coherent control of photoassociation at ultracold temperatures: opportunities and fundamental limits

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work done in collaboration with

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principle of coherent control

wave properties of matter (superposition principle)

variation of phase between
different, but indistinguishable quantum pathways:

constructive *interference*
in desired channel

destructive *interference*
in all other channels

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how to solve the inversion problem?

'intuitive' approaches

optimal control theory

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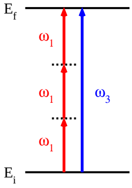
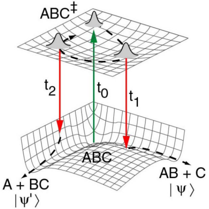
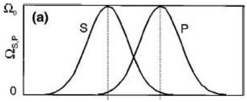
Brumer & Shapiro



Tannor & Rice



STIRAP



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'intuitive' approaches

- bichromatic control
- pump-dump/probe
- STIRAP
  $\rightsquigarrow$ DFS & other
  symmetry-adapted control

optimal control theory

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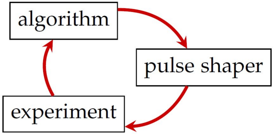
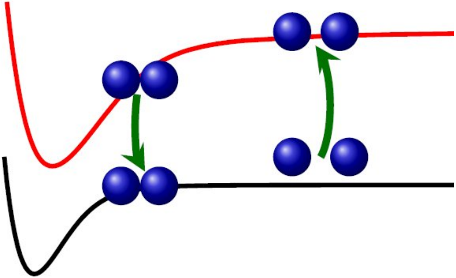
optimal control theory

- theory: iterative solution of control equations
- exp.:



photoassociation

= optical production of molecules



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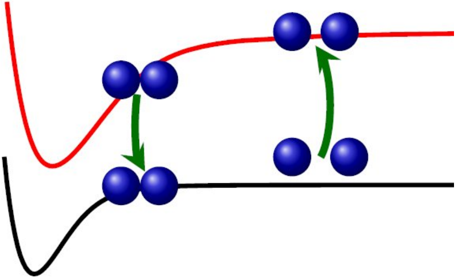

- photoassociation possible

  requires only optical transition
- photoassociation difficult

  phase space compression

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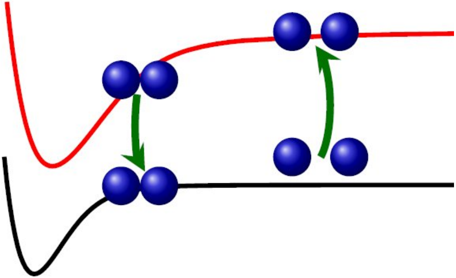

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⟶ **coherence distillation**

⟶ **Franck-Condon filtering**

control versus entropy: thermal effects

coherent time evolution does not change 'quantumness' of the sample

$$\mathrm{Tr}\{\hat{\boldsymbol{\rho}}_T^2\} \qquad \hat{\boldsymbol{\rho}}_T = \frac{1}{Z} e^{-\hat{\mathbf{H}}/k_B T}$$

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example: photoassociation

- **assembling molecules from atoms using laser light**

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- ***short-pulse* photoassociation: after bond formation we can play the usual games of coherent control**
  - pump-probe & pump-dump-probe schemes
  - engineering (coherent) wave packet dynamics
  - optical interference in multi-photon absorption

Koch & Shapiro, Chem Rev 212, 4928 (2012)

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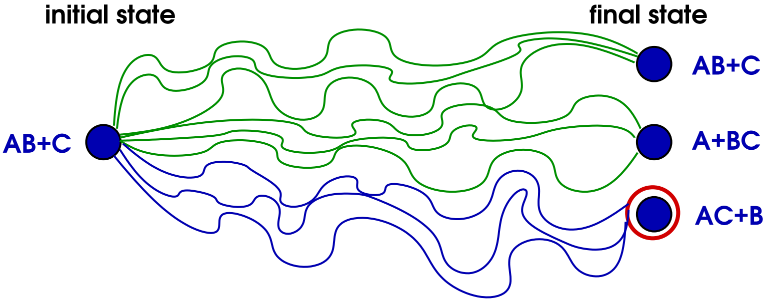
- **prototype of a light-induced binary reaction**

controlling binary reactions

quantum system + light + interaction = pathway

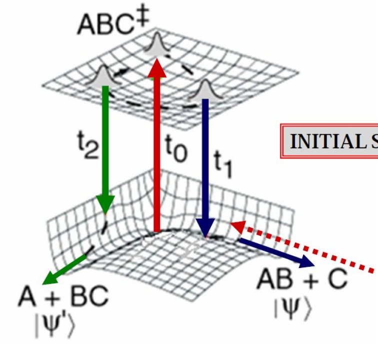


- a femtosecond pulse induces a manifold of such state-to-state transitions
- the interferences are manipulated by shaping the exciting pulse and controlling the time delay between pulses

laser light = {frequency, amplitude, phase, polarization}

controlling a binary reaction

Tannor & Rice, J Chem Phys 83, 5013 (1985)
Tannor, Kosloff, Rice, J Chem Phys 85, 5805 (1986)



INITIAL STATE = FREE

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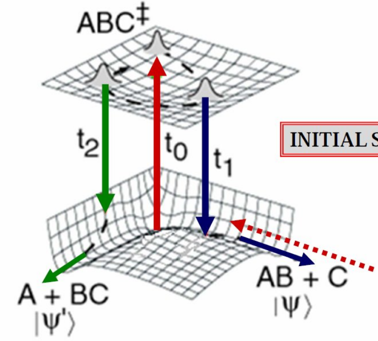


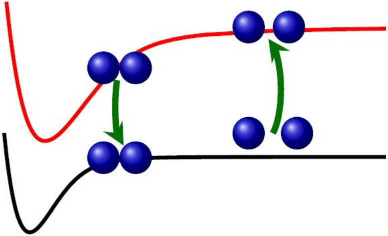
INITIAL STATE = FREE

coherent control

- experimentally : extremely successful in **unimolecular, destructive** processes (*dissociation*, *ionization*, . . .)
- **open challenge: coherent control of bond formation / binary reactions**
  photoassociation = very simple binary reaction

photoassociation

= how to enhance reaction rate?



control versus entropy:

$$\mathrm{Tr}\{\hat{\boldsymbol{\rho}}_T^2\} \qquad \hat{\boldsymbol{\rho}}_T = \frac{1}{Z} e^{-\hat{\mathbf{H}}/k_B T}$$

two steps: photo-association & photo-stabilization

1. **more efficient bond formation:**
   - coherent control of tunneling resonances
   - multi-photon femtosecond photoassociation
2. more efficient transitions to $X^1\Sigma_g^+(v=0)$:
   - strong spin-orbit interaction in heavy atoms

     SrYb: *Tomza, Pawłowksi, Jeziorska, Koch, Moszynski, Phys Chem Chem Phys 13, 18893 (2011)*

     Sr_2: *Skomorowski, Moszynski, Koch, Phys Rev A 85, 043414 (2012)*
   - engineered wavepacket dynamics

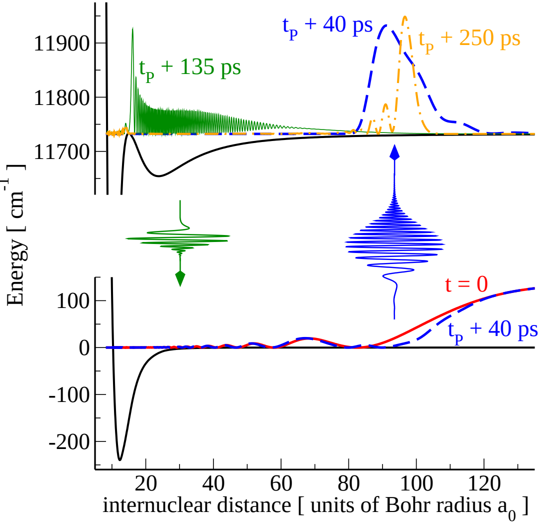
     Koch & Moszynski, Phys Rev A 78, 043417 (2008)

coherent photoassociation

what is different from previous pump-probe schemes?

- initial state
- timescales

↷ bandwidths



Koch, Luc-Koenig, Masnou-Seeuws, Phys Rev A 73, 033408 (2006)

initial state: cold collisions

photoassociation is difficult

initial state

$$\begin{aligned}\hat{\boldsymbol{\rho}}_T &= \frac{1}{Z_{eq}} e^{-\frac{\hat{\mathsf{H}}_g}{k_B T}} \\ &= \frac{1}{Z_{eq}} \sum_{n,J} (2J+1) \\ & \quad e^{-\frac{E_{n,J}}{k_B T}} \left|E_{n,J}\right\rangle \left\langle E_{n,J}\right|\end{aligned}$$

=thermal ensemble

Koch, Kosloff, Luc-Koenig, Masnou-Seeuws, Crubellier, J Phys B 39, S1017 (2006)

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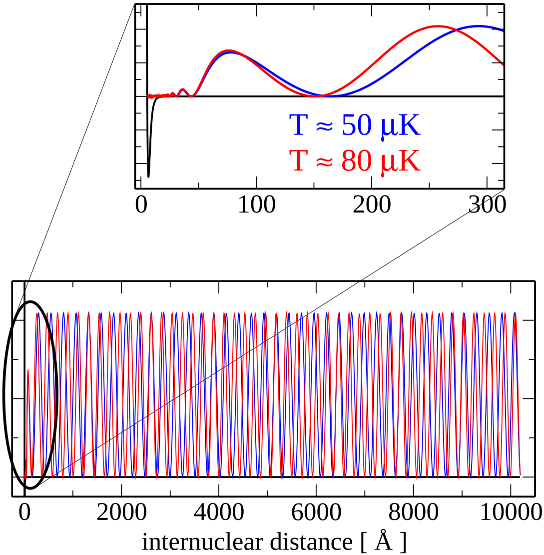

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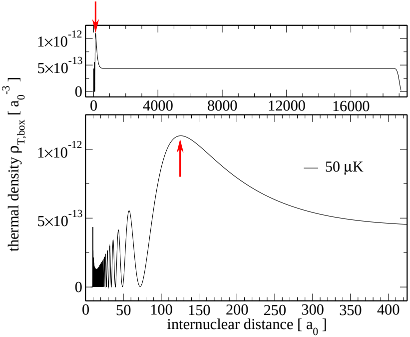
hot vs cold photoassociation

cold



- only few lowest partial waves
  $\longrightarrow$ high initial purity $\mathrm{Tr}[\hat{\boldsymbol{\rho}}_T^2]$
- photoassociation at large *R*
- huge influence of resonances

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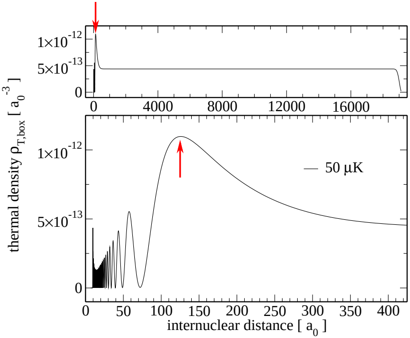

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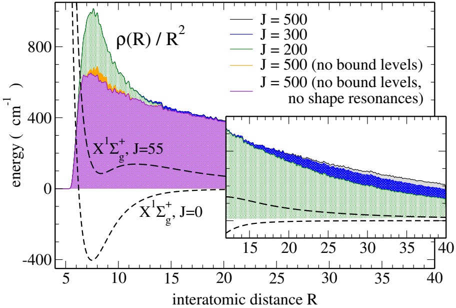


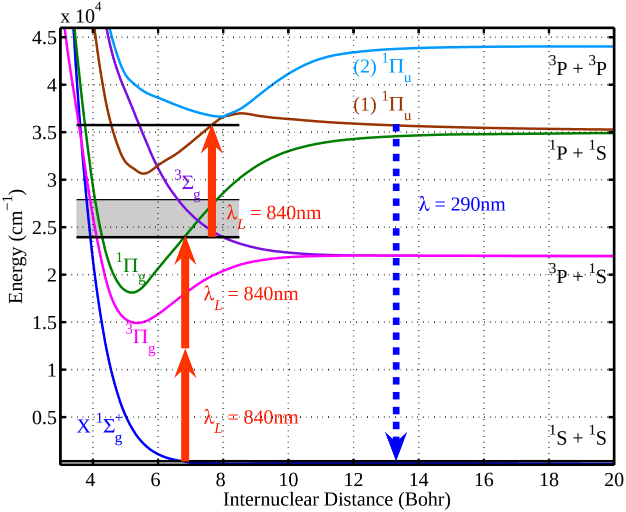
- many partial waves → almost zero initial purity $\mathrm{Tr}[\hat{\rho}_T^2]$
- photoassociation at short R
- some influence of resonances

hot photoassociation: FC filtering at short R

Rybak, Amaran, Levin, Tomza, Moszynski, Kosloff, Koch, Amitay, Phys Rev Lett 107, 273001 (2011)

Rybak, Amitay, Amaran, Kosloff, Tomza, Moszynski, Koch, Faraday Discuss. 153, 383 (2011)

Mg + Mg $\longrightarrow$ **Mg**$_2^*$ **hot:** $T = 1000K$



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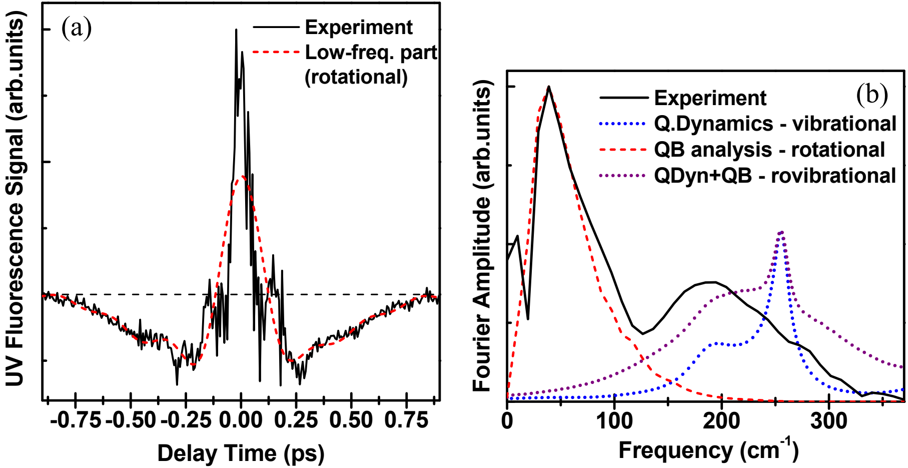

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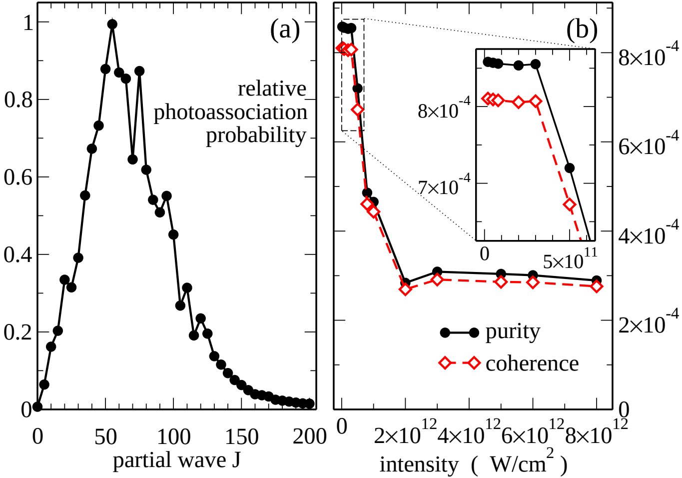
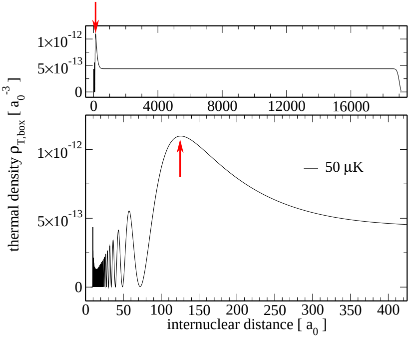


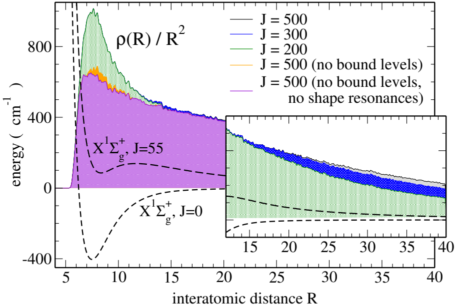
photoassociated molecules = sub-ensemble of higher purity

hot vs cold photoassociation

cold



hot



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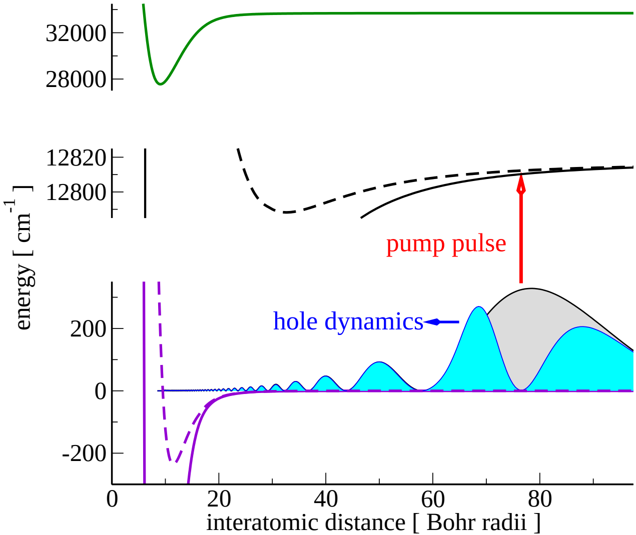
cold atoms: pump-probe spectroscopy

of two-body correlations in the thermal ensemble

Koch & Kosloff, Phys Rev Lett 103, 260401 (2009)



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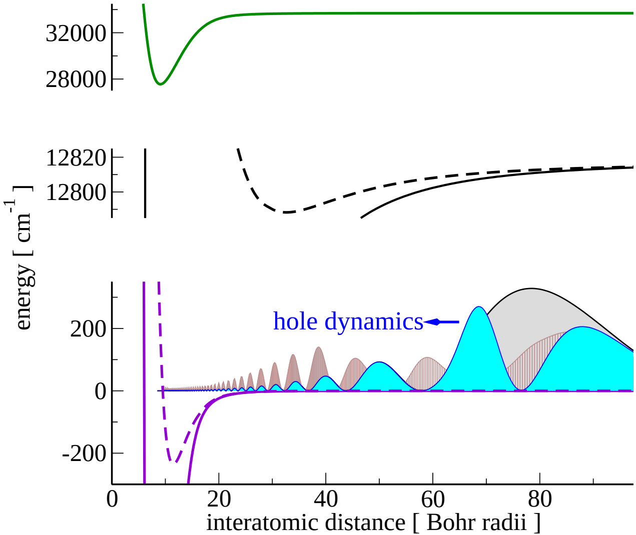

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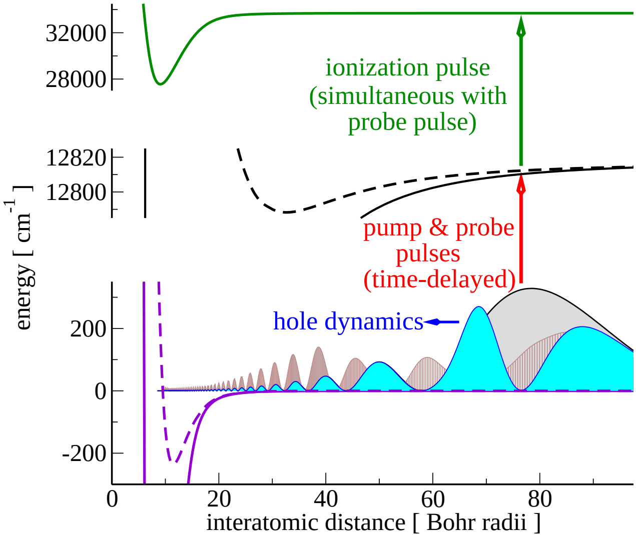

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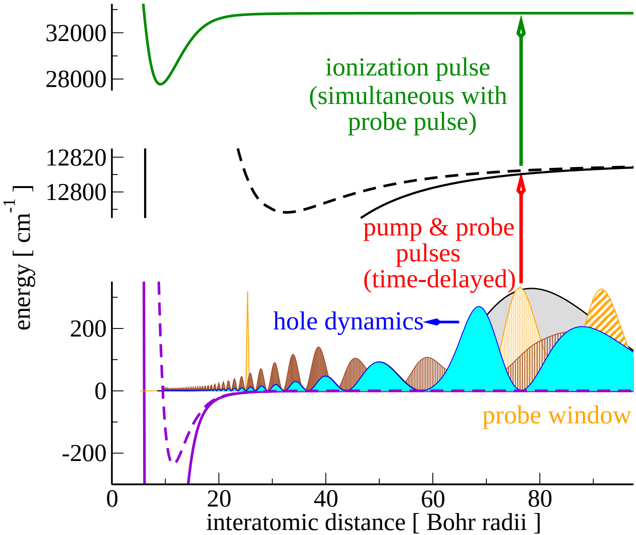

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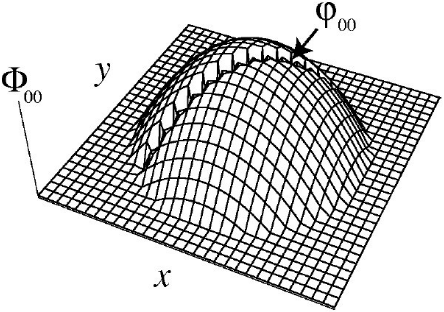
reduced pair wave function

$$\varphi(x,y;t) = \frac{\langle \hat{\psi}(x;t)\hat{\psi}(y;t)\rangle}{\langle \hat{\psi}(x;t)\rangle\langle \hat{\psi}(y;t)\rangle}$$



$$\Phi_{00}(x,y) = \frac{1}{\sqrt{2}}\Psi_0(x)\Psi_0(y)\varphi(x,y)$$

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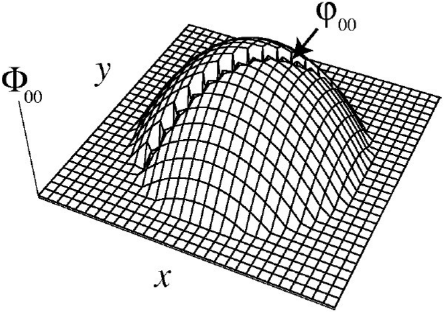
if

1. extent of $\varphi(x,y;t) \ll$ condensate length scale
2. higher than 2nd order terms do not affect $\varphi(x,y;t)$



then

$$i\hbar\frac{\partial\varphi}{\partial t} = \left(-\frac{\hbar^2}{2m}\Delta_x + \Delta_y + V_2(x-y)\right)\varphi(x,y;t)$$

$$\Phi_{00}(x,y) = \frac{1}{\sqrt{2}}\Psi_0(x)\Psi_0(y)\varphi(x,y)$$

equivalent result obtained for 1st order cumulant expansion

Köhler & Burnett, Phys Rev A 65, 033601 (2002)

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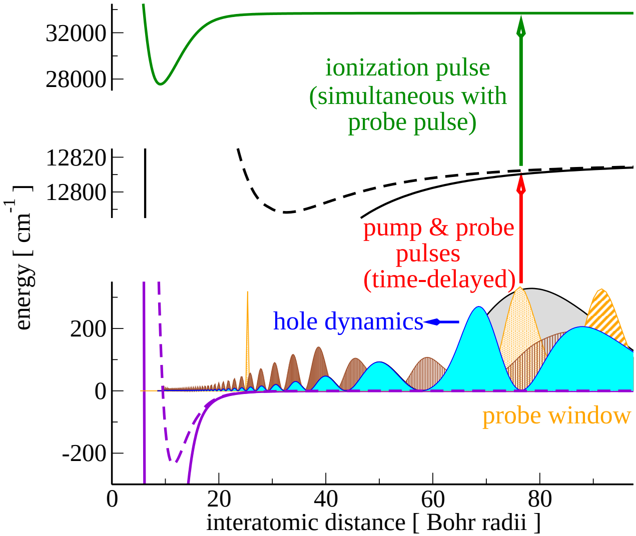
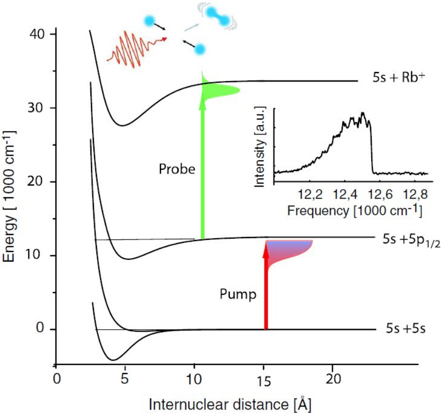
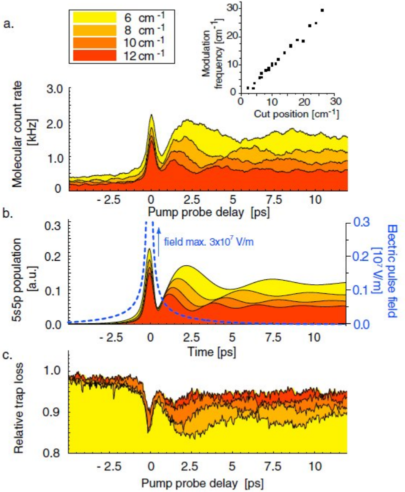


first experiment

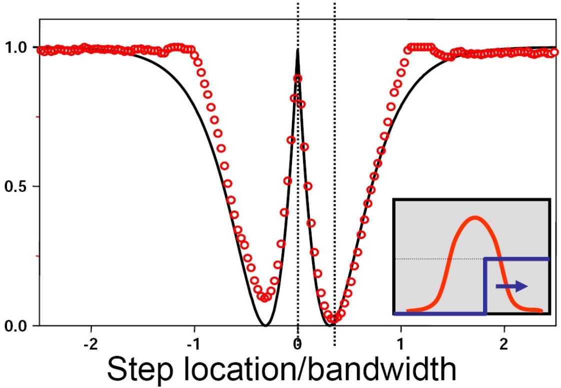
demonstrating femtosecond photoassociation of ultracold atoms

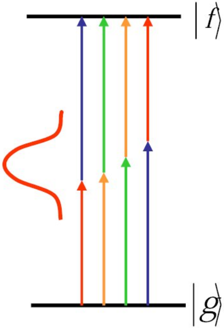
Salzmann et al., PRL 100, 233003 (2008) [Weidemüller & Wöste groups]





narrow transitions & broad-band light





certain phase functions annihilate the two-photon absorption

Meshulach & Silberberg, Nature 396, 239 (1998)

two-photon photoassociation

$$\hat{\mathbf{H}}(t) = \begin{pmatrix} \hat{\mathbf{T}} + V_g(\hat{\mathbf{R}}) + \omega_g^S(t) & \chi(t)e^{-i\varphi(t)} \\ \chi(t)e^{i\varphi(t)} & \hat{\mathbf{T}} + V_e(\hat{\mathbf{R}}) + \Delta_{2P} + \omega_e^S(t) \end{pmatrix}$$

generalization of model for two-photon absorption of Trallero-Herrero et al., Phys Rev A 71, 013423 (2005)

we seek broadband excitation which is dark for the atoms but excites molecules

Koch, Ndong, Kosloff, Faraday Discuss. 142, 389 (2009)

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two-photon couplings:

$$\chi(t) = -\frac{1}{4}E_0^2|S(t)|^2 \sum_m \frac{\mu_{em}\mu_{mg}}{\omega_{mg} - \omega_L}$$

dynamic Stark shifts:

$$\omega_i^S(t) = -\frac{1}{2}E_0^2|S(t)|^2 \sum_m |\mu_{mi}|^2 \frac{\omega_{mi}}{\omega_{mi}^2 - \omega_L^2}\,, \quad i = g, e$$

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Koch, Ndong, Kosloff, Faraday Discuss. 142, 389 (2009)

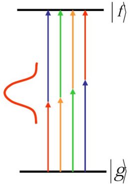
atoms: two-photon dark states

analytical solutions

weak field

strong field

- two-photon absorption
  $\sim \int d\omega E(\omega) E(\omega_L - \omega)$



- phase function:
  destructive IF

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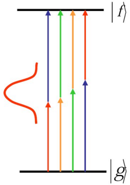

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- chirped pulse
- phase locking: laser phase compensates for matter phase due to dynamical Stark shift
- Rabi cycling: two-photon 2π pulse

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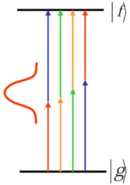

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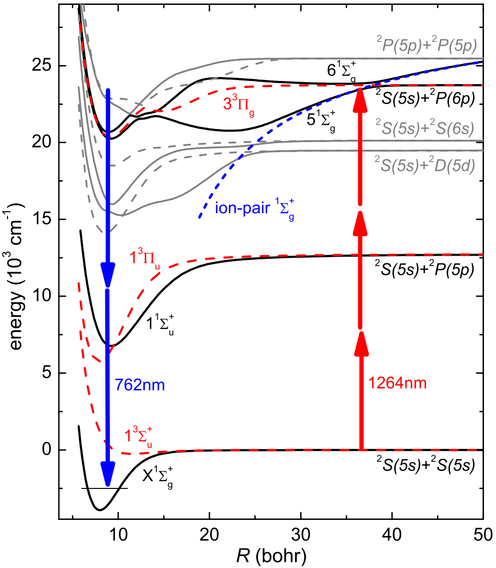
can be generalized to multi-photon transitions

three-photon photoassociation: Rb_2

Tomza, Goerz, Musiał, Moszynski, Koch, Phys Rev A 86, 043424 (2012)



- $1/R^3$ excited states
- multi-photon selection rules
- strong spin-orbit coupling
- crossing of ion-pair state

three-photon photoassociation: Rb_2

Tomza, Goerz, Musiał, Moszynski, Koch, Phys Rev A 86, 043424 (2012)

$$\hat{\mathbf{H}}_{pump}(t) = \begin{pmatrix} \hat{\mathbf{H}}^{a^3\Sigma_u^+}(R) & 0 & \epsilon^*(t)^3\chi^{(3)}(\omega_L, R) & 0 \\ 0 & \hat{\mathbf{H}}^{(5)^1\Sigma_g^+}(R) & \xi_3(R) & A(R) \\ \epsilon(t)^3\chi^{(3)}(R) & \xi_3(R) & \hat{\mathbf{H}}^{(3)^3\Pi_g}(R) - \xi_4(R) & \xi_5(R) \\ 0 & A(R) & \xi_5(R) & \hat{\mathbf{H}}^{(6)^1\Sigma_g^+}(R) \end{pmatrix}$$

- $\hat{\mathbf{H}}^{2S+1|\Lambda|} = \hat{\mathbf{T}} + V^{2S+1|\Lambda|}(R) + \omega_S^{2S+1|\Lambda|}(t, R) + \Delta_{\omega_L}$
- $\chi^{(3)}(\omega_L, R)$ three-photon coupling
- ξ_j spin-orbit couplings
- $A(R)$ non-adiabatic radial coupling

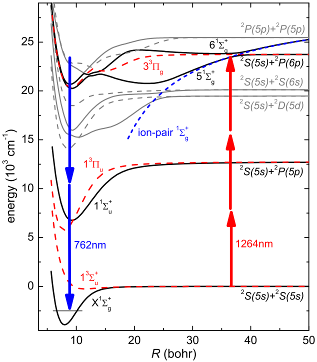
optimal control calculations in progress

poster next week

two-photon dump: Rb$_2$

Tomza, Goerz, Musiał, Moszynski, Koch, Phys Rev A 86, 043424 (2012)

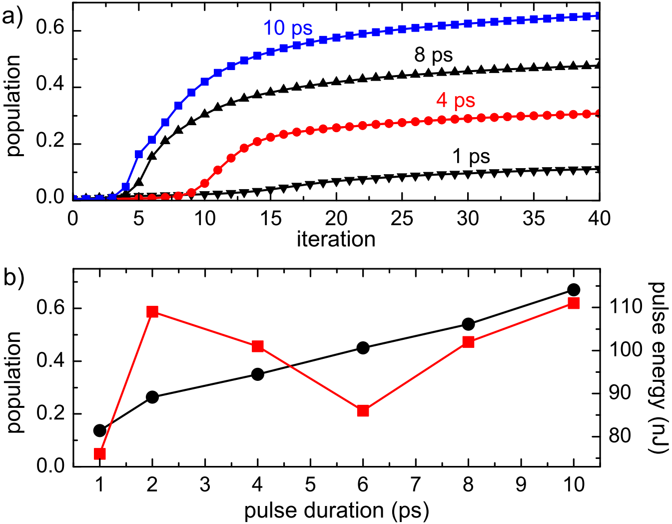
$$\hat{\mathbf{H}}_{dump}(t) = \begin{pmatrix} \hat{\mathbf{H}}^{X^1\Sigma_g^+}(R) & \epsilon^*(t)d_1(R) & 0 & 0 & 0 & 0 \\ \epsilon(t)d_1(R) & \hat{\mathbf{H}}^{A^1\Sigma_u^+}(R) & \xi_1(R) & \epsilon^*(t)d_2(R) & 0 & \epsilon^*(t)d_4(R) \\ 0 & \xi_1(R) & \hat{\mathbf{H}}^{b^3\Pi_u}(R) - \xi_2(R) & 0 & \epsilon^*(t)d_3(R) & 0 \\ 0 & \epsilon(t)d_2(R) & 0 & \hat{\mathbf{H}}^{(5)^1\Sigma_g^+}(R) & \xi_3(R) & A(R) \\ 0 & 0 & \epsilon(t)d_3(R) & \xi_3(R) & \hat{\mathbf{H}}^{(3)^3\Pi_g}(R) - \xi_4(R) & \xi_5(R) \\ 0 & \epsilon(t)d_4(R) & 0 & A(R) & \xi_5(R) & \hat{\mathbf{H}}^{(6)^1\Sigma_g^+}(R) \end{pmatrix}$$



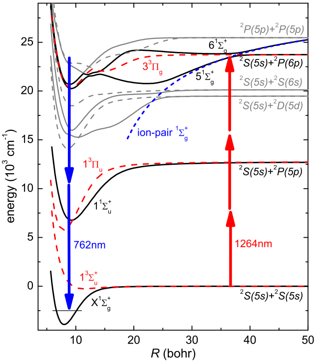
- $\hat{\mathbf{H}}^{2S+1|\Lambda|} = \hat{\mathbf{T}} + V^{2S+1|\Lambda|}(R) + +\Delta^{np}_{\omega_L}$
- $d_j(R)$ transition dipole matrix elements
- ξ_j spin-orbit couplings
- $A(R)$ non-adiabatic radial coupling

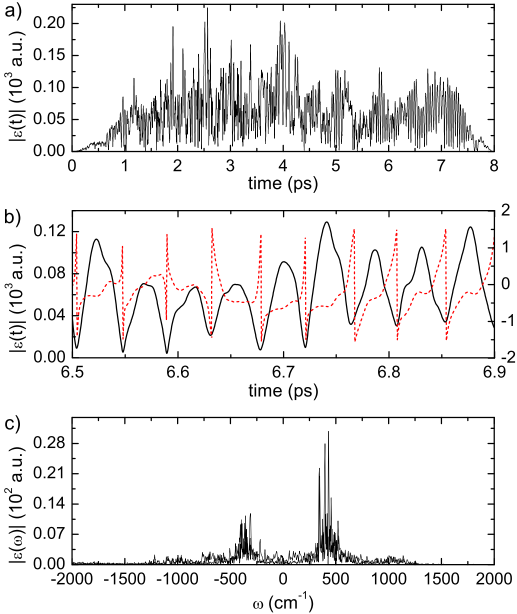
optimized two-photon dump: Rb_2

Tomza, Goerz, Musiał, Moszynski, Koch, Phys Rev A 86, 043424 (2012)



optimized two-photon dump: Rb_2





summary

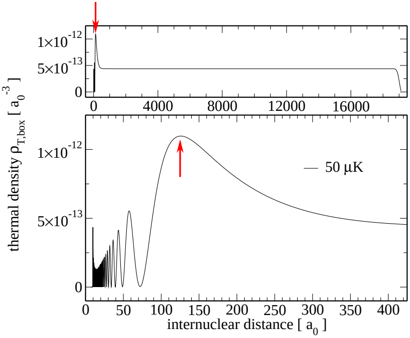
multi-photon photoassociation of Rb_2

Tomza, Goerz, Musiał, Moszynski, Koch, Phys Rev A 86, 043424 (2012)

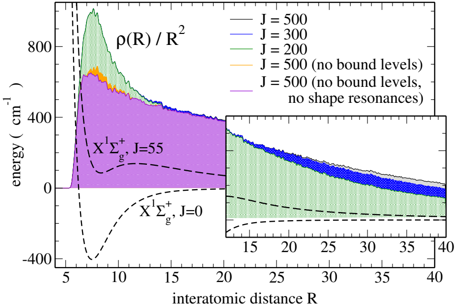
- multi-photon ionization:
  problem of bandwidth, selection rules
- ion-pair state:
  speed up excited state dynamics
- strong spin-orbit coupling:
  singlet-triplet conversion, efficient dumping
- optimal control can teach you how to take full advantage of complex dynamics

hot vs cold photoassociation

cold



hot



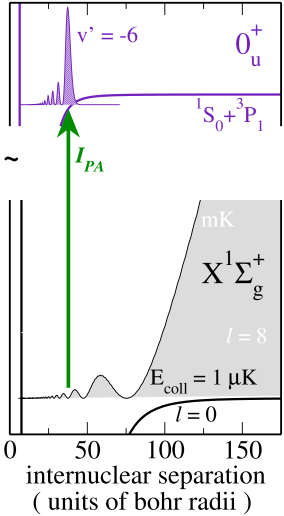
- only few lowest partial waves $\longrightarrow$ high initial purity $\mathrm{Tr}[\hat{\boldsymbol{\rho}}_T^2]$
- photoassociation at large R
- huge influence of resonances

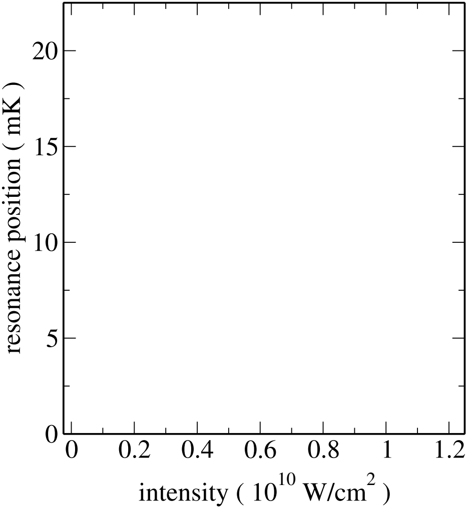
- many partial waves $\longrightarrow$ almost zero initial purity $\mathrm{Tr}[\hat{\boldsymbol{\rho}}_T^2]$
- photoassociation at short R
- some influence of resonances

resonances in the continuum

tunneling resonances enhance the pair density at photoassociation distances

González-Férez & Koch, Phys Rev A 86, 063420 (2012)





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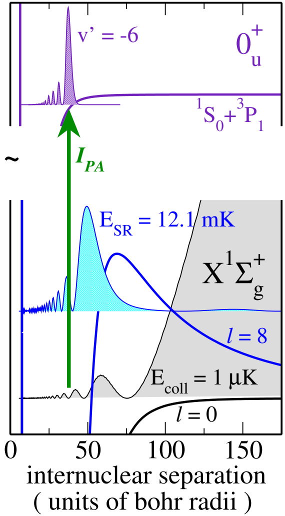

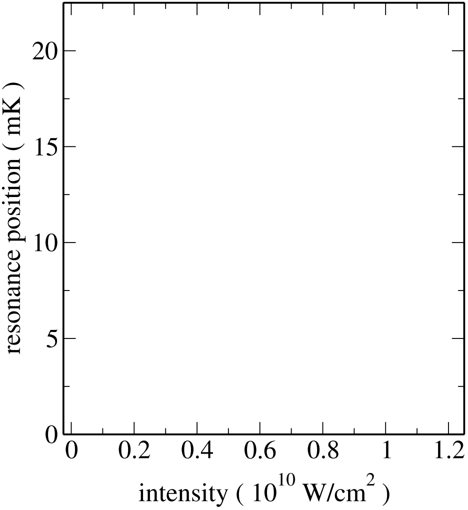

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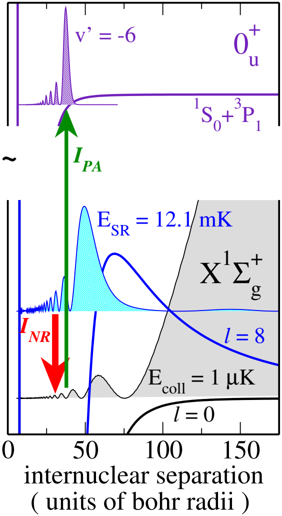

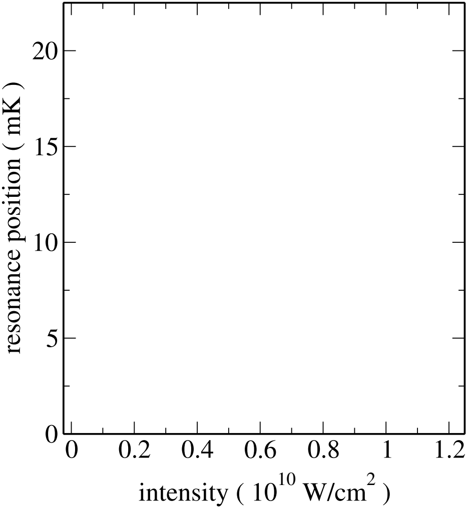

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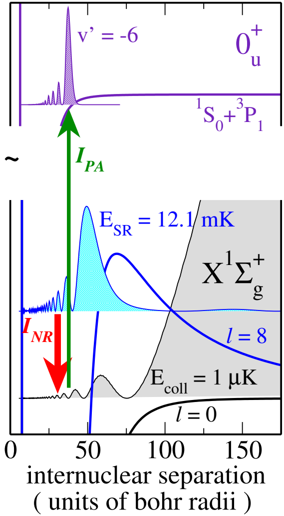

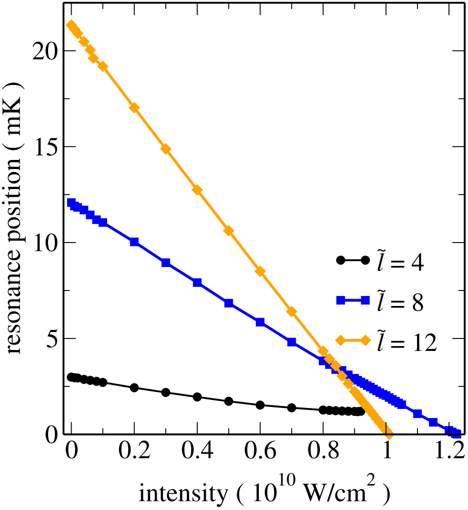

resonances in the continuum

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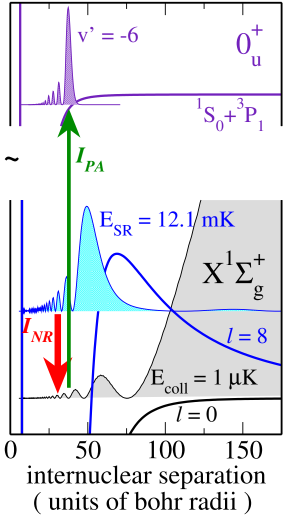
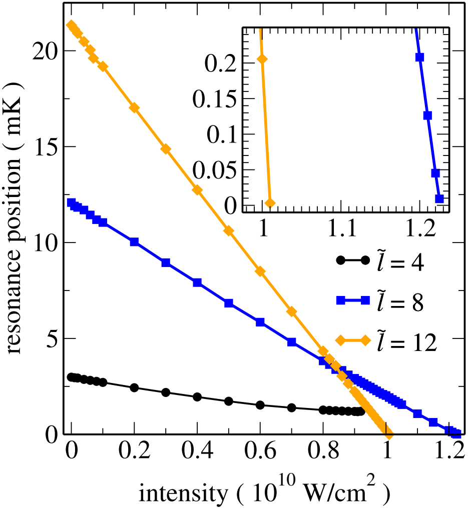
González-Férez & Koch, Phys Rev A 86, 063420 (2012)





non-resonant field control

Ağanoğlu, Lemeshko, Friedrich, González-Férez, Koch, arXiv:1105.0761

González-Férez & Koch, Phys Rev A 86, 063420 (2012)

$$\hat{\mathsf{H}} \;=\; \hat{\mathsf{T}} + V(\hat{\mathsf{R}}) + \frac{1}{2\mu\hat{\mathsf{R}}^2}\hat{\mathsf{J}}^2 - \frac{2\pi I}{c}\left(\Delta\alpha(\hat{\mathsf{R}})\cos^2\hat{\theta} + \alpha_\perp(\hat{\mathsf{R}})\right)$$

coupling of field I to polarizability anisotropy $\Delta\alpha(\hat{\mathsf{R}})$

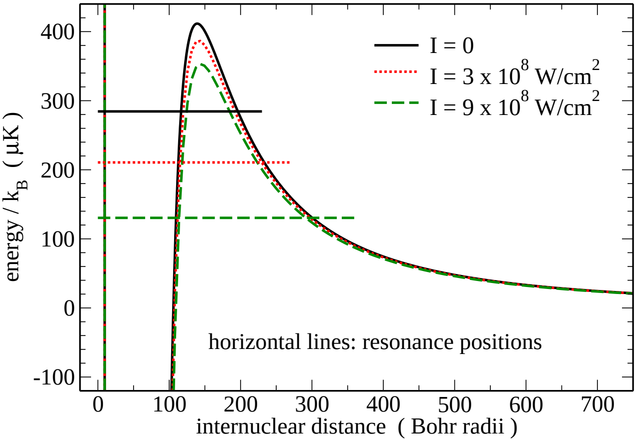
$$\begin{aligned} \alpha_\perp(\hat{\mathsf{R}}) &\approx 2\alpha_0 - 2\alpha_0^2/\hat{\mathsf{R}}^3 + 2\alpha_0^3/\hat{\mathsf{R}}^6 \\ \alpha_\parallel(\hat{\mathsf{R}}) &\approx 2\alpha_0 + 4\alpha_0^2/\hat{\mathsf{R}}^3 + 8\alpha_0^3/\hat{\mathsf{R}}^6 \end{aligned}$$

Silberstein's formula

non-resonant field control

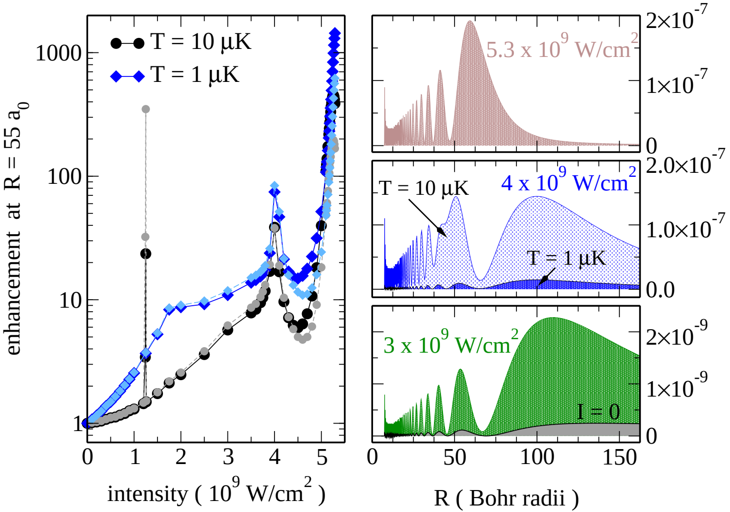
Ağanoğlu, Lemeshko, Friedrich, González-Férez, Koch, arXiv:1105.0761

González-Férez & Koch, Phys Rev A 86, 063420 (2012)



use the non-resonant field to control the position of the shape resonance, bringing it close to $k_B T_{trap}$

enhancement of the pair density: $^{88}Sr_2$



→ **large enhancement**

photoassociation

in the presence of a non-resonant field

$$\hat{\mathbf{H}} = \begin{pmatrix} \hat{\mathbf{T}} + V_g(\hat{\mathbf{R}}) & -\frac{1}{2}D(\hat{\mathbf{R}})\sqrt{\frac{I_{PA}}{2\epsilon_o c}}\cos\hat{\theta} \\ -\frac{1}{2}D(\hat{\mathbf{R}})\sqrt{\frac{I_{PA}}{2\epsilon_o c}}\cos\hat{\theta} & \hat{\mathbf{T}} + V_e(\hat{\mathbf{R}}) + \Delta_{PA} \end{pmatrix}$$

$$+\frac{\hat{\mathbf{J}}^2}{2\mu\hat{\mathbf{R}}^2} - \frac{2\pi I_{NR}}{c}\left[\begin{pmatrix} \Delta\alpha_g(\hat{\mathbf{R}}) & 0 \\ 0 & \Delta\alpha_e(\hat{\mathbf{R}}) \end{pmatrix}\cos^2\hat{\theta}\right.$$

$$\left. + \begin{pmatrix} \alpha_{\perp,g}(\hat{\mathbf{R}}) & 0 \\ 0 & \alpha_{\perp,e}(\hat{\mathbf{R}}) \end{pmatrix}\right]$$

photoassociation rates

- ensemble with Maxwell-Boltzmann velocity distribution
- isolated resonance
- weak PA laser

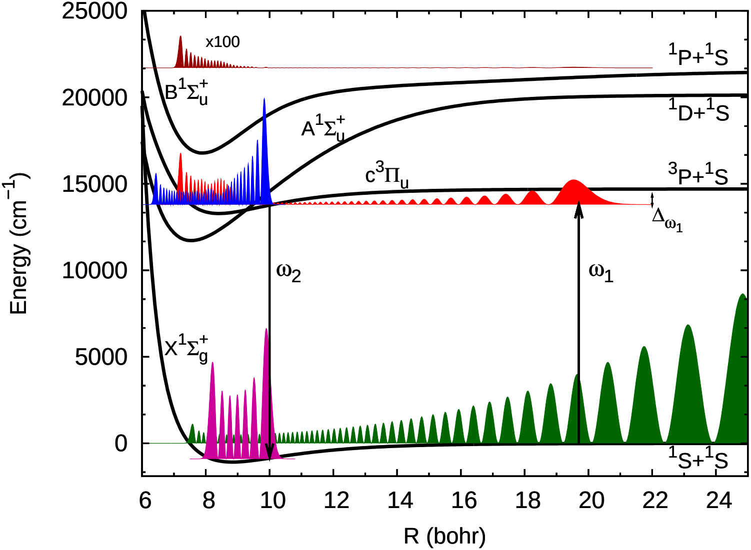
$$K_{v'}(I_{PA},\Delta_{PA},T) \approx \frac{4\pi^2 I_{PA}}{c}\frac{k_B T}{h Q_T} \int_0^\infty \sum_{J=0}^{\infty}\sum_{M=-J}^{J} e^{-\frac{E}{k_B T}} \frac{\gamma_{v'}|D_{v'J'}(E)|^2}{(E-\Delta_{v'J'})^2+(\gamma/2)^2}\frac{dE}{k_B T}$$

$$D_{v'J'}(E) = \langle \psi^e_{v'J'}|D(\hat{\mathbf{R}})\cos\hat{\theta}|\psi^g_J(E)\rangle$$

$|\psi^g_J(E)\rangle$ modified by I_{NR}

photoassociation of Sr_2

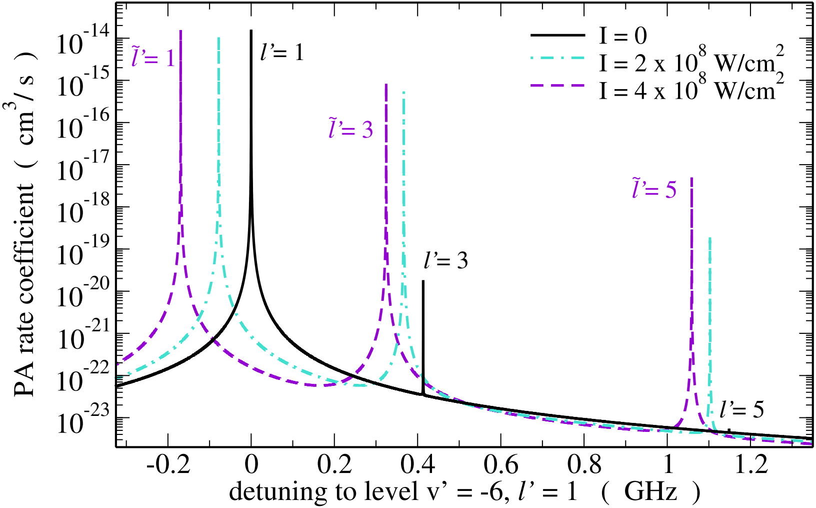
Skomorowski, Moszynski, Koch, Phys Rev A 85, 043414 (2012)



effect of non-resonant light

González-Férez & Koch, Phys Rev A 86, 063420 (2012)

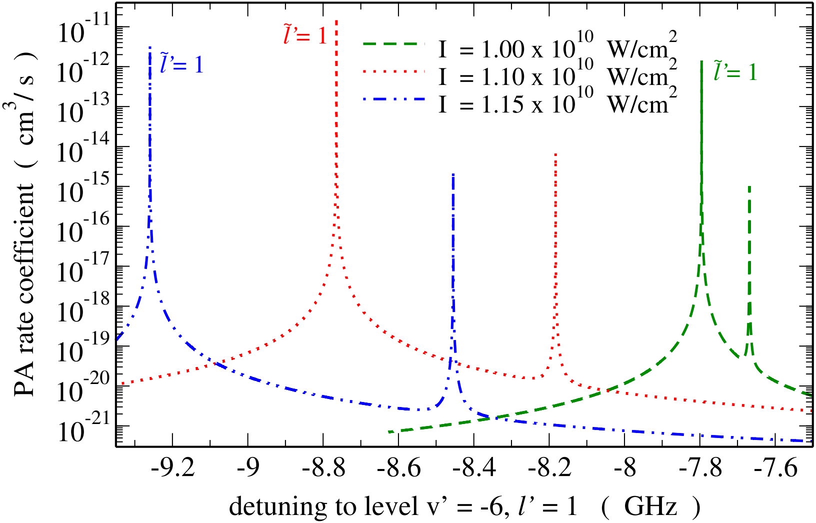
(i) weak field: shift of lines



enhancement of PA rate

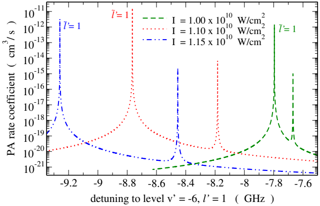
González-Férez & Koch, Phys Rev A 86, 063420 (2012)

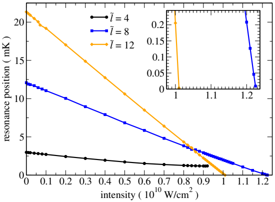
(ii) strong field: large enhancement

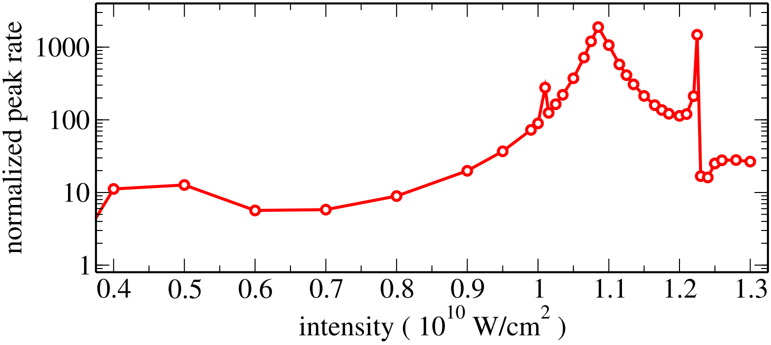


enhanced PA rates by shape resonance control

González-Férez & Koch, Phys Rev A 86, 063420 (2012)







envisioned scheme for PA

1. slowly switching on the non-resonant field

   thermal cloud follows adiabatically

2. photoassociation in presence of non-resonant field

   PA laser finds enhanced pair density
   at relevant interatomic separations
   due to non-resonant field

3. spontaneous decay

   ground state molecules in hybridized levels

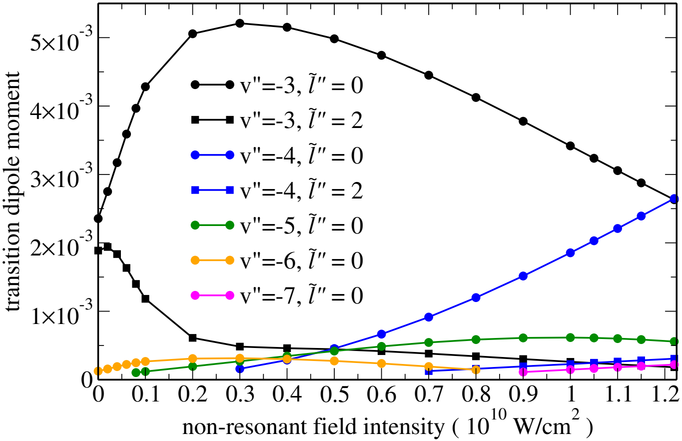
4. slowly/suddenly switching off the non-resonant field

   ground state molecules in field-free levels

5. Raman transfer to $v = 0$

spontaneous decay

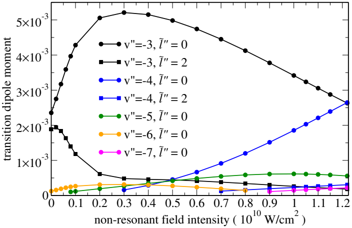
into hybridized ground state levels

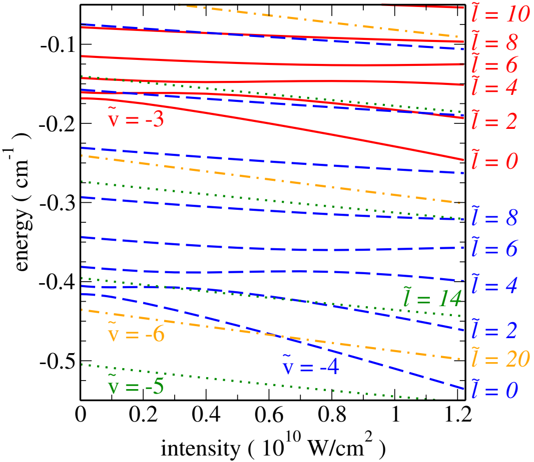


spontaneous decay

into hybridized ground state levels

followed by adiabatic switch off of non-resonant light

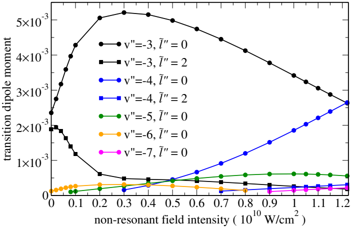


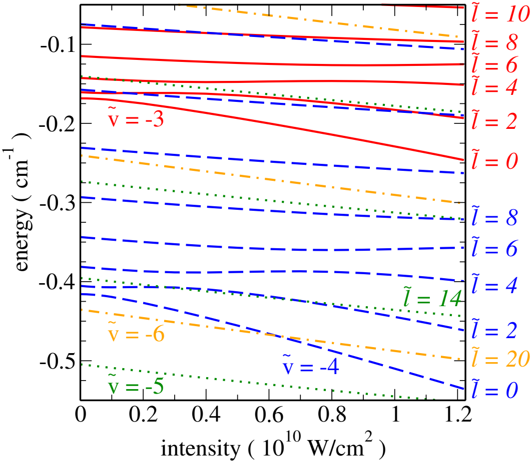


spontaneous decay

into hybridized ground state levels

followed by adiabatic switch off of non-resonant light



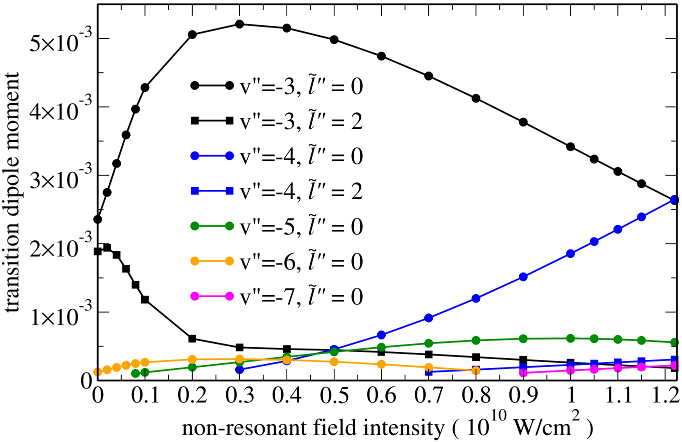


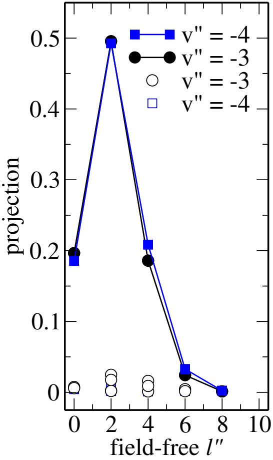
slow switch off of non-resonant field leads to GS molecules in $v = -3$ and $v = -4$ with $\ell = 0$!

spontaneous decay

into hybridized ground state levels

followed by sudden switch off of non-resonant light





50% of GS molecules in $v=-3$ and $v=-4$ with $\ell=2$

envisioned scheme for PA

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   at relevant interatomic separations
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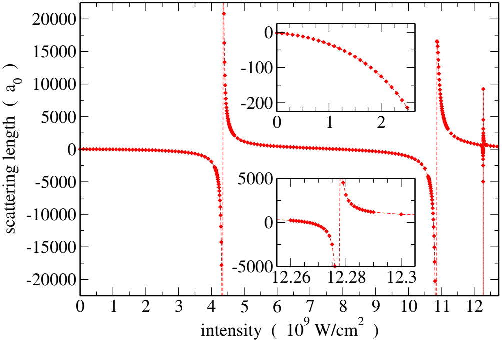
5. Raman transfer to $v = 0$

Skomorowski, Moszynski, Koch,
Phys Rev A 85, 043414 (2012)

outlook:
non-resonant light control of scattering

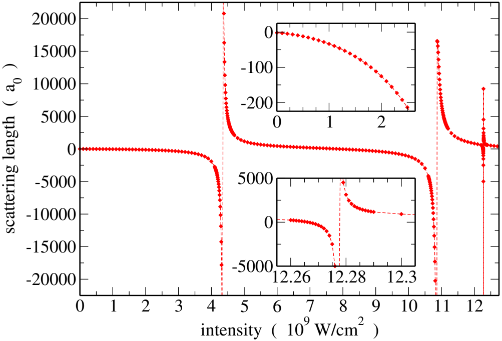
in collaboration with R. González-Férez, P. Julienne, J. Ye



- **heating due to light scattering can be made small by using far off-resonant laser light ($\lambda_{NR} = 10\,\mu$m)**
- **also scattering of higher partial waves will be affected**

outlook:
non-resonant light control of scattering

in collaboration with R. González-Férez, P. Julienne, J. Ye



- **heating due to light scattering can be made small by using far off-resonant laser light ($\lambda_{NR} = 10\,\mu$m)**
- **also scattering of higher partial waves will be affected**

opening the way toward all-optical control of scattering!

summary

photoassociation as a binary reaction

- **photoassociation:**
  coherent control out of scattering continuum
- **initial thermal ensemble can be significantly altered by tuning scattering resonances**
- **here: non-resonant field control of shape resonances**
  related: Feshbach-optimized photoassociation
  Pellegrini, Gacesa, Côté, Phys Rev Lett 101, 053201 (2008)
- **generally applicable**
  best for heavy atoms with large polarizabilities and large scattering lengths

take home messages

- **photoassociation:**

  coherent control out of scattering continuum

  coherence distillation/Franck-Condon filtering

- **coherent evolution after bond formation:**

  play all the games of coherent control

- **low temperature:**

  initial thermal ensemble of high purity

  can be significantly altered
  by tuning scattering resonances