Host-guest interaction in cryogenic solids probed by infrared stimulated photon echoes

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Introduction

Aim: **Probing host-guest weak interactions by means of vibrational dynamics in well-defined systems**

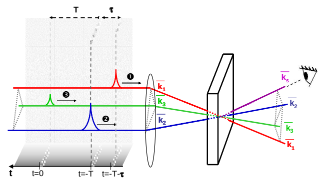
✓ Molecular vibration as a probe of local environment ✓ Environment effects – trapping sites ✓ Influence of long range interactions

Molecular systems

❑ Guest = Metal Carbonyl
Role in organometallic synthesis, catalysis, materials chemistry…[1]
✓$W(CO)_6$: rigid, large transition dipole moment, O_h symmetry
✓$Fe(CO)_5$: « fluxional » [2], D_{3h} symmetry
❑ Host = van der Waals solids
Weak perturbations, low temperatures (4-40K)
✓Noble gas: simple fcc crystal
✓Molecular lattices: N_2, CH_4

Methods

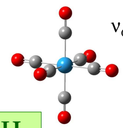
❑ Matrix isolation techniques
❑ IR spectroscopy
❑ **Time resolved IR 1C-DFWM***
Three pulse photon echoes → S(τ,T)
OPA fs IR (3 9μm, 3μJ/pulse, 1 kHz)
Pulses 150 fs. Spectral bandwidth 150 cm^{-1}
Dephasing time T_2- S(τ), T fixed
Life time T_1 – S(T), τ fixed
* One color degenerate 4-wave mixing

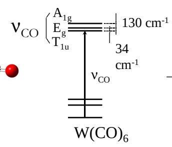


$$\gamma_{homo} = \frac{1}{\pi T_2} = \frac{1}{2\pi T_1} + \frac{1}{\pi T_2^*}$$

$W(CO)_6$

• Solution, amorphous solids: very fast dynamics (ps) [3]
• Noble gas solids: $T_2 \approx 2T_1$ [4]
• **Molecular solids: relationship between crystal properties and vibrational dynamics.**



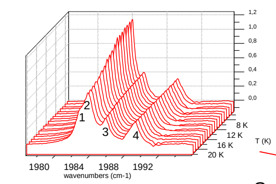


• T_{1u} CO stretching, μ ~ 1 D

	Gas	CCl_4	CH_4	N_2
νCO (cm^{-1})	1998	1980	1981	1983

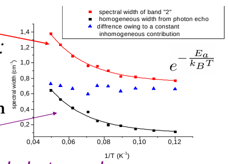
$W(CO)_6$ / N_2

Absorption



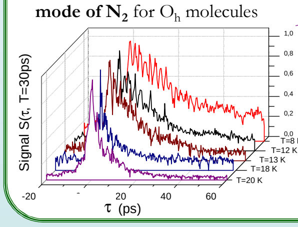
✓ **Molecular distortion**
$O_h \rightarrow D_{2h}$: $T_{1u} \rightarrow B_{1u}, B_{2u}, B_{3u}$
2 1, 3, 4

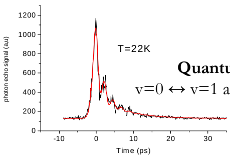
Spectral widths:



✓Narrowing of band 2 follows narrowing of the homogenous width
✓ $e^{-Ea/kT}$, Ea=32 cm^{-1} ↔ **coupling with a libration mode of N_2** for O_h molecules

Stimulated photon echoes

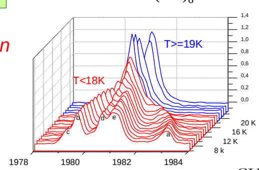




Quantum beats
v=0 ↔ v=1 and v=1 ↔ v=2

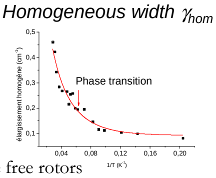
$W(CO)_6$ / CH_4

Absorption



✓ **CH_4 solid: Phase transition @ 20 K**

Homogeneous width γ_{hom}

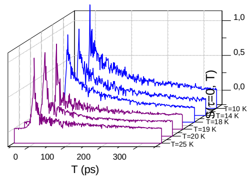


T < 20 K
• ¼ of CH_4 molecules are free rotors.
• Inhomogeneous broadening and degeneracy lift (@ 8 K T_2*~ 100ps; γ_{hom}=0.1cm^{-1})

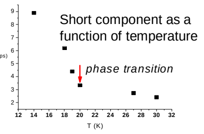
T > 20 K
• CH_4 molecules are free rotors
• Broadening nearly homogeneous (0.5 cm^{-1}) - motional line narrowing

✓ γ_{hom}(T): coupling with rotation of methane in both phases ?

Life time T_1

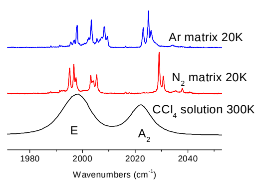


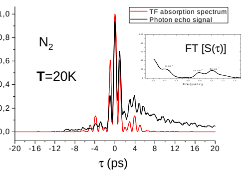
✓A short component at T>20K (~4-6 ps): orientational relaxation?
✓ Long component ≈ 300 ps

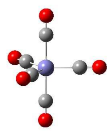


$Fe(CO)_5$

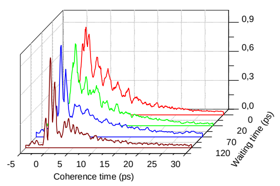
Absorption

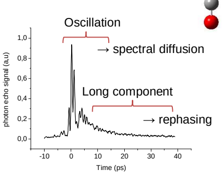






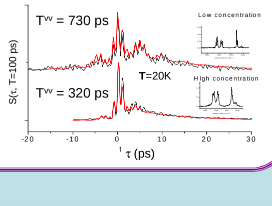
Stimulated photon echo in N_2 matrix.





✓ Influence of the waiting time T_w (population evolution) on the pattern of stimulated photon echoes S(τ, T=T_w).
↳ Spectral diffusion due to vibrational transfers [5](T^{vv} rates)
✓Concentration and temperature effects confirming transfers between different guest molecules:
T^{vv} between 300 ps and 2 ns.

Modeling of partial spectral diffusion



Matrix effects

✓ Very efficient spectral diffusion in nitrogen but not in argon.
✓ T_2= f(T_K) in N_2 [30ps @ 20K, 50 ps @ 10K], not in Ar [T_2 ≈ 70 ps]

↳ Influence of N_2 libration? Influence of N_2 lattice on μ? on fluxionality?

Summary

❑ **$W(CO)_6$** : different trapping sites → different vibrational dynamics
✓ Probe of local environment.
✓ Coupling with molecular modes of the host (libration, rotation) in contrast with the case of noble gas lattices.
✓ Complex relationship between phase transition and vibrational dynamics in solid methane.

❑ **$Fe(CO)_5$**:
✓Quantum beats between different vibrational modes due to spectral diffusion. [6]
✓Spectral diffusion due to vibrational transfers.
✓Important matrix effects.

Outlooks

❑ Toward a better understanding of $W(CO)_6$ / CH_4 => further studies in CD_4
❑ Toward a better understanding of the vibrational dynamics of $Fe(CO)_5$ in cryogenic matrices

References :
[1] G. L. Geoffroy, M.S. Wrighton, Organometallic photochemistry 1979.
[2] Y. Jiang, T. Lee, C.G. Rose-Petruck, J. Phys. Chem. A. 107, 7524 (2003), J. F. Cahoon, K.R. Sawyer, J. P. Schlegel, C.B. Harris, Science, 319, 1820 (2008)
[3] A. Tokmakoff, B. Sauter, M.D. Fayer, J. Chem. Phys. 100, 9035 (1994).
[4] M. Broquier, C. Crépin, H. Dubost, J-P. Galaup, Chem. Phys. 341, 207 (2007)
[5] M. Broquier, C. Crépin, A. Cuisset, H. Dubost, J-P. Galaup, P. Roubin, J. Chem. Phys. 118, 9582 (2003).
[6] C. Crepin, Phys. Rev. A 67 (2003) 013401.