H_2O atomization energy in cc-pV10Z

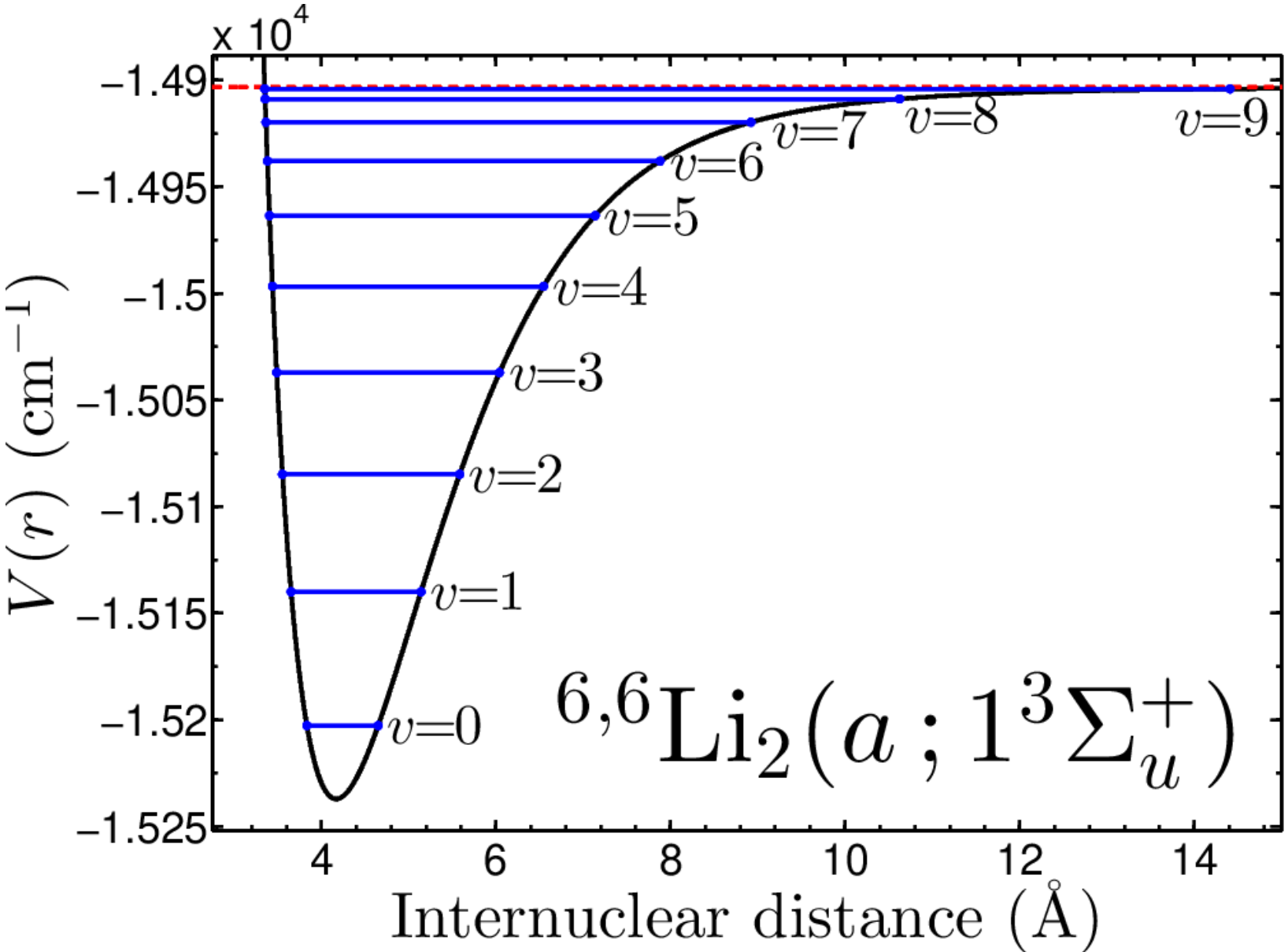
Nike Dattani

21 June 2019

Atomization Energy

$\mathfrak{D}_e$ 333.758 (7)

r_e 4.17005 (3)



An accurate analytic potential function for ground-state N_2 from a direct-potential-fit analysis of spectroscopic data

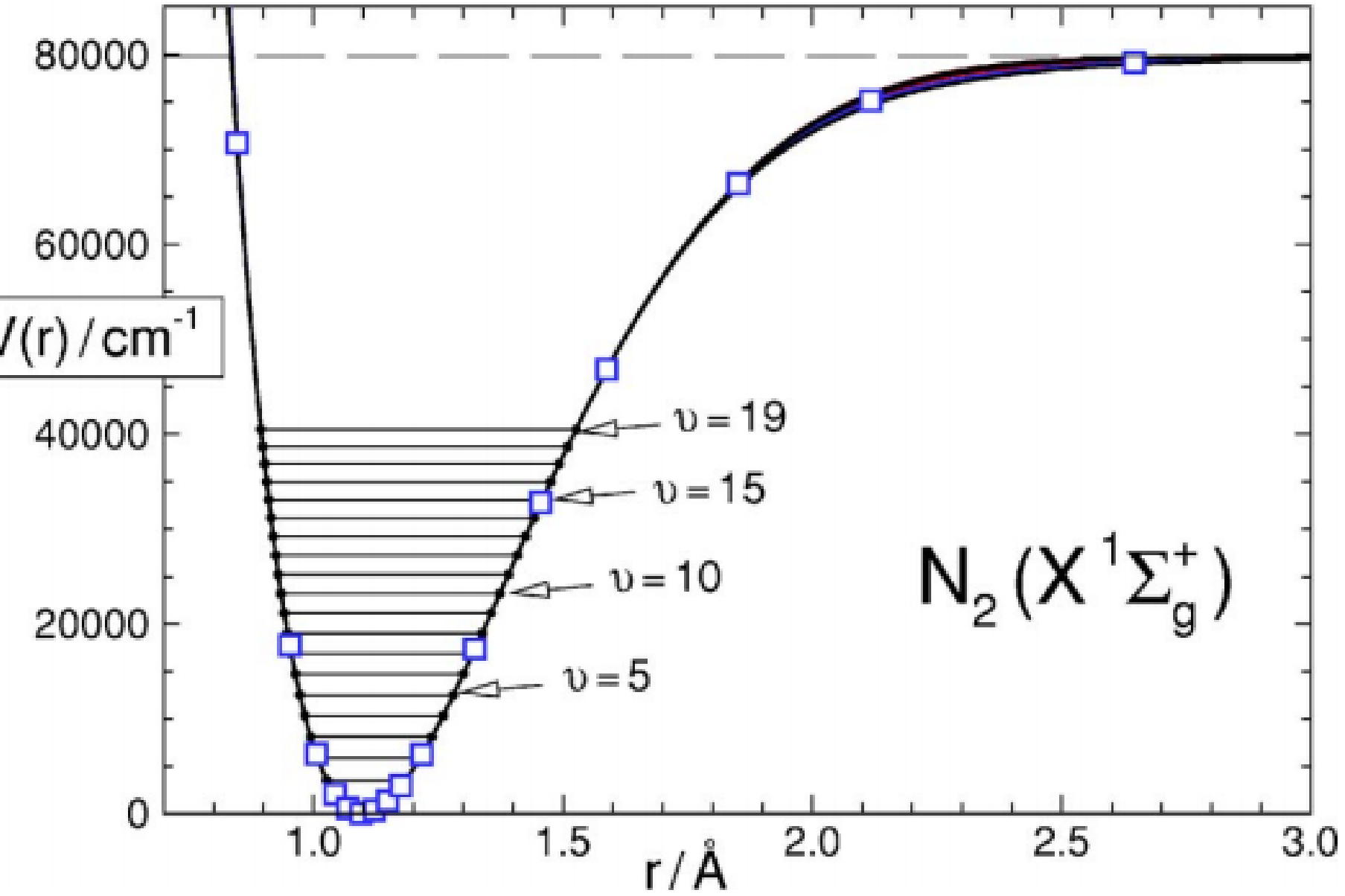
Robert J. Le Roy,[a] Yiye Huang, and Calvin Jary
Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

Species	Type	Δv	v''	J''_{max}	unc./cm^{-1}	No. of lines	Source	Year
$^{14,14}N_2$	Raman	0	0	18	0.001	19	Bendtsen[a]	1974
	CARS	1	0	48	0.01	42	Gilson *et al.*[b]	1980
	CARS	1	1	30	0.02	24	Gilson *et al.*[b]	1980
	Quadrupole	1	0	21	0.004 3	18	Reuter *et al.*[c]	1986
	CARS	1	0	47	0.001 3	15	Tabyoui *et al.*[d]	1990
	CARS	1	1	26	0.002 2	24	Tabyoui *et al.*[d]	1990
	Quadrupole	1	0	22	0.000 6	19	Rinslandet *et al.*[e]	1991
	CARS	1	1	14	0.001 4	15	Orlov *et al.*[f]	1997
	CARS	1	2	20	0.001 8	21	Orlov *et al.*[f]	1997
	CARS	1	3	20	0.004 1	21	Orlov *et al.*[f]	1997
	CARS	1	4	18	0.001 4	19	Orlov *et al.*[f]	1997
	CARS	1	5	17	0.001 6	16	Orlov *et al.*[f]	1997
	CARS	1	6	22	0.003 5	21	Orlov *et al.*[f]	1997
	CARS	1	7	12	0.002 2	6	Orlov *et al.*[f]	1997
	Raman	1	0	24	0.000 54	56	Bendtsen and Rasmussen[g]	2000
	Electronic	n/a	0–19	16–32	0.07	525	Roncin *et al.*[h]	1999
$^{14,15}N_2$	Raman	0	0	19	0.001	18	Bendtsen[a]	1974
	CARS	1	0	48	0.02	37	Gilson *et al.*[b]	1980
	Raman	1	0	26	0.000 54	60	Bendtsen[i]	2001
$^{15,15}N_2$	Raman	0	0	21	0.001	20	Bendtsen[a]	1974
	CARS	1	1	29	0.02	11	Gilson *et al.*[b]	1980
	CARS	1	0	25	0.001 0	25	Orlov *et al.*[f]	1997
	CARS	1	1	27	0.001 6	27	Orlov *et al.*[f]	1997
	CARS	1	2	25	0.001 7	25	Orlov *et al.*[f]	1997
	CARS	1	3	25	0.004 3	24	Orlov *et al.*[f]	1997
	CARS	1	4	23	0.003 0	21	Orlov *et al.*[f]	1997
	CARS	1	5	25	0.003 2	25	Orlov *et al.*[f]	1997
	CARS	1	6	25	0.001 8	12	Orlov *et al.*[f]	1997
	Raman	1	0	25	0.0005 6	55	Bendtsen[i]	2001

Atomization Energy

$\mathfrak{D}_e$ 79 845[±9]

r_e/Å 1.097 679 (1)



Molecule	Expt. kcal/mol
$LiH(^1\Sigma^+)$	**56.00±0.01** WS
	55.67±0.01 JANAF
$BeH(^2\Sigma^+)$	**46.90±0.01** HH
$CH(^2\Pi)$	**79.90±0.02** HH
	80±4 JANAF
$CH_2(^3B_1)$	**179.6** LZ
	181±1 JANAF
$CH_2(^1A_1)$	**170.6** MBSESS
$CH_3(^2A_2'')$	**289.3±0.2** JANAF
$CH_4(^1A_1)$	**392.5±0.1** JANAF
$NH(^3\Sigma^-)$	**79.0±0.4** GGB
	74.2±4 JANAF
$NH_2(^2B_1)$	**170.0±0.3** GGB
$NH_3(^1A_1)$	**276.7±0.1** JANAF
$OH(^2\Pi)$	**101.4±0.3** JANAF
$H_2O(^1A_1)$	**219.35±0.01** JANAF
$HF(^1\Sigma^+)$	**135.2±0.2** JANAF
$SiH_2(^1A_1)$	**144.4±0.7** BGCR
$SiH_2(^3B_1)$	**123.4±0.7** BGCR
$SiH_3(^2A_2'')$	**213.8±1.2** DW
$SiH_4(^1A_1)$	**302.6±0.5** JANAF

Laboratory spectrometers

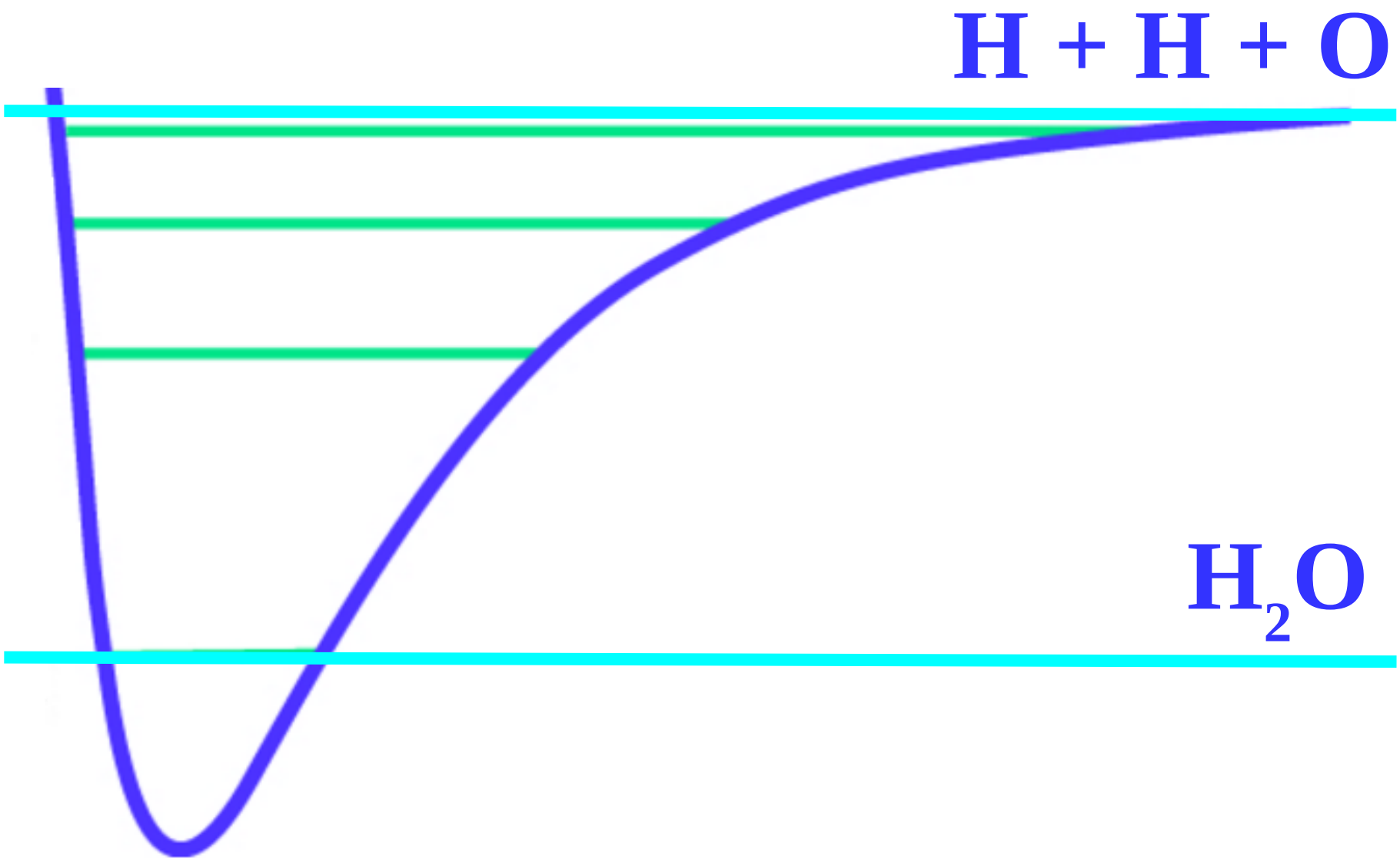
Laboratory spectrometer

Computer spectrometer

Laboratory spectrometer

Computer spectrometer

Type in the name of the molecule:
Get it's spectrum.


H + H + O
H_2O

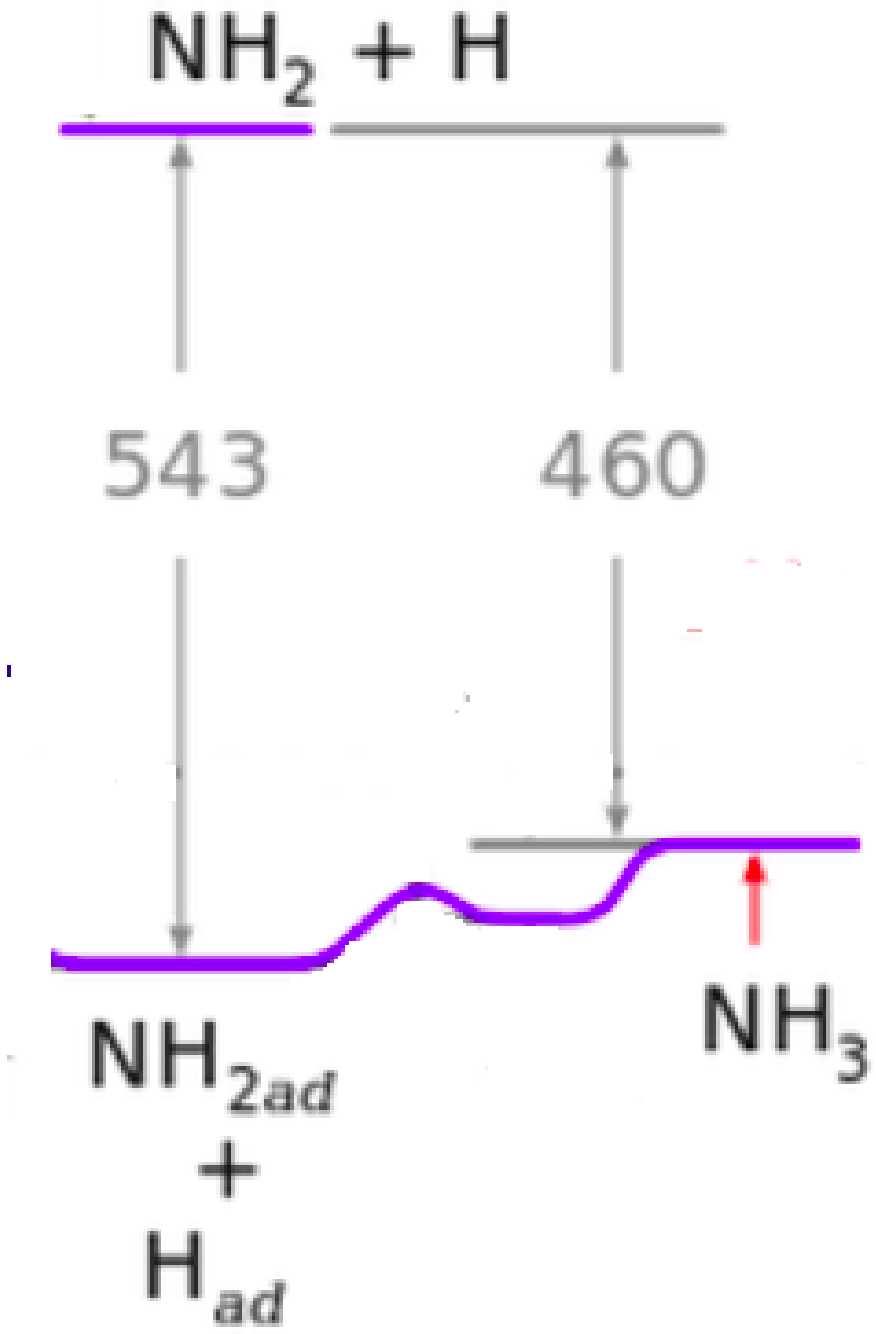
$\mathrm{C}\left(^3P\right)$ $[E_{\mathrm{Hartree}}]$	$\mathrm{C}^+\left(^2P\right)$ $[E_{\mathrm{Hartree}}]$	$2^3P \rightarrow 2^2P$ $[\mathrm{cm}^{-1}]$
-37.844 251 5(05)	-37.430 345 1(01)	90 841.955(028)

$\mathrm{C}\left(^3P\right)$ $[E_{\mathrm{Hartree}}]$	$\mathrm{C}^+\left(^2P\right)$ $[E_{\mathrm{Hartree}}]$	$2^3P \rightarrow 2^2P$ $[\mathrm{cm}^{-1}]$
-37.844 251 5(05)	-37.430 345 1(01)	90 841.955(028)

COMPUTER SPECTROMETERS

NIKE DATTANI, *Department of Chemistry, Kyoto University, Kyoto, Japan.*

Ideally, the cataloguing of spectroscopic linelists would not demand laborious and expensive experiments.


NH2 + H
543
460
NH2ad
+
Had
NH3

NIST

PHYSICAL MEASUREMENT LABORATORY

Atomic Spectra Database

At. Num.	El. name	Ionization Energy [a] (cm^{-1})
33	Arsenic	78 950(2)
57	Lanthanum	44 981(5)
58	Cerium	44 672(3)
59	Praseodymium	[44 120(3)]
60	Neodymium	44 562(5)
61	Promethium	[44 980(140)]
93	Neptunium	50 535(2)
94	Plutonium	48 601(2)
95	Americium	48 182(2)
96	Curium	48 324(2)
97	Berkelium	49 989(2)
98	Californium	50 665(2)
99	Einsteinium	51 358(2)
100	Fermium	[52 400(600)]
101	Mendelevium	[53 100(600)]
102	Nobelium	[53 600(600)]
103	Lawrencium	40 000(600)
104	Rutherfordium	(48 500(800))
105	Dubnium	(55 000(4000))
106	Seaborgium	[63 000(4000)]
107	Bohrium	[62 000(4000)]
108	Hassium	[61 000(4000)]

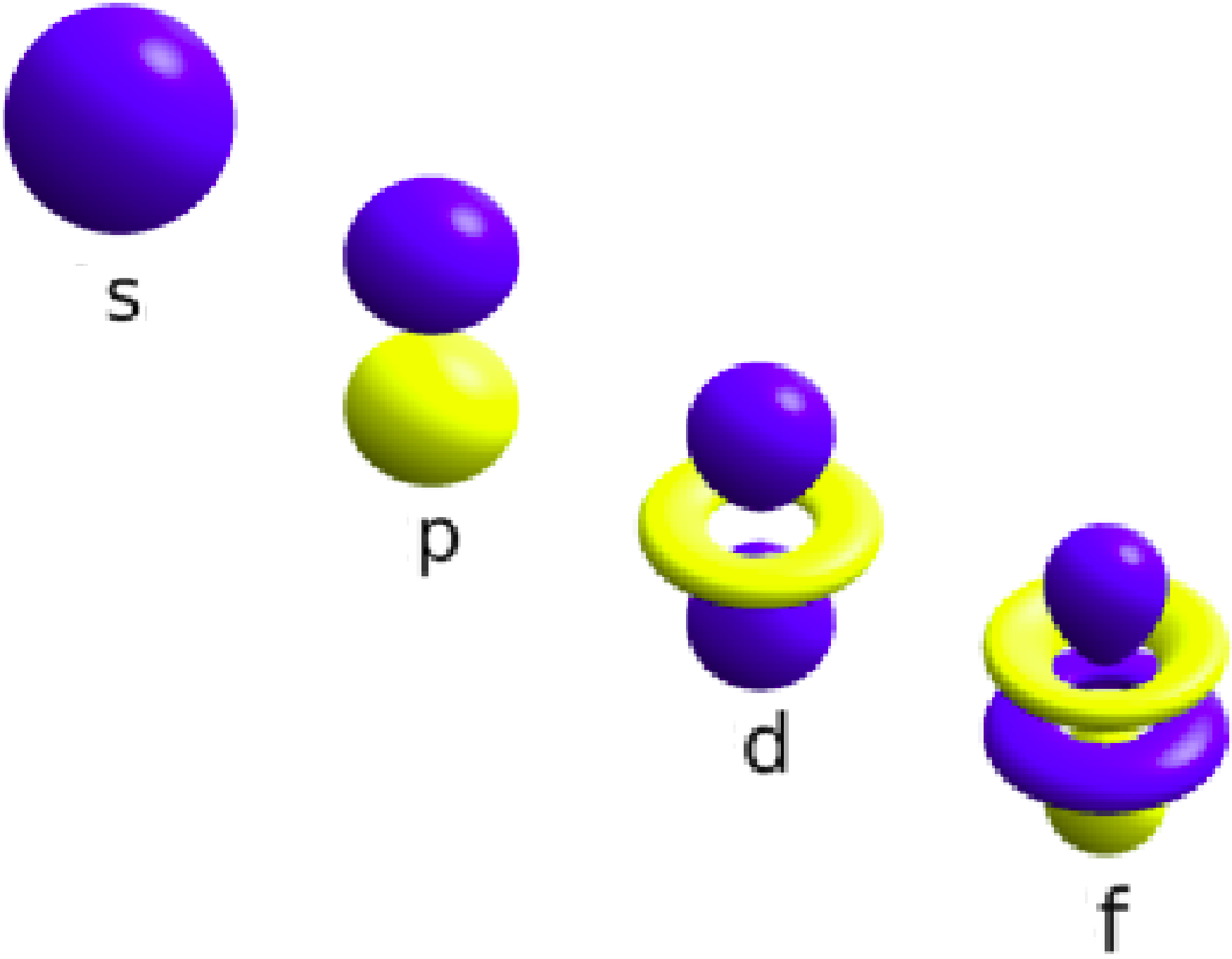
At. Num.	El. name	Ionization Energy [a] (cm^{-1})
1	Hydrogen	(109 678.77174307(10))
2	Helium	198 310.66637(20)
2	Helium	(438 908.8785(2))
3	Lithium	43 487.11420(18)
3	Lithium	[610 078.526(10)]
3	Lithium	(987 661.014(2))
4	Beryllium	75 192.64(6)
4	Beryllium	146 882.86(30)
4	Beryllium	[1 241 256.60(3)]
4	Beryllium	(1 756 018.822(8))
5	Boron	66 928.040(22)
5	Boron	202 887.4(4)
5	Boron	305 930.8(6)
5	Boron	2 091 972(20)
5	Boron	(2 744 107.936(20))
6	Carbon	90 820.45(10)
6	Carbon	[196 674(7)]
6	Carbon	386 241.0(10)
6	Carbon	520 175.3(15)
6	Carbon	[3 162 423.3(2)]
6	Carbon	(3 952 061.67(5))
7	Nitrogen	117 225.7(3)
7	Nitrogen	[238 750.2(7)]
7	Nitrogen	[382 672(20)]

	Transition	Experiment [cm^{-1}]		Theory [cm^{-1}]		Calc - Obs [cm^{-1}]	$\left\lvert\frac{\text{Calc - Obs}}{\text{Uncertainty in obs}}\right\rvert$	More precise
^{1}H	$H^{+}\left(1^{1}S\right) \leftarrow H\left(1^{2}S\right)$	109 678.771 732(23)	[14]	109 678.771 743 07(10)	[a]	0.000 011	0.48	Theory
^{4}He	$He^{+}\left(1^{2}S\right) \leftarrow He\left(1^{1}S\right)$	198 310.666 37(2)	[19]	198 310.665 07(1)	[20]	-0.001 3	65.00	Theory
^{3}Li	$Li^{+}\left(1^{1}S\right) \leftarrow Li\left(2^{2}S\right)$	43 487.159 40(18)	[21]	43 487.159 7(7)	[1]	-0.000 3	1.66	Experiment
^{9}Be	$Be^{+}\left(2^{2}S\right) \leftarrow Be\left(2^{1}S\right)$	75 192.64(6)	[22]	75 192.699(7)	[3]	0.059	0.98	Theory
^{11}B	$B^{+}\left(2^{1}S\right) \leftarrow B\left(2^{2}P\right)$	66 928.036(22)	[23]	66 927.91(21)	[4]	-0.126	5.73	Experiment
^{12}C	$C^{+}\left(2^{2}P\right) \leftarrow C\left(2^{3}P\right)$	90 833.171(15)[b]	[24]	90 832.299	-	-0.872	58.13	Experiment

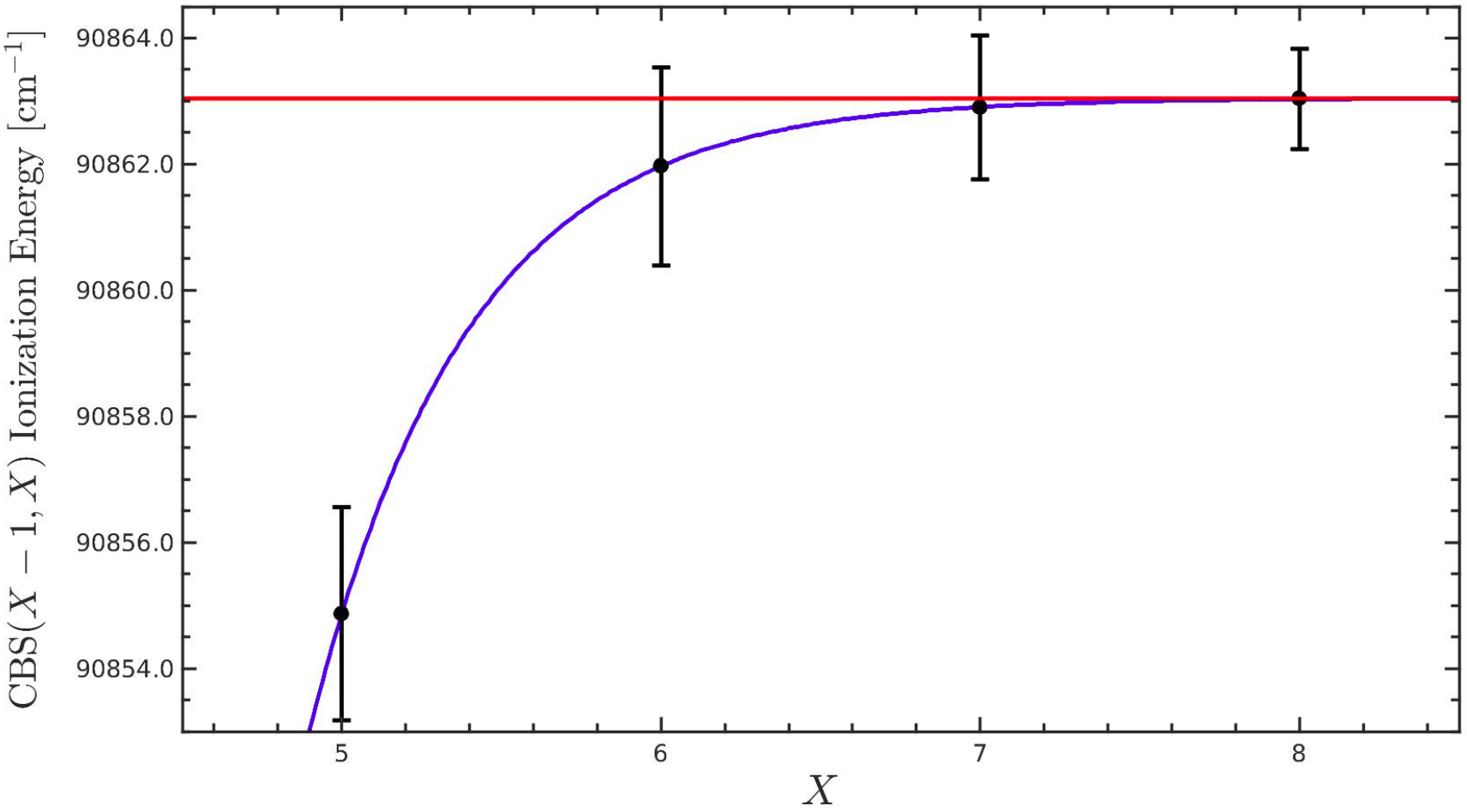
You all now know:

- **What an “atomization energy” is**
- **What “computer spectroscopy” is**

What is: cc-pV10Z ?


s
p
d
f

s,p,d	**cc-pVDZ**
s,p,d,f	**cc-pVTZ**
s,p,d,f,g	**cc-pVQZ**
s,p,d,f,g,h	**cc-pV5Z**
s,p,d,f,g,h,i	**cc-pV6Z**
s,p,d,f,g,h,i,k	**cc-pV7Z**
s,p,d,f,g,h,i,k,l	**cc-pV8Z**
s,p,d,f,g,h,i,k,l,m	**cc-pV9Z**
s,p,d,f,g,h,i,k,l,m,n	**cc-pV10Z**


90864.0
90862.0
90860.0
90858.0
90856.0
90854.0
CBS$(X-1, X)$ Ionization Energy [cm^{-1}]
5
6
7
8
X

MOLPRO can't use k-functions (limit: cc-pV6Z)
GAMESS can't use k-functions (limit: cc-pV6Z)
NWChem can't use k-functions (limit: cc-pV6Z)
CFOUR can't use k-functions (limit: cc-pV6Z)
COLUMBUS can't use k-functions (limit: cc-pV6Z)
ORCA can't use k-functions (limit: cc-pV6Z)

.

.

MRCC can't use m-functions (limit: cc-pV8Z)

Dalton can do n-functions (cc-pV10Z), but:
- **only closed shell systems**
- **only CCSD and CCSD(T), not CCSDT, CCSDT(Q), etc.**

MOLCAS can do n-functions (cc-pV10Z), but:
- **only CCSD and CCSD(T), not CCSDT, CCSDT(Q), etc.**

H_2O (frozen core, 8 electrons)

cc-pVDZ: CCSDTQPHSO. 0.4GB, 5 hours
cc-pVTZ: CCSDTQPH. 228GB, 7 days
cc-pVQZ: CCSDTQP. 47GB, 32 days
cc-pV5Z: CCSDTQ. 147GB, 22 days
cc-pV6Z: CCSDTQ. 519GB, 72 days
cc-pV7Z: CCSDT. 255GB, 3 days
cc-pV8Z: CCSDT. 2.4TB, 57GB, 15 days
cc-pV9Z: CCSD(T). 9 Terabytes
cc-pV10Z: Hartree-Fock

H_2O (frozen core, 8 electrons)

cc-pV9Z, CCSD(T):

- **24 trillion 2e- integrals (9 Terabytes on disk)**
- **equivalent to 125 atoms in C_{2v} with cc-pVDZ**
- **example: $C_{13}H_{10}BrCl_2O_2PS$ (leptophos: pesticide)**
- **thousands of atoms if we screen integrals**

H_2O (frozen core, 8 electrons)

cc-pV9Z, CCSD(T):

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- **example: $C_{13}H_{10}BrCl_2O_2PS$ (leptophos: pesticide)**
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cc-pV10Z:

- **New atomization energy of Water:**

3.5x more precise than best empirical value.