Vibrational relaxation of small molecules isolated in low-temperature matrices

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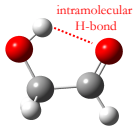
Introduction

Aim: **Determine the relaxation dynamics of small organic systems**

Glycolaldehyde [1]

- Product of alkenes-ozone reactions in atmosphere
- Isomer of acetic acid and methylformate, found in the interstellar medium



cis-cis conformer

Issues

- Vibrational dynamics
- Influence of the environment
- Effect of H-bonding ↔ Isomerisation

Methods

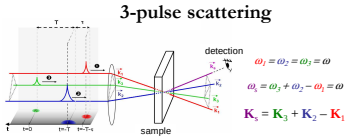
Matrix isolation spectroscopy

- Low temperatures (4-40K)
- Inert gases → less perturbations
- Isolated molecules, intrinsic properties
- Simplified spectroscopy

IR TR-DFWM techniques

- Photon echo, pump-probe
- **3-pulses photon echo**
- **→ controlled S(τ,T)**

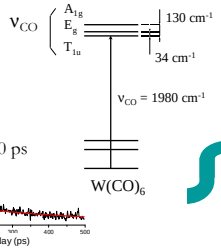
↳ IR fs-OPA (3-9 µm, 3µJ/pulse) – collaboration with Drs. B. Bourguignon and A. Ouvrard (ISMO, Orsay)

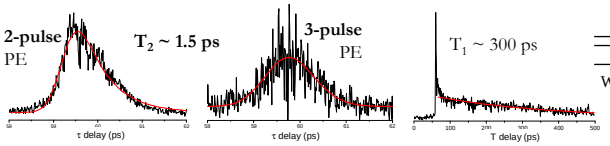


- T_2 dephasing time - S(τ), T fixed
- T_1 vibrational lifetime – S(T), τ fixed
- Preliminary tests with $W(CO)_6$ in CCl_4 and N_2 matrix
- UV irradiation for glycolaldehyde isomerisation studies (Nd:YAG @266nm)

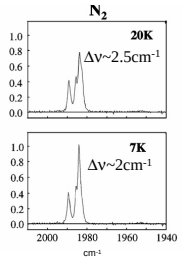
$W(CO)_6$/ 'test molecule'

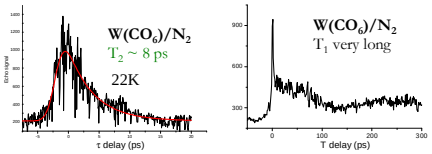
- CO stretching mode, µ ≈ 1 D
  ν_{gaz} = 1998 cm^{-1} / ν_{CCl4} = 1980 cm^{-1}
- **$W(CO)_6/CCl_4$**: Dynamics measured with a fs laser



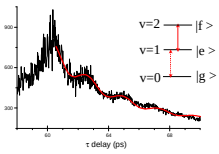


- **Ar, N_2, CH_4 matrices** [2]: ν_{mat} = 1983 cm^{-1} band structure ∝ triply degenerate T_{1u} level?
- In N_2 matrix at higher T(K)
  T_2 ~ 8ps at 22K instead of 40ps at 7K





- Oscillations observed with stimulated photon echo due to excitation of v=2 ←v=1 vibrational state ⇒ anharmonicity ~ 15 cm-1



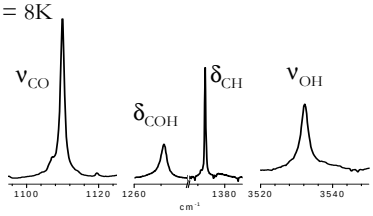
Summary $W(CO)_6$

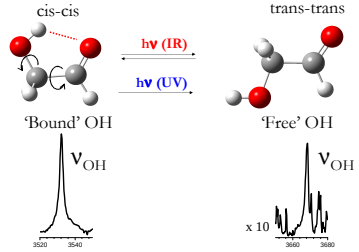
- **In CCl_4**: T_1 and T_2 measured by fs IR source ⇒ T_1 consistent with Ref [3], **T_2 = 1.5±0.5 ps** & 3-pulse PE ⇒ homogeneously broadened
- Long T_1>100 ps in matrices [2], T_1 'infinite' in N_2 at 22K
- T_2 more sensitive probe of the environment
  - CO stretch inhomogeneously broadened in Ar, CH_4 matrices
  - Homogeneous behaviour in N_2 at higher T(K) ∝ libration of N_2?
  - ↳ T_2 as a function of temperature… to be done

Glycolaldehyde

IR spectroscopy

GA/N_2
T = 8K





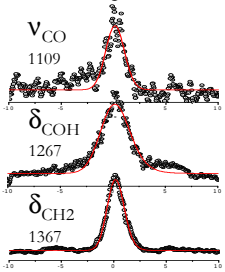
- GA isolated in matrices (Ar[4], N_2, pH_2)
- Cis-cis conformer predominant
- Trans-trans minor conformer observed

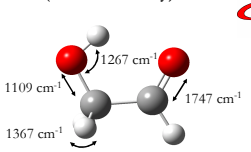
- Reduced site effect in N_2 and pH_2 ⇒ well isolated bands
- Δν ~ 1cm^{-1} even in pH_2 [5] inhomogeneous broadening?

- Different bandwidth
- ↳ **Influence of the intramolecular H-bond** on the dynamics breaking of the H-bond: cis-cis vs. trans-trans
- IR and UV-induced isomerisation

Photon echo

Preliminary results with CLIO-FEL (Orsay) – collaboration with Drs. M. Broquier and P. Çarçabal (ISMO, Orsay)





Subps dynamics (CLIO pulse)

⇒ fs measurements under way

Outlooks

- Vibrational dynamics (T_1 and T_2) of glycolaldehyde (GA) monomer under way
- Larger systems
- Effect of the environment
  - Different matrices (N_2, rare gas, pH_2)
  - Effect of H-bonding: Tt conformer, $(GA)_2$ dimers
  - Solvation effect: GA-H_2O complexes

References :

[1] C.J. Bennett, R.I. Kaiser, Ap. J. 661, 899 (2007); C. Bacher, G. S. Tyndall, J. J. Orlando, J. Atm. Chem. 39, 171 (2001). [2] A. Tokmakoff, B. Sauter, M.D. Fayer, J. Chem. Phys. 100, 9035 (1994). [3] M. Broquier, C. Crépin, H. Dubost, J-P. Galaup, Chem. Phys. 341, 207 (2007). [4] A. Aspiala, J. Murto, P. Stén. Chem. Phys. 106, 399 (1986). [5] J.Ceponkus, W. Chin, M. Chevalier, A. Limongi, M. Broquier, C. Crépin, J.Chem. Phys. 133, 094502 (2010).

Acknowledgements

The authors are thankful to Julien Vincent for his technical assistance.