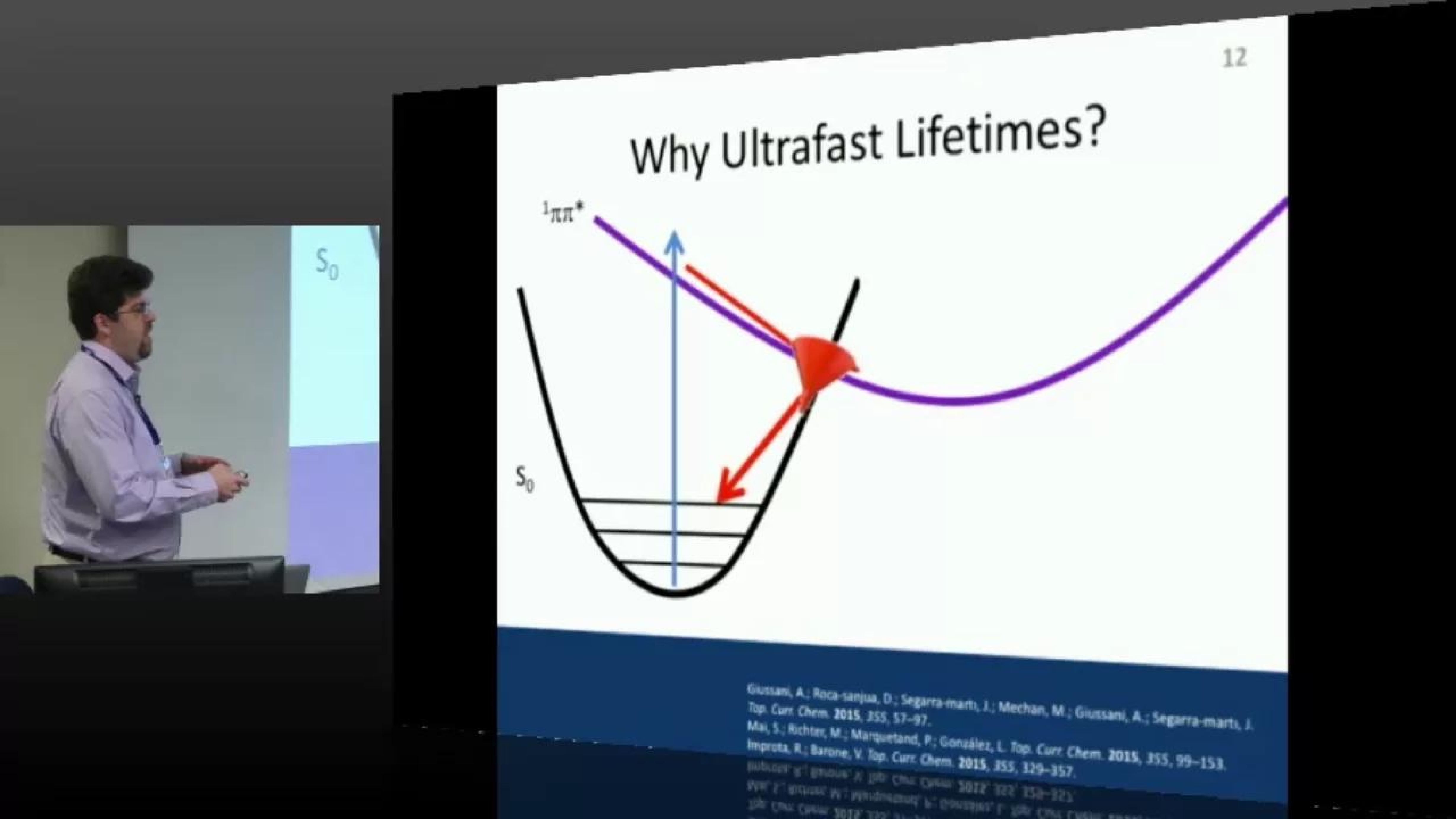

12
Why Ultrafast Lifetimes?
$^1\pi\pi^*$
S_0
S_0
Giussani, A.; Roca-sanjua, D.; Segarra-marti, J.; Mechan, M.; Giussani, A.; Segarra-marti, J.
Top. Curr. Chem. 2015, 355, 57–97.
Mai, S.; Richter, M.; Marquetand, P.; González, L. Top. Curr. Chem. 2015, 355, 99–153.
Improta, R.; Barone, V. Top. Curr. Chem. 2015, 355, 329–357.

1
00:00:12,490 --> 00:00:10,430
okay hi thanks again my name is Matthew

2
00:00:15,560 --> 00:00:12,500
bristan i'll be talking about ancestry

3
00:00:17,359 --> 00:00:15,570
nuclear bases so i'm going to completely

4
00:00:20,769 --> 00:00:17,369
change subjects and talk about physical

5
00:00:23,200 --> 00:00:20,779
chemistry so my group is interested in

6
00:00:25,370 --> 00:00:23,210
photochemistry so it's the monitoring of

7
00:00:27,529 --> 00:00:25,380
photochemical and photophysical events

8
00:00:29,150 --> 00:00:27,539
so when you think of a photo physical

9
00:00:30,830 --> 00:00:29,160
event it's the conservation of energy a

10
00:00:32,810 --> 00:00:30,840
photochemical event is the breaking of

11
00:00:36,049 --> 00:00:32,820
chemical bonds so to help illustrate

12
00:00:37,790 --> 00:00:36,059
that can I have just the Jablonski

13
00:00:39,979 --> 00:00:37,800

diagram so we have our ground state

14
00:00:41,270 --> 00:00:39,989
energy a singlet manifold and triple

15
00:00:42,530 --> 00:00:41,280
manifold when we talk about manifold

16
00:00:44,569 --> 00:00:42,540
we're talking about multiple excited

17
00:00:47,270 --> 00:00:44,579
states so what we're interested in is

18
00:00:49,490 --> 00:00:47,280
what happens after photo excitation so

19
00:00:51,680 --> 00:00:49,500
if you have a photo excitation we

20
00:00:53,779 --> 00:00:51,690
populate the singlet manifold from there

21
00:00:56,119 --> 00:00:53,789
we can have internal conversion down to

22
00:00:58,670 --> 00:00:56,129
the lowest energy singlet state once

23
00:01:01,160 --> 00:00:58,680
there the population can either emit a

24
00:01:02,420 --> 00:01:01,170
photon through fluorescence not

25
00:01:04,520 --> 00:01:02,430
immediately decay back to the ground

26
00:01:06,859 --> 00:01:04,530
state or inner system cross to the

27
00:01:08,840 --> 00:01:06,869
triple manifold again once in the trip

28
00:01:11,230 --> 00:01:08,850
manifold we can see internal conversion

29
00:01:14,679 --> 00:01:11,240
to the lowest energy triplet state and

30
00:01:16,999 --> 00:01:14,689
then we can see emission of a photon

31
00:01:18,499 --> 00:01:17,009
phosphorescent or under a big lead okay

32
00:01:21,410 --> 00:01:18,509
so it's important to note that these are

33
00:01:22,910 --> 00:01:21,420
all photophysical events okay but we

34
00:01:24,649 --> 00:01:22,920
also are interested in photochemical

35
00:01:26,570 --> 00:01:24,659
events photochemical events can occur

36
00:01:28,719 --> 00:01:26,580
from either the single manifold or the

37
00:01:31,190 --> 00:01:28,729
triple manifold the longer and the

38
00:01:32,569 --> 00:01:31,200

population stays excited obviously the

39
00:01:36,649 --> 00:01:32,579
higher the probability for a photo

40
00:01:38,719 --> 00:01:36,659
chemistry to occur also a majority of

41
00:01:41,630 --> 00:01:38,729
organic compounds when exposed to UV

42
00:01:43,069 --> 00:01:41,640
light dudu photochemistry either they

43
00:01:47,499 --> 00:01:43,079
break down and form photo products or

44
00:01:49,490 --> 00:01:47,509
they just degrade so in order to monitor

45
00:01:51,469 --> 00:01:49,500
photophysical and photochemical vents we

46
00:01:53,870 --> 00:01:51,479
use what's called transient absorption

47
00:01:57,620 --> 00:01:53,880
spectroscopy so when we think of it

48
00:01:59,300 --> 00:01:57,630
think of a uv-vis uv-vis monitors ground

49
00:02:02,380 --> 00:01:59,310
state to electronic state transitions

50
00:02:04,459 --> 00:02:02,390
what we're monitoring our electronic

51
00:02:06,200 --> 00:02:04,469
transitions to hire excited state

52
00:02:08,389 --> 00:02:06,210
transitions so in order to do that we

53
00:02:10,669 --> 00:02:08,399
use a pump probe technique so we have a

54
00:02:13,680 --> 00:02:10,679
pump pulse excite a portion of the

55
00:02:16,090 --> 00:02:13,690
population and a probe pulse is going to

56
00:02:18,250 --> 00:02:16,100
monitor the transition from one excited

57
00:02:20,580 --> 00:02:18,260
state to the other so our experiment

58
00:02:24,220 --> 00:02:20,590
begins when the pump and probe both

59
00:02:25,870 --> 00:02:24,230
aligned in space and time so what we can

60
00:02:27,970 --> 00:02:25,880
do is we can monitor this transition

61
00:02:29,470 --> 00:02:27,980
here and we can get some spectral

62
00:02:31,570 --> 00:02:29,480
information just like with the uv-vis

63
00:02:34,180 --> 00:02:31,580

but in this case we're monitoring let's

64
00:02:36,700 --> 00:02:34,190
say this transition we can also delay

65
00:02:38,470 --> 00:02:36,710
our probe pulse in time to get temporal

66
00:02:41,230 --> 00:02:38,480
information so we can monitor the

67
00:02:43,750 --> 00:02:41,240
population decaying over time and obtain

68
00:02:46,810 --> 00:02:43,760
lifetime so we can get both spatial and

69
00:02:50,860 --> 00:02:46,820
temporal information from our spectral

70
00:02:53,140 --> 00:02:50,870
data so what are they the fundamental

71
00:02:54,610 --> 00:02:53,150
questions we're trying to answer one or

72
00:02:57,250 --> 00:02:54,620
whatever may like the origins of life

73
00:03:00,550 --> 00:02:57,260
and why did nature select the nuclear

74
00:03:02,290 --> 00:03:00,560
bases of DNA and RNA so first off the

75
00:03:04,120 --> 00:03:02,300
current form of RNA is thought to come

76
00:03:07,930 --> 00:03:04,130
through a complex chemical and

77
00:03:09,850 --> 00:03:07,940
biological evolution event to understand

78
00:03:11,920 --> 00:03:09,860
the molecular origins of life you need

79
00:03:14,070 --> 00:03:11,930
to identify promising ancestor RNA

80
00:03:16,570 --> 00:03:14,080
candidates so we can no longer find

81
00:03:18,130 --> 00:03:16,580
ancestral RNA like sequestered somewhere

82
00:03:21,340 --> 00:03:18,140
on earth so essentially we have to

83
00:03:24,750 --> 00:03:21,350
actually just rediscover it or find

84
00:03:27,010 --> 00:03:24,760
plausible candidates to that effort

85
00:03:29,730 --> 00:03:27,020
california and hyde took essentially a

86
00:03:31,930 --> 00:03:29,740
bunch of molecules in this case 81 and

87
00:03:34,420 --> 00:03:31,940
pull them from the prebiotic soup and

88
00:03:36,580 --> 00:03:34,430

applied selection criteria to them one

89
00:03:38,830 --> 00:03:36,590
of them was the ability to hydrogen bond

90
00:03:41,770 --> 00:03:38,840
with the canonical nucleobases so that

91
00:03:45,070 --> 00:03:41,780
eliminated up to half the other would be

92
00:03:49,240 --> 00:03:45,080
able to show a synthetic pathway for

93
00:03:51,400 --> 00:03:49,250
sugar attachment to these ancestral

94
00:03:55,120 --> 00:03:51,410
candidates and finally being able to

95
00:03:56,650 --> 00:03:55,130
self-assemble in water so that left with

96
00:03:59,800 --> 00:03:56,660
Barbra tear-gassing we're going to

97
00:04:03,610 --> 00:03:59,810
abbreviate ba and 246 try me no

98
00:04:07,470 --> 00:04:03,620
pyrimidine abbreviated GA p so when we

99
00:04:09,699 --> 00:04:07,480
look at Barbra touareg acid and tiap

100
00:04:14,500 --> 00:04:09,709
against the canonical nucleases of

101
00:04:16,420 --> 00:04:14,510
uracil thymine guanine cytosine quantity

102
00:04:18,370 --> 00:04:16,430
and Adnan we can see some similarities

103
00:04:20,620 --> 00:04:18,380
between VA and uracil we see a

104
00:04:23,380 --> 00:04:20,630
substitution of the carboxylic at the

105
00:04:25,660 --> 00:04:23,390
sixth position where for ta p we see a

106
00:04:27,760 --> 00:04:25,670
substitution at the sixth position and

107
00:04:32,380 --> 00:04:27,770
the two position here with an amine

108
00:04:35,380 --> 00:04:32,390
group so one of the interesting

109
00:04:37,540 --> 00:04:35,390
phenomenon of the niccola basis is the

110
00:04:39,850 --> 00:04:37,550
ability to be what's called photo staple

111
00:04:42,100 --> 00:04:39,860
the idea is we can excite the

112
00:04:44,590 --> 00:04:42,110
nucleobases they can take this high

113
00:04:47,110 --> 00:04:44,600

electronic energy internally convert

114
00:04:48,640 --> 00:04:47,120
them an ultra-fast time scale back to

115
00:04:51,250 --> 00:04:48,650
the ground state and essentially stay

116
00:04:55,870 --> 00:04:51,260
relatively stable and not photo degrade

117
00:04:57,790 --> 00:04:55,880
or do photo chemistry so one of the

118
00:05:00,190 --> 00:04:57,800
important criterion that we postulate

119
00:05:02,470 --> 00:05:00,200
that was overlooked in this study was

120
00:05:05,950 --> 00:05:02,480
obviously the ability to be photo stable

121
00:05:07,900 --> 00:05:05,960
so we can see here with and without the

122
00:05:10,300 --> 00:05:07,910
ozone layer against the normalized

123
00:05:11,800 --> 00:05:10,310
absorption of RNA and DNA you see that

124
00:05:13,840 --> 00:05:11,810
even though there's a small cross

125
00:05:15,400 --> 00:05:13,850
section here we all know that if you

126
00:05:16,750 --> 00:05:15,410
stay out in the Sun long enough you're

127
00:05:18,910 --> 00:05:16,760
going to get a sunburn and then

128
00:05:21,610 --> 00:05:18,920
eventually form skin cancer so even

129
00:05:23,410 --> 00:05:21,620
though you can there's a small cross

130
00:05:25,810 --> 00:05:23,420
section here and the ozone is filtering

131
00:05:28,420 --> 00:05:25,820
out a lot of the UV radiation we can

132
00:05:30,490 --> 00:05:28,430
still you take our DNA so this is even

133
00:05:32,230 --> 00:05:30,500
more important the idea for the

134
00:05:33,490 --> 00:05:32,240
stability when you think of the

135
00:05:35,860 --> 00:05:33,500
prebiotic earth because they wouldn't

136
00:05:40,110 --> 00:05:35,870
have the protection of the ozone layer

137
00:05:42,550 --> 00:05:40,120
at the time so as I said before the

138
00:05:44,050 --> 00:05:42,560

niccola basis of the canonical

139
00:05:46,750 --> 00:05:44,060
nucleobases have been shown to have

140
00:05:51,040 --> 00:05:46,760
ultra-fast internal conversion lifetimes

141
00:05:53,800 --> 00:05:51,050
of about less than a picosecond okay so

142
00:05:54,850 --> 00:05:53,810
why is this ultra-fast so first off when

143
00:05:56,880 --> 00:05:54,860
I was talking with the debacle site

144
00:05:59,560 --> 00:05:56,890
Jablonski diagram it's a super

145
00:06:01,810 --> 00:05:59,570
simplification you have to think of it

146
00:06:03,310 --> 00:06:01,820
as a potential energy surfaces so when

147
00:06:05,350 --> 00:06:03,320
you excite from one potential energy

148
00:06:06,490 --> 00:06:05,360
surface to another you essentially

149
00:06:08,200 --> 00:06:06,500
saying according the Jablonski diagram

150
00:06:09,700 --> 00:06:08,210
you're going to follow the potential

151
00:06:12,460 --> 00:06:09,710
energy held down to a minimum then

152
00:06:13,930 --> 00:06:12,470
internally convert what X ends up

153
00:06:17,200 --> 00:06:13,940
happening for the canonical nucleobases

154
00:06:19,690 --> 00:06:17,210
is there is what's called a conical

155
00:06:22,480 --> 00:06:19,700
intersection a point where we can bypass

156
00:06:25,570 --> 00:06:22,490
this minimum and go directly to in this

157
00:06:27,790 --> 00:06:25,580
case to the ground state upon photo

158
00:06:29,950 --> 00:06:27,800
excitation in this case it gets to the

159
00:06:31,450 --> 00:06:29,960
what's called a hot ground state so it's

160
00:06:34,300 --> 00:06:31,460
essentially the ground state electronic

161
00:06:37,670 --> 00:06:34,310
state with extra vibrational energy ok

162
00:06:41,900 --> 00:06:37,680
and that eventually dissipates as heat

163
00:06:44,330 --> 00:06:41,910

so what we've learned so far we got the

164
00:06:45,650 --> 00:06:44,340
longer molecule stay excited the higher

165
00:06:48,260 --> 00:06:45,660
the probability for photochemistry to

166
00:06:50,330 --> 00:06:48,270
occur we have Nicola basis exhibit

167
00:06:53,060 --> 00:06:50,340
ultra-fast lifetimes contain conical

168
00:06:55,129 --> 00:06:53,070
intersections and photo stability is a

169
00:06:57,590 --> 00:06:55,139
definite key requirement for any

170
00:07:00,499 --> 00:06:57,600
ancestral candidate so to that effort we

171
00:07:03,219 --> 00:07:00,509
took barbituric acid and BA and I do a

172
00:07:06,140 --> 00:07:03,229
show you the day that does look better

173
00:07:11,839 --> 00:07:06,150
it's just the conversion between mac and

174
00:07:13,790 --> 00:07:11,849
pc but so we who yeah we excited at 270

175
00:07:18,890 --> 00:07:13,800
in this case so you can see here with

176
00:07:21,200 --> 00:07:18,900
giap NBA in a PBS buffer solution so

177
00:07:23,060 --> 00:07:21,210
when we did our transient sorption when

178
00:07:24,920 --> 00:07:23,070
we first did it for BA we are

179
00:07:26,990 --> 00:07:24,930
essentially populating a what's called

180
00:07:29,420 --> 00:07:27,000
the pipe icing let's say upon photo

181
00:07:33,080 --> 00:07:29,430
excitation around 500 nanometers from

182
00:07:37,100 --> 00:07:33,090
there we can see this band decrease

183
00:07:39,080 --> 00:07:37,110
about 500 disband increase at 350 we've

184
00:07:41,240 --> 00:07:39,090
assigned that to the internal conversion

185
00:07:43,909 --> 00:07:41,250
from the pipe i single state down to a

186
00:07:45,890 --> 00:07:43,919
hot vibronic Gram stain from there we

187
00:07:47,750 --> 00:07:45,900
can see that vibrant ground state this

188
00:07:51,189 --> 00:07:47,760

long absorption tale start to decay to

189
00:07:57,230 --> 00:07:51,199
essentially have no change in absorption

190
00:08:01,399 --> 00:07:57,240
for ta p we have absorption at around

191
00:08:03,500 --> 00:08:01,409
600 fun photo excitation you see the 600

192
00:08:06,800 --> 00:08:03,510
nanometer band set to decrease 300

193
00:08:09,080 --> 00:08:06,810
nanometer band increased during a very

194
00:08:10,850 --> 00:08:09,090
short time scales and so you can see

195
00:08:13,550 --> 00:08:10,860
here in this case we assigned it from a

196
00:08:15,890 --> 00:08:13,560
pipe I transition to a Empire transition

197
00:08:18,499 --> 00:08:15,900
in the singlet manifold and from there

198
00:08:20,810 --> 00:08:18,509
it would just a non radiative decay back

199
00:08:24,350 --> 00:08:20,820
to the ground state so both of these

200
00:08:27,469 --> 00:08:24,360
processes happened in for BA on a sub

201
00:08:28,879 --> 00:08:27,479
picosecond time scale and this for tha

202
00:08:32,300 --> 00:08:28,889
it took about I think of three

203
00:08:38,000 --> 00:08:32,310
picoseconds so in somewhere we can see

204
00:08:40,969 --> 00:08:38,010
here we have the kinetic traces of both

205
00:08:43,040 --> 00:08:40,979
be a and T AP we can see here with our

206
00:08:46,370 --> 00:08:43,050
time scale that's happening again an

207
00:08:49,490 --> 00:08:46,380
ultra-fast lifetime in here we can see

208
00:08:50,930 --> 00:08:49,500
it takes about roughly 20 picoseconds

209
00:08:54,710 --> 00:08:50,940
but the lifetime of that event is

210
00:08:56,330 --> 00:08:54,720
actually five as I said before ba and ta

211
00:08:59,540 --> 00:08:56,340
PA look very similar to uracil and

212
00:09:01,460 --> 00:08:59,550
cytosine since no high-level

213
00:09:04,760 --> 00:09:01,470

computational results have been done for

214
00:09:09,320 --> 00:09:04,770
be a pap we can theorize what is

215
00:09:11,420 --> 00:09:09,330
possible from the library of comical

216
00:09:13,700 --> 00:09:11,430
information from the eurozone this case

217
00:09:15,590 --> 00:09:13,710
and cytosine that have been done so they

218
00:09:18,650 --> 00:09:15,600
have shown conical intersections for

219
00:09:20,000 --> 00:09:18,660
your soul to be at what this five six

220
00:09:22,580 --> 00:09:20,010
carbon so it's an essentially an

221
00:09:24,500 --> 00:09:22,590
ethylenic twist so when you photo excite

222
00:09:26,230 --> 00:09:24,510
your uracil in this case you get this

223
00:09:28,880 --> 00:09:26,240
ethylene a twist which twists that

224
00:09:31,130 --> 00:09:28,890
torsional angle enforces the comical

225
00:09:33,470 --> 00:09:31,140
intersection so we hypothesized since

226
00:09:35,900 --> 00:09:33,480
for BA we actually don't have a double

227
00:09:39,730 --> 00:09:35,910
bond making that twist even more likely

228
00:09:43,780 --> 00:09:39,740
so it would exhibit even a faster

229
00:09:46,280 --> 00:09:43,790
lifetime then uracil does and forward

230
00:09:49,160 --> 00:09:46,290
site is in actually has a couple of

231
00:09:51,200 --> 00:09:49,170
conical intersections one out of an

232
00:09:53,720 --> 00:09:51,210
out-of-plane puckering of the amino

233
00:09:55,130 --> 00:09:53,730
group at the 4-position and an

234
00:09:57,950 --> 00:09:55,140
out-of-plane puckering at the six

235
00:10:00,980 --> 00:09:57,960
position so if you know they're similar

236
00:10:04,390 --> 00:10:00,990
analogues we can theorize that again 40

237
00:10:06,740 --> 00:10:04,400
AP it could possibly do a c4

238
00:10:08,870 --> 00:10:06,750

out-of-plane puckering to access that

239
00:10:12,920 --> 00:10:08,880
conical intersection much like cytosine

240
00:10:14,540 --> 00:10:12,930
does and i'd like to thank everyone for

241
00:10:17,540 --> 00:10:14,550
listening the National Science

242
00:10:20,060 --> 00:10:17,550
Foundation dr. Carlos crespo my advisor

243
00:10:27,060 --> 00:10:20,070
and my current group members and I'll be

244
00:10:42,059 --> 00:10:38,560
questions for Matthew just out of

245
00:10:45,519 --> 00:10:42,069
curiosity has anybody actually tried

246
00:10:48,850 --> 00:10:45,529
synthesizing DNA with these new nuclear

247
00:10:51,160 --> 00:10:48,860
bases in them and a method to my

248
00:10:54,540 --> 00:10:51,170
knowledge okay so yeah people are

249
00:10:57,999 --> 00:10:54,550
looking into the cytosines I know for

250
00:11:00,069 --> 00:10:58,009
they've been able to show like prebiotic

251
00:11:02,079 --> 00:11:00,079
synthesis so the idea is being an attack

252
00:11:04,780 --> 00:11:02,089
with the sugar group but I don't know if

253
00:11:06,400 --> 00:11:04,790
anyone's actually gone beyond like doing

254
00:11:08,769 --> 00:11:06,410
the oligomers and they trying to make

255
00:11:22,689 --> 00:11:08,779
hydrogen bonding occur like that okay

256
00:11:24,579 --> 00:11:22,699
that'd be cool yeah all right one

257
00:11:27,730 --> 00:11:24,589
comment on that last comment before I

258
00:11:30,550 --> 00:11:27,740
ask you a question we have to so this

259
00:11:32,650 --> 00:11:30,560
work is based upon work in my group the

260
00:11:35,439 --> 00:11:32,660
hut group at Georgia Tech we have done

261
00:11:38,319 --> 00:11:35,449
some substitutions into DNA and have

262
00:11:40,509 --> 00:11:38,329
shown that it still does base pair from

263
00:11:42,250 --> 00:11:40,519

there I mean it reduces it but it still

264
00:11:45,430 --> 00:11:42,260
can effectively do it so it doesn't

265
00:11:48,280 --> 00:11:45,440
completely destroy it all right now for

266
00:11:49,960 --> 00:11:48,290
you have you considered them attaching

267
00:11:53,350 --> 00:11:49,970
sugars to it and checking for their

268
00:11:55,600 --> 00:11:53,360
photostability yeah so we're a physical

269
00:11:58,180 --> 00:11:55,610
chemist group so we actually don't do

270
00:12:01,629 --> 00:11:58,190
much synthesis at all we we actually

271
00:12:03,850 --> 00:12:01,639
purchased our molecules from Sigma so if

272
00:12:06,400 --> 00:12:03,860
somebody has them if you guys make them

273
00:12:08,860 --> 00:12:06,410
we'll take a look at them oh yeah we can

274
00:12:12,340 --> 00:12:08,870
talk about it's shockingly easy to

275
00:12:14,590 --> 00:12:12,350
attach ribose to yeah right it is a very

276
00:12:16,900 --> 00:12:14,600
simple synthesis but we like I said we

277
00:12:19,780 --> 00:12:16,910
don't do it most of our lab space is all

278
00:12:22,629 --> 00:12:19,790
instrumental it's just all laser tables

279
00:12:24,340 --> 00:12:22,639
and we have a small little cramped

280
00:12:26,259 --> 00:12:24,350
workspace for wet work is that an

281
00:12:28,090 --> 00:12:26,269
experiment you'd be interested in sir