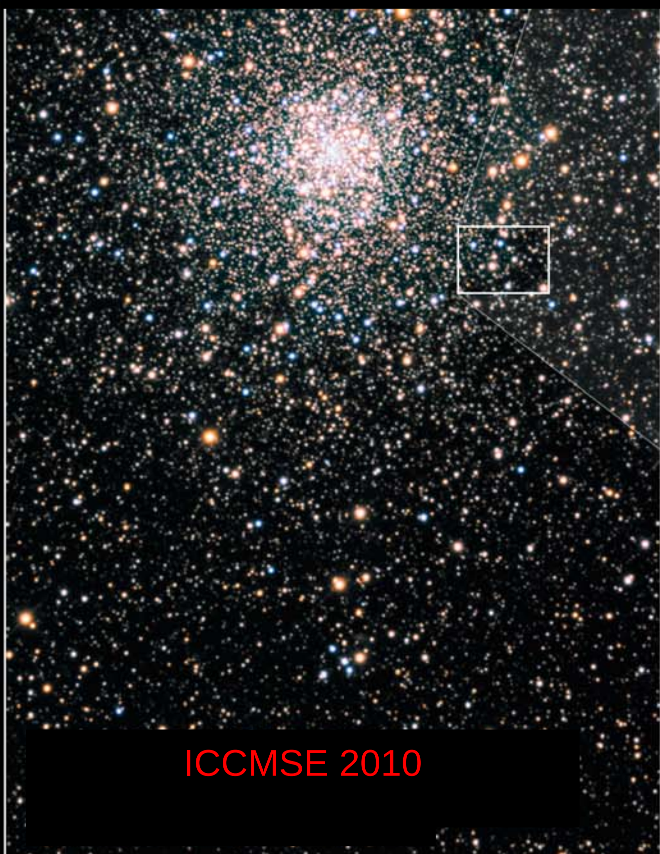
Absorption of Radiation due to Collisions of Hydrogen Molecules with Helium Atoms at High Temperatures

Xiaoping Li, Anirban Mandal, Evangelos Miliordos,
Katharine L. C. Hunt, Martin Abel and Lothar Frommhold



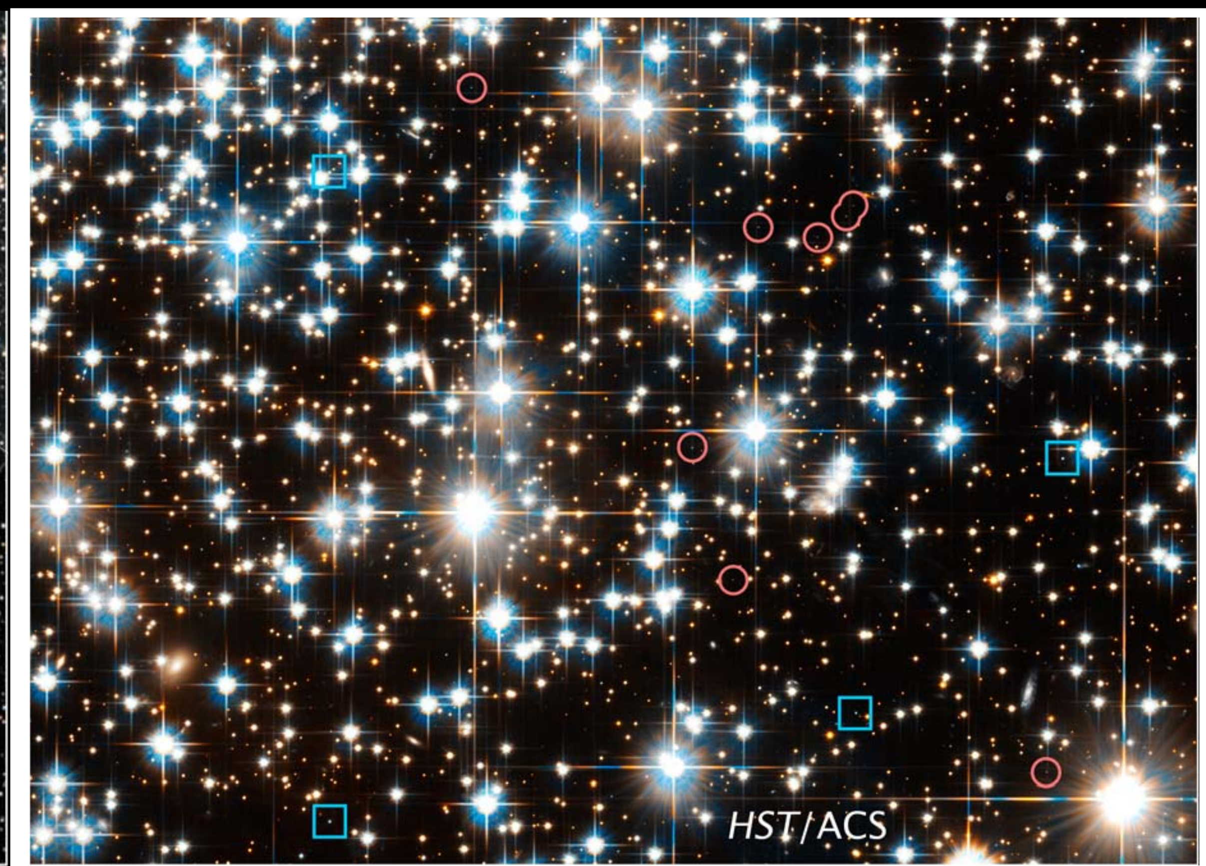
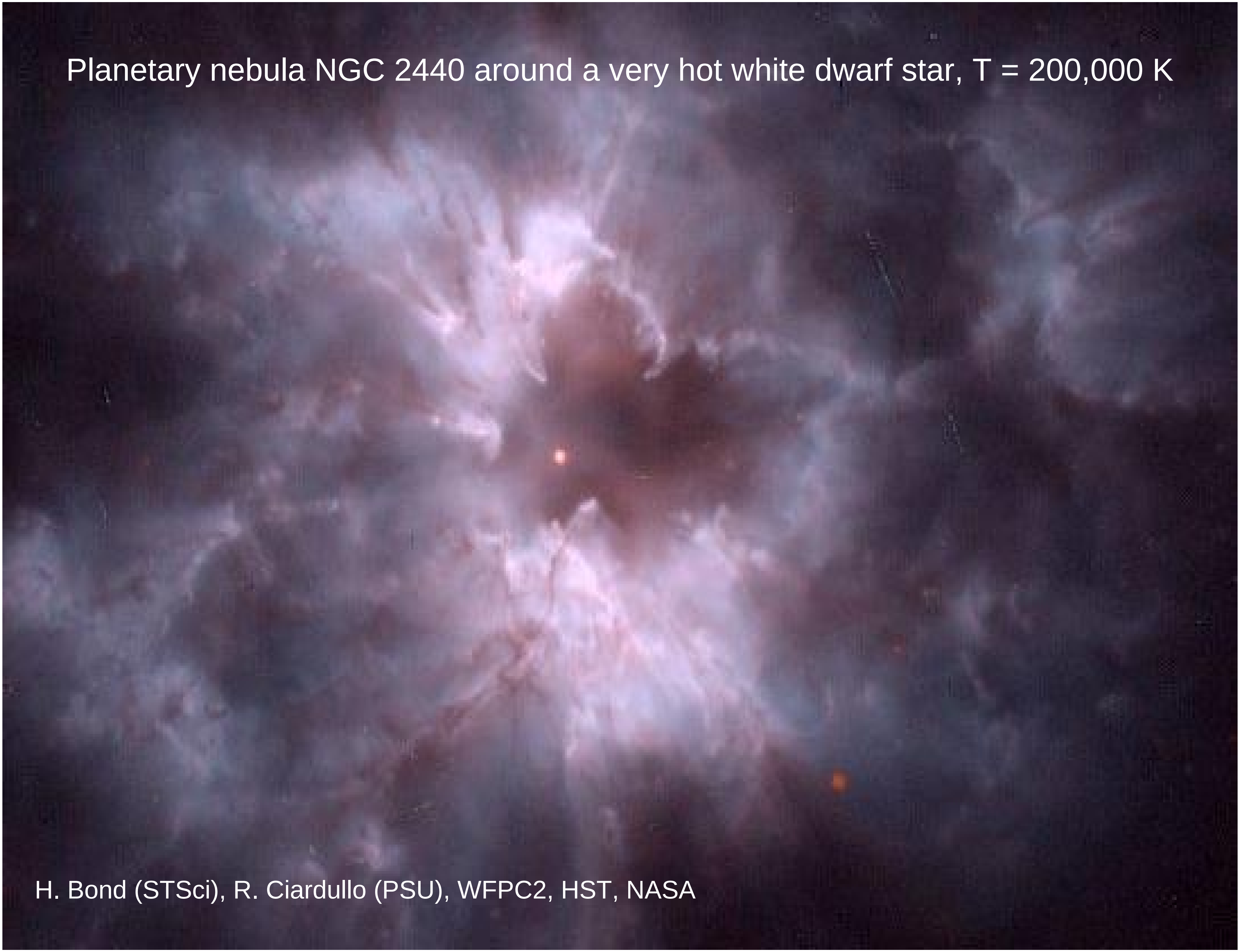
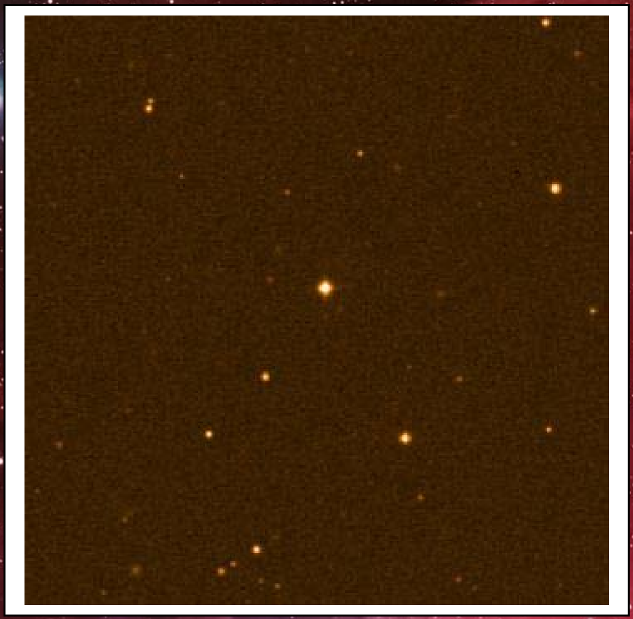


Photo credits: NASA, ESA, and H. Richer (Univeristy of British Columbia), HST ACS/WFC, D. Verschatse, Antilhue

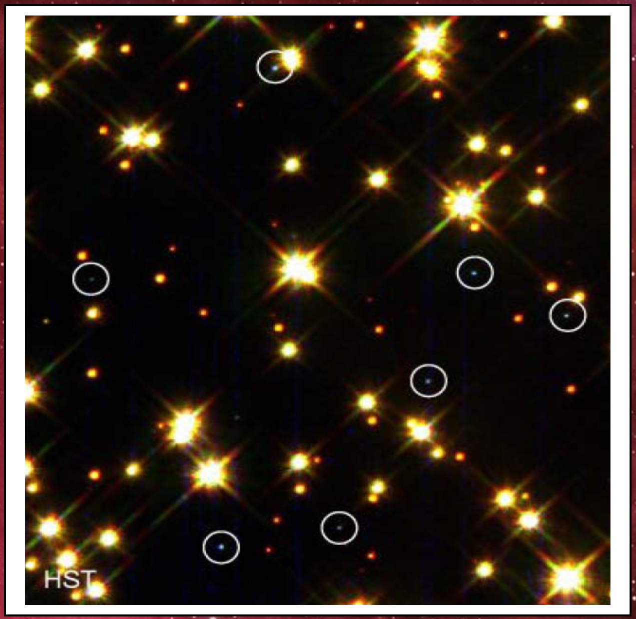

Planetary nebula NGC 2440 around a very hot white dwarf star, T = 200,000 K
H. Bond (STScI), R. Ciardullo (PSU), WFPC2, HST, NASA

Very Cool White Dwarf Stars



Van Maanen's Star
ESO Online Digitized Sky Survey

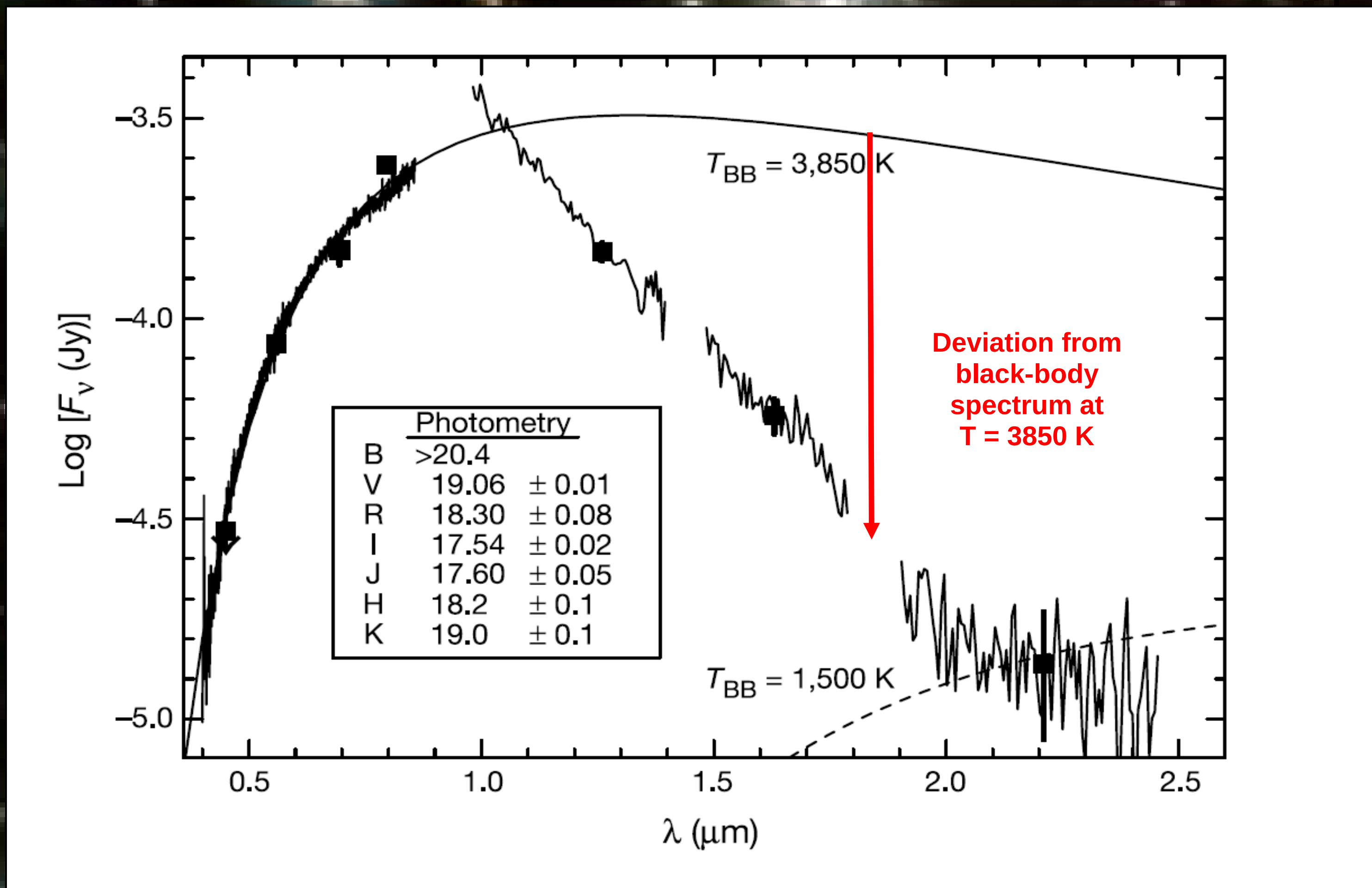
~10 billion years old
14.13 light years away
Mass = 0.7 * Sun
Luminosity = 0.000182 * Sun
Diameter = 0.013 * Sun
(in constellation Pisces)



White Dwarf Stars in Globular Cluster M4
NASA and H. Richer,
University of British Columbia

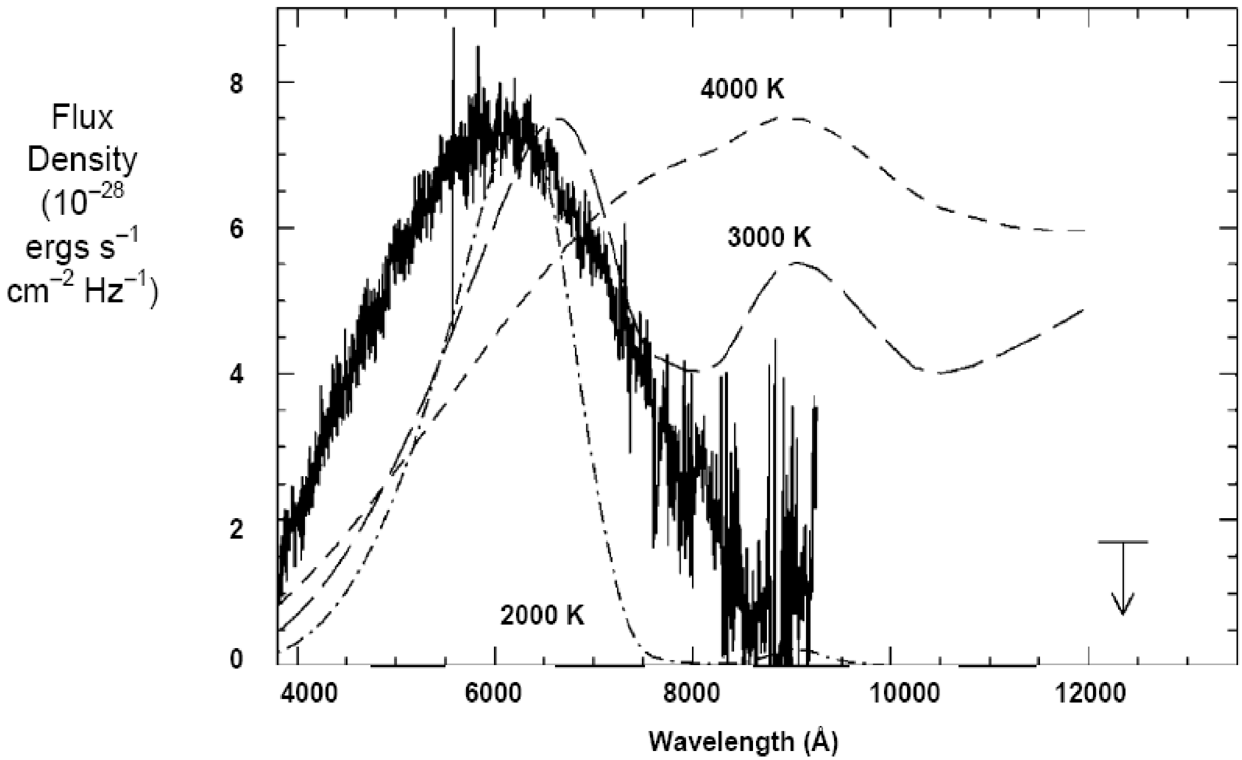
Luminosity: 100 Watt light bulb,
seen from 239,000 miles away
8 days exposure time over 67-day period
Hubble Space Telescope
5,600 light years away

Spectrum of the cool white dwarf WD0346+246



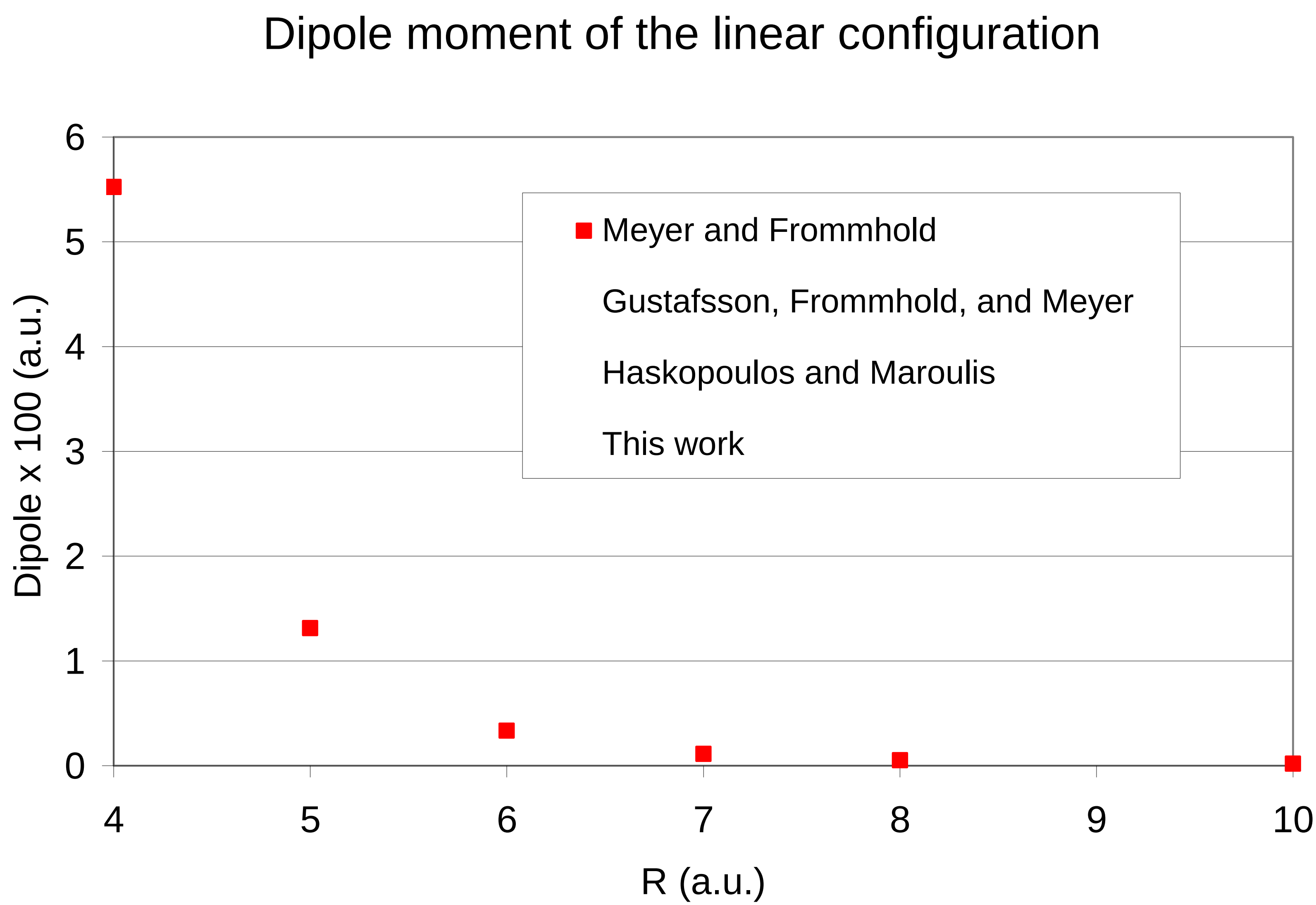
S. T. Hodgkin, B. R. Oppenheimer, N. C. Hambly, R. F. Jameson, S. J. Smartt, and I. A. Steele, *Nature*, **403**, 57-59 (2000).

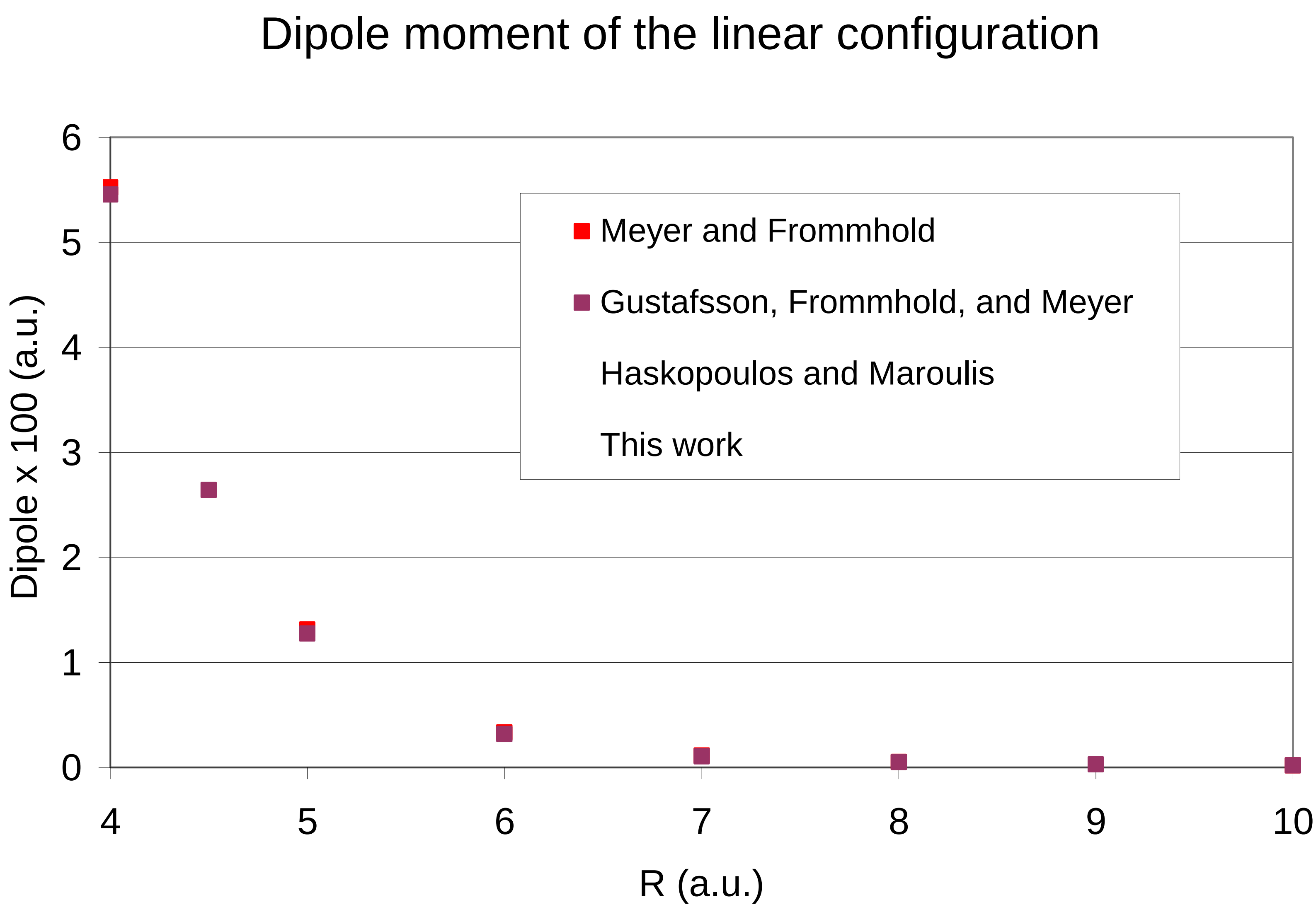
Preliminary Spectral Modeling of SDSS 1337+00

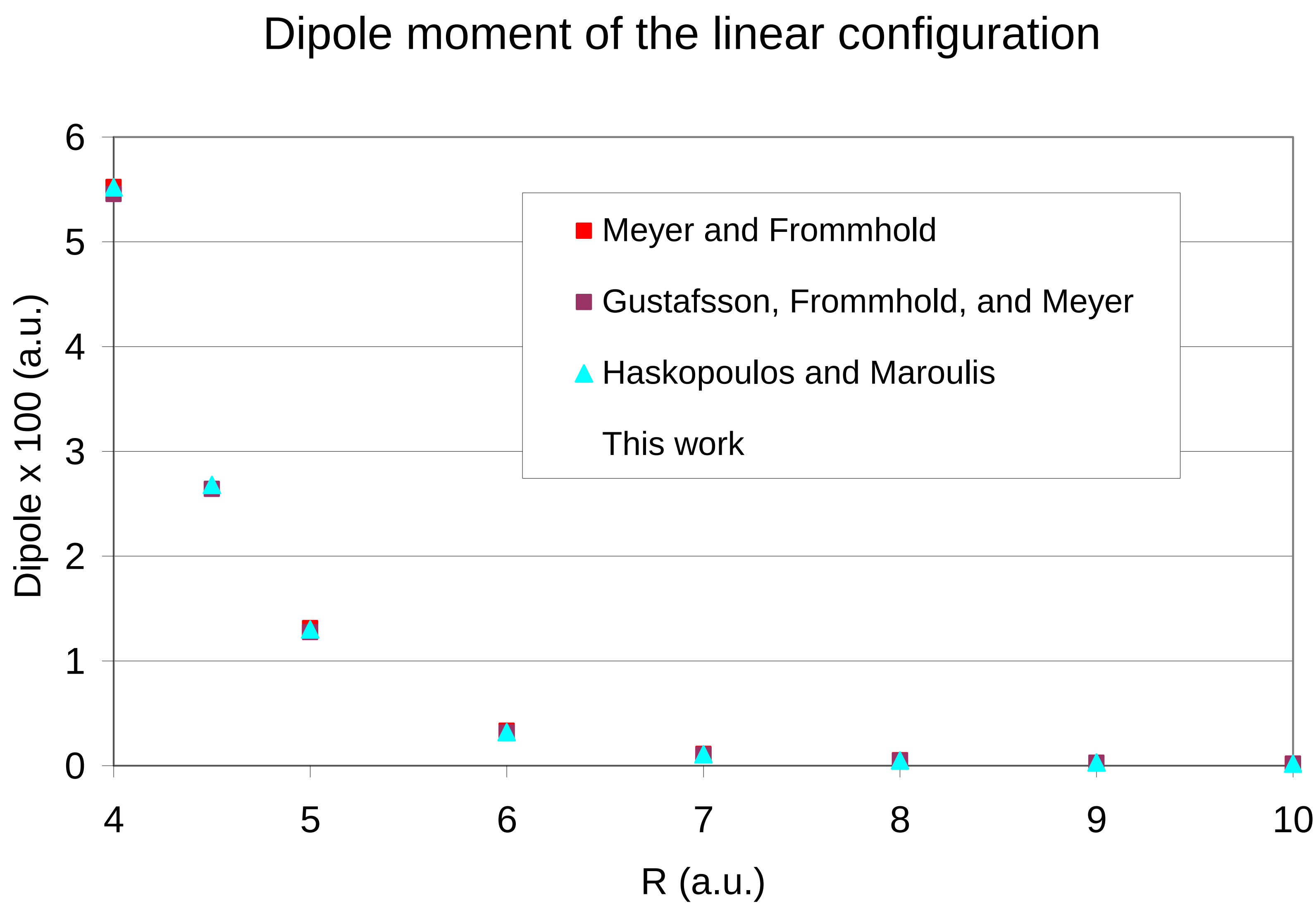


H. C. Harris, B. M. S. Hansen, J. Liebert, D. E. Vanden Berk, S. F. Anderson, G. R. Knapp, X. Fan, B. Margon, J. A. Munn, R. C. Nichol, J. R. Pier, D. P. Schneider, J. A. Smith, D. E. Winget, D. G. York, J. E. Anderson, Jr., J. Brinkmann, S. Burles, B. Chen, A. J. Connolly, I. Csabai, J. A. Frieman, J. E. Gunn, G. S. Hennessy, R. B. Hindsley, Ž. Ivezić, S. Kent, D. Q. Lamb, R. H. Lupton, H. J. Newberg, D. J. Schlegel, S. Smee, M. A. Strauss, A. R. Thakar, A. Uomoto, and B. Yanny, *Astrophys. J.* **549**: L109-113 (2001).

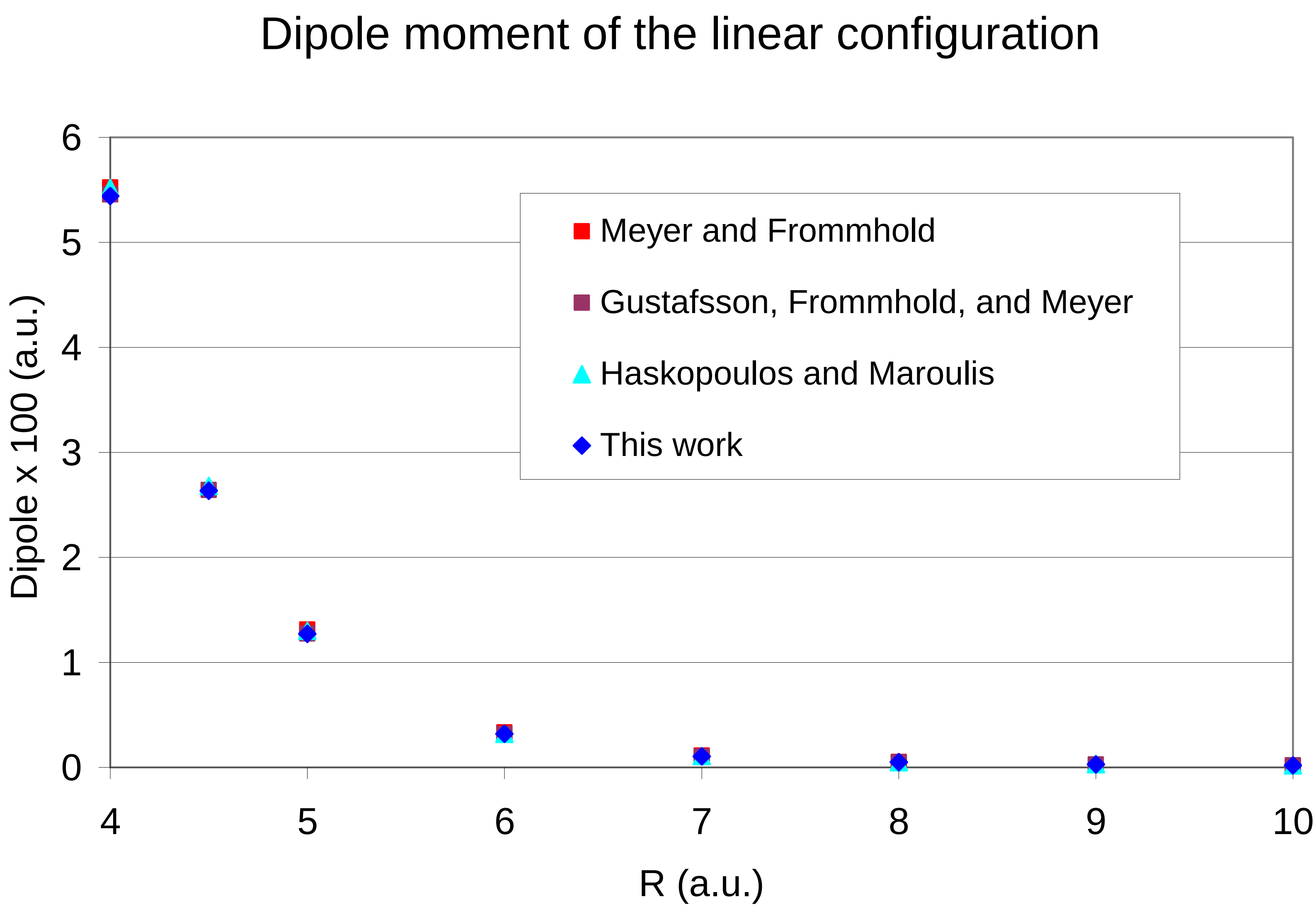
Comparison of *ab initio* calculations of the collision-induced dipole of $H_2 \cdots He$						
	Computational method	Basis sets	Intermolecular separations	Bond lengths	Relative orientations	Properties computed
Meyer and Frommhold (1986)	SCEP	H: [3s 1p] H2 center: (3s 2p 2d) He: [6s 3p1d]	7	3	3	μ
Gustafsson, Frommhold, and Meyer (2000)	MRCI	H: (9s 3p) H2 center: (2s 3p 3d 2f) He: (9s 4p 3d 2f)	10	5	4	μ
Haskopoulos and Maroulis (2010)	MP2, CCSD	H: [6s, 4p, 3d] He: [6s 4p 3d] H: [6s 4p 3d 1f] He: [6s 4p 3d 1f] H: (14s 9p 5d) He: (12s 9p 5d)	13	1	3	μ, $\Delta\alpha$, β
This work	CCSD(T)	H and He: aug-cc-pV5Z (spdfg) (9s 5p 4d 3f 2g)/ [6s 5p 4d 3f 2g] 240 functions	15	8	19	μ

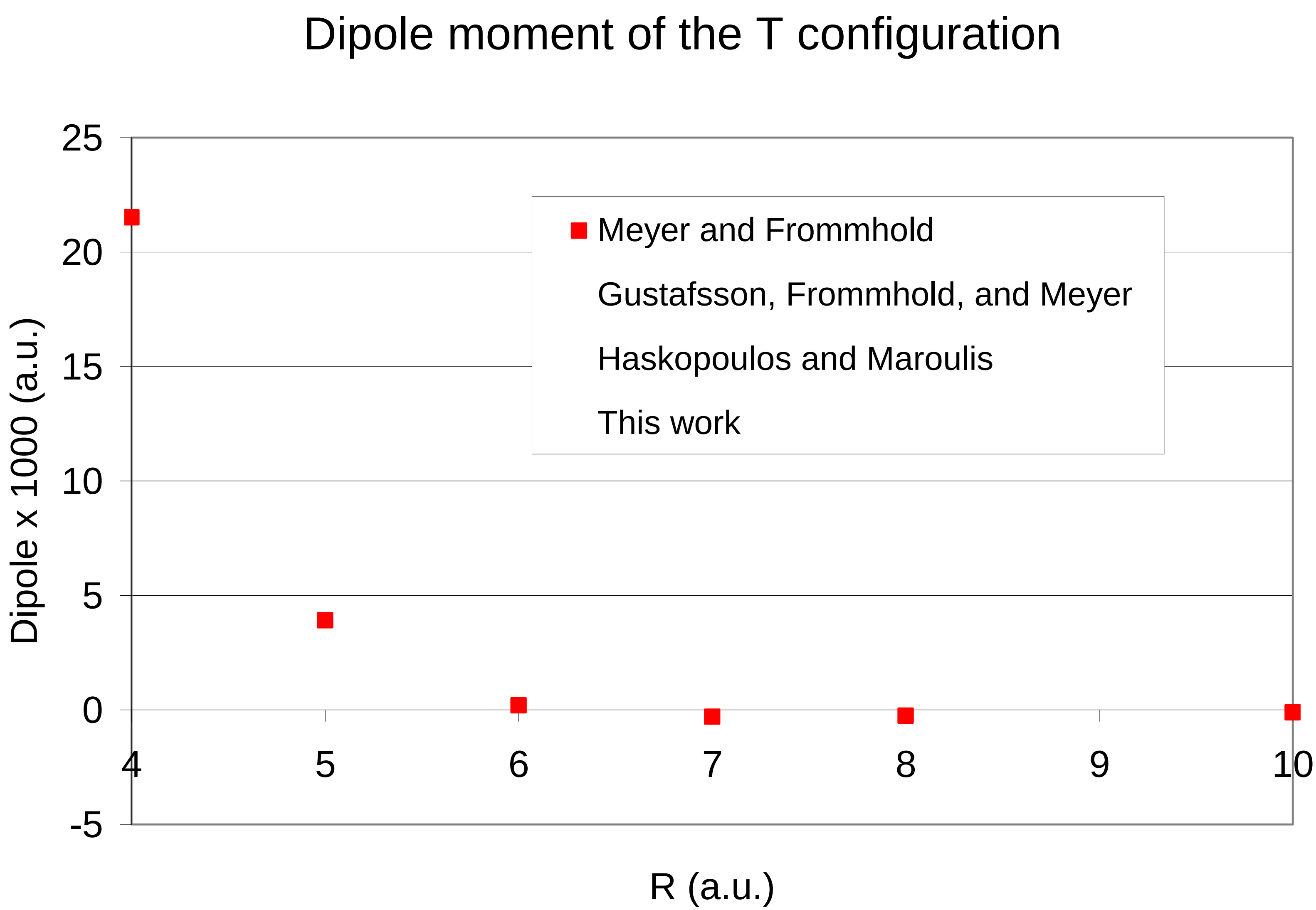

Dipole moment of the linear configuration
Meyer and Frommhold
Gustafsson, Frommhold, and Meyer
Haskopoulos and Maroulis
This work
Dipole x 100 (a.u.)
R (a.u.)
0
1
2
3
4
5
6
4
5
6
7
8
9
10


Dipole moment of the linear configuration
Dipole x 100 (a.u.)
R (a.u.)
0
1
2
3
4
5
6
4
5
6
7
8
9
10
Meyer and Frommhold
Gustafsson, Frommhold, and Meyer
Haskopoulos and Maroulis
This work

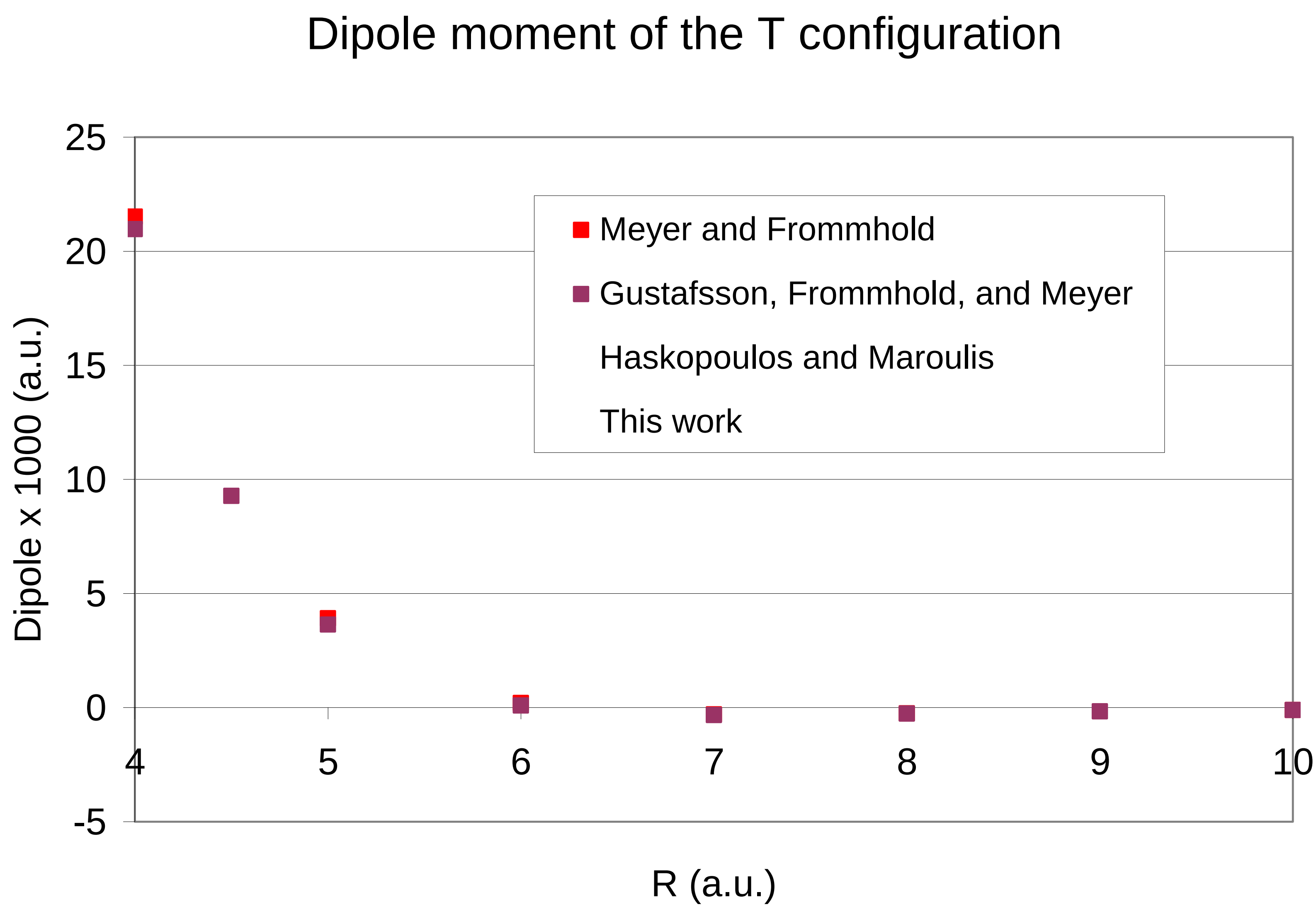


Dipole moment of the linear configuration
6
5
4
3
2
1
0
Dipole x 100 (a.u.)
4
5
6
7
8
9
10
R (a.u.)
Meyer and Frommhold
Gustafsson, Frommhold, and Meyer
Haskopoulos and Maroulis
This work

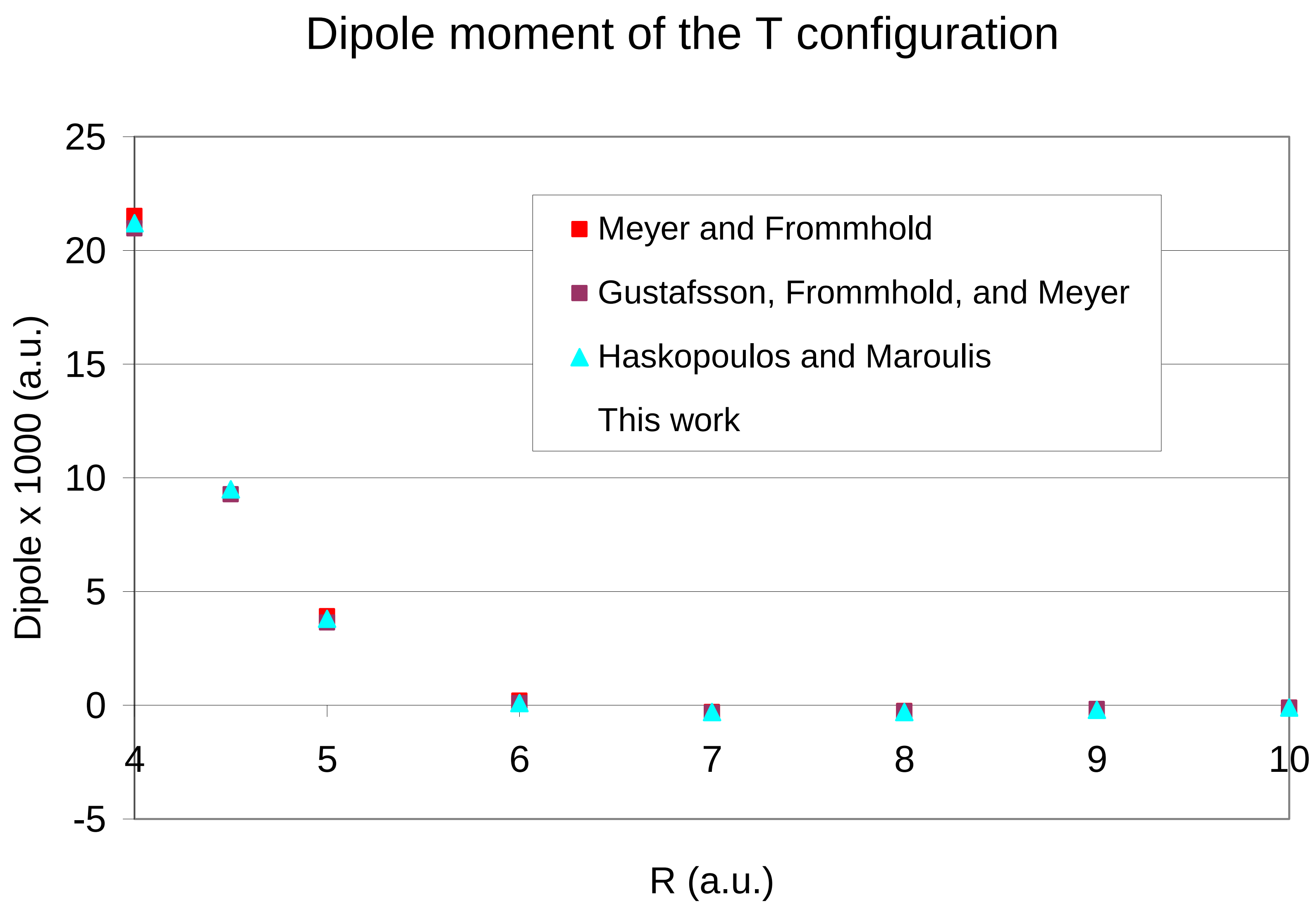

Dipole moment of the linear configuration
Meyer and Frommhold
Gustafsson, Frommhold, and Meyer
Haskopoulos and Maroulis
This work
Dipole x 100 (a.u.)
6
5
4
3
2
1
0
4
5
6
7
8
9
10
R (a.u.)



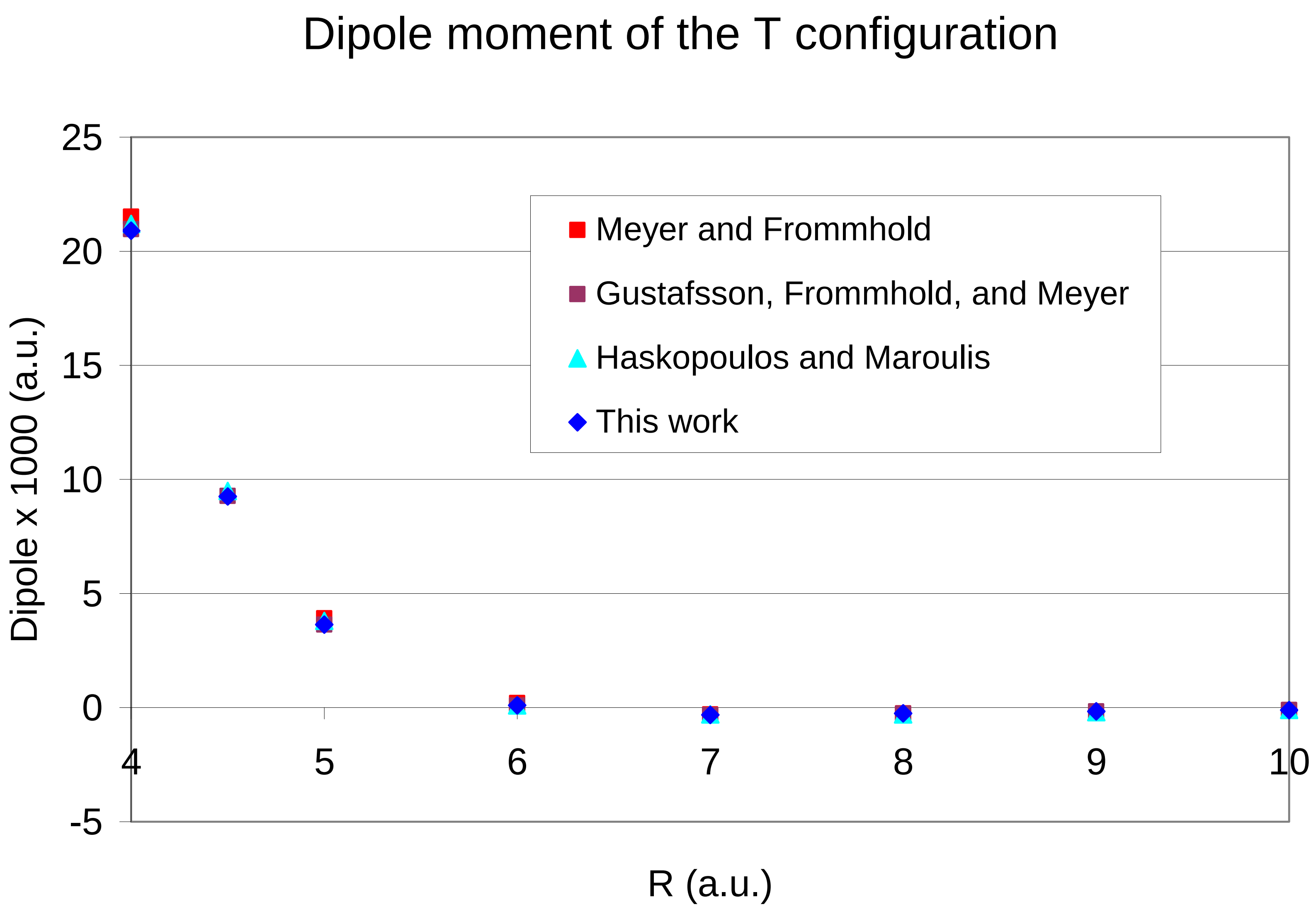
Dipole moment of the T configuration
25
20
15
10
5
0
-5
Dipole x 1000 (a.u.)
4
5
6
7
8
9
10
R (a.u.)
Meyer and Frommhold
Gustafsson, Frommhold, and Meyer
Haskopoulos and Maroulis
This work

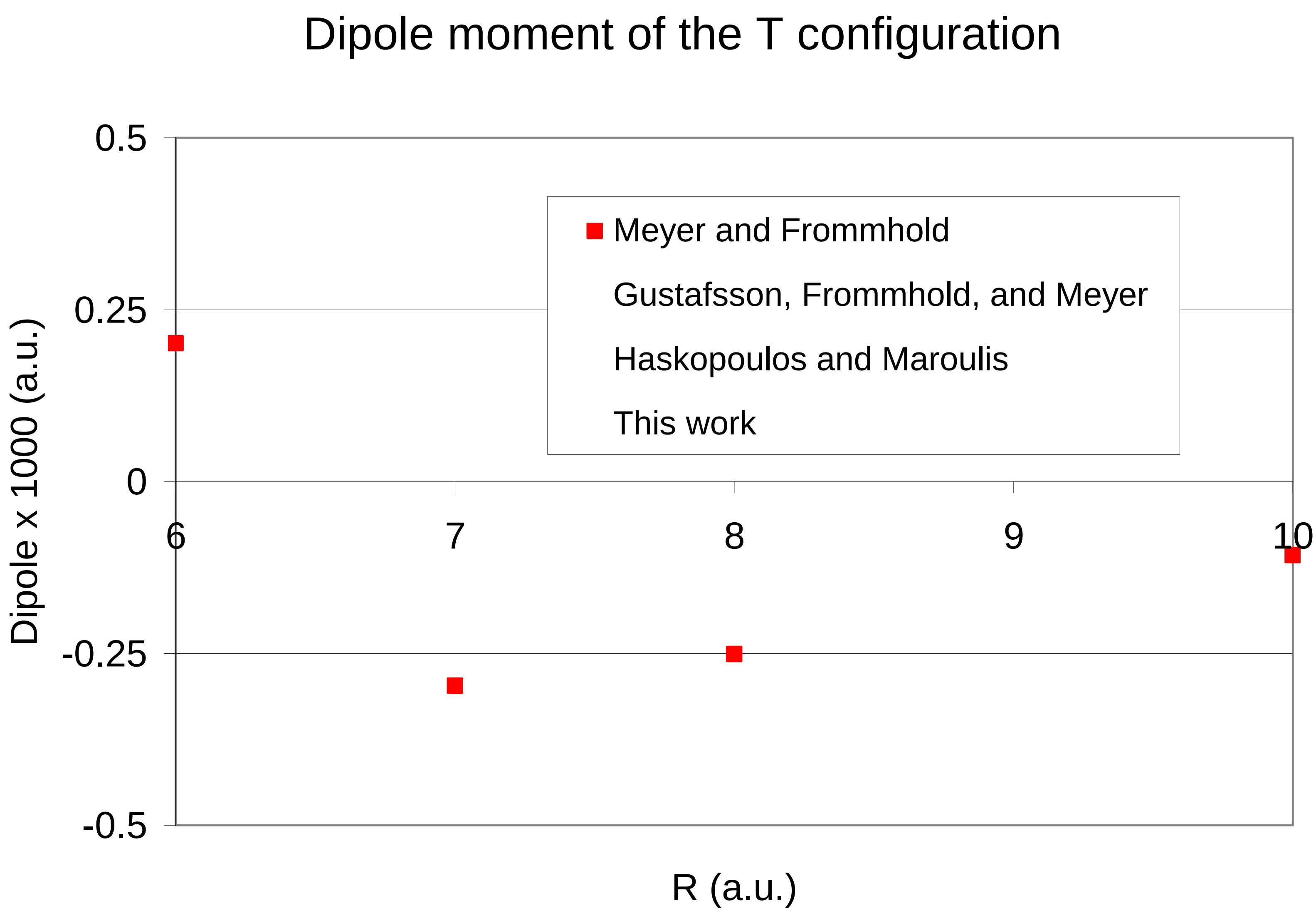


Dipole moment of the T configuration
Meyer and Frommhold
Gustafsson, Frommhold, and Meyer
Haskopoulos and Maroulis
This work
Dipole x 1000 (a.u.)
25
20
15
10
5
0
-5
4
5
6
7
8
9
10
R (a.u.)

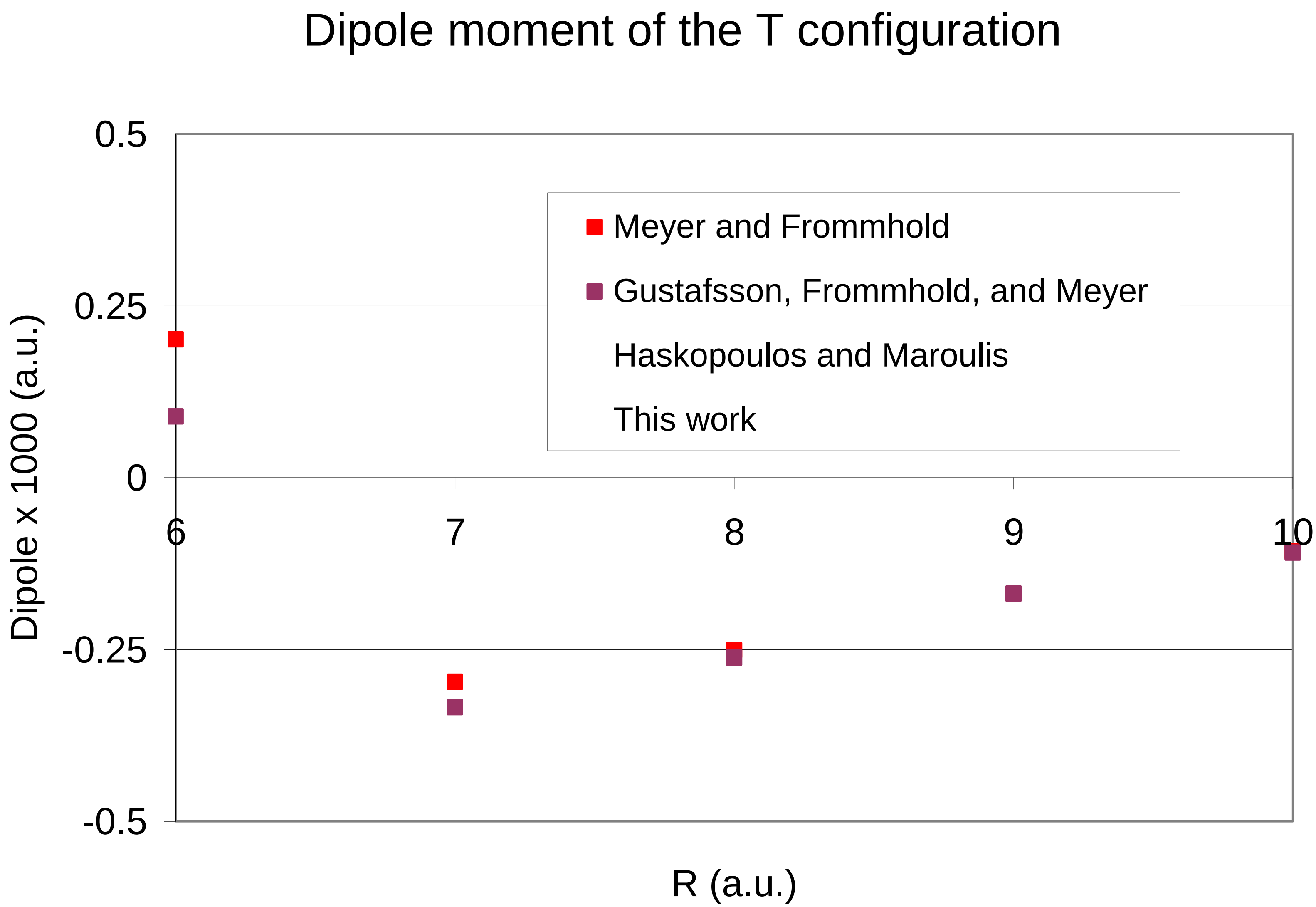


Dipole moment of the T configuration
25
20
15
10
5
0
-5
Dipole x 1000 (a.u.)
4
5
6
7
8
9
10
R (a.u.)
Meyer and Frommhold
Gustafsson, Frommhold, and Meyer
Haskopoulos and Maroulis
This work


Dipole moment of the T configuration
Dipole x 1000 (a.u.)
25
20
15
10
5
0
-5
4
5
6
7
8
9
10
R (a.u.)
Meyer and Frommhold
Gustafsson, Frommhold, and Meyer
Haskopoulos and Maroulis
This work



Dipole moment of the T configuration
Dipole x 1000 (a.u.)
0.5
0.25
0
-0.25
-0.5
6
7
8
9
10
R (a.u.)
Meyer and Frommhold
Gustafsson, Frommhold, and Meyer
Haskopoulos and Maroulis
This work



Dipole moment of the T configuration
0.5
0.25
0
-0.25
-0.5
Dipole x 1000 (a.u.)
6
7
8
9
10
R (a.u.)
Meyer and Frommhold
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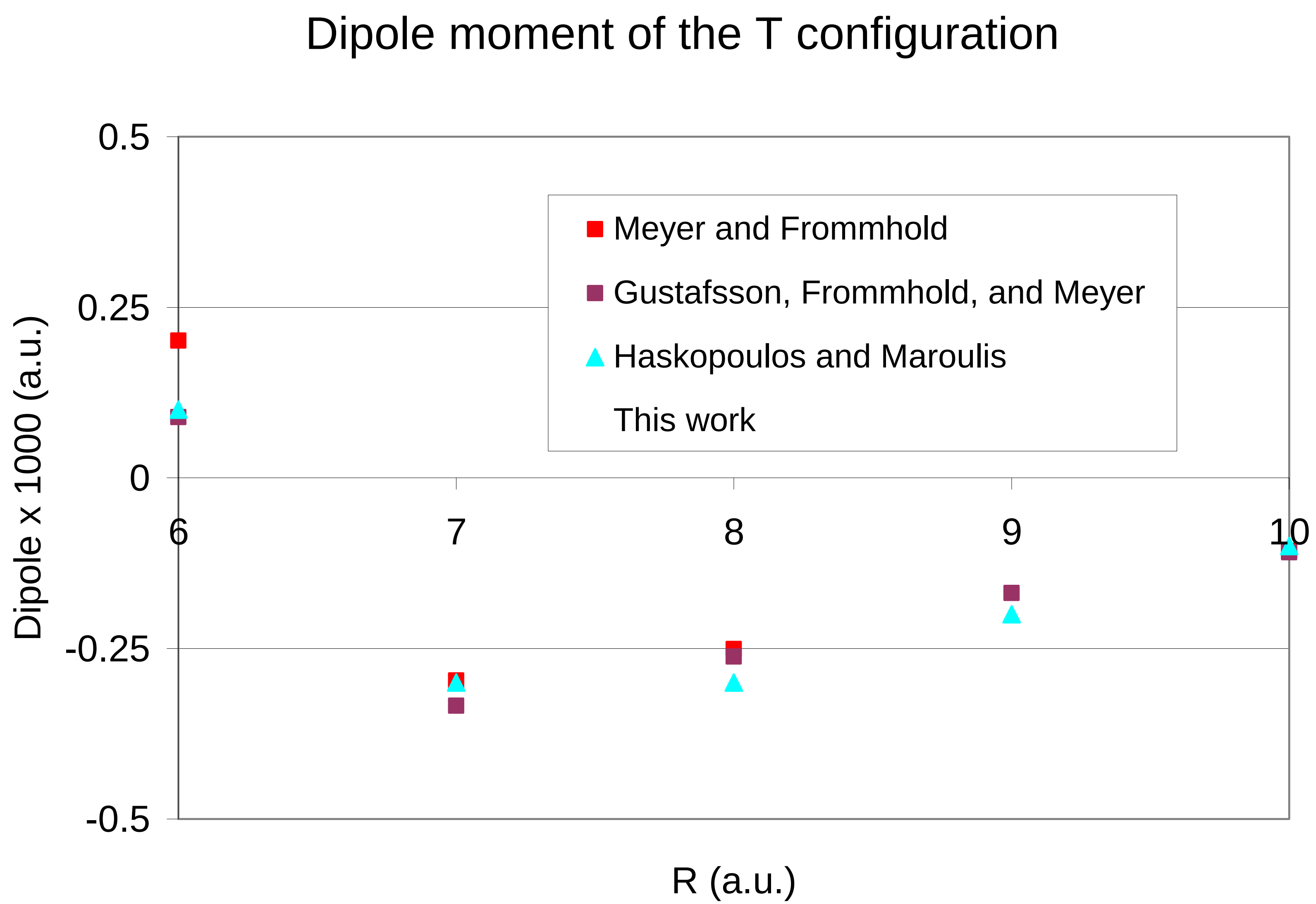
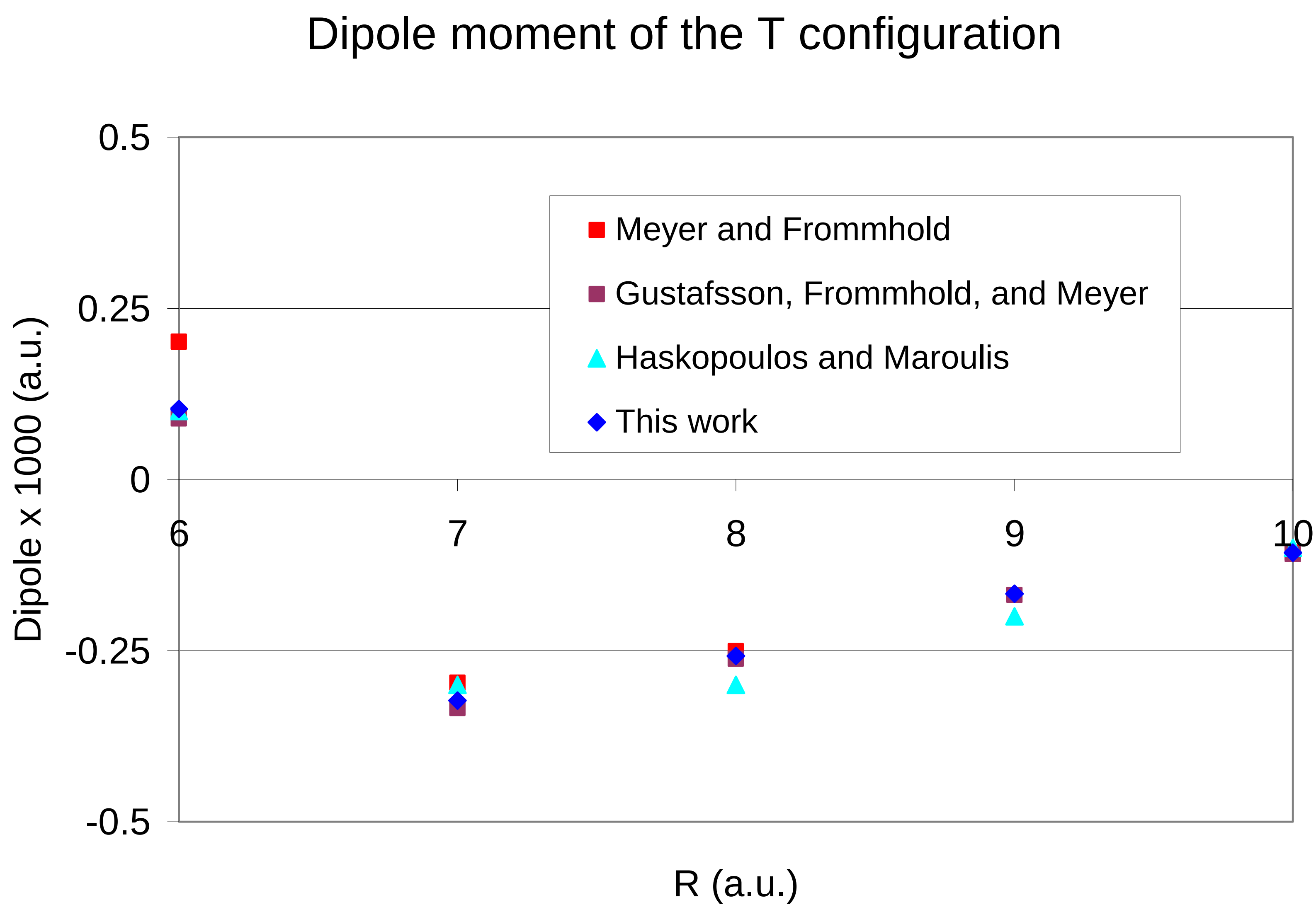

Dipole moment of the T configuration
0.5
0.25
0
-0.25
-0.5
Dipole x 1000 (a.u.)
6
7
8
9
10
R (a.u.)
Meyer and Frommhold
Gustafsson, Frommhold, and Meyer
Haskopoulos and Maroulis
This work



Dipole moment of the T configuration
0.5
0.25
0
-0.25
-0.5
Dipole x 1000 (a.u.)
6
7
8
9
10
R (a.u.)
Meyer and Frommhold
Gustafsson, Frommhold, and Meyer
Haskopoulos and Maroulis
This work

Expansion of the collision-induced dipole in spherical harmonics

1) Convert Cartesian components of the dipole to spherical-tensor components

$$\mu_0 = \mu_z$$

$$\mu_{\pm 1} = -(\mu_x \pm i\,\mu_y)/\sqrt{2}$$

2) Find coefficients for series expansion of the collision-induced dipole moment

$$\mu_M(\mathbf{r}, \mathbf{R}) = 4\pi/3^{1/2} \sum_{\lambda,L,m} D_{\lambda L}(r, R)\, Y_\lambda^{\,m}(\hat{\mathbf{r}})\, Y_L^{\,M-m}(\hat{\mathbf{R}})\, \langle \lambda\ L\ m\ M-m \mid 1\ M \rangle$$

$D_{\lambda L}(r, R)$: Dipole expansion coefficients

$Y_\lambda^{\,m}(\hat{\mathbf{r}})$: Spherical harmonics of the H_2 orientation

$Y_L^{\,M-m}(\hat{\mathbf{R}})$: Spherical harmonics of the orientation of the intermolecular vector **R**

$\langle \lambda\ L\ m\ M-m \mid 1\ M \rangle$: Clebsch-Gordan coefficients

Advantages:

Separates out different polarization mechanisms into different coefficients

Ties directly to rotational selection rules, Δj goes up to $\pm\lambda$ for $D_{\lambda L}(r, R)$ component

Spherical Dipole Coefficients for $H_2 \cdots He$

Bond length of H_2 = 1.449 a.u.

$D_{nm} \cdot 10^6$		R								
n	m	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
0	1	-471155	-126781	-31034	-6444	-1077	-122	10	15	7
2	1	139471	29280	5701	1017	158	18	1	0	-1
2	3	-87454	-26898	-7781	-2567	-1035	-509	-289	-179	-117
4	3	6527	2311	450	81	15	3	0	0	0
4	5	-2871	-1614	-386	-96	-28	-10	-4	-2	-1
6	5	-127	94	17	3	0	-1			
6	7	52	-63	-15	-4	-2	-1			
8	7	-24	2	0						
8	9	-4	-1	-1						
10	9	-2	1							
10	11	-2	1							
12	11	-1								
12	13	-1								
14	13	-1								

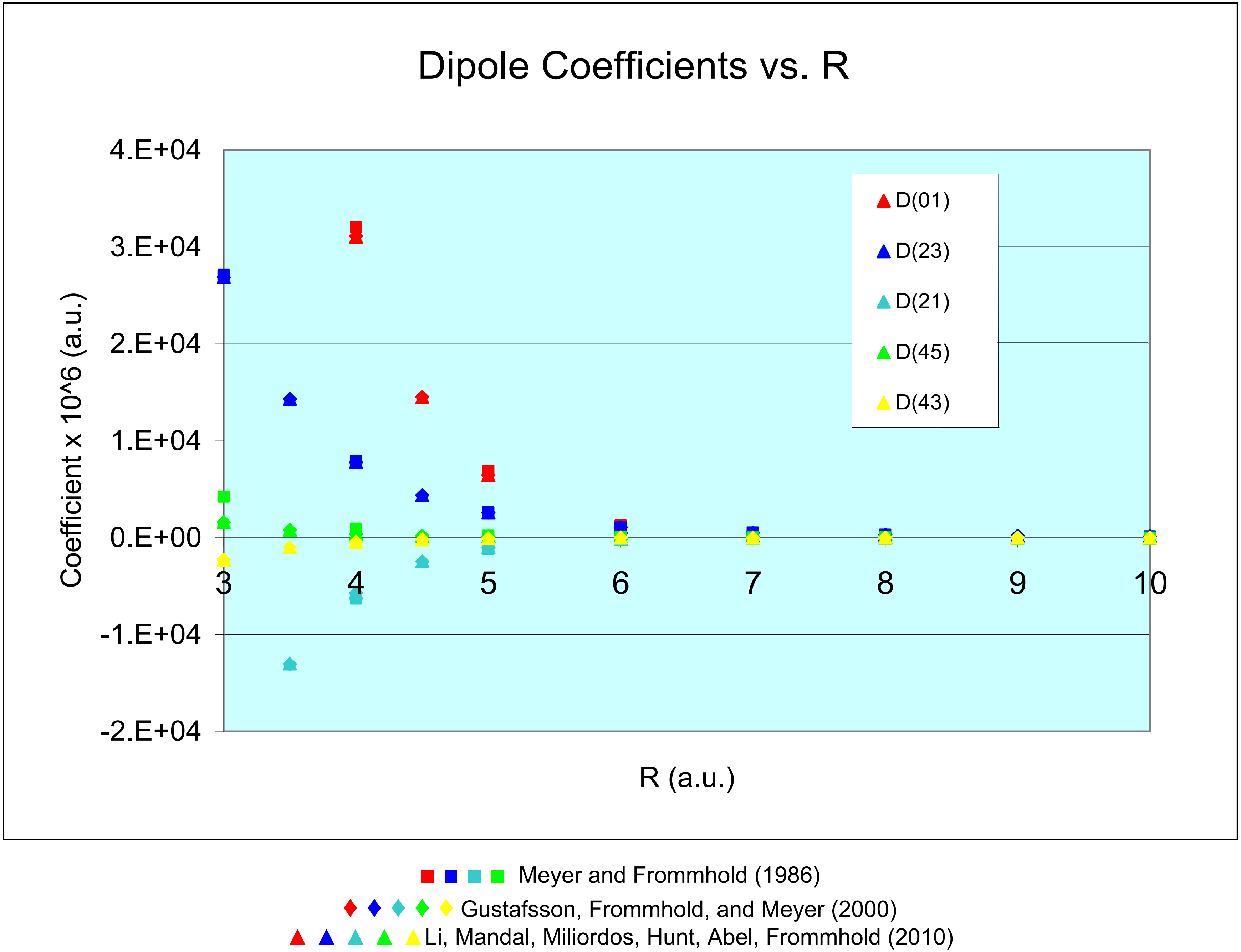
Spherical Dipole Coefficients for $H_2 \cdots He$

$H_2 \cdots He$ separation R = 3.0 a.u.

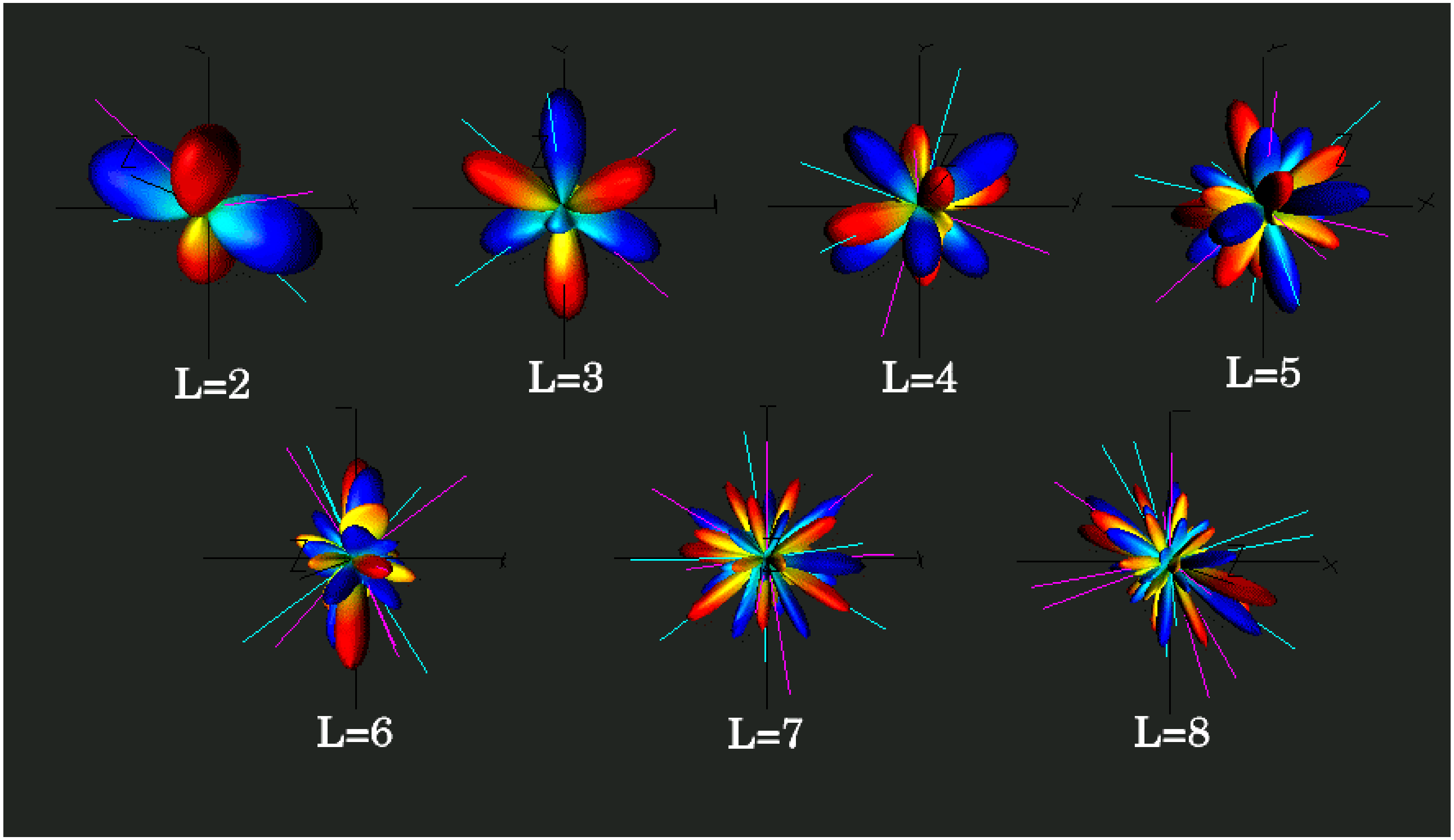
$D_{nm} \cdot 10^6$ — $r(H_2)$ in a.u.

n	m	0.942	1.111	1.280	1.449	1.787	2.125	2.463	2.801
0	1	-59053	-79092	-101720	-126781	-183143	-244943	-307098	-363451
2	1	8079	13181	20162	29280	54523	88783	129269	171526
2	3	-9192	-13705	-19535	-26898	-47171	-76460	-116602	-169003
4	3	298	647	1274	2311	6299	14242	28037	49554
4	5	-249	-506	-938	-1614	-4087	-8948	-17826	-33373
6	5	7	17	41	94	381	1238	3470	8737
6	7	-2	-11	-29	-63	-225	-644	-1616	-3785
8	7	1	1	1	2	11	54	232	867
8	9	1			-1	-7	-21	-27	45
10	9	1	1		1	-1	-2	-16	-68
10	11				1		3	20	139
12	11				1		-3	-11	-70
12	13						-1	4	37
14	13	-2					1		-8
14	15	2					1	-1	1

For r = 2.801 a.u., we continue to find large values of D_{nm} through (at least) n = 24, m = 23


Dipole Coefficients vs. R
4.E+04
3.E+04
2.E+04
1.E+04
0.E+00
-1.E+04
-2.E+04
Coefficient x 10^6 (a.u.)
3
4
5
6
7
8
9
10
R (a.u.)
D(01)
D(23)
D(21)
D(45)
D(43)
Meyer and Frommhold (1986)
Gustafsson, Frommhold, and Meyer (2000)
Li, Mandal, Miliordos, Hunt, Abel, Frommhold (2010)

Multipoles Acting as Field Sources



Classical induction terms in the dipole coefficients

Atom A interacting with diatomic molecule B, **R** runs from the center of the molecule to the atom

$$D_{01} = (6/5)\,(\alpha^B_{zz} - \alpha^B_{xx})\,\alpha^A\,\Theta^B\,R^{-7}$$

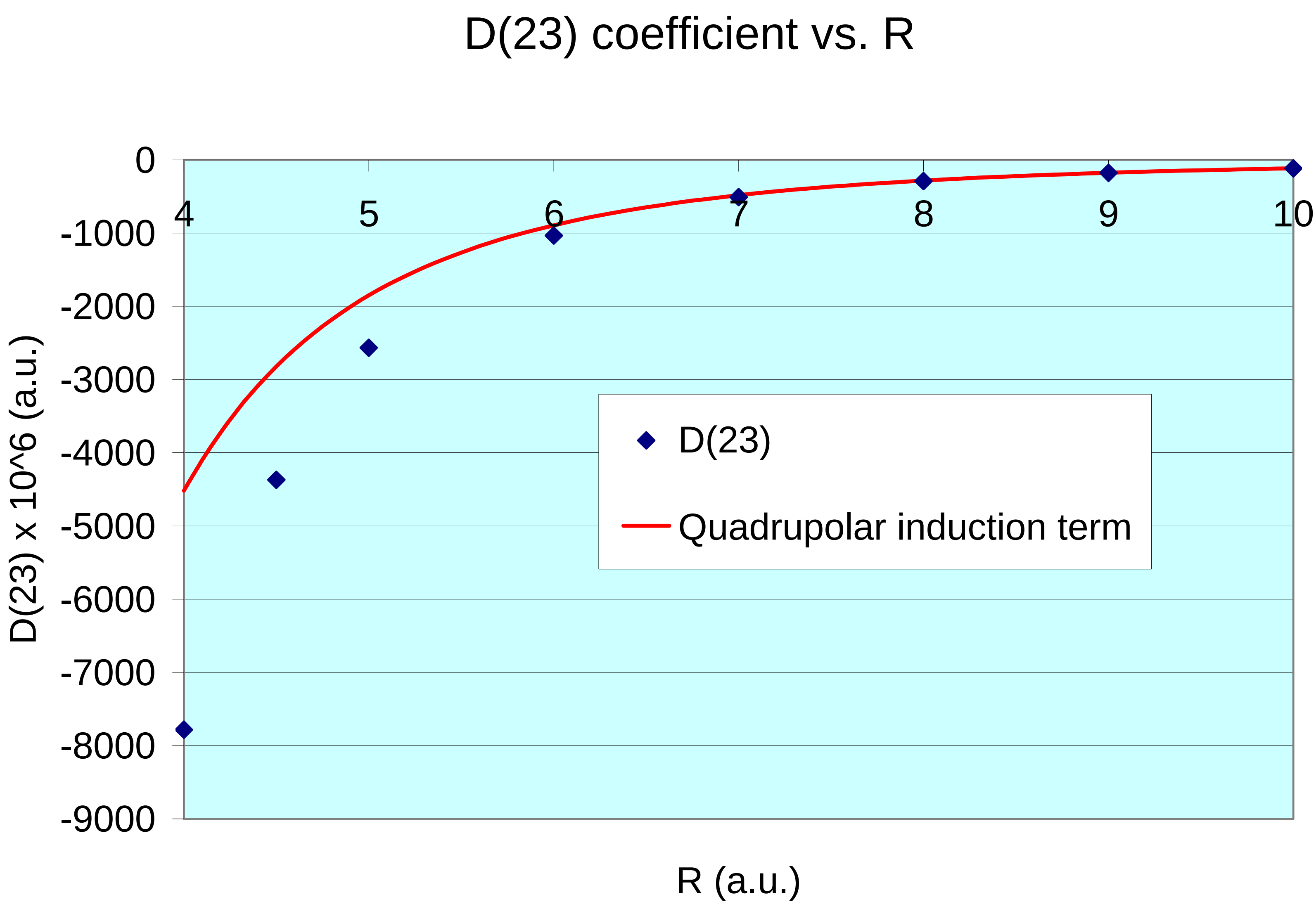
$$D_{21} = -3\,(2^{1/2}/5)\,(2\,\alpha^B_{zz} + \alpha^B_{xx})\,\alpha^A\,\Theta^B\,R^{-7}$$

$$D_{23} = 3^{1/2}\,\alpha^A\,\Theta^B\,R^{-4} + 4\,(3^{1/2}/35)\,(3\,\alpha^B_{zz} + 4\,\alpha^B_{xx})\,\alpha^A\,\Theta^B\,R^{-7}$$

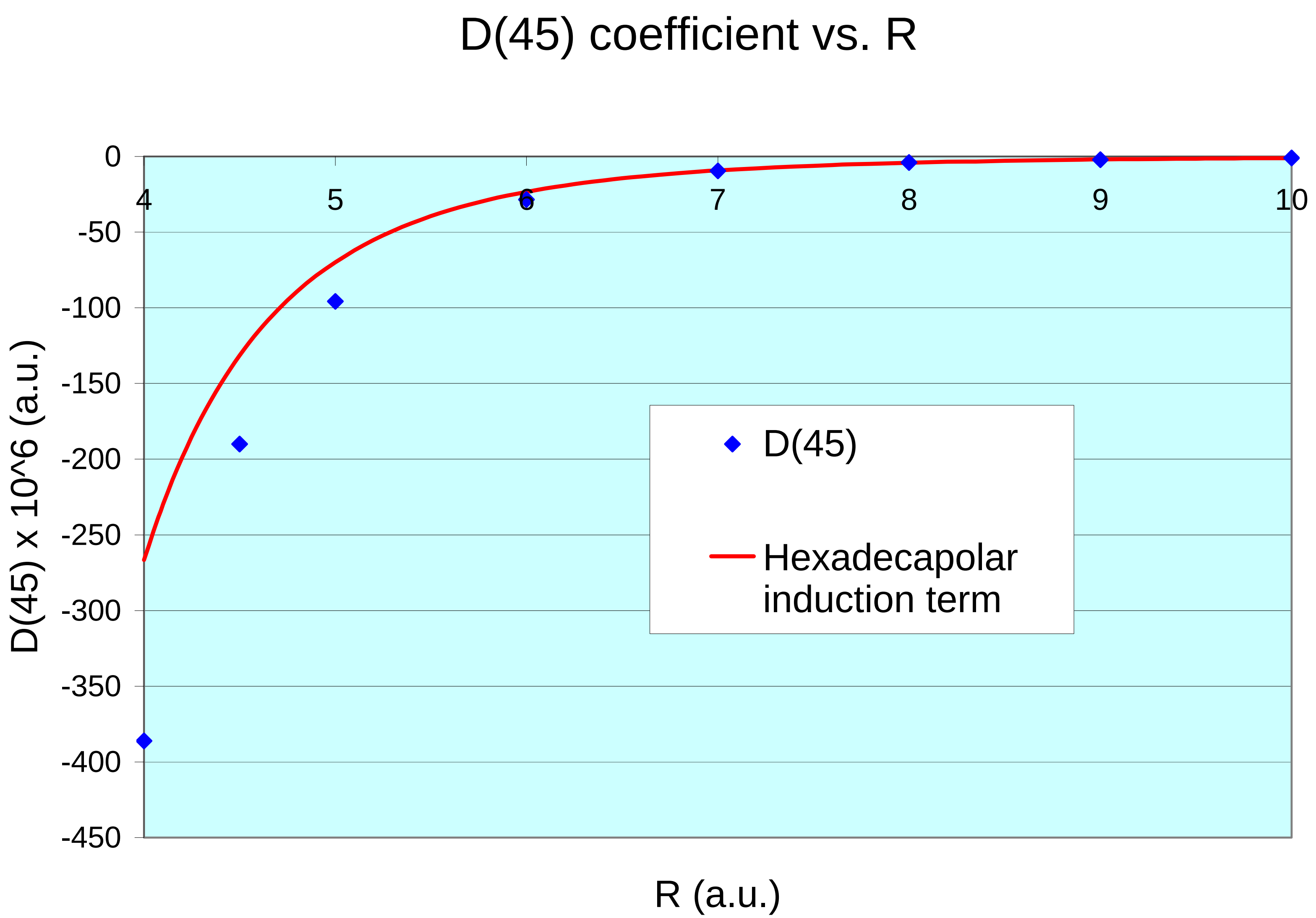
$$D_{43} = -24/35\,(\alpha^B_{zz} - \alpha^B_{xx})\,\alpha^A\,\Theta^B\,R^{-7}$$

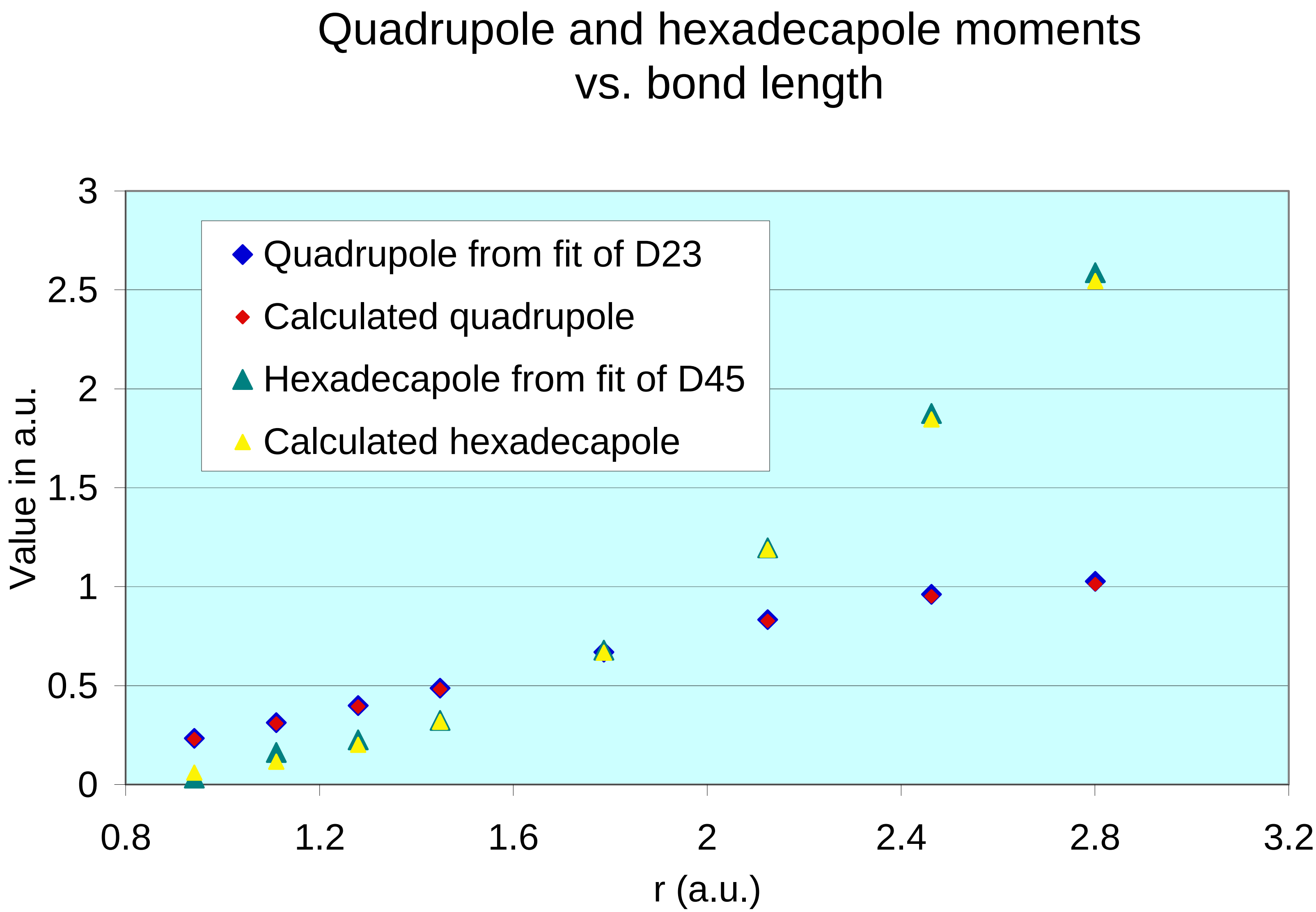
$$D_{45} = 5^{1/2}\,\alpha^A\,\Phi^B\,R^{-6}$$

Quadrupolar induction: $\alpha^A\,\Theta^B$ term varies as R^{-4}
Hexadecapolar induction: $\alpha^A\,\Phi^B$ term varies as R^{-6}
Remaining terms come from back-induction and vary as R^{-7}



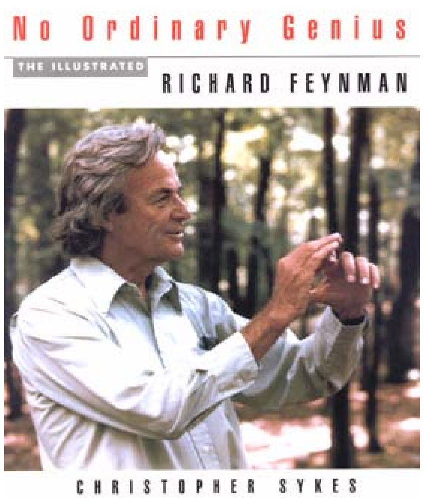
D(23) coefficient vs. R
0
-1000
-2000
-3000
-4000
-5000
-6000
-7000
-8000
-9000
4
5
6
7
8
9
10
D(23) x 10^6 (a.u.)
R (a.u.)
D(23)
Quadrupolar induction term

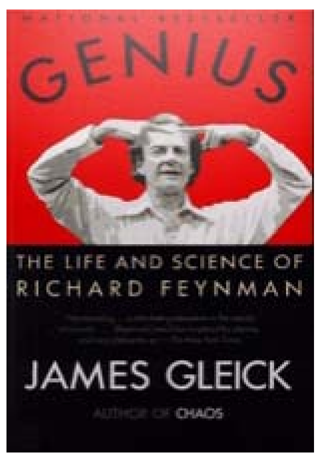

D(45) coefficient vs. R
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
4
5
6
7
8
9
10
D(45) x 10^6 (a.u.)
R (a.u.)
D(45)
Hexadecapolar induction term



Quadrupole and hexadecapole moments
vs. bond length
Quadrupole from fit of D23
Calculated quadrupole
Hexadecapole from fit of D45
Calculated hexadecapole
Value in a.u.
r (a.u.)
0
0.5
1
1.5
2
2.5
3
0.8
1.2
1.6
2
2.4
2.8
3.2

THE FEYNMAN “CONJECTURE”





Dispersion energy depends on linear response, but dispersion dipole depends on nonlinear response?

Centrosymmetric molecules:
Dispersion energy depends on u states, but dispersion dipole depends on g and u states?

Noncentrosymmetric molecules:
Dispersion energy varies as R^{-6}
Dispersion force varies as R^{-7}
Dispersion dipole varies as R^{-6}

The *origin* of dispersion forces should not depend on molecular symmetry.

Explanation

Derivative of the susceptibility with respect to a nuclear coordinate depends on the density of the nonlinear response of the next higher order

$\partial\alpha/\partial R^K$ depends on $\beta(r, r', r'')$

E^{disp} depends on α, $\therefore F^{disp}$ depends on β

Distance dependence of dispersion forces

Force on an individual nucleus: R^{-6}

Force on the center of mass: R^{-7}

Dispersion terms in the dipole coefficients

$$D_{01} = (9\hbar/\pi)\, R^{-7} \int_0^\infty [\alpha^A(i\omega)\, B^B{}_0(0,i\omega) - \bar{\alpha}^B(i\omega)\, B^A(0,i\omega)]\, d\omega$$

$$D_{21} = -3\hbar/(5\ 2^{1/2}\, \pi)\, R^{-7} \int_0^\infty \{4\,\alpha^A(i\omega)\, B^B{}_{2a}(0,i\omega) - [\alpha^B{}_{zz}(i\omega) - \alpha^B{}_{xx}(i\omega)]\, B^A(0,i\omega)\}\, d\omega$$

$$D_{23} = (4\ 3^{1/2}\, \hbar/\pi)\, R^{-7} \int_0^\infty \{2\,\alpha^A(i\omega)\, B^B{}_{2b}(0,i\omega) - [\alpha^B{}_{zz}(i\omega) - \alpha^B{}_{xx}(i\omega)]\, B^A(0,i\omega)\}\, d\omega$$

$$D_{43} = (-16\hbar/\pi)\, R^{-7} \int_0^\infty [\alpha^A(i\omega)\, B^B{}_4(0,i\omega)]\, d\omega$$

$B(0,i\omega)$ denotes the dipole-dipole quadrupole hyperpolarizability
Integrals have been evaluated with high accuracy by D. M. Bishop and J. Pipin, for $H_2 \cdot\cdot\cdot He$, with B components of ranks 0, 2, and 4

Dispersion contributions to the dipole moment

Equations: J. E. Bohr and K. L. C. Hunt, *J. Chem. Phys*. **86**, 5441 (1987).
Accurate numerical values: D. M. Bishop and J. Pipin, *J. Chem. Phys*. **98**, 4003 (1993).

Dispersion dipole coefficients for H_2-He:

$D_{01}{}^{d} = -86.87\ R^{-7}$

$D_{21}{}^{d} = 12.91\ R^{-7}$

$D_{23}{}^{d} = 0.23\ R^{-7}$

$D_{43}{}^{d} = 0.06\ R^{-7}$

Classical induction contribution:

$D_{43}{}^{b} = (6/5)\ (\alpha^{B}{}_{zz} - \alpha^{B}{}_{xx})\ \alpha^{A}\ \Theta^{B}\ R^{-7}$

Polarizabilities and permanent quadrupole of H2 at r = 1.449 a.u.

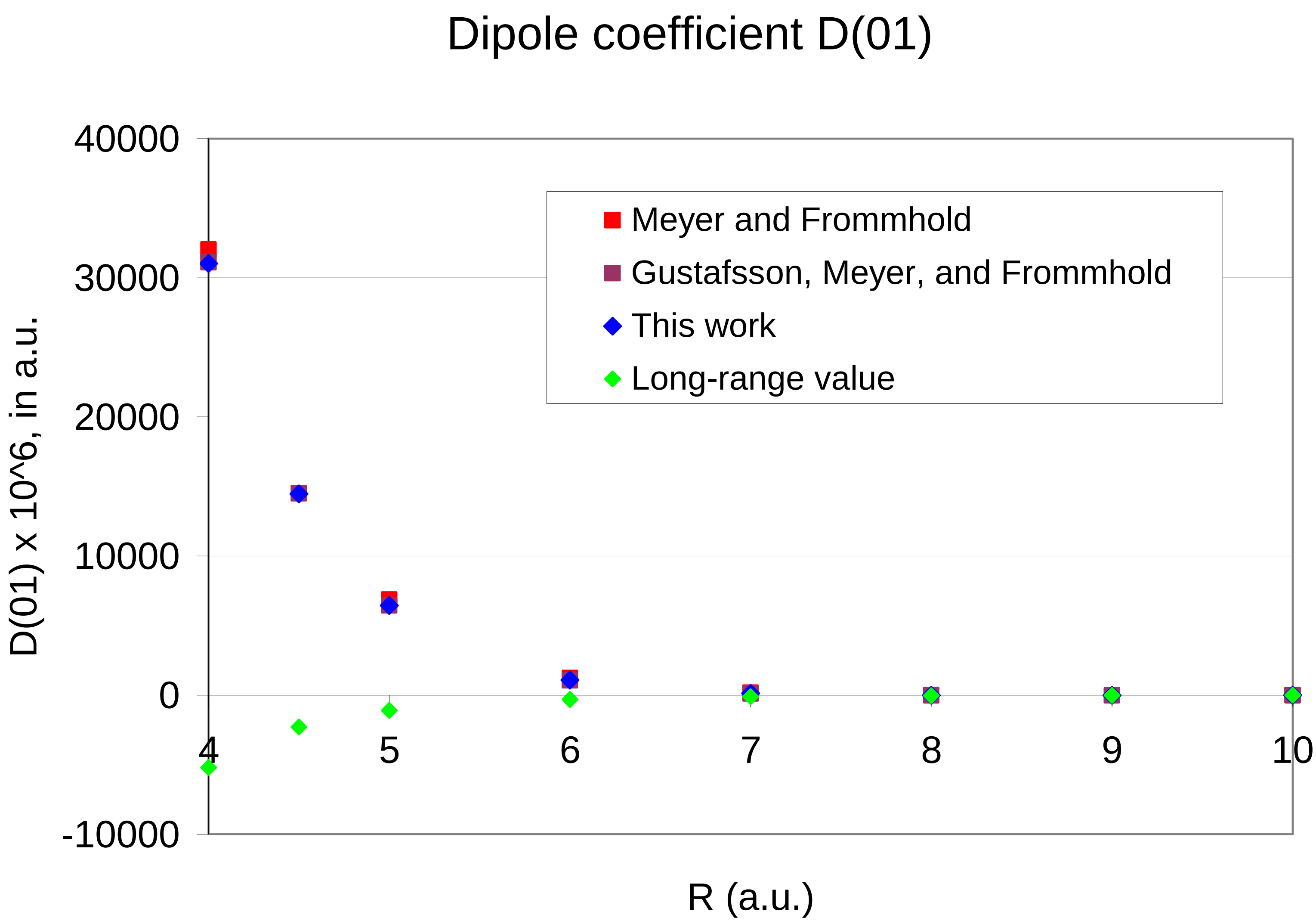
$\Theta^{B} = 0.4828$ a.u.

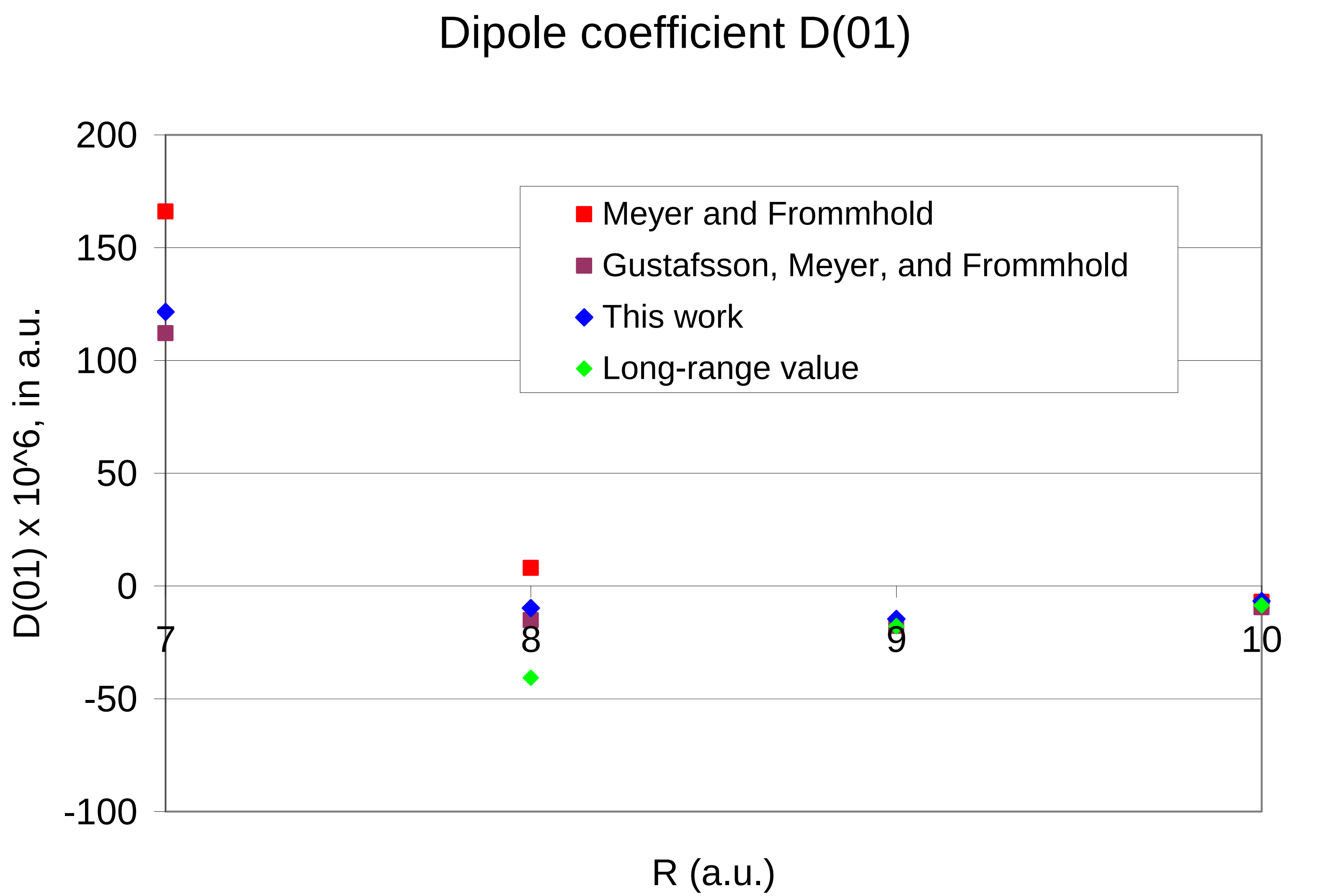
$\alpha^{B}{}_{zz} - \alpha^{B}{}_{xx} = 1.9793$ a.u.

$\alpha^{A} = 1.383192$ a.u.

Resulting value for D_{01}: $-85.28\ R^{-7}$

Can we see this in the *ab initio* results?


Dipole coefficient D(01)
D(01) x 10^6, in a.u.
40000
30000
20000
10000
0
-10000
4
5
6
7
8
9
10
R (a.u.)
Meyer and Frommhold
Gustafsson, Meyer, and Frommhold
This work
Long-range value

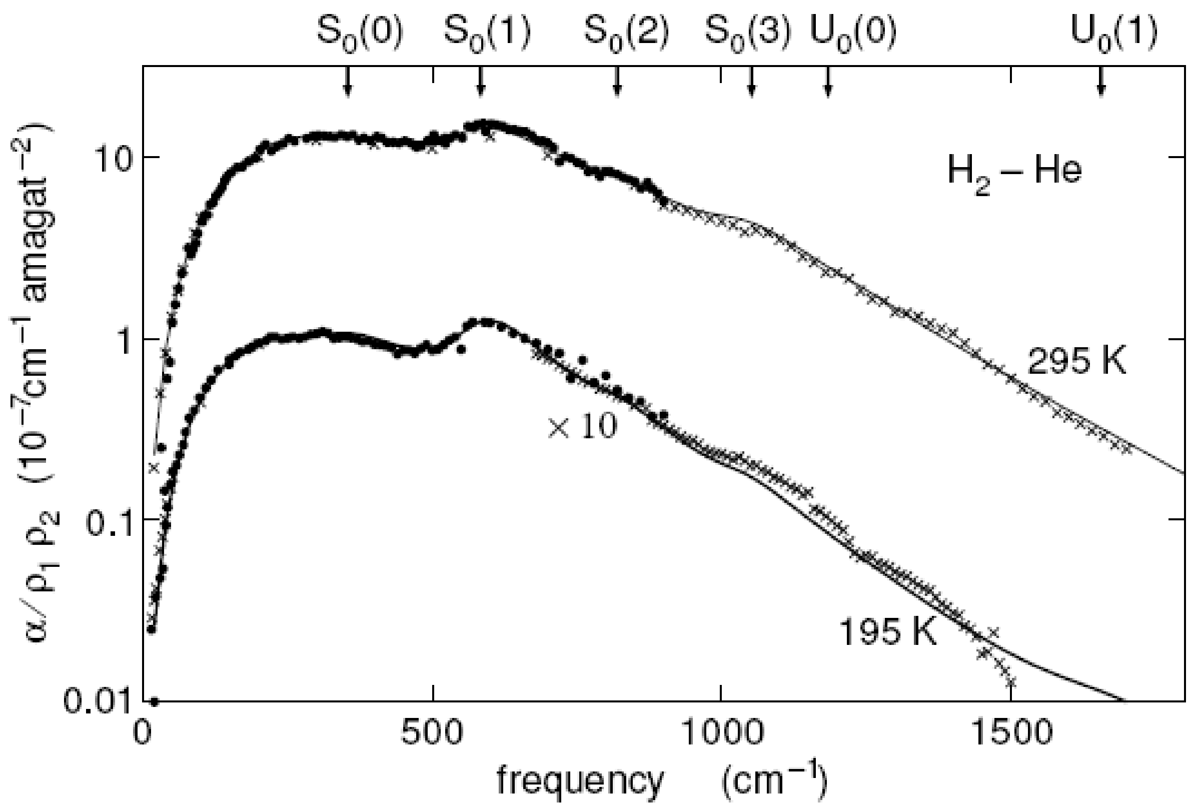

Dipole coefficient D(01)
Meyer and Frommhold
Gustafsson, Meyer, and Frommhold
This work
Long-range value
D(01) x 10^6, in a.u.
R (a.u.)
200
150
100
50
0
-50
-100
7
8
9
10

Experimental Results

Binary, collision-induced spectra of H_2-He pairs

1) Rototranslational band (195 K, 295 K)
2) Fundamental vibrational band (298 K)
3) Calculated spectra including overtone bands (300 K-9000 K)

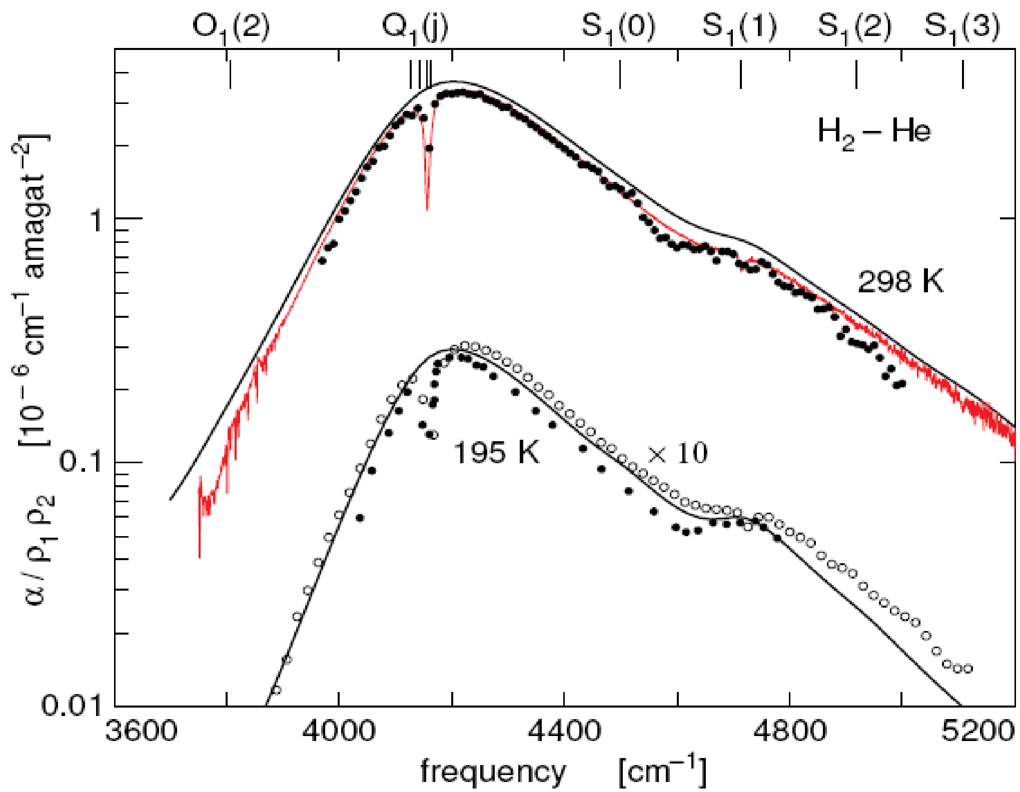
Rototranslational Absorption Spectrum of $H_2 \cdots He$



Theory: Solid line from Abel, Frommhold, Li and Hunt, 2010.

Experiments:
- • G. Birnbaum, *J. Quant. Spectrosc. Rad. Transfer* **19**, 51 (1978).
- x G. Birnbaum, G. Bachet, and L. Frommhold, *Phys. Rev. A* **36**, 3729 (1987).

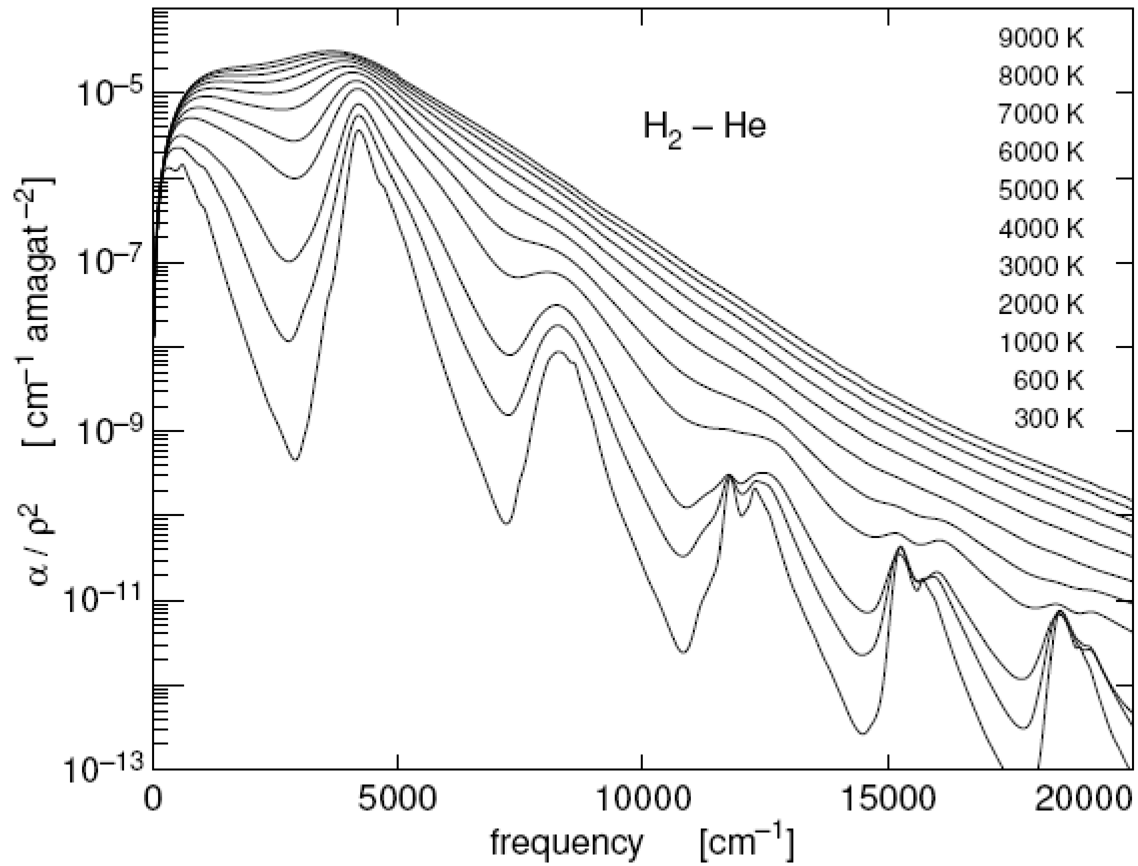
Fundamental Vibrational Band in the $H_2 \cdots He$ Spectrum



Theory: Solid lines from Abel, Frommhold, Li, and Hunt (2010).
Experiment: Red trace with noise, C. Brodbeck, Nguyen-van-Thanh, J. P. Bouanich, and L. Frommhold, *Phys. Rev. A* **51**, 1209 (1995).

- ● T = 298 K, G. Birnbaum, A. Borysow, and G. S. Orton, *Icarus* **123**, 4 (1996).
- ● T = 195 K, J. L. Hunt and H. L. Welsh, *Can. J. Phys*. **42**, 873 (1964).
- ○ T = 195 K, S. P. Reddy, in *Phenomena Induced by Intermolecular Interactions*, edited by G. Birnbaum (Plenum, New York, 1985), pp. 129-168.

Normalized Two-Body Absorption Spectrum for $H_2 \cdots He$



Calculations for temperatures from 300 K to 9000 K, from Abel, Frommhold, Li, and Hunt (2010).

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