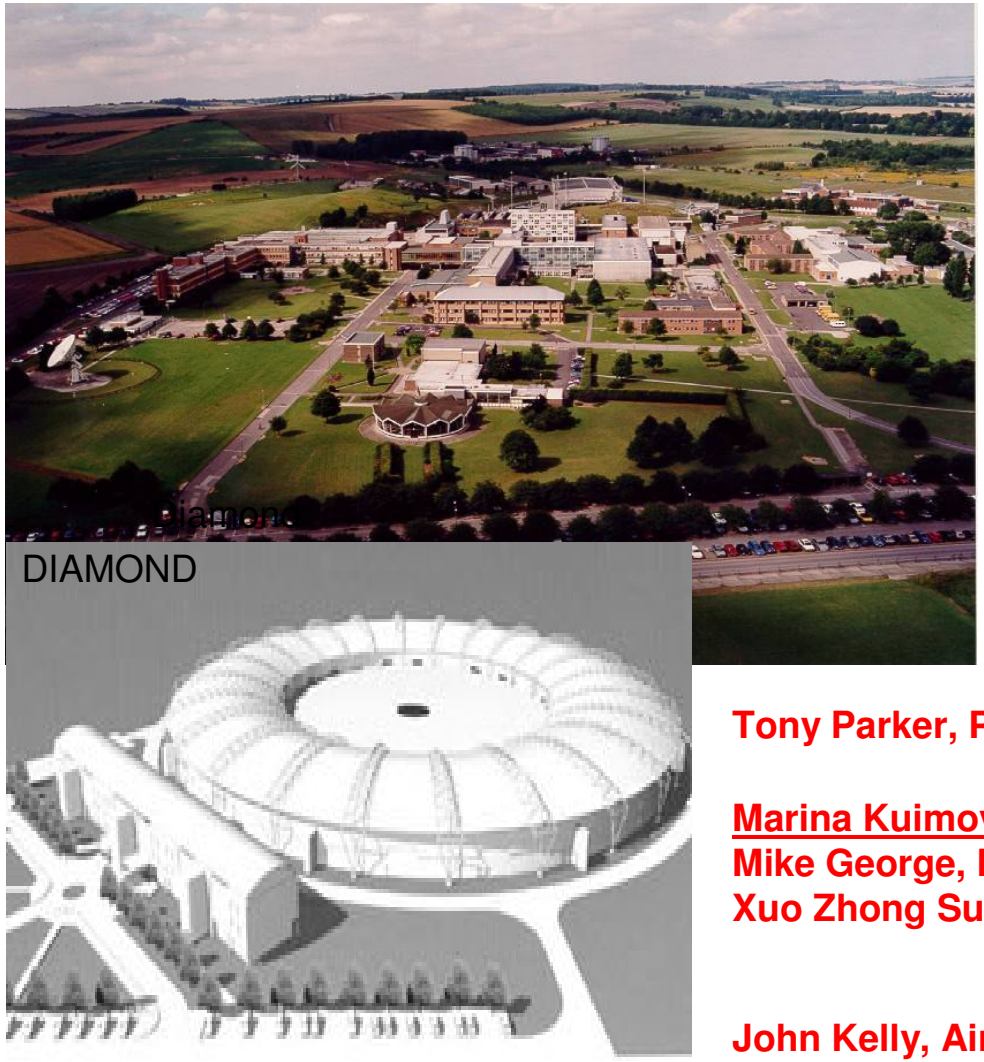
# Ultrafast deactivation of the electronic excited states of DNA bases and polynucleotides following 267 nm laser excitation explored using picosecond time-resolved infrared spectroscopy

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# UV Excitation of DNA & Components



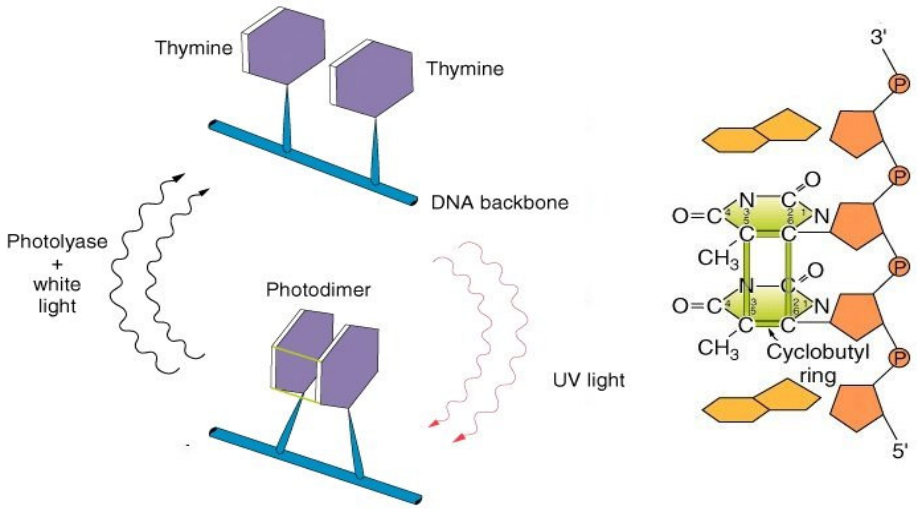
- **DNA is remarkably photostable**
- **UV excitation of singlet leads to**
  ps to sub-ps *internal conversion*
  $\Phi_f \leq 10^{-4}$

  *Low yield of potentially damaging triplets & photo-reactions*

  **Photochemical reactions**
  UVB - Pyrimidine dimers

  **Photoionisation**
  Base + hν → Base$^{\cdot+}$ + electron
  IP in solution:- 5 eV to 6 eV

- **Ultrafast Techniques**
  Transient absorption
  Fluorescence up-conversion




http://www.mun.ca/biology/scarr/Gr16-20,25.htm

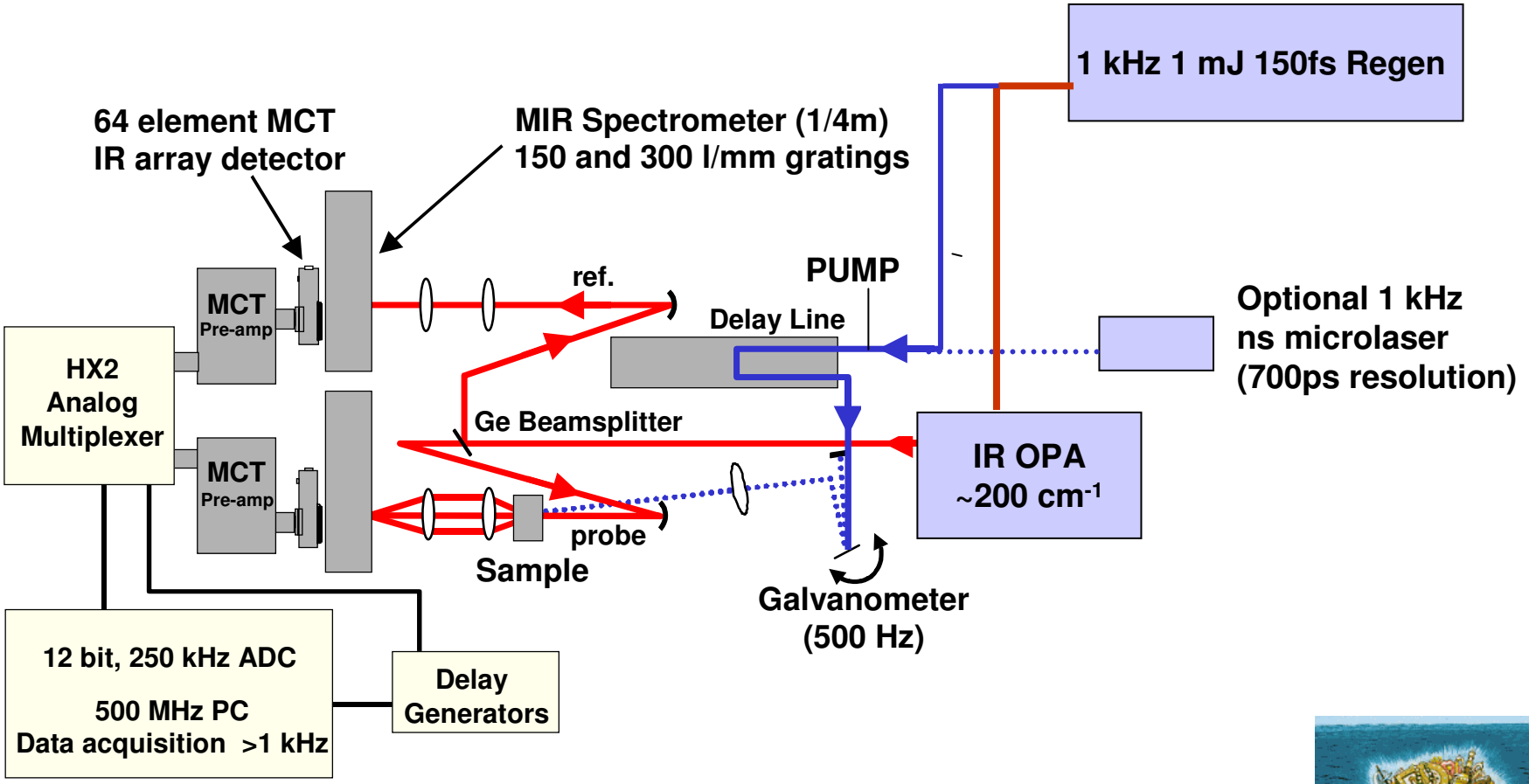
**UV induced dimerisation can induce**

**Block to transcription**
**Cell death**
**Mutation**



*Review: Kohler et al Chem Rev **2004** vol 104 p1977*

# The Broadband Pump-Probe TRIR Spectrometer



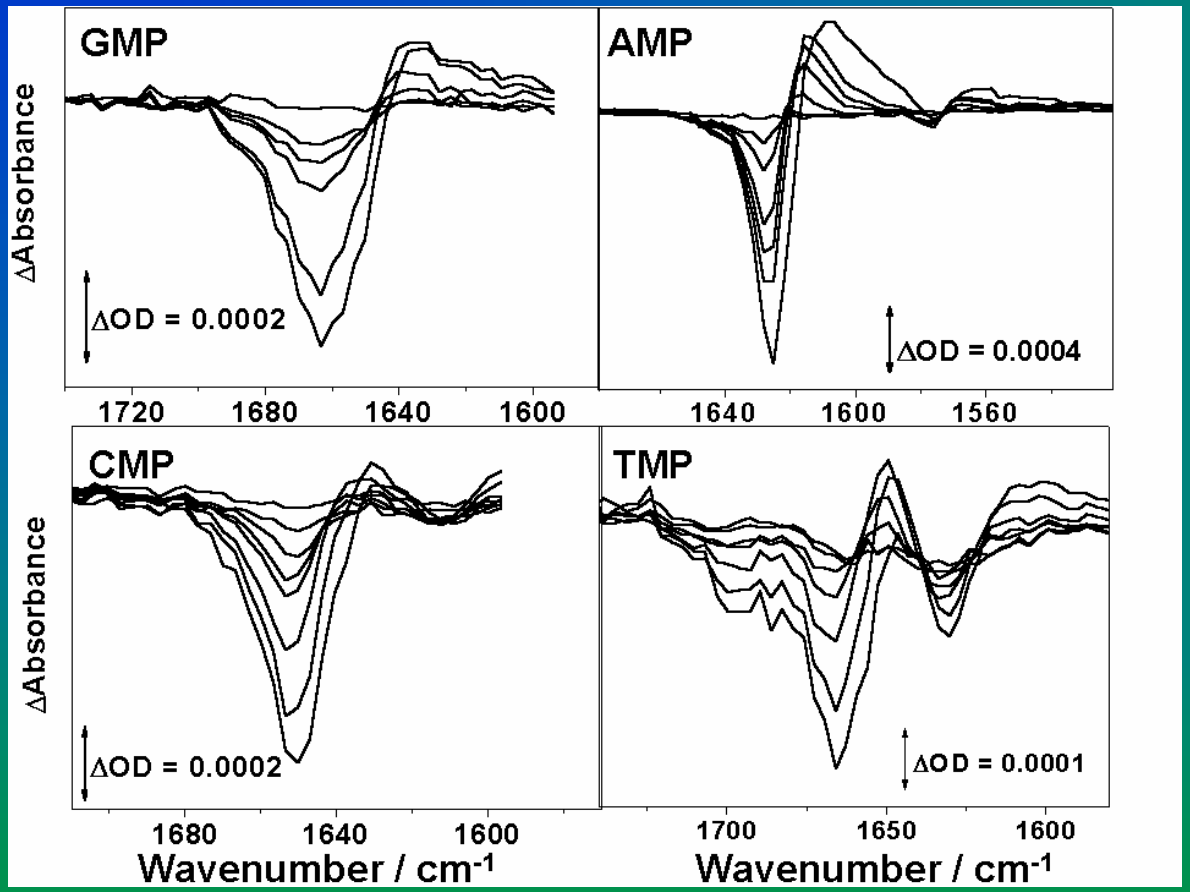

| | |
|---|---|
| SENSITIVITY | $10^{-4}$ ΔA (1 s) |
| Femtosecond time range: | 0-2 ns (< 1ps resolution) |
| Nanosecond time range: | 0-100 μS (700 ps resolution) |

CCLRC

# 267 nm pump IR probe in C=O stretch region

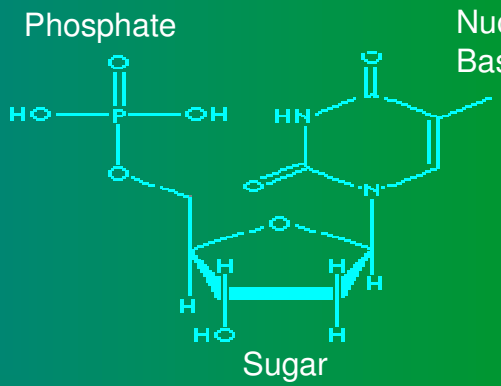


**ps-TRIR spectra (1-50 ps)**
**following 267 nm excitation**




## NUCLEOTIDES

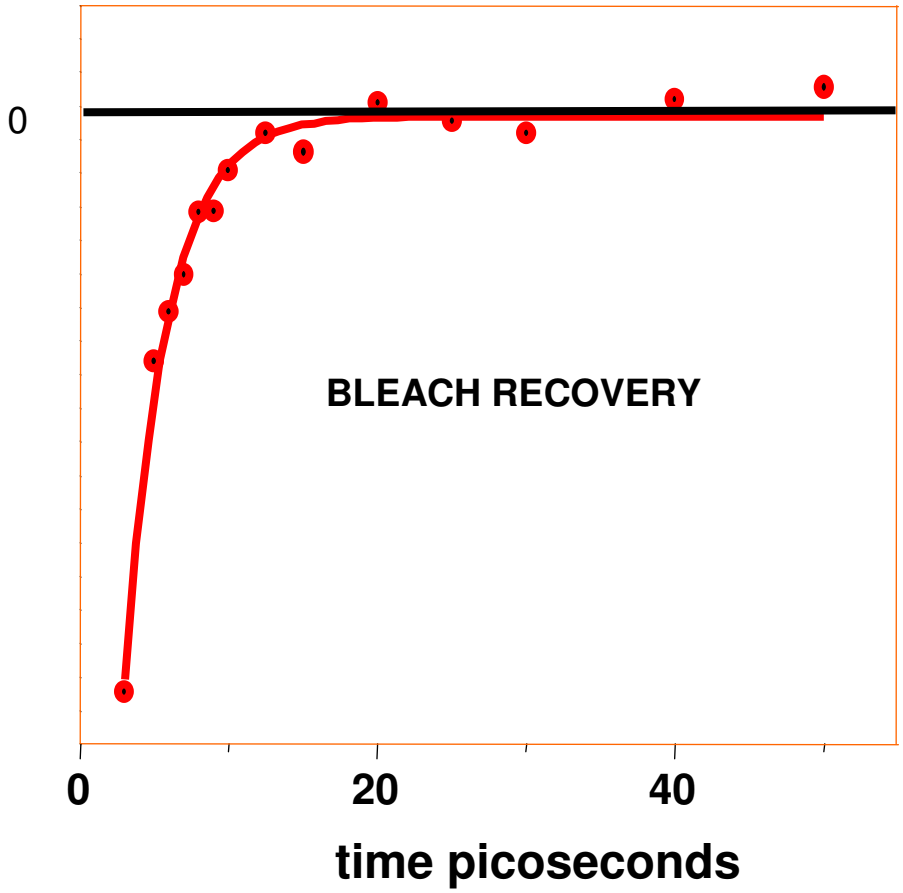
**AMP adenosine monophospate**
**TMP thymidine monophosphate**
**GMP guanosine monophosphate**
**CMP cytidine monophosphate**




TMP

**5'-nucleotides (10 mM) in 50 mM phosphate $D_2O$ buffer.**

# Kinetics – e.g. 5’ dGMP ~



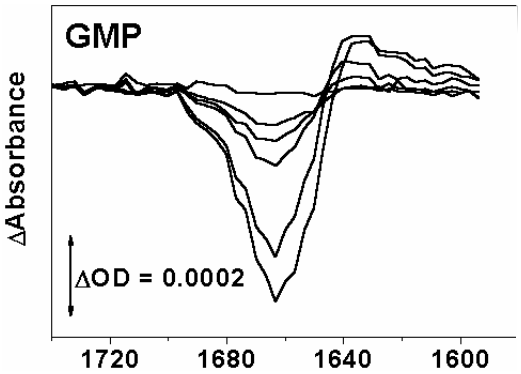

| Base | lifetime |
|---|---|
| 5’-dGMP | 2.9 (±0.2) ps |
| 5’-dCMP | 4.7 (±0. 3) ps |
| 5’-dAMP | 4.3 (±0.2) ps |
| 5’-TMP | 2.2 (±0.1) ps |

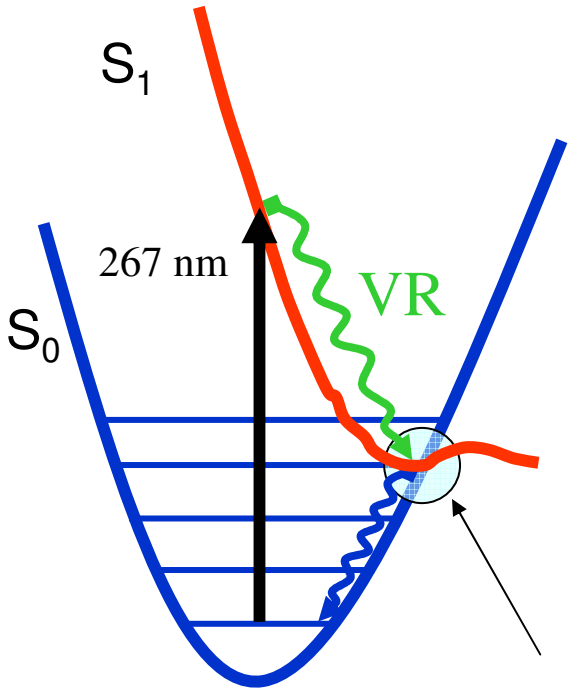
Electronic state lifetime <1ps
(see Kohler review)



*Kohler et al Chem Rev **2004** vol 104 p1977*

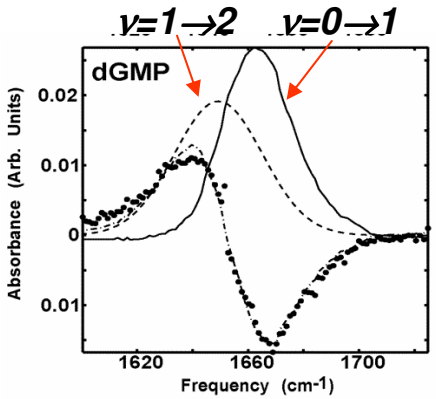
# What are the 2-5 ps dynamics?




**Martin Zanni et al**

*IR Pump-IR Probe*
*Anharmonic downshift of 10 $cm^{-1}$*




**Intramolecular Vibrational Relaxation, IVR**
*Using UV transient absorption Pecourt et al Reported ~2 ps IVR in nucleosides.*

**Cooling**:- Temperature jump ~1000K
Coupling of excited low frequency modes to the high frequency modes.

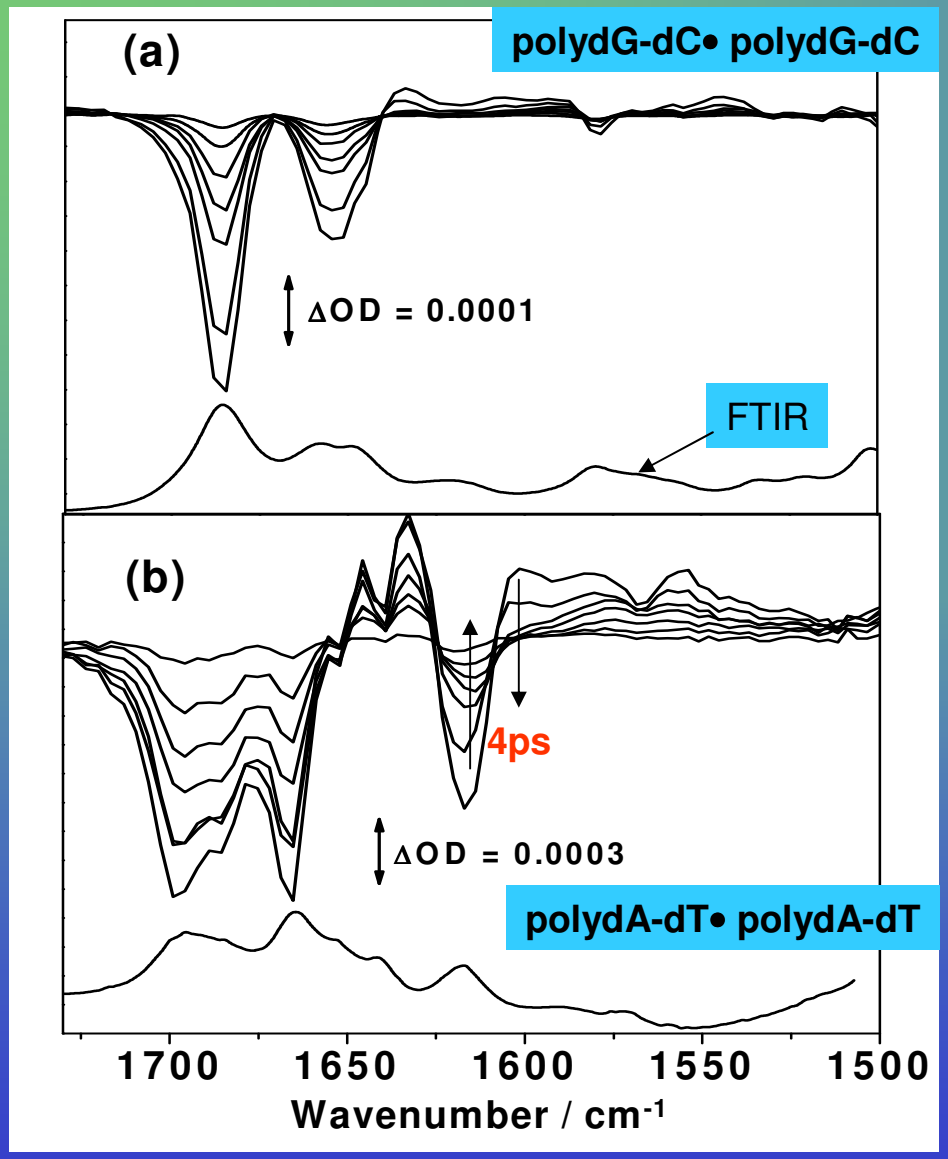
**Hydrogen Bond Breaking?** Would expect frequency upshift

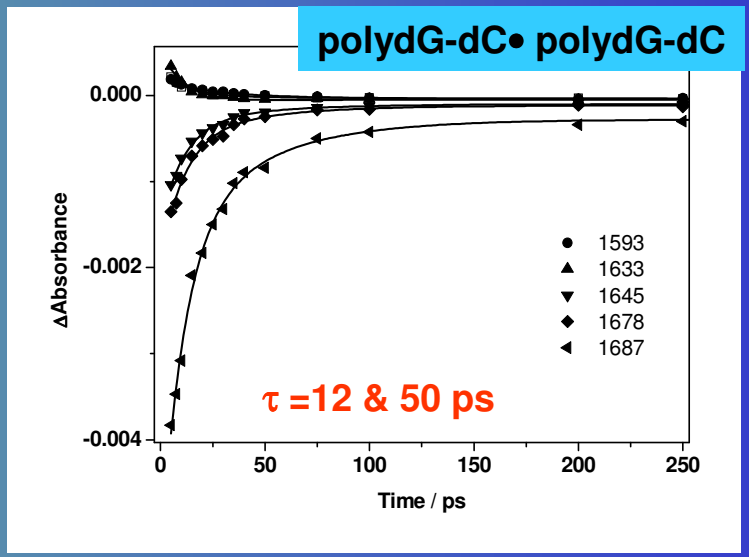
**<1 ps relaxation to ground state**

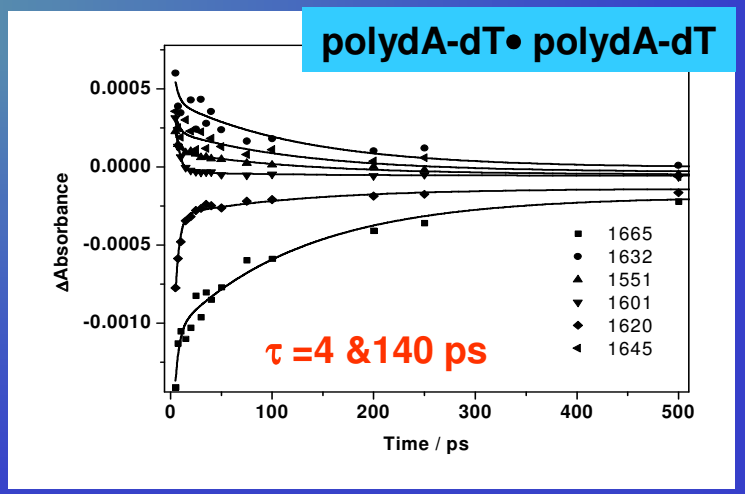
One possibility:- Internal conversion through a conical intersection involving $\pi\,\pi^*$ or dark $n\pi^*$ and $\pi\sigma^*$ states?


*A. T. Krummel, P. Mukherjee and M. Zanni, J. Phys. Chem. B., 2003, **107**, 9165.*
*J.M. Pecourt, J. Peon, B. Kohler, J. Am. Chem. Soc **123** (2001) 10370*

# UV pump IR probe (poly-strands B-form)

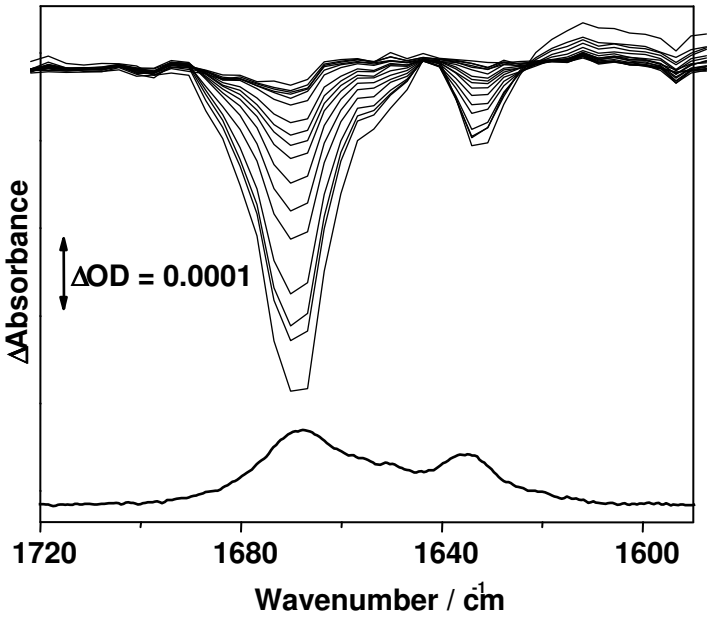


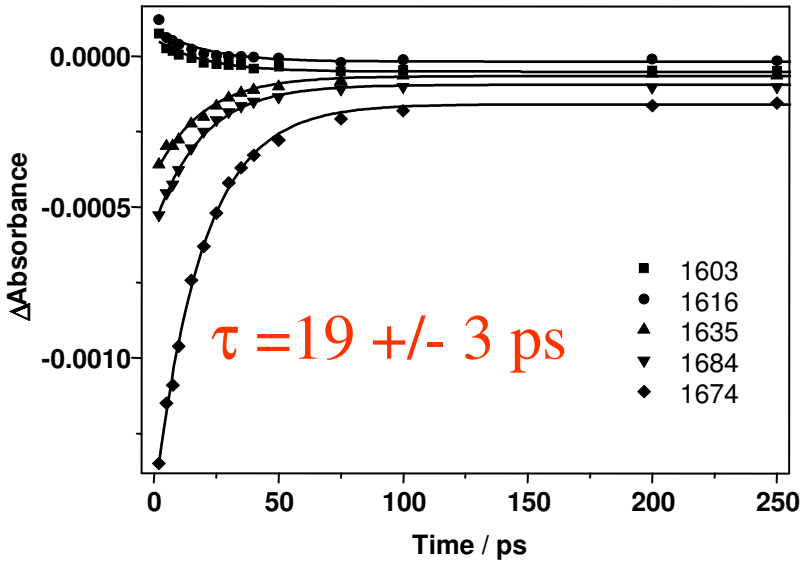




ps-TRIR spectra (1-1000 ps) obtained following 300 fs, 267 nm excitation. 50mM Phosphate Buffer

# Z-Form of polydGdC



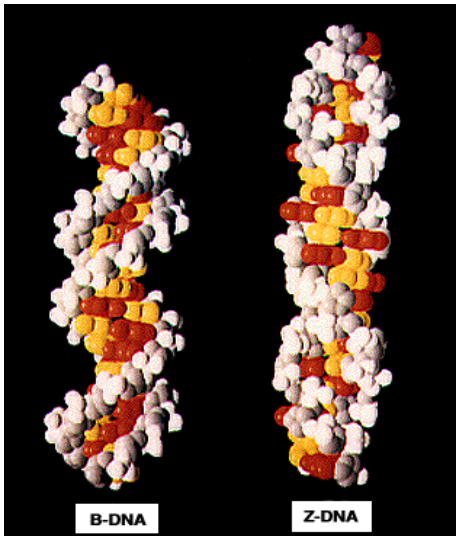



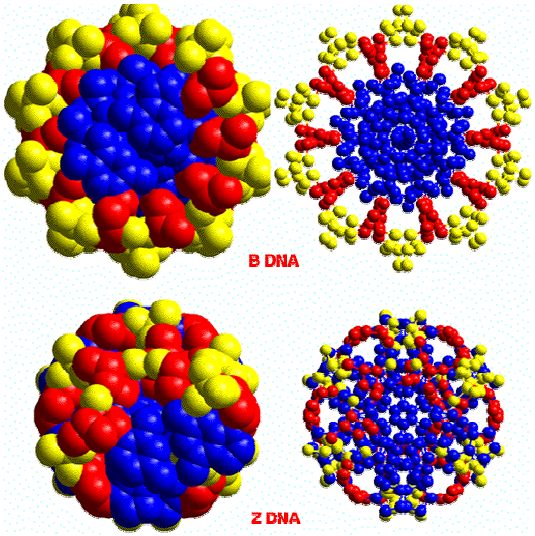

4 M NaCl

*http://www.albany.edu/~achm110/abzdna.html*
*http://www.albany.edu/~achm110/abztopview.html*

**Expect TRIR spectroscopy to report on changes in**

- Base pairing & stacking
- Tautomerism
- Hydrogen bonding
- Hydration (not like bulk water)
- Solvent Accessibility




Bases (Blue)
Sugars (Red)
Phosphates (Yellow)

# Conclusions

- Demonstrated that fs-TRIR can be used to follow ultrafast dynamics in DNA and its constituent nucleobases
- Electronic excitation leads to rapid $S_1$ to $S_0$ relaxation
  *(in agreement with other workers)*
- We have directly observed the rapid formation and decay of vibrationally hot ($S_o\nu \geq 1$) ground state nucleobases after relaxation of their electronic excited states.
- Poly nucleotide strands give complex spectra with transients living rather longer than individual bases with differing IR spectral features
- Future work will help define role of base pairing, stacking, conformation, solvent interactions and H-bonding.



*Kuimova et al Chem. Comm (2005) p1182*

# Acknowledgements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CCLRC bbsrc biotechnology and biological sciences research council