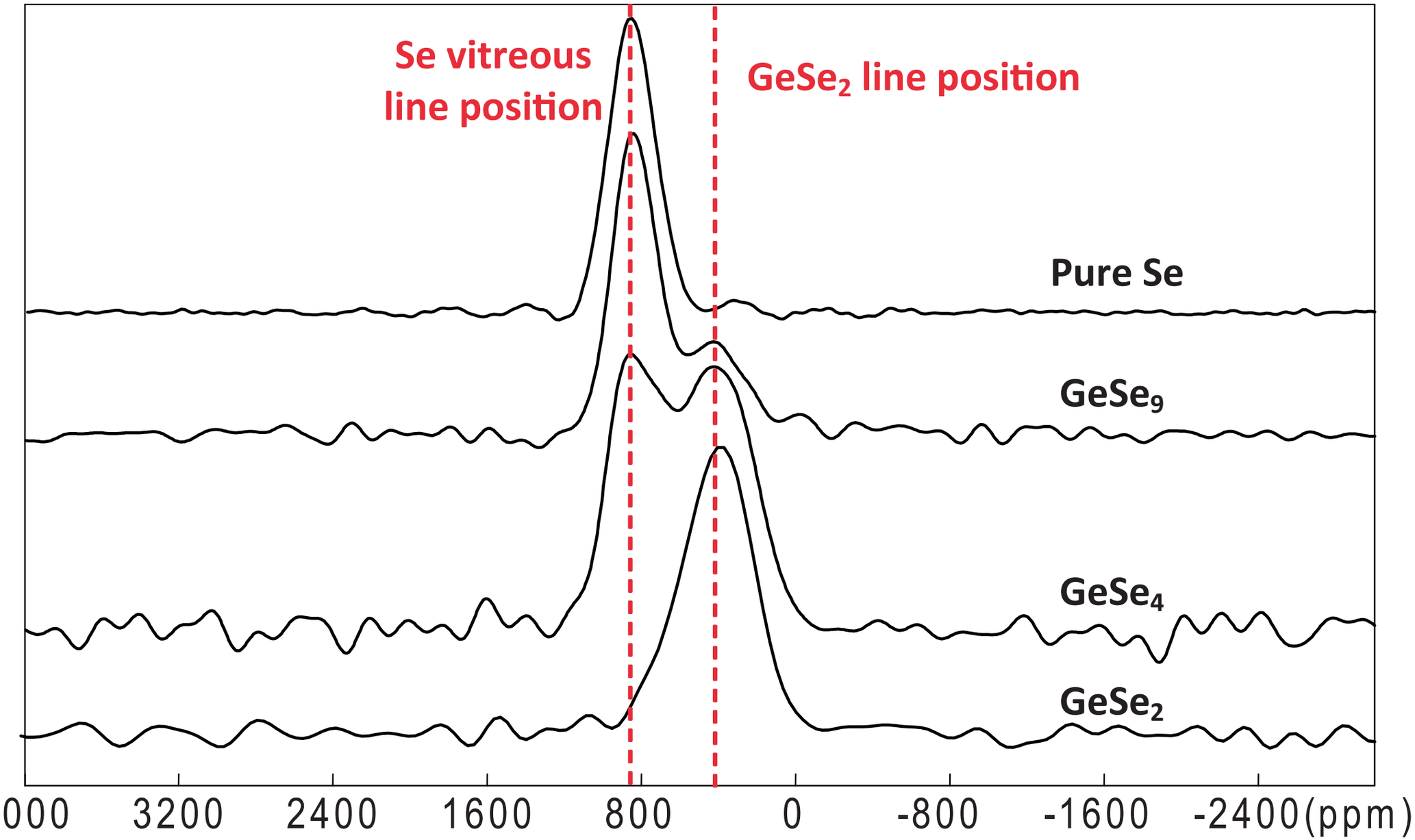
2. fully bonded with intermediate configurations[2]



[1] P. Lucas ..., and B. Bureau, Phys. Rev. B 80, 214114 (2009)
[2] E. L. Gjersing, S. Sen, and B. G. Aitken, J. Phys. Chem. C 114, 8601 (2010)

Introduction: $Ge_xSe_{\{1-x\}}$ glasses

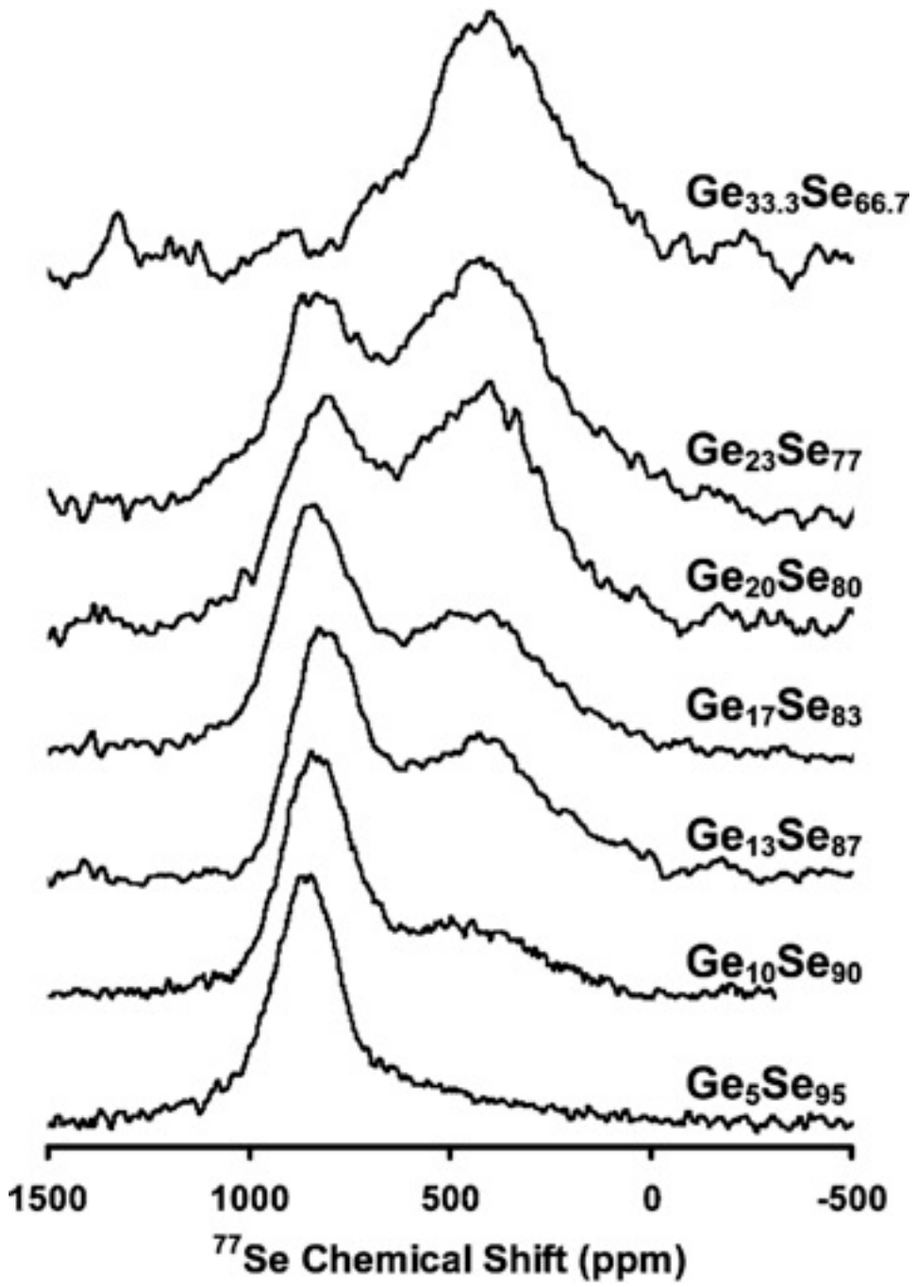
experimental spectra used to justify bimodal phase: Se-Se-Se bonds and Ge-Se-Ge bonds only[1]



[1] P. Lucas ..., and B. Bureau, Phys. Rev. B 80, 214114 (2009)

Introduction: $Ge_xSe_{\{1-x\}}$ glasses

experimental spectra used to justify fully bonded model with intermediate configurations[2]

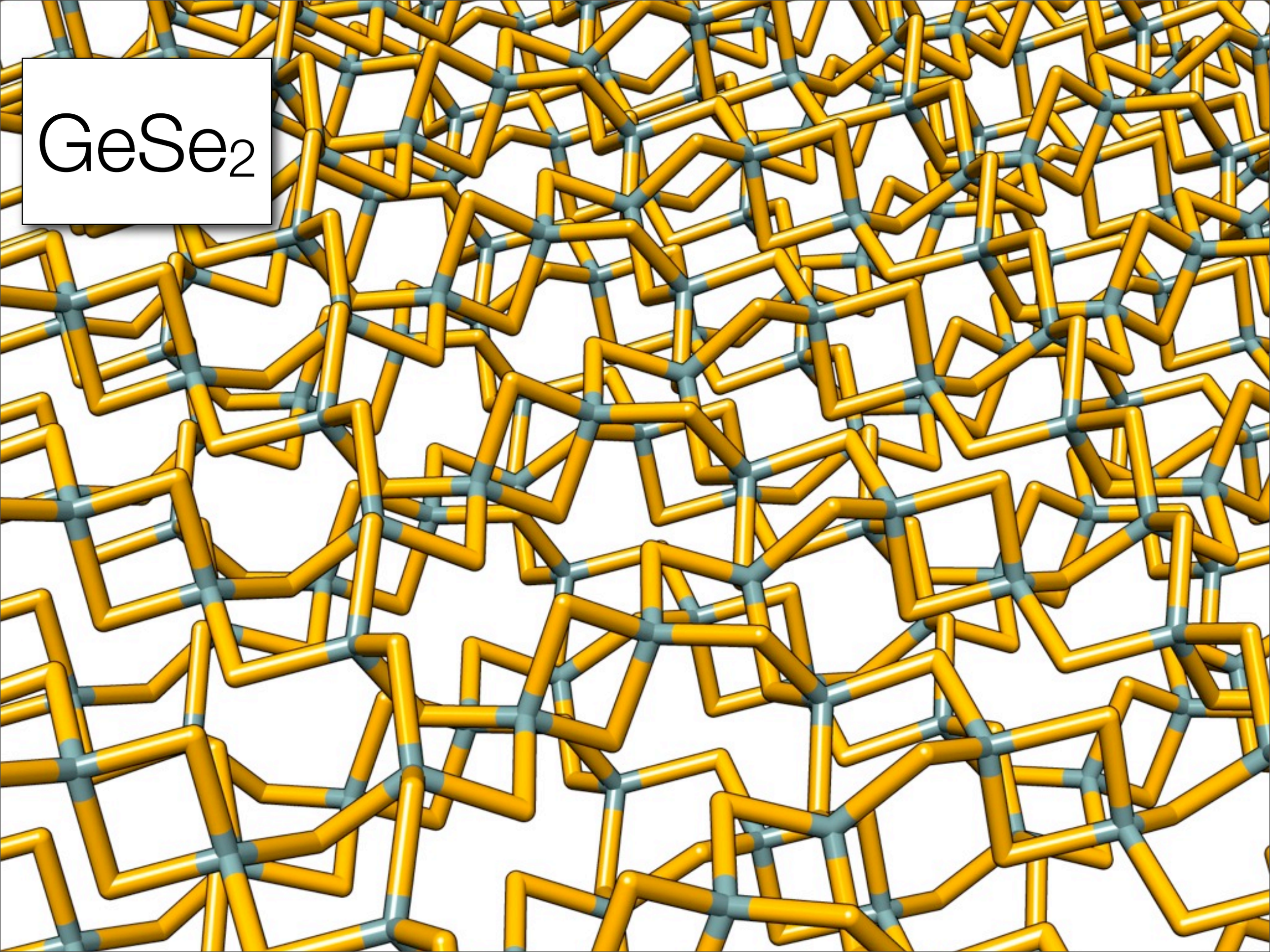


[2] E. L. Gjersing, S. Sen, and B. G. Aitken, J. Phys. Chem. C 114, 8601 (2010)

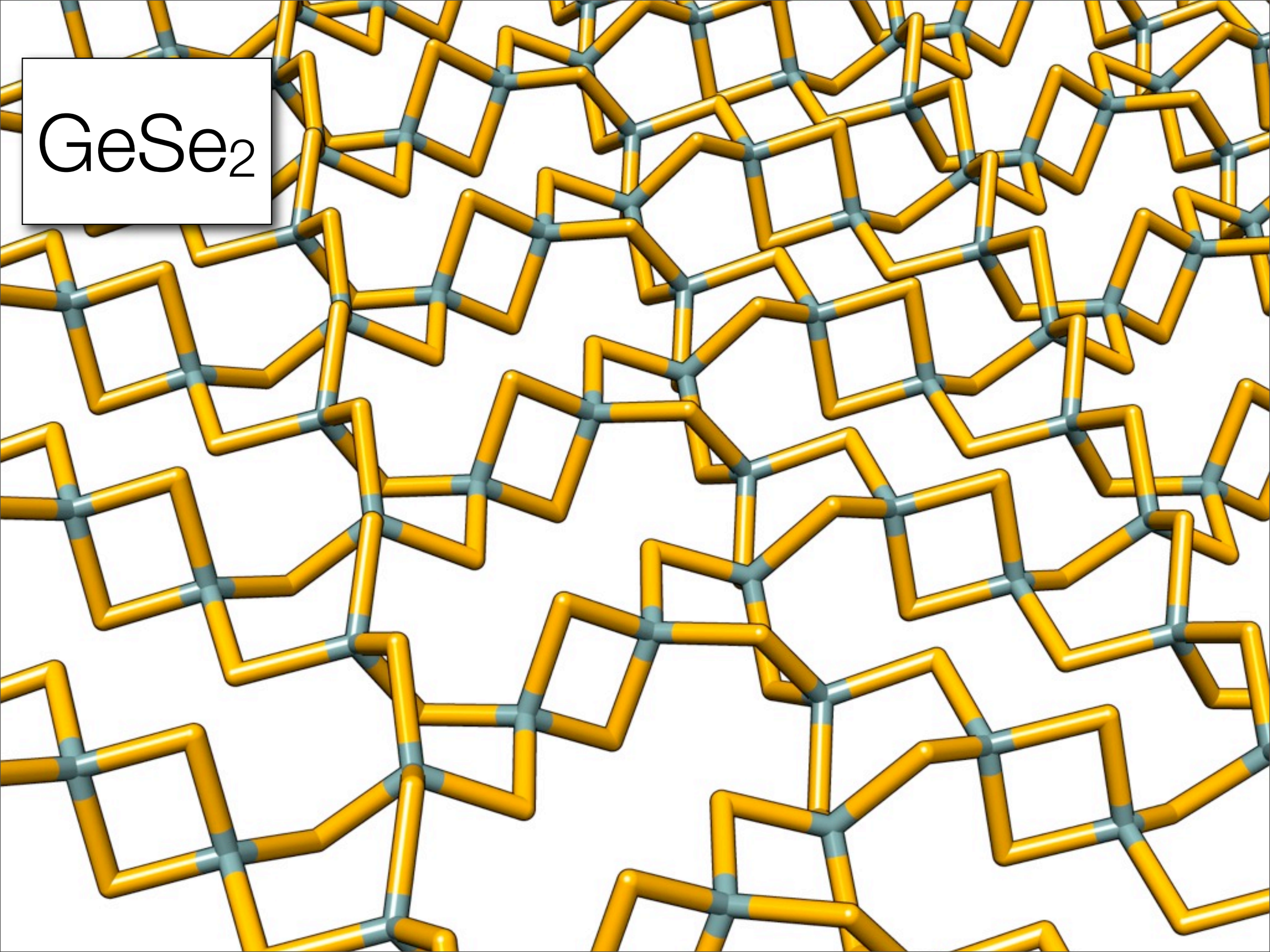
Aim

To provide structural assignments for the experimentally measured NMR spectra

$GeSe_2$



$GeSe_2$

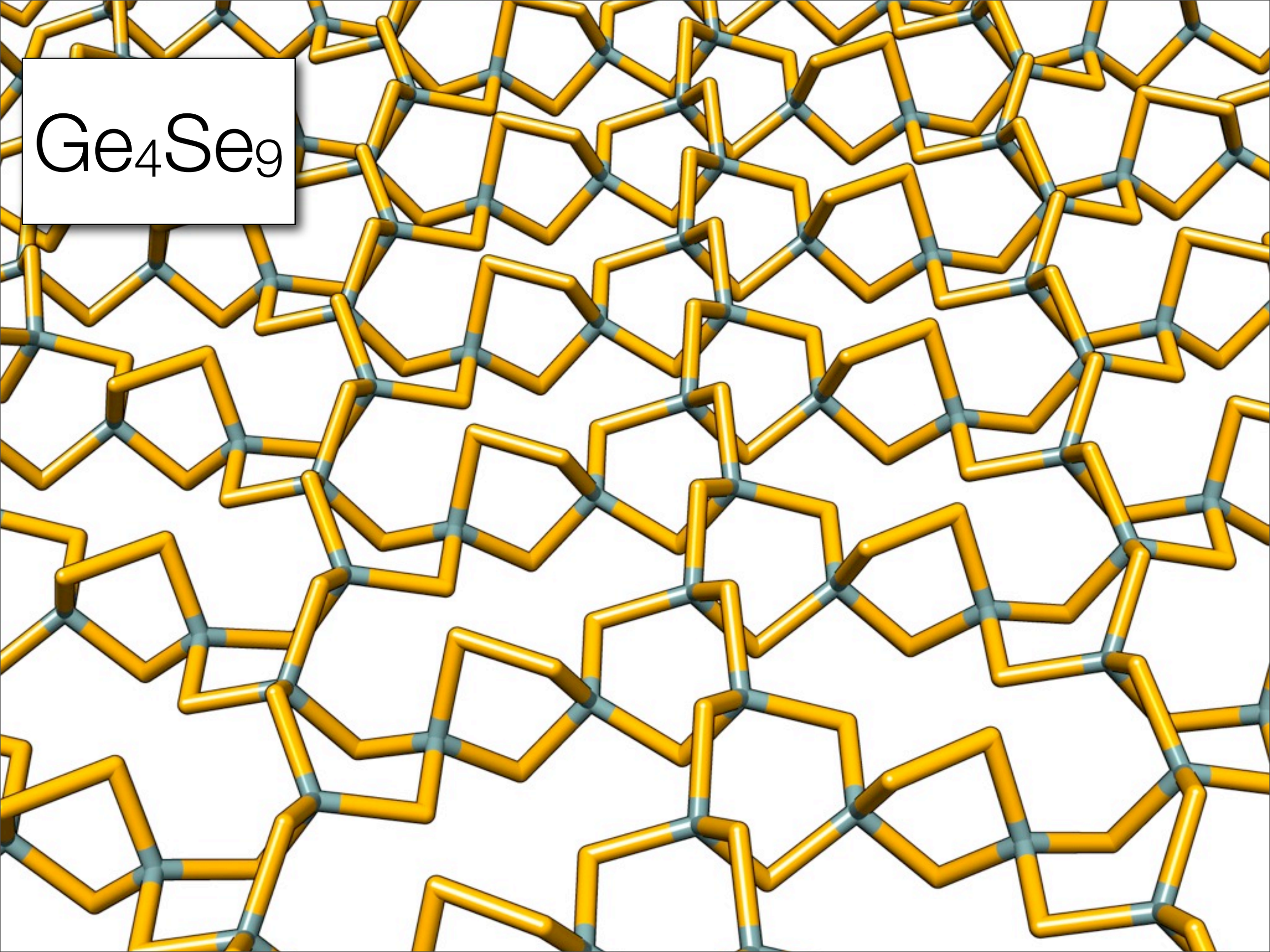


$GeSe_2$

ES

CS

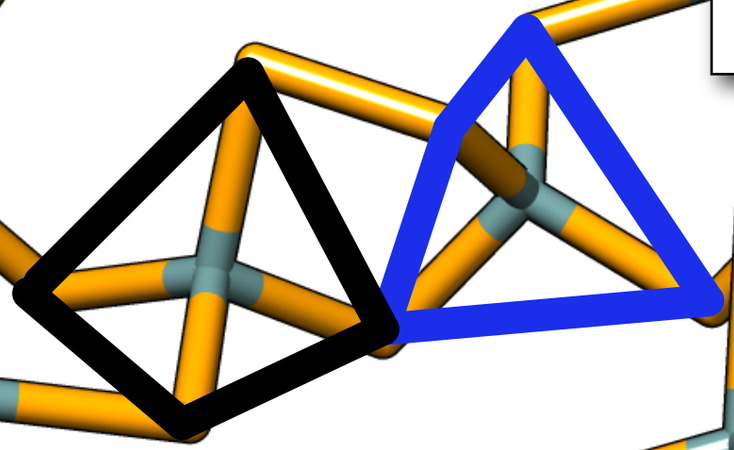
Ge_4Se_9



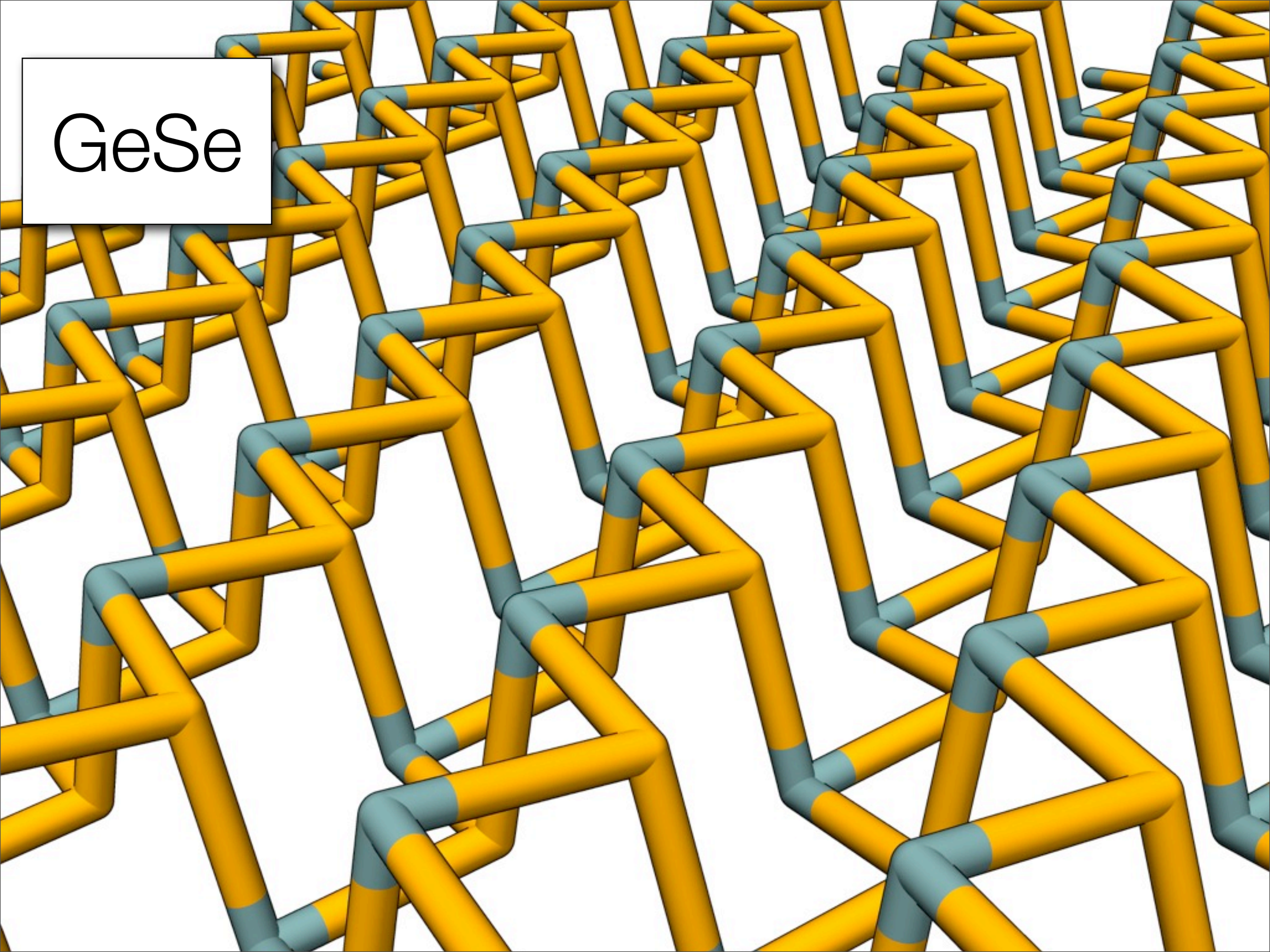
Ge_4Se_9

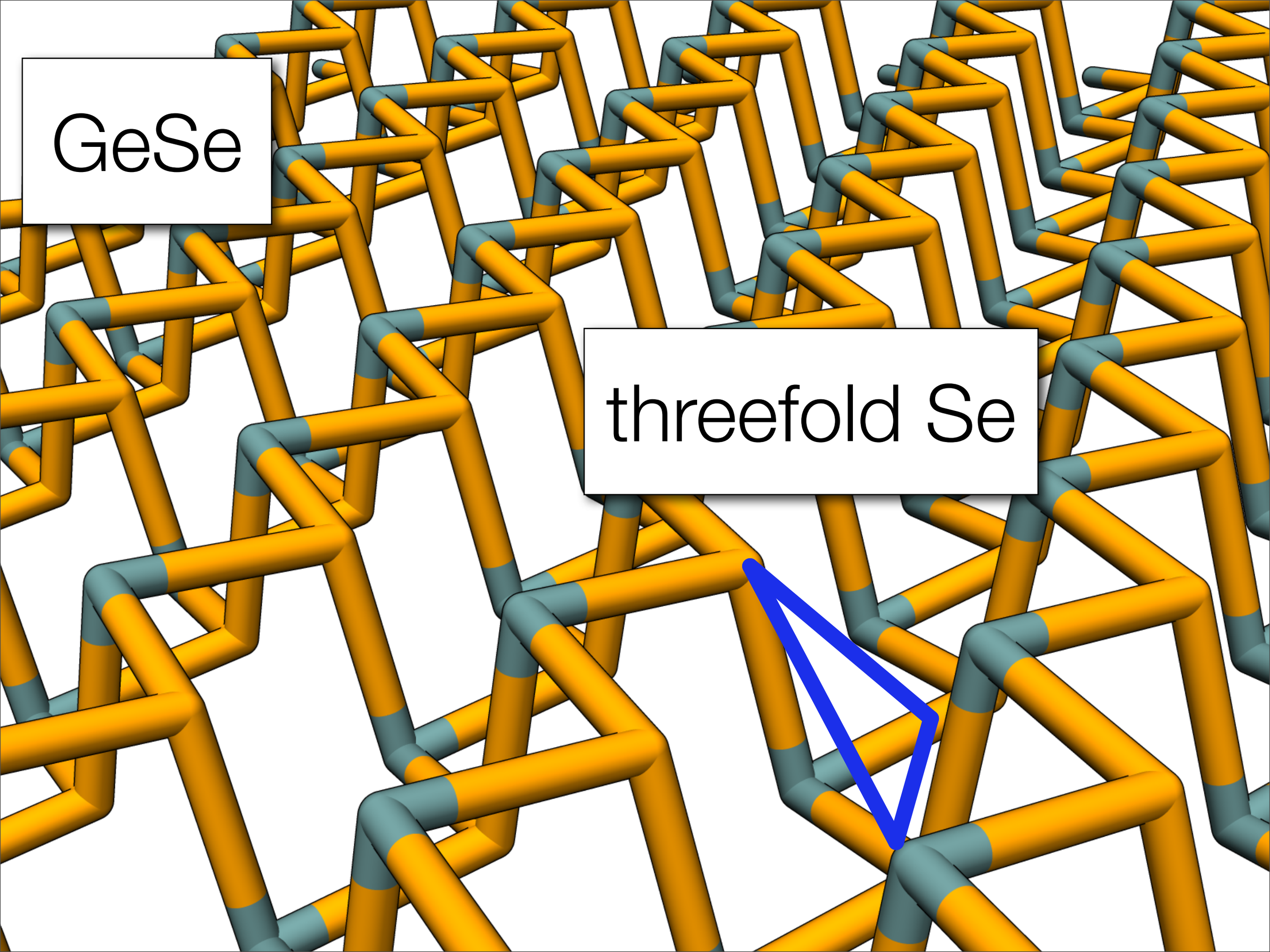
Se-Se-Ge

CS



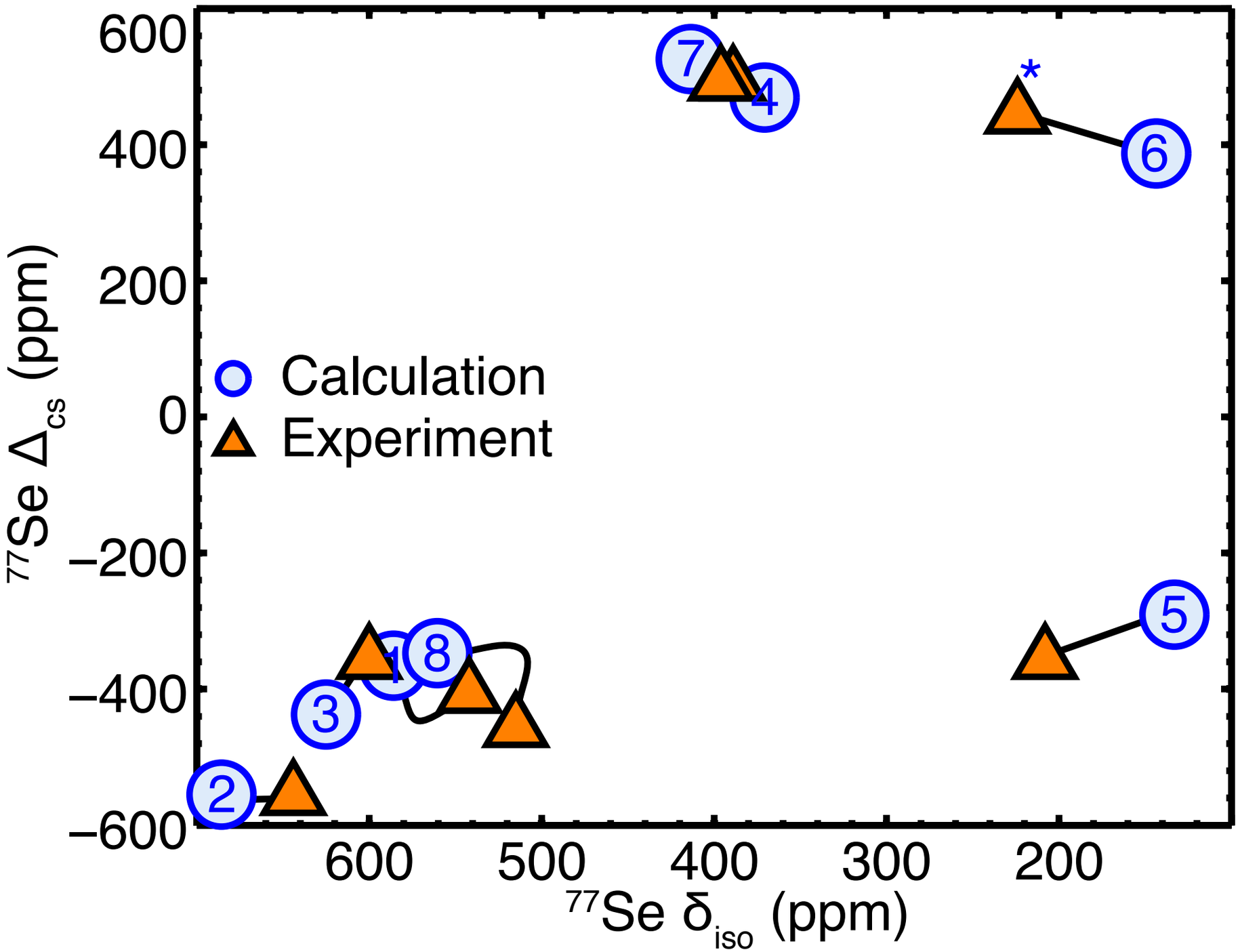
GeSe

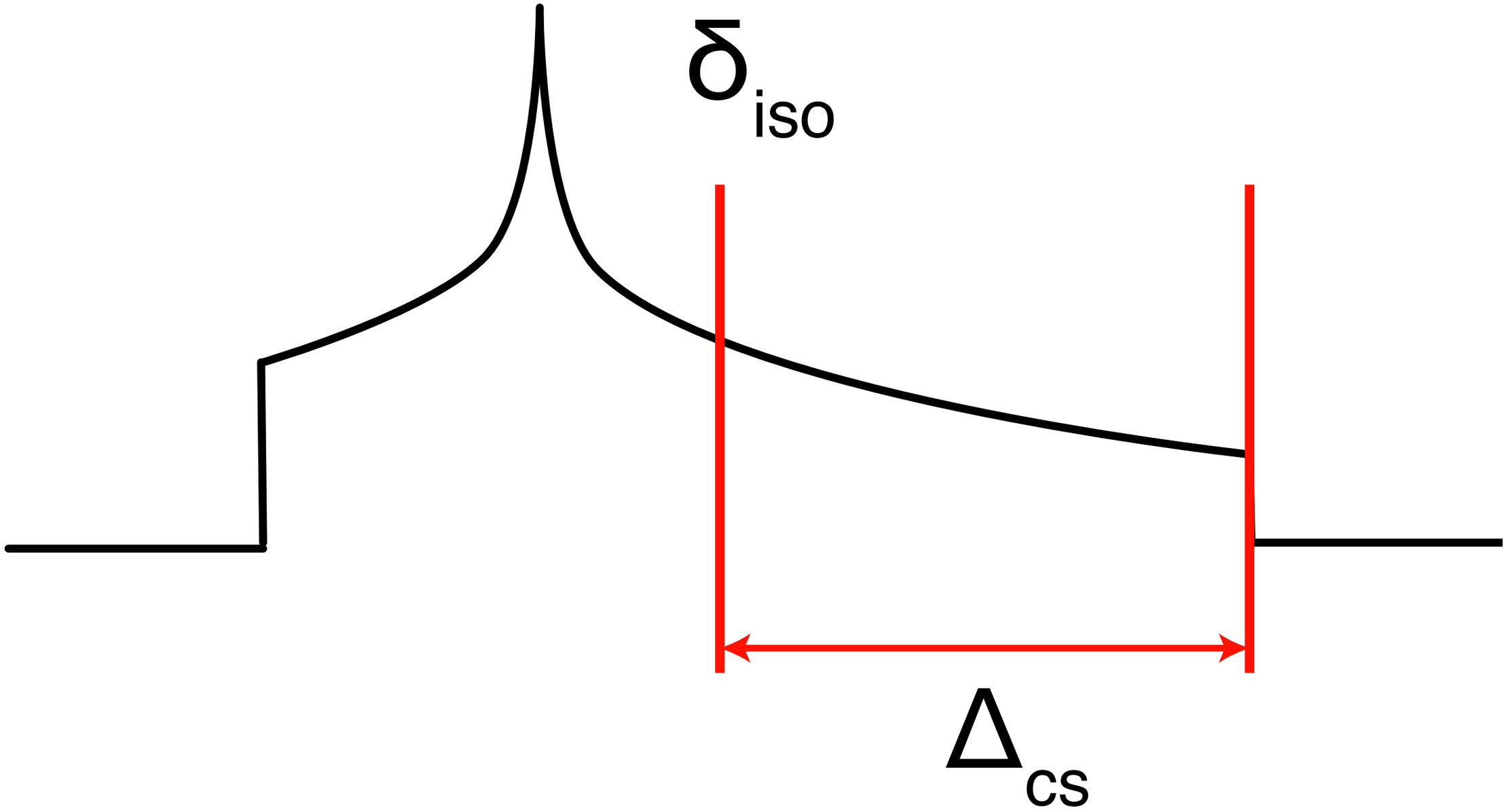



GeSe
threefold Se

Establishing reliability of calculation

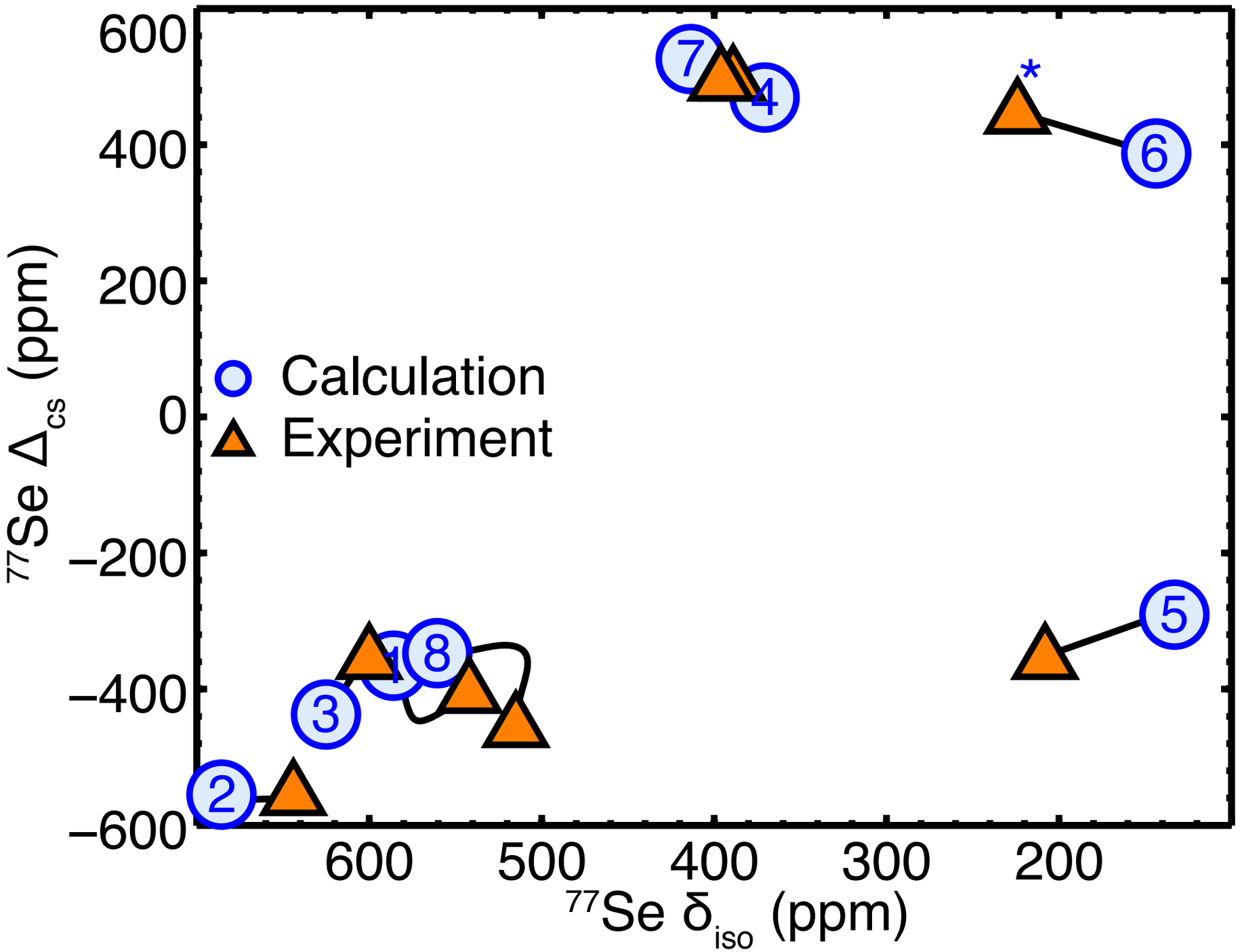
$GeSe_2$



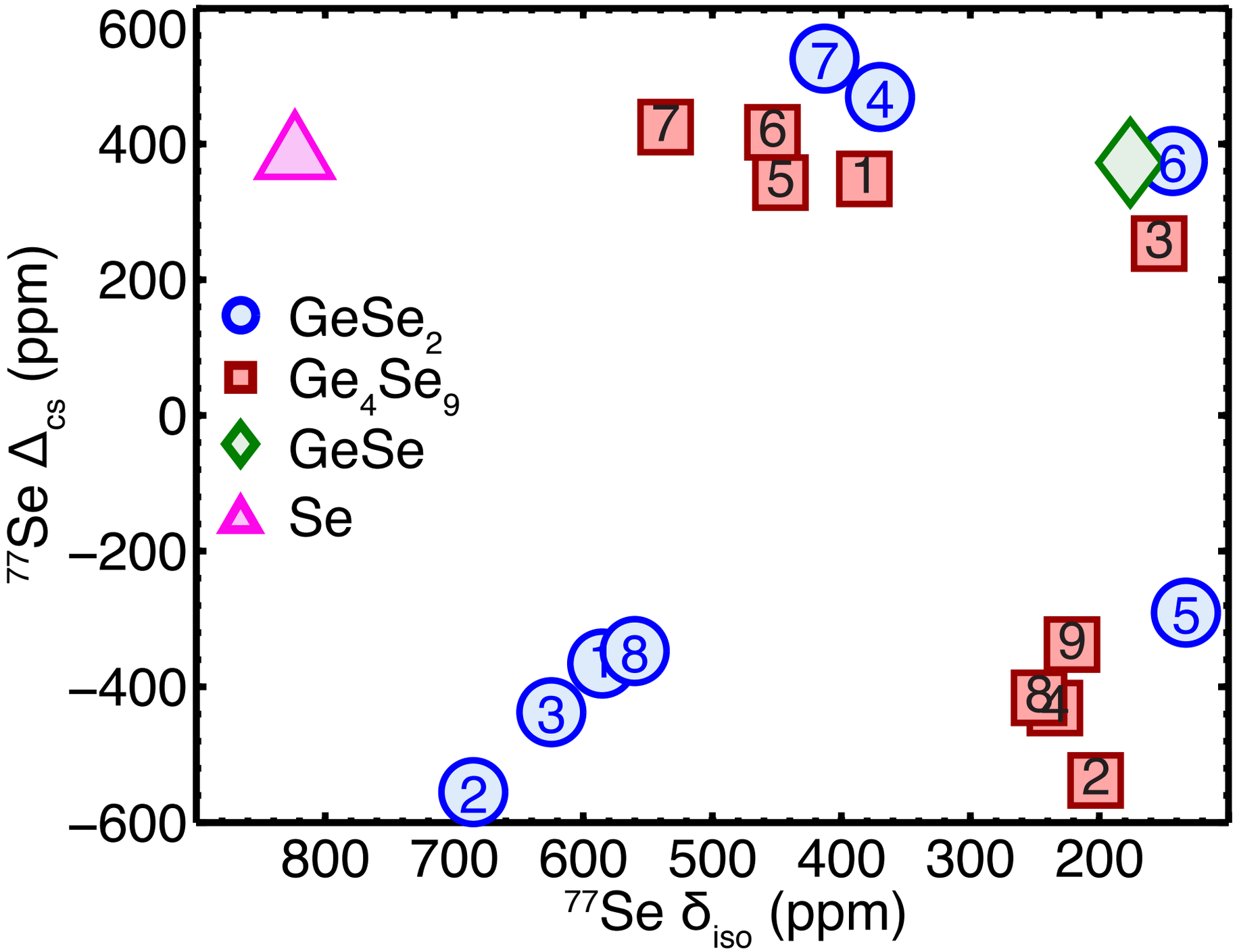

δ
iso
Δ
CS

Establishing reliability of calculation

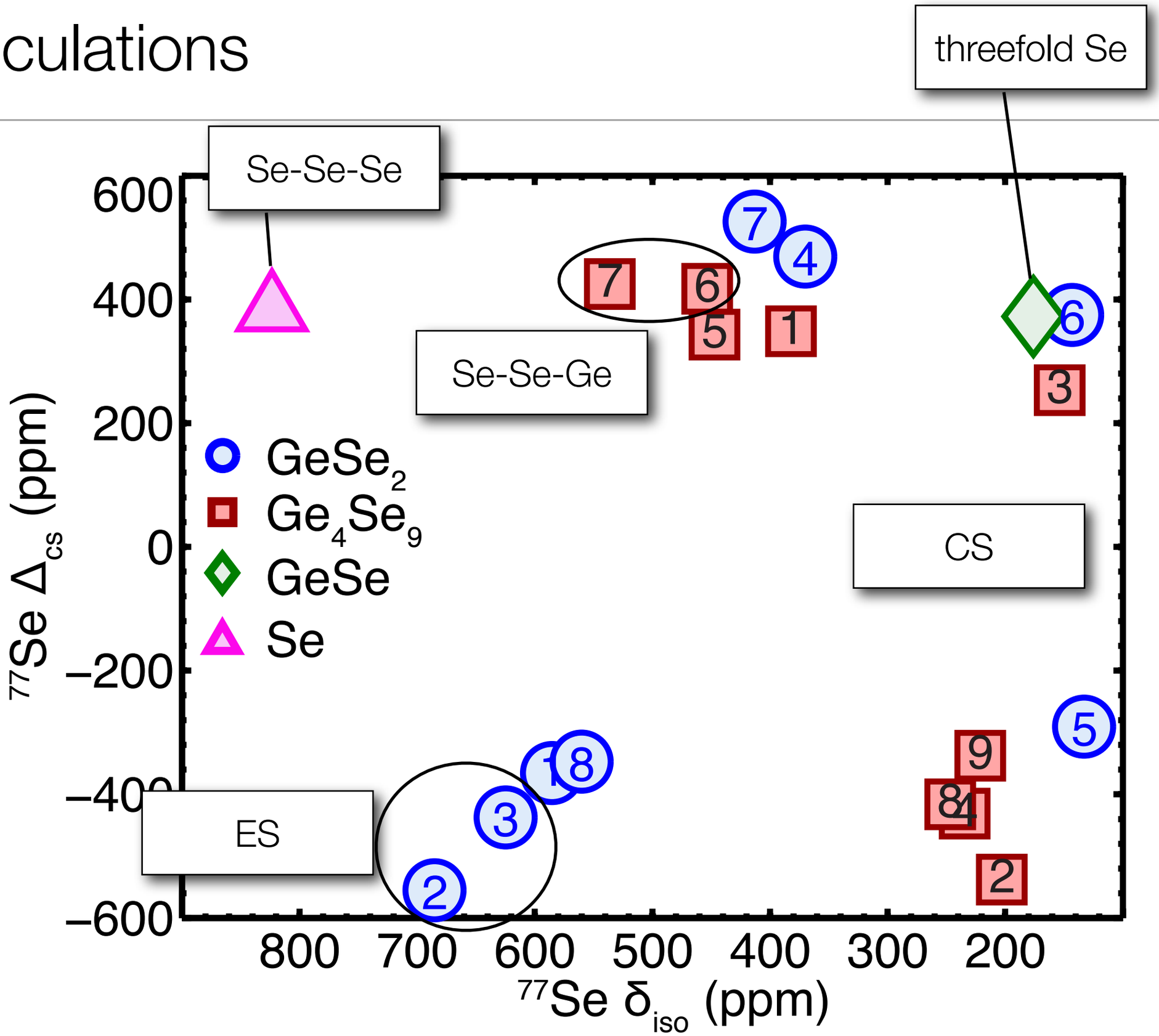
$GeSe_2$

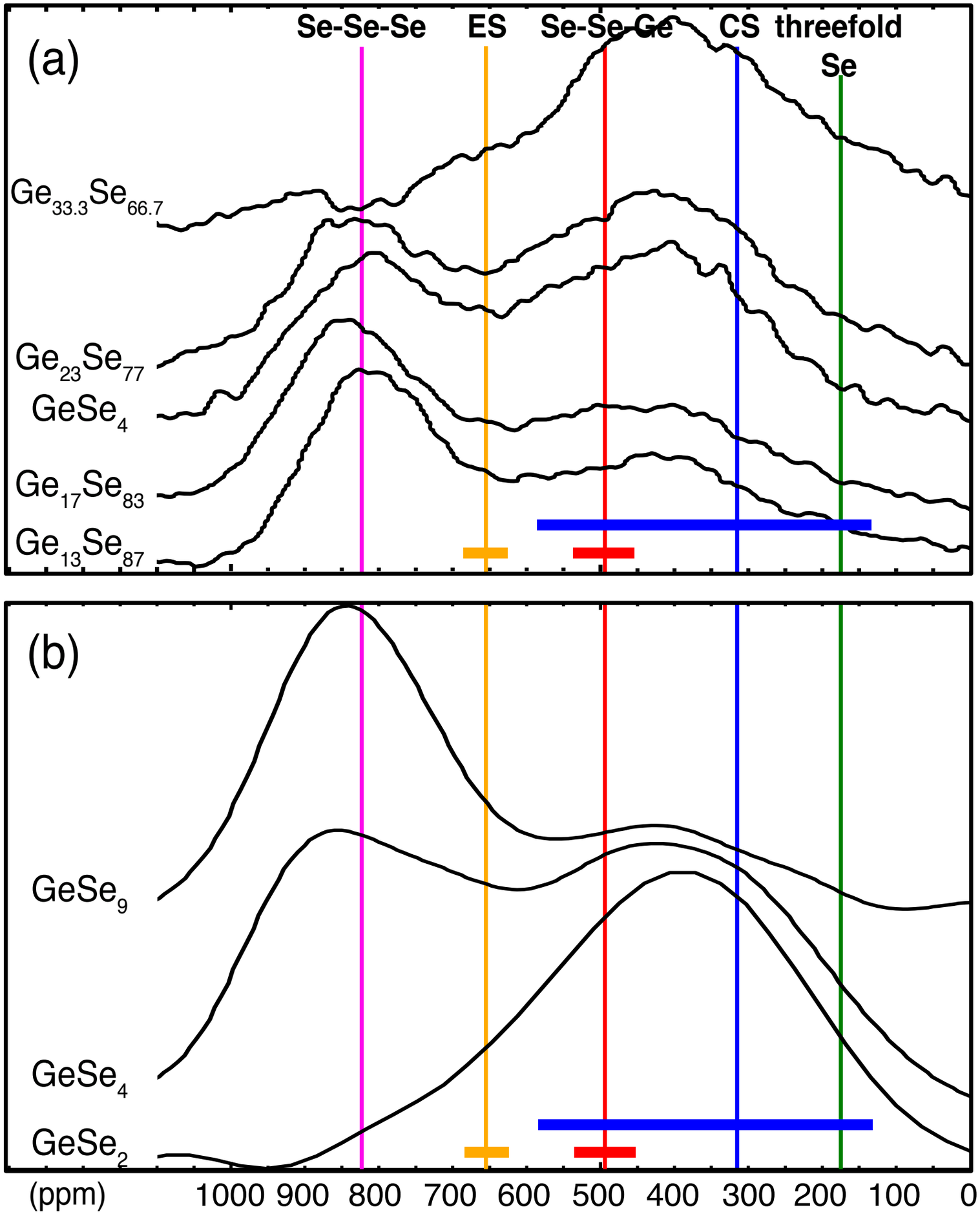


Calculations



Calculations




(a)
Se-Se-Se
ES
Se-Se-Ge
CS
threefold
Se
Ge33.3Se66.7
Ge23Se77
GeSe4
Ge17Se83
Ge13Se87
(b)
GeSe9
GeSe4
GeSe2
(ppm)
1000 900 800 700 600 500 400 300 200 100 0

Conclusion

- one of the experimentally observed peak results from overlapping contributions from various bonding configurations
- our interpretation is consistent with the occurrence of Ge-Se-Se linkages
- bimodal description is not necessary

Acknowledgements

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  Institut de Physique et de Chimie des Materiaux de Strasbourg, France

- Alfredo Pasquarello
  EPFL, Switzerland

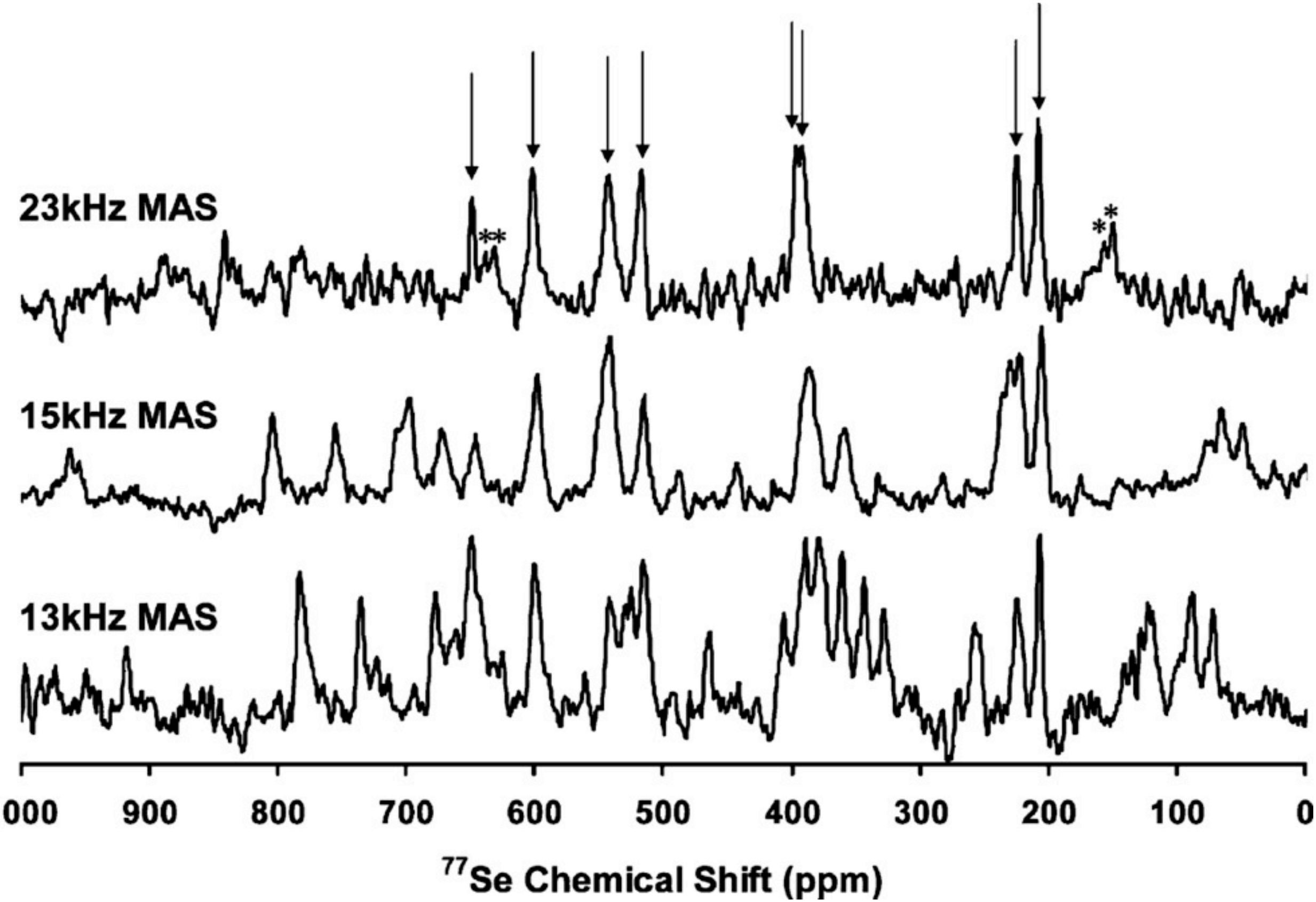
TCM

EPSRC

Thank you for listening

back up slides

[2] E. L. Gjersing, S. Sen, and B. G. Aitken, J. Phys. Chem. C 114, 8601 (2010)



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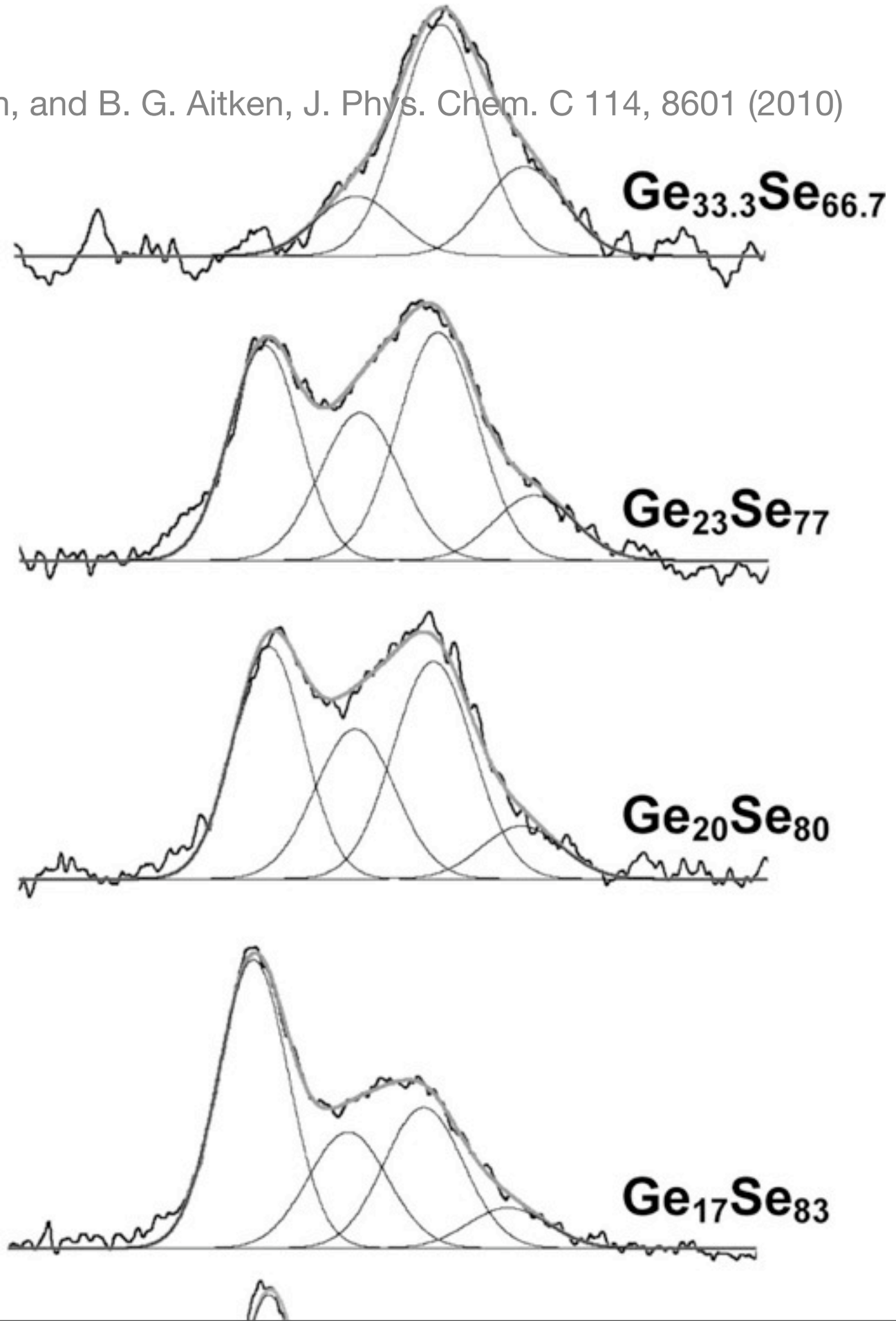

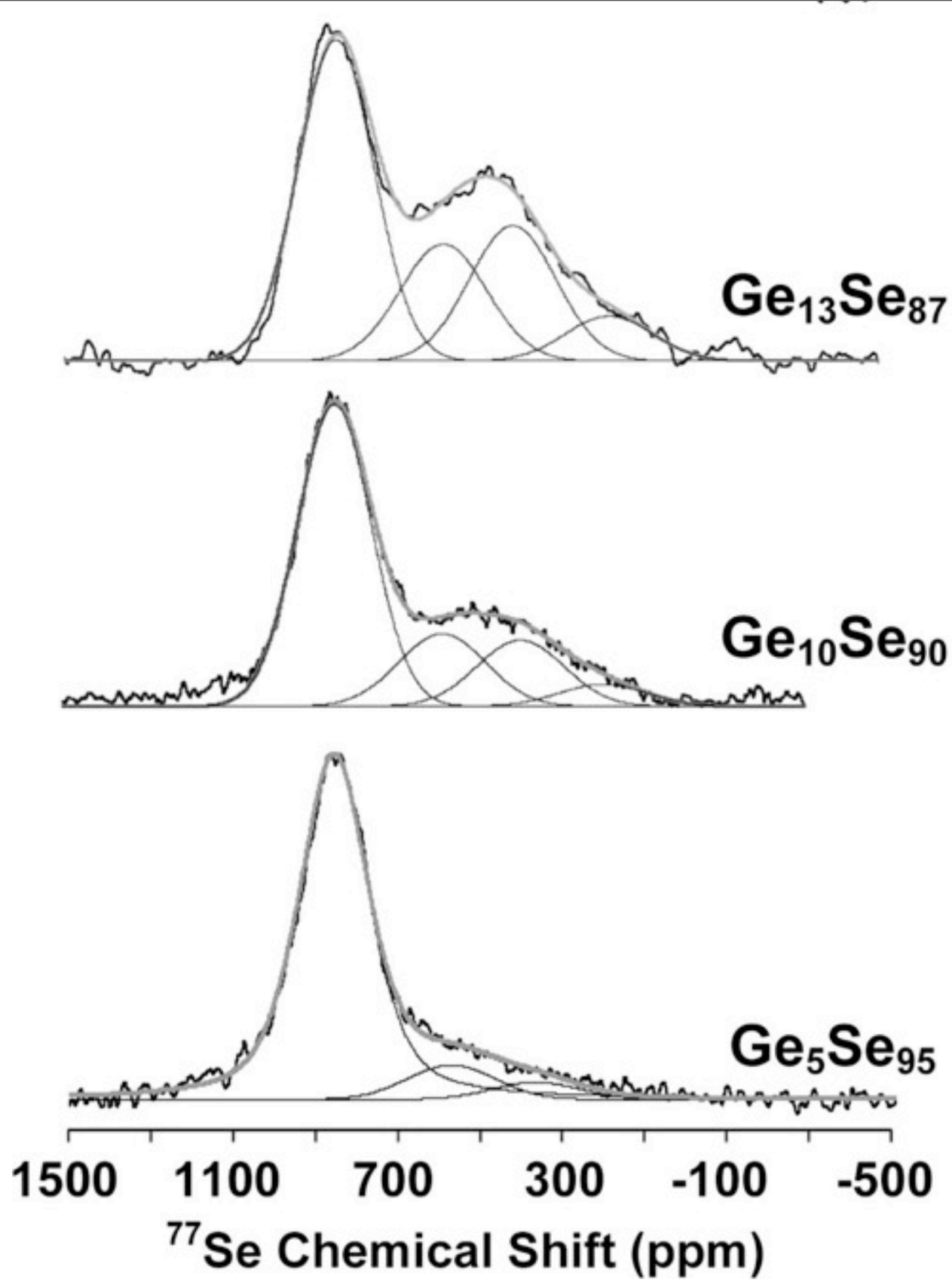

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