
AbSciCon
2019

1
00:00:00,790 --> 00:00:07,320
[Music]

2
00:00:13,000 --> 00:00:09,240
[Applause]

3
00:00:15,970 --> 00:00:13,010
Thank You Michel cassava I'm gonna talk

4
00:00:19,600 --> 00:00:15,980
about biomolecular synthesis again but

5
00:00:23,080 --> 00:00:19,610
from a quantum chemical perspective so

6
00:00:25,510 --> 00:00:23,090
we all first let me let me acknowledge

7
00:00:29,139 --> 00:00:25,520
my collaborators my theoretical

8
00:00:30,880 --> 00:00:29,149
collaborators here dr. Jim Lee proposed

9
00:00:34,660 --> 00:00:30,890
the Martin had gotten professor Thomas

10
00:00:37,660 --> 00:00:34,670
Tyne and my collaborators at NASA Ames

11
00:00:40,200 --> 00:00:37,670
experimental side notice Scott Sanford

12
00:00:42,819 --> 00:00:40,210
Michele Louisville and Chris matarese

13
00:00:47,139 --> 00:00:42,829

and funding from NASA Astrobiology

14
00:00:50,979 --> 00:00:47,149
Institute as well so we all know by now

15
00:00:54,029 --> 00:00:50,989
that that that biomolecules are organic

16
00:00:57,340 --> 00:00:54,039
molecules are formed on the surfaces of

17
00:01:00,970 --> 00:00:57,350
on the surfaces of are found in the

18
00:01:05,219 --> 00:01:00,980
services of meteorites and bodies that

19
00:01:08,380 --> 00:01:05,229
have are extraterrestrial in origin I

20
00:01:11,170 --> 00:01:08,390
stick to we stick to answering questions

21
00:01:14,770 --> 00:01:11,180
of how they're formed and why their form

22
00:01:17,740 --> 00:01:14,780
and by which processes so here is a

23
00:01:19,750 --> 00:01:17,750
cartoon of what may be molecular

24
00:01:22,300 --> 00:01:19,760
synthesis in the gas phase which may

25
00:01:25,660 --> 00:01:22,310
then be incorporated into into parent

26
00:01:28,000 --> 00:01:25,670
bodies such as meteor as such as you

27
00:01:30,160 --> 00:01:28,010
know grains or it could be formed on the

28
00:01:32,020 --> 00:01:30,170
surface of the grains or on the surfaces

29
00:01:33,850 --> 00:01:32,030
of the grains that is covered with a

30
00:01:37,150 --> 00:01:33,860
little bit of ice and we know these

31
00:01:40,320 --> 00:01:37,160
molecules can be as complex as sugars

32
00:01:43,210 --> 00:01:40,330
nuclear bases alcohols etc we try to

33
00:01:45,460 --> 00:01:43,220
look at what physical processes that

34
00:01:47,020 --> 00:01:45,470
that create the reactants what reactions

35
00:01:49,750 --> 00:01:47,030
are possible what's not possible what

36
00:01:52,690 --> 00:01:49,760
products are more likely to happen what

37
00:01:57,130 --> 00:01:52,700
what is less likely to happen

38
00:01:58,960 --> 00:01:57,140

so this is again in sort of motivated by

39
00:02:02,500 --> 00:01:58,970
and in collaboration with experiments

40
00:02:04,780 --> 00:02:02,510
where Michelle Kristin and Scott has

41
00:02:07,390 --> 00:02:04,790
done this and others have many others

42
00:02:09,400 --> 00:02:07,400
have done this they'd looked at Isis

43
00:02:13,270 --> 00:02:09,410
that in the laboratory and then exposed

44
00:02:19,240 --> 00:02:13,280
the ISIS with UV light and seen organic

45
00:02:27,040 --> 00:02:23,170
at low temperature deposited on aluminum

46
00:02:31,090 --> 00:02:27,050
foil ionized with or irradiated with UV

47
00:02:33,010 --> 00:02:31,100
lamp and and and experimented with HPLC

48
00:02:34,810 --> 00:02:33,020
and GCMs and found all sorts of

49
00:02:37,210 --> 00:02:34,820
interesting molecules including hypo

50
00:02:40,660 --> 00:02:37,220
xanthine adenine guanine I saw burn in

51
00:02:43,600 --> 00:02:40,670
xanthine and and so on and so we tried

52
00:02:48,250 --> 00:02:43,610
to understand what might have happened

53
00:02:52,690 --> 00:02:48,260
in between in between between depositing

54
00:02:54,880 --> 00:02:52,700
and and identifying the molecules so

55
00:02:56,949 --> 00:02:54,890
what might have happened was you have

56
00:02:59,050 --> 00:02:56,959
about ten point two five little folds of

57
00:03:01,870 --> 00:02:59,060
energy that may break water into

58
00:03:03,670 --> 00:03:01,880
hydroxyl may break or ammonia into amino

59
00:03:05,740 --> 00:03:03,680
group it does not iein eyes water

60
00:03:08,440 --> 00:03:05,750
because two point six electron volt is

61
00:03:11,380 --> 00:03:08,450
not available but it can ionize ammonia

62
00:03:14,590 --> 00:03:11,390
it can break ammonia or and it can even

63
00:03:16,890 --> 00:03:14,600

ionize and break purine into their

64
00:03:19,780 --> 00:03:16,900
components so all these reactants are

65
00:03:24,729 --> 00:03:19,790
are available in this and the sister

66
00:03:27,670 --> 00:03:24,739
said for h2o radical cation they then go

67
00:03:31,210 --> 00:03:27,680
on to react in various ways so here is a

68
00:03:33,190 --> 00:03:31,220
just a few of those and we look at each

69
00:03:37,150 --> 00:03:33,200
one of these but I'm going to point out

70
00:03:41,250 --> 00:03:37,160
just couple of them so here's a neutral

71
00:03:43,870 --> 00:03:41,260
purine reacting with water or ammonia

72
00:03:48,400 --> 00:03:43,880
neutral peirong reacting with a hydroxyl

73
00:03:51,430 --> 00:03:48,410
or ammonium or amino group radical

74
00:03:53,949 --> 00:03:51,440
reacting with the radical radical cation

75
00:03:56,320 --> 00:03:53,959
of purine reacting with hydroxyl or

76
00:03:58,330 --> 00:03:56,330
amino group and so on so I'm going to

77
00:04:02,650 --> 00:03:58,340
stick to this and for a good reason

78
00:04:06,400 --> 00:04:02,660
should be clear later stick to reactions

79
00:04:09,850 --> 00:04:06,410
between purine cation and and hydroxyl

80
00:04:12,940 --> 00:04:09,860
and amino radicals these are radical

81
00:04:14,740 --> 00:04:12,950
radical reactions so easier but there's

82
00:04:17,380 --> 00:04:14,750
a good reason for it but all these

83
00:04:19,930 --> 00:04:17,390
reactions we have actually explored and

84
00:04:23,380 --> 00:04:19,940
is available in our papers you can

85
00:04:24,510 --> 00:04:23,390
always go and look at those we use

86
00:04:26,920 --> 00:04:24,520
[Applause]

87
00:04:29,500 --> 00:04:26,930
primarily for these work density

88
00:04:31,750 --> 00:04:29,510

functional theory using one of the most

89
00:04:32,460 --> 00:04:31,760
modern density functions called Omega B

90
00:04:35,430 --> 00:04:32,470
97

91
00:04:37,830 --> 00:04:35,440
viii along with a large enough basis set

92
00:04:41,070 --> 00:04:37,840
and for condensed phase calculations we

93
00:04:42,750 --> 00:04:41,080
do a conductor like polarized continuum

94
00:04:45,380 --> 00:04:42,760
models so these are two sets of

95
00:04:48,300 --> 00:04:45,390
calculations between gas phase and

96
00:04:51,300 --> 00:04:48,310
explicitly condensed phase calculations

97
00:04:53,880 --> 00:04:51,310
and sometimes we use molar + @

98
00:04:58,500 --> 00:04:53,890
perturbation theory as well depending on

99
00:05:00,750 --> 00:04:58,510
the need so what we really do we try to

100
00:05:02,640 --> 00:05:00,760
explore the mechanism of these reactions

101
00:05:05,010 --> 00:05:02,650
so here is purine cation for you

102
00:05:06,810 --> 00:05:05,020
reacting with a hydroxyl radical giving

103
00:05:09,570 --> 00:05:06,820
you an intermediate that needs to then

104
00:05:11,280 --> 00:05:09,580
lose a proton to give you the product

105
00:05:14,190 --> 00:05:11,290
the products in this case is two

106
00:05:15,570 --> 00:05:14,200
hydroxyl two hydroxy purine it can

107
00:05:17,820 --> 00:05:15,580
happen in a different way as well

108
00:05:21,090 --> 00:05:17,830
feeding cattle reacting with water give

109
00:05:23,220 --> 00:05:21,100
you in between a few steps giving you

110
00:05:26,790 --> 00:05:23,230
the same thing and those same reaction

111
00:05:30,870 --> 00:05:26,800
scanning even happen with amino group

112
00:05:32,790 --> 00:05:30,880
and many other many other reactants so

113
00:05:34,380 --> 00:05:32,800

if we look at each one of these

114
00:05:38,340 --> 00:05:34,390
reactions let's look at the amino

115
00:05:39,870 --> 00:05:38,350
reaction first it is a reaction diagram

116
00:05:44,370 --> 00:05:39,880
so the x-axis is your reaction

117
00:05:48,510 --> 00:05:44,380
coordinate unitless and y axis is energy

118
00:05:50,969 --> 00:05:48,520
in kilocalories per mole here's the the

119
00:05:54,600 --> 00:05:50,979
reactants you have the purine cation the

120
00:05:56,610 --> 00:05:54,610
amino group and and the water and the

121
00:05:59,130 --> 00:05:56,620
intermediates here and the products

122
00:06:01,650 --> 00:05:59,140
there now the intermediates form in this

123
00:06:03,510 --> 00:06:01,660
case without any barrier because you

124
00:06:05,969 --> 00:06:03,520
have a reaction between a radical and a

125
00:06:08,400 --> 00:06:05,979
radical and that gives you the covalent

126
00:06:11,010 --> 00:06:08,410
bond formation here but that this this

127
00:06:13,560 --> 00:06:11,020
these molecules still need to lose a

128
00:06:16,020 --> 00:06:13,570
proton and that proton is lost because

129
00:06:18,330 --> 00:06:16,030
of the because of the water around it

130
00:06:21,630 --> 00:06:18,340
the water water's proton affinity

131
00:06:24,570 --> 00:06:21,640
actually pulls the proton out and gives

132
00:06:26,850 --> 00:06:24,580
you these products if you didn't include

133
00:06:29,850 --> 00:06:26,860
this water in this in this equation

134
00:06:30,840 --> 00:06:29,860
these energies for the products would be

135
00:06:32,700 --> 00:06:30,850
somewhere around here

136
00:06:34,830 --> 00:06:32,710
which means the reactions will not be

137
00:06:37,409 --> 00:06:34,840
favorable you need to include at least

138
00:06:39,420 --> 00:06:37,419

one water actually more than one water

139
00:06:41,250 --> 00:06:39,430
but in this case with even with one

140
00:06:43,620 --> 00:06:41,260
water the reaction main energies become

141
00:06:45,750 --> 00:06:43,630
favorable this already tells you that

142
00:06:47,730 --> 00:06:45,760
pure gas phase reaction

143
00:06:51,000 --> 00:06:47,740
is kind of difficult pure gas phase

144
00:06:52,860 --> 00:06:51,010
reaction between this radical cation and

145
00:06:54,990 --> 00:06:52,870
a radical will give you the intermediate

146
00:06:56,580 --> 00:06:55,000
but not the products because the protons

147
00:06:58,770 --> 00:06:56,590
still going to be stuck there and you

148
00:07:02,760 --> 00:06:58,780
need something to pull that proton out

149
00:07:04,860 --> 00:07:02,770
water does that right here you can show

150
00:07:06,630 --> 00:07:04,870
this using condensed phase calculations

151
00:07:09,210 --> 00:07:06,640
explicitly here

152
00:07:13,920 --> 00:07:09,220
so these RC PCM calculations and again

153
00:07:15,660 --> 00:07:13,930
we make the reactants 0 arbitrarily and

154
00:07:17,190 --> 00:07:15,670
and see the what happens to

155
00:07:19,080 --> 00:07:17,200
intermediates and products here you see

156
00:07:21,120 --> 00:07:19,090
that the the effect of the condensed

157
00:07:23,750 --> 00:07:21,130
phase clearly it pulls the energy is

158
00:07:28,110 --> 00:07:23,760
down further and makes a reaction go

159
00:07:30,480 --> 00:07:28,120
better similar things you can now start

160
00:07:32,760 --> 00:07:30,490
now the other point I want to make from

161
00:07:34,290 --> 00:07:32,770
this is that that you have two products

162
00:07:37,260 --> 00:07:34,300
that is six amino purine and two men

163
00:07:39,390 --> 00:07:37,270

amino purine that is the most likely

164
00:07:41,040 --> 00:07:39,400
what's most stable products in this six

165
00:07:43,740 --> 00:07:41,050
I mean appear in is nothing but adenine

166
00:07:46,860 --> 00:07:43,750
adenine is your most favorable product

167
00:07:50,040 --> 00:07:46,870
if you take one of these two and or both

168
00:07:52,860 --> 00:07:50,050
and do the next step that is an addition

169
00:07:54,990 --> 00:07:52,870
of either amine group amino group or a

170
00:07:55,590 --> 00:07:55,000
hydroxyl group you would find something

171
00:07:59,190 --> 00:07:55,600
like this

172
00:08:02,070 --> 00:07:59,200
so here's an example of adenine reacting

173
00:08:04,170 --> 00:08:02,080
with hydroxyl and and you have the

174
00:08:06,290 --> 00:08:04,180
reactants their intermediates and

175
00:08:10,440 --> 00:08:06,300
products here so if you start from

176
00:08:13,230 --> 00:08:10,450
adenine you get to I so guanine if you

177
00:08:15,210 --> 00:08:13,240
start from too high to amino purine you

178
00:08:18,150 --> 00:08:15,220
get to go on in

179
00:08:19,800 --> 00:08:18,160
here's going in and again you see the

180
00:08:21,810 --> 00:08:19,810
same thing happening this is a pure gas

181
00:08:24,480 --> 00:08:21,820
phase calculation in in black and blue

182
00:08:25,980 --> 00:08:24,490
you see the reactants of the

183
00:08:27,390 --> 00:08:25,990
intermediates forming the products for

184
00:08:30,480 --> 00:08:27,400
me in the product intermediates are

185
00:08:32,880 --> 00:08:30,490
still a little bit lower in energy so

186
00:08:35,040 --> 00:08:32,890
that the reaction shouldn't go if you

187
00:08:36,719 --> 00:08:35,050
actually include the condensed phase and

188
00:08:39,300 --> 00:08:36,729

the condenses calculations clearly

189
00:08:41,880 --> 00:08:39,310
showed that that the reactions go in in

190
00:08:43,740 --> 00:08:41,890
the products direction so so you have

191
00:08:45,690 --> 00:08:43,750
you need the matrix you need the water

192
00:08:47,400 --> 00:08:45,700
matrix these reactions do not go in the

193
00:08:50,370 --> 00:08:47,410
gas phase so gasp your gas phase

194
00:08:55,550 --> 00:08:50,380
formation oxidation or amino ammunition

195
00:08:59,060 --> 00:08:55,560
of purines to adenine or guanine is

196
00:09:02,210 --> 00:08:59,070
unlikely but condensed phase

197
00:09:08,440 --> 00:09:02,220
with covered with ice phase followed by

198
00:09:12,860 --> 00:09:08,450
ionization formation is very likely so

199
00:09:15,230 --> 00:09:12,870
we may ask why I work with cation all

200
00:09:17,900 --> 00:09:15,240
the time so here's the pure in cation

201
00:09:19,550 --> 00:09:17,910
and seen pigeon cations before it's a

202
00:09:22,880 --> 00:09:19,560
good reason for it now and it became

203
00:09:25,370 --> 00:09:22,890
clear later so here's an example that

204
00:09:27,290 --> 00:09:25,380
has is out of place here's an example of

205
00:09:29,690 --> 00:09:27,300
an experiment that Chris and Michelle

206
00:09:40,250 --> 00:09:29,700
did where they deposited I was time to

207
00:09:43,460 --> 00:09:40,260
have okay okay so I mean a purine in

208
00:09:45,770 --> 00:09:43,470
pure ammonia and ionized and right

209
00:09:48,140 --> 00:09:45,780
followed by radiation and we did the

210
00:09:50,390 --> 00:09:48,150
calculations ensure that you should be

211
00:09:52,790 --> 00:09:50,400
able to make adenine from it because you

212
00:09:54,680 --> 00:09:52,800
know I mean any NEC has strong enough

213
00:09:58,910 --> 00:09:54,690

return affinity to pull that proton out

214
00:10:01,490 --> 00:09:58,920
so you should you should get adenine and

215
00:10:03,620 --> 00:10:01,500
and all other amino purine products

216
00:10:07,910 --> 00:10:03,630
except when they do the experiments they

217
00:10:11,600 --> 00:10:07,920
don't see any now this this is an

218
00:10:14,900 --> 00:10:11,610
interesting case it became clearer later

219
00:10:17,240 --> 00:10:14,910
when we found this paper by quill ethyl

220
00:10:19,700 --> 00:10:17,250
where they make this observation that

221
00:10:21,380 --> 00:10:19,710
the ice matrix acts as an electronic

222
00:10:22,880 --> 00:10:21,390
solitaire switch where the relative

223
00:10:25,160 --> 00:10:22,890
amount of water and ammonia determines

224
00:10:28,160 --> 00:10:25,170
whether the positively or the negatively

225
00:10:33,050 --> 00:10:28,170
charged PA is in this case but in our

226
00:10:36,740 --> 00:10:33,060
case purine is formed so in pure water

227
00:10:38,420 --> 00:10:36,750
you have cations and in pure ammonia you

228
00:10:40,400 --> 00:10:38,430
have a neurons produced that's because

229
00:10:42,680 --> 00:10:40,410
of the low ionization energy of ammonia

230
00:10:45,020 --> 00:10:42,690
and hire an additional energy of water

231
00:10:47,690 --> 00:10:45,030
low ionization of energy of ammonia

232
00:10:49,520 --> 00:10:47,700
makes ammonium cat or ammonia cation

233
00:10:53,030 --> 00:10:49,530
plus an electron electron is captured by

234
00:10:55,280 --> 00:10:53,040
the the purine or the pH and you have

235
00:10:57,890 --> 00:10:55,290
the anion so when you have the Anna and

236
00:11:00,350 --> 00:10:57,900
the reactions don't go go like the way I

237
00:11:02,390 --> 00:11:00,360
should and you don't see any product

238
00:11:04,280 --> 00:11:02,400

that kind of proves the cationic

239
00:11:07,940 --> 00:11:04,290
mechanism because the moment you have

240
00:11:09,740 --> 00:11:07,950
the water water helps create the cations

241
00:11:11,780 --> 00:11:09,750
of the purine or the pyrimidine or

242
00:11:14,090 --> 00:11:11,790
whatever you have working with

243
00:11:15,650 --> 00:11:14,100
the cationic reaction goes forward this

244
00:11:17,600 --> 00:11:15,660
is kind of the proof of the cationic

245
00:11:19,670 --> 00:11:17,610
mechanism that's why we chose the

246
00:11:22,520 --> 00:11:19,680
cationic mechanism of all the of the

247
00:11:24,620 --> 00:11:22,530
mechanisms here so now going forward we

248
00:11:27,710 --> 00:11:24,630
just can do the same experiment in

249
00:11:31,010 --> 00:11:27,720
Reverse you say how about the hydroxyl

250
00:11:32,660 --> 00:11:31,020
if the hydroxyl attaches first you see

251
00:11:34,970 --> 00:11:32,670
the same thing in this case you would

252
00:11:39,260 --> 00:11:34,980
see hypose Anthon instead of amino

253
00:11:41,600 --> 00:11:39,270
purines and then those can then take in

254
00:11:42,770 --> 00:11:41,610
each amino group later and we'll give

255
00:11:45,110 --> 00:11:42,780
you the similar products basically

256
00:11:48,320 --> 00:11:45,120
guanine I said one in and see similar

257
00:11:50,780 --> 00:11:48,330
ordering of energy but now what is

258
00:11:55,790 --> 00:11:50,790
available will be important at the first

259
00:11:57,200 --> 00:11:55,800
step so if you started from purine if

260
00:11:59,870 --> 00:11:57,210
your first step was an amino group

261
00:12:01,940 --> 00:11:59,880
addition then you expect to find

262
00:12:04,040 --> 00:12:01,950
adenine if your first step was a

263
00:12:06,830 --> 00:12:04,050

hydroxyl group addition you expect to

264
00:12:09,980 --> 00:12:06,840
make hypose and thin but this actually

265
00:12:11,990 --> 00:12:09,990
makes a very interesting case if water

266
00:12:14,870 --> 00:12:12,000
is more abundant so if you make hypo

267
00:12:17,270 --> 00:12:14,880
Santi and you expect that in the next

268
00:12:20,330 --> 00:12:17,280
step if it is a amination then you would

269
00:12:22,070 --> 00:12:20,340
expect to form guanine and if it is a

270
00:12:24,770 --> 00:12:22,080
hydroxylation then you expect to forms

271
00:12:26,750 --> 00:12:24,780
xanthine on the other hand if you if

272
00:12:29,090 --> 00:12:26,760
your first step was an ammunition then

273
00:12:30,680 --> 00:12:29,100
you make adenine and then the next step

274
00:12:33,500 --> 00:12:30,690
would takes you takes you to I so

275
00:12:35,990 --> 00:12:33,510
guanine all these products are possible

276
00:12:39,620 --> 00:12:36,000
it just depends on what is available at

277
00:12:44,840 --> 00:12:39,630
the NIR environment and what reaction is

278
00:12:46,520 --> 00:12:44,850
statistically more feasible so with all

279
00:12:50,510 --> 00:12:46,530
these I'm just going to skip next few

280
00:12:52,700 --> 00:12:50,520
slides and come to my broad conclusions

281
00:12:56,000 --> 00:12:52,710
is that that the that the cationic

282
00:12:58,700 --> 00:12:56,010
mechanism is likely the way this these

283
00:13:00,680 --> 00:12:58,710
reactions go it needs the presence of

284
00:13:02,900 --> 00:13:00,690
the water matrix for for two reasons

285
00:13:06,350 --> 00:13:02,910
water actually plays the devil and and

286
00:13:09,260 --> 00:13:06,360
the do-gooder here is a catalyst because

287
00:13:11,420 --> 00:13:09,270
it helps create the cations it provides

288
00:13:13,490 --> 00:13:11,430

a matrix for the reaction and also

289
00:13:14,810 --> 00:13:13,500
provides the hydroxyl radicals for for

290
00:13:17,240 --> 00:13:14,820
the reaction so it provides the

291
00:13:19,250 --> 00:13:17,250
reactants to but also acts as a as a

292
00:13:21,470 --> 00:13:19,260
competitor because once the hydroxyl is

293
00:13:23,060 --> 00:13:21,480
produced it attacks everything in the

294
00:13:24,440 --> 00:13:23,070
amino group does not have the

295
00:13:27,880 --> 00:13:24,450
opportunity to to

296
00:13:31,460 --> 00:13:27,890
sort of a catalyst and a competitor and

297
00:13:34,370 --> 00:13:31,470
from our other experiments we found that

298
00:13:37,250 --> 00:13:34,380
that the uracil adenine and guanine are

299
00:13:38,960 --> 00:13:37,260
kind of easily formed but timing is not

300
00:13:41,570 --> 00:13:38,970
so easily formed and that's the part I

301
00:13:44,720 --> 00:13:41,580
skip but you can always go back and read

302
00:13:46,610 --> 00:13:44,730
the papers previous papers and so which

303
00:13:49,520 --> 00:13:46,620
is kind of goes along with the absence

304
00:13:52,400 --> 00:13:49,530
of timing in the meteorite examples thus

305
00:13:55,400 --> 00:13:52,410
far so with that I'm just going to skip

306
00:13:57,440 --> 00:13:55,410
next few slides and come to and say

307
00:13:58,780 --> 00:13:57,450
thank you and take any questions you may