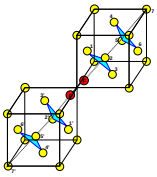
UP2: CONTROL OF CAGE EXIT OF MATRIX-ISOLATED MOLECULES

R. B. Gerber, O. Kühn



AGENDA

Spectroscopy of caging and dissociation dynamics
Laser control of cage exit and intersystem crossing
Laser-induced synthesis of new molecules

COWORKERS

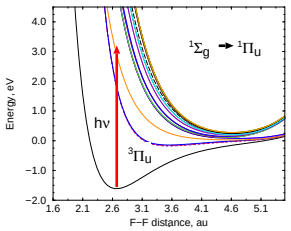
G. Chaban (Jerusalem)
A. Cohen (Jerusalem)
M. Y. Niv (Jerusalem)
M. Schröder (Berlin)
D. Shemesh (Jerusalem)

COOPERATIONS

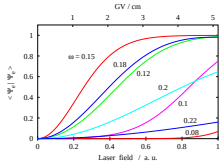
TP A3 (Schwentner/Dietrich)
TP C5 (Schütte/Schmidt)
P. Jungwirth (Prag)
M. Korolkov (Minsk)
N. Makri (Urbana-Champaign)
M. Thoss (München)

RESULTS: F_2 in Argon

DIATOMICS-IN-MOLECULES POTENTIALS

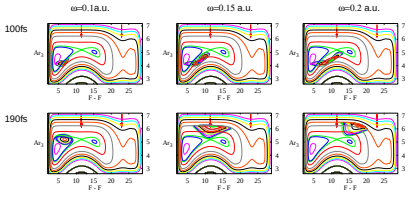


Excitation quantum yield

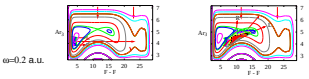


QUANTUM DYNAMICS IN TWO DIMENSIONS

Relief reflections

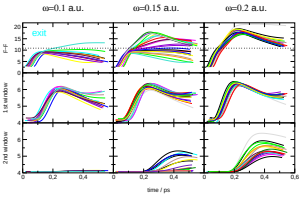


Cage pre-excitation

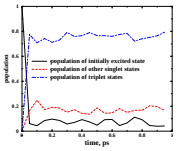


CLASSICAL DYNAMICS WITH NONADIABATIC TRANSITIONS

Caging vs. dissociation

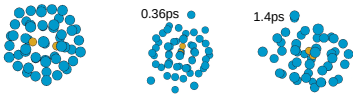


Intersystem crossing in 60 fs



Ultrafast recombination dynamics

$^1\Pi_u \rightarrow {}^3\Pi_u$



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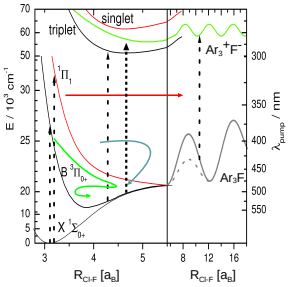
FUTURE

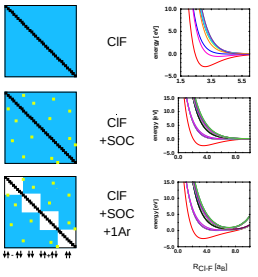
CIF IN RARE GAS MATRIX: SPECTROSCOPY AND LASER CONTROL

Processes



cage exit
recombination and intersystem crossing
damped wave packet motion and dissipation

Diatomics-in-Molecules



Diatomics-in-Ionic-Systems

configurations

A: F(P) + Cl(P) + Ar(S)
B: F^-(S) + Cl^+(P) + Ar(S)
C: F^-(S) + Cl(P) + Ar^+(P)

Classical dynamics with nonadiabatic transitions

- adiabatic potentials and nonadiabatic couplings "on the fly"
- "surface hopping" using Tully's fewest switches criterion

Semiclassical dynamics

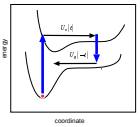
- propagator in coherent state representation

$$\langle \mathbf{x}_f|U(t_f,t_0)|\mathbf{x}_0\rangle \sim (2\pi\hbar)^{-d}\int d\mathbf{x}_{t_0}\int d\mathbf{p}_{t_0}\langle \mathbf{x}_f|\mathbf{x}_{t_f},\mathbf{p}_{t_f}\rangle D(\mathbf{x}_{t_0},\mathbf{p}_{t_0};t_f) \times \exp\left\{\frac{i}{\hbar}S(\mathbf{x}_{t_0},\mathbf{p}_{t_0};t_f)\right\}\langle \mathbf{x}_{t_0},\mathbf{p}_{t_0}|\mathbf{x}_0\rangle$$

- correlation functions

$$\langle A(t)B(0)\rangle = \mathrm{Tr}[U(-t)AU(t)B\rho_{eq}]$$

$A = \mu_{ge}|g\rangle\langle e|$
$B = \mu_{eg}|e\rangle\langle g|$



combined forward-backward dynamics
→ smoothing of integrand

- nonadiabatic transitions
  → discrete-continuous mapping (bosonization)
- mixed-order dynamics

total system = relevant system (semiclassical) + bath (classical)

Quantum dynamics

- reduced dimensionality model
- time-dependent Schrödinger equation in diabatic representation

Topics

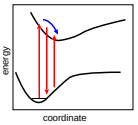
- dynamics of caging, relaxation, dissociation, and ISC
- pump-probe spectroscopy
  (1) Golden rule

$$S_{pp}(t) \propto \sum_{ij}\int d\mathbf{R}\,\rho_i(\mathbf{R};t)\,|\mu_{ij}(\mathbf{R})|^2\,\delta(\Delta V_{ij}(\mathbf{R})-h\nu_p)$$

  (2) response function approach

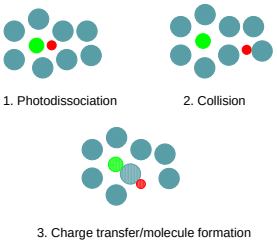
$$C_{pp}^{(3)}(t_3,t_2,t_1) = \mathrm{Tr}_{mol}[U_0(-t_1)\mu_{ge}U_e(-t_2)\mu_{eg}U_f(-t_3)\mu_{fe}U_e(t_3+t_2+t_1)\mu_{eg}\rho_g]$$

  → multiple forward-backward dynamics
- laser pulse control
  → cage exit (via Cl + Ar^+F^-) vs. recombination (via Cl^+F^-)
  → ISC control: nonstatistical singlet/triplet population
  → non-Franck-Condon excitation and trapping using strong fields



CONTROLLED PHOTOCHEMICAL SYNTHESIS OF NEW MOLECULES: FROM HHeF TO ClXeF

Scenario



1. Photodissociation
2. Collision
3. Charge transfer/molecule formation

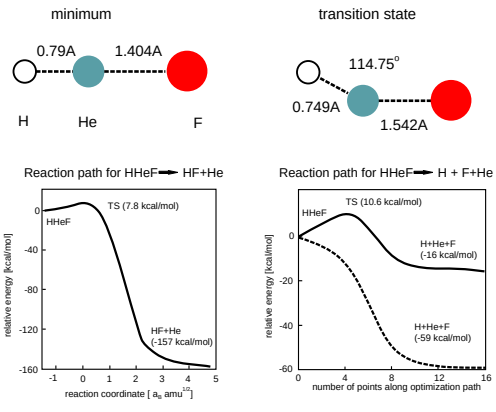
Triatomics-in-Medium (TRIMED) Method

$$\Psi = C_A\Psi_A + C_B\Psi_B + C_C\Psi_C$$

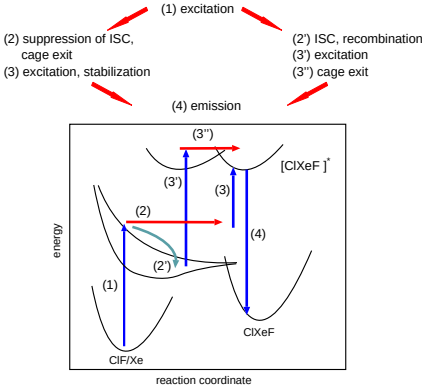
A: Xe + [H(S) + Cl(P)]
B: [H(S) + Xe^+ (P)] + Cl^-
C: H^- + [Xe^+ (P) + Cl(P)]

→ calibration of TRIMED Hamiltonian using ab initio quantum chemistry

Model Study: HHeF



Laser Control Strategies



- characterization via vibrational spectroscopy of F-Xe-Cl
  → electronic structure data plus anharmonic coupled mode treatment of nuclei
- rotational/librational preexcitation (TP C5)

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