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H4.SMR/381-45

COLLEGE ON ATOMIC AND MOLECULAR PHYSICS: PHOTON ASSISTED COLLISIONS IN ATOMS AND MOLECULES

(30 January - 24 February 1989)

LASER CONTROL OF UNIMOLECULAR REACTIONS

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UNIMOLECULAR REACTIONS

LET US STUDY DISSOCIATION BY PHOTOEXCITATION OF SELECTED QUASI-BOUND STATES

$$ABC \xrightarrow{\omega} (ABC)^* \begin{cases} A + BC & \alpha \\ AB + C & \beta \end{cases}$$

$(ABC)^* \equiv |\alpha_{ABC}\rangle$ α = vector of quantum numbers

$|\alpha_{ABC}\rangle$ is an eigenstate of an incomplete Hamiltonian, H_0

$$H = H_0 + V$$

V is responsible of the decay of $|\alpha_{ABC}\rangle$ into the continua

$|\alpha'_A, \alpha'_{BC}, \varepsilon'\rangle$ translational α

$|\beta'_C, \beta'_{AB}, \varepsilon''\rangle$ β

The lifetime of $|\alpha_{ABC}\rangle$ depends on the cross sections for channels α and β (summed over all the

So, for a given excited state of ABC (above the dissociation threshold), the relative yield of channel α and β is out of our control.

If we want to promote, say, channel α, the best we can do is to excite the state ~~that~~ for which

$$\frac{\tau_\alpha}{\tau_\alpha + \tau_\beta} = \frac{\tau_\alpha}{\tau_{tot}} \quad \text{minimum}$$

(τ_α = lifetime for channel α etc.)

What happens if we excite not a single state $|\alpha_{ABC}\rangle$ but a wave packet, i.e.

$$|\psi\rangle = \sum C_{\alpha_{ABC}} |\alpha_{ABC}\rangle \qquad ?$$

Initially:

$$\rho = |\psi\rangle\langle\psi| = \sum_{\alpha\alpha'} C^*_\alpha C_{\alpha'} |\alpha'\rangle\langle\alpha| =$$

$$= \sum_\alpha \underbrace{|C_\alpha|^2}_{\rho_{\alpha\alpha}} |\alpha\rangle\langle\alpha| + {\sum_{\alpha\alpha'}}' \underbrace{C^*_\alpha C_{\alpha'}}_{\rho_{\alpha'\alpha}} |\alpha'\rangle\langle\alpha|$$

In usual conditions $\rho_{\alpha'\alpha}$ goes rapidly to zero due to ensemble averaging (dephasing):

$$\langle \rho_{\alpha'\alpha} \rangle \rightarrow \rho_{\alpha\alpha}\, \delta_{\alpha'\alpha}$$

(before the reaction ~~to~~ can take place)

In this situation there is no advantage in exciting wavepackets.

Is it possible to utilize coherent superpositions of states for promoting a given channel? (working with beams or at low pressure)

The answer is affirmative.

Several theoretical papers on this subject:

e.g.

M. Shapiro and P. Brumer J. Chem. Phys. 84 (1986) 4103

Laser control of product quantum state populations in unimolecular reactions

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D. J. Tannor, R. Kosloff and S. A. Rice J. Chem. Phys. 85 (1986) 5805

coherent pulse sequence induced control of selectivity of reactions

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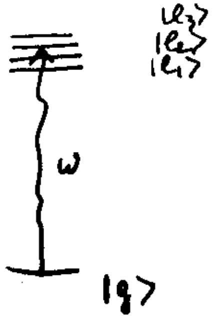
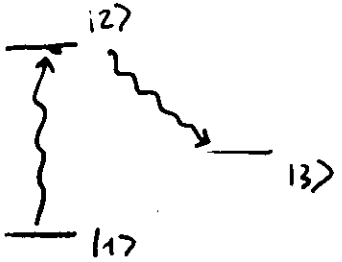
A. Lami and G. Villani J. Phys. Chem. 92 4368 (1988)

control of the yield of competing unimolecular reactions through double-resonance coherent trapping



With a monochromatic source only a few molecular states can be simultaneously excited (nearly degenerate)

$$E_g + \omega \cong E_{e_j}$$



with two laser sources (ω, ω) we can excite linear combinations involving molecular eigenstates with very different energies

$$E_1 + \omega_1 \sim E_2 \sim E_3 + \omega_2$$

In terms of molecule ⊗ photon states

$|1\rangle \rightarrow |1; \omega_1, \omega_2\rangle$
$|2\rangle \rightarrow |2, \omega_2\rangle$
$|3\rangle \rightarrow |3, 2\omega_2\rangle$

Lasers can be used
constructively to build up
linear combinations involving molecular
states (very far in energy) having
the desired properties.

The properties of such linear
combinations may be quite
different from the ones of the
individual states

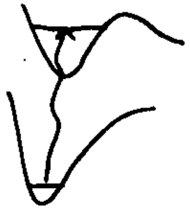
This is the general idea

I am going to discuss just a
simple, particular, application of
this quite intriguing idea.

GENERAL CONSIDERATIONS

SEVERAL UNIMOLECULAR REACTIONS AT
ENERGY JUST ABOVE THE THRESHOLD ARE
PREDISSOCIATIONS

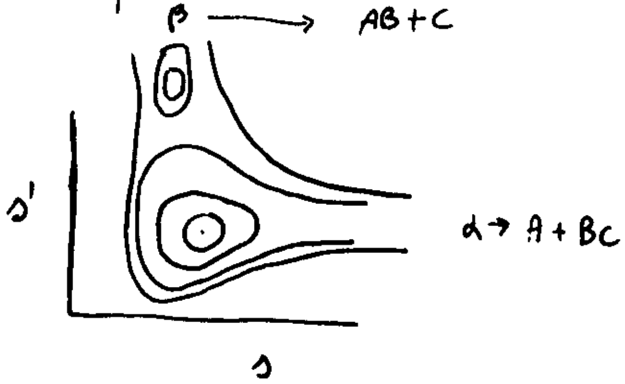
PROMPT PHOTODISSOCIATION



PHOTOPREDISSOCIATION

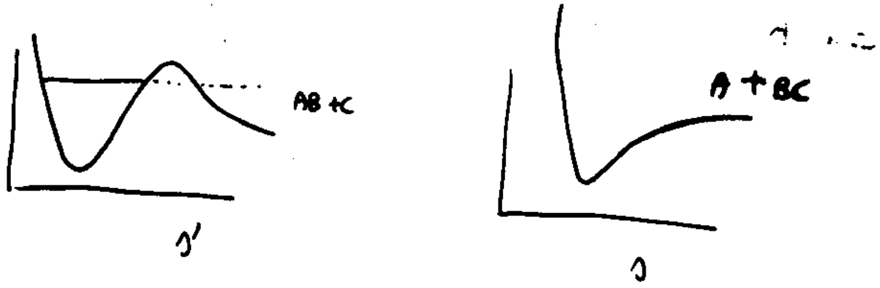
THE ABOVE IS AN UNIDIMENSIONAL PICTURE
CONSIDER A TRIATOMIC MOLECULE

SUPPOSE φ FIXED



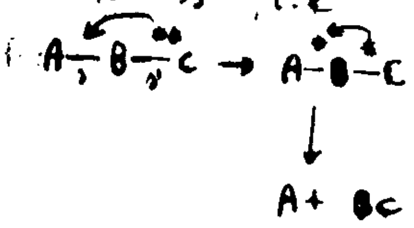
SECTION

SECTIONS

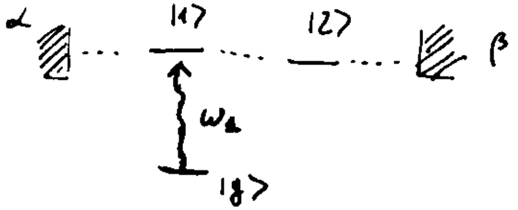


IF ONE EXCITES ALONG s' ONE MAY HAVE A DIRECT PREDISSOCIATION $ABC \rightarrow AB+C$

AN ALTERNATIVE PATHWAY CONSISTS IN TRANSFERRING VIBRATIONAL ENERGY TO s. AFTER A FEW STEPS ONE CAN REACH THE CONTINUUM FOR s, i.e.



IN INFRARED PHOTOCHEMISTRY THE ~~[illegible]~~ EASIEST BOND TO EXCITE DOES NOT USUALLY CORRESPOND TO THE BOND EFFECTIVELY BROKEN (WHICH MEANS THAT THE VIBRATIONAL ENERGY IS TRANSFERRED VERY FAST)



RECALL : $|g\rangle$ both s and s' unexcited

$|1\rangle$ s' excited

$|2\rangle$ energy transferred in part fro s' to s

$|1\rangle$ decays by tunneling into the continuum α

$|2\rangle$ decays by vibrational predissociation into the continuum β corresponding to excitation of s above the dissociation threshold

γ_1 imaginary part of the energy for state $|1\rangle$ due to α

γ_2 imaginary part of the energy for $|2\rangle$ due to β (The coupling to the conti is due to $T_{ss'} + V_{ss'}$

$|1\rangle$ and $|2\rangle$ are coupled because they are eigenstates of the incomplete Hamiltonian $H_0 = H_s + H_{s'}$

$$H = H_s + H_{s'} + \underbrace{V_{ss'} + T_{ss'}}$$

$H_s \equiv$ Hamiltonian for oscillator s (potential = section along s)

$H_{s'} \equiv$ Hamiltonian for s'

potential and kinetic coupling

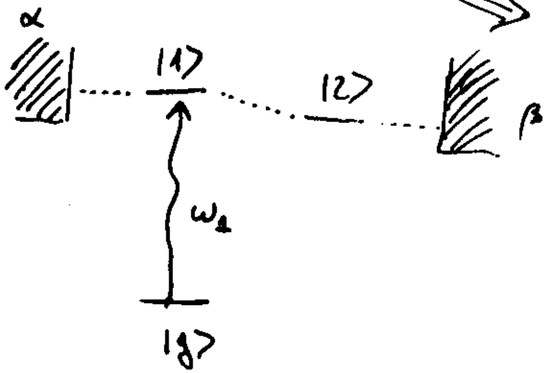
$$V_{ss'} = V^{\text{true}}(s,s') - (V_s + V_{s'})$$

$$T_{ss'} = -\frac{2\cos\phi}{m_B}\frac{\partial^2}{\partial s\,\partial s'}$$

$|g\rangle \equiv |v_{s'}=0\,;\,v_s=0\rangle$

$|1\rangle \equiv |v_{s'}=m\,;\,v_s=0\rangle \Rightarrow$ predissociation (s' broken) α

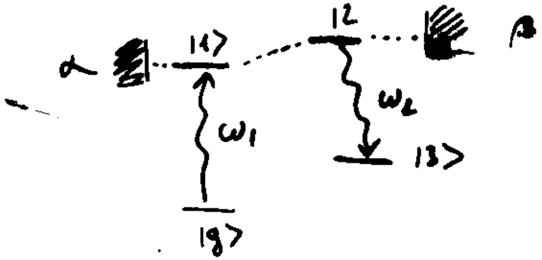
$|2\rangle \equiv |v_{s'}=m'\,;\,v_s=n\rangle \Rightarrow$ vibrational predissociation (bond s broken) β



BY EXCITING WITH ω_1 A CERTAIN FRACTION OF THE MOLECULES DECAYS IN CHANNEL α (X_α), OTHERS IN β (X_β). AS PREVIOUSLY MENTIONED X_α IS USUALLY QUITE SMALL, i.e. $X_\beta \gg X_\alpha$

FOR PROMOTING CHANNEL α WE PROPOSE OF USING ANOTHER LASER ω_2 TO PERMIT TO ANOTHER MOLECULAR STATE, $|3\rangle$, TO COME INTO PLAY.

HERE $|3\rangle$ IS ANOTHER BOUND STATE DIFFERENT FROM $|g\rangle$



$$H^{\text{eff}} \equiv \begin{pmatrix} E_g+\omega_1+\omega_2 & V_{g1} & 0 & 0 \\ & E_1+\omega_2-i\gamma_1 & V_{12} & 0 \\ & & E_2+\omega_2-i\gamma_2 & V_{23} \\ & & & E_3+2\omega_2 \end{pmatrix}$$

symmetric

Let us consider, for simplicity, the case of ω_1 weak.
Then ω_1 simply acts as a pump of population into the excited manifold spanned by $|1\rangle$ $|2\rangle$ $|3\rangle$

$|1\rangle \equiv |1;\ \omega_2\rangle$
$|2\rangle \equiv |2;\ \omega_2\rangle$
$|3\rangle \equiv |3;\ 2\omega_2\rangle$

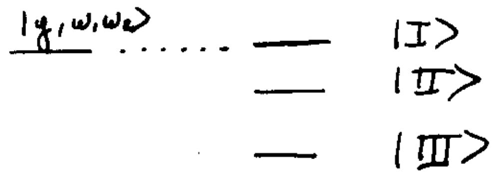
By diagonalizing the 3x3 effective hamiltonian one has three dissipative dressed states (i.e eigenstates of $H_{mol} + H_{rad} + H_{mol\text{-}rad}$)

$|I\rangle$ $|II\rangle$ $|III\rangle$

The three widths $\Gamma_I, \Gamma_{II}, \Gamma_{III}$ (as well as the energies E_I, E_{II}, E_{III}) depend on ω_2, I_2

$\Gamma_I, \Gamma_{II}, \Gamma_{III}$ contain contributions from α and β.

THE FUNDAMENTAL POINT IS THAT ω_2 AND I_2 MAY BE USED AS CONTROL PARAMETERS TO MAKE ONE OF THE THREE Γ's, SAY Γ_I, BE COMPOSED MAINLY BY CONTRIBUTIONS COMING FROM α



$|g, \omega_1, \omega_2\rangle$ can then positioned in front of Γ_I (by suitably tuning ω_1)

Since the coupling is small the population flows from $|g, \omega_1 \omega_2\rangle$ to $|I\rangle$, which means that the yield of channel α is enhanced

WARNING: IF $E_I \sim E_{II} \sim E_{III}$ IT IS IMPORTANT TO BE SURE THAT THE RADIATIVE COUPLING ~~TO~~ OF
IS THE MAXIMUM

$$H^{eff} = \begin{pmatrix} E_g+\omega_1+\cancel{\omega_2} & V_{g1} & 0 & 0 \\ & E_1+\cancel{\omega_2}-i\gamma_1 & V_{12} & 0 \\ & & E_2+\cancel{\omega_2}-i\gamma_2 & V_{23} \\ & & & E_3+2\cancel{\omega_2} \end{pmatrix}$$

$$\begin{pmatrix} E_1-i\gamma_1 & V_{12} & 0 \\ V_{12} & E_2-i\gamma_2 & V_{23} \\ 0 & V_{23} & E_3+\omega_2 \end{pmatrix}$$

Suppose γ_1, γ_2 small. Then one of the eigenstates is $\begin{pmatrix} p \\ 0 \\ q \end{pmatrix}$ if $E_3+\omega_2 = E_1$

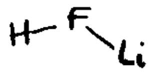
In fact

$$\begin{pmatrix} E_1 & V_{12} & 0 \\ V_{12} & E_2 & V_{23} \\ 0 & V_{23} & E_1 \end{pmatrix} \begin{pmatrix} p \\ 0 \\ q \end{pmatrix} = E_1 \begin{pmatrix} p \\ \frac{1}{E_1}(pV_{12}+qV_{23}) \\ q \end{pmatrix}$$

$$pV_{12}+qV_{23}=0 \qquad p = -q\frac{V_{23}}{V_{12}} \qquad (p^2+q^2=1)$$

This eigenstate is a linear combination of $|1\rangle$ and $|3\rangle$. One may think that nearly the same holds also inserting $-i\gamma_1$ and $-i\gamma_2$ in the 3×3 H^{eff}. If this is true then Γ must receive contributions mainly by γ_1 (decay into channel α)

THE CALCULATIONS SHOW THAT THIS IS INDEED THE CASE

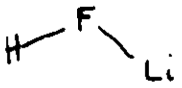
A CONCRETE EXAMPLE : THE INFRARED PHOTOPREDISSOCIATION OF 

A. LANI AND G. VILLANI J. PHYS. CHEM. 92 (1988) 4368

THE AB-INITIO PES FOR THE COLLISION

H–F + Li

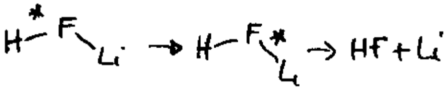
SHOW THAT THERE IS A MINIMUM FOR



IT IS NOT SURE WHETER THE MINIMUM IS SUFFICIENTLY DEEP TO SUPPORT BOUND STATES. IN ANY CASE THERE IS A QUITE LONG-LIVING STATE WHICH WE HAVE CONSIDERED AS BOUND

THE H-F BOND MAY BE EASILY EXCITED BY AN INFRARED LASER TO PROMOTE THE REACTION

THE CALCULATIONS HOWEVER SHOW THAT THE VIBRATIONAL ENERGY IS RAPIDLY TRANSFERRED TO F–Li AND THE REACTION IS



CALCULATIONS : M.M.L. CHEN AND
H.F. SCHAEFER J. CHEM PHYS:
72 (1980) 4376

FITTING : S. CARTER AND J.N. MURREL
J. MOL. PHYS. 41 (1980) 567

570 S. Carter and J. N. Murrell

As starting point for the minimization, we took $R_i^\circ = 1$ Å and $\gamma_i = 2$ Å^{-1} in (4). The minimization was well behaved with no local minima being found that were not recognized as such by the minimization procedure [12]. The optimum three-body term for a quartic polynomial is given in table 2. This has a standard deviation of 7·8 kJ mol^{-1} with a maximum error of 28 kJ mol^{-1} on the scaled *ab initio* points. The saddle point is fitted to within 1 kJ mol^{-1}.

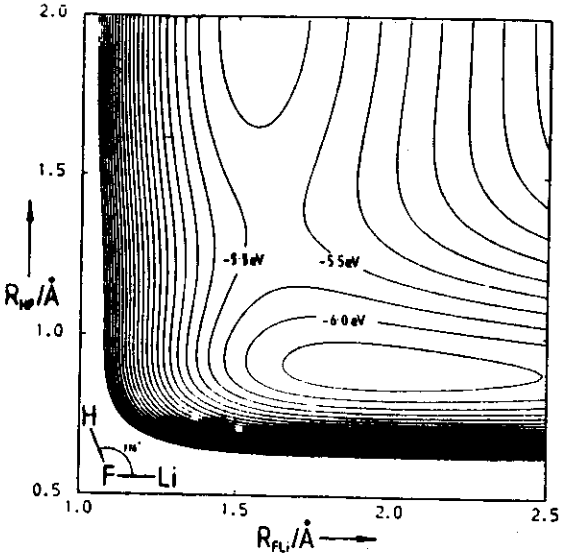
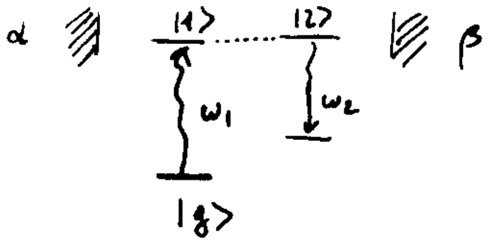


Figure 1. Contours of the LiFH potential for $\widehat{LiFH} = 114°$. Contour interval 0·25 eV. The complex has dimensions $R_{HF} = 0·93$ Å, $R_{FLi} = 1·90$ Å and has an energy of −6·38 eV.



$\alpha \equiv H + F\text{-}Li\,(v$

$\beta \equiv HF(v=1) + Li$

$|g\rangle \equiv |v_{H-F}=0,\ v_{Li-F}=0\rangle$

$|1\rangle \equiv |v_{H-F}=2,\ v_{Li-F}=0\rangle$

$|2\rangle \equiv |v_{H-F}=1,\ v_{Li-F}=8\rangle$

$|3\rangle \equiv |v_{H-F}=0,\ v_{Li-F}=8\rangle$

$H = H_s + H_{s'} + V_{ss'} + T_{ss'}$

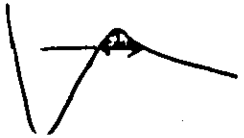
H_s = Morse oscillator for H–F

$H_{s'}$ = Morse oscillator for Li–F

$V_{ss'}$ = potential coupling $= V^{\text{true}}_{(s,s')} - V_{(\text{sum of Morse})}$

$T_{ss'}$ = Kinetic coupling $= -\frac{2}{m_F}\cos\theta_{eq}\cdot\frac{\partial^2}{\partial s\,\partial s'}$

γ_1 = width for channel α ≃ 3 cm^{-1}



estimated from the potential barrier parameters

$\gamma_2 \equiv$ width for channel β

$$\gamma_2 = \pi \left| \langle v_{HF=1}, v_{Li-F}=8 \,|\, H' \,|\, v_{HF=0}, E \rangle \right|^2$$

$\gamma_2 \cong 7\,cm^{-1}$ $\qquad H' = V_{ss'} + T_{ss'}$

$$V_{12} = \langle 1 | H' | 2 \rangle \cong 62\,cm^{-1}$$

The total yield $Y_\alpha(\omega_1, \omega_2, I_2)$ for channel α is defined as

$$Y_\alpha = \frac{\sigma_\alpha(\omega_1, \omega_2, I_2)}{\sigma_\alpha(\omega_1, \omega_2, I_2) + \sigma_\beta(\omega_1, \omega_2, I_2)}$$

where σ_α and σ_β are the cross sections for channel α and β, respectively

σ_α and σ_β calculated from time-dependent Schriödinger equation