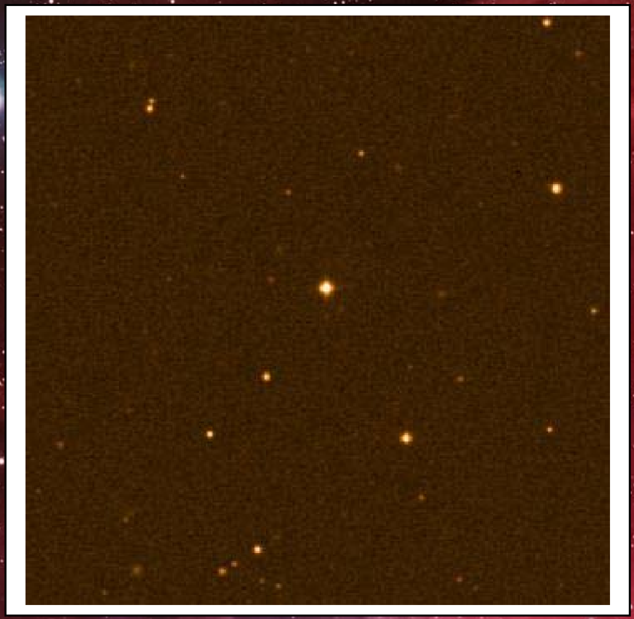
Collision-induced absorption in the stellar atmospheres of very cool white dwarf stars

Katharine L. C. Hunt
Michigan State University

Collaborators:
Professor Lothar Frommhold, University of Texas, Austin
Dr. Magnus Gustafsson, University of Gothenburg, Sweden
Dr. Xiaoping Li, Michigan State University
Martin Abel, University of Texas, Austin

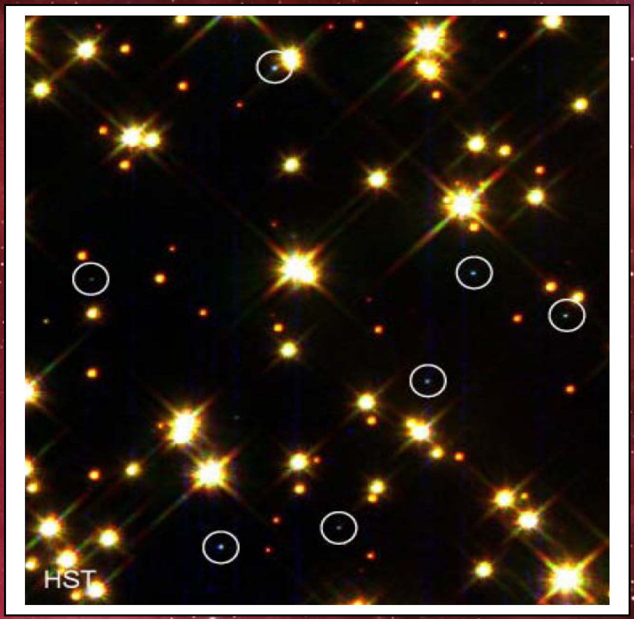
QSCP XV, Cambridge, England, 2010

Very Cool White Dwarf Stars



Van Maanen's Star
ESO Online Digitized Sky Survey

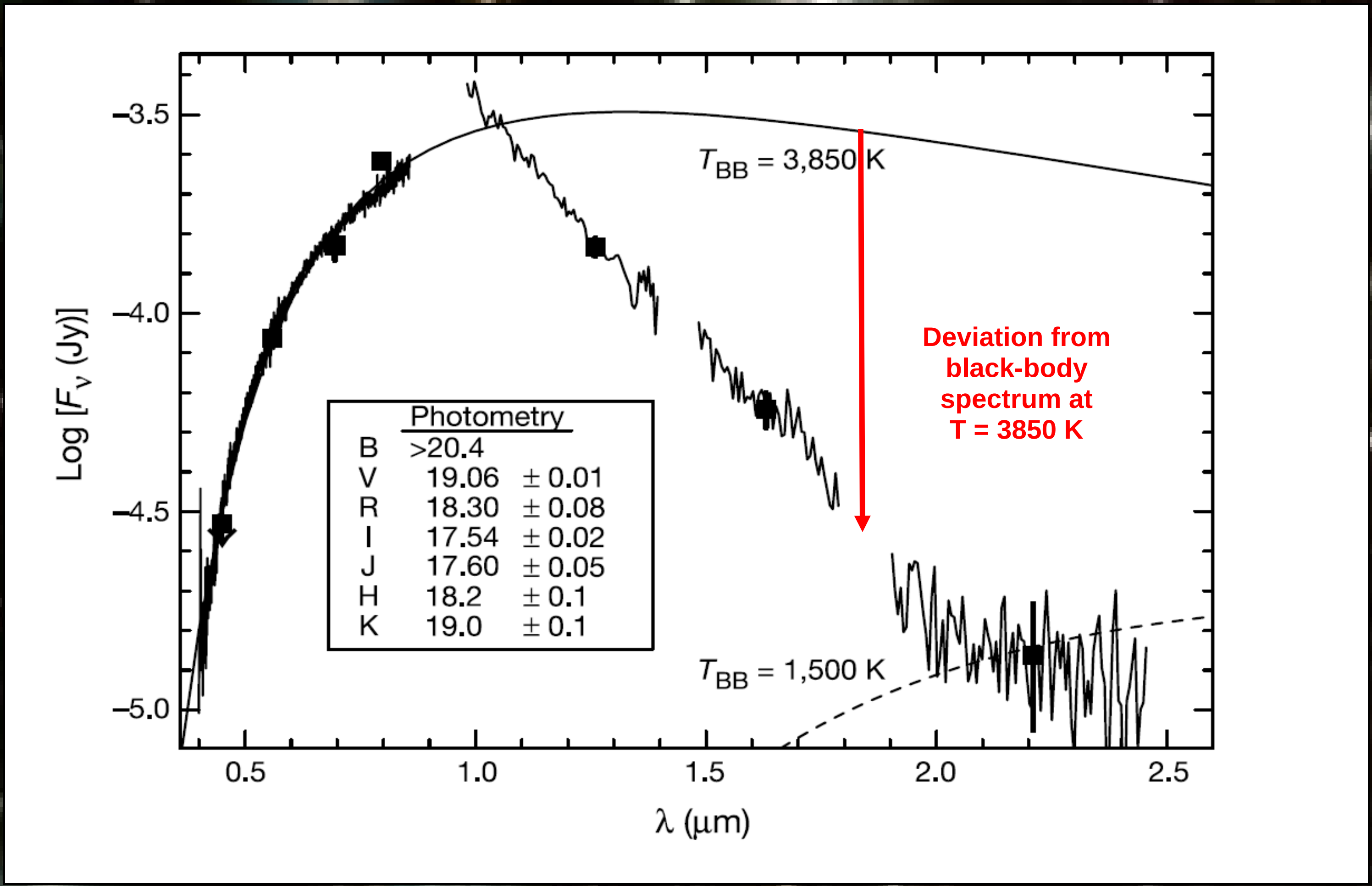
~10 billion years old
14.13 light years away
Mass = 0.7 * Sun
Luminosity = 0.000182 * Sun
Diameter = 0.013 * Sun
(in constellation Pisces)



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

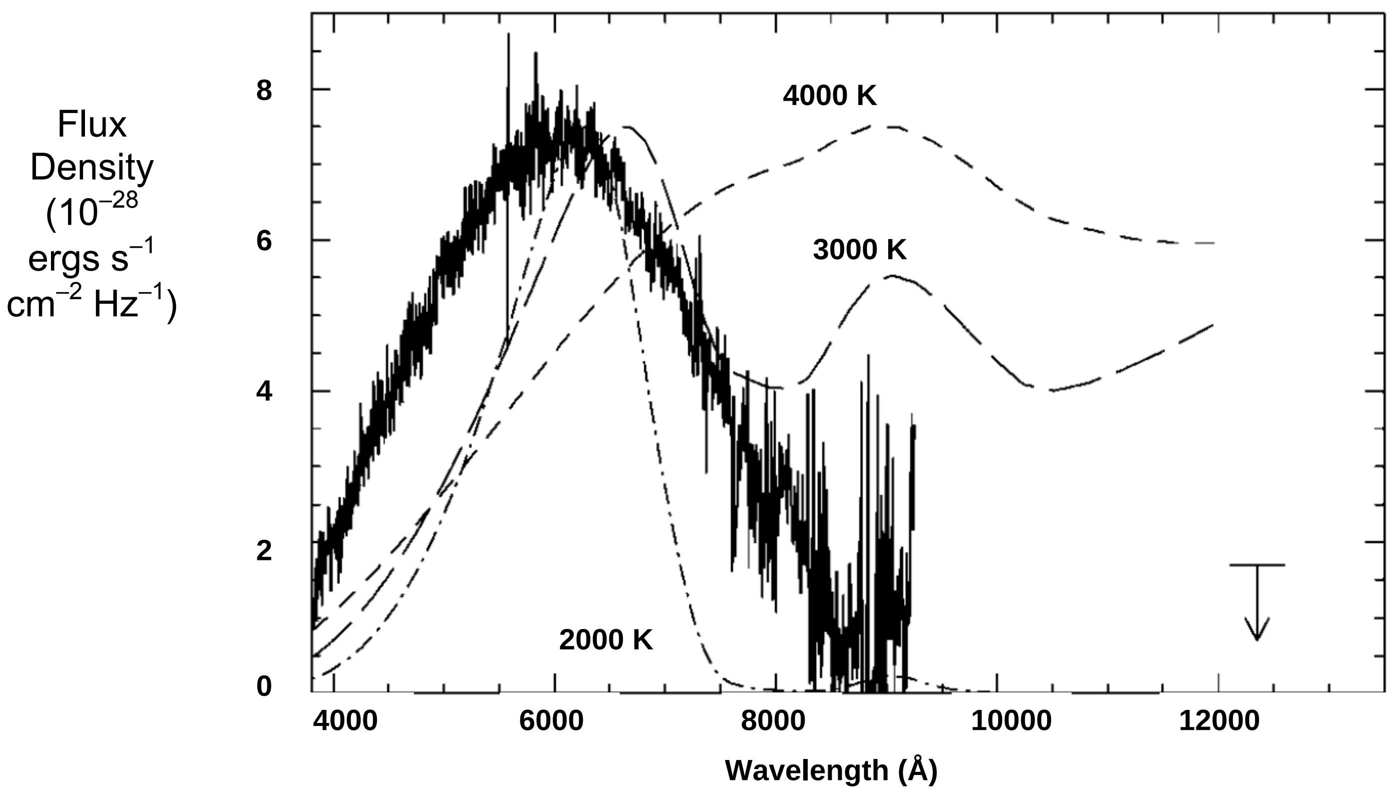
Luminosity: 100 Watt light bulb,
seen from 239,000 miles away
8 days exposure time over 67-day period
Hubble Space Telescope
5,600 light years away

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).

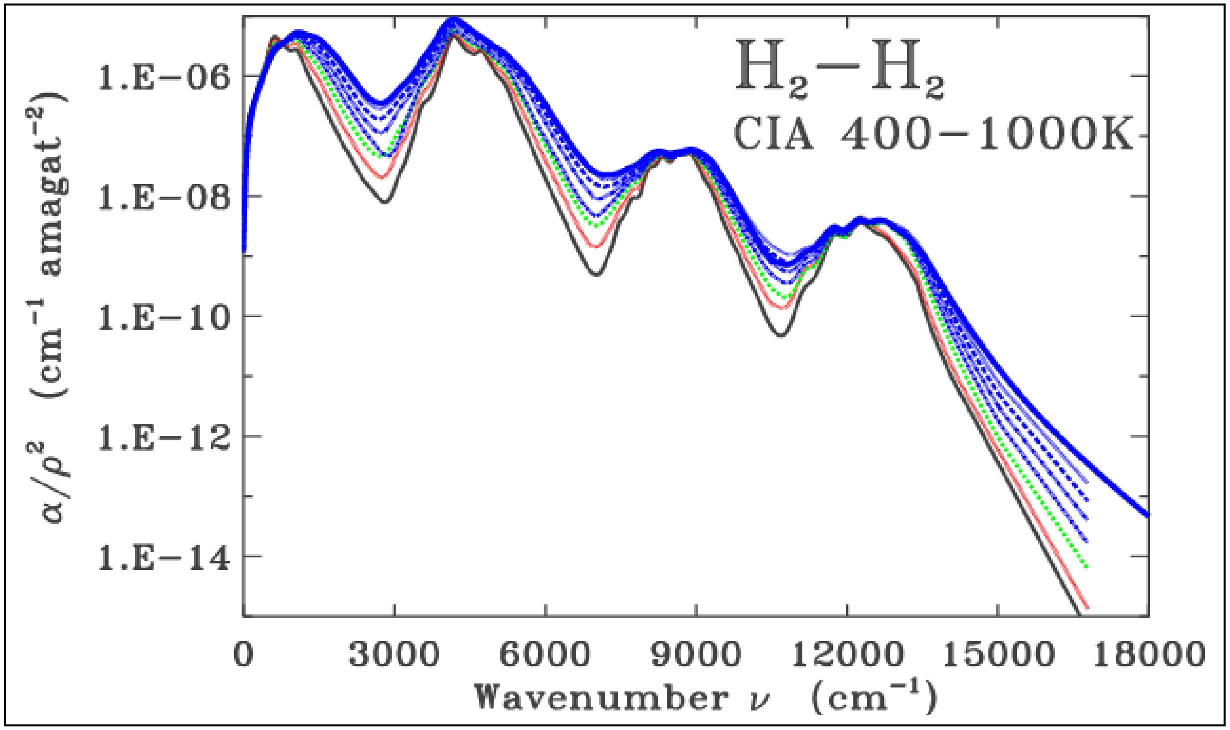
Preliminary Spectral Modeling of SDSS 1337+00



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).

COLLISION-INDUCED ABSORPTION IN H_2

- Sub-picosecond time scale
- Molecular interactions break symmetry
- Single-molecule forbidden transitions can occur



ABSORPTION BY HYDROGEN

Vibrational transitions in H_2:

Fundamental
4162 cm^{-1} = 2.4 mm

First overtone
8089 cm^{-1} = 1.2 mm

Second overtone
11786 cm^{-1} = 0.8 mm

Aleksandra Borysow, *Astronomy and Astrophysics* **390**, 779 (2002).

Ab initio Calculations

CCSD(T), MOLPRO 2000

CR-CC(2,3), GAMESS

Basis: aug-cc-pV5Z (spdf)

Finite-field approach

$\Delta\mu$: 6 field strengths in each direction, analytic fit to find

$\Delta\mu_\alpha = -\lim_{F_\alpha \to 0} \partial E / \partial F_\alpha$

17 pair orientations, range of separations from 3-10 a.u.

28 bond-length combinations, from the set:

{0.942 a.u., 1.111 a.u., 1.280 a.u., 1.449 a.u., 1.787 a.u., 2.125 a.u., 2.463 a.u., 2.801 a.u.}

X. Li, C. Ahuja, J. F. Harrison, and K. L. C. Hunt, *J. Chem. Phys*. **126**, 214302 (2007); X. Li, K. L. C. Hunt, F. Wang, M. Abel, and L. Frommhold, *Int. J. Spectroscopy* **2010**, 371201 (2010).

TABLE 1. Dipole Moment of $H_2 \ldots H_2$ with $r_1 = r_o = 1.449$ a.u. and $r_2 = r_- = 1.111$ a.u. Cartesian components (in a.u., multiplied by 10^6).

R (a.u.)	4.0	5.0	6.0	7.0	8.0	9.0	10.0
(θ_1, θ_2, φ_{12})			μ_z				
(π/12, π/6, π/3)	–38855	–10233	–2908	–1042	–501	–294	–192
(π/12, π/4, π/6)	-49050	–14121	–4639	–1932	–1009	–608	–396
(π/12, π/3, π/6)	–58504	–17749	–6279	–2786	–1500	–910	–595
(π/12, 5π/12, π/6)	–65027	–20268	–7431	–3391	–1850	–1127	–737
(π/6, π/4, π/3)	–35860	–9931	–3044	–1183	–596	–356	–234
(π/6, π/3, π/4)	–45319	–13548	–4673	–2030	–1083	–657	–431
(π/6, 5π/12, π/3)	–51734	–16002	–5789	–2617	–1423	–868	–570
(π/4, π/3, π/6)	–28836	–8221	–2593	–1033	–527	–317	–209
(π/4, 5π/12, π/6)	–35159	–10620	–3680	–1604	–858	–522	–345
(π/3, 5π/12, π/6)	–20071	–5619	–1669	–617	–303	–180	–121
(7π/12, π/12, π/6)	22791	9980	5124	2864	1692	1054	690
(7π/12, π/6, π/4)	15484	7298	3956	2270	1353	846	554
(7π/12, π/4, π/6)	5967	3779	2408	1474	897	563	370
(7π/12, π/3, π/6)	–3194	359	888	684	443	281	183
(π/2, π/12, π/6)	25966	11030	5555	3081	1818	1132	742
(π/2, π/6, π/3)	18630	8341	4385	2485	1478	923	606
(π/2, π/4, π/6)	9115	4819	2835	1688	1021	640	420
			μ_x				
(π/12, π/6, π/3)	–357	293	245	156	96	61	41
(π/12, π/4, π/6)	-3266	–1435	–717	–390	–228	–141	–91
(π/12, π/3, π/6)	–2594	–1058	–513	–278	–164	–103	–66
(π/12, 5π/12, π/6)	–576	102	127	81	47	28	19
(π/6, π/4, π/3)	533	1171	797	475	285	178	117
(π/6, π/3, π/4)	–318	632	488	296	176	109	72
(π/6, 5π/12, π/3)	1221	1604	1038	607	360	224	147
(π/4, π/3, π/6)	–68	787	577	348	207	128	84
(π/4, 5π/12, π/6)	1781	1833	1149	667	395	245	160
(π/3, 5π/12, π/6)	1212	1361	866	506	301	187	122
(7π/12, π/12, π/6)	–5770	–3703	–2114	–1206	–718	–449	–294
(7π/12, π/6, π/4)	–6702	–4239	–2408	–1370	–815	–509	–333
(7π/12, π/4, π/6)	–8207	–5076	–2865	–1626	–965	–603	–394
(7π/12, π/3, π/6)	–7218	–4500	–2547	–1447	–860	–536	–351
(π/2, π/12, π/6)	–2862	–1628	–891	–499	–295	–184	–120
(π/2, π/6, π/3)	–2825	–1609	–882	–495	–292	–182	–119
(π/2, π/4, π/6)	–5580	–3180	–1747	–982	–581	–362	–237

Spherical Tensor Analysis of Dipole Components

$$\mu_1^{0} = \mu_Z$$

$$\mu_1^{\pm 1} = \mp(\mu_X \pm i\,\mu_Y)$$

Tensor components are expressed in terms of the spherical harmonics of the orientation angles for molecular axes and for the intermolecular vector:

$$\Delta\mu^{M}(\mathbf{r}^{A}, \mathbf{r}^{B}, \mathbf{R}) = (4\pi)^{3/2}\, 3^{-1/2} \sum \mathbf{D}_{\lambda^A\lambda^B\Lambda L}(r^{A}, r^{B}, R)$$
$$\times\, Y_{\lambda^A}^{m_A}(\Omega^{A})\, Y_{\lambda^B}^{m_B}(\Omega^{B})\, Y_{L}^{M-m}(\Omega^{R})$$
$$\times \langle\, \lambda^A\, \lambda^B\, m_A\, m_B \mid \Lambda\, m \,\rangle \langle\, \Lambda\, L\, m\, (M-m) \mid 1\, M \,\rangle$$

Summation runs over λ^A, λ^B, Λ, L, m_A, m_B, and m

X. Li and K. L. C. Hunt, *J. Chem. Phys*. **100**, 9276 (1994).
J. Van Kranendonk, *Physica* **24**, 347 (1958).
J. D. Poll and J. L. Hunt, *Can. J. Phys*. **54**, 461 (1976); **59**, 1448 (1981).

Dipole Expansion Coefficients $D_{\lambda_A \lambda_B \Lambda L}$ (in a.u., multiplied by 10^6) for $H_2 ... H_2$, $r_A = r_B = 1.449$ a.u.
Comparison with results of Meyer, Borysow, and Frommhold (MBF) and Fu, Zheng, and Borysow (FZB).

R(a.u.)	4.0	5.0	6.0	7.0	8.0	9.0	10.0
D_{2021}							
This work	9983	2123	407	73	13	4	2
MBF	10401	2190	429	84	20	7	–
FZB	10385	2184	427	83	19	6	–
D_{2023}							
This work	–20065	–8076	–3725	–1950	–1124	–695	–455
MBF	–19967	–7953	–3688	–1939	–1119	–692	–
FZB	–19949	–7946	–3685	–1938	–1118	–692	–
D_{2233}							
This work	2020	977	514	289	171	107	70
MBF	1992	949	498	280	166	104	–
FZB	1991	949	498	279	166	104	–
D_{4043}							
This work	690	180	42	9	2	0	0
MBF	–	–	–	–	–	–	–
FZB	–	–	–	–	–	–	–
D_{4045}							
This work	–845	–283	–97	–37	–16	–8	–4
MBF	–1523	–450	–135	–47	–19	–9	–
FZB	–1517	–447	–134	–46	–19	–9	–

Long-range Polarization Effects from Perturbation Theory

Polarization Mechanisms through order R^{-7}:

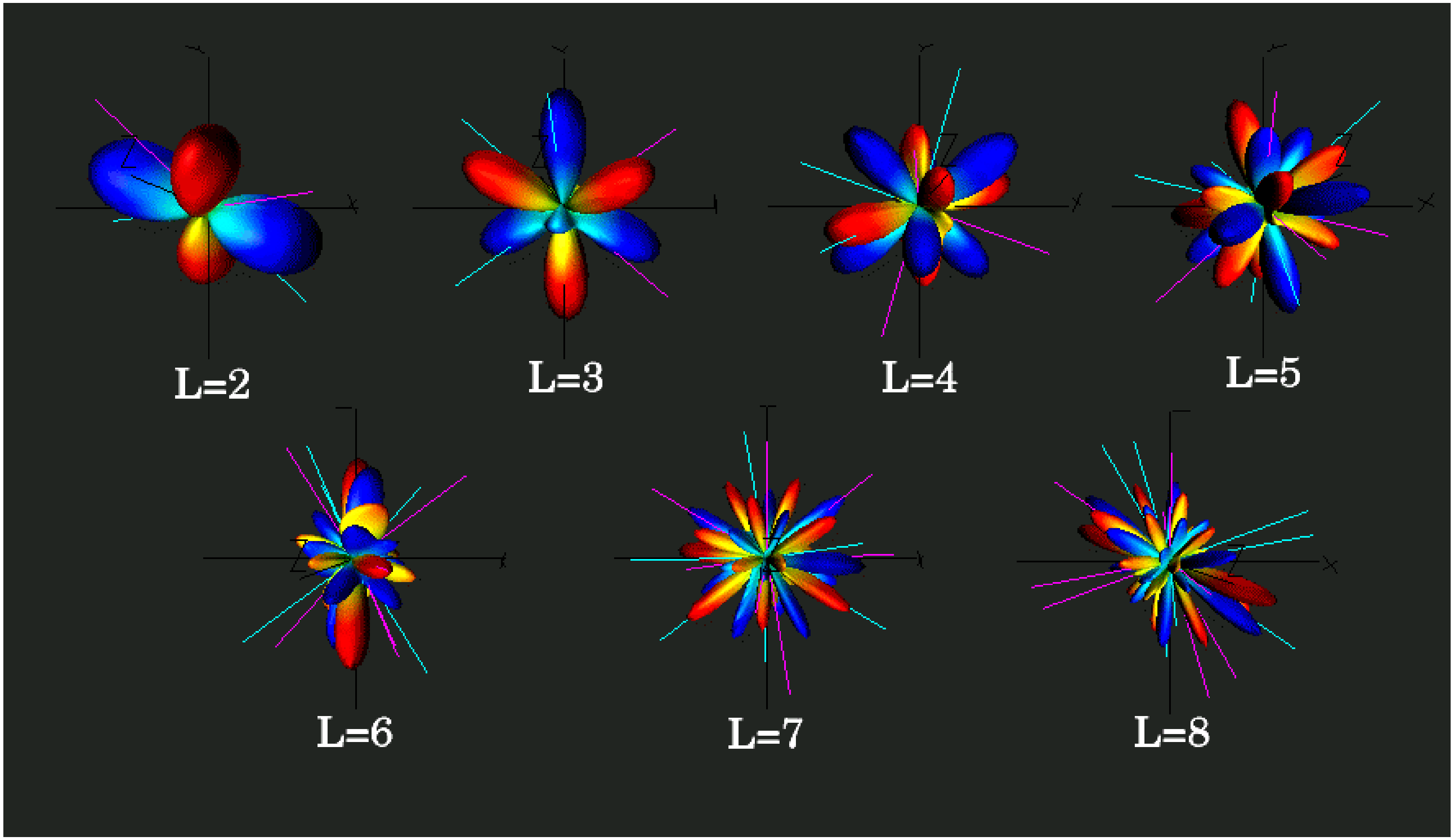
- Quadrupolar Induction
- Hexadecapolar Induction
- Back-induction
- Non-uniform Field Effects (E-tensor terms)
- Van der Waals Dispersion

Dispersion Dipole:

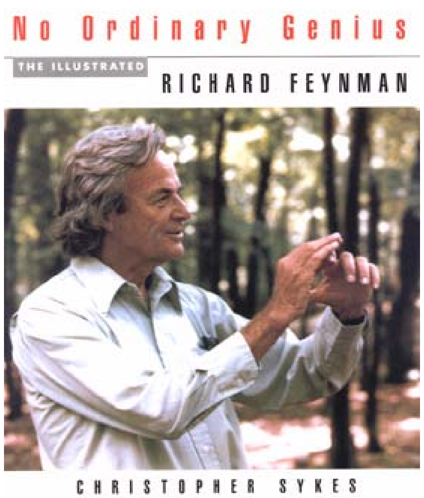
$$\mu_\phi = (\hbar/3\pi)\,(1 - \mathscr{P}^{AB}) \int_0^\infty d\omega\; \alpha^A_{\beta\gamma}(i\omega)\; B^B_{\alpha\phi,\delta\varepsilon}(0, i\omega)\; T_{\alpha\beta}(\mathbf{R})\; T_{\gamma\delta\varepsilon}(\mathbf{R})$$

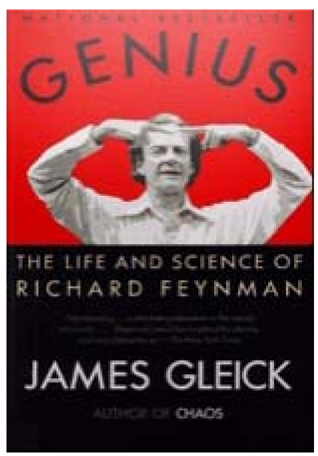
J. E. Bohr and K. L. C. Hunt, *J. Chem. Phys*. **87**, 3821 (1987).
X. Li and K. L. C. Hunt, *J. Chem. Phys*. **100**, 9276 (1994).

Multipoles Acting as Field Sources



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.

Spherical Tensor Analysis

Examples:

Quadrupole-induced Dipole

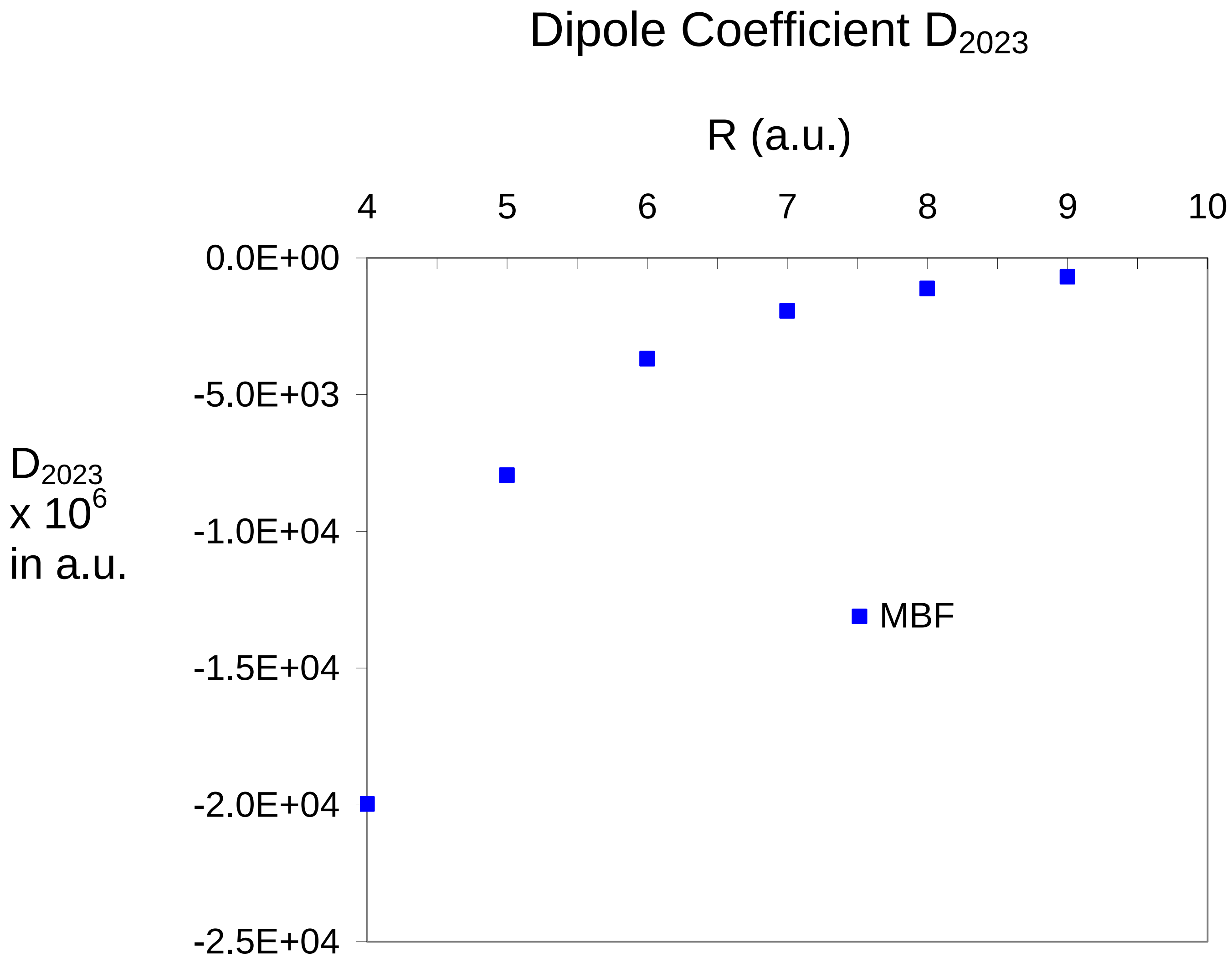
$$D_{2\lambda_B\Lambda 3} = \sqrt{2}\,(-1)^{\lambda+1}\,(2\lambda+1)^{1/2} \begin{Bmatrix} 3 & 2 & 1 \\ \lambda^B & 1 & \Lambda \end{Bmatrix} \Theta^A(2,0)\,\alpha^B(\lambda^B,0)\,R^{-4}$$

Dispersion Dipole Coefficients

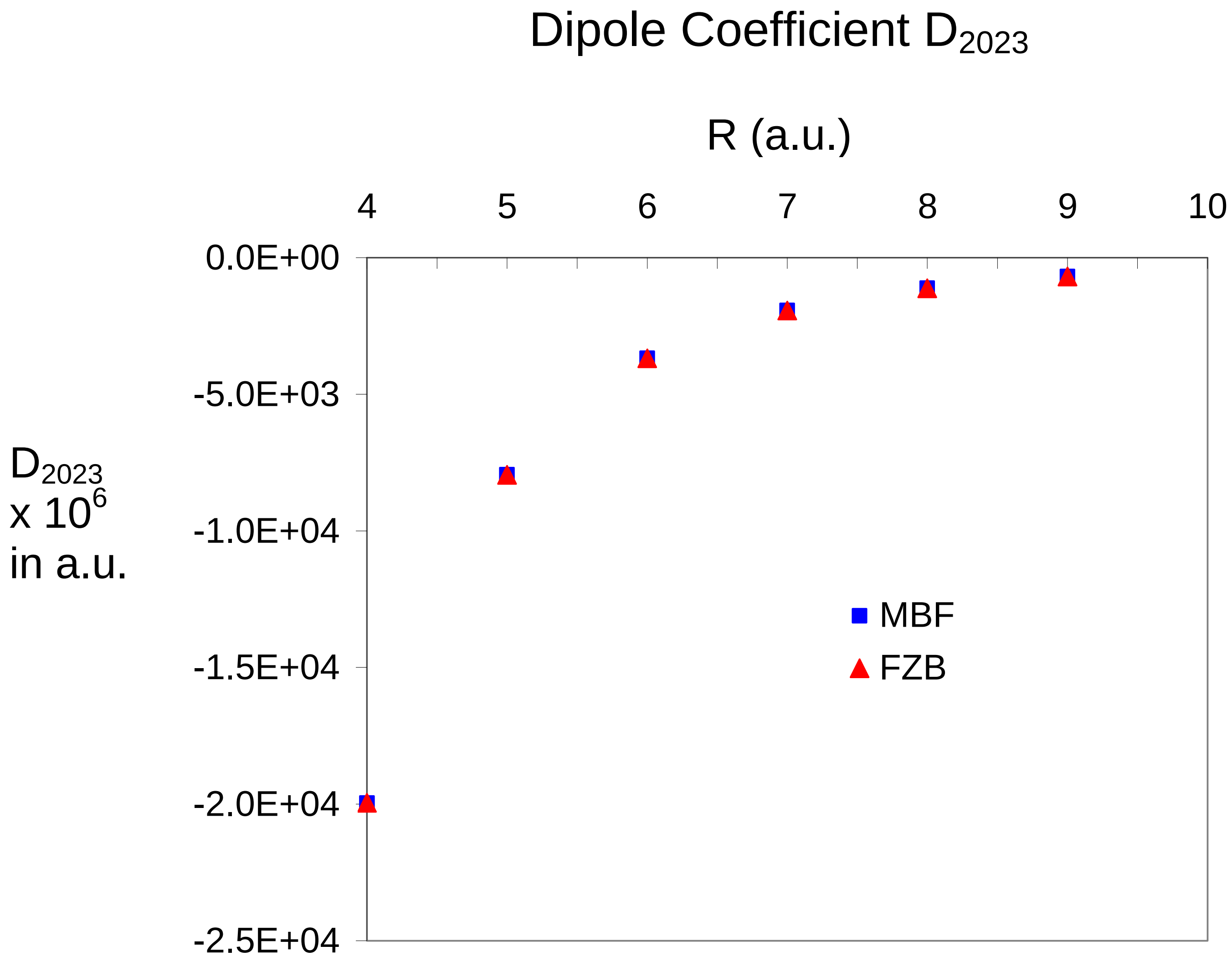
$$D_{\lambda_A\lambda_B\Lambda L} = 15\sqrt{14}\,\hbar/\pi\,R^{-7}\;\langle 2\,3\,0\,0\,|\,L\,0\rangle\,[1+(-1)^{\lambda+1}\mathscr{P}^{AB}]\,\Sigma_{a,g}\,(-1)^{a+g+\lambda^A}$$

$$(2g+1)\,\Pi_{a\lambda}\int_0^\infty d\omega\,B^{(a)}(\lambda^A,0;0,i\omega)\,\alpha^B(\lambda^B,0;i\omega)$$

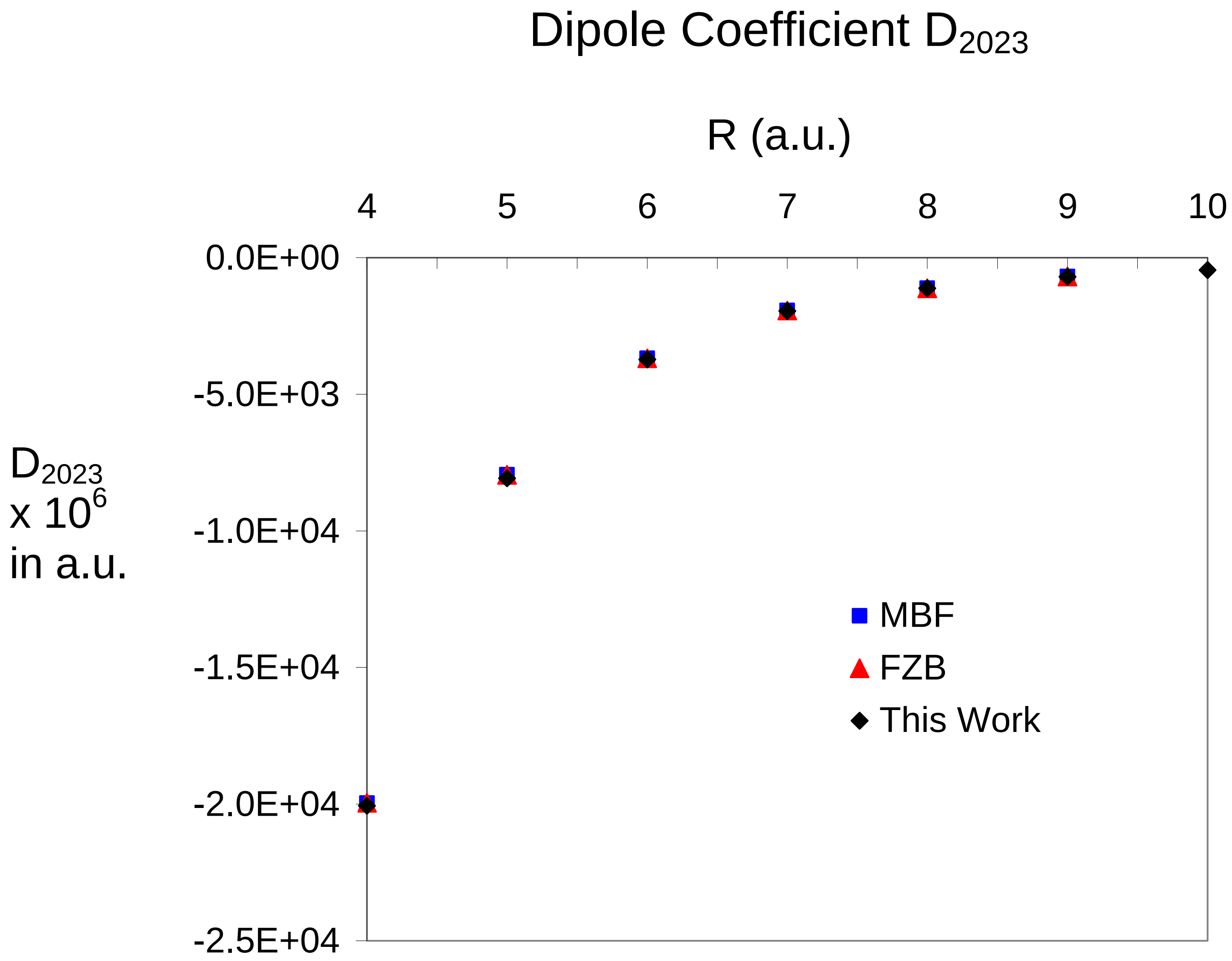
$$\begin{Bmatrix} 1 & 2 & 1 \\ 1 & 3 & 2 \\ \lambda^B & L & g \end{Bmatrix} \begin{Bmatrix} g & \lambda^A & 1 \\ a & 1 & 2 \end{Bmatrix} \begin{Bmatrix} \lambda^B & \lambda^A & \Lambda \\ 1 & L & g \end{Bmatrix}$$



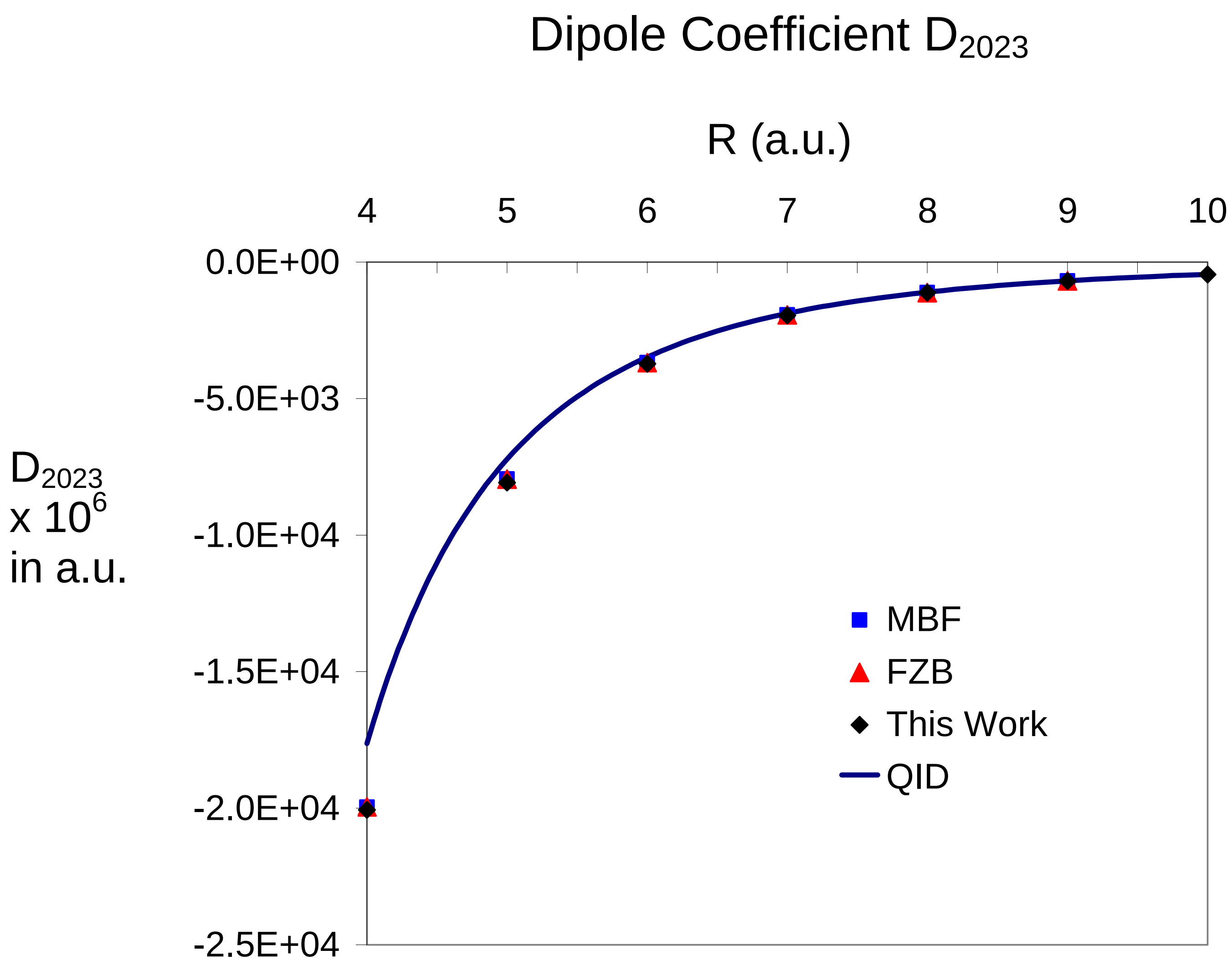
Dipole Coefficient D_{2023}
R (a.u.)
4
5
6
7
8
9
10
0.0E+00
-5.0E+03
-1.0E+04
-1.5E+04
-2.0E+04
-2.5E+04
D_{2023} x 10^6 in a.u.
MBF

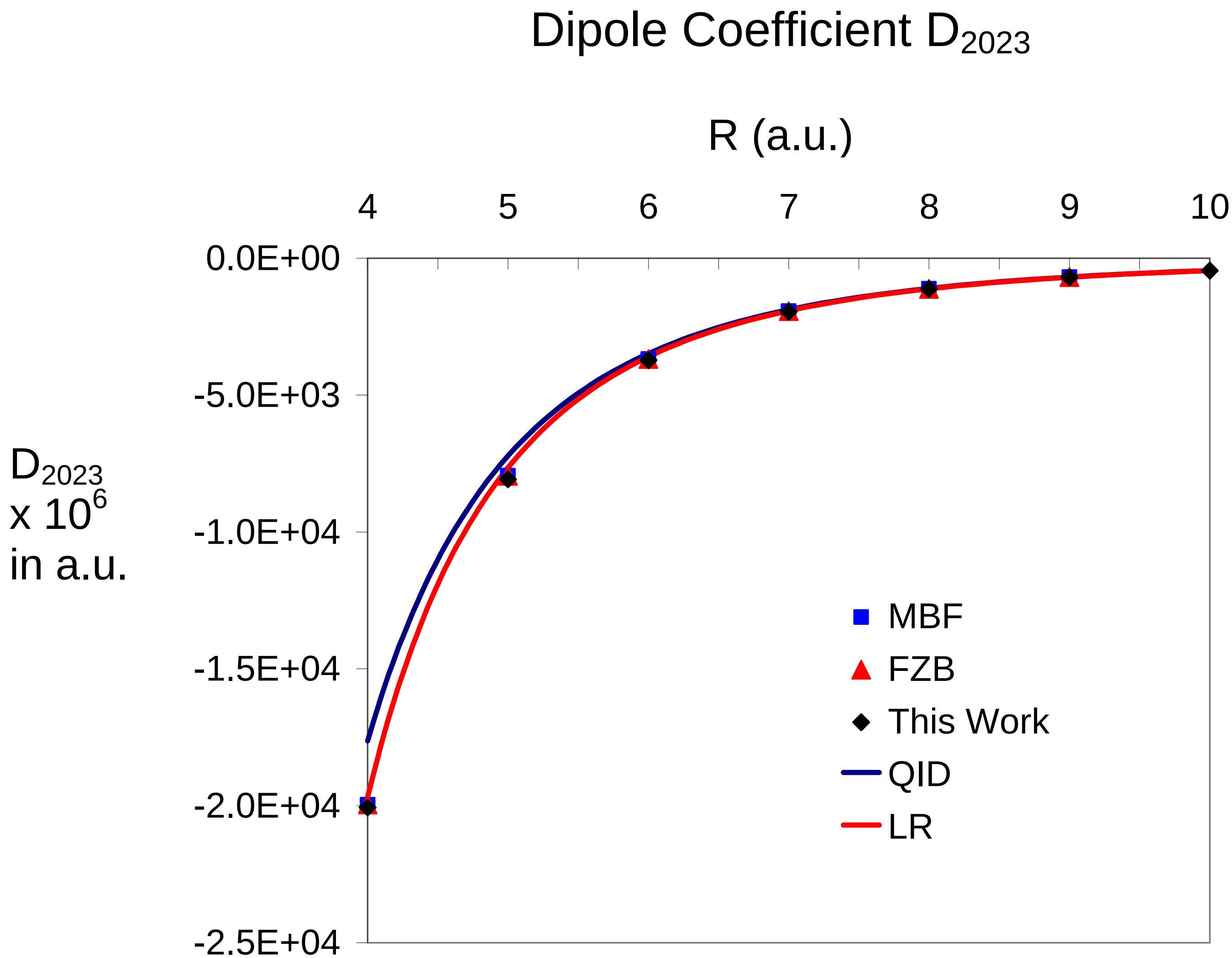


Dipole Coefficient D2023
R (a.u.)
4
5
6
7
8
9
10
0.0E+00
-5.0E+03
-1.0E+04
-1.5E+04
-2.0E+04
-2.5E+04
D2023
x 10
6
in a.u.
MBF
FZB

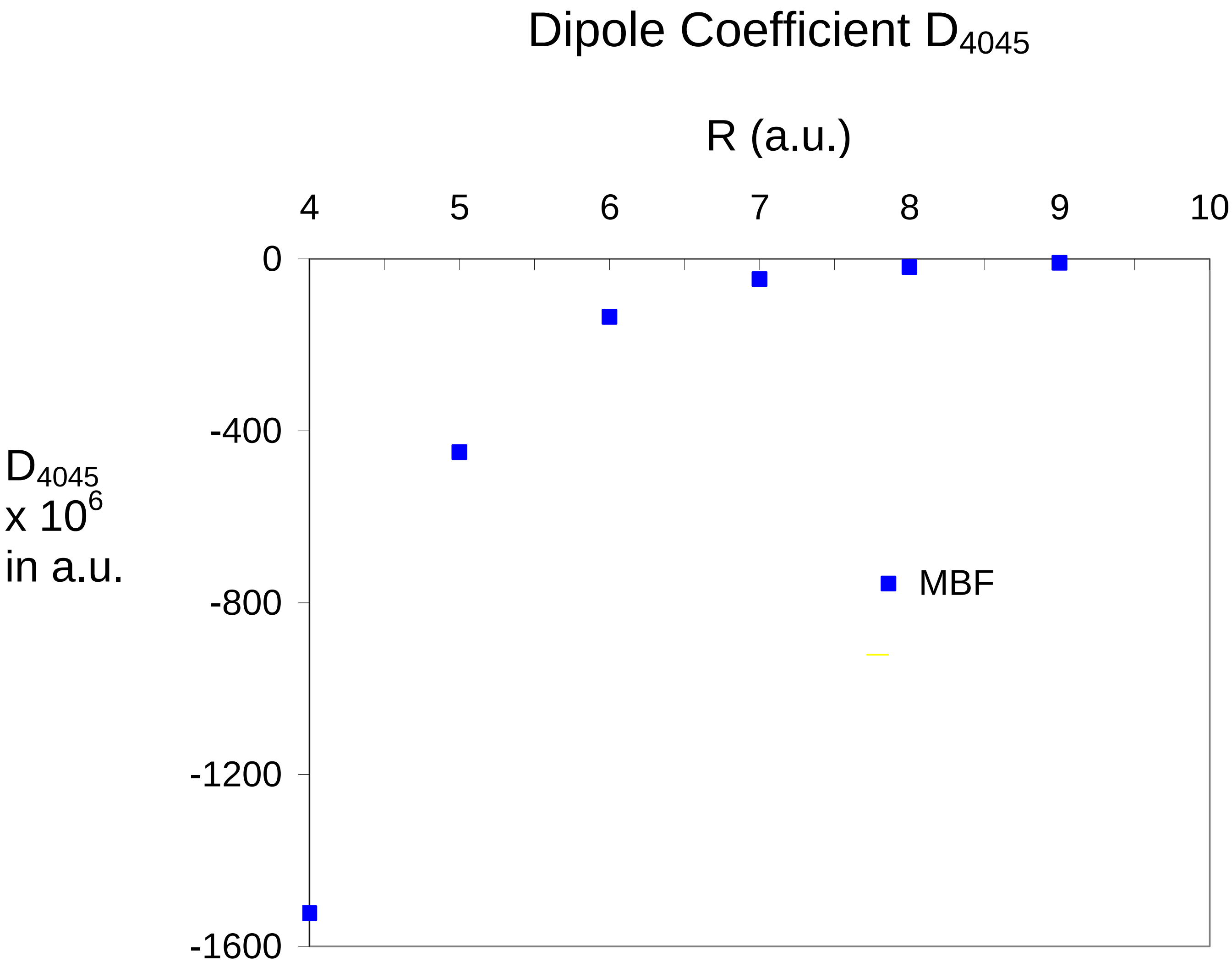


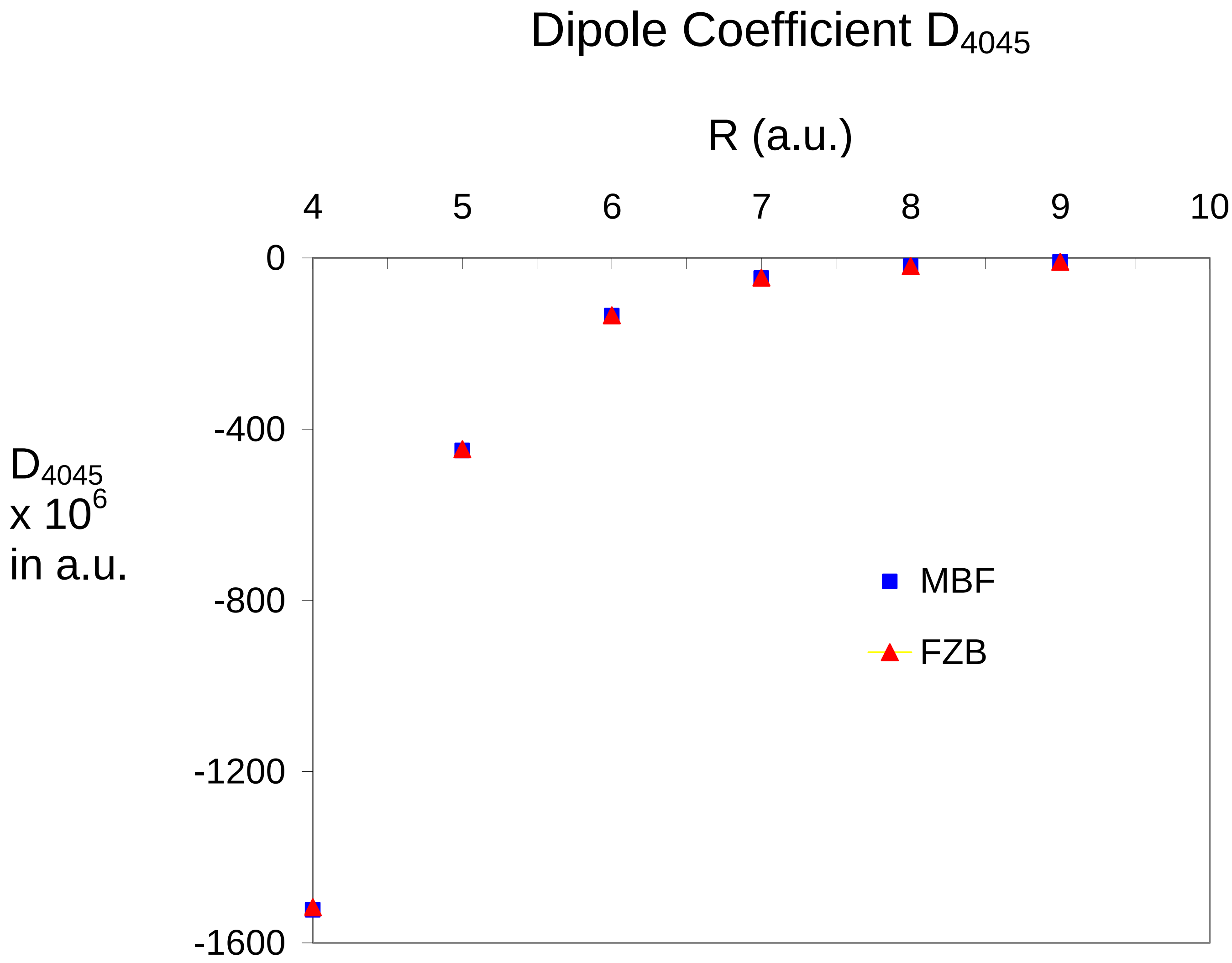
Dipole Coefficient D2023
R (a.u.)
4
5
6
7
8
9
10
0.0E+00
-5.0E+03
-1.0E+04
-1.5E+04
-2.0E+04
-2.5E+04
D2023
x 10^6
in a.u.
MBF
FZB
This Work


Dipole Coefficient D_{2023}
R (a.u.)
4
5
6
7
8
9
10
0.0E+00
-5.0E+03
-1.0E+04
-1.5E+04
-2.0E+04
-2.5E+04
D_{2023} x 10^6 in a.u.
MBF
FZB
This Work
QID

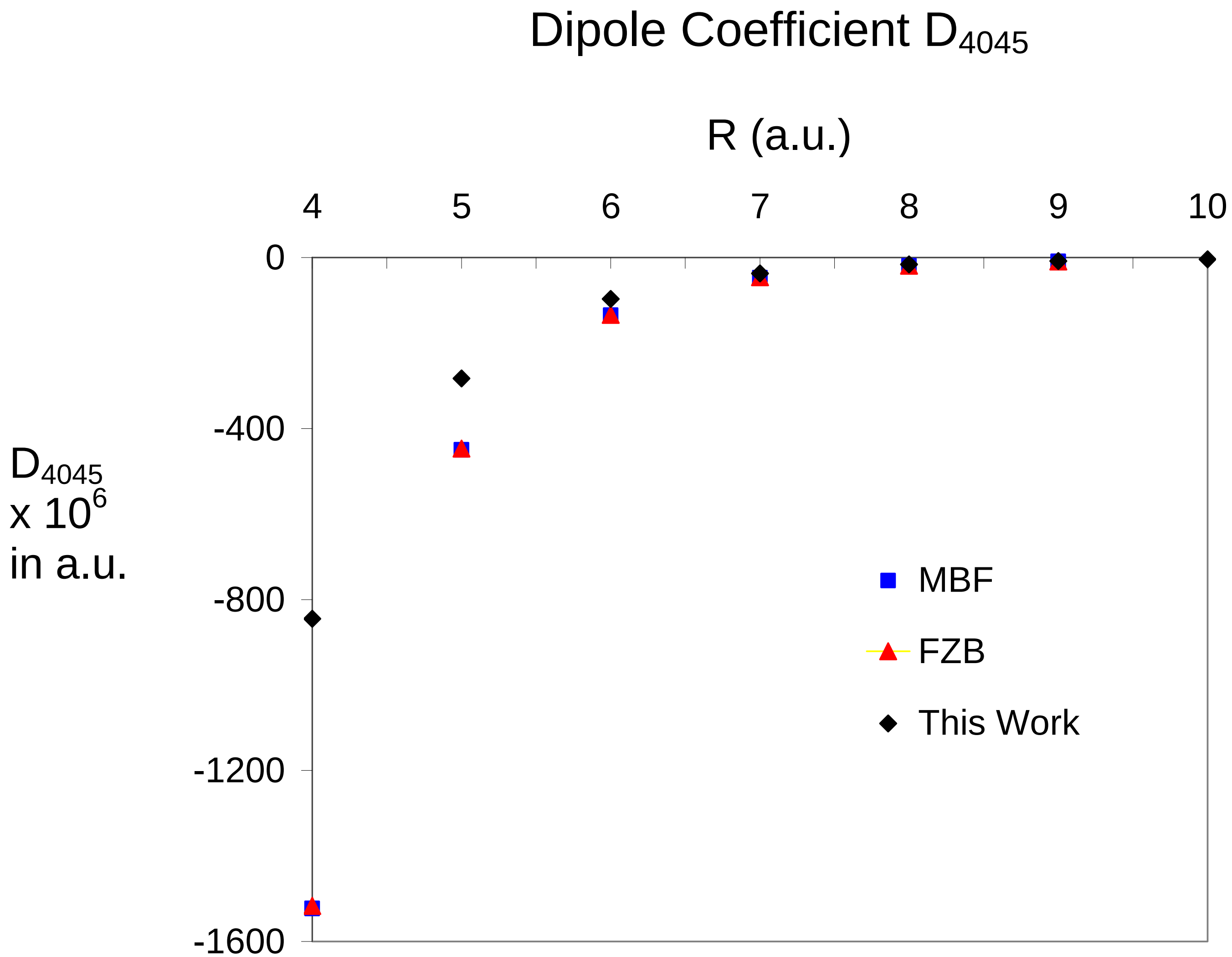


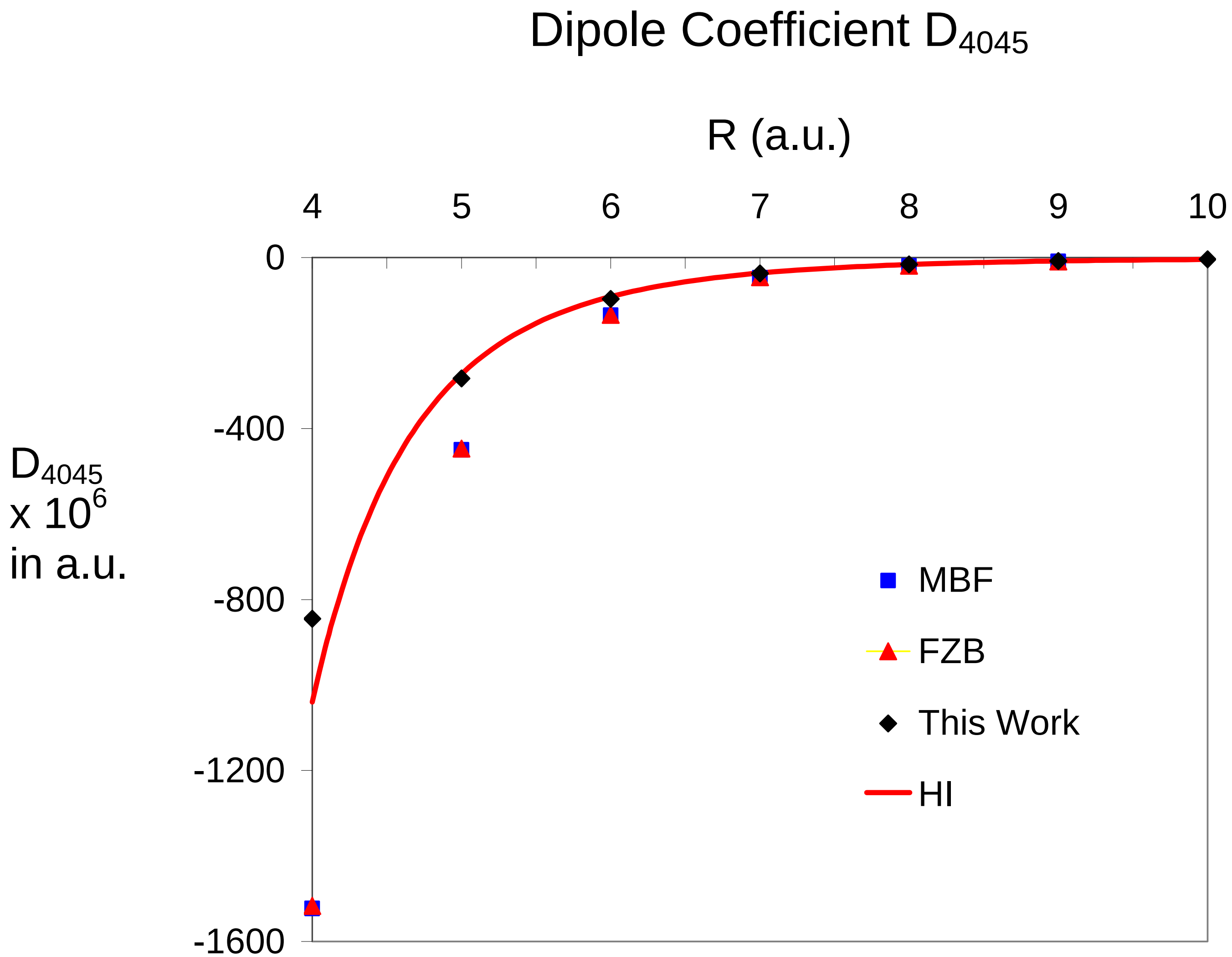
Dipole Coefficient D_{2023}
R (a.u.)
4
5
6
7
8
9
10
0.0E+00
-5.0E+03
-1.0E+04
-1.5E+04
-2.0E+04
-2.5E+04
D_{2023} x 10^6 in a.u.
MBF
FZB
This Work
QID
LR


Dipole Coefficient D_{4045}
R (a.u.)
4
5
6
7
8
9
10
0
-400
-800
-1200
-1600
D_{4045}
x 10^6
in a.u.
MBF



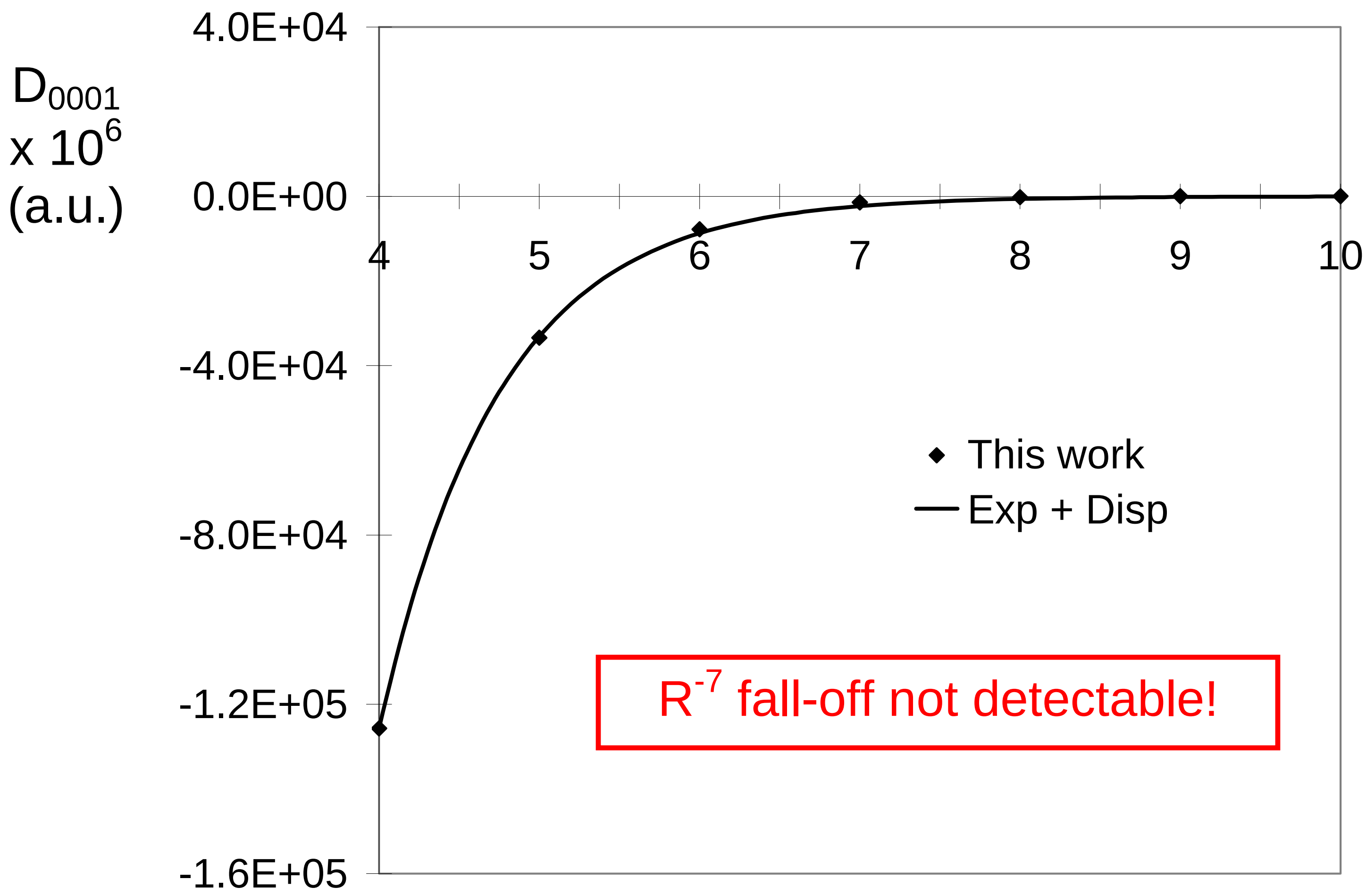
Dipole Coefficient D4045
R (a.u.)
4
5
6
7
8
9
10
0
-400
-800
-1200
-1600
D4045
x 10^6
in a.u.
MBF
FZB


Dipole Coefficient D4045
R (a.u.)
4
5
6
7
8
9
10
0
-400
-800
-1200
-1600
D4045
x 10^6
in a.u.
MBF
FZB
This Work

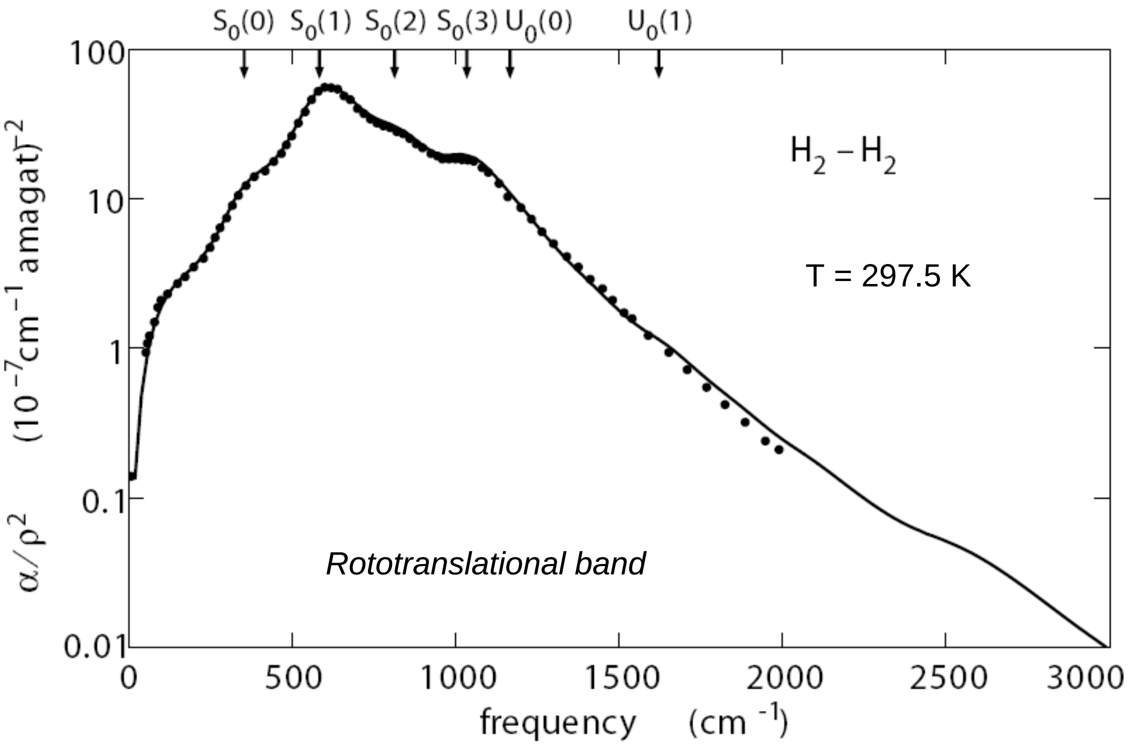


Dipole Coefficient D4045
R (a.u.)
4
5
6
7
8
9
10
0
-400
-800
-1200
-1600
D4045
x 10^6
in a.u.
MBF
FZB
This Work
HI

Dipole Expansion Coefficient D_{0001}

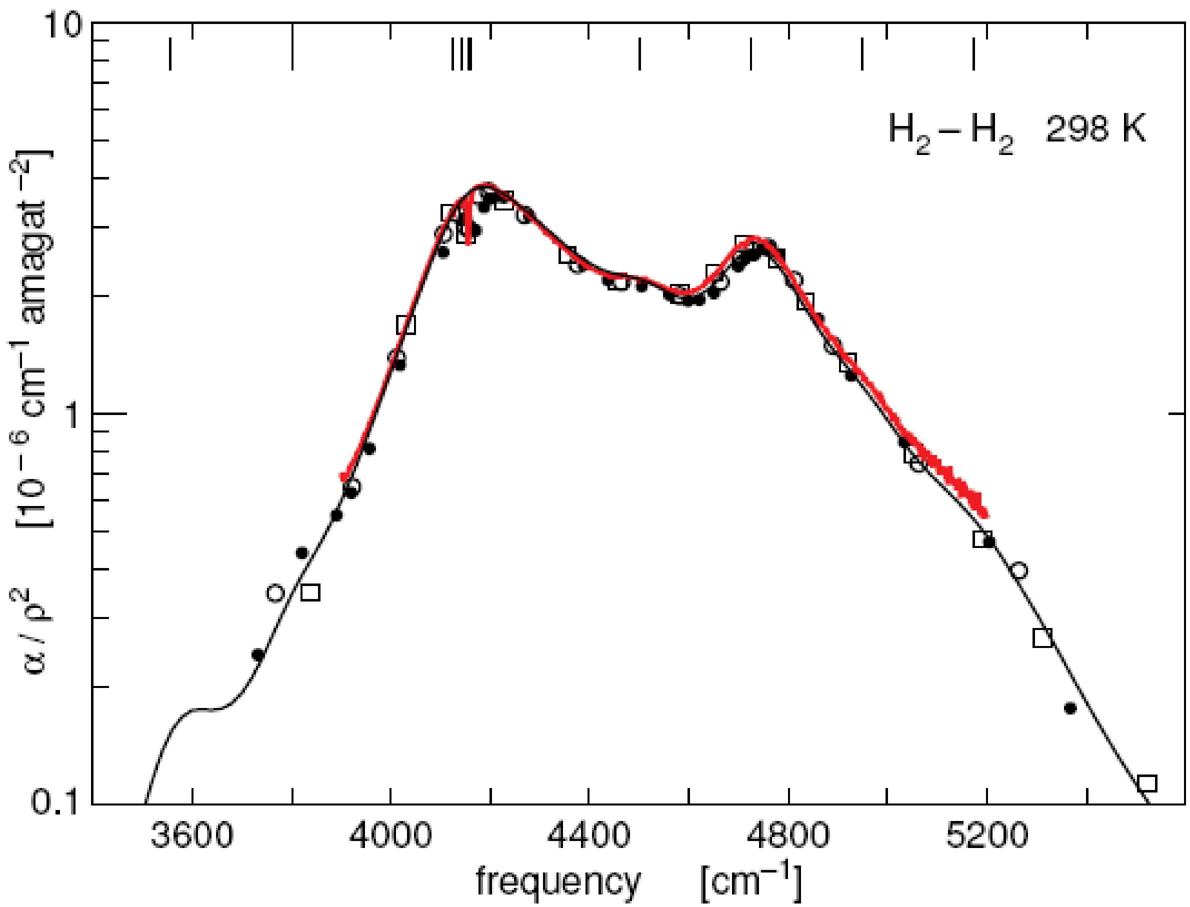


Comparison of Calculated Absorption Spectrum of $H_2 \ldots H_2$ with Experiment



Calculations (solid line): X. Li, K. L. C. Hunt, F. Wang, M. Abel, and L. Frommhold, *Int. J. Spectroscopy* **2010**, 371201 (2010).
Laboratory Measurements (•): G. Bachet, E. R. Cohen, P. Dore, and G. Birnbaum, *Can. J. Phys*. **61**, 591-603 (1983).

Collision-Induced Absorption Spectrum of $H_2 ... H_2$: Fundamental Band



Calculations: M. Abel, L. Frommhold, F. Wang, X. Li, and K. L. C. Hunt, to be submitted to *J. Chem. Phys*. (2010).

● A. Watanabe, Ph.D. thesis, University of Toronto (1964).

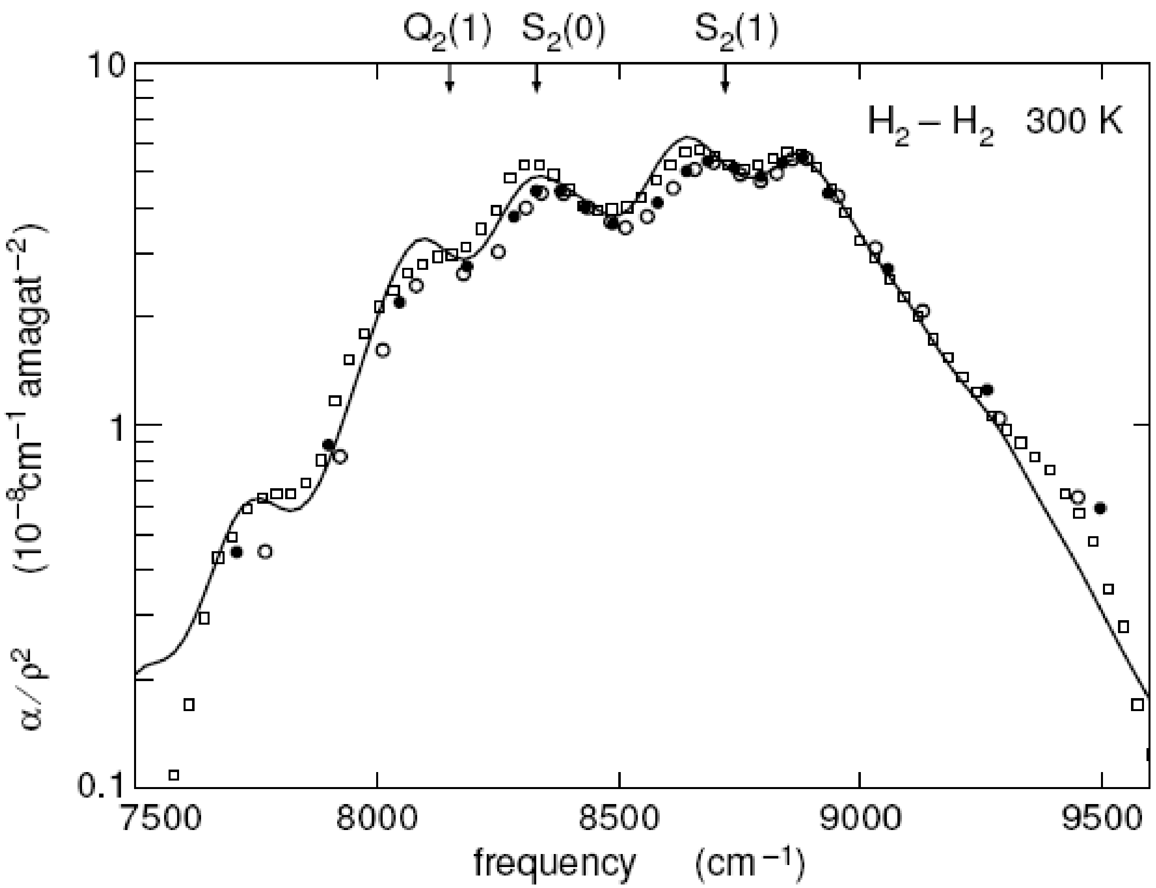
○ J. L. Hunt and H. L. Welsh, *Can. J. Phys*. **42**, 873 (1964).

■ S. P. Reddy, G. Varghese, and R. D. G. Prasad, *Phys. Rev. A* **15**, 975 (1977).

□ C. Brodbeck, Nguyen van Thanh, A. Jean-Louis, J. P. Bouanich, and L. Frommhold, *Phys. Rev. A* **50**, 484 (1994).

— A. Watanabe, *Can. J. Phys*. **49**, 1320 (1971).

Collision-induced First Overtone of $H_2 \ldots H_2$



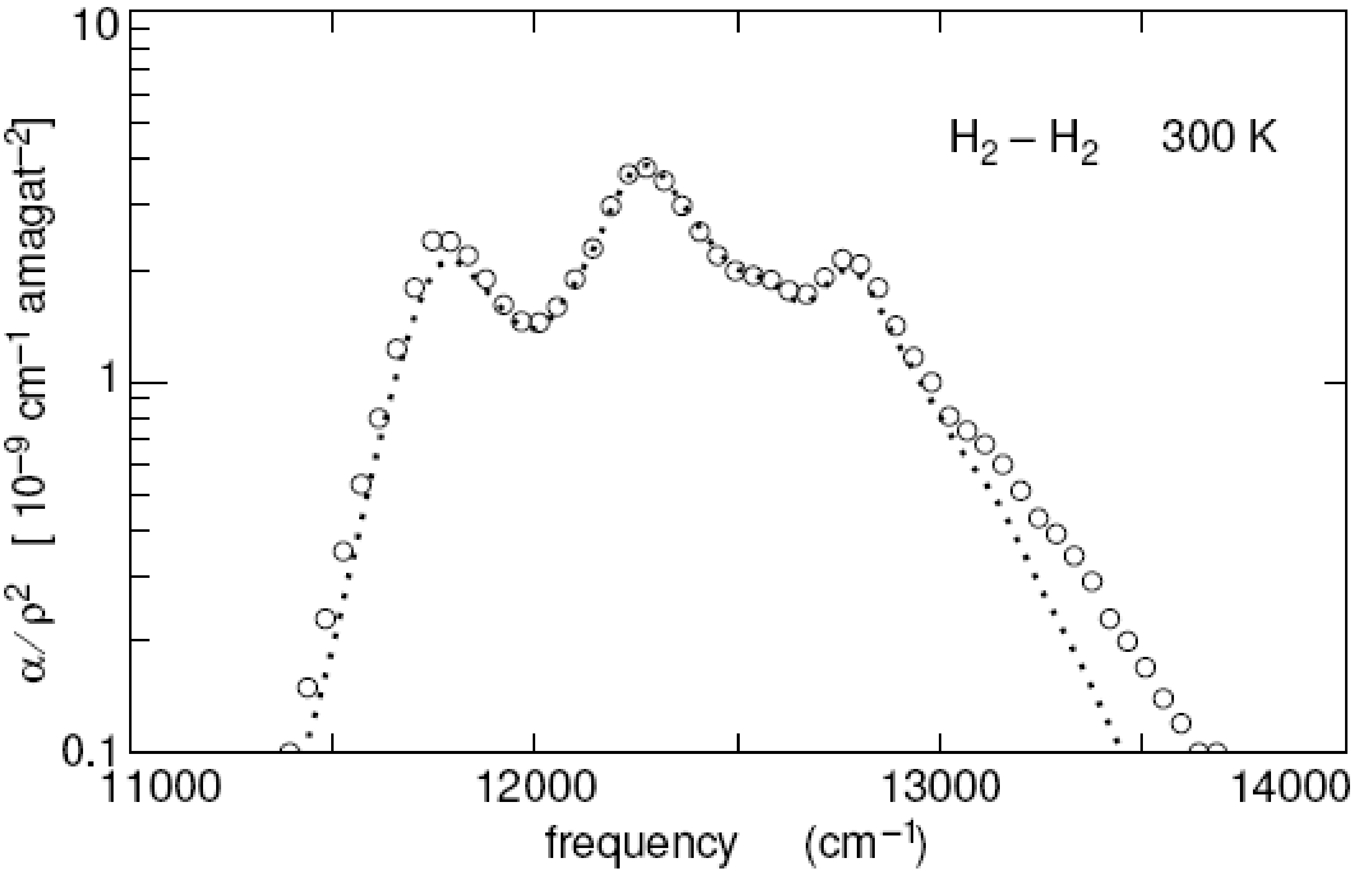
Calculations: M. Abel, L. Frommhold, F. Wang, X. Li, and K. L. C. Hunt, to be submitted to *J. Chem. Phys*. (2010).

□ Communication to L. Frommhold.

○ A. Watanabe, *Can. J. Phys*. **49**, 1320 (1971).

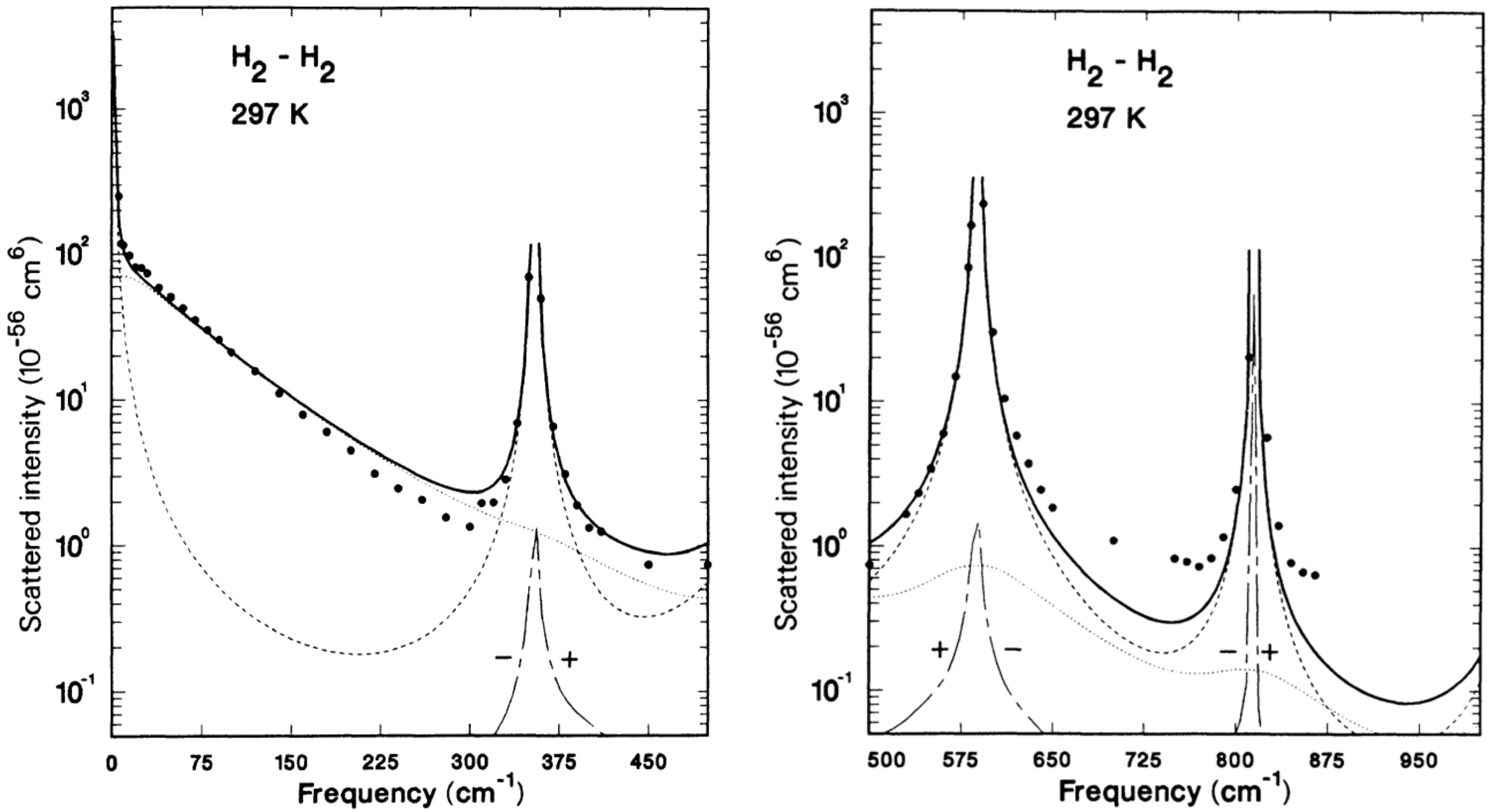
● A. Watanabe, Ph.D. thesis, University of Toronto (1964).

Collision-induced Second Overtone of $H_2 \ldots H_2$



Calculations: M. Abel, L. Frommhold, F. Wang, X. Li, and K. L. C. Hunt, to be submitted to *J. Chem. Phys*. (2010).
○ C. Brodbeck, J.-P. Bouanich, Nguyen-Van-Thanh, Y. Fu, and A. Borysow, *J. Chem. Phys*. **110**, 4750 (1999).

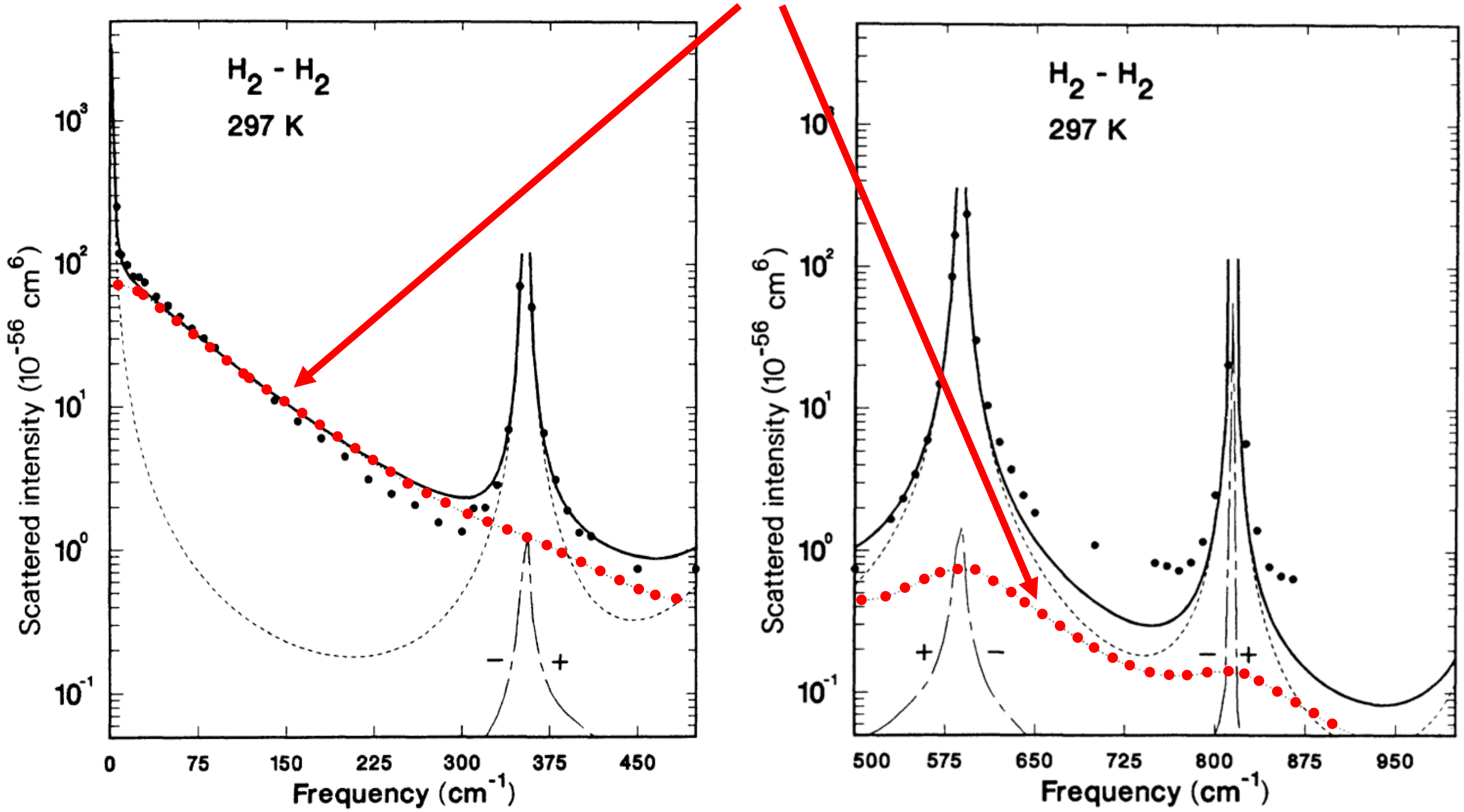
Roto-translational Raman Scattering by $H_2 \ldots H_2$



A. Borysow and M. Moraldi, *Phys. Rev. A* **40**, 1251 (1989).

Roto-translational Raman Scattering by H_2 . . . H_2

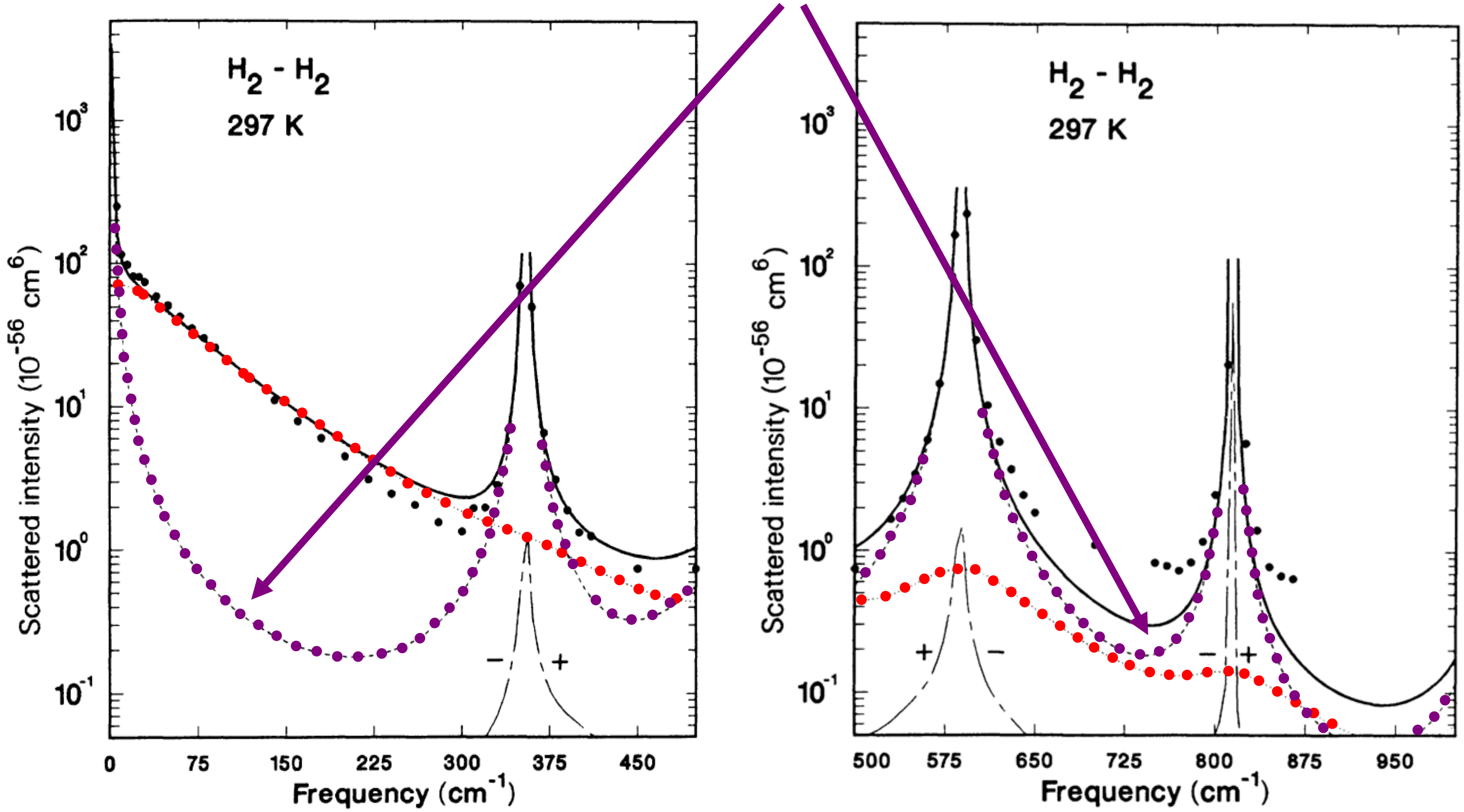
Collision-Induced Scattering



A. Borysow and M. Moraldi, *Phys. Rev. A* **40**, 1251 (1989).

Roto-translational Raman Scattering by H_2 . . . H_2

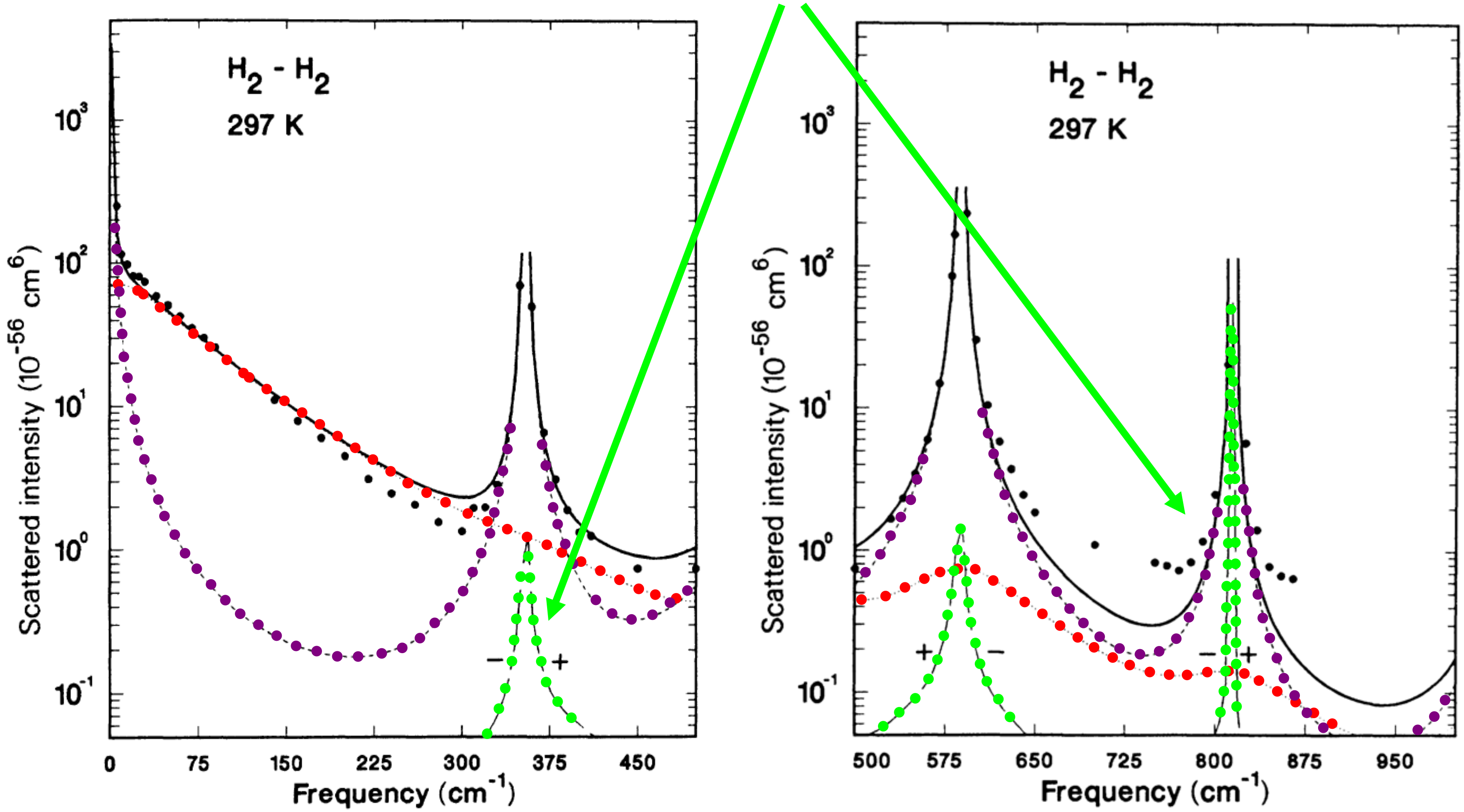
Pressure Broadening



A. Borysow and M. Moraldi, *Phys. Rev. A* **40**, 1251 (1989).

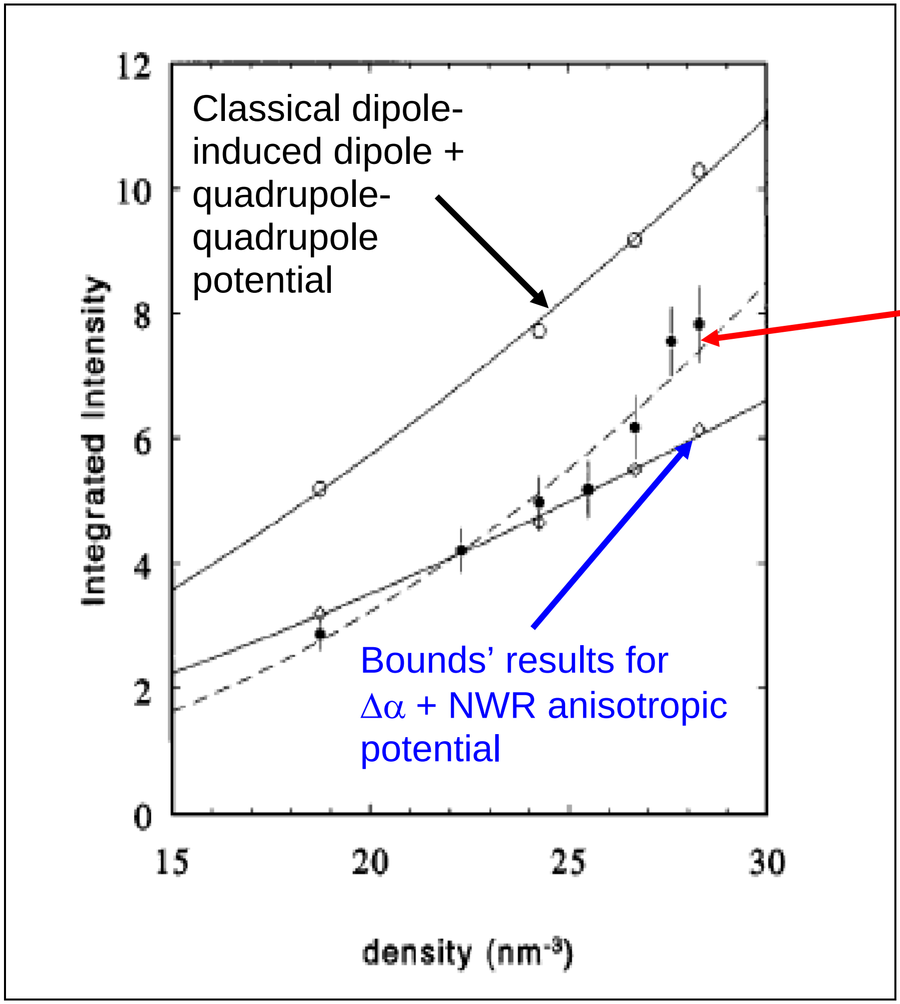
Roto-translational Raman Scattering by $H_2 \ldots H_2$

Cross Terms



A. Borysow and M. Moraldi, *Phys. Rev. A* **40**, 1251 (1989).

Double transition intensities, $S_0(0) + S_0(0)$:



F. Barocchi, M. Moraldi, M. Santoro, L. Ulivi, and M. Zoppi, *Phys. Rev. B* **55**, 12223 (1997).

Experiment

Intensity is overestimated by the DID model
80% at 18.73 nm^{-3}
30-35% at 28.30 nm^{-3}
and 30.89 nm^{-3}

Bounds' results underestimate the density by 20% near 30 nm^{-3}

Slope of intensity vs. density is too low

Ab initio Calculations

CCSD(T), MOLPRO 2000; CR-CC(2,3), GAMESS

Basis: aug-cc-pV5Z (spdf)

Finite-field approach

$\Delta\alpha$: 80-120 different field directions and strengths (0.001 to 0.01 a.u.) for each pair geometry

Fit to quartic polynomial in field: E, μ, α, β, γ

Extract quadratic term α

Subtract isolated-molecule contributions yielding $\Delta\alpha$

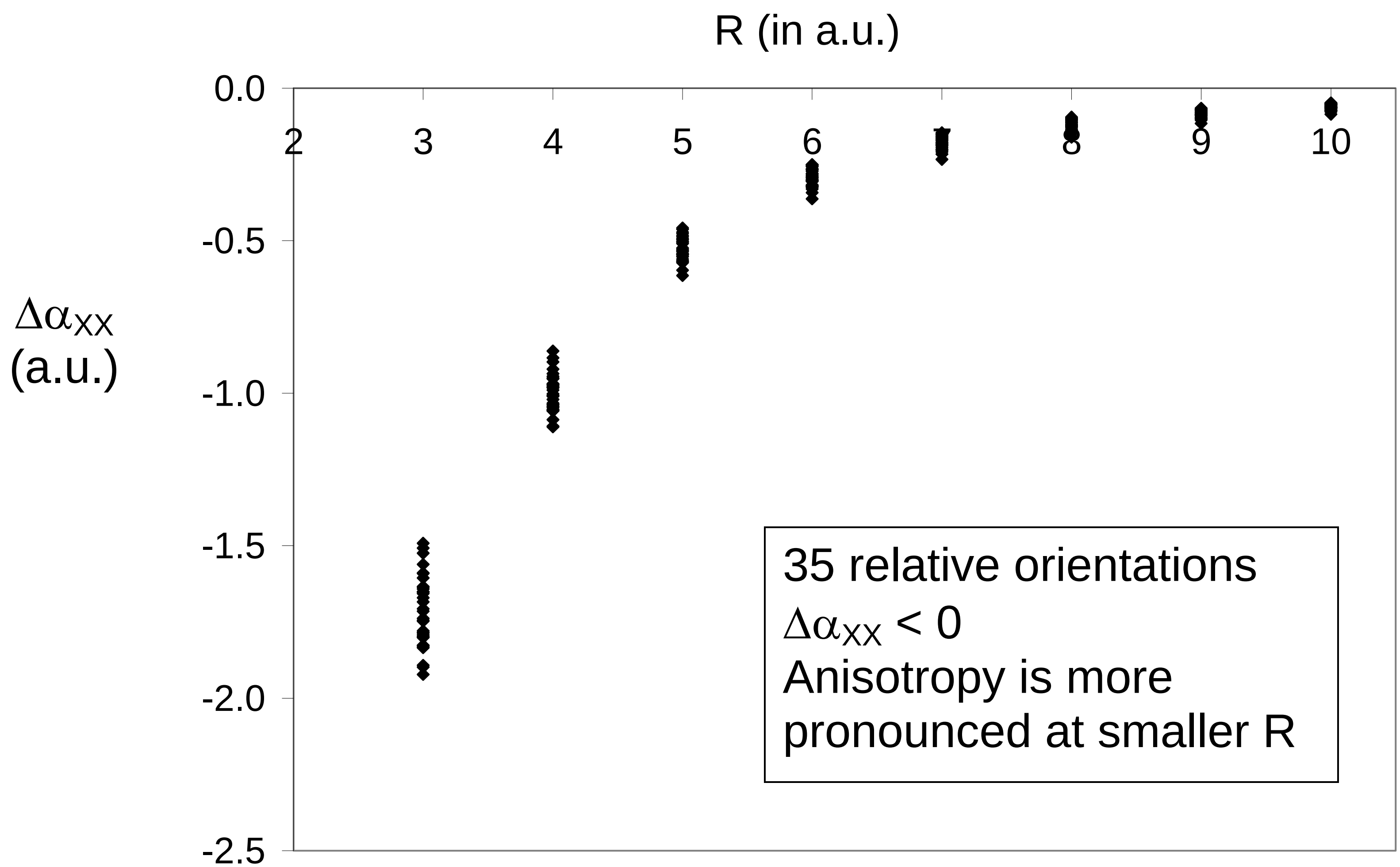
35 pair orientations (now), range of separations (R) from 2-10 a.u. (3-10 a.u. for co-linear molecules)

$\Delta\mu$: 6 field strengths in each direction, analytic fit

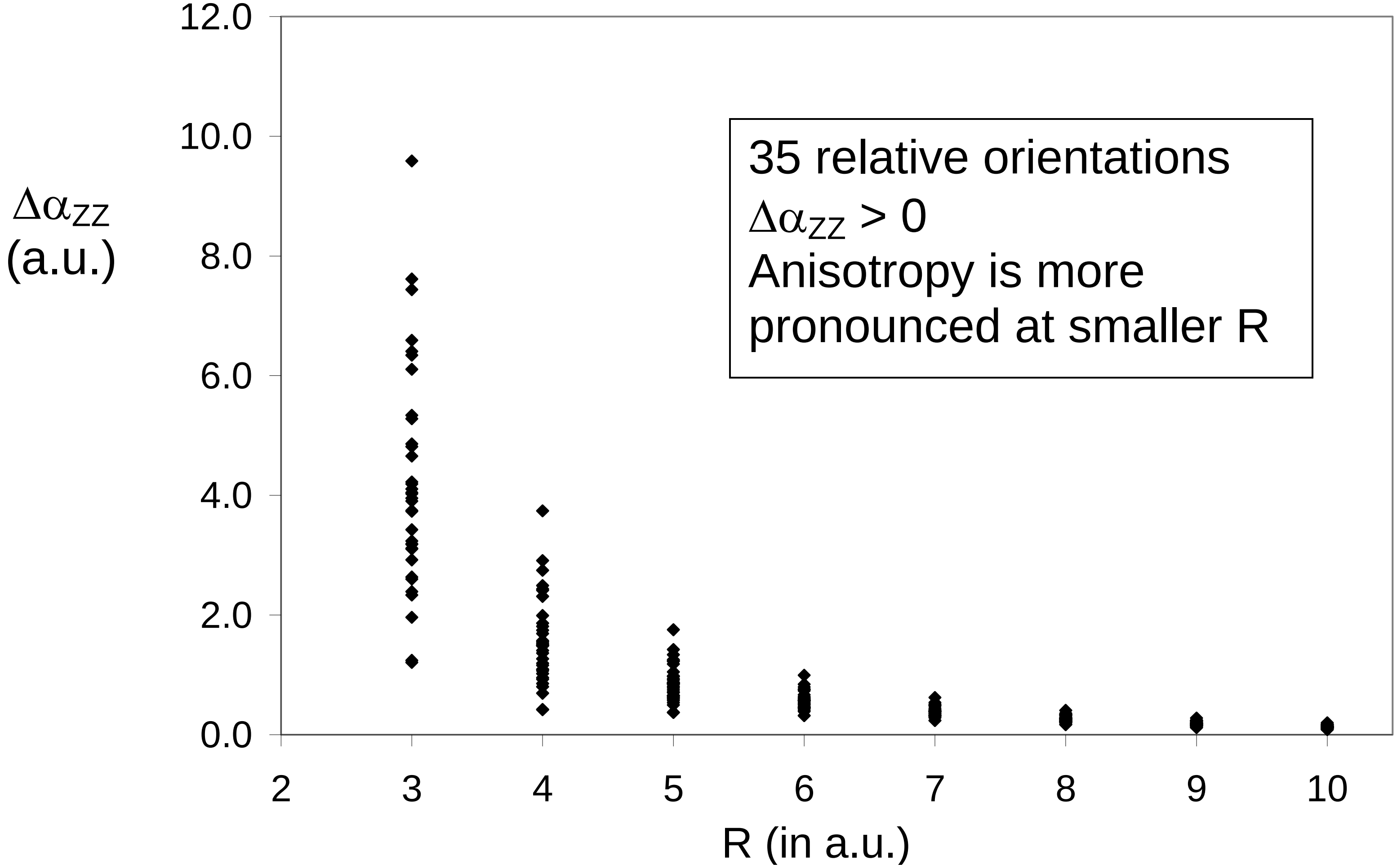
17 pair orientations, range of separations from 4-10 a.u.

X. Li, C. Ahuja, J. F. Harrison, and K. L. C. Hunt, *J. Chem. Phys*. **126**, 214302 (2007); X. Li, K. L. C. Hunt, F. Wang, M. Abel, and L. Frommhold, *Int. J. Spectroscopy*, accepted (2009).

Collision-Induced Polarizability $\Delta\alpha_{XX}$ for H_2 . . . H_2



Collision-Induced Polarizability $\Delta\alpha_{ZZ}$ for H_2 . . . H_2



Long-Range Models for $\Delta\alpha$: Physical Effects

- First-order and second-order dipole-induced-dipoles (DID)

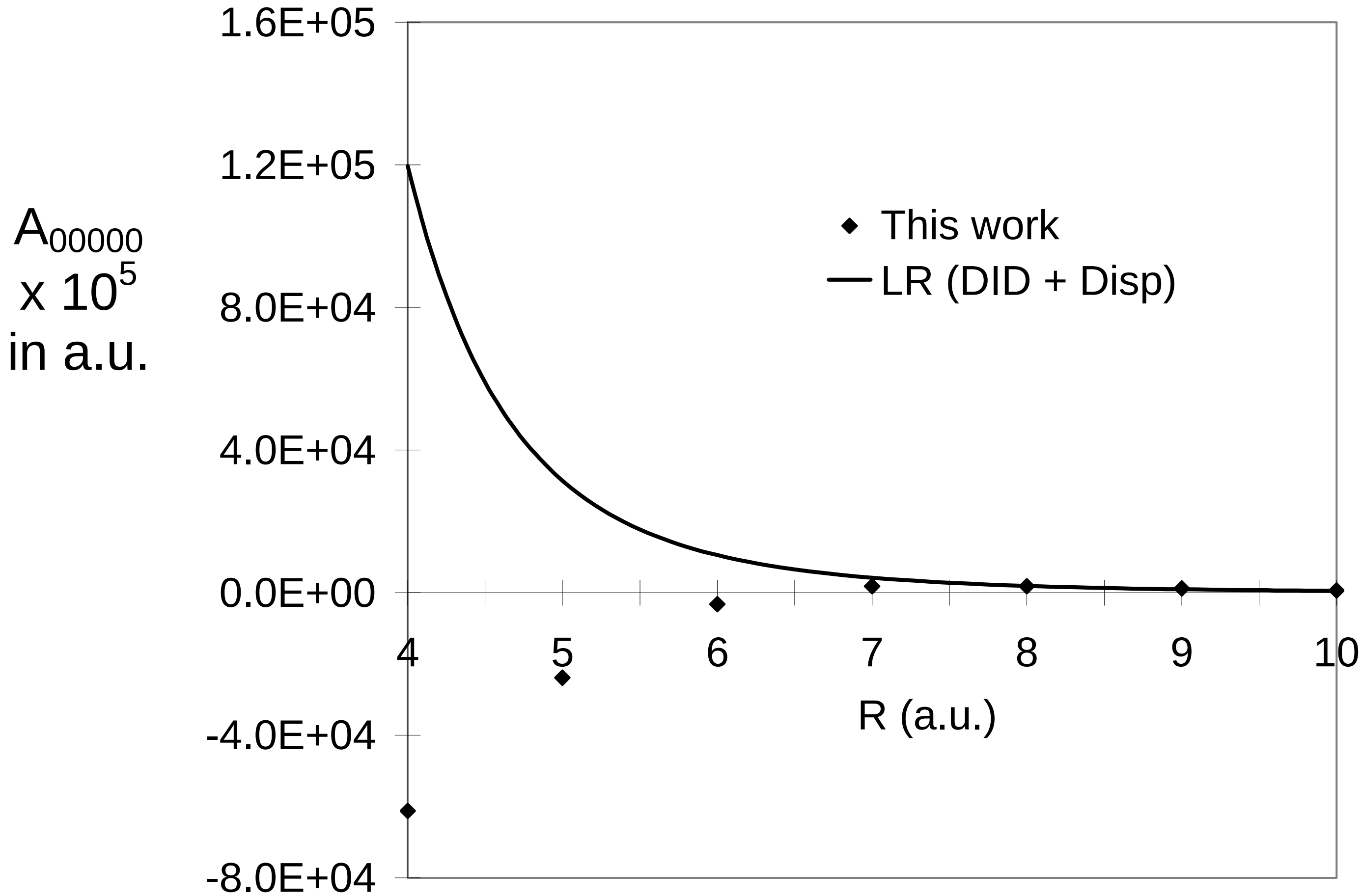
- Higher multipole induction ← E-tensor
- Nonuniform field effects ←

- Hyperpolarization B-tensor, Θ^0

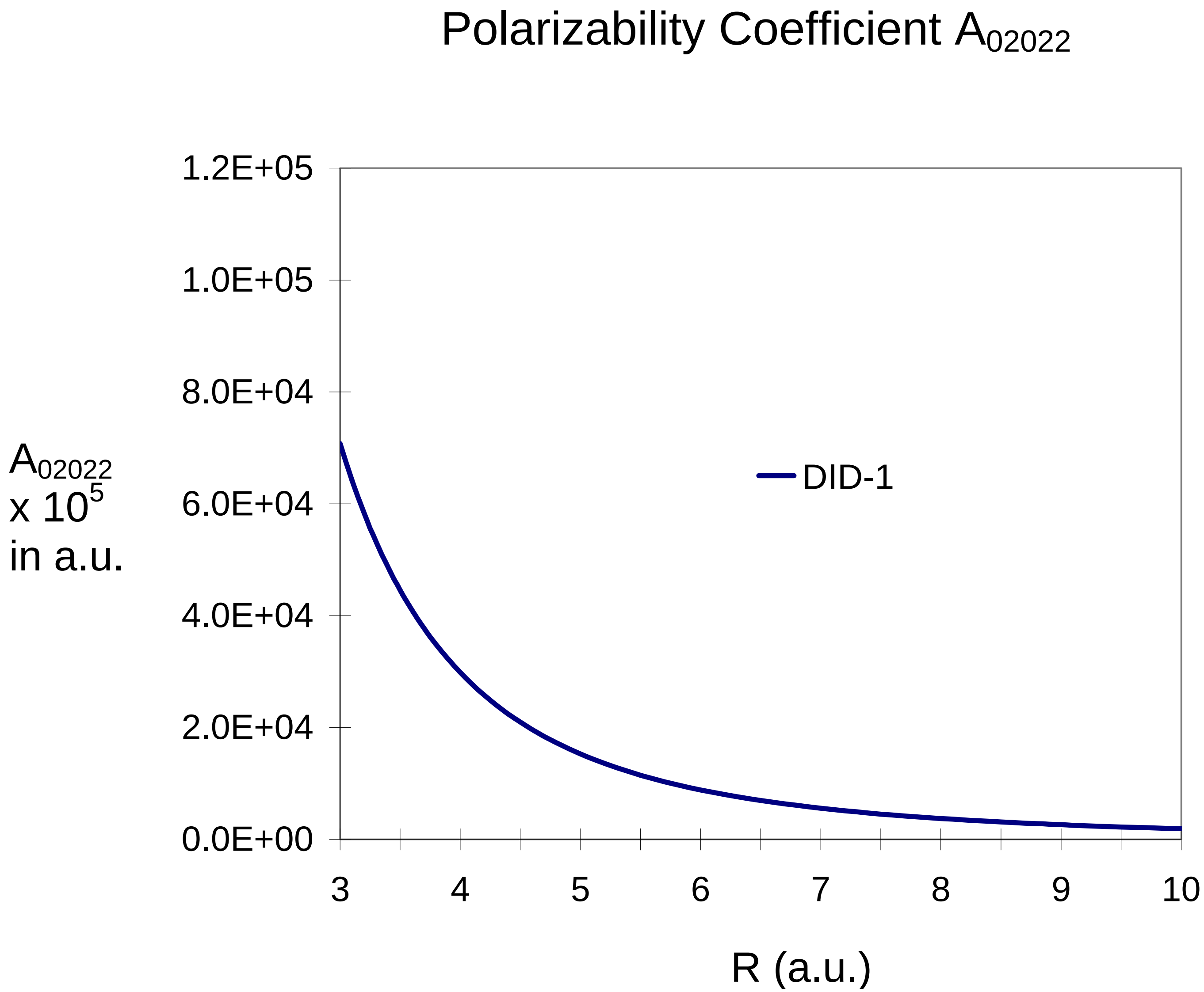
- Dispersion:
  Hyperpolarization
  Field-induced fluctuation correlations

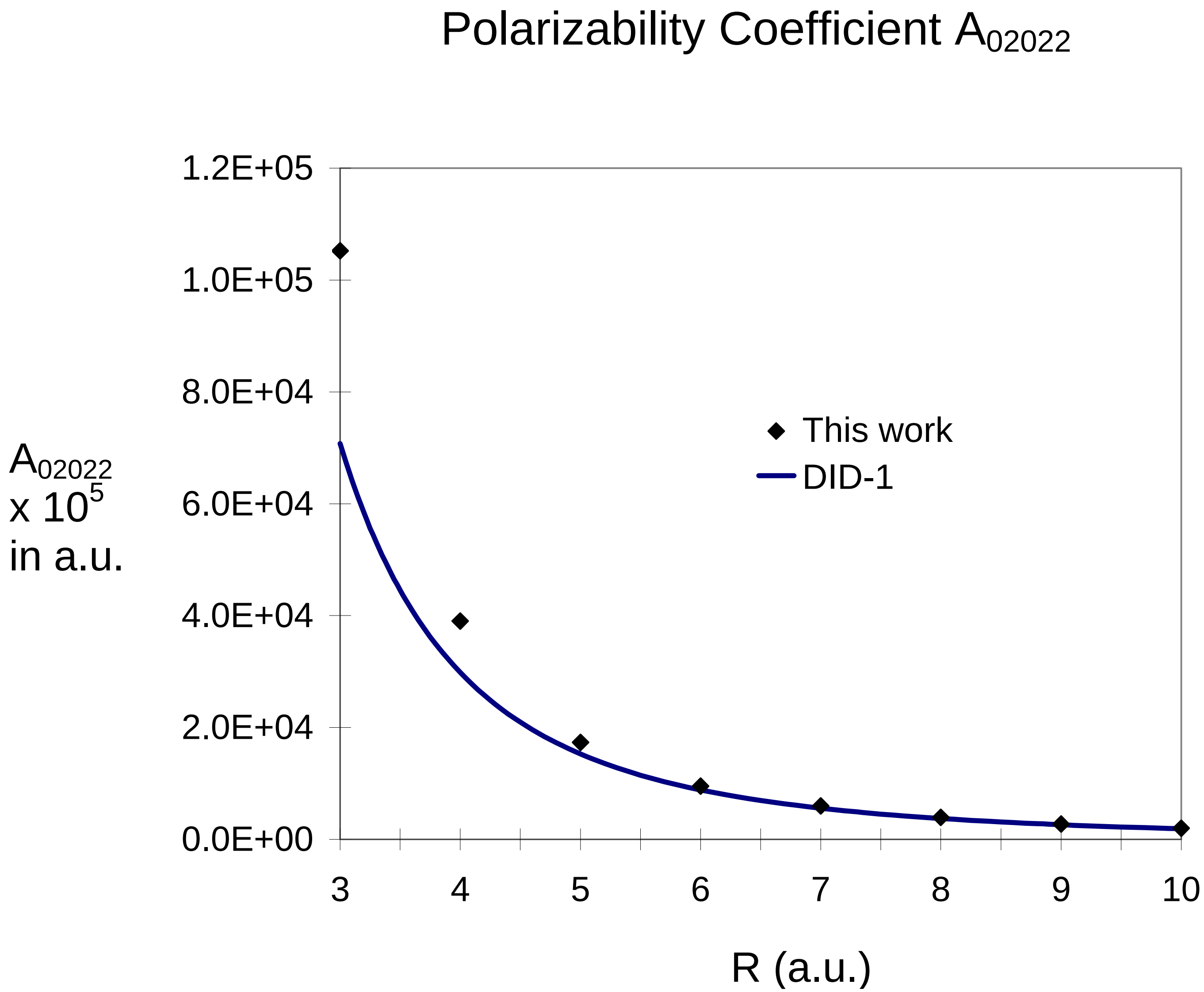
Spherical tensor analysis gives A coefficients

Polarizability Coefficient A_{00000}

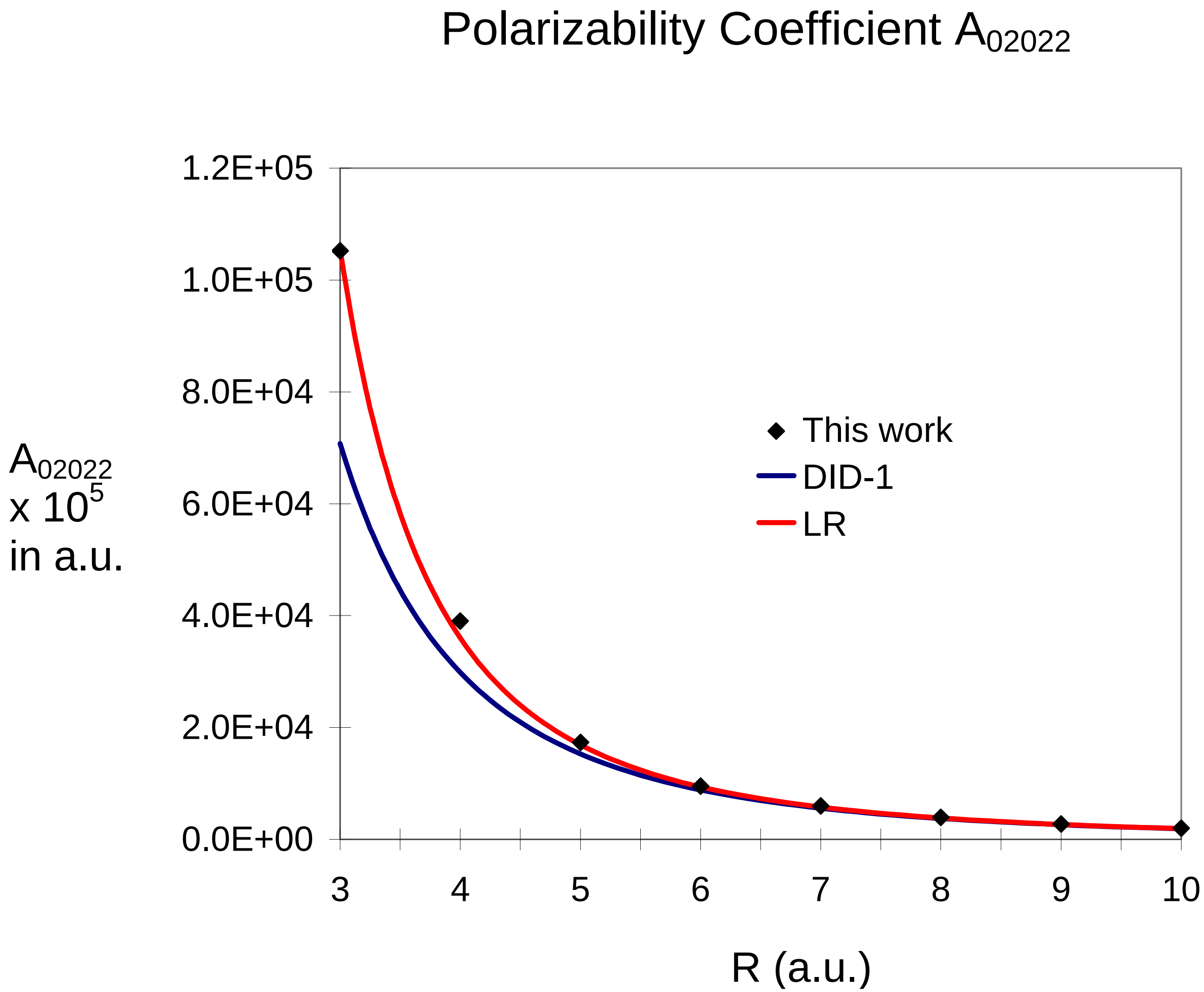


Limiting slope of log-log plot at long range (*ab initio* data): –5.83

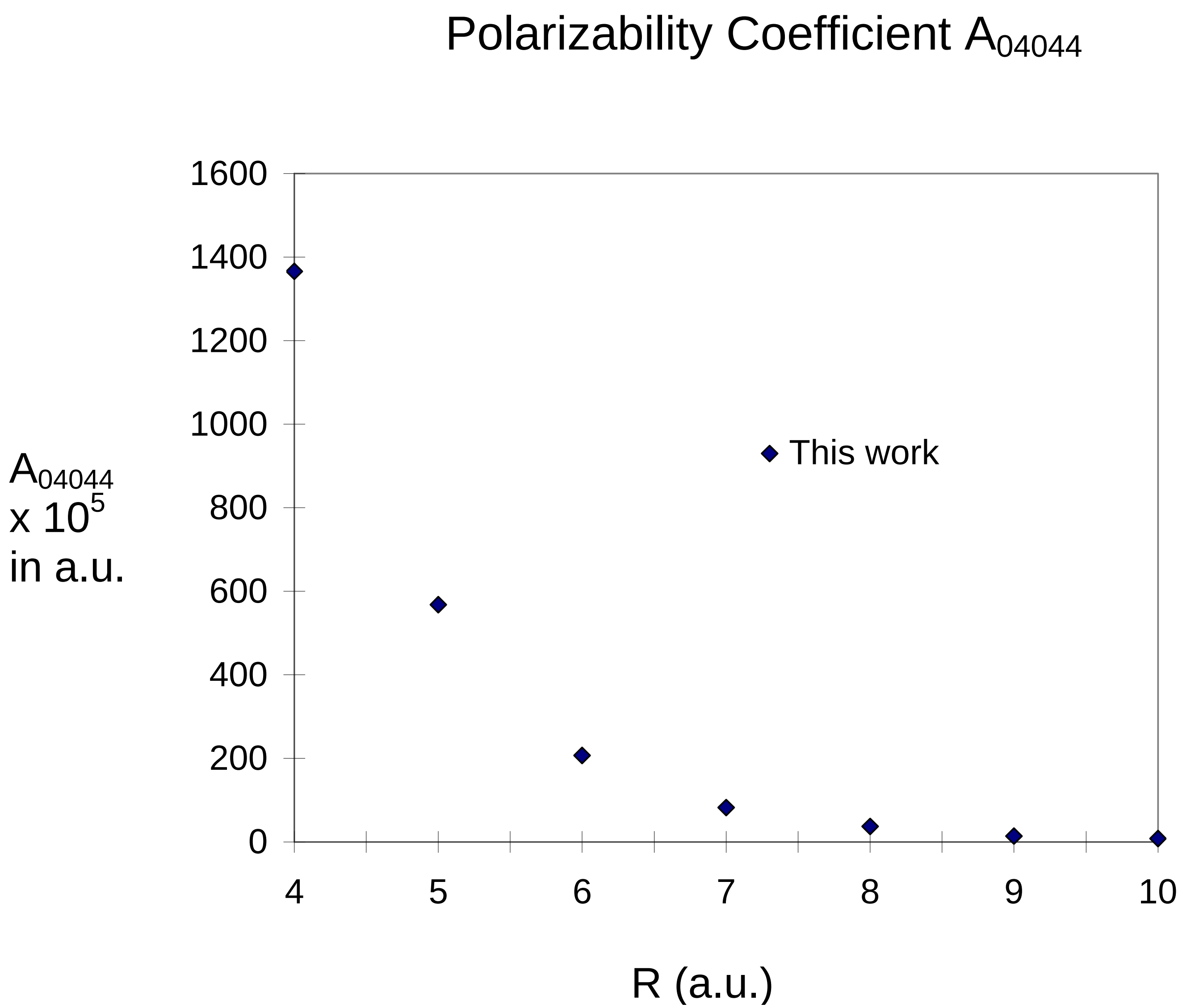

Polarizability Coefficient A_{02022}
A_{02022} x 10^5 in a.u.
1.2E+05
1.0E+05
8.0E+04
6.0E+04
4.0E+04
2.0E+04
0.0E+00
3
4
5
6
7
8
9
10
R (a.u.)
DID-1

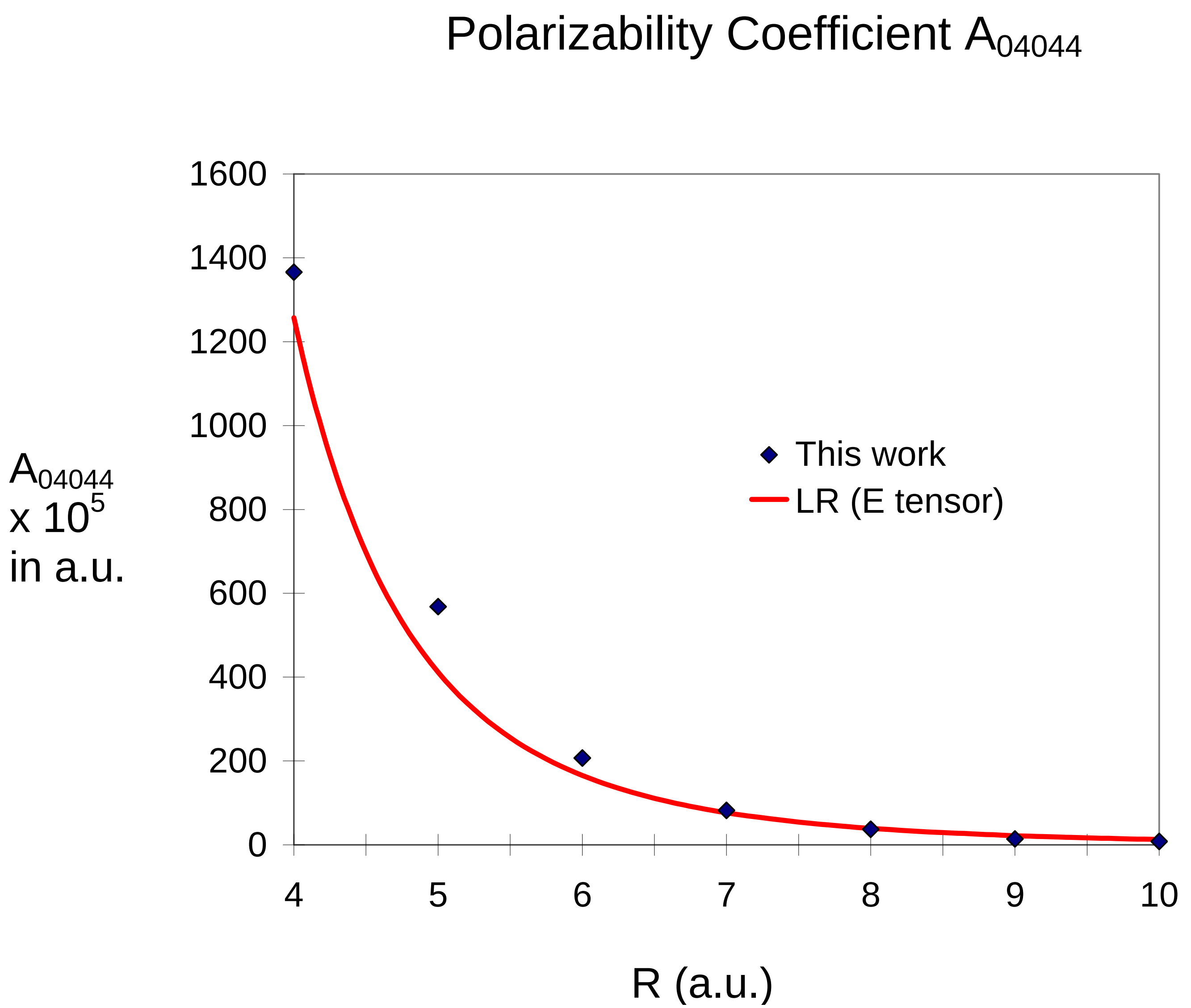


Polarizability Coefficient A_{02022}
1.2E+05
1.0E+05
8.0E+04
6.0E+04
4.0E+04
2.0E+04
0.0E+00
A_{02022} x 10^5 in a.u.
This work
DID-1
3
4
5
6
7
8
9
10
R (a.u.)

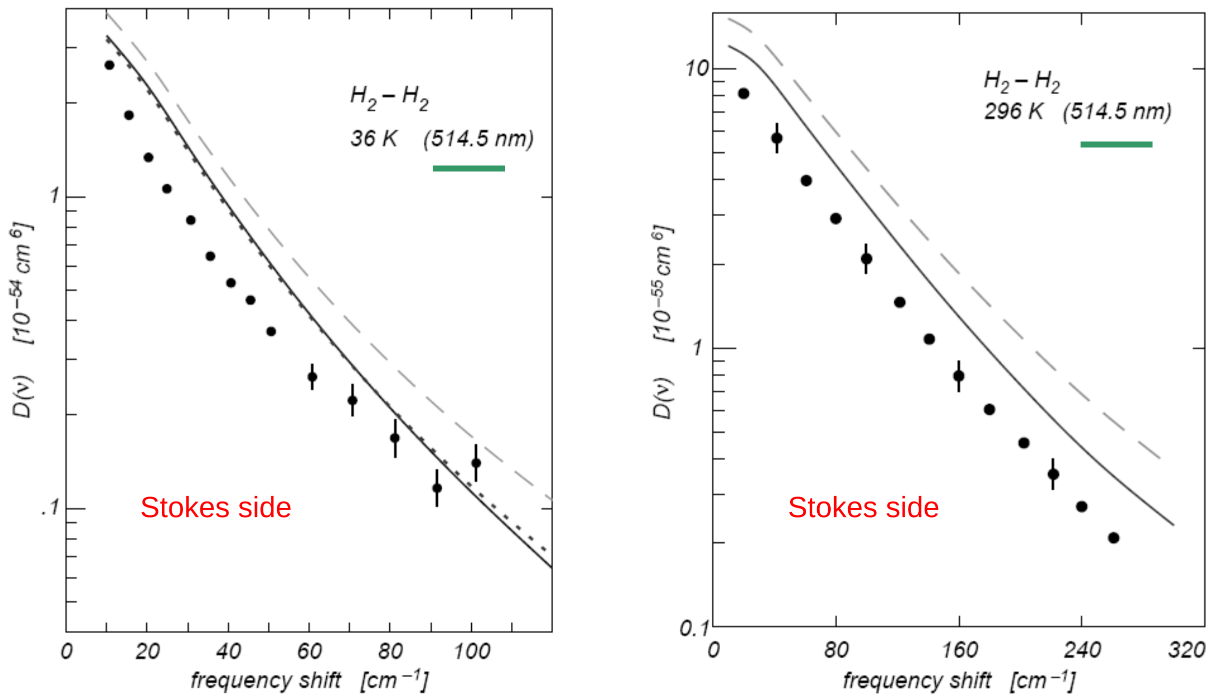


Polarizability Coefficient A02022
1.2E+05
1.0E+05
8.0E+04
6.0E+04
4.0E+04
2.0E+04
0.0E+00
A02022
x 10^5
in a.u.
This work
DID-1
LR
3
4
5
6
7
8
9
10
R (a.u.)


Polarizability Coefficient A04044
1600
1400
1200
1000
800
600
400
200
0
This work
A04044
x 10^5
in a.u.
4
5
6
7
8
9
10
R (a.u.)


Polarizability Coefficient A_{04044}
A_{04044} x 10^5 in a.u.
1600
1400
1200
1000
800
600
400
200
0
4
5
6
7
8
9
10
R (a.u.)
This work
LR (E tensor)

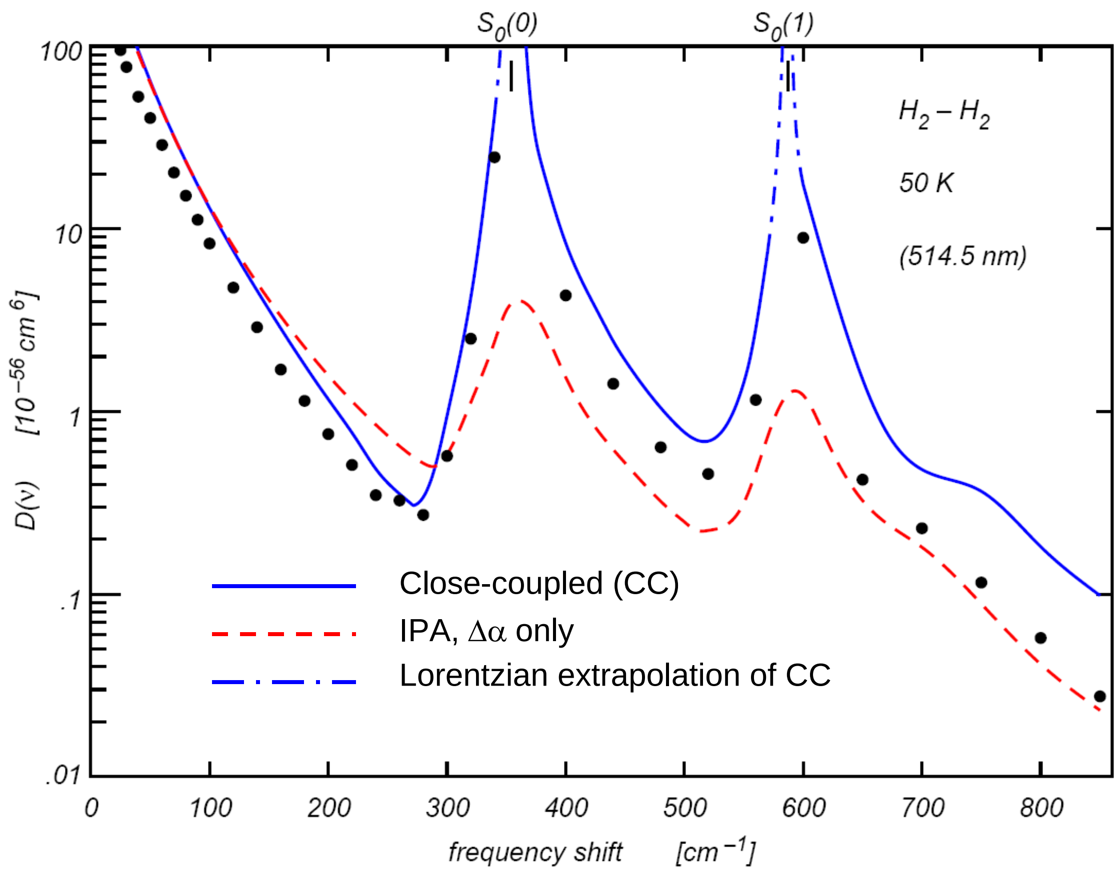
Depolarized Collision-Induced Light Scattering Spectrum of $H_2 \ldots H_2$
Comparison of Experiment and Calculations



Calculations: M. Gustafsson, L. Frommhold, X. Li, and K. L. C. Hunt, *J. Chem. Phys*. **130**, 164314 (2009).
36 K: Solid line, close-coupled scattering theory; dotted line, isotropic potential approximation; dashed line, DID
296 K: Solid line, IPA; dashed line, DID

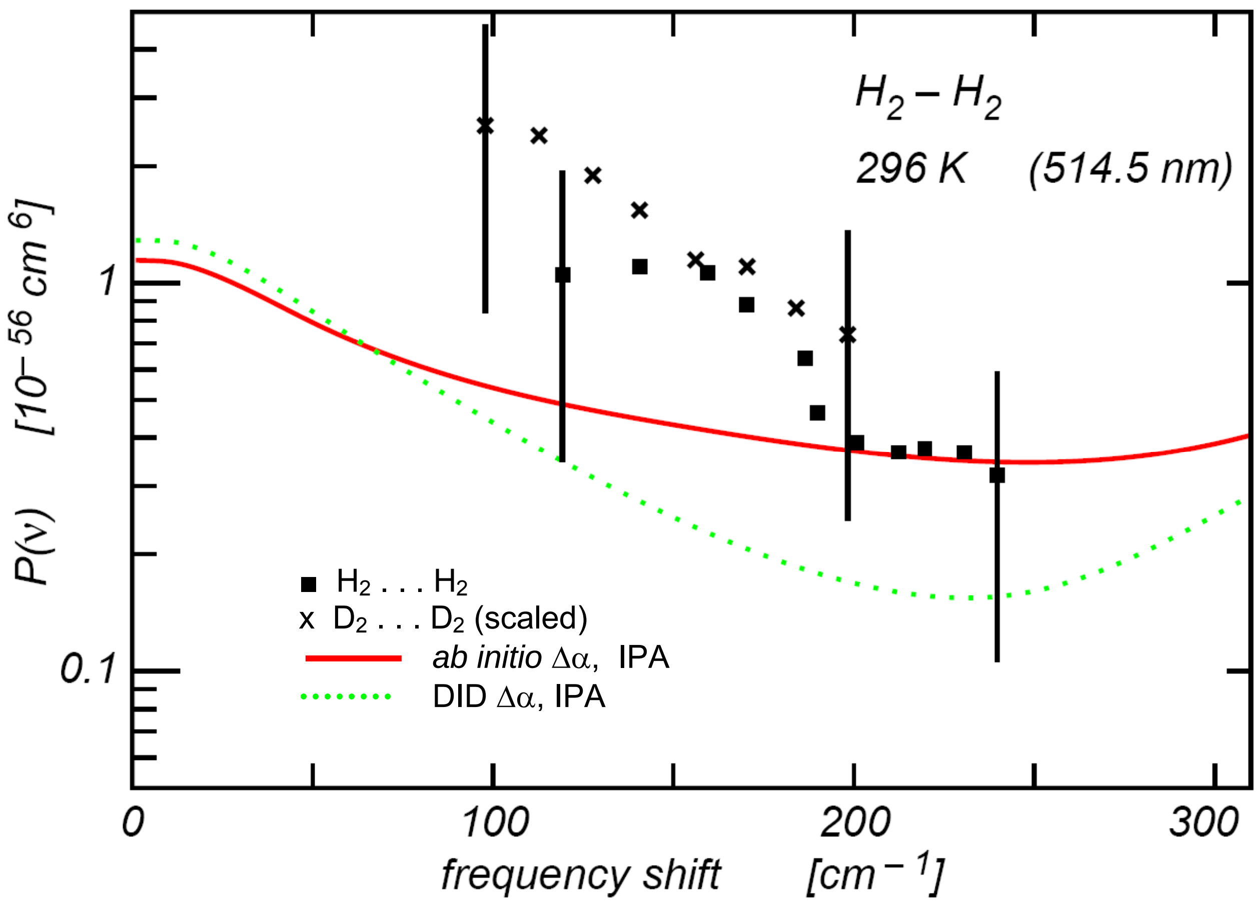
Measurements (•):
36 K: U. Bafile, M. Zoppi, F. Barocchi, M. S. Brown, and L. Frommhold, *Phys. Rev. A* **40**, 1654 (1989).
296 K: M. S. Brown, S. K. Wang, and L. Frommhold, *Phys. Rev. A* **40**, 2276 (1989).

Depolarized Rototranslational Raman Intensity of $H_2 ... H_2$ at 50 K



Calculations: M. Gustafsson, L. Frommhold, X. Li, and K. L. C. Hunt, *J. Chem. Phys*. **130**, 164314 (2009).
Measurements (•): U. Bafile, L. Ulivi, M. Zoppi, F. Barocchi, M. Moraldi, and A. Borysow, *Phys. Rev. A* **42**, 6916 (1990).

Polarized Translational Raman Spectra, Stokes Side



Calculations, *ab initio* $\Delta\alpha$: M. Gustafsson, L. Frommhold, X. Li, and K. L. C. Hunt, *J. Chem. Phys*. **130**, 164314 (2009).

Calculations, DID $\Delta\alpha$: M. S. Brown, S. K. Wang, and L. Frommhold, *Phys. Rev. A* **40**, 2276 (1989).

Experiments: M. S. Brown, S. K. Wang, and L. Frommhold, *Phys. Rev. A* **40**, 2276 (1989).

Summary

New *ab initio* values of $\Delta\mu$ and $\Delta\alpha$ for $H_2 \ldots H_2$ and for coefficients in spherical-harmonic expansion

Differences from quadrupolar induction are evident in $\Delta\mu$; differences from first-order DID are evident in $\Delta\alpha$

Ab initio values converge to full long-range model (LR) as R increases; highly isotropic coefficients are an exception

Good fit for rototranslational Raman spectrum of $H_2 \ldots H_2$ with remaining differences probably due to difference between $\Delta\alpha(\omega = 0)$ and $\Delta\alpha(\omega)$

Excellent fit of rototranslational absorption, IR fundamental and overtones

Research Group and Collaborators

Prof. Lothar Frommhold, UT, Austin

Prof. Magnus Gustafsson, Gothenburg

Prof James F. Harrison, MSU

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