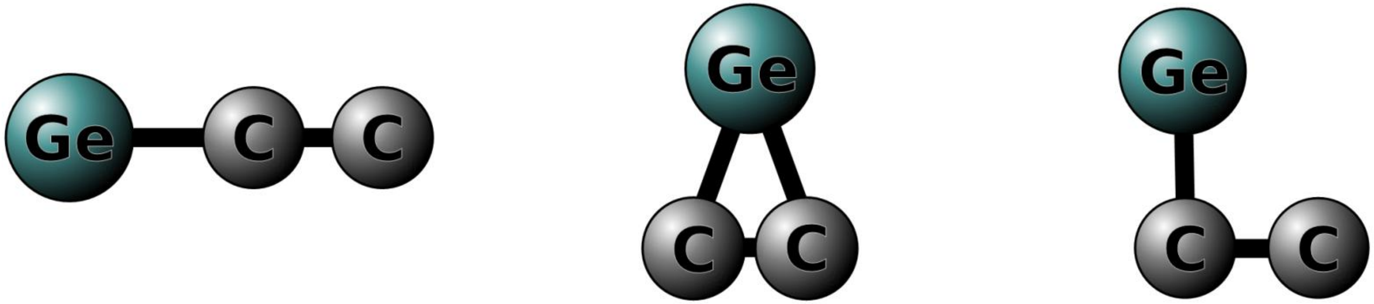
Germanium Dicarbide: Evidence for a T-shaped Ground State Structure



O. Zingsheim, M.A. Martin-Drumel, S. Thorwirth,
S. Schlemmer, C.A. Gottlieb, J. Gauss, and M.C. McCarthy

72nd ISMS 2017

GeC_2 – A vivid example

- **Since the late 1950s:**
  Discussion about the structure of GeC_2
- **Isovalent to SiC_2 (C_{2V} structure[1])**
- **Metal Dicarbides MC_2 are detected in space (e.g. C_2O[2] and SiC_2[3])**
- **Carbon-rich Group 14 materials: Attractive for nanoelectronics and material science**

[1] Michalopoulos et al., *J. Chem. Phys.* **80** (1984)
[2] Ohishi et al., *Astrophys. J.* 3**80** (1991)
[3] Thaddeus et al., *Astrophys. J.* **283** (1984)

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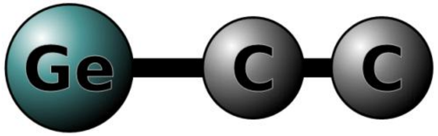
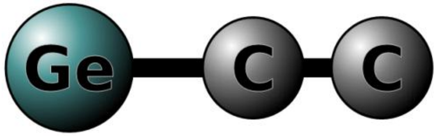
GeC_2 – Structural debate

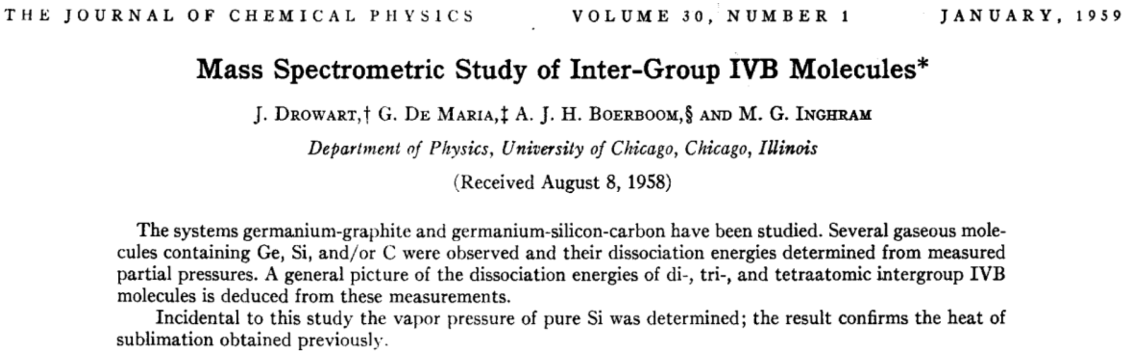
linear



GeC_2 – Structural debate

linear




THE JOURNAL OF CHEMICAL PHYSICS VOLUME 30, NUMBER 1 JANUARY, 1959

Mass Spectrometric Study of Inter-Group IVB Molecules*

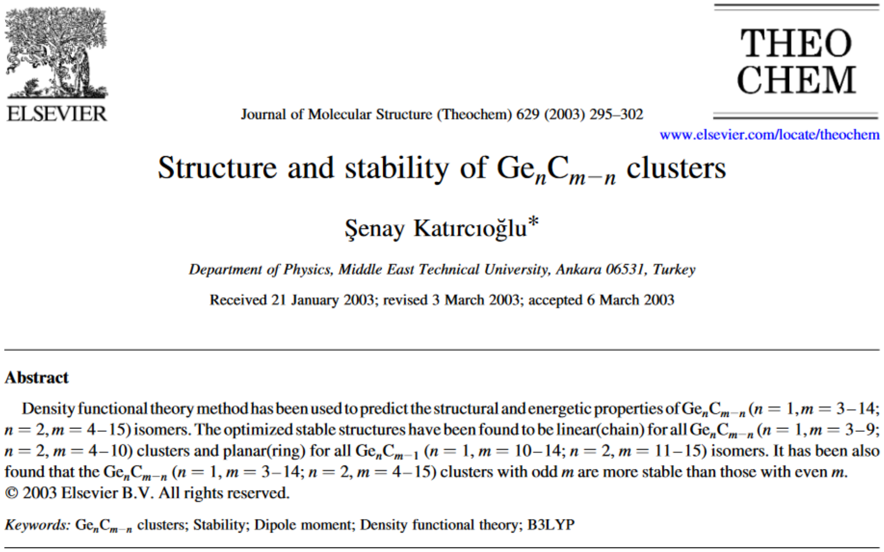
J. Drowart,† G. De Maria,‡ A. J. H. Boerboom,§ and M. G. Inghram

Department of Physics, University of Chicago, Chicago, Illinois

(Received August 8, 1958)

The systems germanium-graphite and germanium-silicon-carbon have been studied. Several gaseous molecules containing Ge, Si, and/or C were observed and their dissociation energies determined from measured partial pressures. A general picture of the dissociation energies of di-, tri-, and tetraatomic intergroup IVB molecules is deduced from these measurements.

Incidental to this study the vapor pressure of pure Si was determined; the result confirms the heat of sublimation obtained previously.


ELSEVIER

Journal of Molecular Structure (Theochem) 629 (2003) 295–302

THEO CHEM

www.elsevier.com/locate/theochem

Structure and stability of Ge_nC_{m-n} clusters

Şenay Katırcıoğlu*

Department of Physics, Middle East Technical University, Ankara 06531, Turkey

Received 21 January 2003; revised 3 March 2003; accepted 6 March 2003

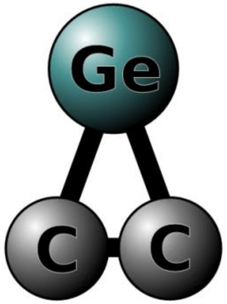
Abstract

Density functional theory method has been used to predict the structural and energetic properties of Ge_nC_{m-n} ($n = 1, m = 3-14$; $n = 2, m = 4-15$) isomers. The optimized stable structures have been found to be linear(chain) for all Ge_nC_{m-n} ($n = 1, m = 3-9$; $n = 2, m = 4-10$) clusters and planar(ring) for all Ge_nC_{m-1} ($n = 1, m = 10-14$; $n = 2, m = 11-15$) isomers. It has been also found that the Ge_nC_{m-n} ($n = 1, m = 3-14$; $n = 2, m = 4-15$) clusters with odd m are more stable than those with even m.

Keywords: Ge_nC_{m-n} clusters; Stability; Dipole moment; Density functional theory; B3LYP

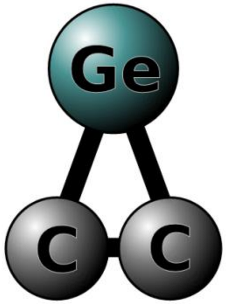
GeC_2 – Structural debate

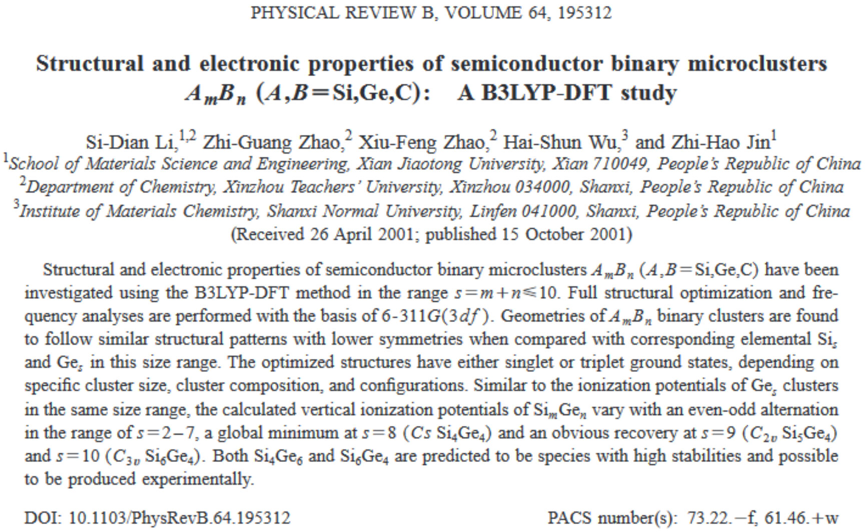
T-shaped



GeC_2 – Structural debate

T-shaped





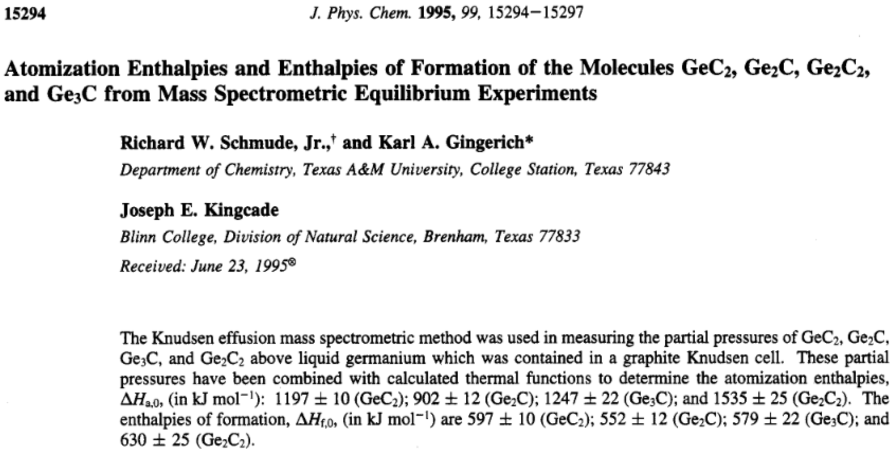
PHYSICAL REVIEW B, VOLUME 64, 195312

Structural and electronic properties of semiconductor binary microclusters A_mB_n ($A,B=$Si,Ge,C): A B3LYP-DFT study

Si-Dian Li,[1,2] Zhi-Guang Zhao,[2] Xiu-Feng Zhao,[2] Hai-Shun Wu,[3] and Zhi-Hao Jin[1]
[1]*School of Materials Science and Engineering, Xian Jiaotong University, Xian 710049, People's Republic of China*
[2]*Department of Chemistry, Xinzhou Teachers' University, Xinzhou 034000, Shanxi, People's Republic of China*
[3]*Institute of Materials Chemistry, Shanxi Normal University, Linfen 041000, Shanxi, People's Republic of China*
(Received 26 April 2001; published 15 October 2001)

Structural and electronic properties of semiconductor binary microclusters A_mB_n ($A,B=$Si,Ge,C) have been investigated using the B3LYP-DFT method in the range $s=m+n\leqslant 10$. Full structural optimization and frequency analyses are performed with the basis of 6-311$G(3df)$. Geometries of A_mB_n binary clusters are found to follow similar structural patterns with lower symmetries when compared with corresponding elemental Si_s and Ge_s in this size range. The optimized structures have either singlet or triplet ground states, depending on specific cluster size, cluster composition, and configurations. Similar to the ionization potentials of Ge_s clusters in the same size range, the calculated vertical ionization potentials of Si_mGe_n vary with an even-odd alternation in the range of $s=2-7$, a global minimum at $s=8$ (Cs Si_4Ge_4) and an obvious recovery at $s=9$ (C_{2v} Si_5Ge_4) and $s=10$ (C_{3v} Si_6Ge_4). Both Si_4Ge_6 and Si_6Ge_4 are predicted to be species with high stabilities and possible to be produced experimentally.

DOI: 10.1103/PhysRevB.64.195312 PACS number(s): 73.22.−f, 61.46.+w



15294 *J. Phys. Chem.* **1995,** *99,* 15294−15297

Atomization Enthalpies and Enthalpies of Formation of the Molecules GeC_2, Ge_2C, Ge_2C_2, and Ge_3C from Mass Spectrometric Equilibrium Experiments

Richard W. Schmude, Jr.,† and Karl A. Gingerich*
Department of Chemistry, Texas A&M University, College Station, Texas 77843

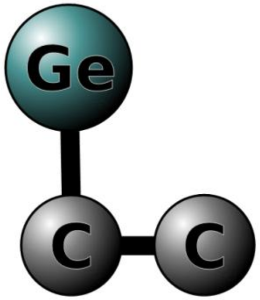
Joseph E. Kingcade
Blinn College, Division of Natural Science, Brenham, Texas 77833

Received: June 23, 1995®

The Knudsen effusion mass spectrometric method was used in measuring the partial pressures of GeC_2, Ge_2C, Ge_3C, and Ge_2C_2 above liquid germanium which was contained in a graphite Knudsen cell. These partial pressures have been combined with calculated thermal functions to determine the atomization enthalpies, $\Delta H_{a,0}$, (in kJ mol^{-1}): 1197 ± 10 (GeC_2); 902 ± 12 (Ge_2C); 1247 ± 22 (Ge_3C); and 1535 ± 25 (Ge_2C_2). The enthalpies of formation, $\Delta H_{f,0}$, (in kJ mol^{-1}) are 597 ± 10 (GeC_2); 552 ± 12 (Ge_2C); 579 ± 22 (Ge_3C); and 630 ± 25 (Ge_2C_2).

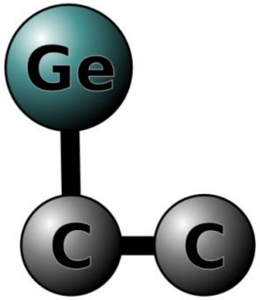
GeC_2 – Structural debate

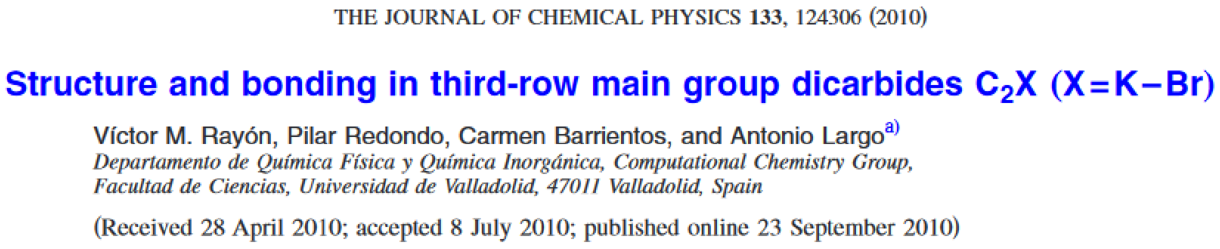
L-shaped



GeC_2 – Structural debate

L-shaped

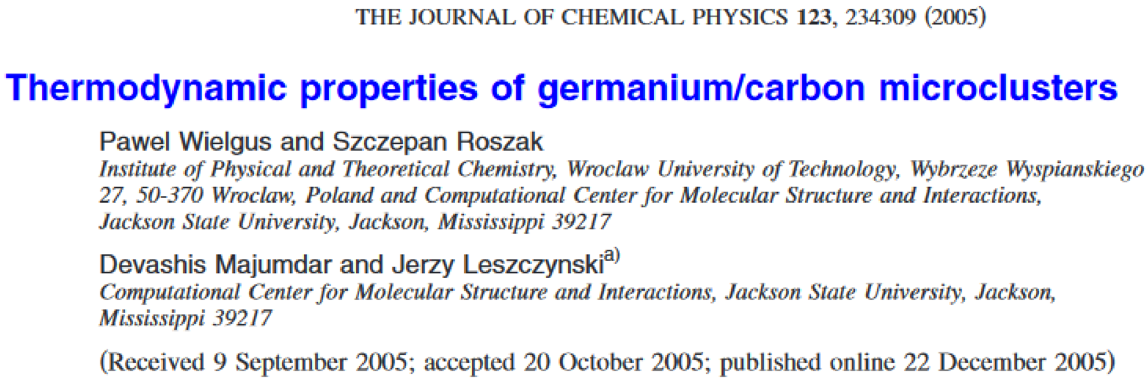



THE JOURNAL OF CHEMICAL PHYSICS **133**, 124306 (2010)

Structure and bonding in third-row main group dicarbides C_2X (X=K–Br)

Víctor M. Rayón, Pilar Redondo, Carmen Barrientos, and Antonio Largo[a)]
Departamento de Química Física y Química Inorgánica, Computational Chemistry Group, Facultad de Ciencias, Universidad de Valladolid, 47011 Valladolid, Spain

(Received 28 April 2010; accepted 8 July 2010; published online 23 September 2010)

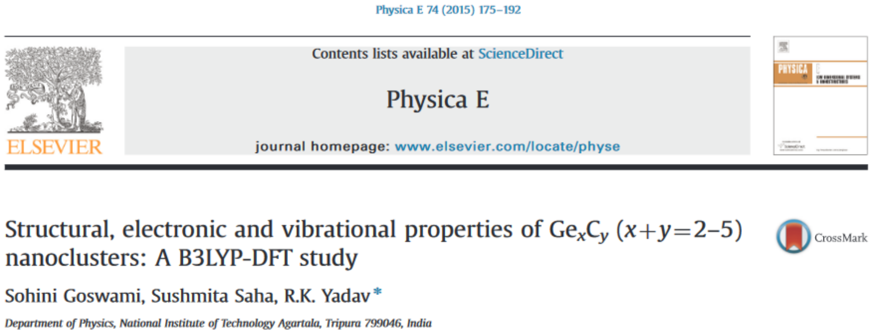

THE JOURNAL OF CHEMICAL PHYSICS **123**, 234309 (2005)

Thermodynamic properties of germanium/carbon microclusters

Pawel Wielgus and Szczepan Roszak
Institute of Physical and Theoretical Chemistry, Wroclaw University of Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland and Computational Center for Molecular Structure and Interactions, Jackson State University, Jackson, Mississippi 39217

Devashis Majumdar and Jerzy Leszczynski[a)]
Computational Center for Molecular Structure and Interactions, Jackson State University, Jackson, Mississippi 39217

(Received 9 September 2005; accepted 20 October 2005; published online 22 December 2005)


Physica E 74 (2015) 175–192

Contents lists available at ScienceDirect

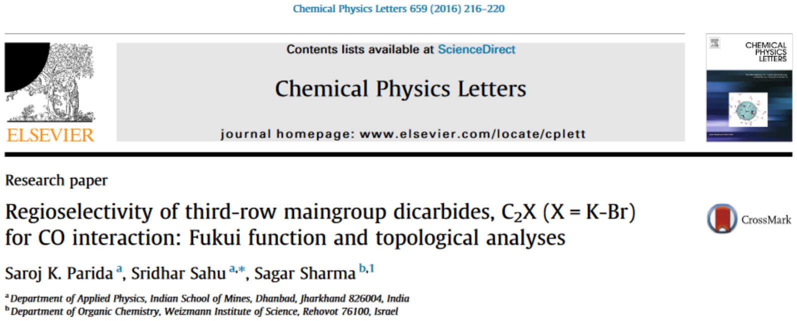
Physica E

journal homepage: www.elsevier.com/locate/physe

Structural, electronic and vibrational properties of Ge_xC_y $(x+y=2–5)$ nanoclusters: A B3LYP-DFT study

Sohini Goswami, Sushmita Saha, R.K. Yadav*

Department of Physics, National Institute of Technology Agartala, Tripura 799046, India


Chemical Physics Letters 659 (2016) 216–220

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

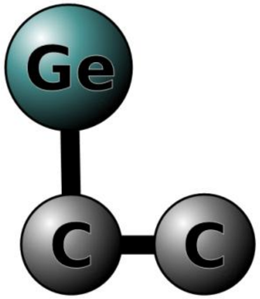
Regioselectivity of third-row maingroup dicarbides, C_2X (X = K-Br) for CO interaction: Fukui function and topological analyses

Saroj K. Parida[a], Sridhar Sahu[a,*], Sagar Sharma[b,1]

[a] *Department of Applied Physics, Indian School of Mines, Dhanbad, Jharkhand 826004, India*
[b] *Department of Organic Chemistry, Weizmann Institute of Science, Rehovot 76100, Israel*

JOURNAL OF CHEMICAL PHYSICS VOLUME 117, NUMBER 22 8 DECEMBER 2002

An L-shaped equilibrium geometry for germanium dicarbide (GeC_2)? Interesting effects of zero-point vibration, scalar relativity, and core–valence correlation

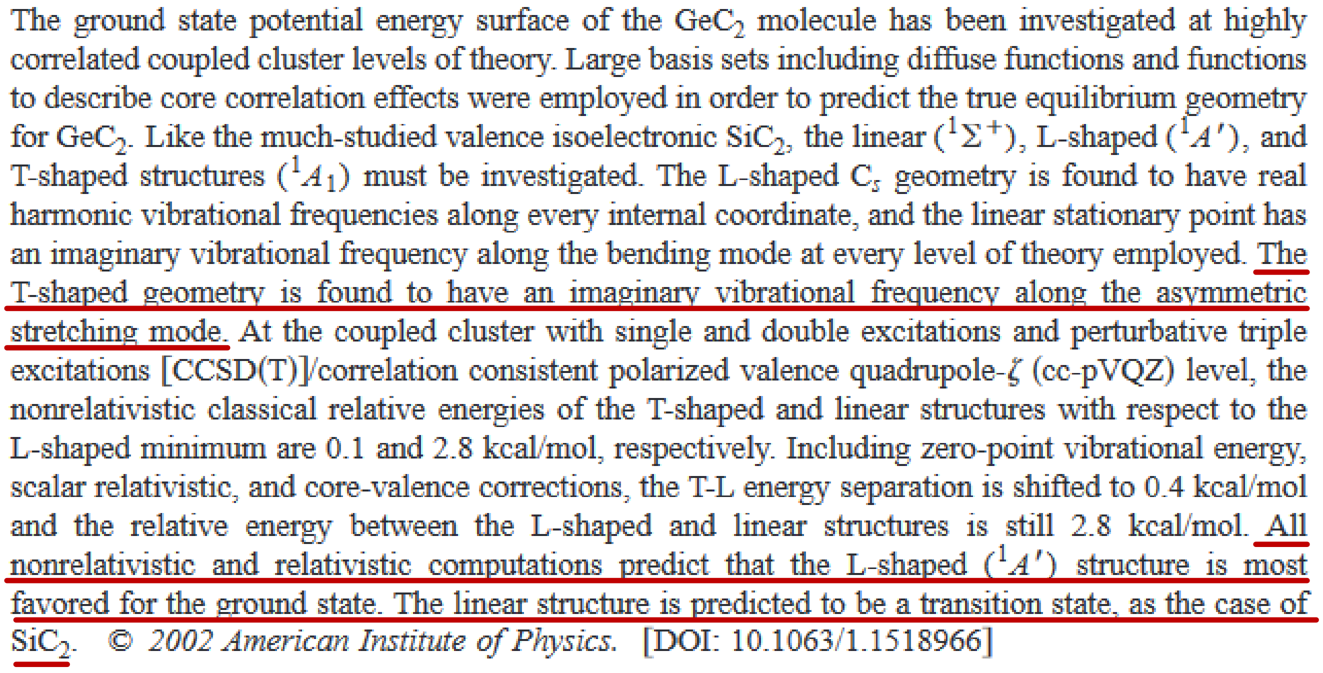


Levent Sari
Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602-2525

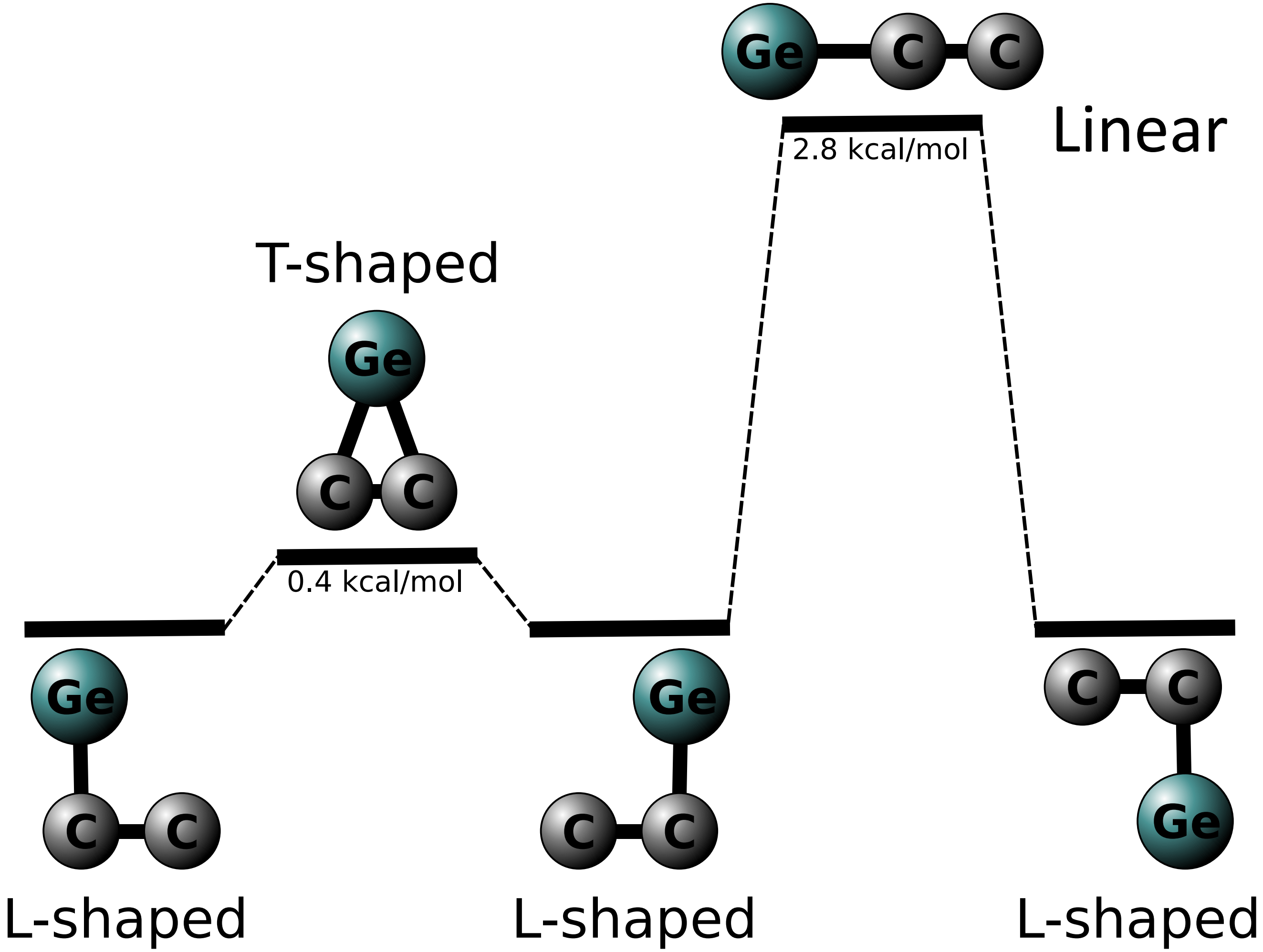
Kirk A. Peterson
Department of Chemistry, Washington State University, Richland, Washington 99352

Yukio Yamaguchi and Henry F. Schaefer III[a)]
Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602-2525

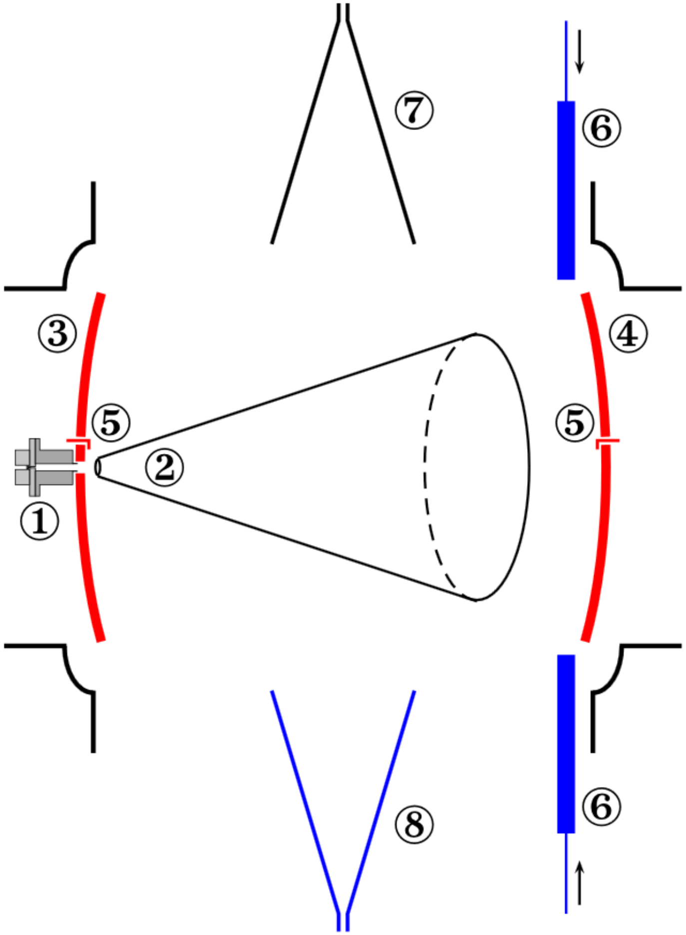
(Received 11 July 2002; accepted 12 September 2002)


The ground state potential energy surface of the GeC_2 molecule has been investigated at highly correlated coupled cluster levels of theory. Large basis sets including diffuse functions and functions to describe core correlation effects were employed in order to predict the true equilibrium geometry for GeC_2. Like the much-studied valence isoelectronic SiC_2, the linear ($^1\Sigma^+$), L-shaped ($^1A'$), and T-shaped structures ($^1A_1$) must be investigated. The L-shaped C_s geometry is found to have real harmonic vibrational frequencies along every internal coordinate, and the linear stationary point has an imaginary vibrational frequency along the bending mode at every level of theory employed. The T-shaped geometry is found to have an imaginary vibrational frequency along the asymmetric stretching mode. At the coupled cluster with single and double excitations and perturbative triple excitations [CCSD(T)]/correlation consistent polarized valence quadrupole-ζ (cc-pVQZ) level, the nonrelativistic classical relative energies of the T-shaped and linear structures with respect to the L-shaped minimum are 0.1 and 2.8 kcal/mol, respectively. Including zero-point vibrational energy, scalar relativistic, and core-valence corrections, the T-L energy separation is shifted to 0.4 kcal/mol and the relative energy between the L-shaped and linear structures is still 2.8 kcal/mol. All nonrelativistic and relativistic computations predict that the L-shaped ($^1A'$) structure is most favored for the ground state. The linear structure is predicted to be a transition state, as the case of SiC_2. [DOI: 10.1063/1.1518966]

GeC_2 – Structural debate



Chirped-Pulse Spectrometer



① Pulsed nozzle

② Supersonic expansion

③ Fixed mirror

④ Movable mirror

⑤ Microwave emitter/receiver

⑥ Micrwave absorbers

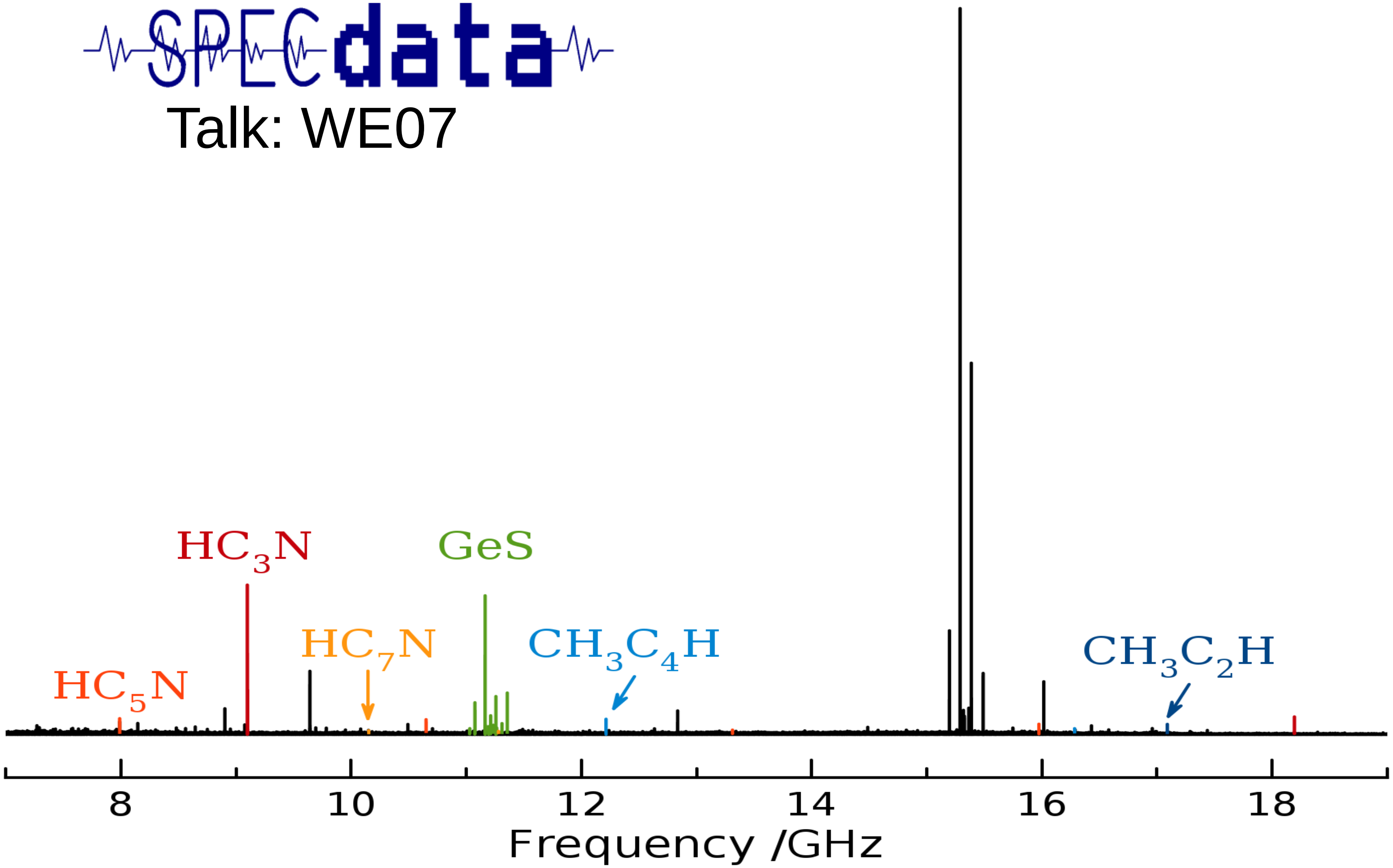
⑦ Horn antenna

⑧ Horn antenna

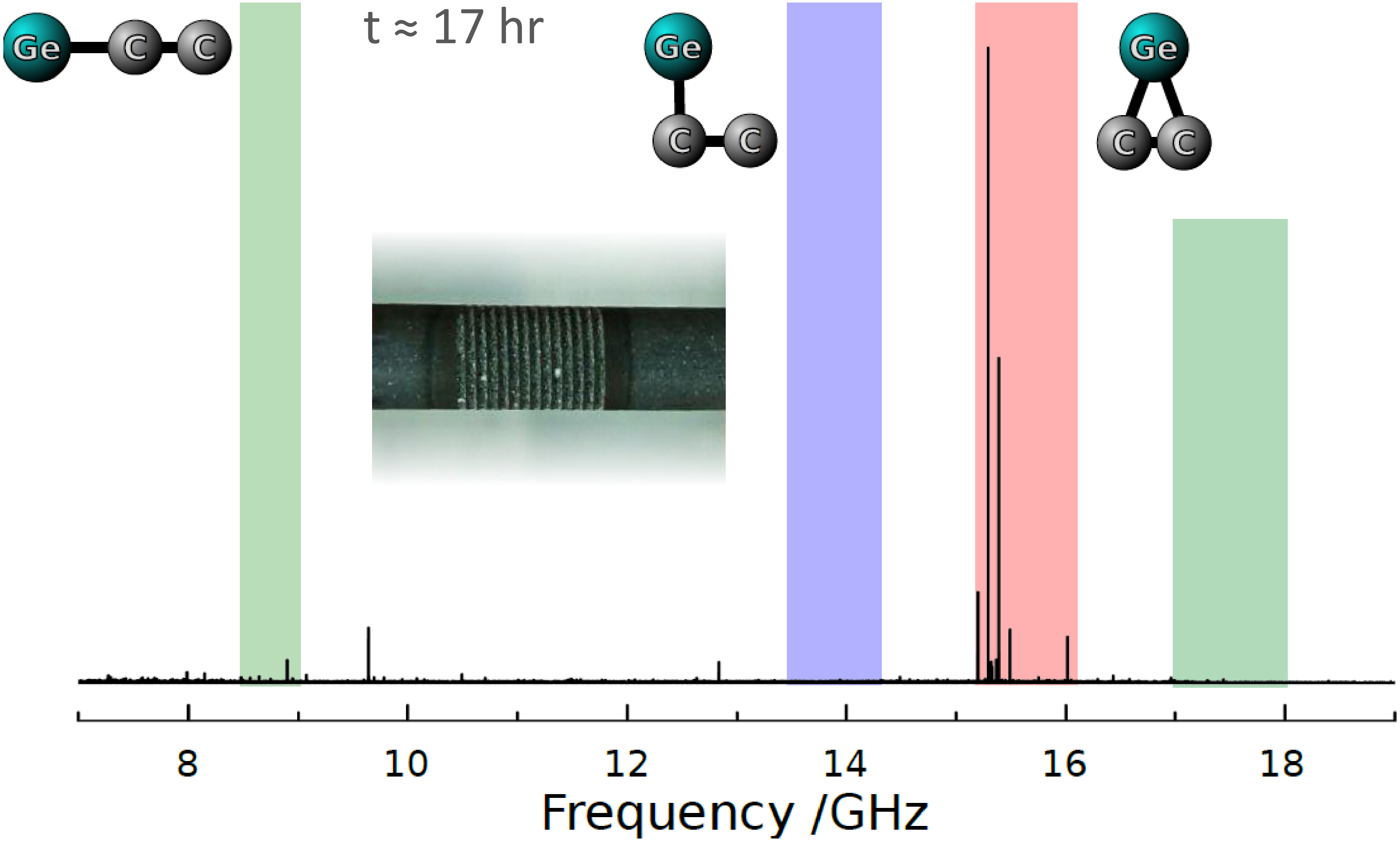
Crabtree et al, *J. Chem. Phys.* **144** *(2016)*

Broadband measurement

Talk: WE07

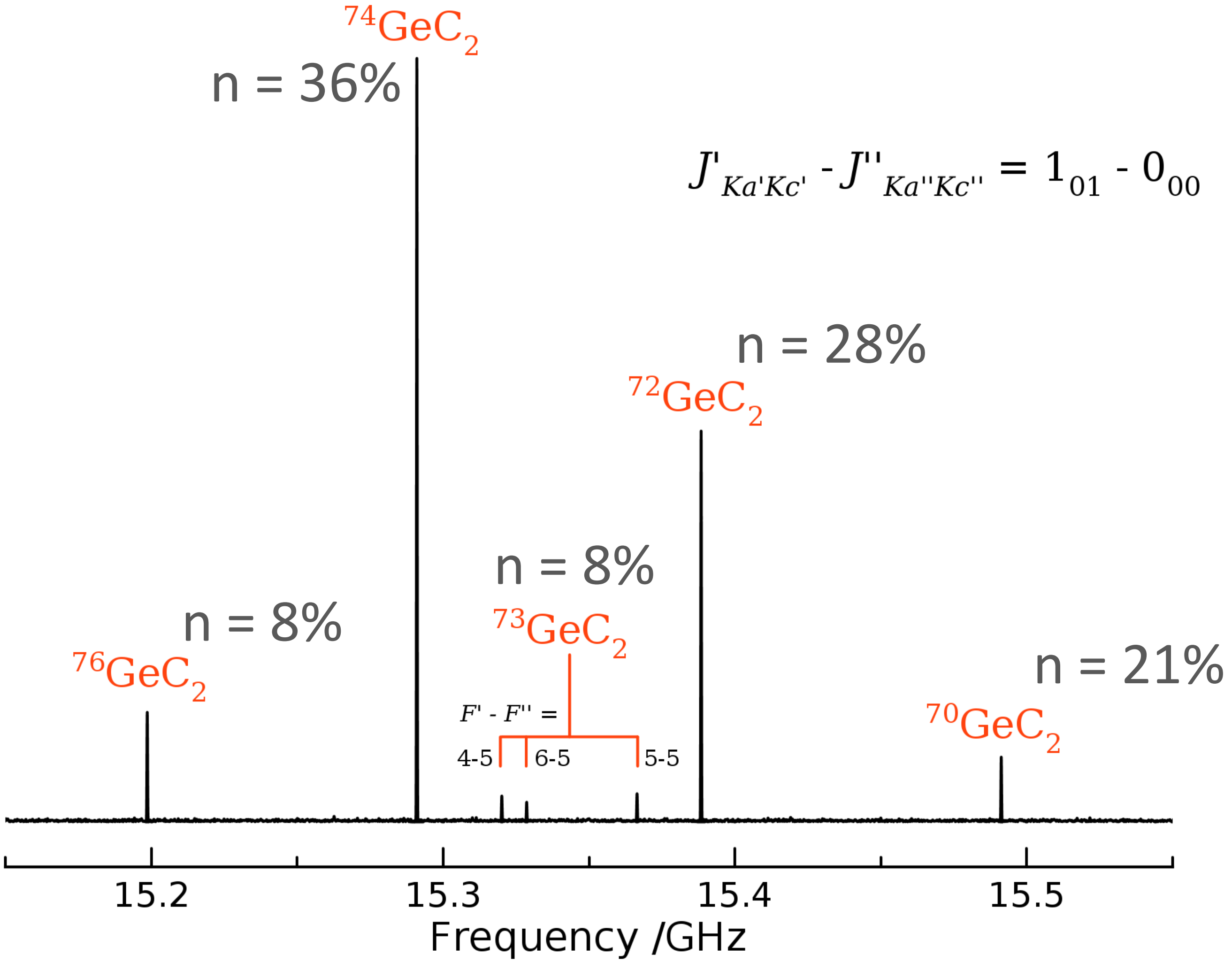


Broadband measurement

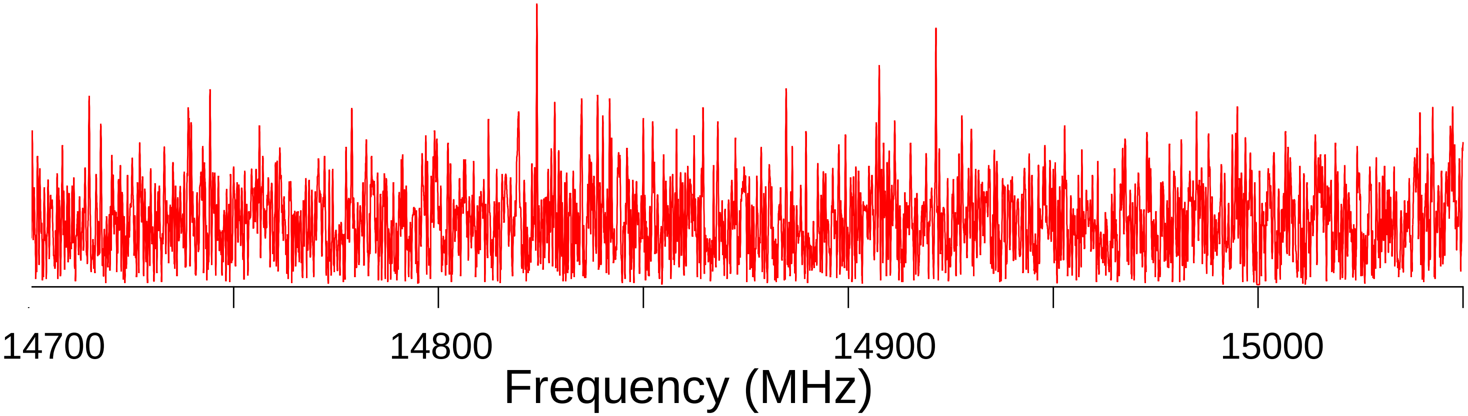


t ≈ 17 hr

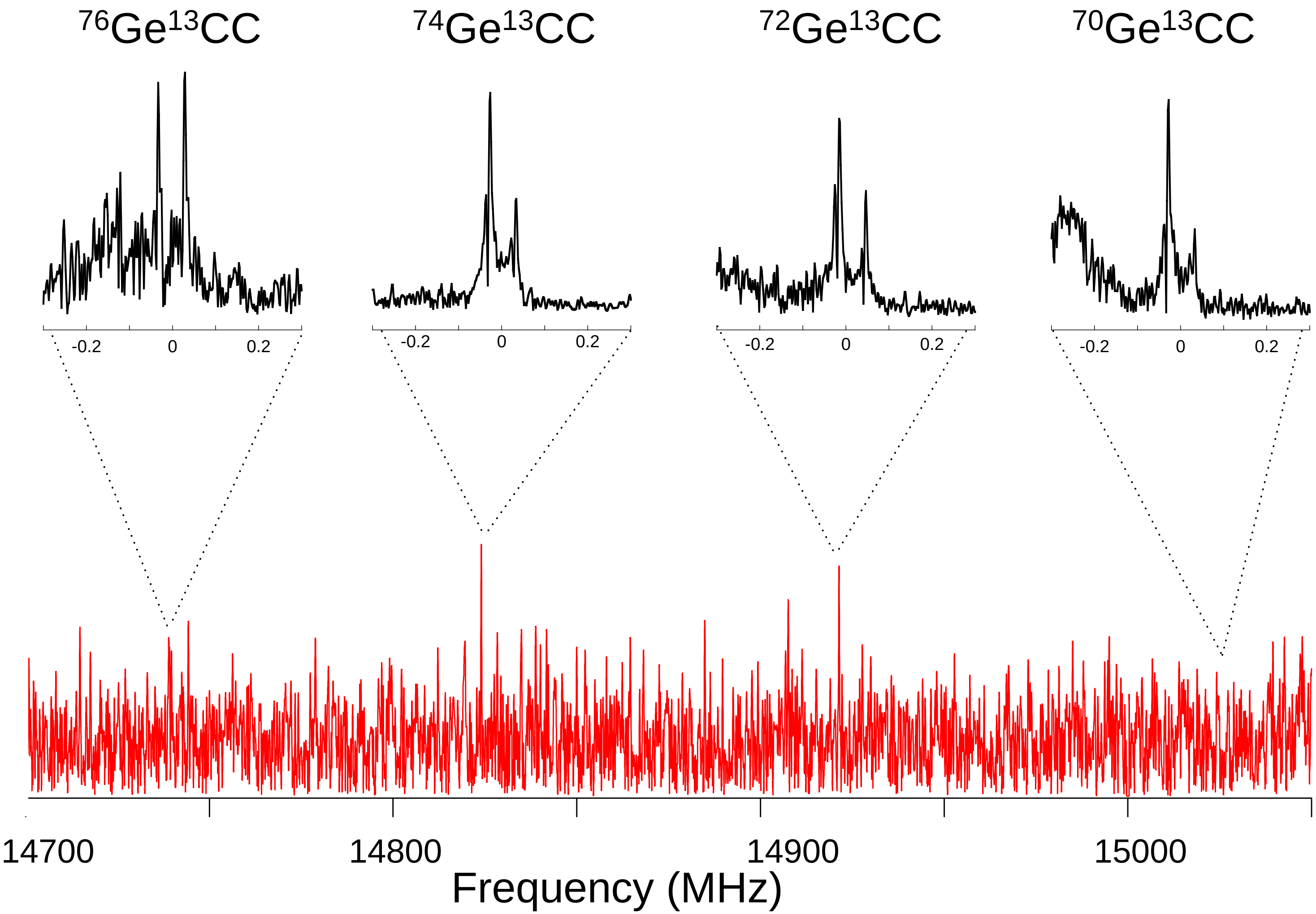
Zoom


$^{74}GeC_2$
n = 36%
$J'_{Ka'Kc'} - J''_{Ka''Kc''} = 1_{01} - 0_{00}$
n = 28%
$^{72}GeC_2$
n = 8%
$^{73}GeC_2$
n = 8%
$^{76}GeC_2$
$F' - F'' =$
4-5
6-5
5-5
n = 21%
$^{70}GeC_2$
15.2
15.3
15.4
15.5
Frequency /GHz

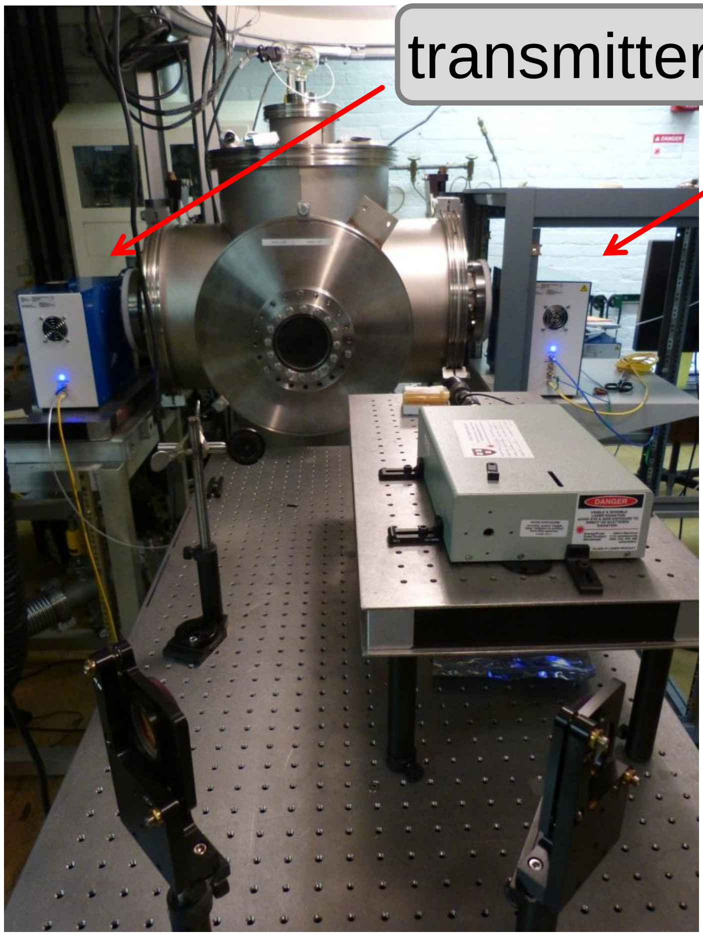
Wealth of Isotopologues



Wealth of Isotopologues



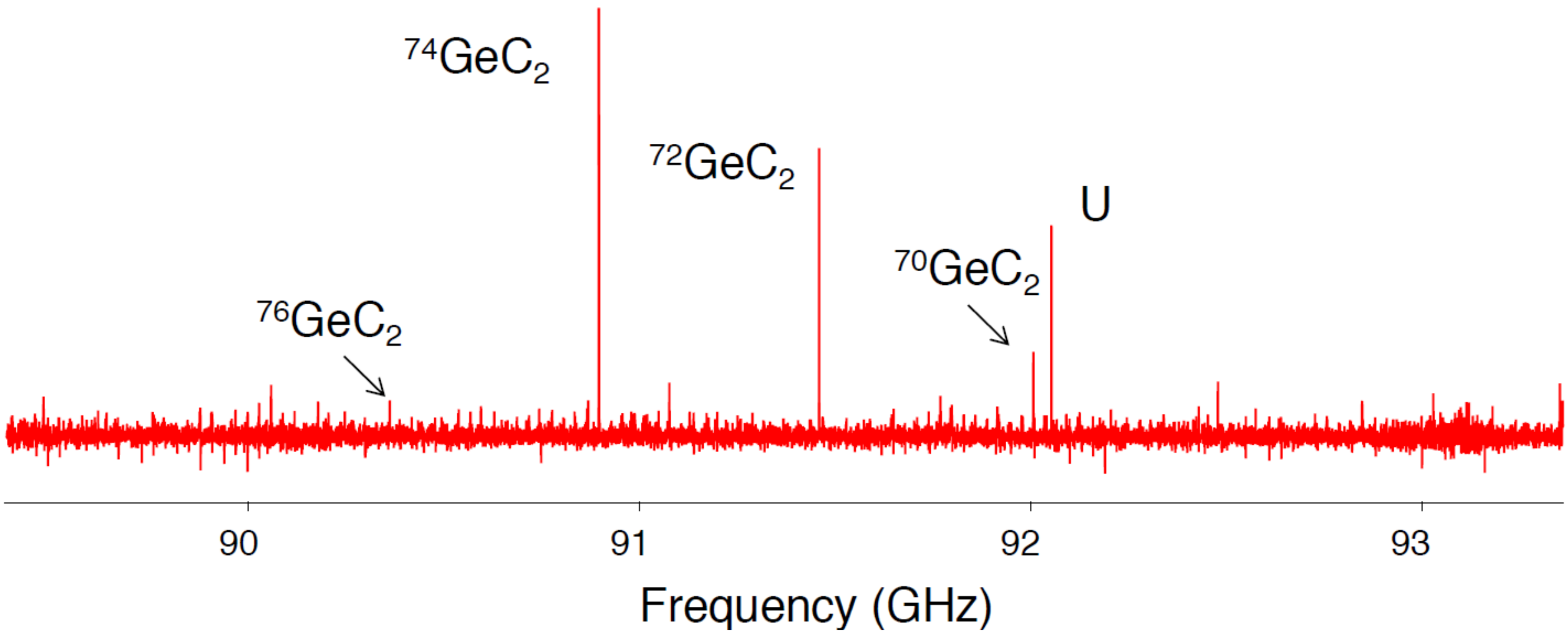
W-Band spectrometer



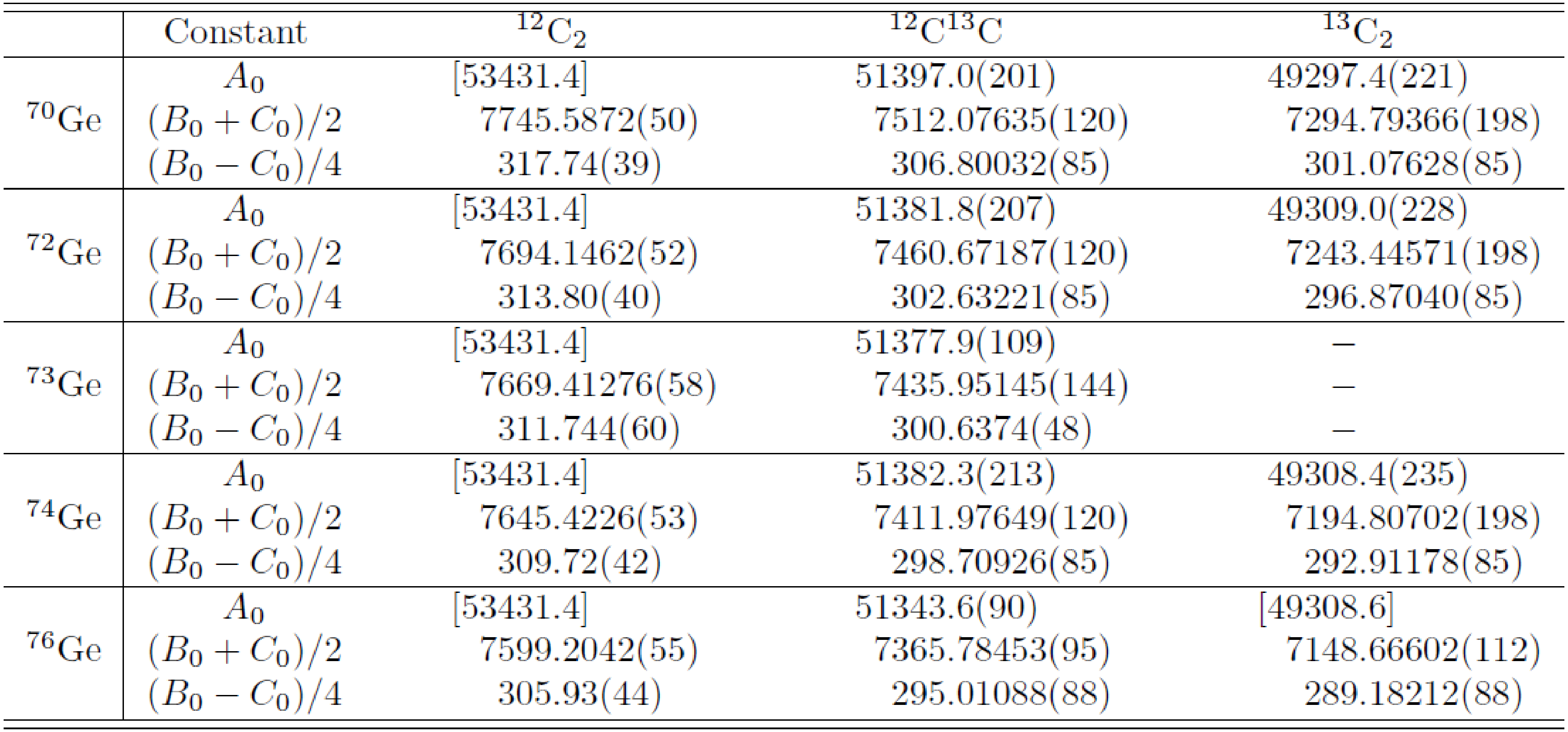
- Commercial chirped spectrometer
- 75-115 GHz

BrightSpec

W-Band measurement



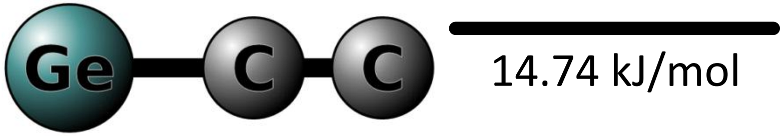
Rotational parameters

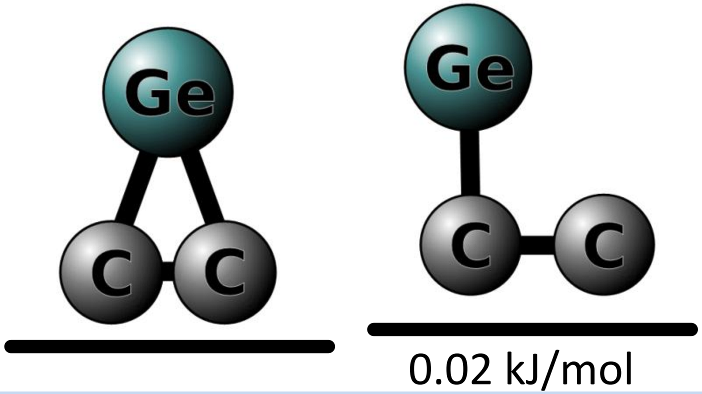


	Constant	$^{12}C_2$	$^{12}C^{13}C$	$^{13}C_2$
^{70}Ge	A_0	[53431.4]	51397.0(201)	49297.4(221)
	$(B_0 + C_0)/2$	7745.5872(50)	7512.07635(120)	7294.79366(198)
	$(B_0 - C_0)/4$	317.74(39)	306.80032(85)	301.07628(85)
^{72}Ge	A_0	[53431.4]	51381.8(207)	49309.0(228)
	$(B_0 + C_0)/2$	7694.1462(52)	7460.67187(120)	7243.44571(198)
	$(B_0 - C_0)/4$	313.80(40)	302.63221(85)	296.87040(85)
^{73}Ge	A_0	[53431.4]	51377.9(109)	–
	$(B_0 + C_0)/2$	7669.41276(58)	7435.95145(144)	–
	$(B_0 - C_0)/4$	311.744(60)	300.6374(48)	–
^{74}Ge	A_0	[53431.4]	51382.3(213)	49308.4(235)
	$(B_0 + C_0)/2$	7645.4226(53)	7411.97649(120)	7194.80702(198)
	$(B_0 - C_0)/4$	309.72(42)	298.70926(85)	292.91178(85)
^{76}Ge	A_0	[53431.4]	51343.6(90)	[49308.6]
	$(B_0 + C_0)/2$	7599.2042(55)	7365.78453(95)	7148.66602(112)
	$(B_0 - C_0)/4$	305.93(44)	295.01088(88)	289.18212(88)

Structural parameters

CCSD(T)/cc-pwCVQZ - level





Structural parameters

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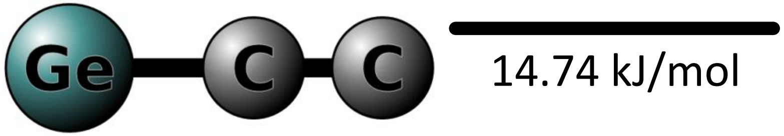
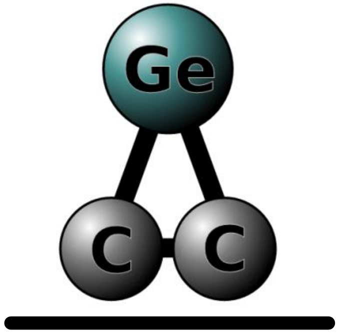
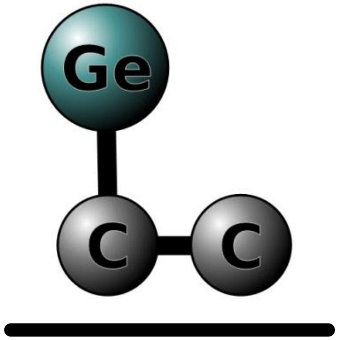


	Experimental	T-shaped	L-shaped	Linear
$r_{Ge\text{-}C}$ /Å	1.952(1)	1.9296	1.8184	1.7717
$r_{Ge\text{-}C}$ /Å	1.294	1.2750	1.2810	1.2836
Apex angle /°	38.7(2)	38.58	86.29	

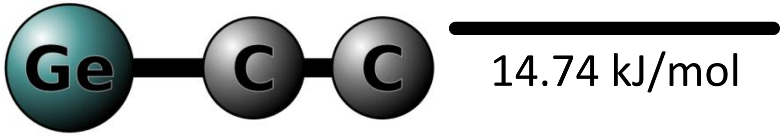




0.02 kJ/mol

Structural parameters

CCSD(T)/cc-pwCVQZ - level



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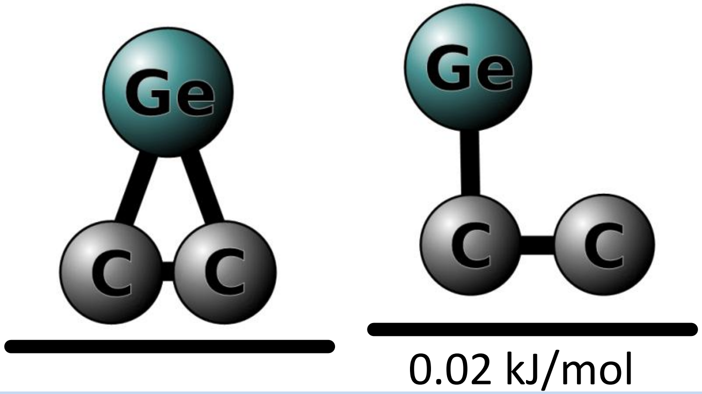

Acknowledgments

Thank you for your attention!

NSF

AST-1615847

BrightSpec

- Justin Neill and Matt Muckle

VE RI TAS

CfA

+ P. Antonucci

DFG Deutsche Forschungsgemeinschaft

ph1 Universität zu Köln

bcgs
Bonn-Cologne Graduate School of Physics and Astronomy

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