

# **Non-adiabatic effects in molecular systems**

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## **Born-Oppenheimer or adiabatic approximation**

The B.O. or adiabatic approximation represents one of the cornerstones of molecular physics and chemistry. Many chemical processes can be described by using this approximation. (The dynamics of the atomic nuclei can be treated on a single B.O. potential-energy surface (PES).)

- The local versus normal mode description of molecular vibrations
- The decay of excited vibrational levels in polyatomic molecules
- Calculation of reaction cross section in atom-molecule collisions etc. . . .

## **Non-adiabatic processes**

Chemical processes, which involve nuclear dynamics on at least two coupled PES and thus cannot be described within the B.O. adiabatic approximation.

Typical processes are:

- Photochemical, photobiological processes
- Radiationless relaxation of excited electronic states
- Isomerization processes of polyatomic molecules
- Photoninduced unimolecular decay etc. . . .

## **Non-adiabatic processes**

During the last few decades there were rapid change of paradigms in non-adiabatic chemistry (experiment, theory).

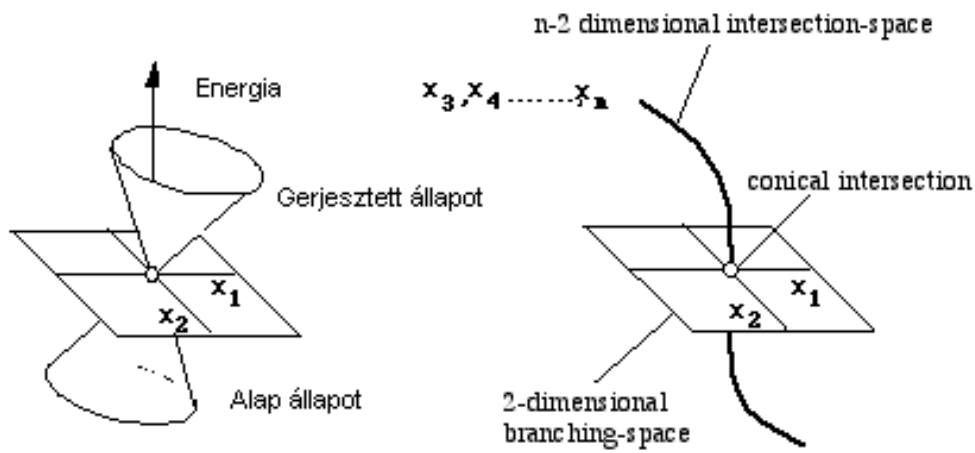
1. Femto-sec. laser technology and time-resolved spectroscopy have revealed that the radiationless decay of excited electronic states may take place much faster than previously thought. The traditional theory of the radiationless decay processes, developed in (60-70th years) cannot explain the femtoseconds time scale!!!

2. The development and widespread application of multi-reference electronic structure methods. Using these methods for the calculation of excited states potential energy surfaces, it was shown that so-called CONICAL INTERSECTIONS (CI) of these multidimensional surfaces (predicted by J. Neumann and E. Wigner in 1929) are very important. The concept of CI-s has become widely known in recent years. CI-s are responsible for ultrafast radiationless processes as it was predicted by E. Teller in 1937.

Conical intersections can be found already between low lying electronic states of triatomic molecules. Their abundance grows with increasing number of atoms in the system and with increasing density of electronic states. FOR truly LARGE POLYATOMIC MOLECULES, CONICAL INTERSECTIONS are UBIQUITOUS!!!

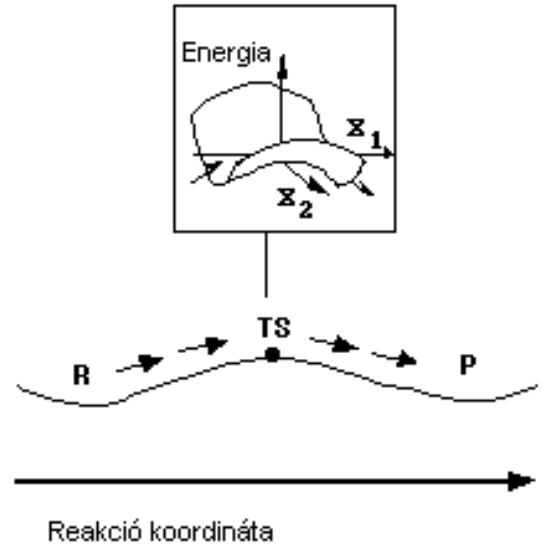
## Some important review papers and books

1. H. Köppel, W. Domcke and L. S. Cederbaum, *Adv. Chem. Phys.* 57, 59 (1984).
2. M. Baer and G. D. Billing, *Adv. Chem. Phys. The Role of Degenerate States in Chemistry*, 124, (2002)
3. M. Baer, *Phys. Rep.* 358, 75 (2002).
4. W. Domcke, D. R. Yarkony and H. Köppel, *Adv. Ser. in Phys. Chem. Conical Intersections*, 15 (2004).
5. G. A. Worth and L. S. Cederbaum, *Annu. Rev. Phys. Chem.* 55, 127 (2004).
6. M. Baer, *Beyond Born-Oppenheimer: Electronic Non-adiabatic Coupling Terms and Conical Intersections* New York, Wiley (2006).
7. ....

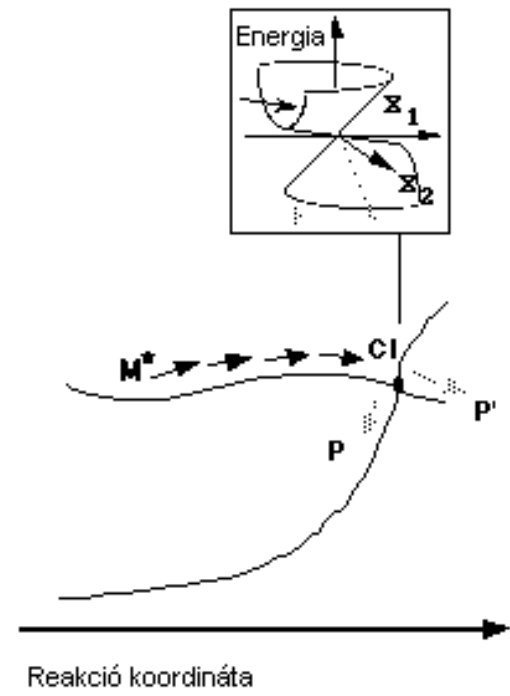


(a)

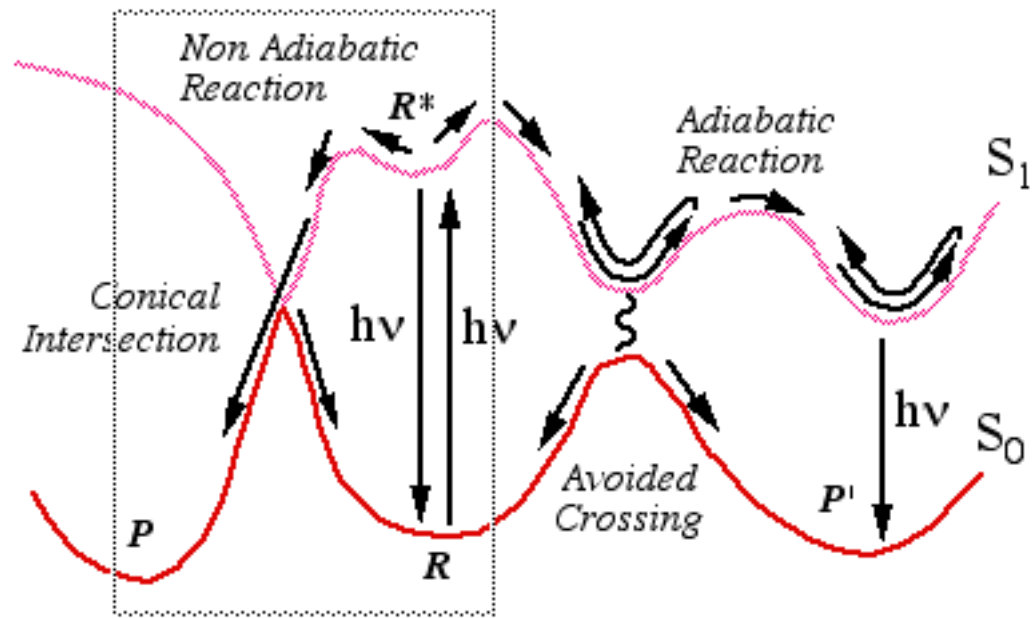
(b)



(a)



(b)



"Branching Space" ( $X_1, X_2$ )

$$X_1 = \frac{\partial(E_1 - E_2)}{\partial q}$$

$$X_2 = \langle \phi_1 | \frac{\partial H}{\partial q} | \phi_2 \rangle$$



## Consequences

Thus, if there is only one degree of freedom and the two states have the same symmetry, one arrives to the well-known noncrossing rule („an avoided crossing”).

If the states of the diatomic have different symmetries, the surfaces can cross because, by symmetry arguments,  $W_{12} = 0$  everywhere.

In polyatomics the number of degree of freedom means that the conditions for the degeneracy may, in principle, always be fulfilled irrespective of the symmetry of the states involved.

Near the degeneracy,  $\Delta \propto \delta \cdot R$  and  $\omega \propto \lambda \cdot R$ . Thus, to first order, the degeneracy is lifted in the space spanned by the vectors  $\delta$  and  $\lambda$ . It can also be seen from the eq. of V that the topology of the surfaces are a double-cone meeting at the point of degeneracy. This two dimensional space is called „branching” space. Orthogonal to the b.s. is the intersection space in which the degeneracy is not lifted. This space forms a N-2 dimensional seam, at each point of which is a conical intersection.

## The Classification of Conical Intersection

Symmetry plays a crucial role in the classification of CIs.

1. Two states of different symmetries can form a conical intersection. (The point group of molecule says which degrees of freedom are involved in the branching space, „symmetry-induced” CI).
2. If the two states involved are symmetrically degenerate this necessarily leads to vibronic coupling and a symmetry-determined conical intersection. (Jahn-Teller effect.)

3. If the two states have the same symmetry or where no symmetry is present and the conditions exist that  $\Delta$  and  $W_{12}$  are independent, CI still possible to be present („accidental conical intersection”).

4. Renner-Teller effect. In linear molecules, a doubly degenerate state arises when the orbital angular momentum around the molecular axis,  $\lambda$  is greater than 0. The degeneracy is split on bending the molecule.

## **Our results related to localizing conical intersections (last years)**

(H+H<sub>2</sub>, Na+H<sub>2</sub>, H<sub>2</sub>O, C<sub>2</sub>H<sub>2</sub><sup>+</sup>, C<sub>2</sub>H<sub>2</sub>, CH<sub>3</sub>NH<sub>2</sub>, THC)

JCP 119,6588,(2003); Faraday Discuss., 127 337,(2004);

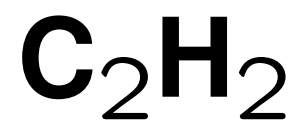
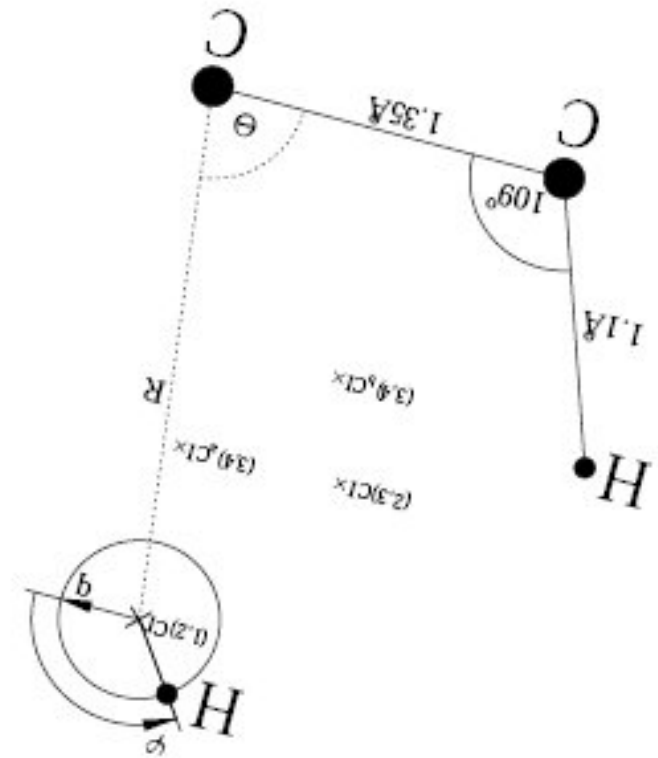
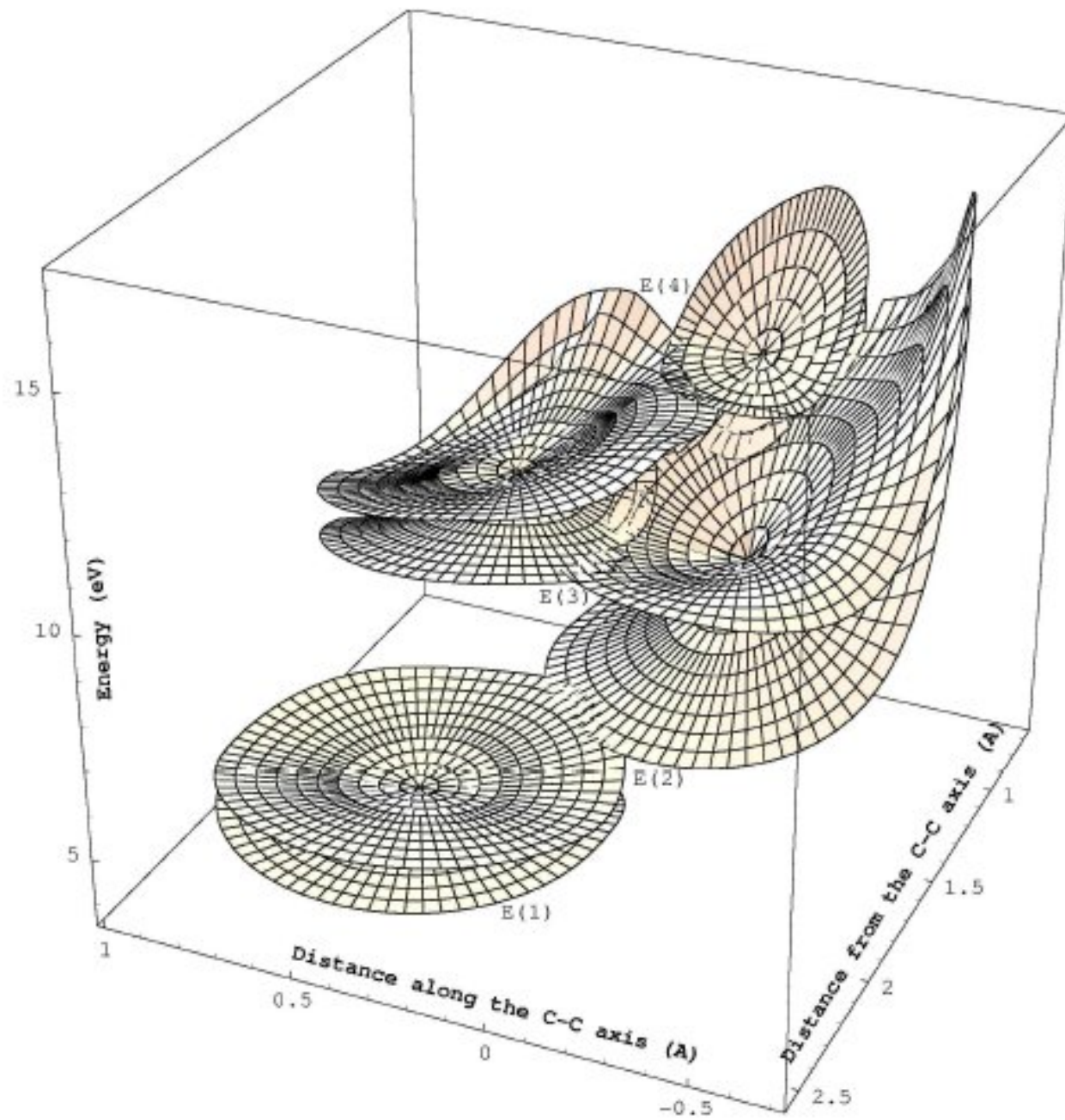
CPL 399,7,(2004); JCP 122, 134109,(2005); CPL 413,226,(2005);

JCP 124,024312,(2006); JCP 124,081106, (2006);

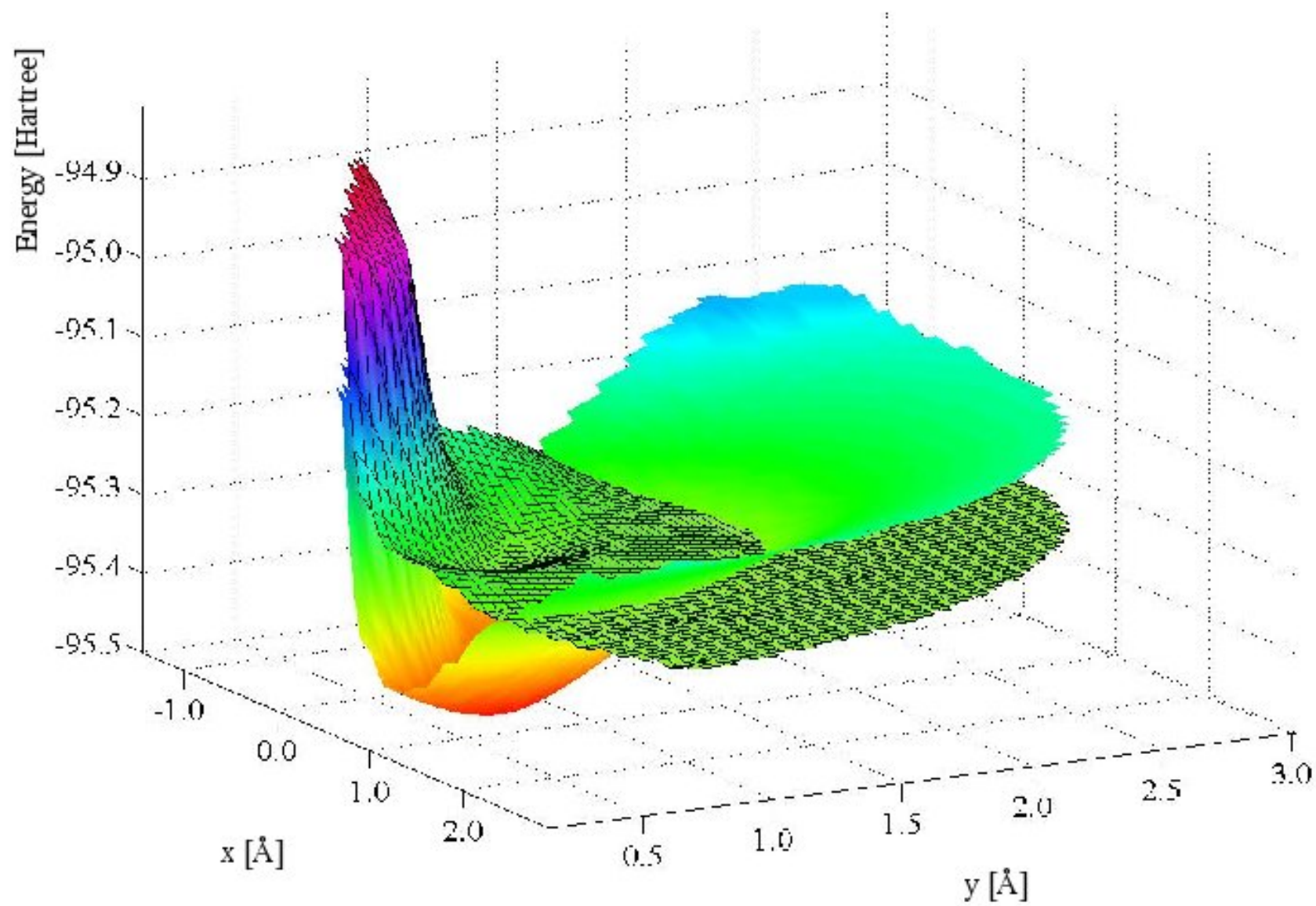
JCP 125,094102,(2006); JCP 127, 144108,(2007);

JCP 126,154309,(2007); JCP 127,244101,(2007);

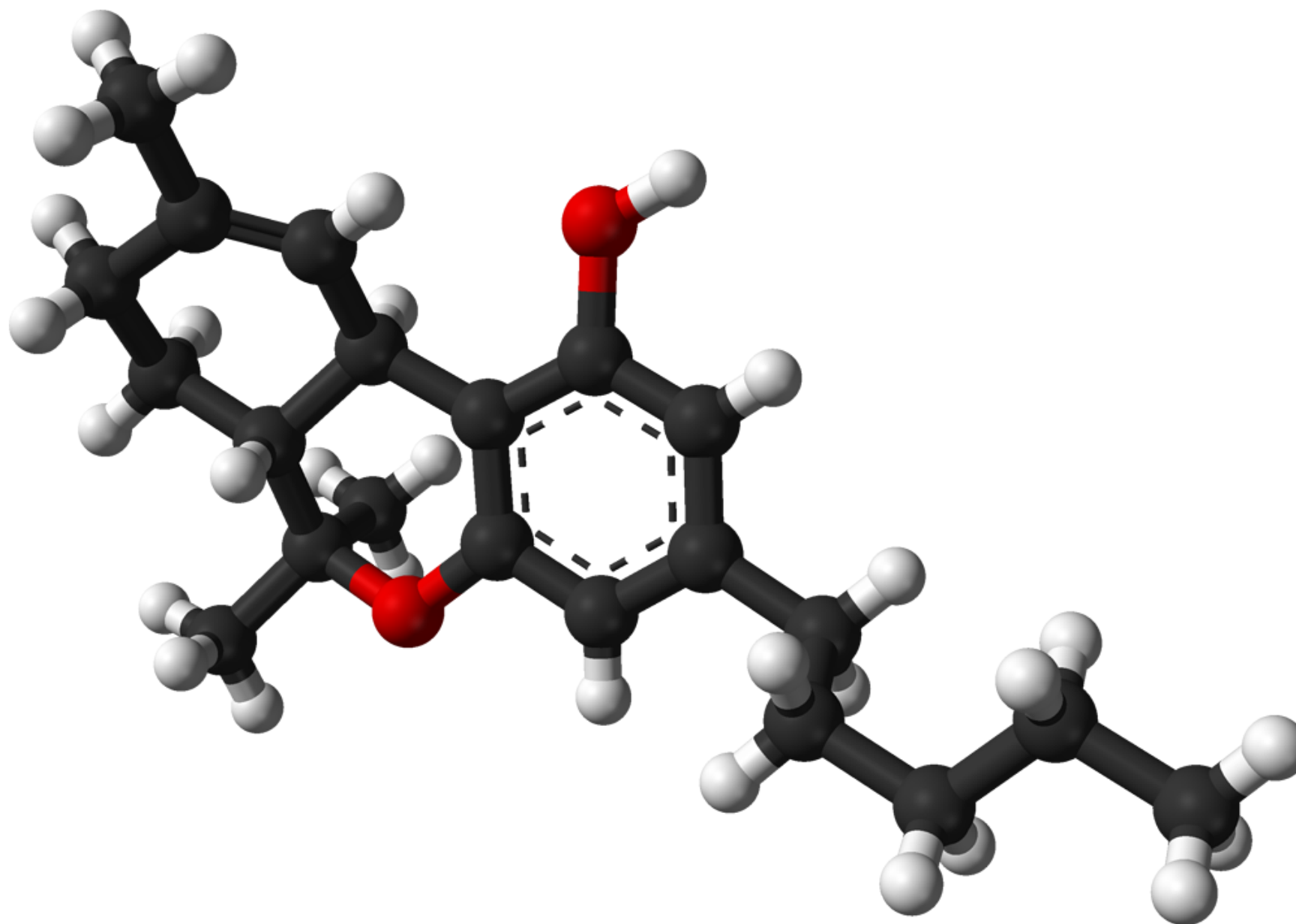
JCP 128,244302, (2008), TCA 125, 3-6, 503, (2010). CPL 494, 150 (2010)...



# Methylamine-CH<sub>3</sub>NH<sub>2</sub>

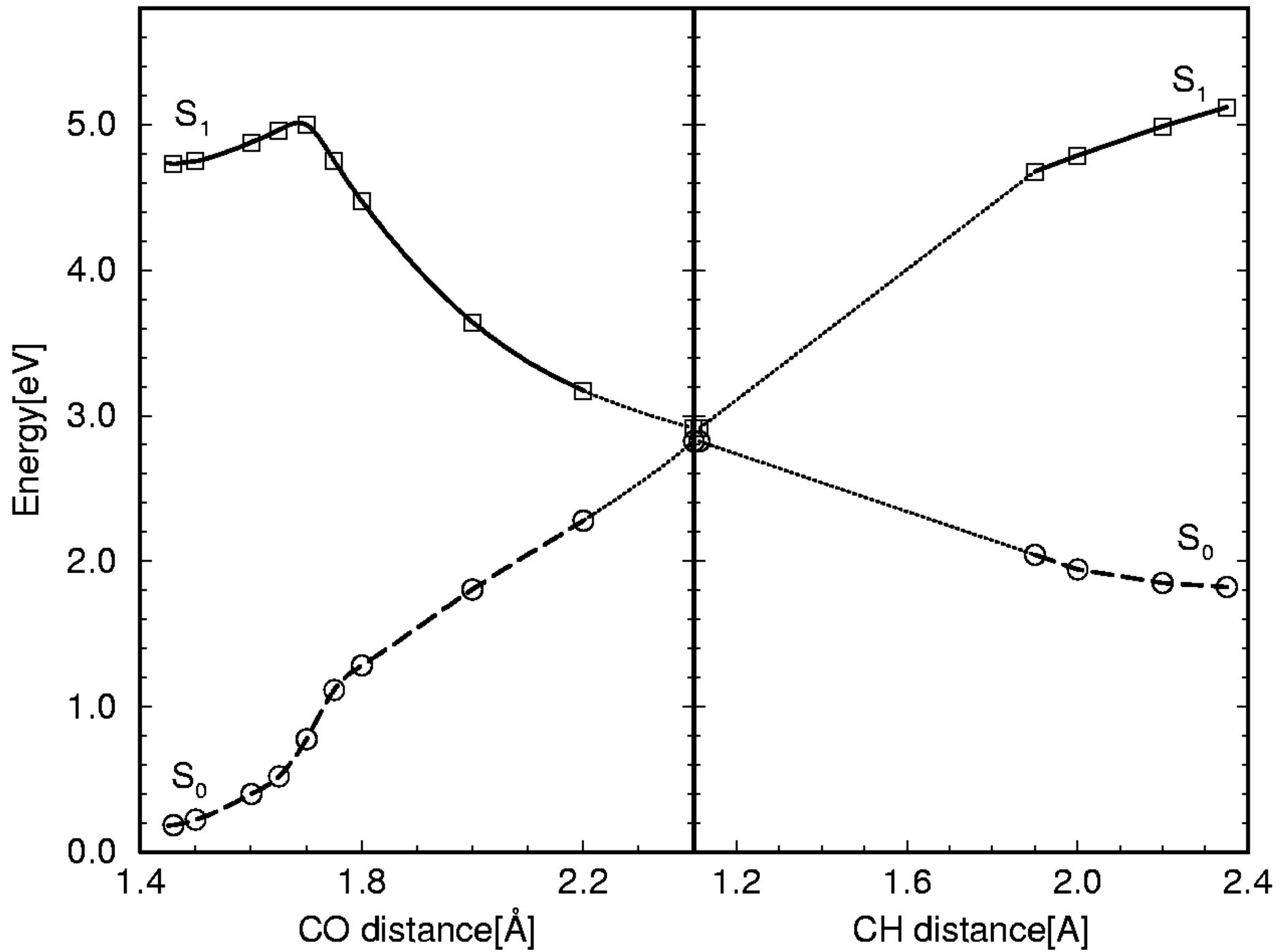


# THC-53





# THC-41



## Conical Intersections induced by light

N. Moiseyev, M. Sindelka and L.S. Cederbaum, J. Phys. B: At. Mol. Opt. Phys. 41 (2008) 221001.

M. Sindelka, N. Moiseyev and L.S. Cederbaum, <http://arxiv.org/abs/1008.0741>.

The Hamiltonian of a diatomic molecule in a linearly polarized laser wave given by formula

$$\mathbf{H}(t) = \hat{T}_{XYZ} + \hat{T}_{R,\theta,\phi} + \mathbf{H}_{el}(R) + \varepsilon_0 \cos(k_L Z) \cos(\omega_L t) \sum_j (z_j \cos \theta + x_j \sin \theta) \quad (1)$$

The  $\omega_L$  laser frequency can couple two electronic states ( $|\psi_1^e\rangle$ ,  $|\psi_2^e\rangle$ ) of the molecule by single photon excitation.

For the case of  $Na_2$  molecule ( $X^1 \Sigma_g^+$  and  $A^1 \Sigma_g^+$ ,  $\lambda = 667nm$ )

Due to symmetry, the only non-vanishing dipole matrix element responsible for light-induced electronic transitions is  $d(R) = \langle \psi_1^e | \sum_j z_j | \psi_2^e \rangle$ .

In the space of the two electronic states the Hamiltonian reduces as follows:

$$\begin{aligned}
 \mathbf{H} = & \left( -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{\mathbf{L}_{\theta\varphi}^2}{2\mu R^2} \right) \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\
 & + \begin{pmatrix} V_X(R) & (\mathcal{E}_0/2) d(R) \cos \theta \\ (\mathcal{E}_0/2) d(R) \cos \theta & V_A(R) - \hbar\omega_L \end{pmatrix} \quad (2)
 \end{aligned}$$

Let us diagonalize the potential matrix in (2) to obtain the two adiabatic (BO) PES  $V_{\pm}^{ad}(R, \theta)$ . One can obtain CI only if the two conditions  $\cos \theta = 0$ , ( $\theta = \pi/2$ ) and  $V_X(R) = V_A(R) - \hbar\omega_L$  are simultaneously fulfilled.

The laser induced CI leads to a breakdown of the B-O picture of single surface dynamics.

Let us diagonalize the potential matrix of  $\hat{H}$  in (2) and thus transform  $\hat{H}$  to the adiabatic representation:

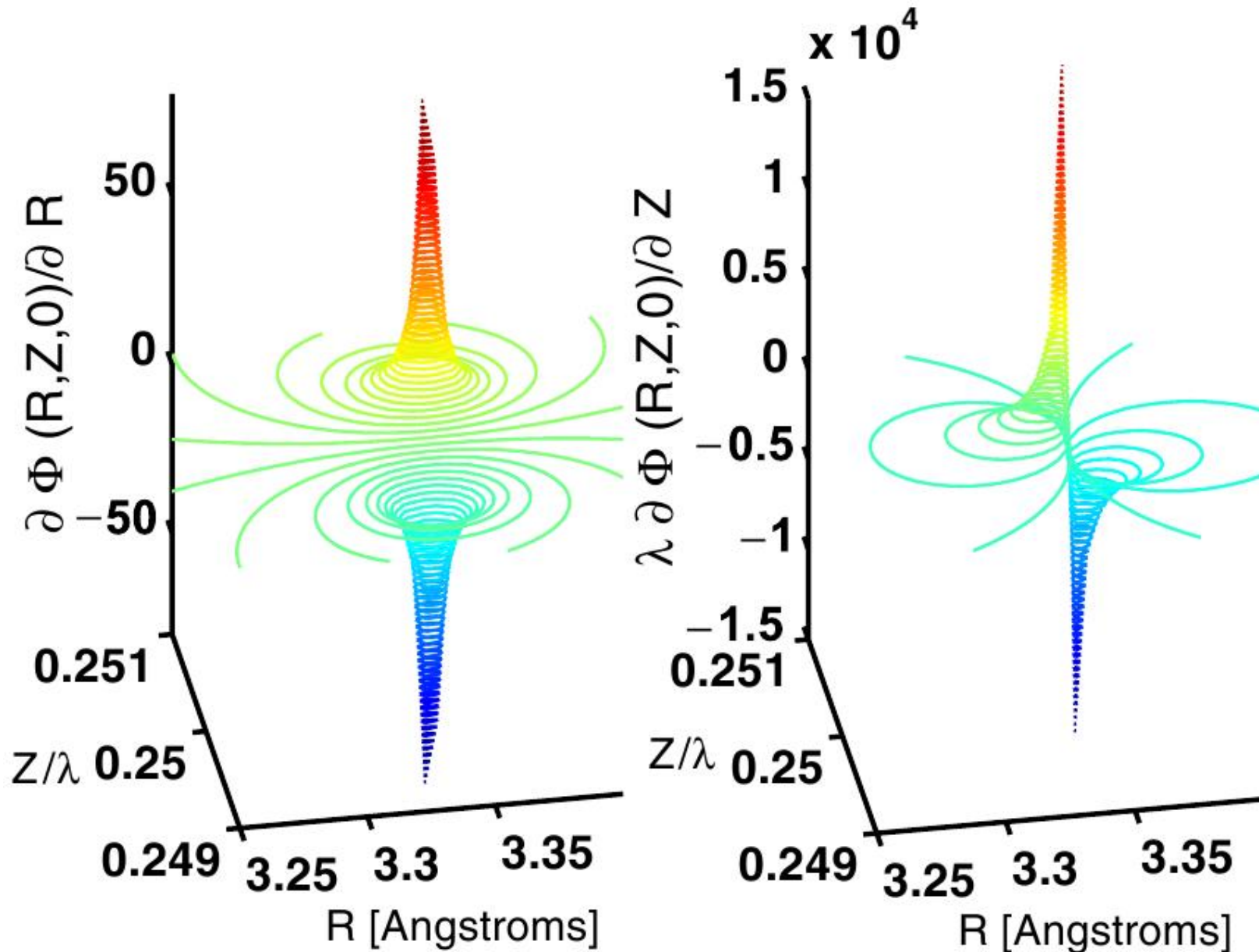
$$\hat{U}(Z, R, \theta) = \begin{pmatrix} \cos \Phi(Z, R, \theta) & \sin \Phi(Z, R, \theta) \\ -\sin \Phi(Z, R, \theta) & \cos \Phi(Z, R, \theta) \end{pmatrix} \quad (3)$$

where

$$\Phi(Z, R, \theta) = \frac{1}{2} \arctan \left( \frac{\varepsilon_0 \cos \theta \cos(k_L Z) d(R)}{E_1(R) - \hbar \omega_L - E_0(R)} \right) \quad (4)$$

In this representation  $\hat{U}\hat{H}\hat{U}^\dagger$  gives the adiabatic PES  $V_{\pm}^{ad}(R, \theta)$  and the kinetic energy operator contains the non-adiabatic couplings.

Light-induced CIs introduce infinitely strong non-adiabatic coupling.



## Summary

1. Diatomic molecules exhibit CIs which are induced by laser waves.
2. In this case the rotational and vibrational degrees of freedom provide the 2 dimensional branching space.
3. These CIs have strong impact on the molecular spectrum and could also be strong impact on other physical quantities.
4. The energetic position of this CI can be controlled by the laser frequency and the strength of its NACs by the laser intensity.
5. In polyatomic systems CIs are given by nature and induced by laser light can interplay and will lead to a wealth of new phenomena.

Thank you for your attention!