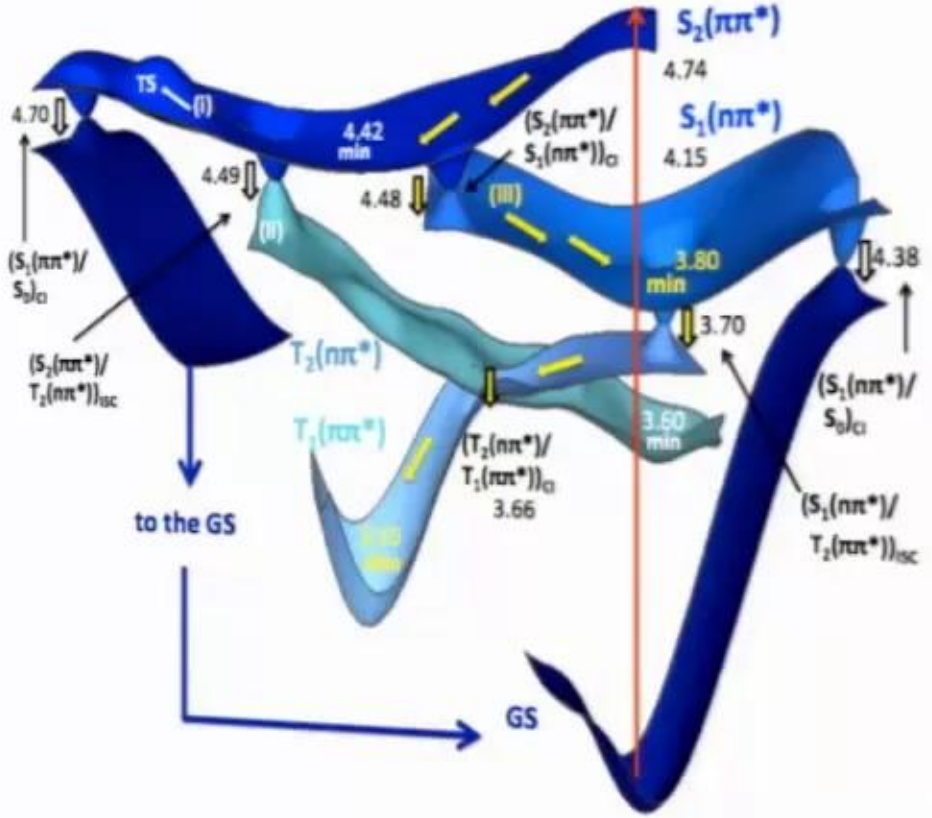
Computational Results

- Minimum energy deactivation paths calculated for purine
  - MS-CASPT2/SA3-CASSCF(16,12) level of theory



Crespo-Hernández, C. E. et. al. *J. Am. Chem. Soc.* **(2015)** 137: 4368. DOI: 10.1021/ja512536c

1
00:00:11,570 --> 00:00:09,110
yeah so today I'm going to talk I think

2
00:00:13,459 --> 00:00:11,580
Samantha touched on it a little bit

3
00:00:16,970 --> 00:00:13,469
about looking at the possibility of

4
00:00:22,609 --> 00:00:16,980
non-canonical DNA bases and evolution of

5
00:00:27,980 --> 00:00:22,619
databases so the harsh UV radiation that

6
00:00:29,660 --> 00:00:27,990
I mentioned is a possible because right

7
00:00:32,560 --> 00:00:29,670
now on earth we are protected from

8
00:00:34,970 --> 00:00:32,570
harsher UV radiation by the ozone layer

9
00:00:38,150 --> 00:00:34,980
reflecting and absorbing some of it and

10
00:00:41,540 --> 00:00:38,160
so in pre Vatican II for the ozone

11
00:00:44,389 --> 00:00:41,550
formation and also in extraterrestrial

12
00:00:48,260 --> 00:00:44,399
situations we would have much more of

13
00:00:53,330 --> 00:00:48,270

this harmful UVA UVB UVC wavelengths

14
00:00:55,430 --> 00:00:53,340
which could shape this evolution so this

15
00:00:59,510 --> 00:00:55,440
is important because the all of the

16
00:01:02,750 --> 00:00:59,520
canonical DNA bases absorb in this UVB

17
00:01:05,179 --> 00:01:02,760
UVC region where we have where we're

18
00:01:09,289 --> 00:01:05,189
essentially protected by the ozone layer

19
00:01:14,840 --> 00:01:09,299
but under solar irradiance we are would

20
00:01:17,120 --> 00:01:14,850
not be so we decided to focus in this

21
00:01:20,590 --> 00:01:17,130
study on the purina family of

22
00:01:25,160 --> 00:01:20,600
nucleobases specifically adenine guanine

23
00:01:29,840 --> 00:01:25,170
and these two bases are shown to be very

24
00:01:32,149 --> 00:01:29,850
photo stable so if you shine a UV light

25
00:01:35,210 --> 00:01:32,159
on them they have mechanisms to get rid

26
00:01:37,580 --> 00:01:35,220
of those that energy within hundreds of

27
00:01:41,330 --> 00:01:37,590
femtoseconds and they go back down to

28
00:01:43,700 --> 00:01:41,340
the ground state very efficiently so

29
00:01:46,460 --> 00:01:43,710
they don't populate long-lived triplet

30
00:01:48,789 --> 00:01:46,470
excited states and they go back to the

31
00:01:52,249 --> 00:01:48,799
ground state but the question that

32
00:01:54,499 --> 00:01:52,259
arises is that ah these have different

33
00:01:57,020 --> 00:01:54,509
structures but they're fairly similar

34
00:02:00,380 --> 00:01:57,030
would this be the case for all other

35
00:02:02,060 --> 00:02:00,390
types of purine derivatives so other

36
00:02:05,929 --> 00:02:02,070
works that have been done in the past

37
00:02:08,600 --> 00:02:05,939
our derivative of guanine hypo xanthine

38
00:02:10,580 --> 00:02:08,610

which I it also has been observed to

39
00:02:13,520 --> 00:02:10,590
ultra-fast inter system cross back to

40
00:02:15,620 --> 00:02:13,530
the ground state um however

41
00:02:17,780 --> 00:02:15,630
just as we saw in the last talk this

42
00:02:20,960 --> 00:02:17,790
derivative of adenine and I guess of

43
00:02:24,170 --> 00:02:20,970
guanine as well is actually fluorescent

44
00:02:26,290 --> 00:02:24,180
and also it is able to populate a

45
00:02:28,130 --> 00:02:26,300
long-lived reactive triplet state

46
00:02:32,600 --> 00:02:28,140
depending on its environmental

47
00:02:35,620 --> 00:02:32,610
conditions so this shows that it's not

48
00:02:38,059 --> 00:02:35,630
definitely all the purine bases that

49
00:02:40,580 --> 00:02:38,069
ultra-fast inter system cross get rid of

50
00:02:42,530 --> 00:02:40,590
that get rid of that energy on an

51
00:02:47,090 --> 00:02:42,540
ultra-fast timescale so then the

52
00:02:51,350 --> 00:02:47,100
question that arises is um is it due to

53
00:02:53,960 --> 00:02:51,360
this purine core or is it the specific

54
00:02:58,300 --> 00:02:53,970
substituent on the peering core that are

55
00:03:01,820 --> 00:02:58,310
moderating this excited state activity

56
00:03:04,400 --> 00:03:01,830
so to begin looking at the purine itself

57
00:03:07,670 --> 00:03:04,410
we looked at the steady state the just

58
00:03:09,530 --> 00:03:07,680
the absorption of the base itself and we

59
00:03:13,520 --> 00:03:09,540
see that just like the natural bases

60
00:03:15,860 --> 00:03:13,530
adenine and guanine it has a absorption

61
00:03:17,930 --> 00:03:15,870
in the UV be around 260 and then a

62
00:03:19,910 --> 00:03:17,940
higher energy stronger absorption and

63
00:03:23,270 --> 00:03:19,920

then a tail going out to about three

64
00:03:25,490 --> 00:03:23,280
hundred and ten nanometers then we

65
00:03:28,400 --> 00:03:25,500
looked at its fluorescence and we see

66
00:03:30,860 --> 00:03:28,410
that like the natural canonical basis it

67
00:03:32,600 --> 00:03:30,870
has very very low fluorescence quantum

68
00:03:36,830 --> 00:03:32,610
yields of 10 to the negative third so

69
00:03:39,280 --> 00:03:36,840
essentially zero fluorescence so this

70
00:03:42,530 --> 00:03:39,290
directly matches with the purine and

71
00:03:44,960 --> 00:03:42,540
derivatives ending and guanine but we

72
00:03:48,620 --> 00:03:44,970
want to know does it ultra-fast inter

73
00:03:52,009 --> 00:03:48,630
system across like those two bases so to

74
00:03:54,560 --> 00:03:52,019
do that we use our pump probe transient

75
00:03:56,960 --> 00:03:54,570
absorption spectroscopy where we use one

76
00:03:59,840 --> 00:03:56,970
laser pulse to pump our sample and send

77
00:04:02,840 --> 00:03:59,850
it to an excited state and then we use a

78
00:04:05,300 --> 00:04:02,850
second pulse at a certain time delay to

79
00:04:07,910 --> 00:04:05,310
look at changes in that excited state

80
00:04:11,330 --> 00:04:07,920
and we detect changes in the absorption

81
00:04:15,229 --> 00:04:11,340
of the sample and we see the change in

82
00:04:17,300 --> 00:04:15,239
absorbance so this is the typical type

83
00:04:20,150 --> 00:04:17,310
of data that we get is a contour plot

84
00:04:23,600 --> 00:04:20,160
where we're seeing a wavelength down the

85
00:04:25,990 --> 00:04:23,610
X here time on the Y and then absorption

86
00:04:29,410 --> 00:04:26,000
intensity as the color with red

87
00:04:32,230 --> 00:04:29,420
the highest so we can see as when we

88
00:04:34,060 --> 00:04:32,240

pump the sample its instantaneously goes

89
00:04:36,460 --> 00:04:34,070
to the excited state so at time zero

90
00:04:39,520 --> 00:04:36,470
we're seeing these signals of excited

91
00:04:42,040 --> 00:04:39,530
state absorption already and this from

92
00:04:44,110 --> 00:04:42,050
this type of contour plot we can extract

93
00:04:47,020 --> 00:04:44,120
kinetic information and then also

94
00:04:49,780 --> 00:04:47,030
spectral information by looking at

95
00:04:54,580 --> 00:04:49,790
either slices in the wavelength regime

96
00:04:57,490 --> 00:04:54,590
or slices in time so these are examples

97
00:04:59,950 --> 00:04:57,500
taken from that contour plot of the type

98
00:05:02,230 --> 00:04:59,960
of kinetic information we get em in

99
00:05:04,930 --> 00:05:02,240
traces or spectral information that we

100
00:05:07,720 --> 00:05:04,940
can see so if we first look at the

101
00:05:12,010 --> 00:05:07,730
kinetic information and we compare it to

102
00:05:15,850 --> 00:05:12,020
the natural adenine base the purine core

103
00:05:18,970 --> 00:05:15,860
does not go back down to the ground

104
00:05:21,610 --> 00:05:18,980
state immediately and in fact in this

105
00:05:24,909 --> 00:05:21,620
timescale we looked out to three nano

106
00:05:26,320 --> 00:05:24,919
seconds with our setup and we can see

107
00:05:29,170 --> 00:05:26,330
that we're actually beginning to

108
00:05:31,120 --> 00:05:29,180
populate even longer lived excited

109
00:05:34,030 --> 00:05:31,130
states at the end here that will go on

110
00:05:38,080 --> 00:05:34,040
for longer and longer time so these

111
00:05:40,480 --> 00:05:38,090
purina excited States live for at least

112
00:05:43,780 --> 00:05:40,490
four orders of magnitude longer than the

113
00:05:46,530 --> 00:05:43,790

natural adenine and guanine basis so

114
00:05:51,969 --> 00:05:46,540
that could be very potentially harmful

115
00:05:54,940 --> 00:05:51,979
for the purine core so to get an idea of

116
00:05:57,909 --> 00:05:54,950
kind of where these excited populations

117
00:05:59,490 --> 00:05:57,919
going we can look at the spectral

118
00:06:02,110 --> 00:05:59,500
information that we get from the

119
00:06:04,510 --> 00:06:02,120
transient but you can see that there's

120
00:06:07,270 --> 00:06:04,520
quite a bit going on here and it's

121
00:06:11,310 --> 00:06:07,280
fairly hard from just experimental point

122
00:06:13,840 --> 00:06:11,320
of view to extract what's happening so

123
00:06:16,750 --> 00:06:13,850
to help us out we turn to some of our

124
00:06:19,150 --> 00:06:16,760
collaborators at Madrid and in Vienna

125
00:06:22,510 --> 00:06:19,160
where they do high-level computational

126
00:06:24,159 --> 00:06:22,520
chemistry and so using their

127
00:06:26,080 --> 00:06:24,169
computational techniques they can

128
00:06:28,719 --> 00:06:26,090
actually model the potential energy

129
00:06:34,330 --> 00:06:28,729
surface of each of these excited states

130
00:06:36,850 --> 00:06:34,340
and then using also surface hopping

131
00:06:39,879 --> 00:06:36,860
dynamic simulations they can predict

132
00:06:42,640 --> 00:06:39,889
which where the excited state population

133
00:06:46,719 --> 00:06:42,650
we'll likely travel along these surfaces

134
00:06:49,480 --> 00:06:46,729
so this this is a pretty complex graphic

135
00:06:53,739 --> 00:06:49,490
but if in the ground state we excite

136
00:06:56,890 --> 00:06:53,749
with the UV photon up to the s2 excited

137
00:06:59,350 --> 00:06:56,900
state then the computations and the

138
00:07:03,670 --> 00:06:59,360

dynamic modeling predict that the most

139
00:07:06,580 --> 00:07:03,680
likely relaxation pathway is a followed

140
00:07:09,519 --> 00:07:06,590
by these yellow arrows so a fast decay

141
00:07:12,399 --> 00:07:09,529
to this conical intersection with the s1

142
00:07:16,149 --> 00:07:12,409
state then a rather slow decay across

143
00:07:17,589 --> 00:07:16,159
this somewhat flat surface to a crossing

144
00:07:21,040 --> 00:07:17,599
point with the triplet and then

145
00:07:23,529 --> 00:07:21,050
efficient population of the t1 minimum

146
00:07:26,050 --> 00:07:23,539
where it gets stuck in this triplet

147
00:07:28,089 --> 00:07:26,060
excited state and it really has no way

148
00:07:32,860 --> 00:07:28,099
to get back to the ground state so it

149
00:07:35,920 --> 00:07:32,870
takes a very very long time so this is

150
00:07:37,360 --> 00:07:35,930
what the computations predicted so now

151
00:07:39,850 --> 00:07:37,370
we want to try and match that up with

152
00:07:41,679 --> 00:07:39,860
our experimental results to see if we

153
00:07:47,950 --> 00:07:41,689
can put together a mechanism that's

154
00:07:50,740 --> 00:07:47,960
fairly concrete for this compound so to

155
00:07:55,300 --> 00:07:50,750
do that we actually chose points along

156
00:07:57,309 --> 00:07:55,310
this predicted surface to do vertical

157
00:08:00,490 --> 00:07:57,319
excitations from like we would do with

158
00:08:03,040 --> 00:08:00,500
our transient setup so when we probe

159
00:08:05,170 --> 00:08:03,050
we're actually probing here and looking

160
00:08:09,490 --> 00:08:05,180
at absorptions from these higher excited

161
00:08:11,409 --> 00:08:09,500
states so we chose these points and try

162
00:08:14,290 --> 00:08:11,419
to simulate our transient spectra with

163
00:08:16,839 --> 00:08:14,300

from these points and so you can

164
00:08:19,300 --> 00:08:16,849
actually see that the experimental

165
00:08:22,119 --> 00:08:19,310
spectra taken at certain time delays and

166
00:08:25,089 --> 00:08:22,129
the simulated transient spectra from the

167
00:08:28,029 --> 00:08:25,099
computations actually match up very very

168
00:08:30,850 --> 00:08:28,039
well and have the same type of

169
00:08:33,630 --> 00:08:30,860
transitions going on which I can discuss

170
00:08:35,709 --> 00:08:33,640
more detail if anybody's interested but

171
00:08:38,500 --> 00:08:35,719
essentially it gave us this mechanism

172
00:08:40,180 --> 00:08:38,510
where that follows just as the

173
00:08:43,000 --> 00:08:40,190
computations predicted where we

174
00:08:45,460 --> 00:08:43,010
eventually lead to a long live triplet

175
00:08:48,809 --> 00:08:45,470
excited state which takes a long time to

176
00:08:52,850 --> 00:08:48,819
relax back down to the ground state so

177
00:08:56,030 --> 00:08:52,860
for from this we learn that a

178
00:08:58,400 --> 00:08:56,040
that the purine core doesn't ultrafast

179
00:09:00,350 --> 00:08:58,410
inner internal conversion to the ground

180
00:09:02,690 --> 00:09:00,360
state rather it in her system crosses to

181
00:09:05,150 --> 00:09:02,700
populate the triplet and that triplet

182
00:09:08,090 --> 00:09:05,160
lives a long time which gives it a lot a

183
00:09:10,790 --> 00:09:08,100
long time to do chemical reactions so

184
00:09:12,980 --> 00:09:10,800
the core of these compounds is not

185
00:09:16,579 --> 00:09:12,990
responsible for the photostability seen

186
00:09:19,340 --> 00:09:16,589
in DNA rather it's ah it seems to be

187
00:09:23,090 --> 00:09:19,350
that having a substituent at the sixth

188
00:09:26,060 --> 00:09:23,100

position is what is really key to their

189
00:09:30,259 --> 00:09:26,070
photostability so if whether it's a mean

190
00:09:33,829 --> 00:09:30,269
of amine group or an ox 0 group the that

191
00:09:39,860 --> 00:09:33,839
provides it with that photostability and

192
00:09:43,759 --> 00:09:39,870
so this lends support to the the these

193
00:09:46,220 --> 00:09:43,769
bases being on prebiotic earth being

194
00:09:49,730 --> 00:09:46,230
photo stable and also provides targets

195
00:09:52,940 --> 00:09:49,740
for searching for other non canonical

196
00:09:55,790 --> 00:09:52,950
basis but from requires that they should

197
00:09:57,949 --> 00:09:55,800
be substituted at the c6 position in

198
00:10:01,370 --> 00:09:57,959
order to be photo stable and survive

199
00:10:16,180 --> 00:10:01,380
harsh UV environments and so with that

200
00:10:21,380 --> 00:10:19,490
so with the energy levels and the

201
00:10:24,290 --> 00:10:21,390
surfaces do you think that with the

202
00:10:26,240 --> 00:10:24,300
substituted purane do you think there's

203
00:10:28,850 --> 00:10:26,250
an additional conical intersection or is

204
00:10:30,550 --> 00:10:28,860
it just that the yeah that's it we're

205
00:10:36,160 --> 00:10:30,560
we're working on that right now some

206
00:10:40,010 --> 00:10:36,170
older computations suggest that this SQ

207
00:10:44,060 --> 00:10:40,020
drop here actually keeps going when you

208
00:10:46,970 --> 00:10:44,070
have that c6 substituent so um the I

209
00:10:48,920 --> 00:10:46,980
guess speed of the wave packet moving

210
00:10:52,160 --> 00:10:48,930
across this potential energy surface

211
00:10:54,199 --> 00:10:52,170
kind of bypasses this crossing point and

212
00:10:56,180 --> 00:10:54,209
just goes back to the ground state but

213
00:11:06,769 --> 00:10:56,190

we're working on that right now okay

214
00:11:08,930 --> 00:11:06,779
cool other questions if their own

215
00:11:11,090 --> 00:11:08,940
experiments just taking that purine core

216
00:11:16,610 --> 00:11:11,100
and hitting it with light and seeing how

217
00:11:19,850 --> 00:11:16,620
stable it is um I not sure I know that

218
00:11:22,460 --> 00:11:19,860
it has been the triplet population has

219
00:11:26,300 --> 00:11:22,470
been measured to be in the micro seconds

220
00:11:28,550 --> 00:11:26,310
or so and I so I would assume it it can

221
00:11:30,710 --> 00:11:28,560
highly react its triplet so it can react

222
00:11:33,050 --> 00:11:30,720
with oxygen and other things in the

223
00:11:36,829 --> 00:11:33,060
environment so yeah that's another

224
00:11:39,560 --> 00:11:36,839
possibility maybe the purine core being

225
00:11:42,290 --> 00:11:39,570
highly reactive is reacting to form

226
00:11:44,930 --> 00:11:42,300
these photo stable DNA bases maybe

227
00:11:46,880 --> 00:11:44,940
that's another route to it but i'm not

228
00:11:54,970 --> 00:11:46,890
sure as the exact photo chemistry that's