L4

Case studies I: Two examples in photochemistry

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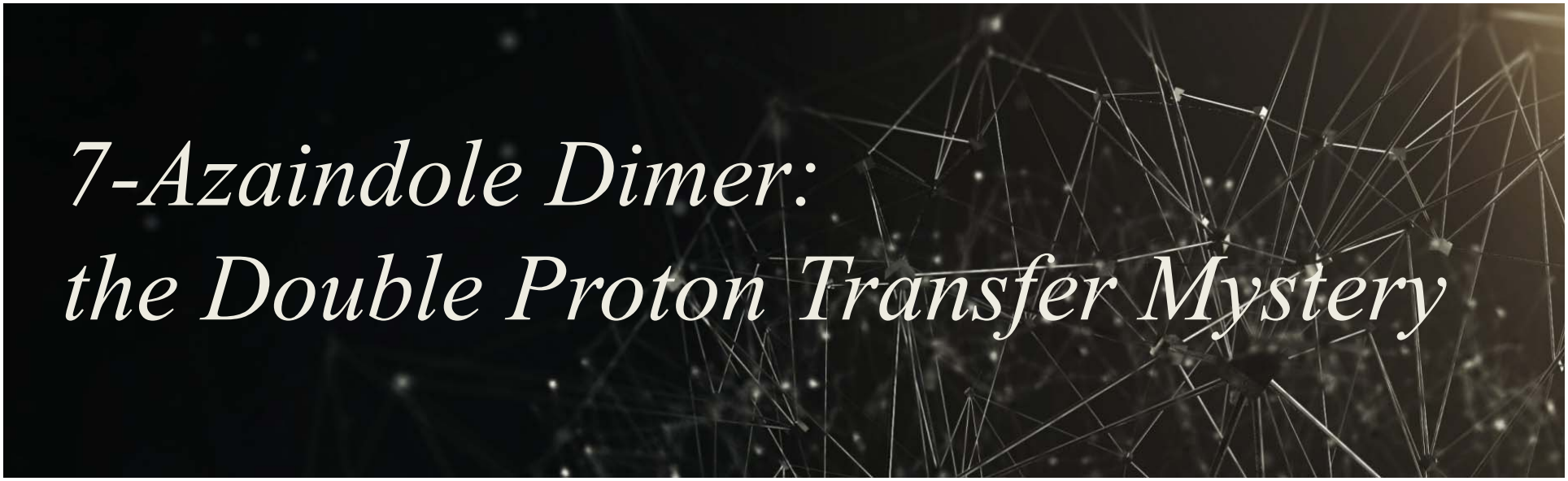
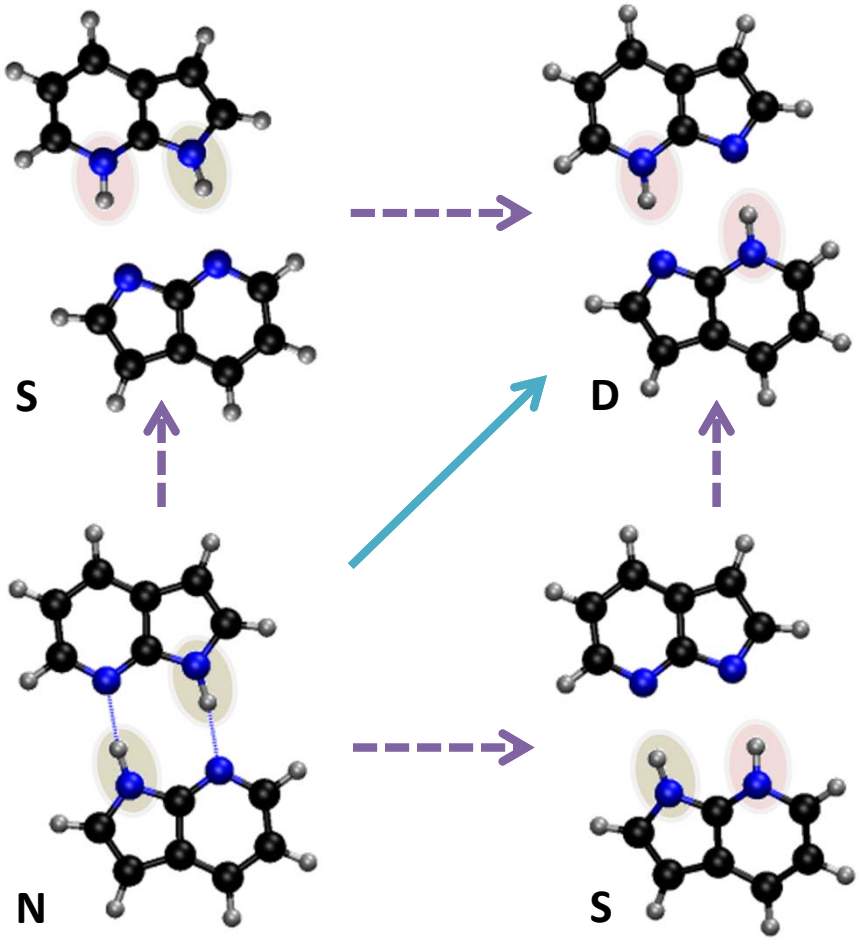
case study



7-Azaindole Dimer: the Double Proton Transfer Mystery

Concerted x Stepwise



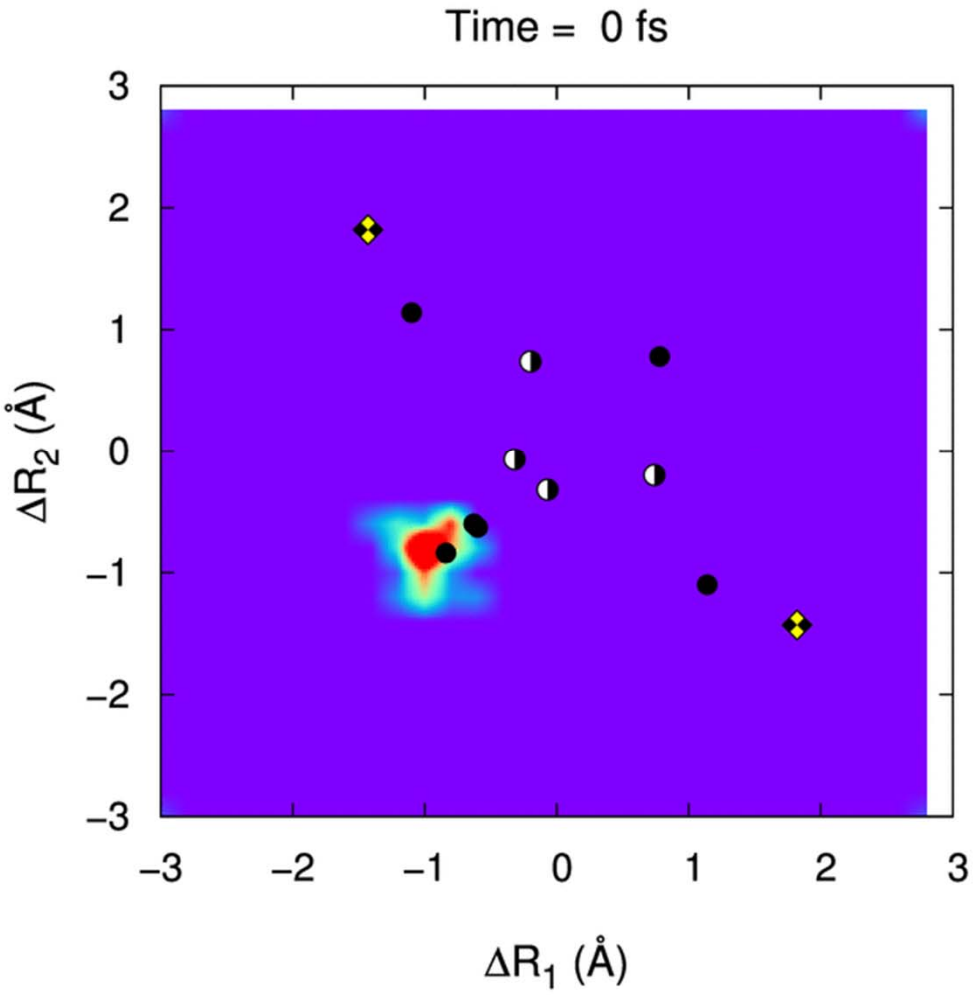
Concerted ESPT

Stepwise ESPT

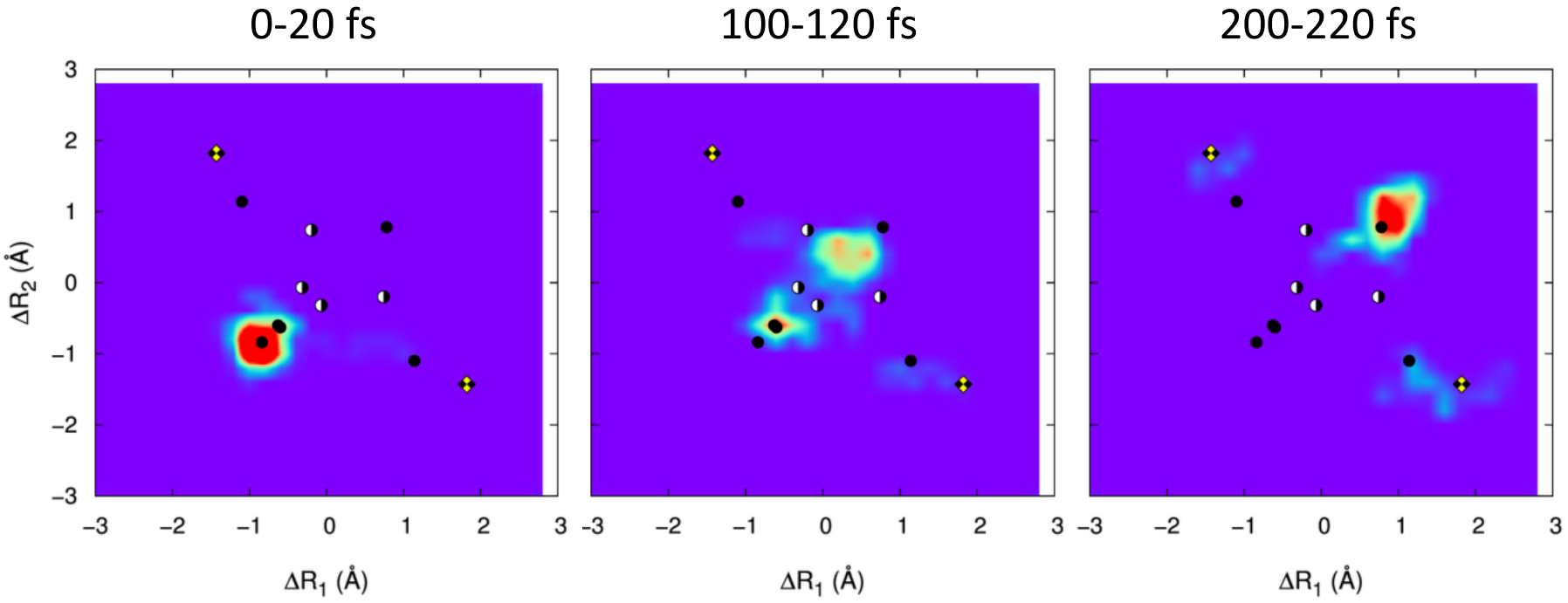
For 20 years people have been discussing whether 7AI dimer PT is concerted or stepwise.

- Douhal, Kim, Zewail, Nature **378**, 260 (1995)
- Catalan, Perez, Jdel Valle, de Paz, Kasha, PNAS **101**, 419 (2004)
- Takeuchi and Tahara, PNAS **104**, 5285 (2007)

youtube.com/user/mbarbatti



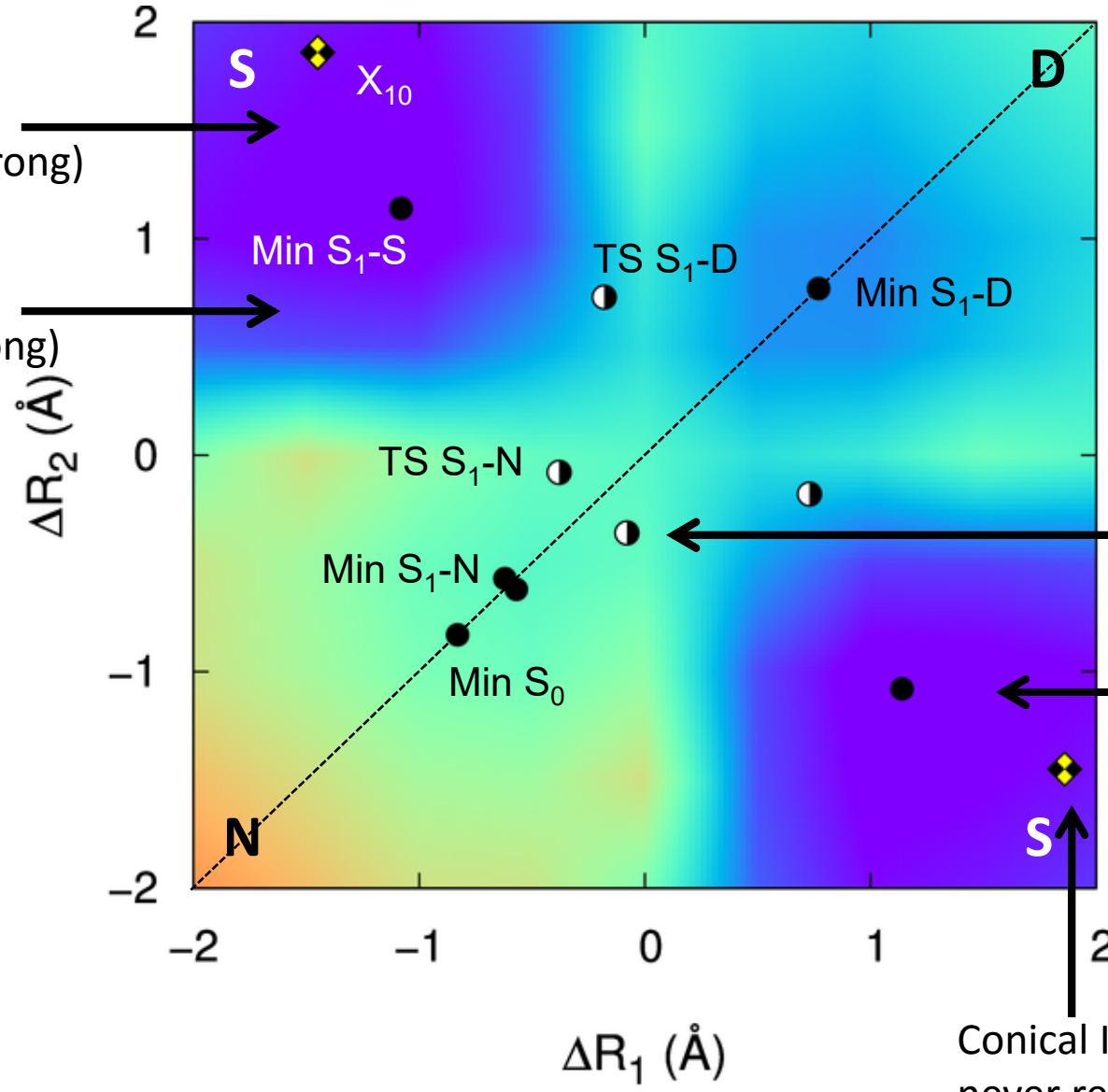
ADC(2)/SVP surface hopping dynamics



Proton transfers are concerted; why so much ado about them?

- Surfaces recomputation at CC2/TZVP
- **Error accessment** with D_1, D_2, and $\%\tau_2$ diagnostics

S_1 Potential Energy (CC2/TZVP)



CIS (2001)
CT > LE (wrong)

CIS (1995)
no CT (wrong)

CASPT2 (2006)
LE min (wrong)

TDDFT (2011)
CT ≈ LE (wrong)

Conical Intersection
never reported

High-level ab-initio theory revealed that:

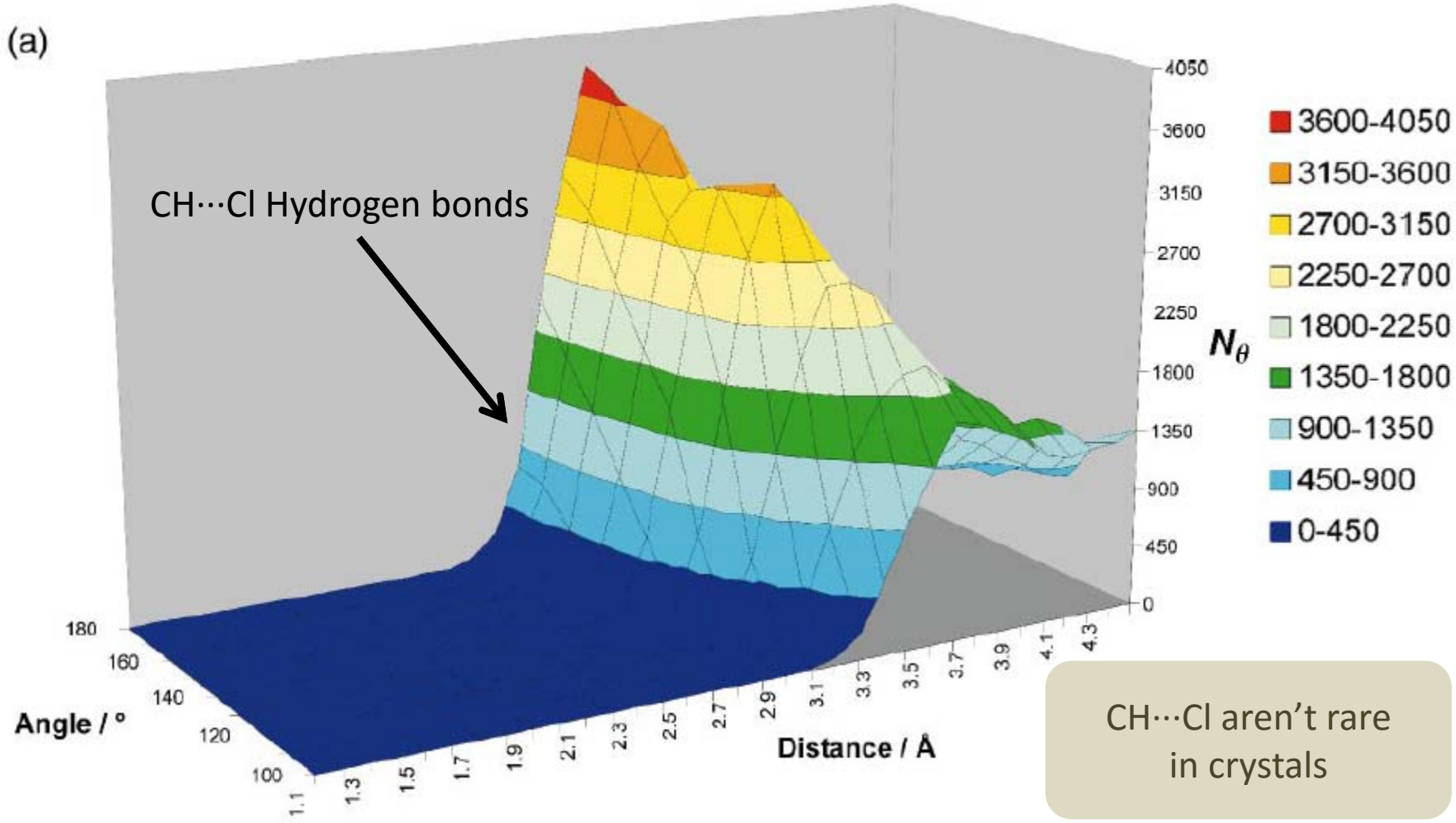
- All theoretical models used to support experiments were wrong!
- CT < LE by 0. 4 eV
- Single PT is possible, but it is followed by internal conversion
- Stepwise PT is *thermodinamically and kinetically* unfavorable
- Double PT can happen only via concerted paths

- Crespo-Otero, Kungwan, Barbatti, Chem Sci **6**, 5762 (2015)

case study

CH-Cl Bonds in Crystals

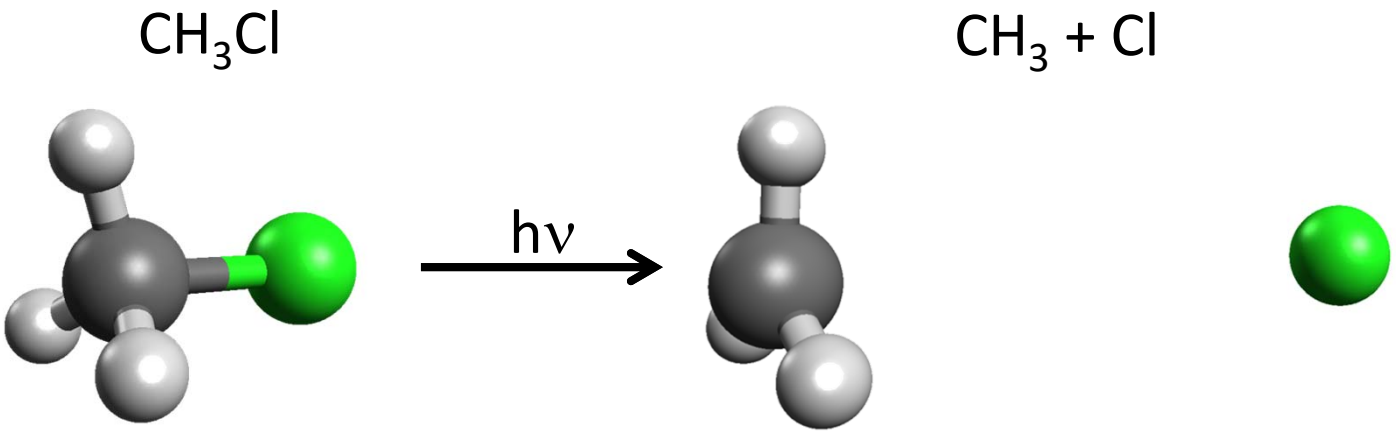
Number of entries in the Cambridge Structural Database



CH···Cl aren't rare in crystals

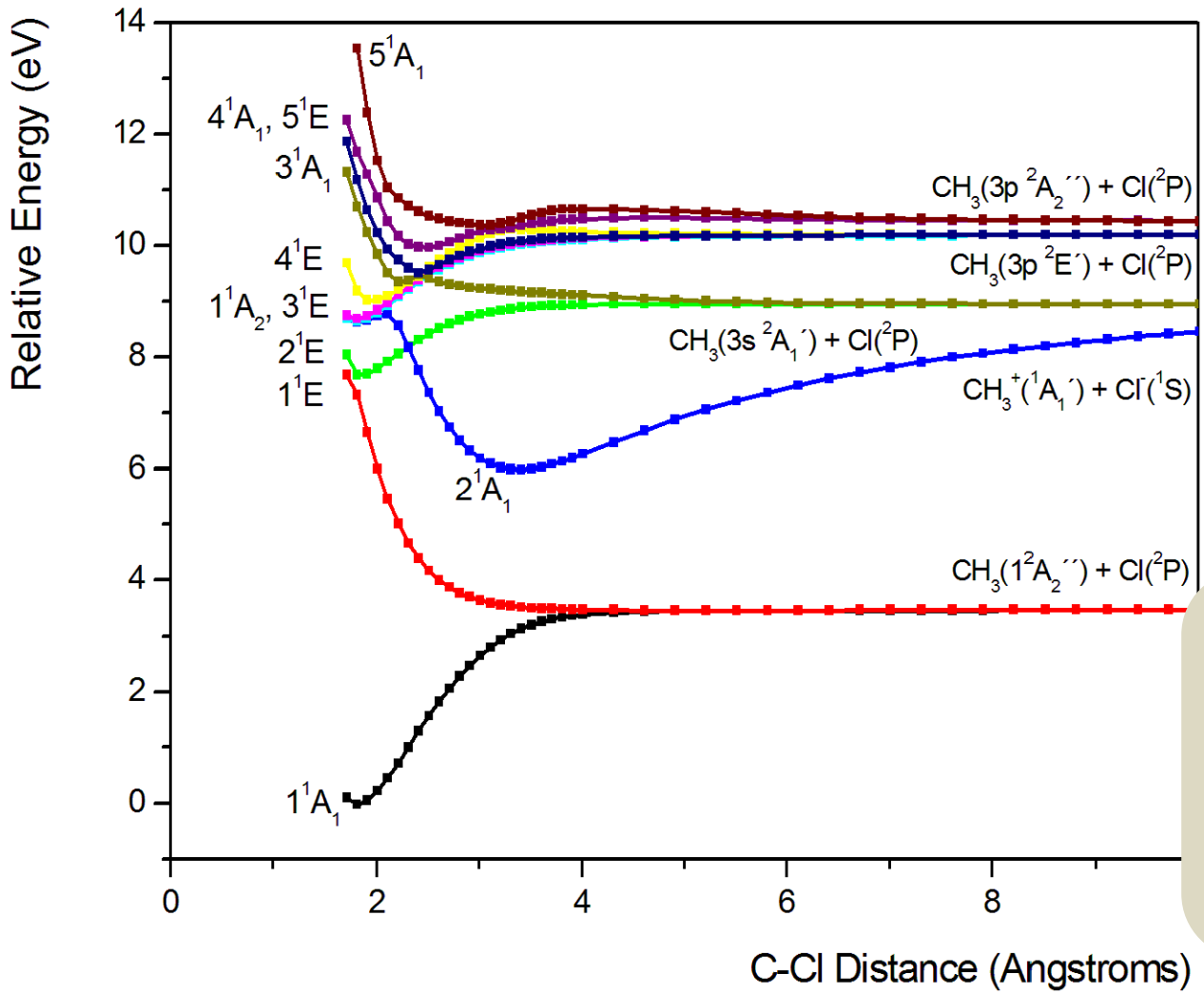
- Aakeröy, Evans, Seddon, Pálinkó, New J Chem **23**, 145 (1999)

Photodissociation of CH_3Cl



- CH_3Cl is one of the main sources of atomic Cl in the high atmosphere.
- This atomic Cl attacks the ozone layer.
- The lowest photodissociation channel is well known.
- There is almost nothing about the other channels.

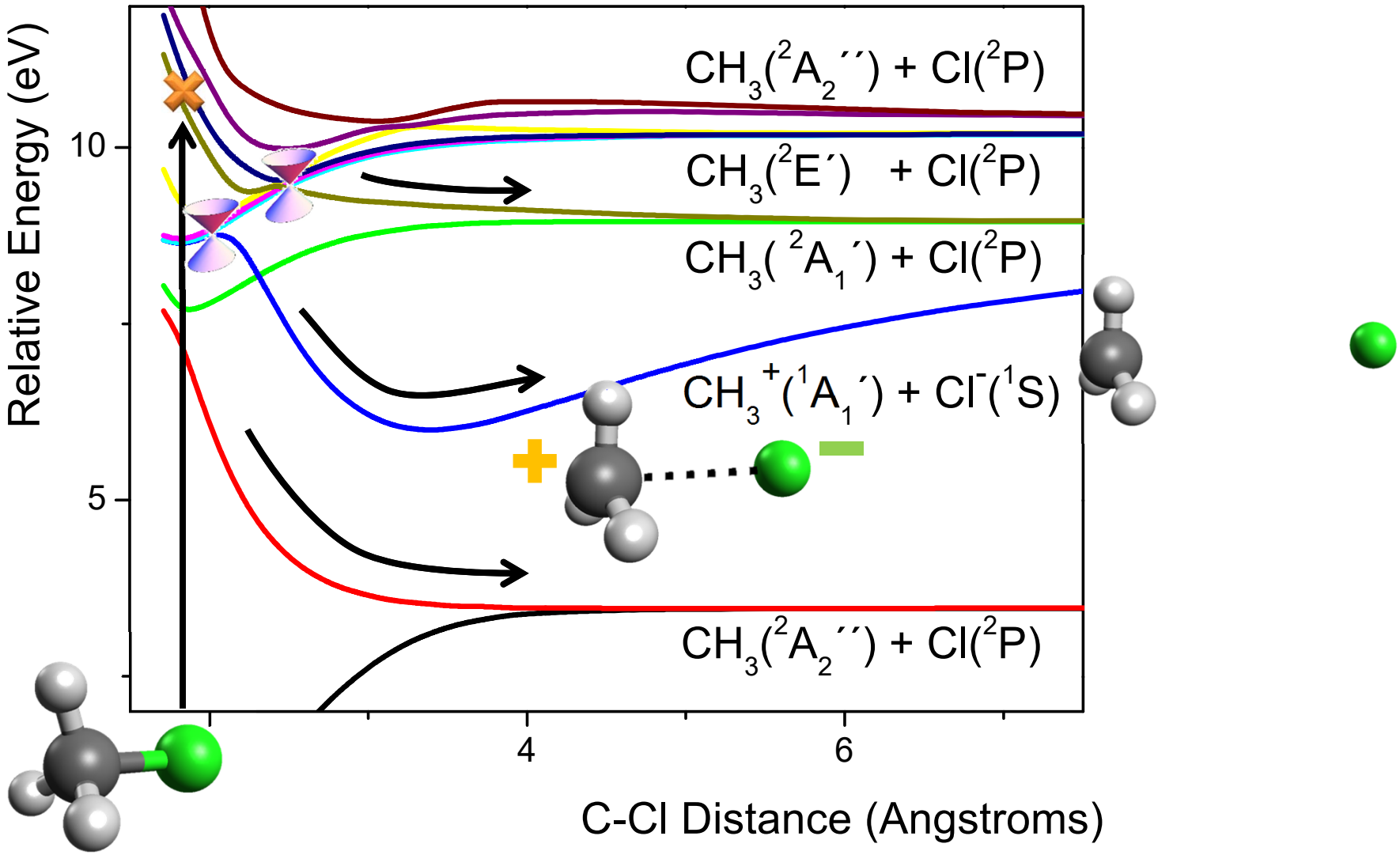
Photodissociation Channels



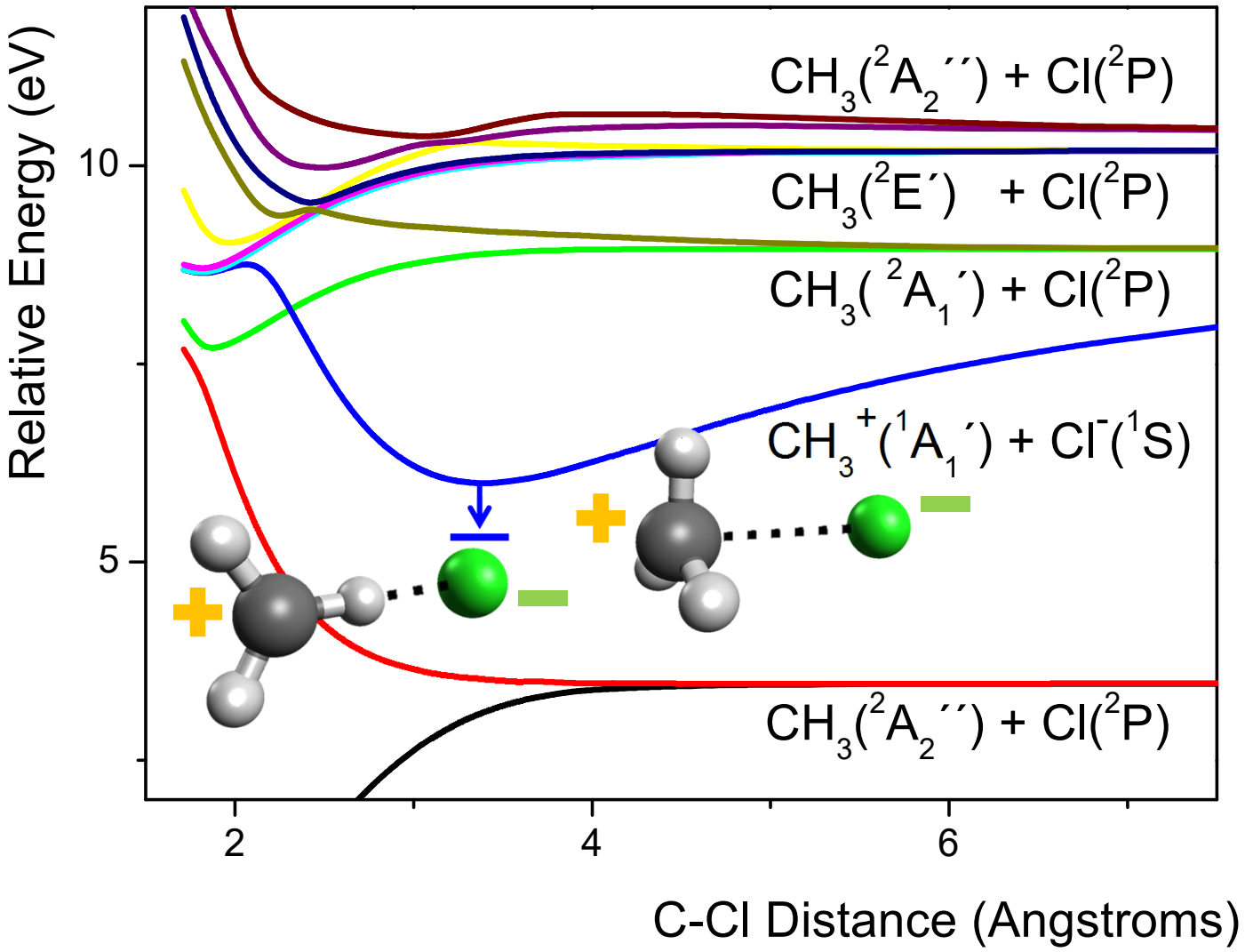
Intricate structure:
Multireference,
Rydbergs states,
Multiple conical intersec,
Electrostatic complex,
Five dissociation limits

MRCI-SD+Q/(d)-aug-cc-pVDZ

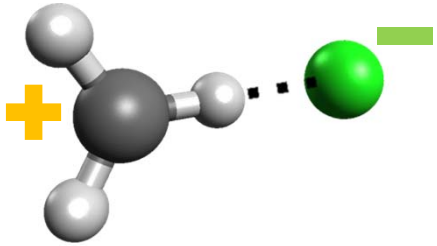
Photodissociation Channels



Photodissociation channels



Is this $CH_3^+\cdots Cl^-$ Hydrogen Bonded?



It is not easy to characterize a H-bond in this complex:

- Exotic species
- Excited state
- Overpowering monopole-monopole interaction

***It satisfies the definition and all conditions** set by IUPAC to characterize H-bonds.*

The $CH_3^+\cdots Cl^-$ complex has a double-charge-assisted CH···Cl hydrogen bond.

- de Medeiros, de Andrade, Leitão, Ventura, Bauerfeldt, Barbatti, do Monte, submitted (2015)

Key points

- Simulations of excited states and nonadiabatic phenomena span a broad area in physical chemistry.
- Diverse methods are available with different degrees of accuracy and different capabilities.
- It is important to be able to judge which methods to use.
- The most reliable quantum chemistry is still the computation of reaction pathways.