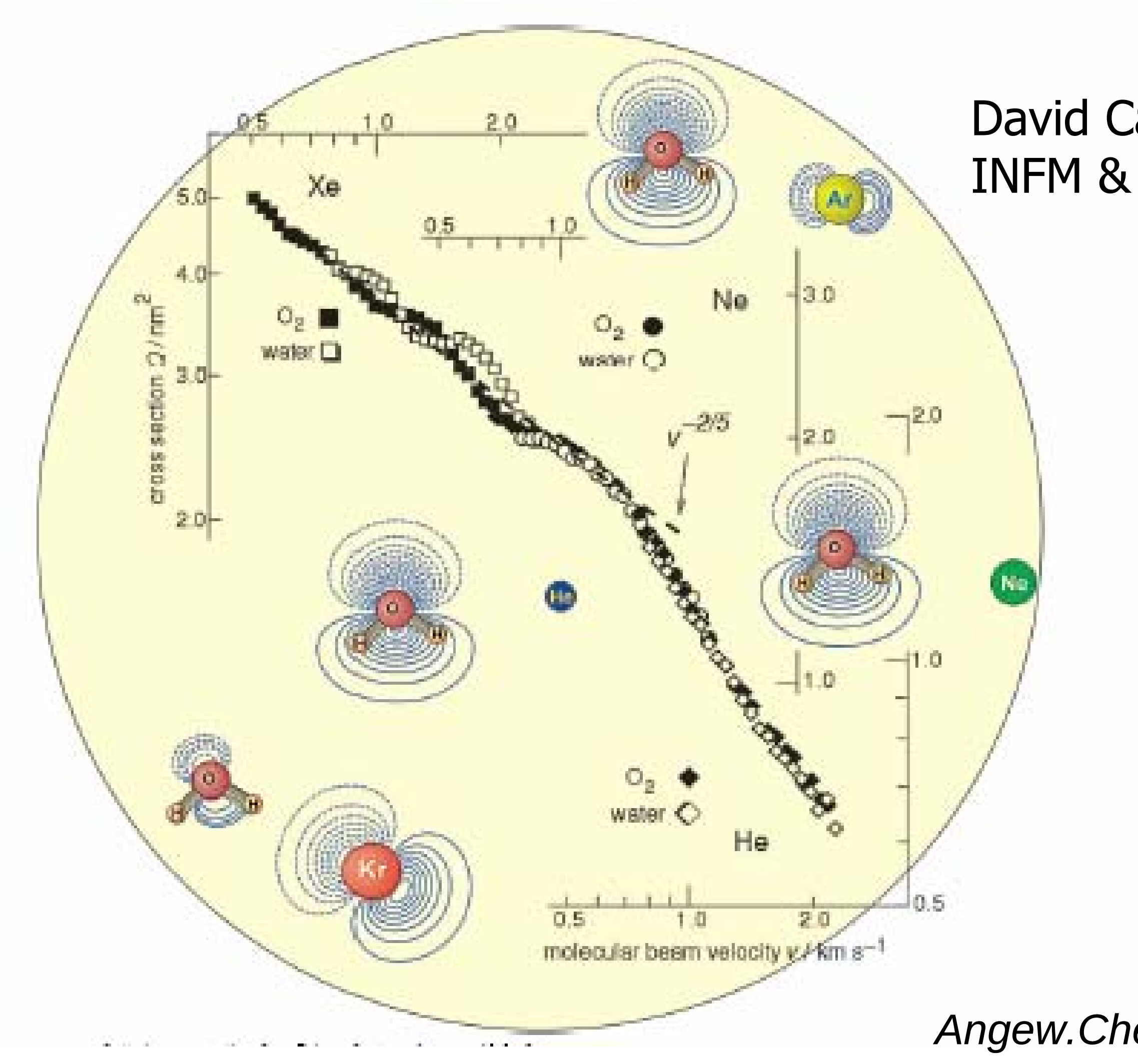
Tales of Glory:
The Birth of the Hydrogen Bond



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Aknowledgments:

MIUR – INFM – CECAM – Galileo exch. Program - IUPAC

Our activity in the field of intermolecular interactions

Molecular beam scattering experiments

	'***van der Waals'***
Ar-Ne, Ar-Kr, ...	
N_2-rare gases , O_2-rare gases	dispersion
O_2-O_2- N_2-N_2, N_2-O_2	induction, electrostatic
C_2H_2, C_2H_4, $C_2H_{6,}$ C_6H_6-– rare gases	repulsion

	'***weak chemical bond'***
F(^{2}P)-rare gases, H_2, CH_4	dispersion
Cl(^{2}P)-rare gases, H2, CH4	induction, electrostatic, ***charge transfer***
S(^{3}P)-rare gases, H2, CH4	repulsion

Role of the different components of the interaction

Role of water complexes in the gas phase

Due to its ubiquity in our environment water is the most studied liquid of the literature

Its role in the gas phase is also very important

•Radiation budget of the atmosphere

H_2O-H_2O K.Pfeilsticker et al. SCIENCE 300, 2078-2080 (2003)

H_2O-O_2 e H_2O-N_2 (may contribute even more)

water vapour continuum

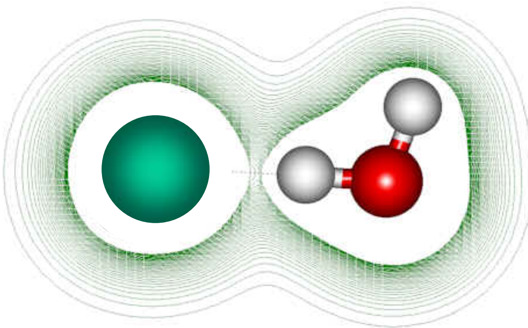
•astrophysical experiments (collisional broadening and pressure induced line shift)

H_2O-He and H_2O-H_2

The key point is the description of its force field !

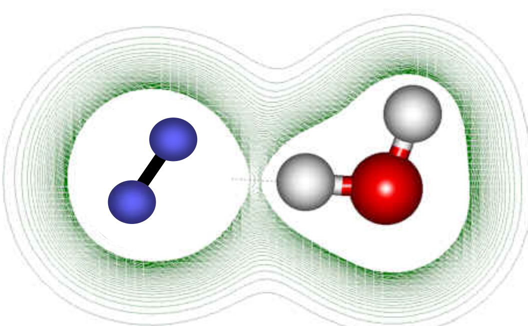
Prototypical gas phase systems involving water

H_2O – rare gases



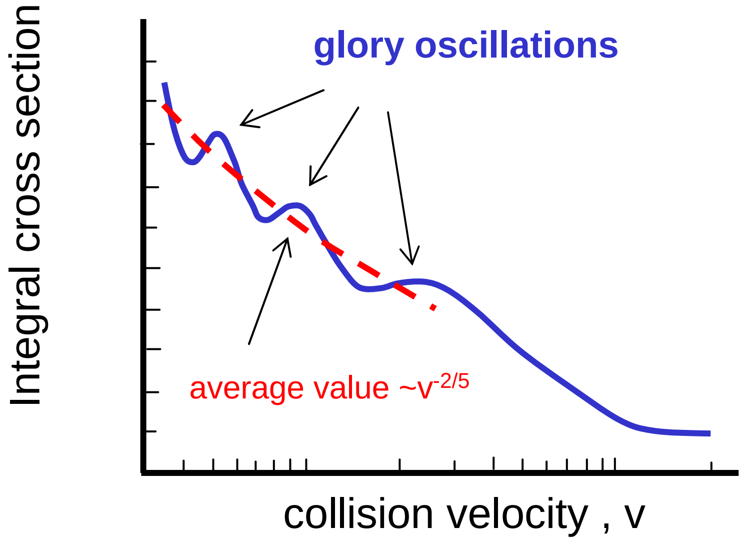
Dispersion Induction	Long range - Attractive
Charge transfer ??	*Intermediate/short range Attractive*
Repulsion	Short range - repulsive

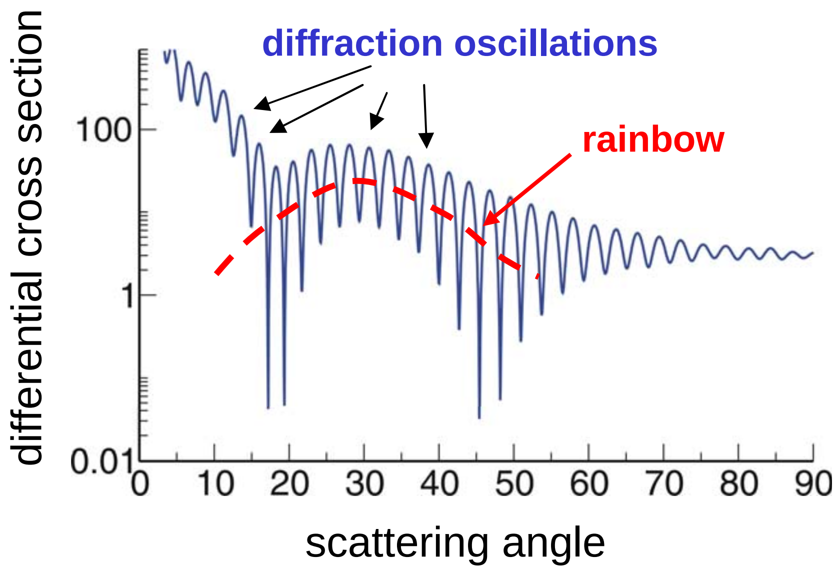
H_2O – apolar diatomic molecules (H_2, N_2, O_2)

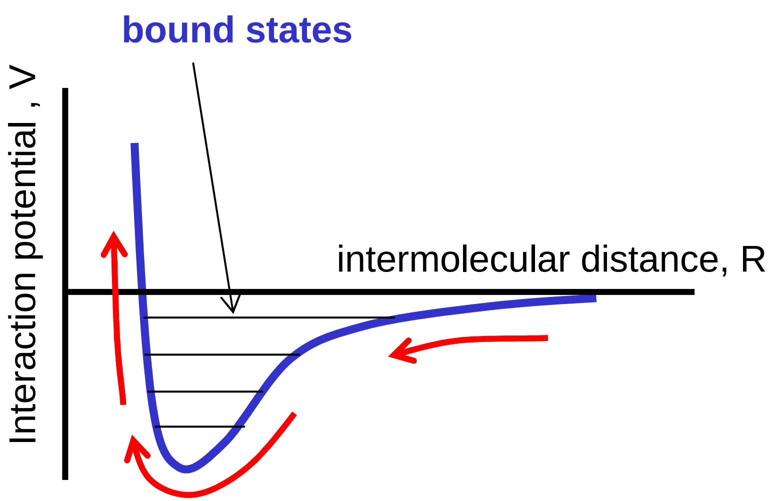


Dispersion Induction	Long range - Attractive
Electrostatic (dipole-quadrupole)	Long range - depends on orientation
Charge transfer ??	*Intermediate/short range Attractive*
Repulsion	Short range - repulsive

Scattering investigations as a probe of intermolecular interactions







Few concepts on 'glory' scattering

$$Q = \frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\sin^2\eta_\ell$$

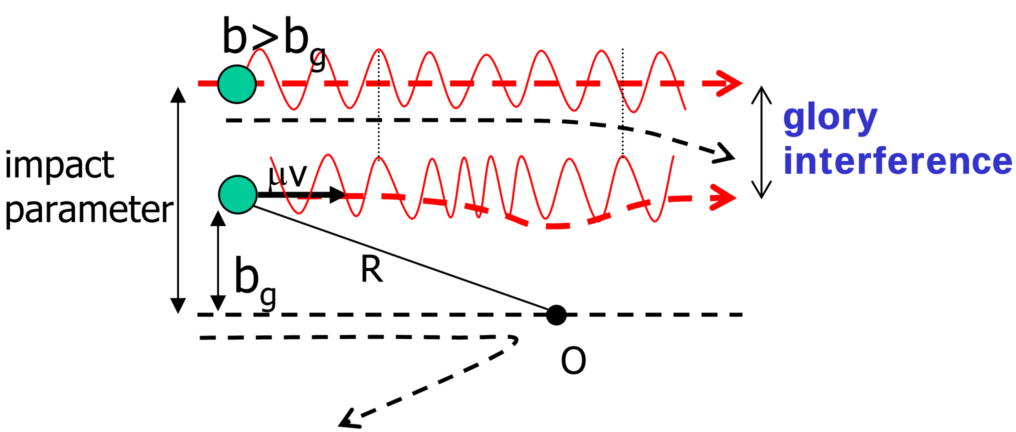
Integral elastic cross section (quantum description)

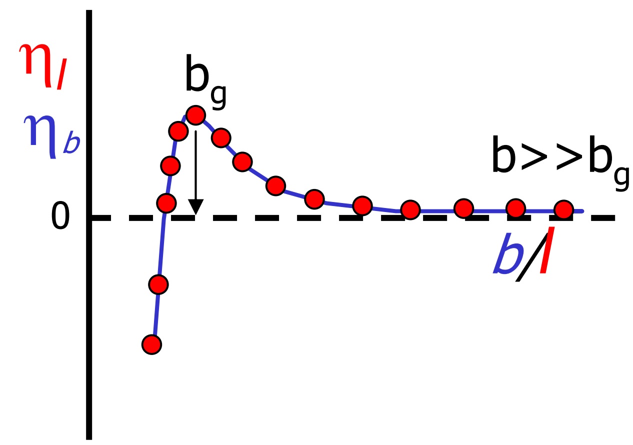
$$Q = 8\pi\int_0^{\infty} b\,\sin^2\eta_b\;\mathrm{d}b$$

Semiclassical description

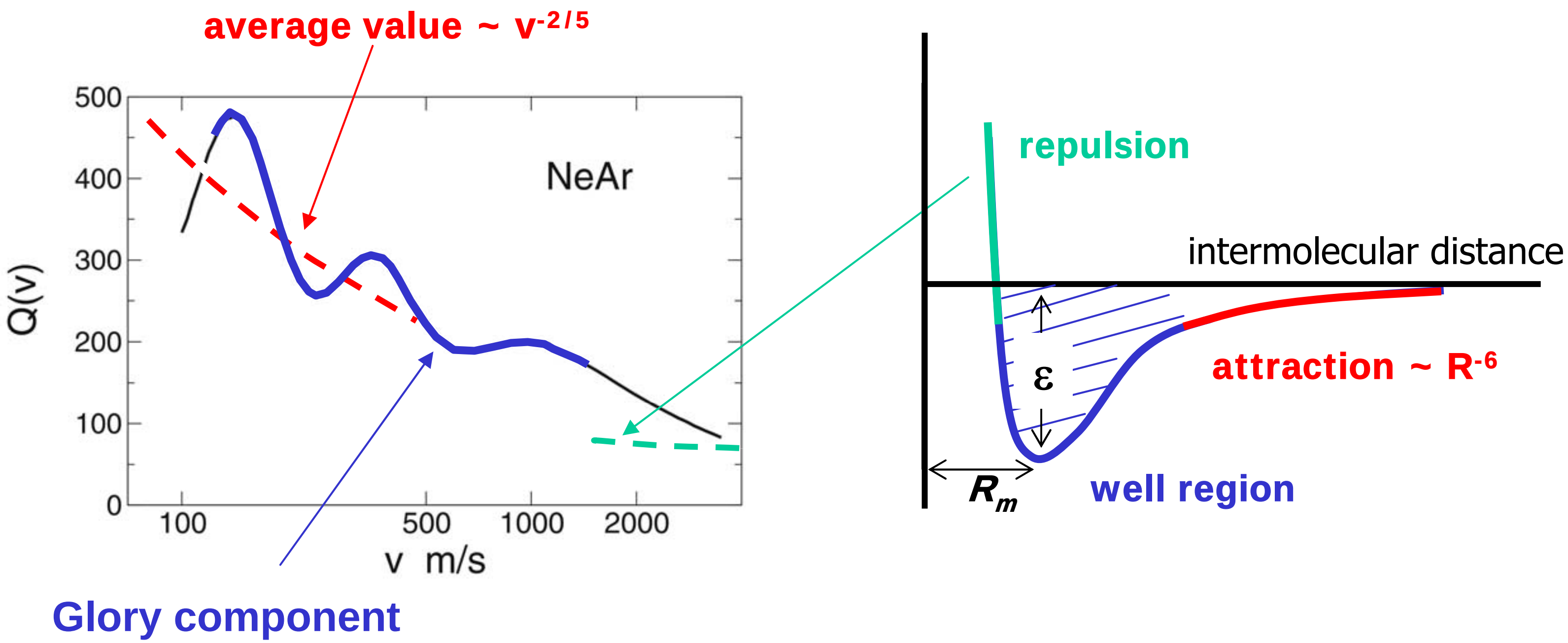
$$b \approx \frac{1}{k}\left(\ell + \frac{1}{2}\right)$$

Phase shift





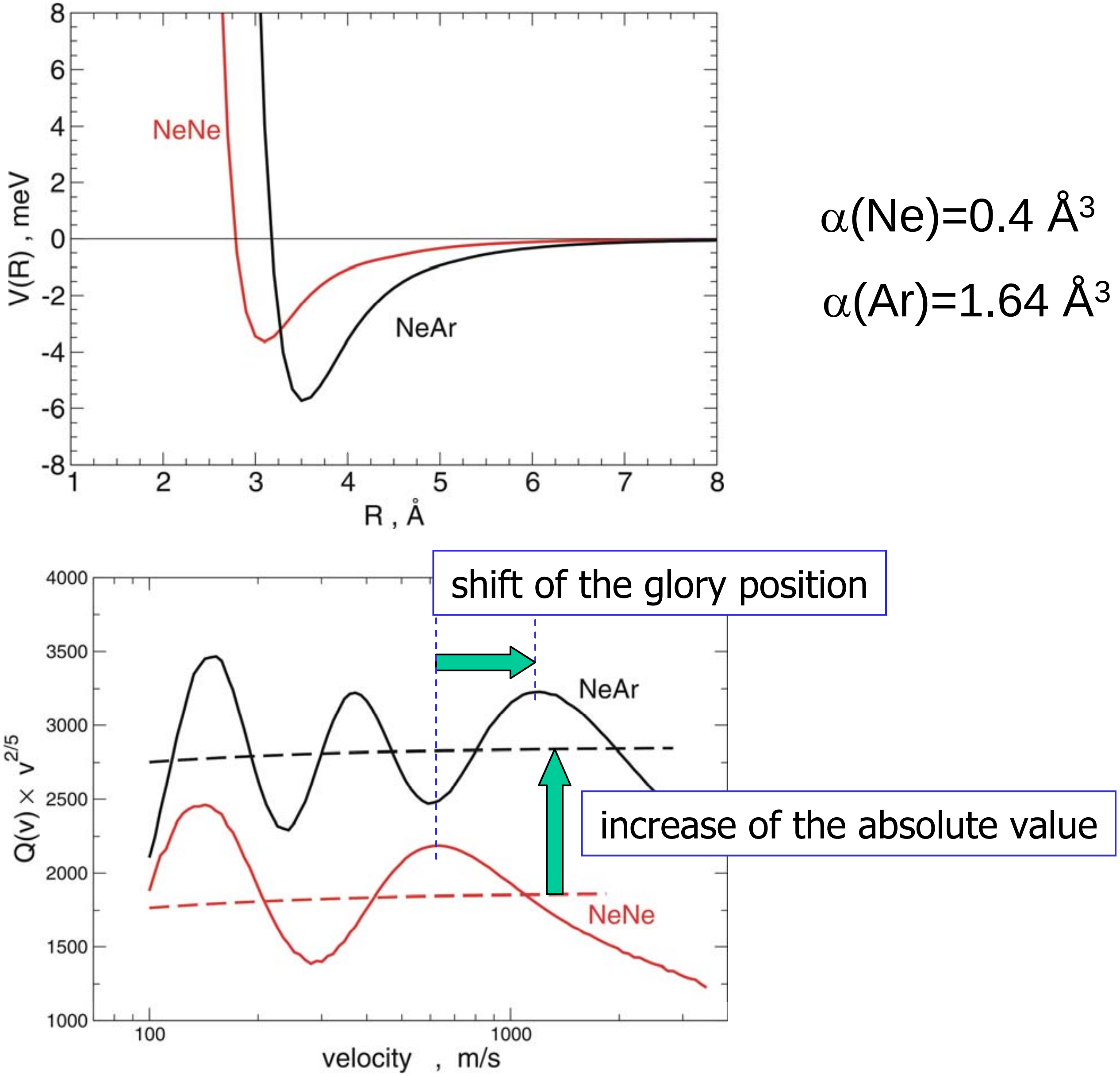
The cross section depends on the interaction potential



In a semiclassical picture: $Q = Q_{av} + \Delta Q$

$$V_{attr} = -\frac{C_s}{R^s} \qquad Q_{av} = g_s \left(\frac{C_s}{\hbar v}\right)^{\left(2/(s-1)\right)}$$

The cross section depends on the interacting system

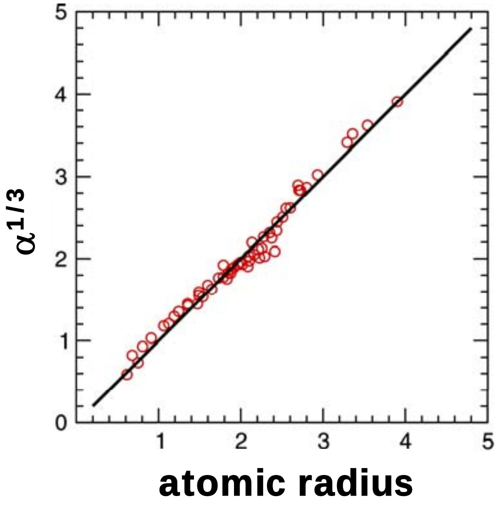


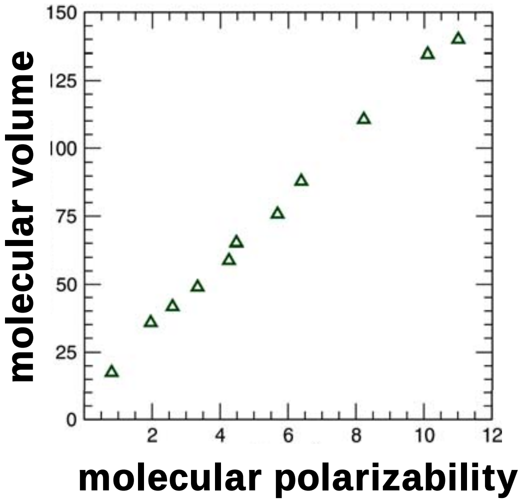
α(Ne)=0.4 Å^3

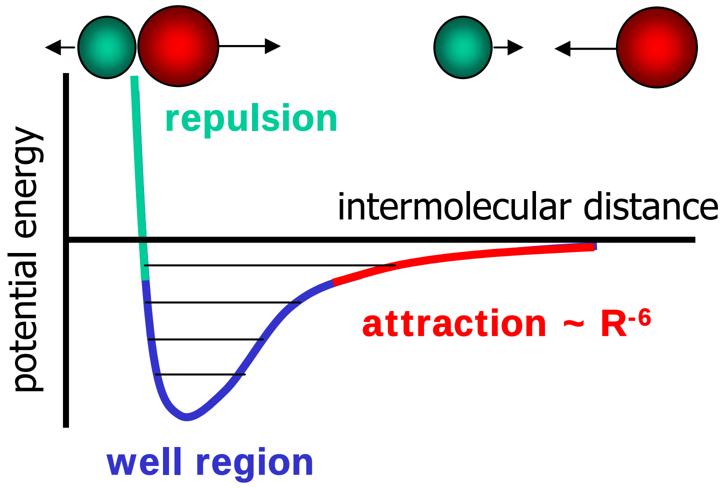
α(Ar)=1.64 Å^3

Polarizability is a good scale for both attraction and repulsion

When only dispersion forces are operative!







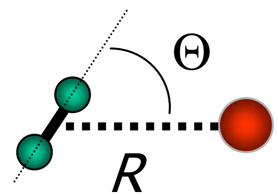
Neutral-neutral J. Chem. Phys., **95**, 1852 (1991) CORRELATION FORMULAS FOR VDW SYSTEMS

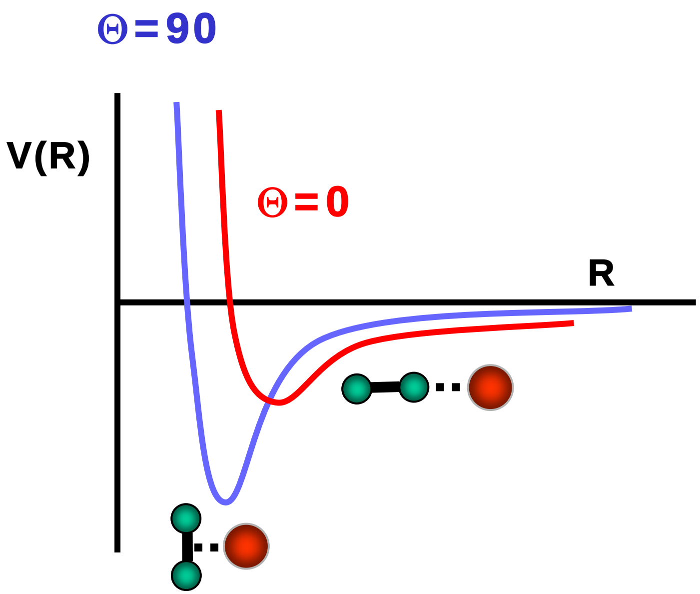
Further applications:

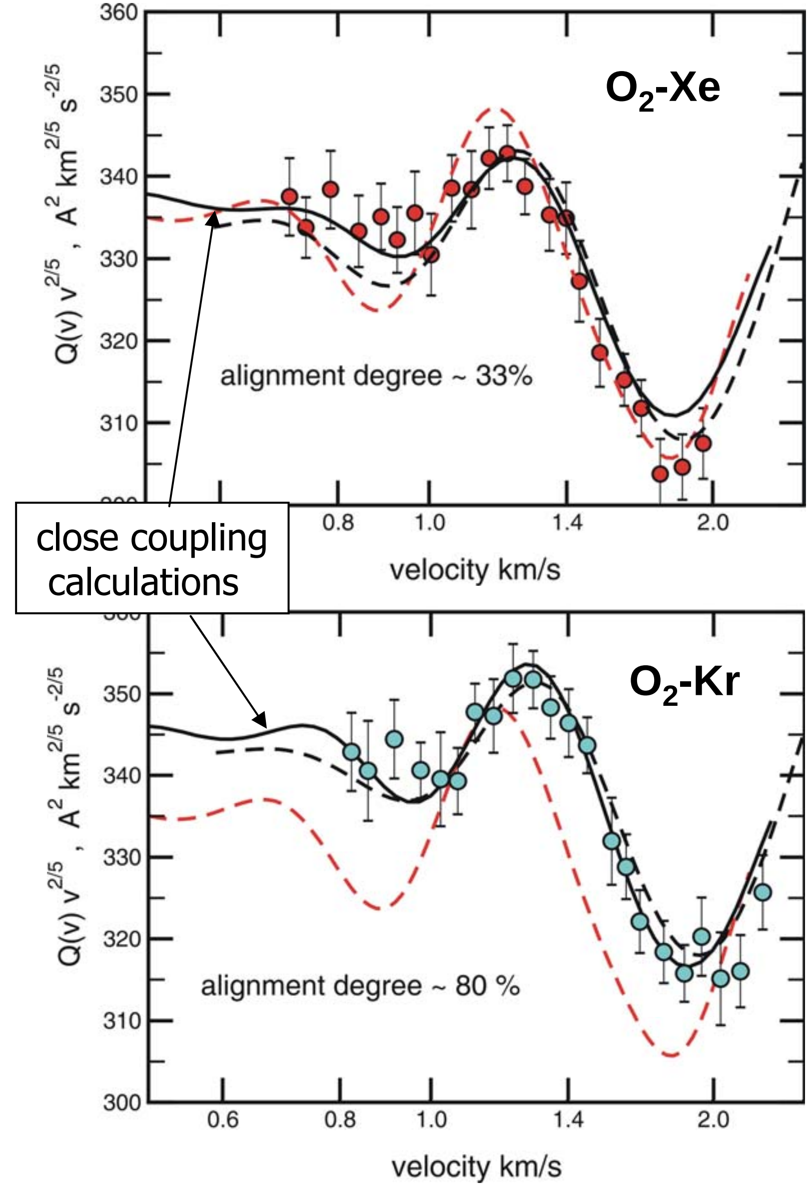
ion–neutral Chem.Phys.Lett. **183**, 297 (1991)
multicharged ion–neutral and ion–ion Chem.Phys. **209**, 299 (1996)
Atom (ion)-polyatomic molecule – Chem.Phys.Lett **350**, 286 (2001); Chem.Phys.Lett. **394**, 37 (2004)

Dispersion is not isotropic !

$$V(R,\Theta)$$

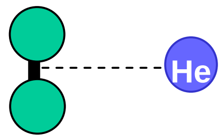




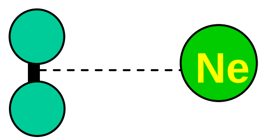


O_2-Xe - PRL, 74, 2929 (1995)
O_2-Kr - JCP, 109, 3839 (1998)
O_2-O_2 - PRL, 82, 69 (1999)
O_2-O_2 - JACS, 121, 10794 (1999)
C_6H_6-Ar,Ne - PRL 86, 5035 (2001)
JCP - 119, 265 (2003)

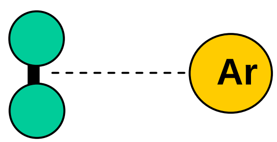
Molecular oxygen complexes with rare gases are always T-shaped in the most stable configuration: a signature of ‘van der Waals’ nature



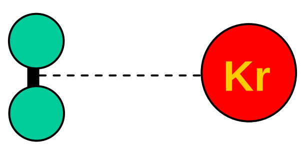
D_e=0.31 kJ/mol
R_e=0.327 nm



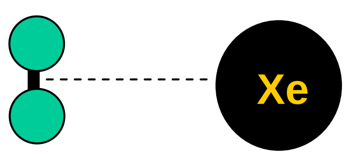
D_e=0.69 kJ/mol
R_e=0.336 nm



D_e=1.4 kJ/mol
R_e=0.35 nm

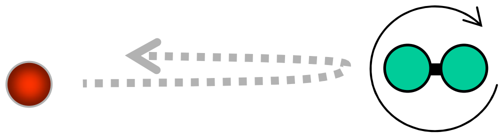


D_e=1.52 kJ/mol
R_e=0.372 nm

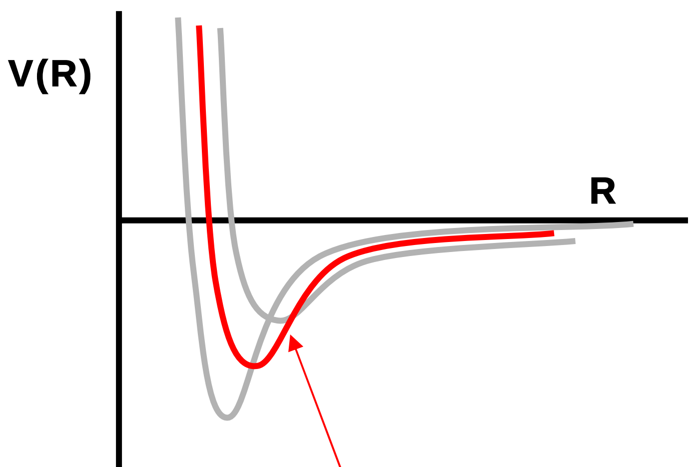


D_e=1.73 kJ/mol
R_e=0.387 nm

We can make dispersion isotropic (heating the molecules)

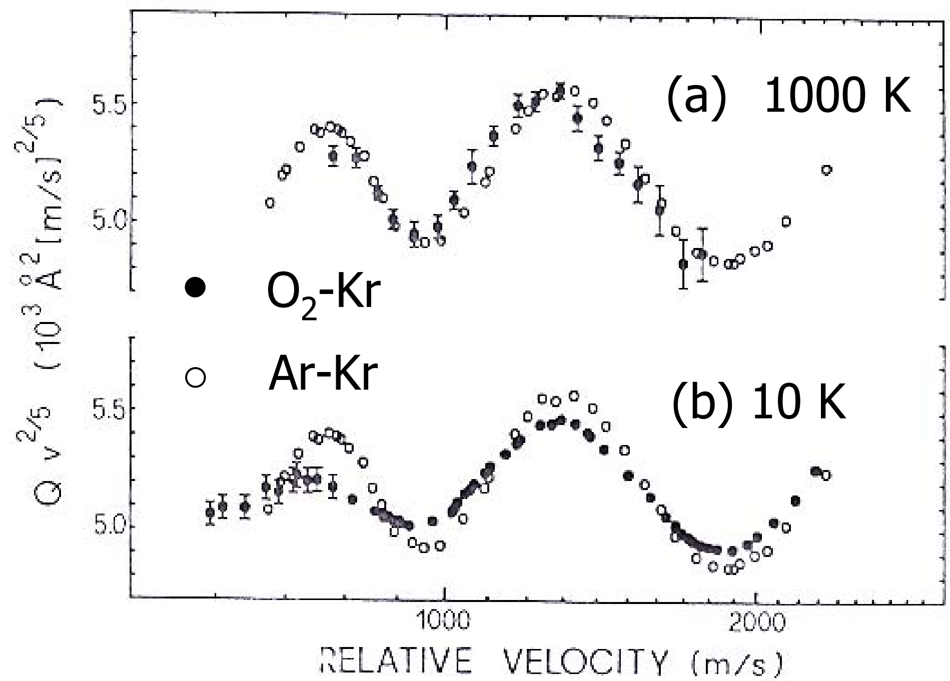


If the molecule rotate faster then the time required for a collision, an effective averaged interaction drives the collision



$$\overline{V} = \frac{1}{2}\int_0^{\pi} V(R,\Theta)\,\sin\Theta\, d\Theta$$

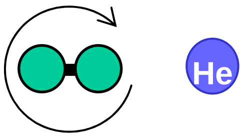
F.Pirani et al. JCP **75**, 1042 (1981)



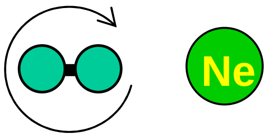
$\alpha(O_2)=1.60$ Å^3

$\alpha(Ar)=1.64$ Å^3

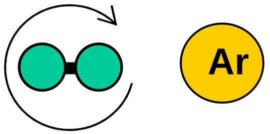
The averaged interaction potential agree with polarizability correlation formulas: Another signature of ‘van der Waals’ nature



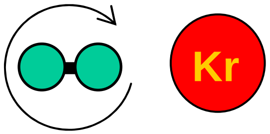
D_e=0.24 **(0.27)** kJ/mol
R_e=0.350 **(0.347)** nm



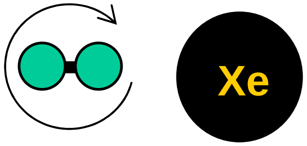
D_e=0.56 **(0.55)** kJ/mol
R_e=0.350 **(0.352)** nm



D_e=1.11 **(1.12)** kJ/mol
R_e=0.372 **(0.379)** nm



D_e=1.29 **(1.36)** kJ/mol
R_e=0.388 **(0.392)** nm

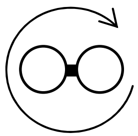


D_e=1.47 **(1.53)** kJ/mol
R_e=0.405 **(0.409)** nm

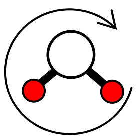
Comparison between water and oxygen (interacting with a rare gas)

$T_{rot} \approx 500K$

$$\bar{V} = \frac{1}{4\pi} \int_0^{\pi} \int_0^{2\pi} V(R, \Theta, \Phi) \sin\Theta d\Theta\, d\Phi$$

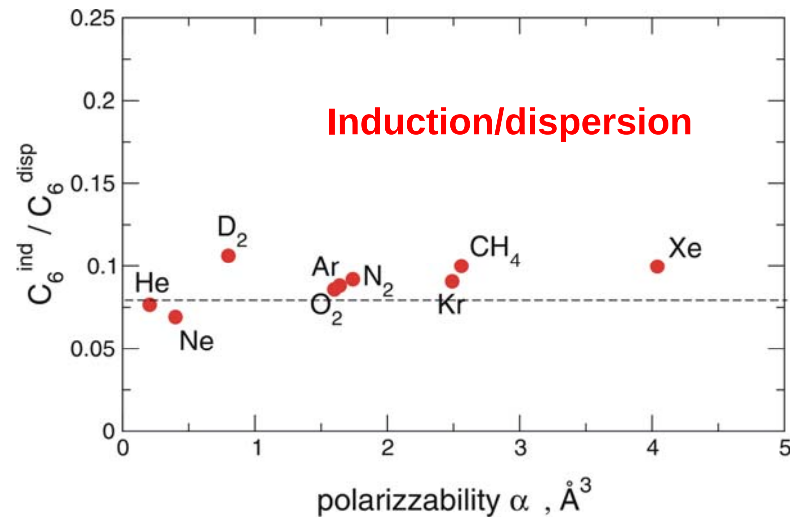


$\alpha(O_2) = 1.60$ Å^3 **dispersion**



$\alpha(H_2O) = 1.46$ Å^3 **dispersion**

$\mu(H_2O) = 1.85$ D **induction**

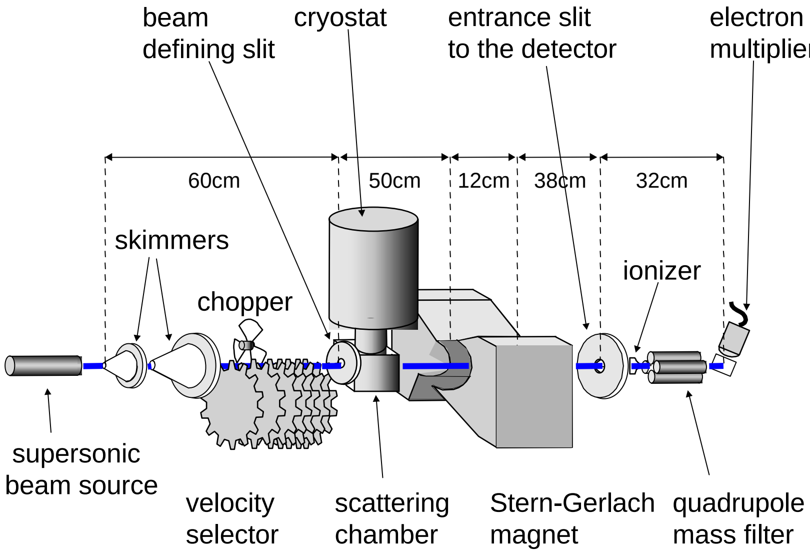


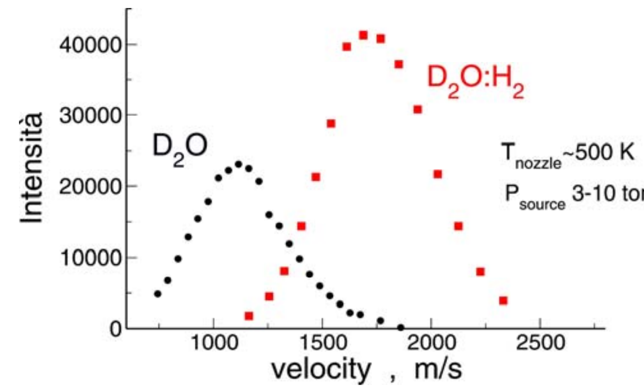
$$V_{tot} = V_{induction} + V_{dispersion}$$

$$V_{induction} = -\frac{C_6^{ind}}{R^6} \qquad V_{dispersion} = -\frac{C_6^{disp}}{R^6}$$

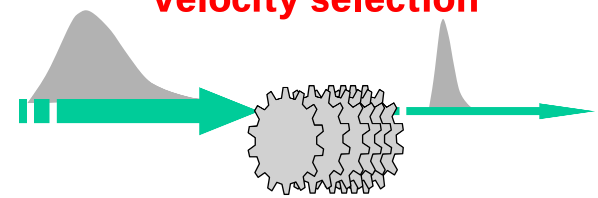
The long range attraction of O_2 and H_2O is very similar :
water rare gas interaction is of ‘van der Waals’ nature?

The experiment

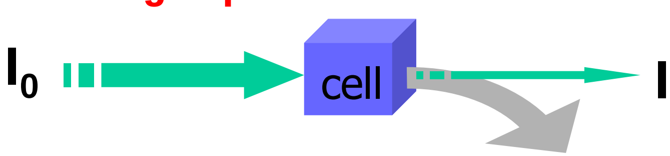




velocity selection



scattering experiments

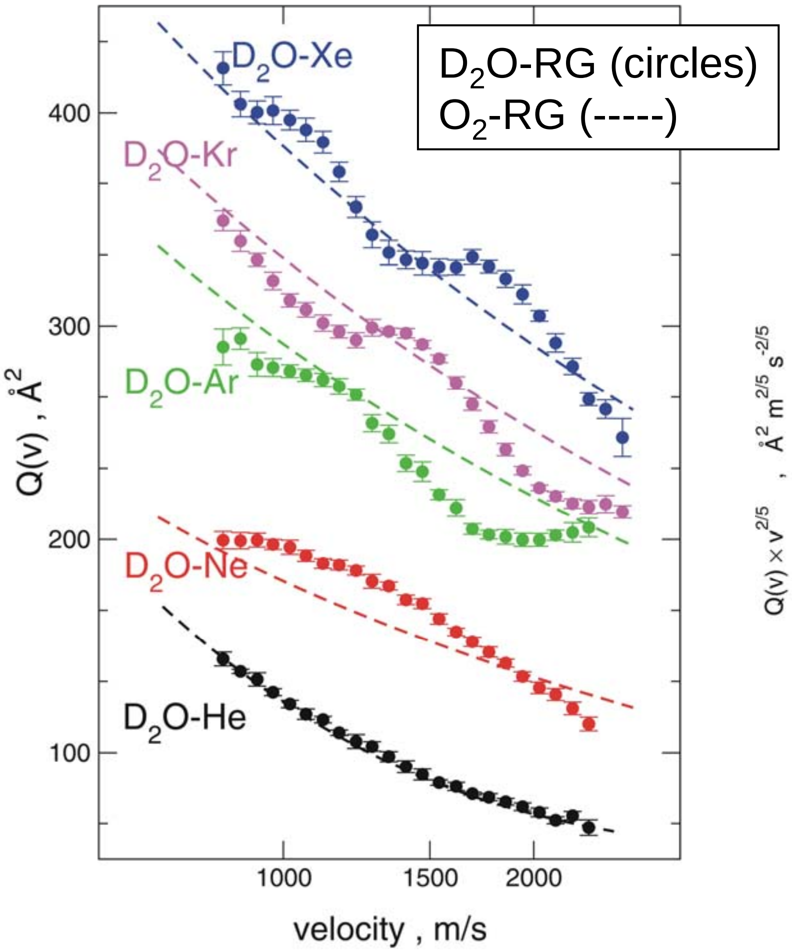


I/I_0 beam attenuation, varies with velocity and intermolecular forces

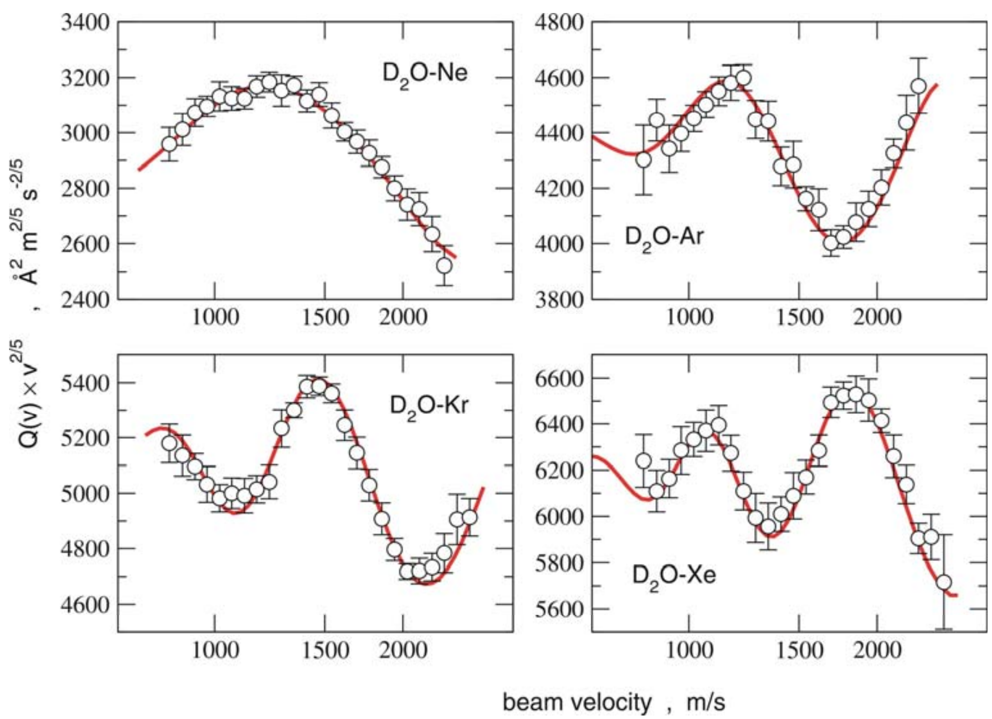
$$Q(v) = \frac{\log\left(I_0 / I \right)}{nL}$$

Experimental results

The average cross section $\boldsymbol{Q}_{av}$ for water and oxygen coincides

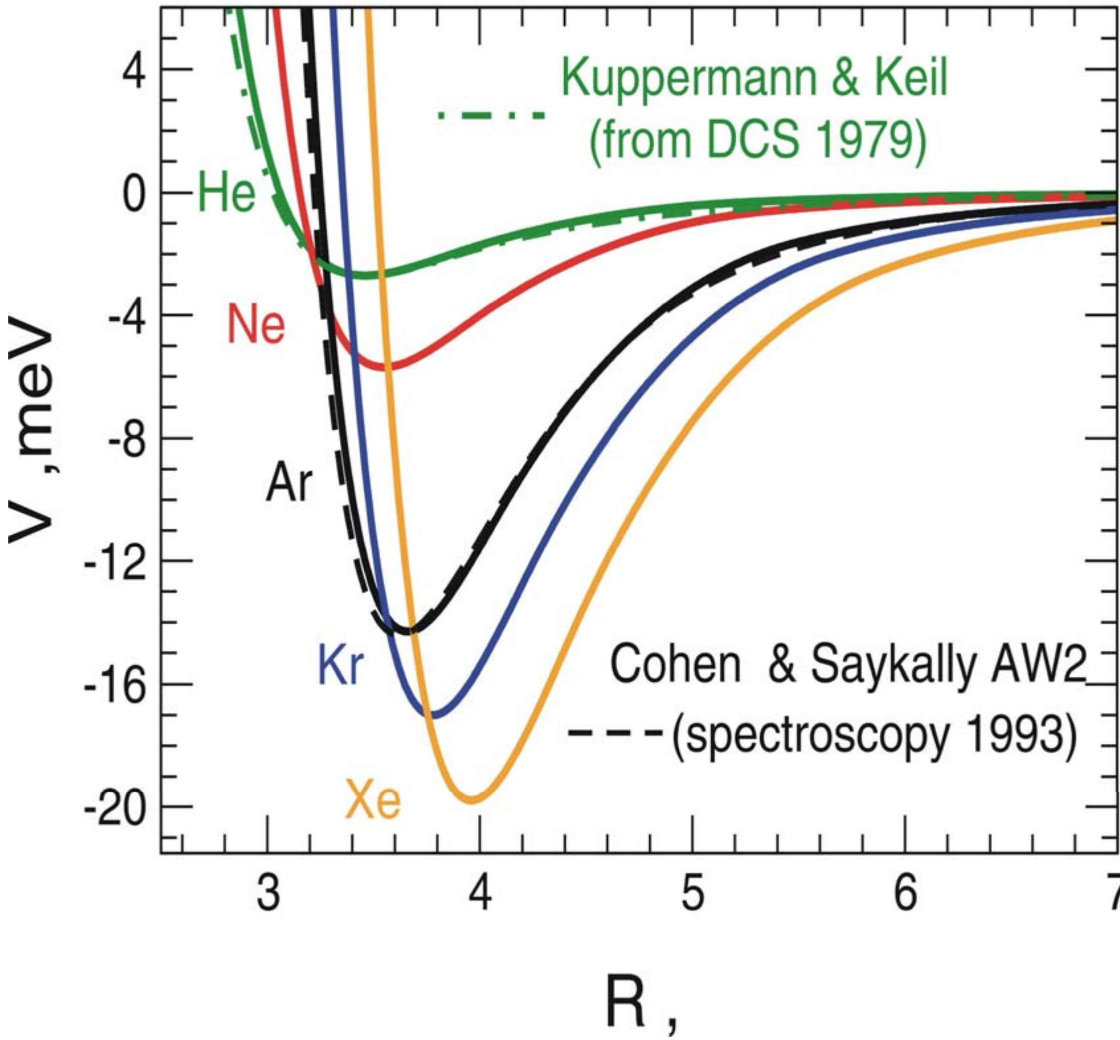


The glory amplitudes $\Delta \boldsymbol{Q}$ are well reproduced by a single spherical potential energy curve



H_2O-rare gases

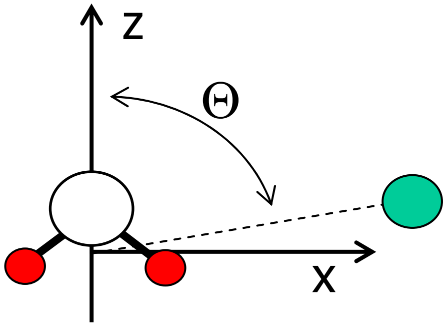
isotropic interaction from integral cross sections



		ε(kJ/mol)	R_m(nm)
He	**D_2O**	**0.26**	**0.345**
		(0.27)	***(0.342)***
Ne		**0.55**	**0.350**
		(0.55)	***(0.346)***
Ar		**1.39**	**0.363** (0.368)*
		(1.13)	***(0.374)***
Kr		**1.65**	**0.375** (0.379)*
		(1.37)	***(0.386)***
Xe		**1.92**	**0.393**
		(1.55)	***(0.404)***

*from rotational spectr.

H_2O - He

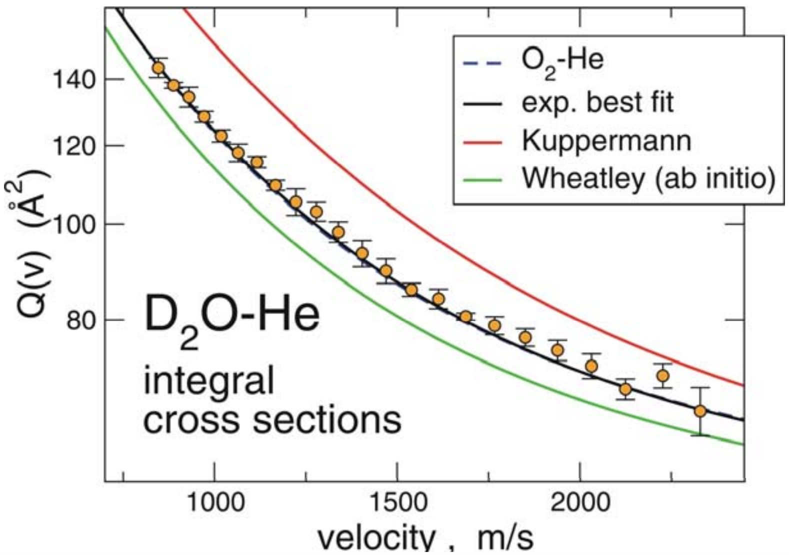


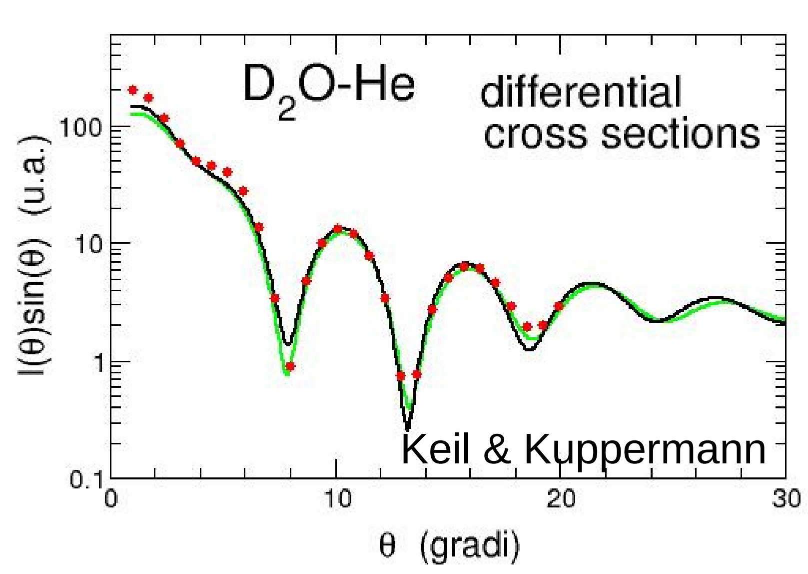
PREVIOUS EXPERIMENTS

Differential Cross Sections

G. Scoles and cow. (1975)	Lennard Jones(12,6)
A. Kuppermann and cow. (1979)	3 different spherical potentials with similar repulsion
U. Buck and cow. (2002)	no fitted potentials

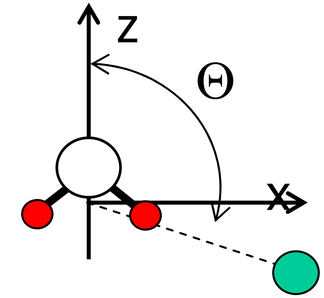
AB INITIO CALCULATIONS	**D_e (meV)**	**R_e (A)**	**Θ(degree)**	**spherical**
A.Palma, S.Green et al. (MP4, 1988-1991)	3.35	3.18	90	**ε = 2.0 meV R_m=3.5 Å**
Kukawska-Tarnawska et al. (SAPT, 1993)	3.71	3.25	80	
F-M. Tao et al. (MP4, 1996)	3.94	3.15	75	
R.J. Wheatley & cow.. (SAPT, 2002)	4.34	3.12	78.3	**ε = 2.42 meV R_m = 3.43 Å**
R. Moszynsky & cow. (SAPT, 2002)	4.34	3.12	78.3	**ε = 2.48 meV R_m = 3.44 Å**
M. Raimondi & Cow. (VB, 2003)	4.19	3.14	74	**ε = 2.63 meV R_m = 3.40 Å**





Oxygen and water have the same cross sections when scattered by He (a very similar interaction)

H_2O-Ar



EXPERIMENTS

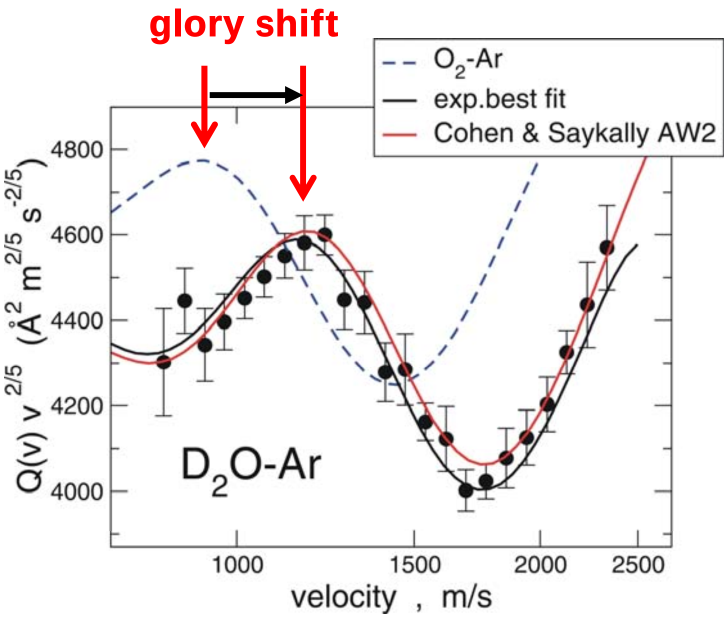
Fraser et al.(1990) Microwave rotational spectra
Gutowsky et al.(1993)
Saykally et al.(1988-1991) Far IR
Suzuki at al.(1991)
Zwart &Meerts (1991) submillimeter bands
Nesbitt et al.(1991-1997) Mid and near IR

EXPERIMENTAL/SEMIEMPIRICAL POTENTIALS

Hutson (1990)
Saykally & Cohen AW2(1993) **H-bonding conf.** **(θ=105.7)**

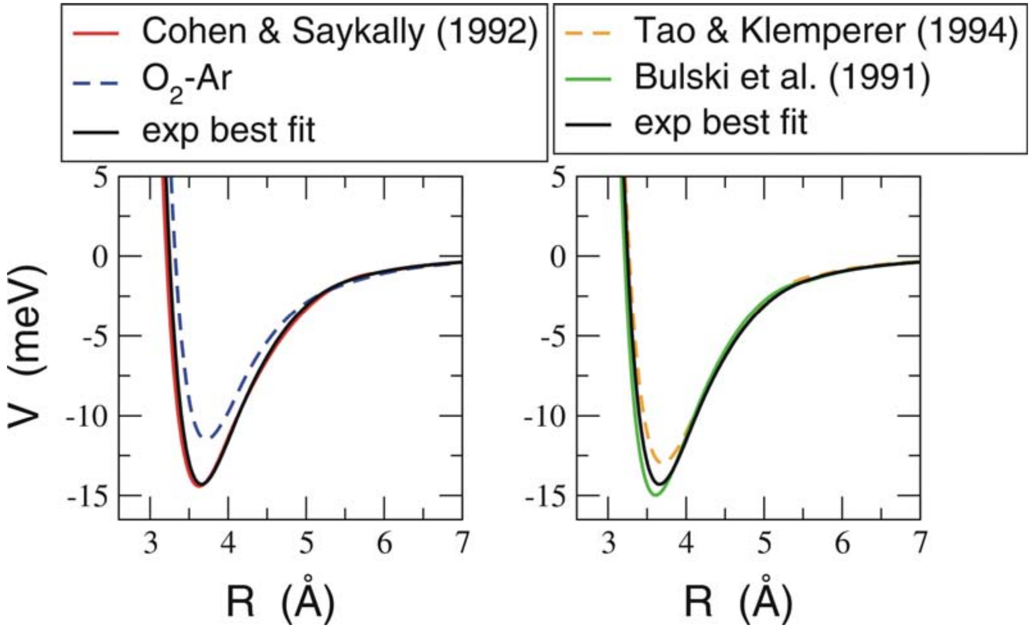
AB-INITIO POTENTIALS

Chalasinski et al. (1991) **anti H-bonding conf.**
Bulski et al. (1991)
Tao & Klemperer (1994) **H-bonding conf.**
Burcl et al. (1995)
Wheatley & cow. (2002)

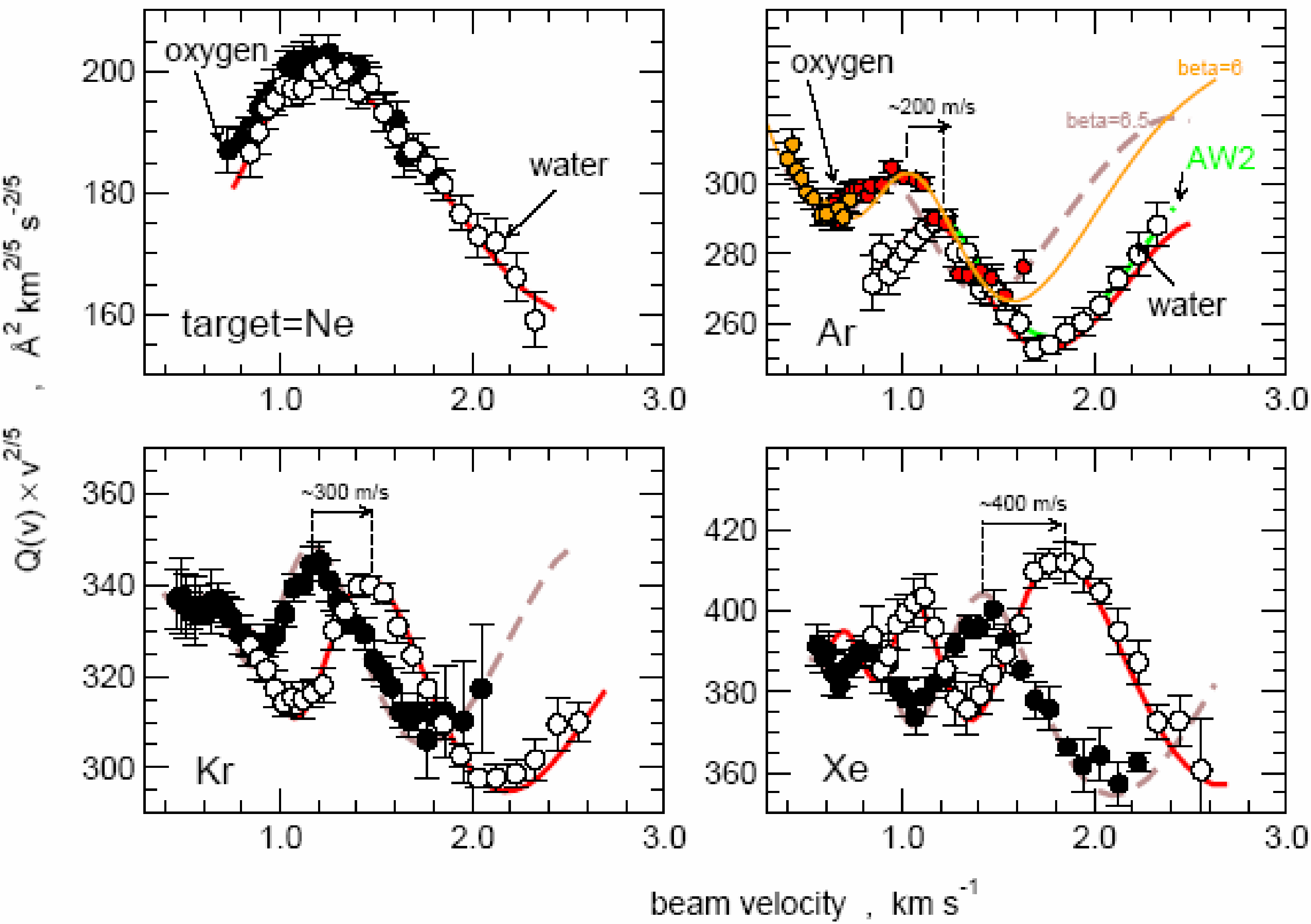


The cross sections of oxygen and water, when scattered by Ar, have the same absolute value but show an energy shift of the glory pattern

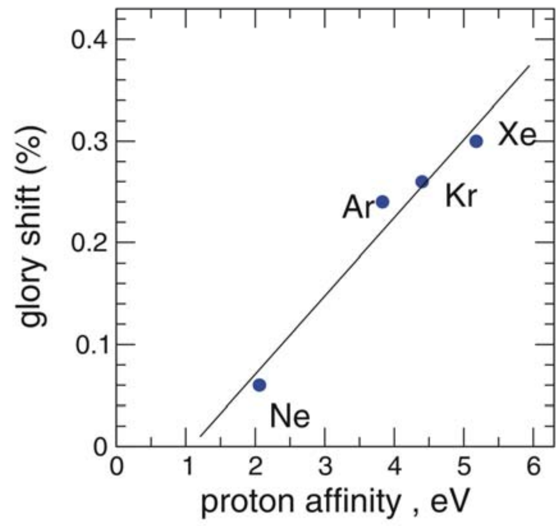
A very similar long range interaction
A different interaction in the well region



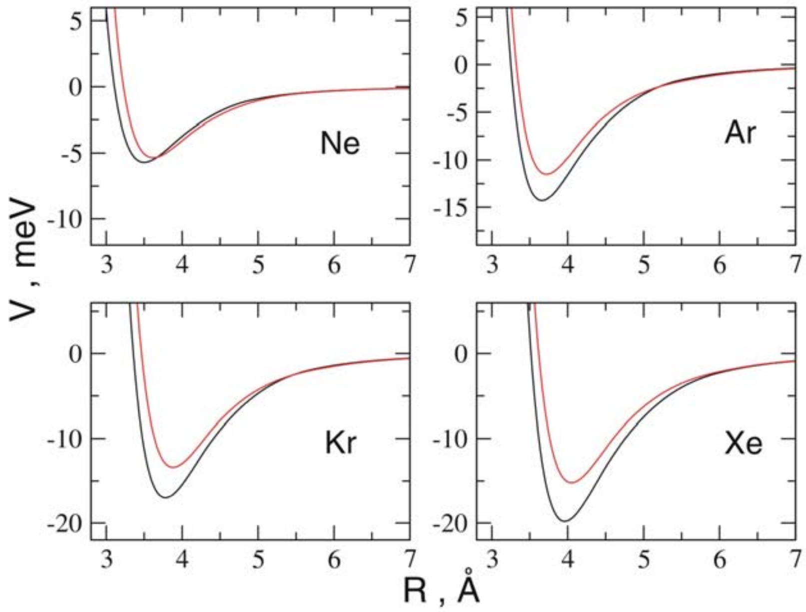
The glory shift increases from Ne to Xe



A signature of charge transfer (embryonic H-bond?) ?

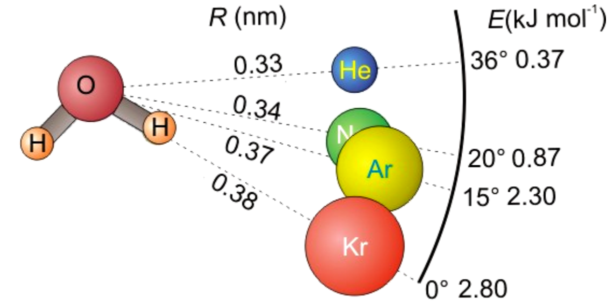


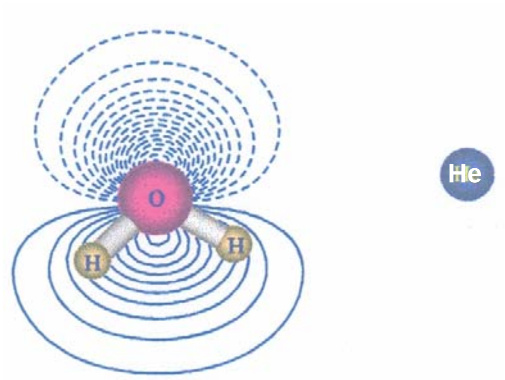
(a)

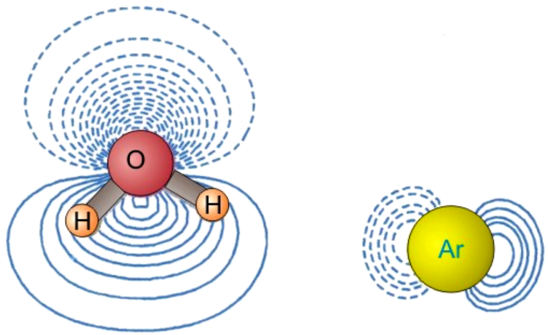


(b)

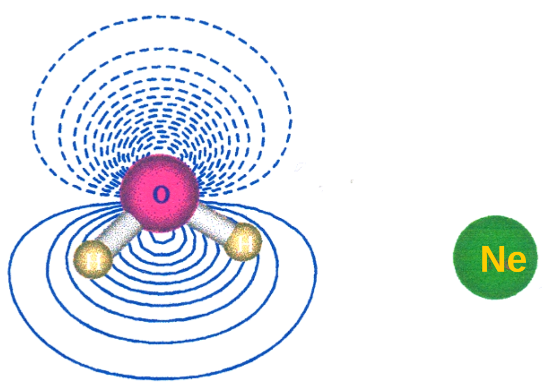
AB-INITIO CALCULATIONS
CCSD(T), Gaussian98
MRCI, MOLCAS4
(aug-cc-VTZ)

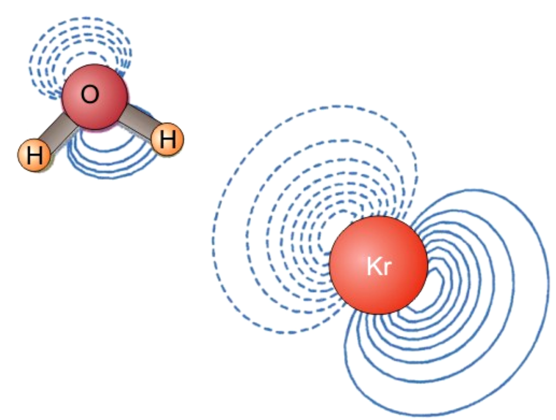




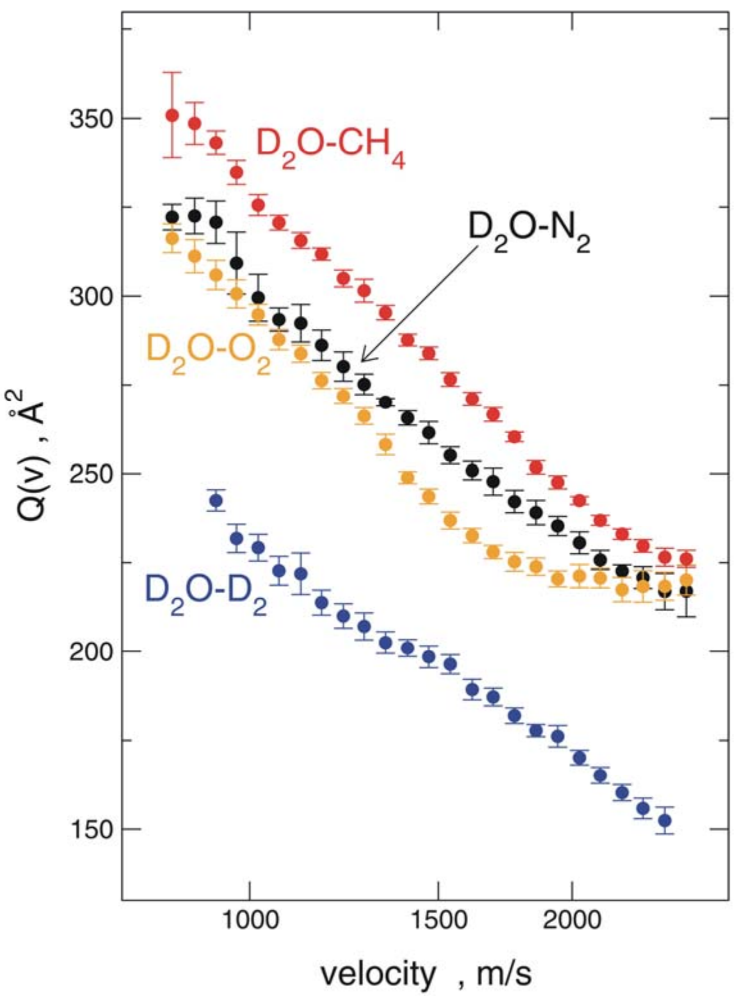


second highest occupied molecular orbital

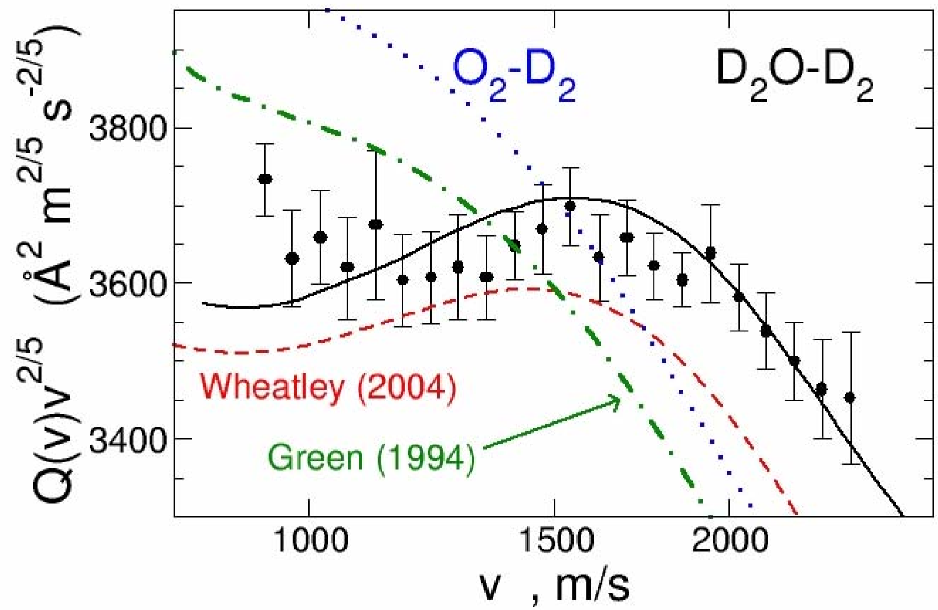




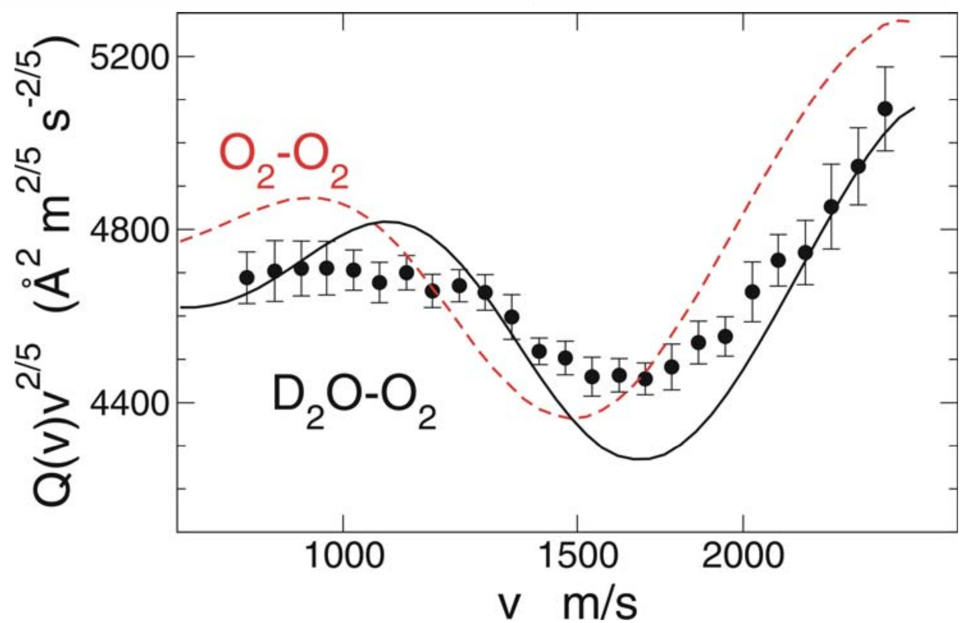
fourth highest occupied molecular orbital



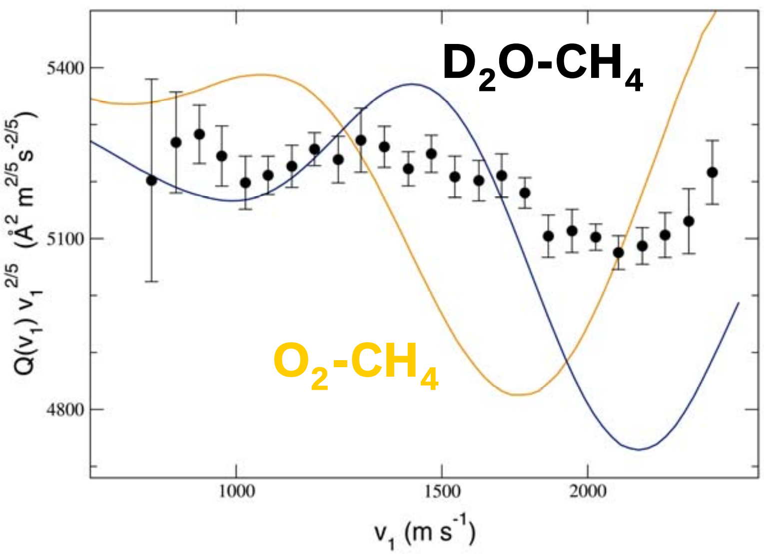
D2O-CH4
D2O-N2
D2O-O2
D2O-D2
350
300
250
200
150
1000
1500
2000
Q(v) , Å2
velocity , m/s



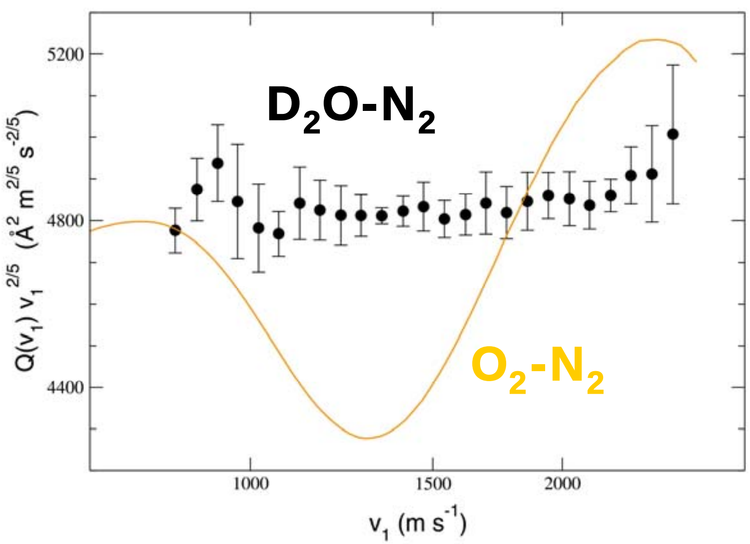
O2-D2
D2O-D2
Wheatley (2004)
Green (1994)
3800
3600
3400
1000
1500
2000
Q(v)v2/5 (Å2 m2/5 s-2/5)
v , m/s



O2-O2
D2O-O2
5200
4800
4400
1000
1500
2000
Q(v)v2/5 (Å2 m2/5 s-2/5)
v m/s



D$_2$O-CH$_4$
O$_2$-CH$_4$
5400
5100
4800
1000
1500
2000
v_1 (m s^{-1})
$Q(v_1)\, v_1^{2/5}$ (Å^2 m$^{2/5}$ s$^{-2/5}$)



D$_2$O-N$_2$
O$_2$-N$_2$
5200
4800
4400
1000
1500
2000
v_1 (m s^{-1})
$Q(v_1)\, v_1^{2/5}$ (Å^2 m$^{2/5}$ s$^{-2/5}$)

Ian H Hiller et al.

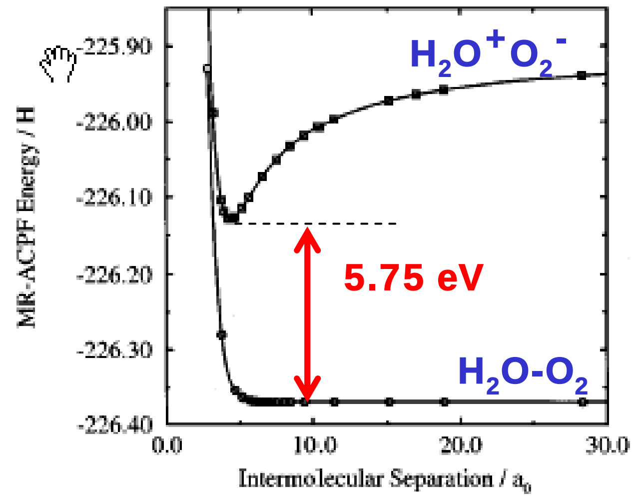
Simulation of the charge transfer absorption of the the H_2O/O_2 complex using ab-initio calculations

J.Chem.Phys. 104 (1996) 3198.

TABLE I. MP2(full)/6-311++G(2d,p) energies (E_{MP2}), binding energies (ΔE_{MP2}), counterpoise estimate of the BSSE (ΔE_{MP2}^{BSSE}) and expectation values of S^2.

Structure[a]	E_{MP2} (Hartrees)	ΔE_{MP2} (eV)	ΔE_{MP2}^{BSSE} (eV)	S^2
1(a)	−226.416 197	−0.033	0.027	2.0489
1(b)	−226.416 178	−0.033	0.021	2.0488
1(c)	−226.415 852	−0.024	0.030	2.0495
1(d)	−226.416 063	−0.029	0.027	2.0492
1(e)	−226.415 962	−0.027	0.024	2.0497
1(f)	−226.416 322	−0.036	0.033	2.0489
1(g)	−150.103 868			2.0494
1(h)	−76.311 112			0.0000

[a]See Fig. 1 for structures of ground state $H_2O \cdot O_2$ complex.



3.15< Rm< 3.48 Å   (**3.50 Å**)
(**8.3 meV**)

Fulvio Cacace et al.

Direct Experimental Evidence for the $H_2O^+O_2^-$ Charge Transfer Complex

Angew.Chem. 39 (2000) 367.

Conclusions

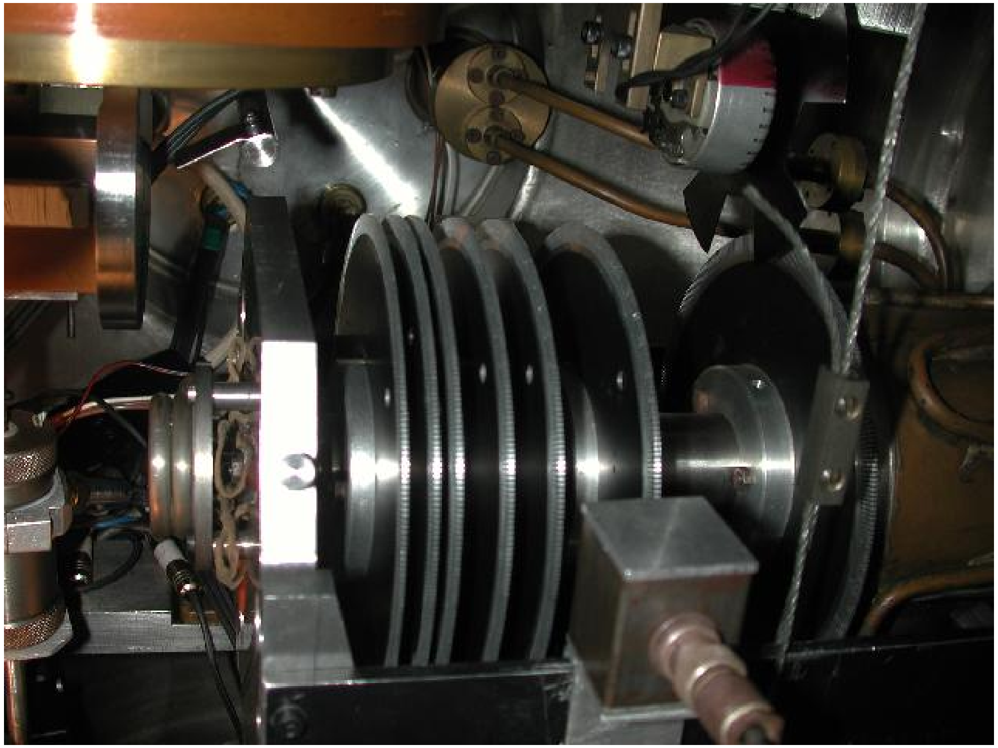
•Present experiments provide important information on range and strenght of the intermolecular potentials in weakly bound complexes involving water

•The non-covalent interaction departs from a van der Waals nature when passing from water-He to water-Xe

•The water-molecule cases exhibit a complex phenomenology. The combination of present results with ab-initio calculations could lead to a proper characterization of such important systems.

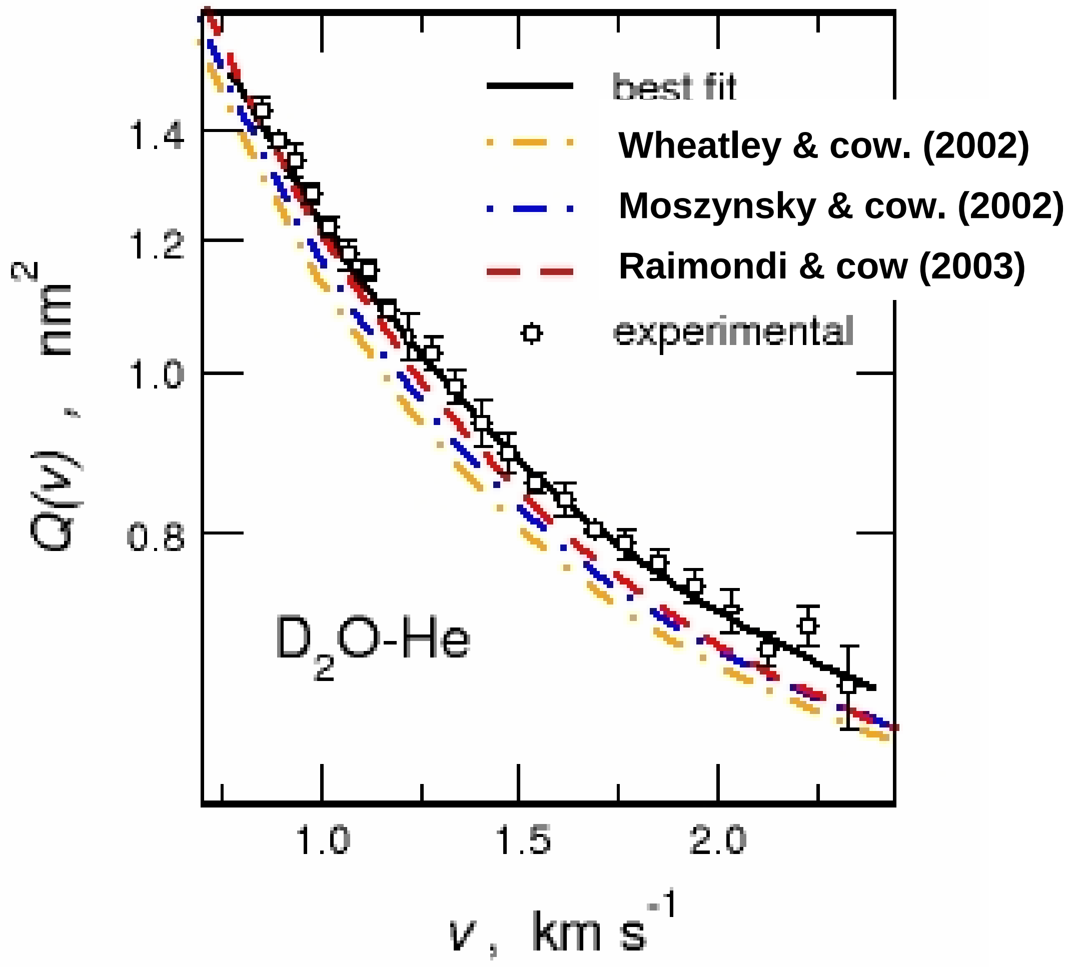
8 disks velocity selector

High resolution (3%) but low transmission (10^{-2})

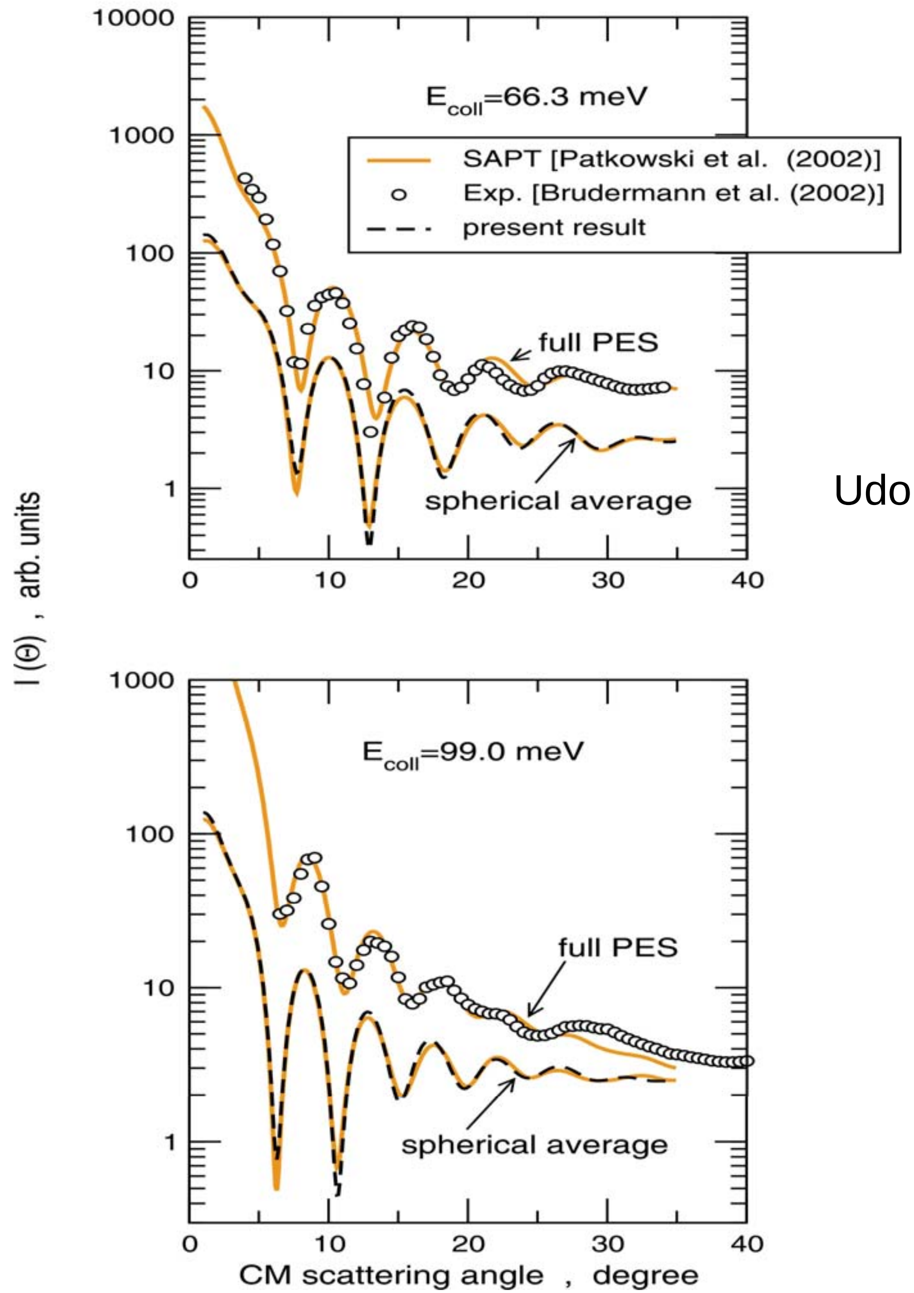


45 cm

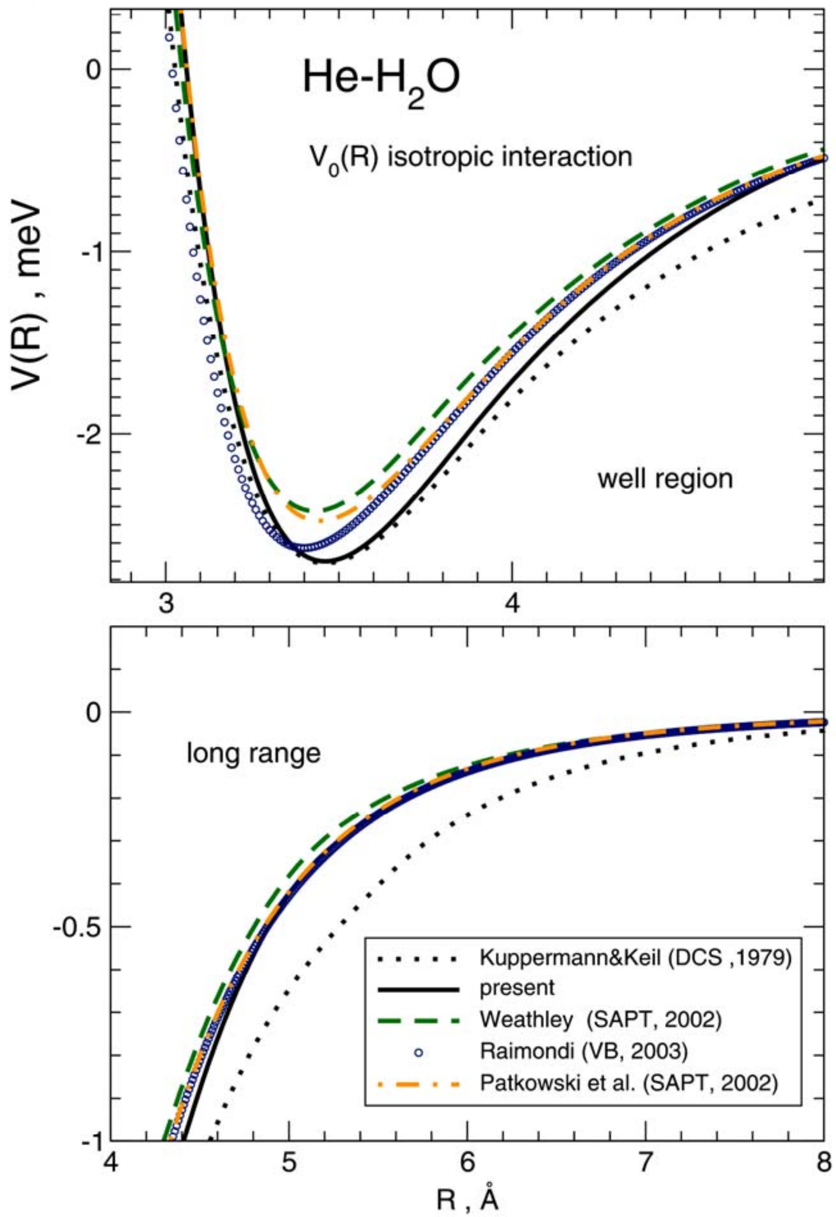
AB-INITIO PES



Differential cross sections for He-H_2O



Udo Buck & cow. (2003)


He-H_2O
$V_0(R)$ isotropic interaction
well region
long range
V(R) , meV
R , Å
0
-1
-2
3
4
0
-0.5
-1
4
5
6
7
8
Kuppermann&Keil (DCS ,1979)
present
Weathley (SAPT, 2002)
Raimondi (VB, 2003)
Patkowski et al. (SAPT, 2002)