

Long-range ultracold atom-dimer photoassociation



Olivier Dulieu

Laboratoire Aimé Cotton, CNRS, Univ. Paris-Sud 11, Orsay, France



**Institut francilien de recherche
sur les atomes froids**

soutenu par la région  **ile de France**



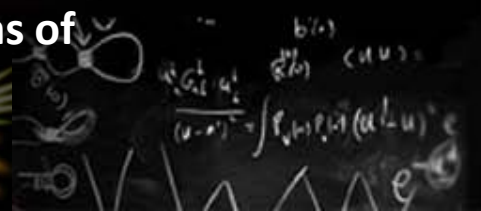
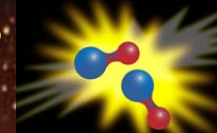
In collaboration with:

Mireille Aymar, Demis Borsalino, Nadia Bouloufa, Anne Crubellier, **Maxence Lepers**,
Eliane Luc, **Jesus Perez-Rios**, **Goulven Quéméner**, Maurice Raoult, **Romain Vexiau**



The Kavli Institute for
Theoretical Physics
University of California, Santa Barbara

Fundamental Science and Applications of
Ultra-cold Polar Molecules
March 7, 2013



Why is there so much enthusiasm about cold and ultracold molecules?

High resolution spectroscopy, test of fundamental theories, quantum simulators of condensed phase phenomena, anisotropy in quantum degenerate gases, quantum information, (other (crazy) ideas)...

a novel « (ultra-)cold photo-physical chemistry »:

Understanding elementary reactions at the single quantum state level,
Role of excited states, quantum resonances,
Control of energy deposition in a molecular system
Reactivity at short/large distances...

PCCP special issue 2011 (eds OD, R. Krems, M. Weidemüller, S. Willitsch): about 55 papers!

Chemical review 2012 (eds J. Ye, D. Jin): 9 review papers!

The hope: to achieve full control of internal and external degrees of freedom of quantum systems

The need: To fully understand the details of molecular structure, i.e. to solve a N-body problem, strongly depending on the value of N

Cold chemistry: enthusiasm or desperation?

PHYSICAL REVIEW A 85, 062712 (2012)

Statistical aspects of ultracold resonant scattering

Michael Mayle, Brandon P. Ruzic, and John L. Bohn

JILA, University of Colorado and National Institute of Standards and Technology, Boulder, Colorado

(Received 30 March 2012; published 28 June 2012)

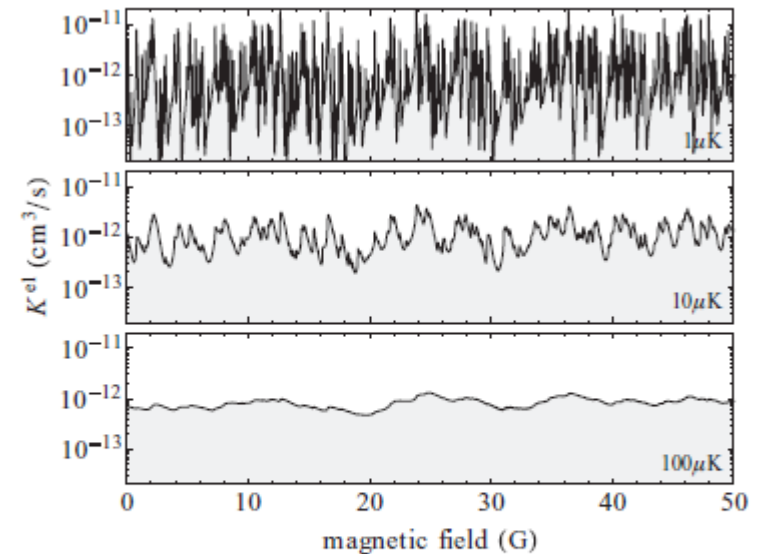
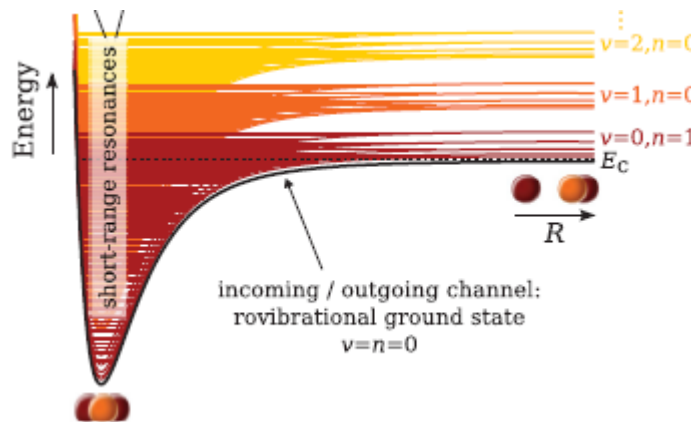
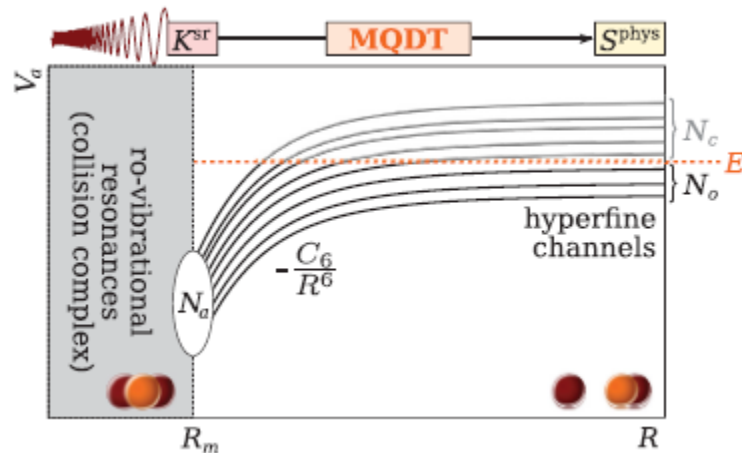


FIG. 5. Elastic s -wave rate constants for Rb + KRB collisions in the absolute ground state. Depicted is the thermalized rate constant for a temperature of $1 \mu\text{K}$, $10 \mu\text{K}$, and $100 \mu\text{K}$, respectively (top to bottom).

PHYSICAL REVIEW A 87, 012709 (2013)

Scattering of ultracold molecules in the highly resonant regime

Michael Mayle, Goulven Quémener, Brandon P. Ruzic, and John L. Bohn

JILA, University of Colorado and National Institute of Standards and Technology, Boulder, Colorado 80309-0440, USA

(Received 16 October 2012; published 24 January 2013)

Compared to purely atomic collisions, ultracold molecular collisions potentially support a much larger number of Fano-Feshbach resonances due to the enormous number of rovibrational states available. In fact, for alkali-metal dimers we find that the resulting density of resonances cannot be resolved at all, even on the sub- μK temperature scale of ultracold experiments. As a result, all observables become averaged over many resonances and can effectively be described by simpler, nonresonant scattering calculations. Two particular examples are discussed: nonchemically reactive RbCs and chemically reactive KRb. In the former case, the formation of a long-lived collision complex may lead to the ejection of molecules from a trap. In the latter case, chemical reactions broaden the resonances so much that they become unobservable.

The vision of an expert...

**CHEMICAL
REVIEWS**

Review

pubs.acs.org/CR

Toward State-to-State Dynamics in Ultracold Collisions: Lessons from High-Resolution Spectroscopy of Weakly Bound Molecular Complexes

David J. Nesbitt*

JILA, National Institute of Standards and Technology, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309, United States

The vision of an expert...

CHEMICAL REVIEWS

Review

pubs.acs.org/CR

ing diatomic molecule.^{7,10–15} From a chemical physics perspective, these diatomic molecules might be considered as relatively arcane objects, with mean bond lengths of many thousands of angstroms and energies only a few megahertz (i.e., a few nano eV) below the dissociation limit.^{7,8,16} However, the

fact that such pairs of separated atoms are formed with center-of-mass velocities corresponding to sub-microkelvin temperatures and therefore essentially stationary in the laboratory frame is both extremely elegant and intellectually compelling.

Indeed, this novel experimental platform of molecules near the dissociation limit offers a fundamentally new and exciting arena for studying three body interactions and ultra low energy atomic collision dynamics.

Although such ultraweakly chemically interacting species might not seem an obvious fit for a *Chemical Reviews* thematic issue, recent advances in this rapidly emerging field of ultracold molecules are now providing a critical change in this way of thinking.^{17–26} In particular, there have been pioneering efforts

in Ultracold Collisions: Lessons from of Weakly Bound Molecular

Department of Chemistry and Biochemistry, University of Colorado,

The vision of an expert...

CHEMICAL REVIEWS

Review

pubs.acs.org/CR

ing diatomic molecule.^{7,10–15} From a chemical physics perspective, these diatomic molecules might be considered relatively arcane objects, with mean bond lengths of thousands of angstroms and energies only a few nano eV below the dissociation limit. The fact that such pairs of separated atoms are moving at low mass velocities corresponding to sub-thermal temperatures and therefore essentially stationary in the laboratory frame is both extremely elegant and intellectually appealing. Indeed, this novel experimental platform of weakly bound complexes just below the dissociation limit offers a fundamentally new approach for studying three body interactions and atomic collision dynamics.

Although such ultraweakly chemically bound complexes might not seem an obvious fit for a *Chemical Reviews* issue, recent advances in this rapidly emerging field of molecules are now providing a critical challenge to our thinking.^{17–26} In particular, there have been

From a chemical physics

The use of weak binding interactions to engineer molecular collisions is not a new idea. In the chemical physics literature, this is what has been referred to as the “half-collision” regime (see Figure 1), whereby the intermolecular potential is used to preorient two reagent species prior to initiating some physical and/or chemical collision event, thereby avoiding the more normal sampling over a broad distribution of scattering angles and collision energies from a “full-collision” perspective.^{58,60,66,67} The point of key relevance to the present work is that any light source with sufficient resolution to spectrally isolate individual rotational, vibrational, and possibly fine/hyperfine transitions in these weakly bound complexes is often able to select and probe a *single pure quantum state* out of a hot (at least from an ultracold 300 nK perspective) distribution of internal states. Thus, high-resolution spectroscopy permits access to elastic, inelastic, and even chemically reactive dynamics arising from pure quantum states of the complex, corresponding in a very real sense to a snapshot of an intermolecular collision for a rigorously well-defined angular momentum state, partial wave, and total parity. Stated

The vision of an expert...

CHEMICAL REVIEWS

Review

pubs.acs.org/CR

ing diatomic molecule.^{17,10-15}

From a chemical physics perspective, these diatomic molecules might be considered relatively arcane objects, with mean bond lengths of thousands of angstroms and energies only a few nano eV below the dissociation limit.

It is a fact that such pairs of separated atoms are moving with mass velocities corresponding to sub-relativistic temperatures and therefore essentially stationary in the laboratory frame is both extremely elegant and intellectually stimulating. Indeed, this novel experimental platform of ultraweakly bound complexes offers a fundamentally new approach for studying three body interactions and atomic collision dynamics.

Although such ultraweakly chemically bound complexes might not seem an obvious fit for a *Chemical Reviews* issue, recent advances in this rapidly emerging field of molecules are now providing a critical challenge to our thinking.¹⁷⁻²⁶ In particular, there have been

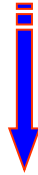
From a chemical physics perspective,

The use of weak binding interactions to engineer molecular collisions is not a new idea. In the chemical physics literature, this is what has been referred to as the “half-collision” approach (see Figure 1), whereby the intermolecular potential is used to preorient two reagent species prior to initiating a physical and/or chemical collision event, thereby allowing for more normal sampling over a broad distribution of scattering angles and collision energies from a “collision” perspective.^{58,60,66,67} The point of interest to the present work is that any light source with sufficient resolution to spectrally isolate individual rotational, and possibly fine/hyperfine transitions in ultraweakly bound complexes is often able to select a single pure quantum state out of a hot (at least from a solid 300 nK perspective) distribution of intermolecular states, high-resolution spectroscopy permits access to elastic, inelastic, and even chemically reactive dynamics arising from pure quantum states of the complex, corresponding in a very real sense to a snapshot of an intermolecular collision for a rigorously well-defined angular momentum state, partial wave, and total parity. Stated

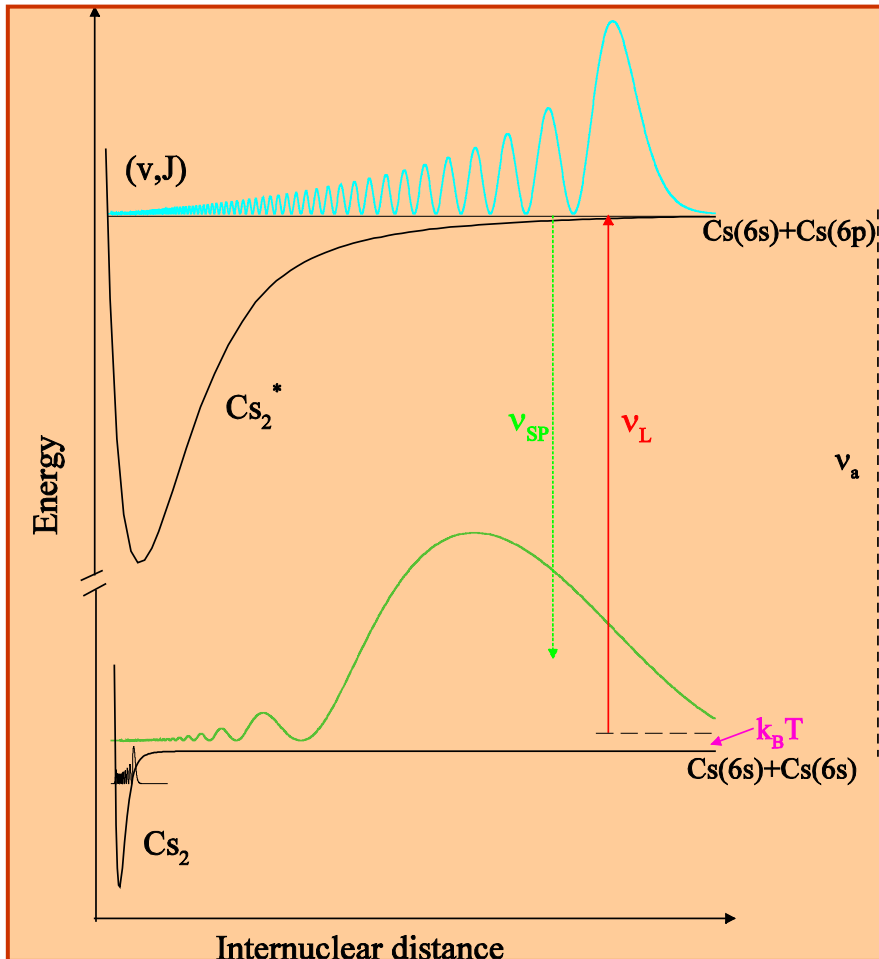
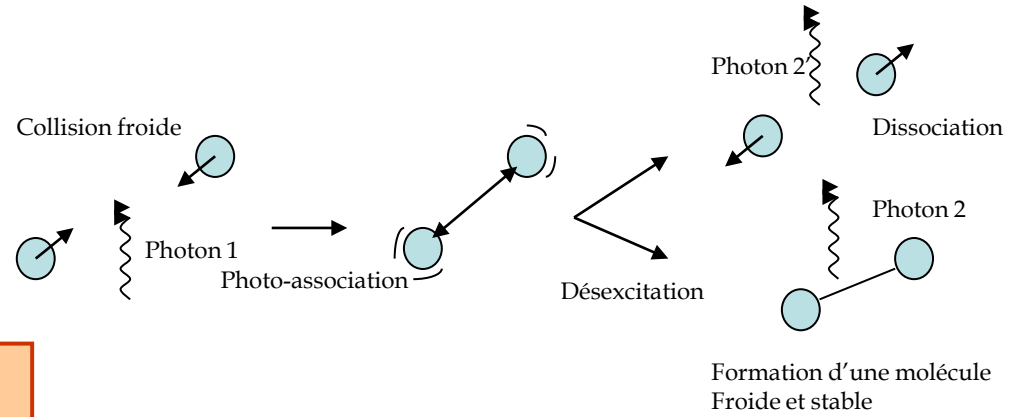
PHOTOASSOCIATION!!!



...associate a pair of ultracold atoms,
to form an ultracold molecule!



PhotoAssociation



Well-known at thermal energies

Marvet&Dantus, Chem. Phys. Lett. 245, 393 (1995)

Cold atoms: "quasibound"-bound transition

Thorsheim et al, PRL, 58, 2420 (1987)

Creates a giant ultracold excited molecule, or
a "long-range molecule"

Stwalley&Wang, J. Mol. Spectrosc. 195, 194, (1999)

Weiner et al, Rev. Mod. Phys. 71, 1 (1999)

Masnou&Pillet, Adv. At. Mol. Opt. Phys. 47, 53 (2001)

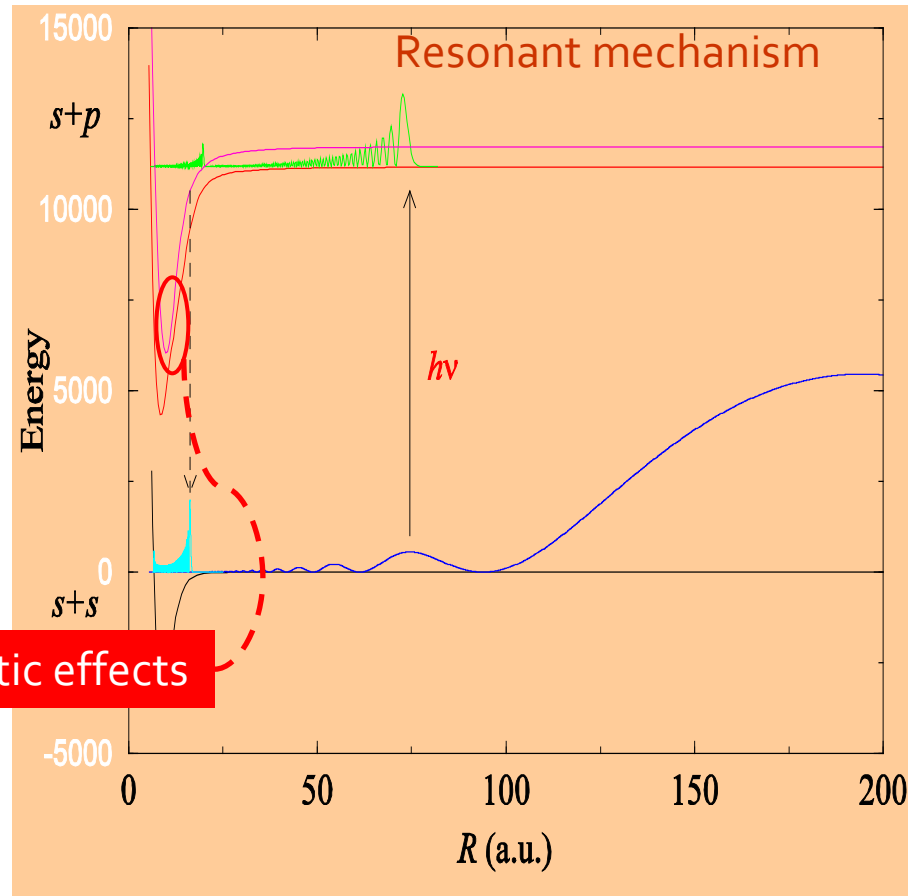
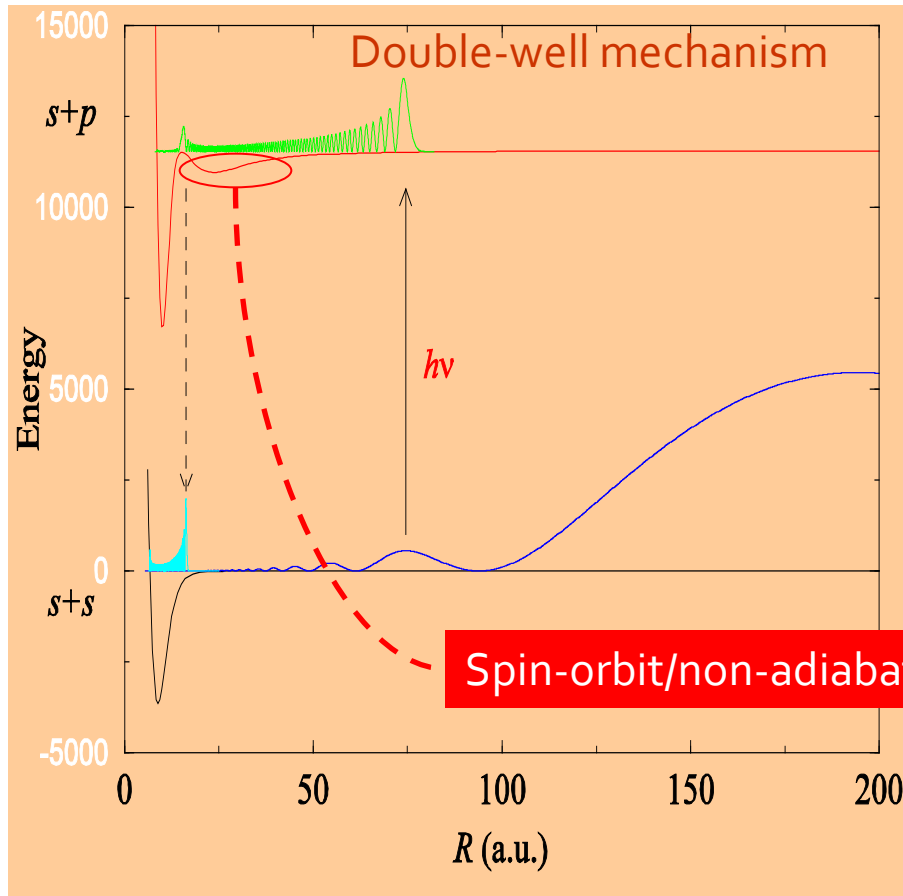
Jones et al, Rev. Mod. Phys., 78 (2006)

- $Li_2, Na_2, K_2, Rb_2, Cs_2; H_2, Ca_2, He_2, Sr_2, Yb_2 \dots$
- $NaCs, RbCs, KRb, LiCs, LiK, YbRb, NaK \dots$

Short-lived ultracold molecules,
stabilization process needed...

UltraCold Molecule Formation through 1-step PA+radiative decay

transfer density of probability inwards, to produce stabilized ultracold molecules



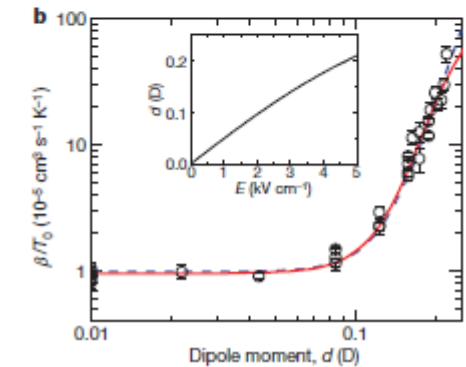
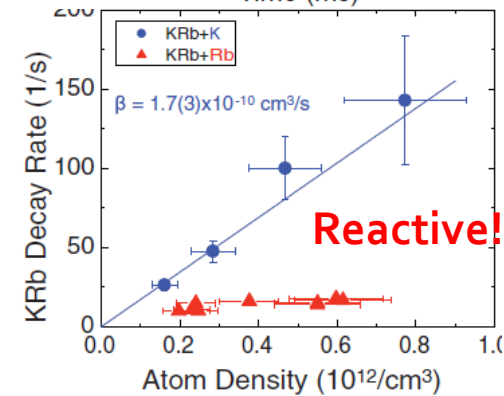
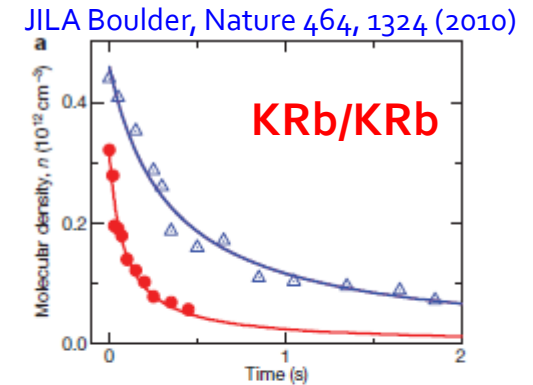
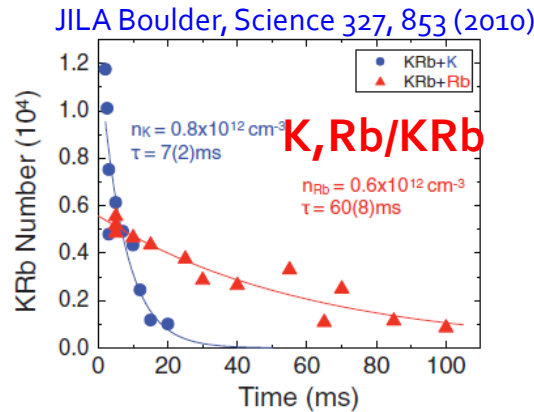
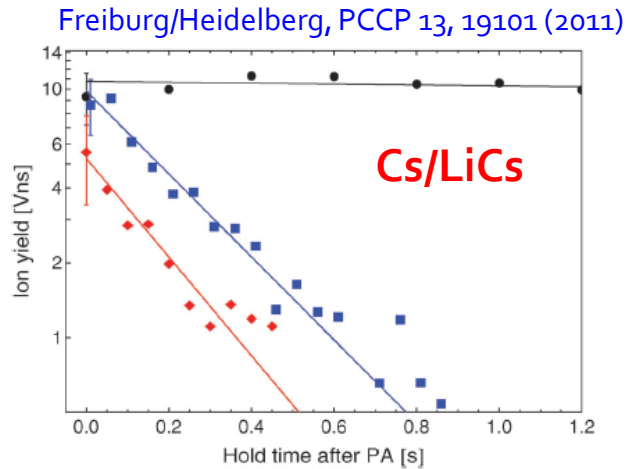
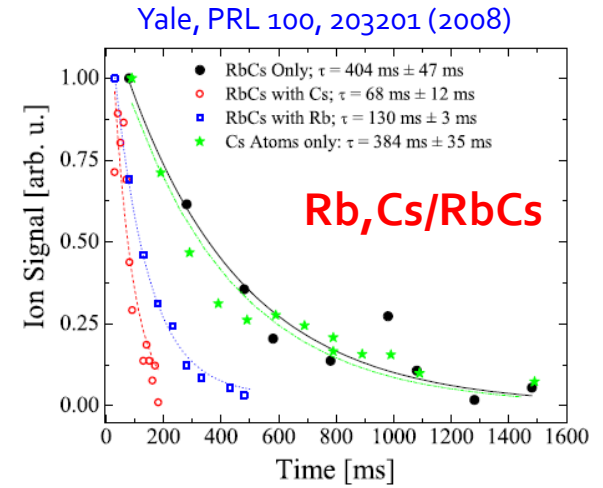
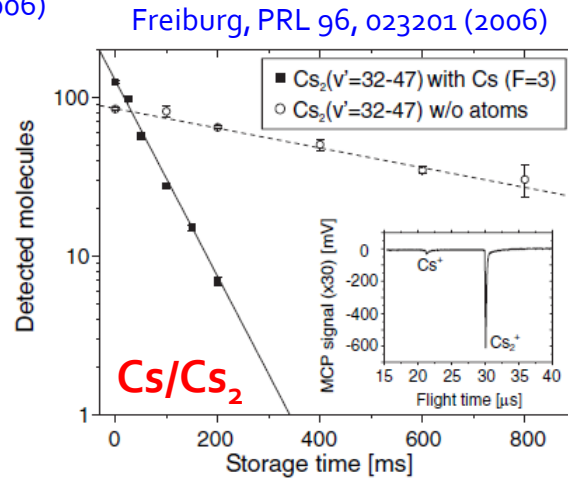
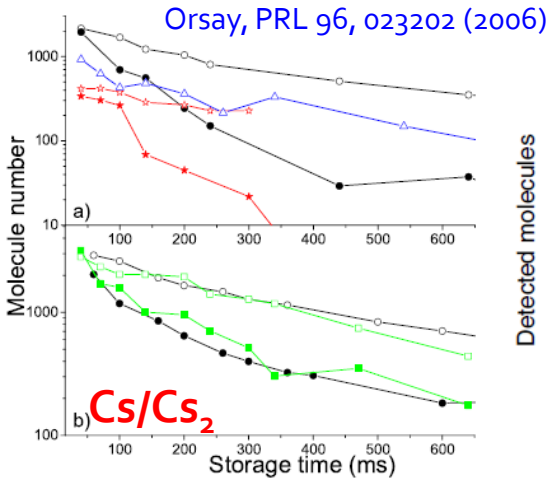
Cs_2 : Orsay, PRL, 80, 4402 (1998);
 Rb_2 : Pisa, PRL, 84, 2814 (2000)

Cs_2 : Orsay, PRL 86, 2253 (2001)

**PHOTOASSOCIATION OF
A and BC**

« the way of desperation »? © (J.B.)

Dense samples of ultracold molecules and atoms are under reach



Excited atom/ground state molecule still to be observed

As for atoms, crucial role of long-range interactions between particles

Long-range interactions between atoms or/and molecules

Standard multipolar long-range expansion

$$V(R) = \frac{1}{4\pi\epsilon_0} \sum_{\ell_A \ell_B m} \frac{f_{\ell_A \ell_B m}}{R^{1+\ell_A+\ell_B}} Q_{\ell_A}^m Q_{\ell_B}^{-m}$$

Multipolar moments

$$Q_{\ell_A}^m = \sqrt{\frac{4\pi}{2\ell_A+1}} \sum_{i \in A} r_i^{\ell_A} Y_{\ell_A}^m(\theta_i, \phi_i), \quad A \rightarrow B, \quad i \rightarrow j$$

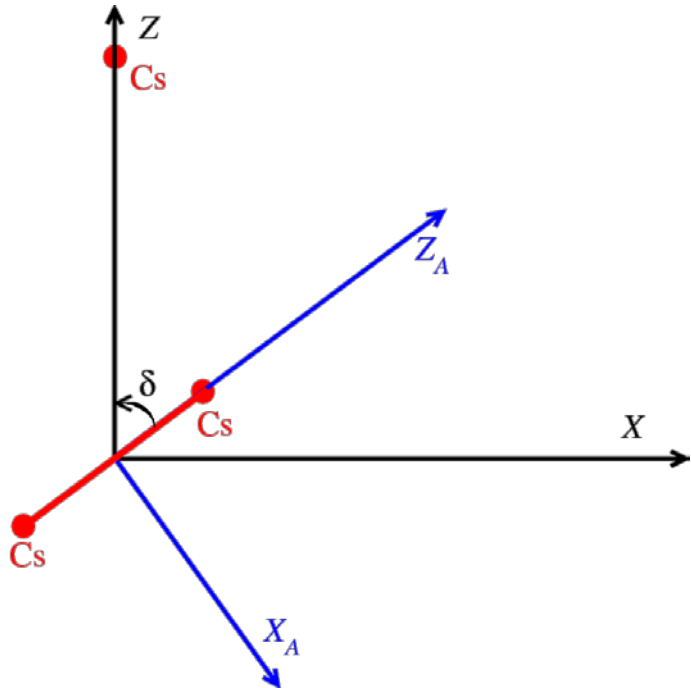
$$f_{\ell_A \ell_B m} = \frac{(-1)^{\ell_B} (\ell_A + \ell_B)!}{\sqrt{(\ell_A + m)! (\ell_A - m)! (\ell_B + m)! (\ell_B - m)!}}$$

See for instance:

B. Bussery-Honvault, et al, J. Chem. Phys. **129**, 234302 (2008).

D. V. M. R. Flannery and V. N. Ostrovsky, J. Phys. B **38**, S279 (2005).

G. C. Groenenboom, et al, J. Chem. Phys. **126**, 204306 (2007).



- Dimer rotation:

$$\text{Cs}_2 : |\Phi_A\rangle \equiv |X\Lambda v_d Nm\rangle = |X^1\Sigma_g^+, v_d = 0, Nm\rangle$$

$$\text{Cs} : |\Phi_B\rangle \equiv |nls(\lambda\sigma) j\omega\rangle = |6^2 P_{j\omega}, (\lambda\sigma)\rangle$$

$$\vec{J} = \vec{N} + \vec{j} + \vec{L}$$

$$\Omega = m + \omega = m + \lambda + \sigma = m_j + \sigma$$

in (XYZ)

Frame transformation $|Nm\rangle$

$$\hat{Q}_{L_A}^M = \sum_{\mu=-L_A}^{L_A} d_{M\mu}^{L_A}(\delta) \hat{q}_{L_A}^\mu$$

in $(X_A Y_A Z_A) |\Lambda v_d\rangle$

DOMINANT TERMS

0th order: $\varepsilon_p^0 = E_A + E_B$ et $|\varphi_p^0\rangle = |\Phi_A\rangle|\Phi_B\rangle$

1st order:

Quadrupole moment of the atom: $\langle n\ell\lambda' | \hat{Q}_2^M | n\ell\lambda \rangle = -e \langle r_{nl}^2 \rangle C_{\ell 0 2 0}^{\ell 0} C_{\ell \lambda 2 M}^{\ell \lambda'} \neq 0$ si $\ell \geq 1$

Quadrupole moment of the molecule: $\langle \Lambda v_d | \hat{q}_2^\mu | \Lambda v_d \rangle = q_2^0$

$$\Rightarrow C_5 / R^5$$

2nd order:

Dimer transitions: $X^1\Sigma_g^+ \rightarrow ^1\Sigma_u^+, ^1\Pi_u$

Atom transitions: $^2P \rightarrow ^2S, ^2D$

$$\Rightarrow C_6 / R^6$$

Note: necessitates the knowledge of MANY PESs and TDMs, calculated on our own

For every N and $\ell(=1)$, $(2N+1) \times (2\ell+1)$ long-range potential curves

$$\varepsilon_{p,i}(R) = B_{Xv_d} N(N+1) + \frac{C_5^{(i)}}{R^5} + \frac{C_6^{(i)}}{R^6}$$

Lepers, Dulieu, Kokoouline Phys. Rev. A, **82**, 042711 (2010),
Lepers, Vexiau, Bouloufa, Dulieu, Kokoouline Phys. Rev. A **83**,
042707 (2011)
Lepers, Dulieu, Eur. Phys. J. D **65**, 113 (2011)
Lepers, Dulieu, Phys. Chem. Chem. Phys. **13**, 19106 (2011)

Long-range coefficients

TABLE I. The C_6 coefficients of the $\text{Cs}_2(X^1\Sigma_g^+, v_d = 0, j) + \text{Cs}(6^2S)$ long-range interaction calculated for $j = 0$ to 4. In analogy to a diatomic molecule, the C_6 are sorted by projections of the total orbital quantum number $m_J = m_j$ on the Z axis (note that $\lambda = 0$) and the parity \pm through the reflection symmetry with respect to a plane containing the axis. This yields the Σ^\pm , Π , Δ , Φ , Γ symmetries for $m_J = 0, \pm 1, \pm 2, \pm 3, \pm 4$, respectively.

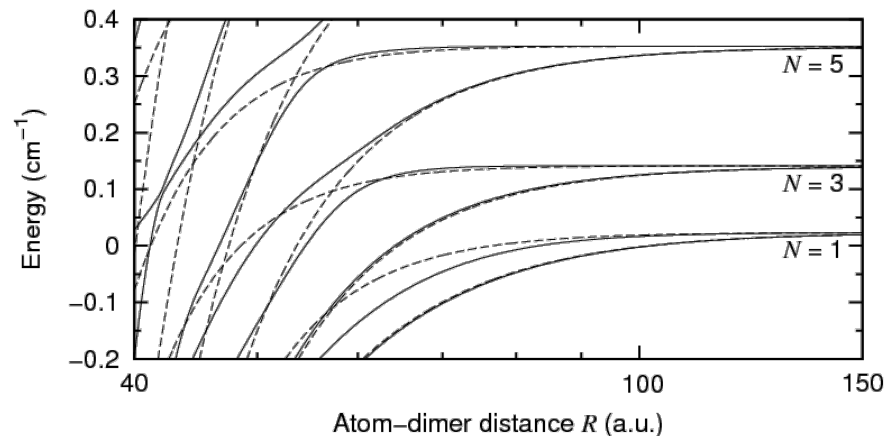
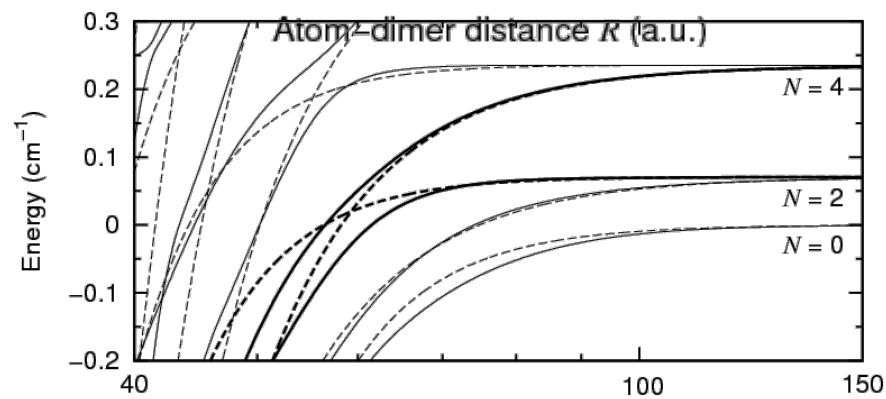
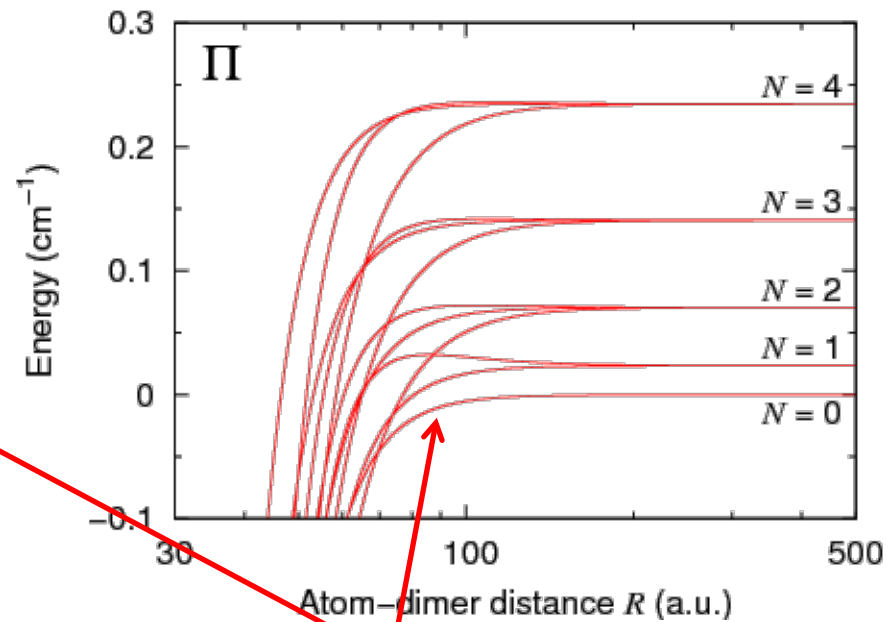
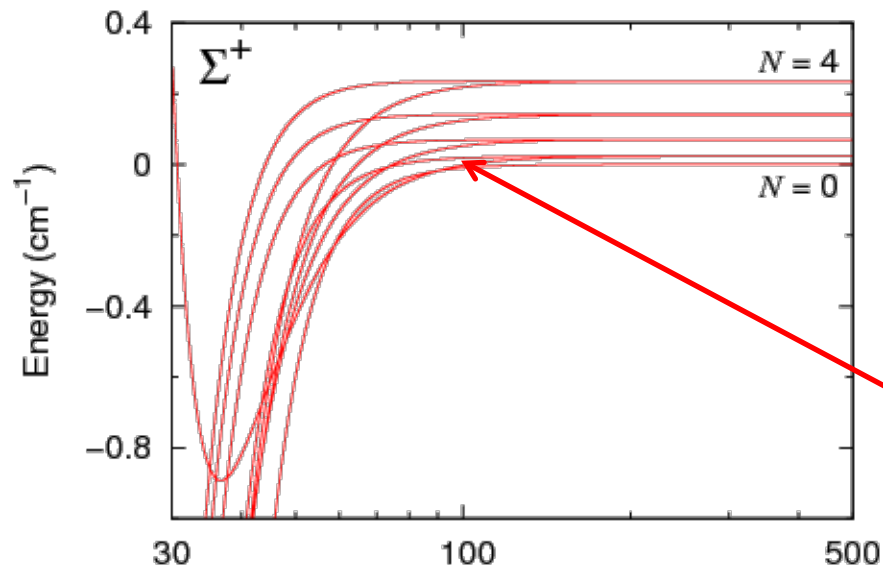
Symmetry	j	C_6 (a.u.)	Symmetry	j	C_6 (a.u.)	
Σ^+	0	-12101	Π	4	-12587	
	1	-12981		Δ	2	-11473
	2	-12729			3	-12101
	3	-12688		4	-12330	
	4	-12672	Φ	3	-11369	
Π	1	-11662	Γ	4	-11902	
	2	-12415		4	-11302	
	3	-12541				

Lepers, Vexiau, Bouloufa, Dulieu, Kokoouline Phys. Rev. A **83**, 042707 (2011)

TABLE II. The C_5 and C_6 coefficients of the $\text{Cs}_2(X^1\Sigma_g^+, v_d = 0, j) + \text{Cs}(6^2P)$ long-range interaction calculated for $j = 0$ to 4. In analogy to a diatomic molecule, the states are sorted by projections of the total orbital quantum number $m_J = m_j + \lambda$ on the Z axis and by the parity \pm after the reflection symmetry through any plane containing this axis. The values for C_5 are taken from paper I.

Symmetry	j	C_5 (a.u.)	C_6 (a.u.)	Symmetry	j	C_5 (a.u.)	C_6 (a.u.)	
Σ^+	0	0	-42704	Π	4	-739	671	
	1	-1674	51249		4	108	-15884	
	1	0	-21562		4	522	-47279	
	2	-913	12128		Δ	1	-279	-18694
	2	116	-16885		2	-140	-21244	
	3	-796	4923	2	1136	-95614		
	3	145	-15420	3	-835	-1624		
	4	-755	2251	3	-87	-19563		
	4	157	-14835	3	736	-65454		
	Σ^-	1	0	-43920	4	-721	-2643	
2		399	-45131	4	-11	-17153		
3		465	-45333	4	623	-56200		
4		489	-45407	Φ	2	-399	-16589	
Π	0	0	-23605	Γ	3	-245	-18030	
	1	0	-29303		3	1175	-103161	
	1	1116	-79756		4	-783	-5057	
	2	-964	7305		4	-161	-17444	
	2	-19	-22961		4	835	-76003	
	2	584	-50736	Γ	3	-465	-15420	
	3	-783	2496	4	-320	-16392		
	3	64	-17295	4	1208	-107555		
	3	532	-48103	H	4	-507	-14676	

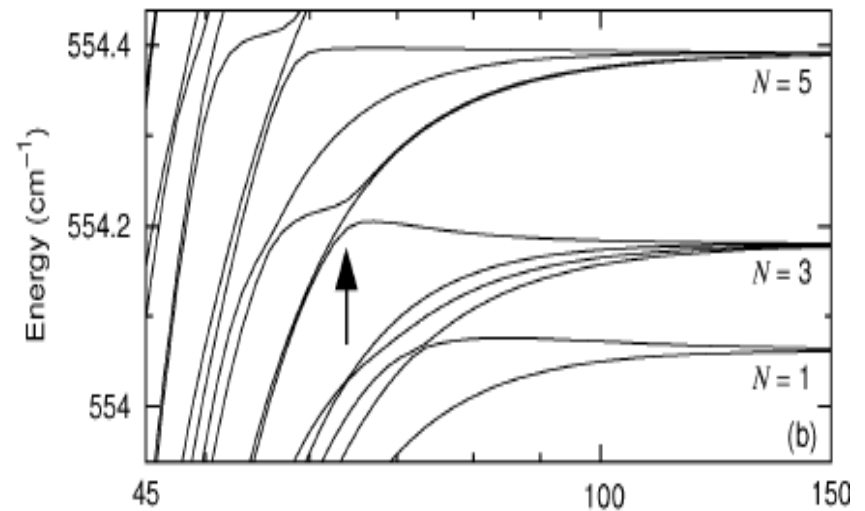
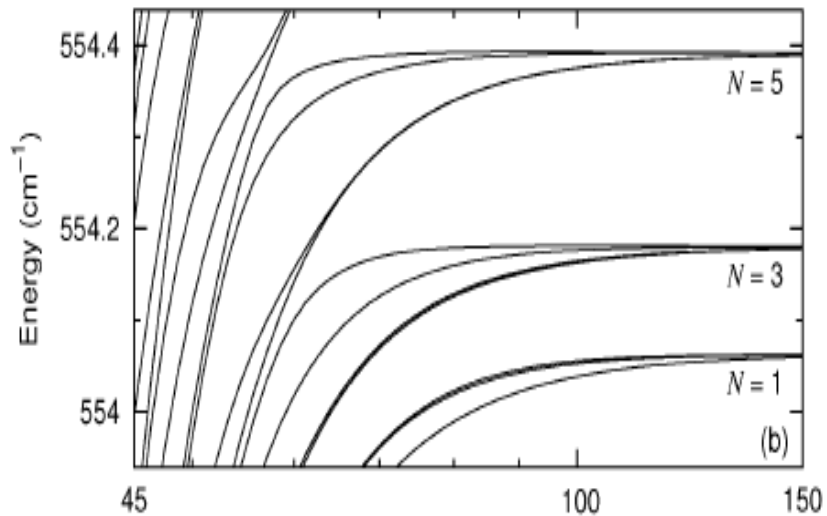
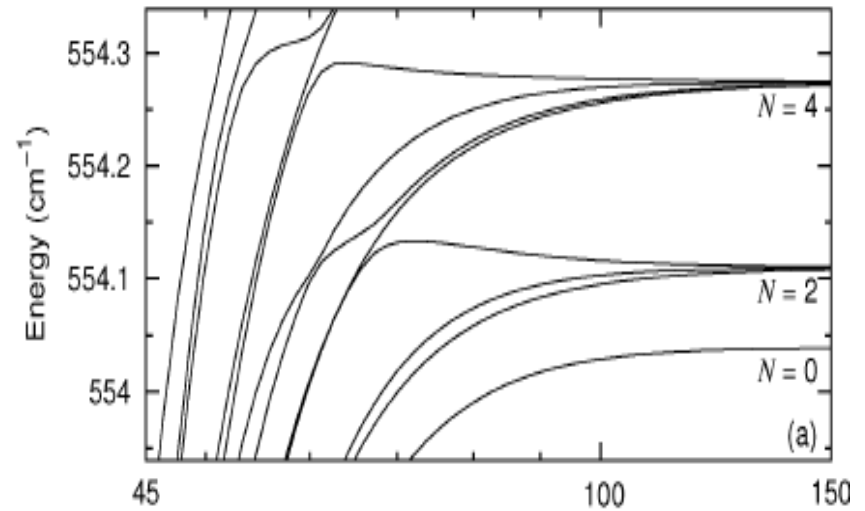
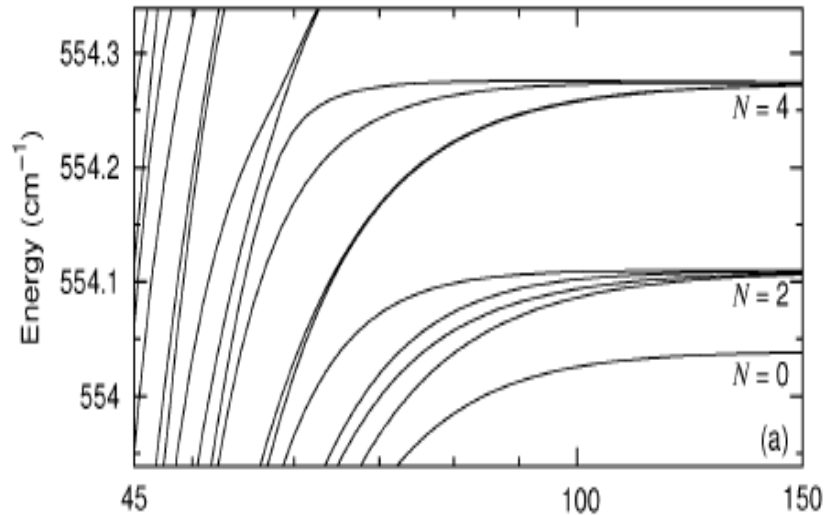
Lepers, Dulieu, Kokoouline Phys. Rev. A, **82**, 042711 (2010),



Around 100 a.u.: electrostatic energy and rotational energy of the same magnitude

2nd order degenerate perturbation theory which will couple various N of the same parity

Add Cs spin-orbit



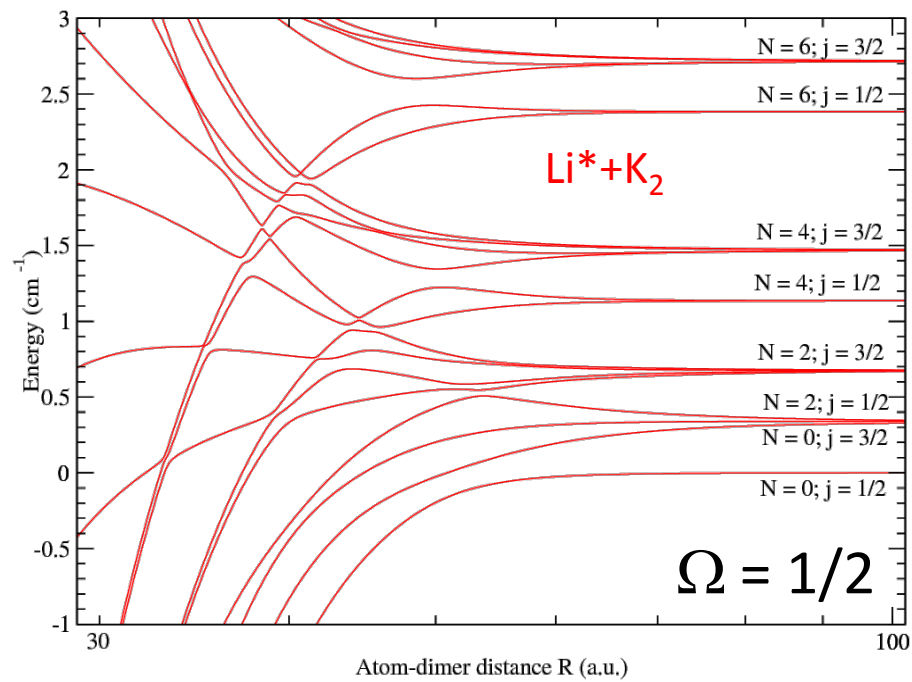
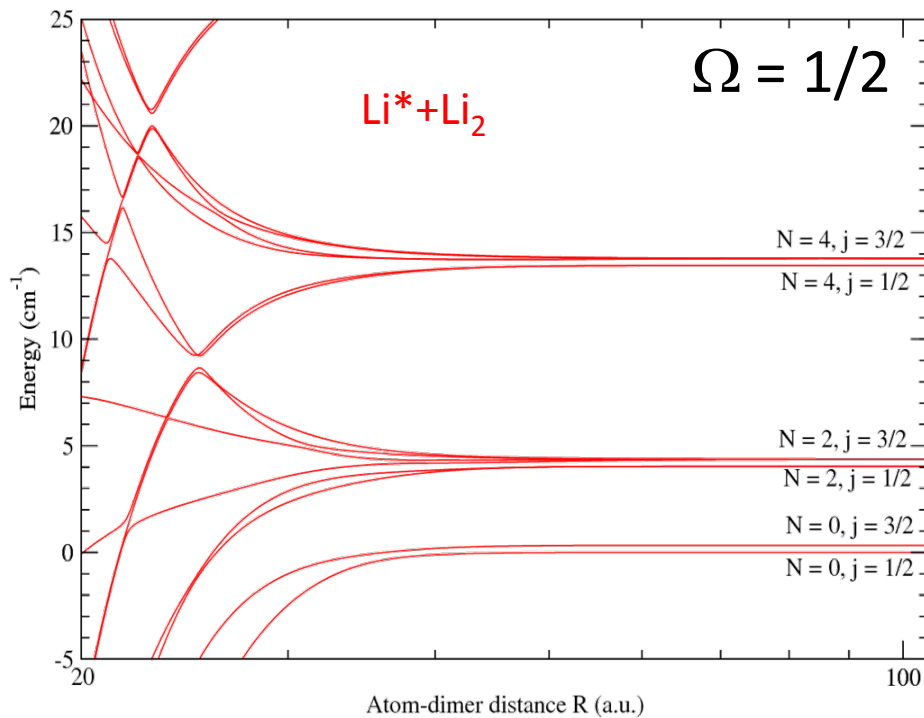
Atom-dimer distance R (a.u.)

$$|\Omega| = 1/2, j = 3/2.$$

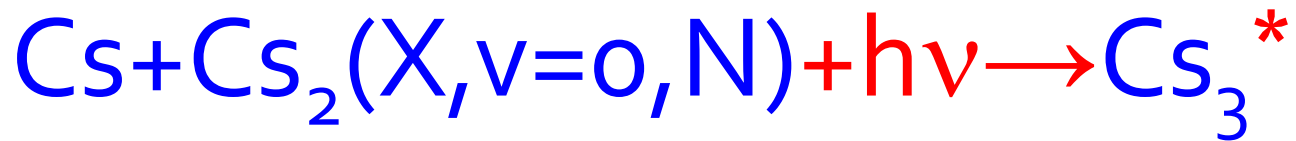
Atom-dimer distance R (a.u.)

$$|\Omega| = 3/2, j = 3/2.$$

Funny (desperated) cases



- Lepers, Dulieu, Kokoouline Phys. Rev. A, **82**, 042711 (2010),
Lepers, Vexiau, Bouloufa, Dulieu, Kokoouline Phys. Rev. A **83**,
042707 (2011), EPJD 2011
Lepers, Dulieu, Eur. Phys. J. D **65**, 113 (2011)
Lepers, Dulieu, Phys. Chem. Chem. Phys. **13**, 19106 (2011)



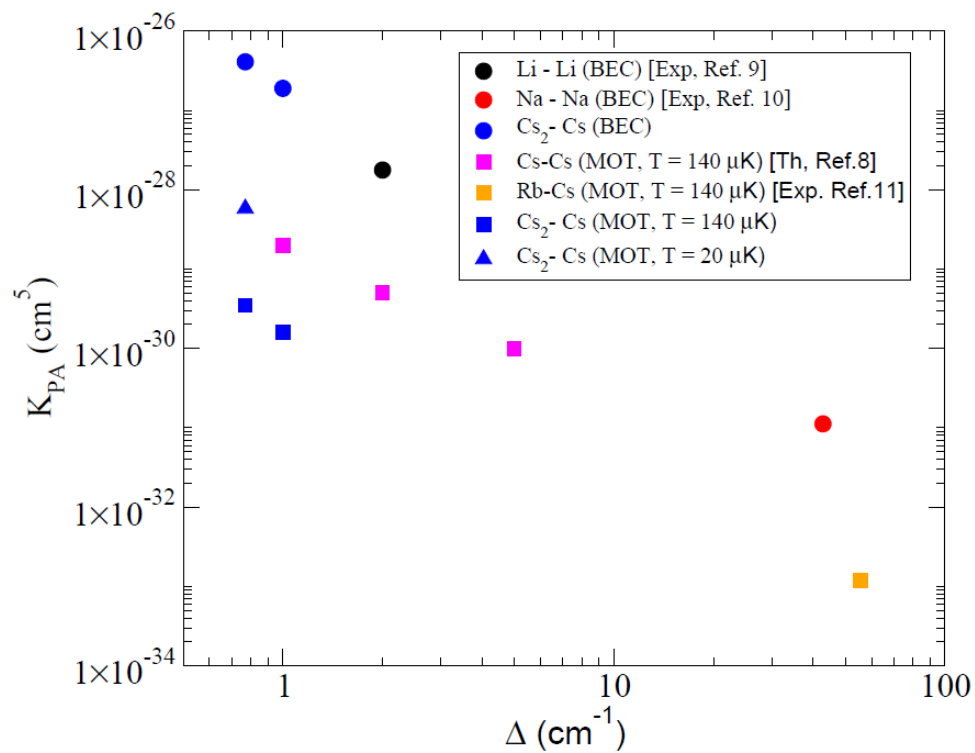
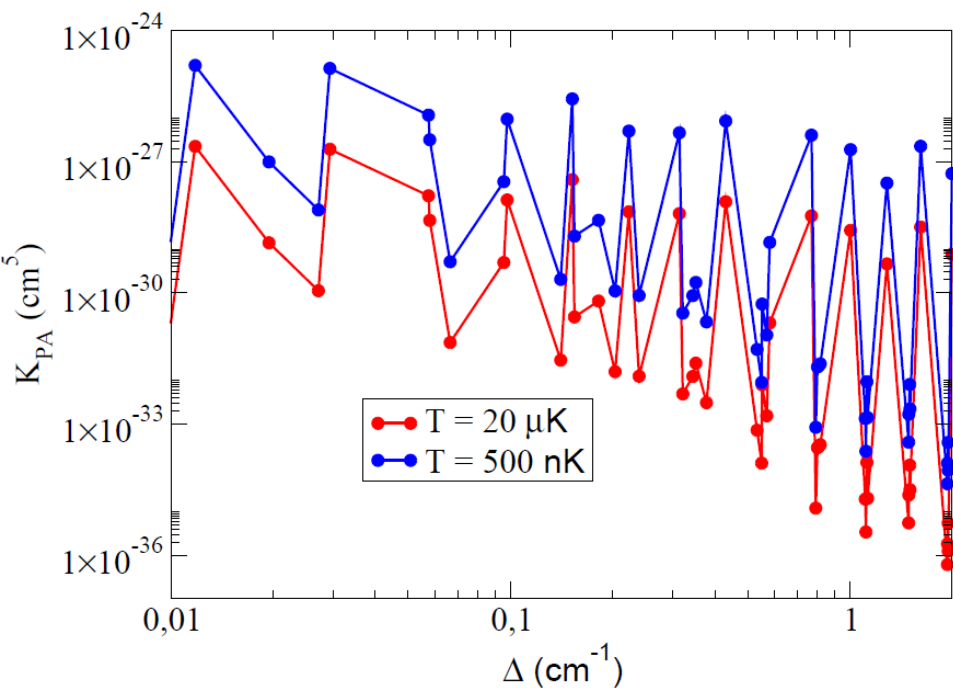
- Consider long-range PESs: $\text{Cs}_3^* \approx \text{Cs}^* \dots \text{Cs}_2$
- Match to a short-range LJ potential at $R_{\text{LR}} \approx 45 \text{a.u.}$
- Compute radial wave functions
- Use standard expression of PA rate for a pair of particles

$$R_{PA} = A(g, e, \epsilon_{PA}) \left(\frac{3}{2\pi} \right)^{3/2} \frac{h}{2} n_{mol} \Lambda^3 e^{-\Delta/k_B T} \Omega^2 \left| \langle \Psi_E | \Psi_b \rangle \right|^2$$

P. Pillet, A. Crubellier, A. Bleton, O. Dulieu, P. Nosbaum, I. Mourachko and F. Masnou-Seeuws, J. Phys. B **30**, 2801 (1997).

- Normalize the rate for the sake of comparison with other cases: $K_{PA} = R_{PA} / n_{mol} \phi$; (in cm^5)

Normalized PA rate



The scenario of **ultracold photochemistry** could be:

- Selection of a particular level as the entrance channel
- This level is probably coupled to many resonances, but could have a decent probability density at large distances
- Something happens in the inner zone, but the complex probably survives long enough to decay radiatively
- The stabilization could occur in bound levels of Cs_3
- The product could be « immediately » detected as chemically distinct from the reactants

- ...now it's time to talk to our best experimental friends....

