Control of ultrafast reactions in molecular clusters

Results 2001-2003

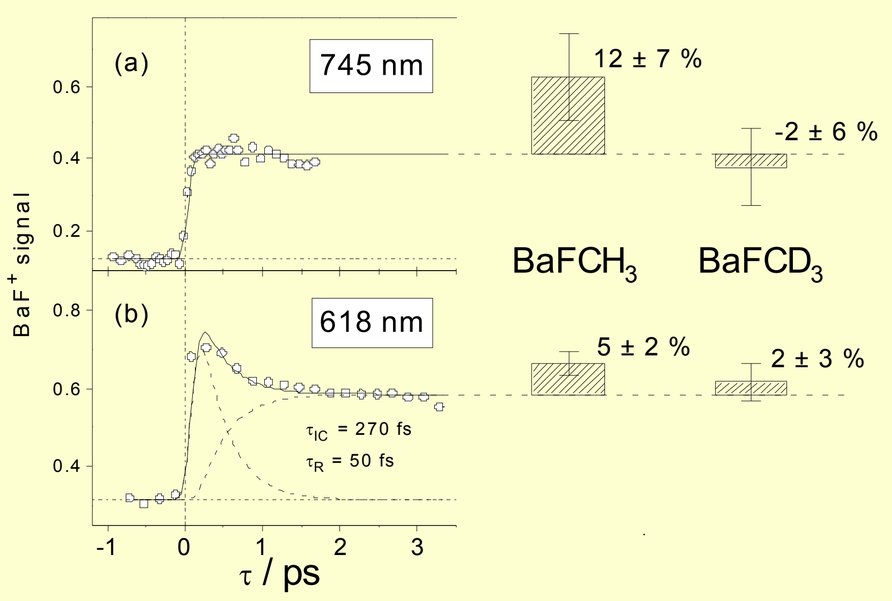
1) Control of the fragmentation of $(NH_3)_n$ clusters via the excited H-transfer state

2) Vibrational preexcitation of the intracluster harpooning reaction in $Ba...FCH_3$

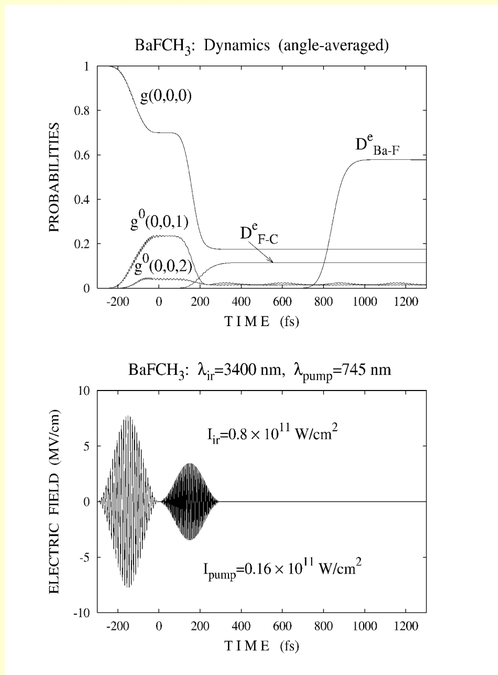
$$Ba...FCH_3\,(\tilde{X},v=0) \xrightarrow{\lambda_{IR}} Ba...FCH_3\,(\tilde{X},v) \xrightarrow{745nm} Ba...FCH_3\,(\tilde{A}',v') \longrightarrow BaF+CH_3$$

λ_{IR}=3.4μm excites the C-H but not the C-D vibrational mode

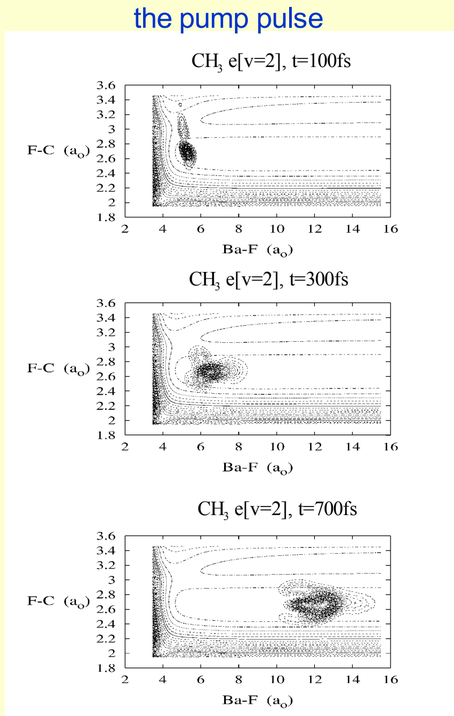
BaF product signal growth for $Ba...FCH_3$ irradiated by the 3.4μm control pulse 1ps prior to the pump pulse at 745nm (a) or 618nm (b)



Calculated time-dependent dissociation probabilities D^e (above) for IR prior pump pulse irradiation (below)



Molecular wave packet dynamics of $BaFCH_3$ at different times t after the pump pulse



Cooperation with TP C1 (Manz/Kühn/Gerber)

Future work

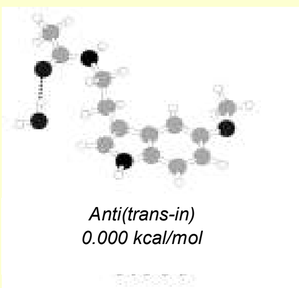
Laser-based selection of isomers of biochromophores

2) Selective preexcitation by ps laser pulses in the IR and UV/VIS region
Example: Selection of melatonin-water conformers by UV hole burning

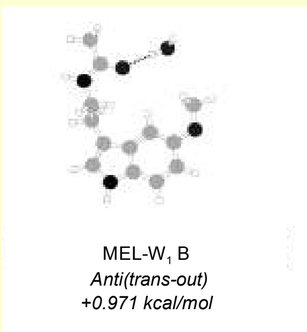
(G.M. Florio, T.S. Zwier, J. Phys. Chem. A, 107 (2003) 974)

The neural hormone melatonin is an indole derivative with a flexible peptidelike side chain that presents five distinct hydrogen-bonding sites for water.

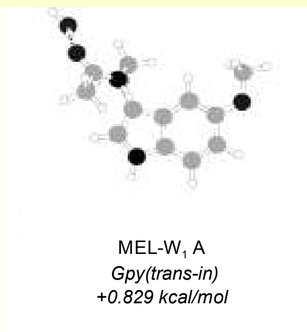
Three of 12 calculated low-energy structures for melatonin-$(H_2O)_1$ clusters corresponding to experimentally observed structures on the right.



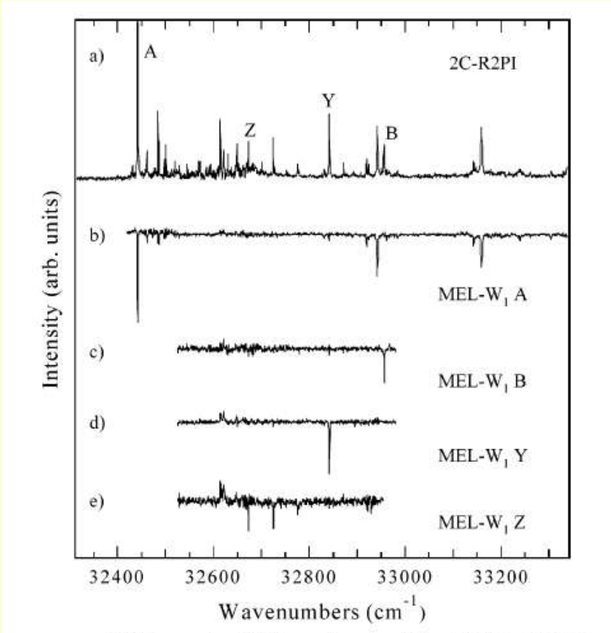
Anti(trans-in)
0.000 kcal/mol



MEL-W_1 B
Anti(trans-out)
+0.971 kcal/mol



MEL-W_1 A
Gpy(trans-in)
+0.829 kcal/mol



(a) Two-color R2PI spectrum and (b−e) UV−UV hole-burning spectra taken with the hole-burning laser tuned to the transitions labeled with the appropriate conformational label in (a). The hole-burning spectra divide the R2PI spectrum into its constituent pieces due to each of the conformations present, identifying four conformations of MEL−W_1.

2) Selection of clusters and isomers by nonadiabatic alignment

(see e.g. E. Peronne, M.D. Poulsen, C.Z. Bisgaard, H. Stapelfeldt, Phys. Rev. Lett. 91 (2003) 043003)