Dynamics of glycolaldehyde in cryogenic matrices

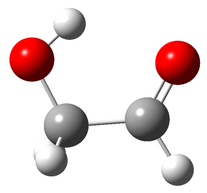
Wutharath Chin[+], Justinas Ceponkus[#], Pierre Çarçabal[+], Michèle Chevalier[+], M. Broquier[+] and C. Crépin[+]

[+] *Institut des Sciences Moléculaires d'Orsay, CNRS – Univ. Paris-Sud, Orsay, France*

[#] *Dept. of General Physics and Spectroscopy, Vilnius University, Vilnius, Lithuania*

Introduction

Aim: **Identify the relaxation pathways of Glycolaldehyde upon laser irradiation**



cis-cis conformer

Glycolaldehyde

- ❑ Possible source of OH radicals
- ❑ Product of alkenes-ozone reactions in atmosphere
- ❑ Isomer of acetic acid and methylformate, found in the interstellar medium

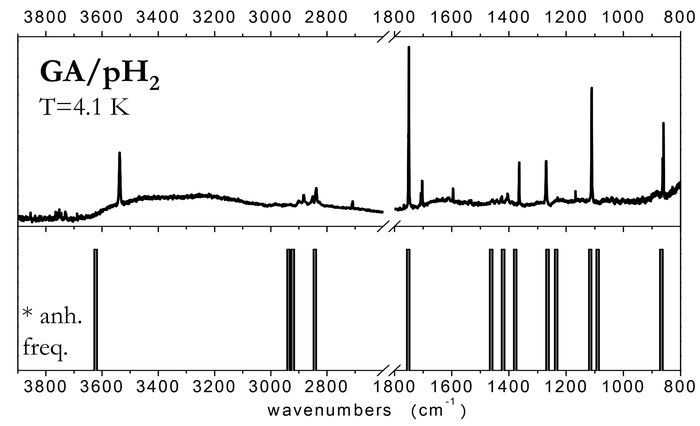
Issues

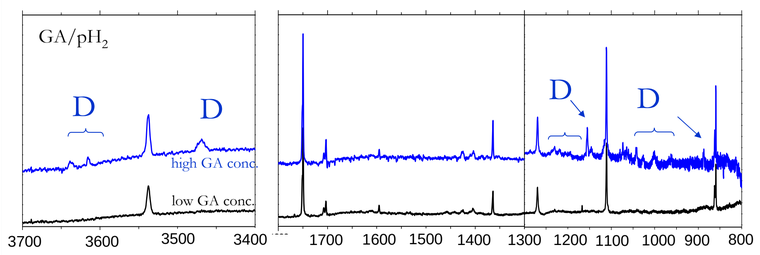
- ❑ Fragmentation vs. isomerisation
- ❑ Identify chemical routes to form complex organic species in interstellar molecular clouds [1]

Methods

Matrix isolation spectroscopy
IR and UV irradiation
Photoproducts monitored by IR spectroscopy

IR spectroscopy





* geometry optimization, anharmonic freq. MP2/6-311++G(df, pd)

GA/pH$_2$ [2]

- Ar and pH$_2$ matrices
- Only Cis-cis (Cc) conformer observed
- Reduced site effect in pH$_2$ ⇒ well isolated bands
- Anharmonic calc. ⇒ Fermi resonances (bands re-assignment)

Dimers

- Band identification
- Need calculations

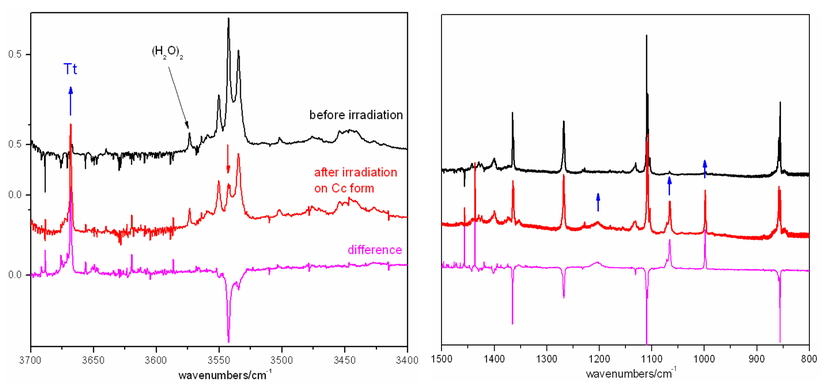
GA-H$_2$O complex

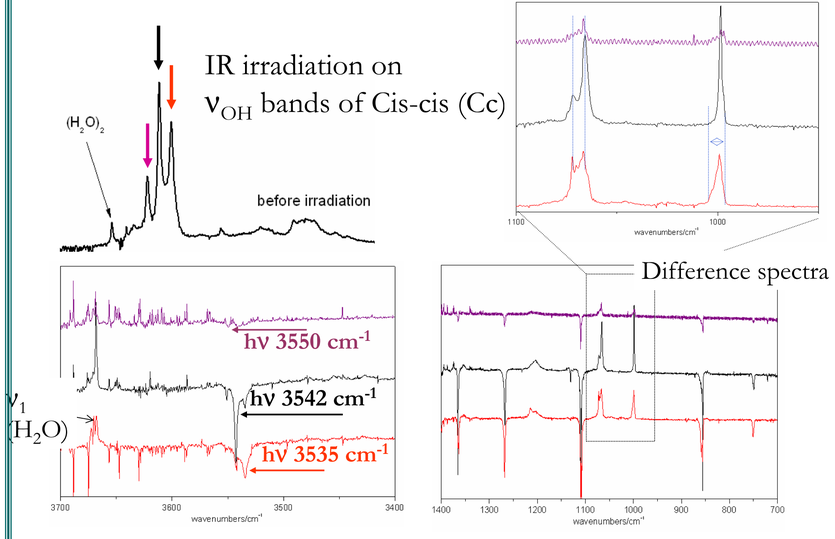
(under way)

IR irradiation GA/Ar

- ps IR OPO laser ($\Delta\nu$~2cm^{-1})
- IR selective excitation

⇒ OH stretch
⇒ different sites





✓ Isomerisation Cc ⇒ Tt [3]
✓ Tt ⇒ Cc reverse process less efficient
✓ Excitation of other vibrational modes

UV irradiation

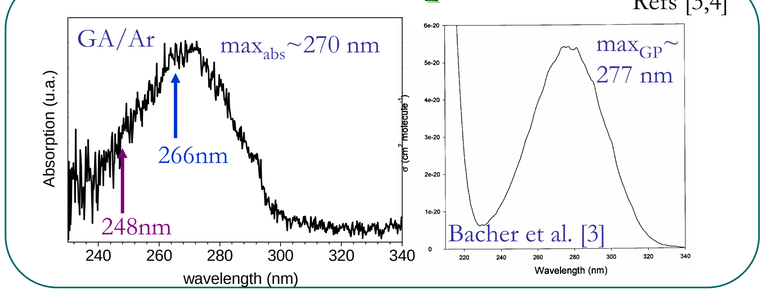
- Three excitation energies: 266, 248, 193 nm

Gas phase reaction pathways [3]:

$HOCH_2CHO + h\nu \rightarrow OH + CH_2CHO$ (1)
$\rightarrow CH_2OH + HCO$ (2)
$\rightarrow CH_3OH + CO$ (3)

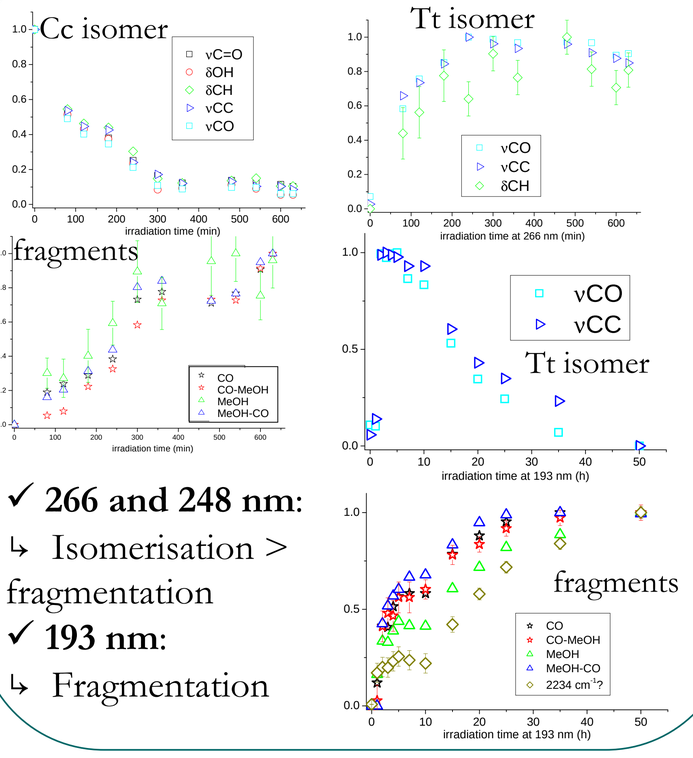
UV absorption

Refs [3,4]



Kinetics

GA/Ar



✓ **266 and 248 nm:**
↳ Isomerisation > fragmentation
✓ **193 nm:**
↳ Fragmentation

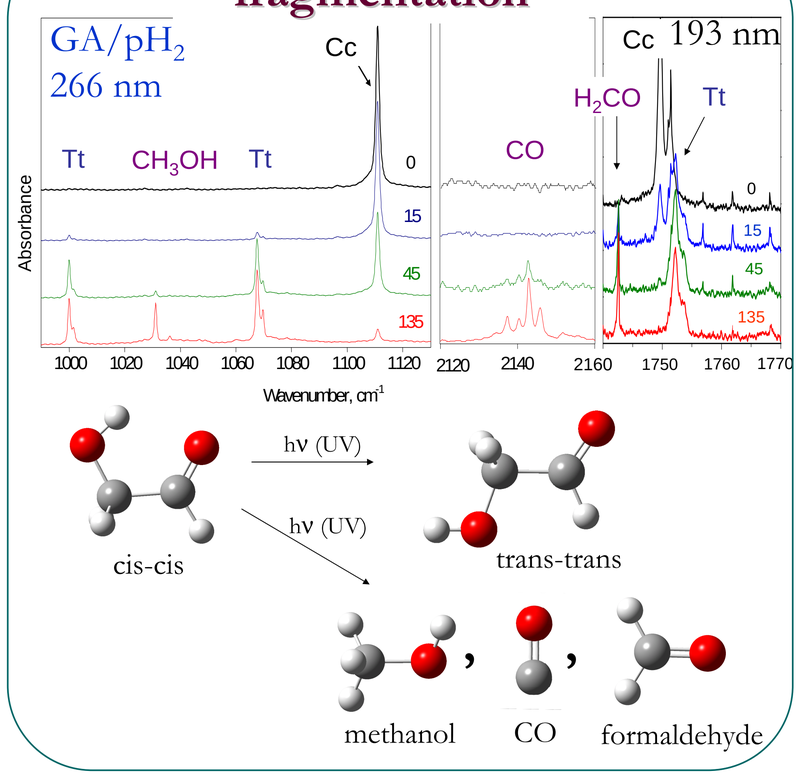
Outlooks

- ❑ Excited states calculations
- ❑ Vibrational dynamics

=> Effect of the environment (Photon echo studies)

- ❑ Different matrices (rare gas, pH$_2$, D$_2$, etc.)
- ❑ Solvation effect (dimers, H$_2$O-complexes)
- ❑ Effect of H-bonding

Isomerisation vs. fragmentation



- ❑ Isomerisation & fragmentation
- ❑ New fragments at 193 nm
- ❑ Different dissociation mechanism at 193 nm

Gas phase [3]: H$_2$CO, CO, CO$_2$, CH$_3$OH, HCOOH

Ar and pH$_2$: CO, CO-CH$_3$OH (Ar), CH$_3$OH, CH$_3$OH-CO (Ar), H$_2$CO (193 nm) + Tt conformer

- **IR & UV-induced isomerisation**
  - Two conformers observed among the four predicted [5]
  - Isomerisation Cis-cis ⇒ Trans-trans
  - Reverse process Trans-trans ⇒ Cis-cis only induced by IR
- UV irradiation
  - Competition between isomerisation and fragmentation
  - Dependence with hν$_{exc}$ => excitation of different electronic states
  - No radicals

Acknowledgements

This work benefited from the support of the French research agency; project ANR-06-BLAN-0314. The authors are thankful to André Limongi for his help in building the experimental setup.

References :

[1] C.J. Bennett and R.I. Kaiser, Ap. J. 661, 899 (2007). [2] J.Ceponkus, W. Chin, M. Chevalier, A. Limongi, M. Broquier, and C. Crépin, J.Chem. Phys. (2010) accepted. [3]C. Bacher, G. S. Tyndall, and J. J. Orlando, J. Atm. Chem. 39, 171 (2001), I. Magneron, A. Mellouki, G. Le Bras, G.K. Moortgat, A. Horowitz, J. Phys. Chem. A 109,4552 (2005) . [3] A. Aspiala, J. Murto and P. Stén. Chem. Phys. 106, 399 (1986). [4] A. Beeby, D. B. H. Mohammed, and J.R. Sodeau, J. Am. Chem. Soc. 109, 857 (1987). [5] Senent et al., J. Phys. Chem.A 108, 6286 (2004).