Large Spin Dichroism Effects Measured in L-histidine

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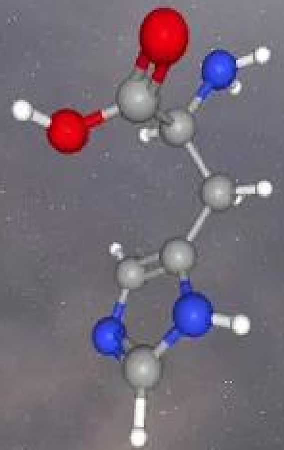

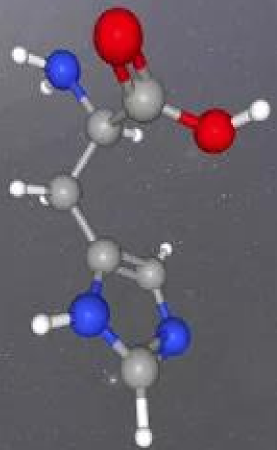

1
00:00:05,829 --> 00:00:03,189
okay great uh thank you to the

2
00:00:07,990 --> 00:00:05,839
uh organizers for giving me a chance to

3
00:00:10,310 --> 00:00:08,000
give this talk and to you all for

4
00:00:12,310 --> 00:00:10,320
watching it uh my name is micah scheibel

5
00:00:14,390 --> 00:00:12,320
i'm from the georgia institute of

6
00:00:16,070 --> 00:00:14,400
technology and today i'll be talking

7
00:00:17,830 --> 00:00:16,080
about some recent measurements where we

8
00:00:20,230 --> 00:00:17,840
explore a mechanism called spin

9
00:00:23,189 --> 00:00:20,240
dichroism and its ability to form

10
00:00:24,630 --> 00:00:23,199
enantiomeric excesses in chiral amino

11
00:00:25,830 --> 00:00:24,640
acids

12
00:00:28,150 --> 00:00:25,840
so i'm sure i don't have to tell this

13
00:00:30,470 --> 00:00:28,160

crowd that chiral amino acids and and

14
00:00:33,590 --> 00:00:30,480
many other types of chiral molecules

15
00:00:36,069 --> 00:00:33,600
are uh found in in many different uh

16
00:00:38,630 --> 00:00:36,079
meteorites as well as in asteroids and

17
00:00:40,630 --> 00:00:38,640
comets uh and here i'm showing a few

18
00:00:43,030 --> 00:00:40,640
different amino acids that have been

19
00:00:45,830 --> 00:00:43,040
identified and in the parentheses is the

20
00:00:48,549 --> 00:00:45,840
largest measured enantiomeric excess of

21
00:00:51,910 --> 00:00:48,559
these chiral amino acids so these being

22
00:00:55,110 --> 00:00:51,920
the l form there's a 20 excess in the l

23
00:00:57,510 --> 00:00:55,120
over the corresponding d form

24
00:01:00,310 --> 00:00:57,520
interestingly enough when we look across

25
00:01:02,389 --> 00:01:00,320
a number of different sources for these

26
00:01:06,149 --> 00:01:02,399
chiral amino acids

27
00:01:10,149 --> 00:01:06,159
we see that very often they are

28
00:01:11,670 --> 00:01:10,159
enhanced towards the l enantiomer so

29
00:01:12,710 --> 00:01:11,680
here showing the

30
00:01:15,510 --> 00:01:12,720
measured

31
00:01:18,950 --> 00:01:15,520
excesses of l-isovalene in a number of

32
00:01:21,429 --> 00:01:18,960
different meteorite types all showing an

33
00:01:22,789 --> 00:01:21,439
excess towards the l-form and none

34
00:01:25,590 --> 00:01:22,799
really showing a statistically

35
00:01:27,109 --> 00:01:25,600
significant excess towards the d-form

36
00:01:29,190 --> 00:01:27,119
so the question that we're asking here

37
00:01:31,910 --> 00:01:29,200
is why do uh seemingly all of these

38
00:01:34,950 --> 00:01:31,920

these primitive meteorites display the

39
00:01:36,710 --> 00:01:34,960
same enantiomeric excesses or this the

40
00:01:38,630 --> 00:01:36,720
enantiomeric excesses of the same

41
00:01:40,630 --> 00:01:38,640
handedness

42
00:01:42,789 --> 00:01:40,640
so different forces in space which can

43
00:01:45,350 --> 00:01:42,799
drive enantioselectivity

44
00:01:48,069 --> 00:01:45,360
uh include several different abiotic

45
00:01:51,830 --> 00:01:48,079
mechanisms um the first being sort of

46
00:01:54,550 --> 00:01:51,840
just a chance or statistical fluctuation

47
00:01:57,030 --> 00:01:54,560
in the molecular populations which lead

48
00:01:59,670 --> 00:01:57,040
to an enhancement in one versus the

49
00:02:01,590 --> 00:01:59,680
other uh now if there's these uh

50
00:02:03,350 --> 00:02:01,600
excesses and meteorites were forming due

51
00:02:05,270 --> 00:02:03,360
to a chance mechanism we would expect

52
00:02:07,749 --> 00:02:05,280
both l and d forms

53
00:02:09,430 --> 00:02:07,759
uh alternatively amplification uh

54
00:02:12,390 --> 00:02:09,440
there's lots of different types of

55
00:02:13,750 --> 00:02:12,400
mechanisms that can drive amplification

56
00:02:17,430 --> 00:02:13,760
of a given

57
00:02:20,710 --> 00:02:17,440
chirality but all of these still require

58
00:02:22,869 --> 00:02:20,720
some initially small excess of one of

59
00:02:24,869 --> 00:02:22,879
the enantiomers versus the other so

60
00:02:27,190 --> 00:02:24,879
ultimately what we're searching for to

61
00:02:29,190 --> 00:02:27,200
explain why all of these meteorites are

62
00:02:30,710 --> 00:02:29,200
pushed in the same direction is

63
00:02:33,830 --> 00:02:30,720

something called a determinant force

64
00:02:37,350 --> 00:02:33,840
where where the excesses are at least

65
00:02:41,030 --> 00:02:37,360
initiated by some sort of physical force

66
00:02:43,190 --> 00:02:41,040
that is not dependent on the environment

67
00:02:46,150 --> 00:02:43,200
um so different determinate mechanisms

68
00:02:48,470 --> 00:02:46,160
which have been explored that uh

69
00:02:51,110 --> 00:02:48,480
induce enantiomeric excesses in organic

70
00:02:54,710 --> 00:02:51,120
molecules uh include first circularly

71
00:02:57,110 --> 00:02:54,720
polarized light uh where uh light from

72
00:03:00,710 --> 00:02:57,120
ionizing radiation such as uv light from

73
00:03:02,830 --> 00:03:00,720
distant stars can obtain a uh circular

74
00:03:05,030 --> 00:03:02,840
or actually a really unknown elliptical

75
00:03:07,110 --> 00:03:05,040
polarization as it passes through dust

76
00:03:08,309 --> 00:03:07,120
clouds on its way towards our solar

77
00:03:10,630 --> 00:03:08,319
system

78
00:03:13,830 --> 00:03:10,640
and those circularly polarized photons

79
00:03:16,390 --> 00:03:13,840
can induce an enantiomeric excess

80
00:03:19,509 --> 00:03:16,400
alternatively you can get preferential

81
00:03:21,910 --> 00:03:19,519
bonding or catalysis on chiral surfaces

82
00:03:24,309 --> 00:03:21,920
uh both of these have been explored and

83
00:03:26,710 --> 00:03:24,319
in general produce fairly small

84
00:03:29,110 --> 00:03:26,720
enantiomeric excesses

85
00:03:31,830 --> 00:03:29,120
a third mechanism which we are exploring

86
00:03:34,229 --> 00:03:31,840
in the current work is interactions of

87
00:03:36,309 --> 00:03:34,239
spin polarized electrons with chiral

88
00:03:38,630 --> 00:03:36,319

molecules uh so the question that we're

89
00:03:41,670 --> 00:03:38,640
asking is can spin polarized electrons

90
00:03:44,550 --> 00:03:41,680
create enantiomeric excesses within

91
00:03:48,229 --> 00:03:44,560
populations of chiral amino acids

92
00:03:51,670 --> 00:03:48,239
uh so first we'll just do a little bit

93
00:03:55,350 --> 00:03:51,680
about where we can expect these spin

94
00:03:57,190 --> 00:03:55,360
polarized electrons to come from um and

95
00:03:59,910 --> 00:03:57,200
what we're doing is we're

96
00:04:02,390 --> 00:03:59,920
looking at the ejection of these spin

97
00:04:05,589 --> 00:04:02,400
polarized electrons from a magnetized

98
00:04:06,470 --> 00:04:05,599
surface so you can imagine here uh our

99
00:04:09,429 --> 00:04:06,480
sort of

100
00:04:11,110 --> 00:04:09,439
schematic of an iron where all of the

101
00:04:13,509 --> 00:04:11,120
spins within the iron or at least the

102
00:04:16,229 --> 00:04:13,519
vast majority of them are pointing in

103
00:04:19,270 --> 00:04:16,239
the same direction

104
00:04:21,189 --> 00:04:19,280
and so when we have ionizing radiation

105
00:04:23,110 --> 00:04:21,199
come in it can excite one of those

106
00:04:24,310 --> 00:04:23,120
electrons which then scatters through

107
00:04:26,310 --> 00:04:24,320
the solid

108
00:04:28,469 --> 00:04:26,320
and then can escape the surface as a

109
00:04:31,670 --> 00:04:28,479
secondary electron

110
00:04:33,749 --> 00:04:31,680
so it turns out that because of the

111
00:04:36,310 --> 00:04:33,759
polarizing or the magnetization of that

112
00:04:39,030 --> 00:04:36,320
surface you have an unequal filling of

113
00:04:41,350 --> 00:04:39,040

the fermi energy levels

114
00:04:43,990 --> 00:04:41,360
within the solid and you get more or

115
00:04:46,629 --> 00:04:44,000
preferential scattering off of the prep

116
00:04:49,189 --> 00:04:46,639
slightly emptier levels so that leads to

117
00:04:51,270 --> 00:04:49,199
then a preferential polarization

118
00:04:53,830 --> 00:04:51,280
direction of the emitted secondary

119
00:04:56,950 --> 00:04:53,840
electrons from that surface

120
00:04:59,350 --> 00:04:56,960
um it turns out that a

121
00:05:01,909 --> 00:04:59,360
spin polarized electron in motion traces

122
00:05:04,230 --> 00:05:01,919
out a helical path um and that by

123
00:05:06,710 --> 00:05:04,240
reversing the substrate magnet

124
00:05:09,350 --> 00:05:06,720
uh magnetization direction we can also

125
00:05:11,990 --> 00:05:09,360
reverse the helicity of the ejected

126
00:05:13,670 --> 00:05:12,000
secondary electrons

127
00:05:17,029 --> 00:05:13,680
so the mechanism that we're exploring

128
00:05:20,230 --> 00:05:17,039
here spin dichroism consists in coupling

129
00:05:22,469 --> 00:05:20,240
between that electron helicity and the

130
00:05:25,390 --> 00:05:22,479
molecular chirality and exploring

131
00:05:27,510 --> 00:05:25,400
whether or not that coupling can lead to

132
00:05:29,510 --> 00:05:27,520
enantioselective damage and formation of

133
00:05:31,350 --> 00:05:29,520
enantiomeric excesses

134
00:05:33,510 --> 00:05:31,360
so here the idea is that we have some

135
00:05:35,909 --> 00:05:33,520
sort of ionizing radiation come in in

136
00:05:38,070 --> 00:05:35,919
these experiments we use x-rays they

137
00:05:41,270 --> 00:05:38,080
excite secondary electrons from the

138
00:05:44,629 --> 00:05:41,280

surface which then are ejected out and

139
00:05:47,110 --> 00:05:44,639
can interact with molecules absorbed

140
00:05:48,870 --> 00:05:47,120
um depending on the magnetization

141
00:05:52,469 --> 00:05:48,880
direction of that substrate you can

142
00:05:55,430 --> 00:05:52,479
either have plus or negative uh

143
00:05:57,510 --> 00:05:55,440
helicity spin polarized electrons

144
00:06:01,350 --> 00:05:57,520
and these may interact differently with

145
00:06:03,670 --> 00:06:01,360
the l or the i r car um

146
00:06:06,550 --> 00:06:03,680
enantiomers

147
00:06:09,189 --> 00:06:06,560
so the experimental setup that we

148
00:06:11,830 --> 00:06:09,199
designed was to first vapor deposit a

149
00:06:13,830 --> 00:06:11,840
molecule l-histidine uh and we used this

150
00:06:16,070 --> 00:06:13,840
one because it was well understood in in

151
00:06:17,990 --> 00:06:16,080
terms of its interactions with surfaces

152
00:06:21,029 --> 00:06:18,000
and and we knew that we could

153
00:06:22,870 --> 00:06:21,039
deposit it reliably on the surface

154
00:06:27,270 --> 00:06:22,880
and then we exposed those films of

155
00:06:28,950 --> 00:06:27,280
l-histidine to 695 ev soft x-rays uh

156
00:06:30,790 --> 00:06:28,960
that were generated by the advanced

157
00:06:32,830 --> 00:06:30,800
photon source synchrotron at argonne

158
00:06:36,469 --> 00:06:32,840
national lab

159
00:06:38,950 --> 00:06:36,479
those x-rays then interacted with our

160
00:06:41,029 --> 00:06:38,960
magnetized cobalt substrate to eject the

161
00:06:46,309 --> 00:06:41,039
spin polarized electrons

162
00:06:48,390 --> 00:06:46,319
could interact with and damage the vapor

163
00:06:50,390 --> 00:06:48,400

deposited l l-histidine

164
00:06:51,990 --> 00:06:50,400
we can then probe that damage using a

165
00:06:53,830 --> 00:06:52,000
technique called x-ray photoelectron

166
00:06:54,710 --> 00:06:53,840
spectroscopy

167
00:06:56,469 --> 00:06:54,720
and then

168
00:06:59,830 --> 00:06:56,479
determine how

169
00:07:01,909 --> 00:06:59,840
that difference in helicity

170
00:07:04,230 --> 00:07:01,919
affects the damaged cross-sections by

171
00:07:06,790 --> 00:07:04,240
reversing the magnetization of our

172
00:07:09,350 --> 00:07:06,800
substrate in situ

173
00:07:11,909 --> 00:07:09,360
what the xps measurements look like is

174
00:07:15,189 --> 00:07:11,919
shown here where i focused on the

175
00:07:17,430 --> 00:07:15,199
nitrogen uh component of our molecules

176
00:07:20,629 --> 00:07:17,440
nitrogen being uh

177
00:07:25,110 --> 00:07:20,639
very unique to the analyte molecule as

178
00:07:28,070 --> 00:07:25,120
all and also um on the chiral center so

179
00:07:29,909 --> 00:07:28,080
we see that the high resolution spectrum

180
00:07:31,909 --> 00:07:29,919
of nitrogen can be fit with five

181
00:07:35,430 --> 00:07:31,919
different peaks

182
00:07:39,029 --> 00:07:35,440
the first two uh being the largest uh

183
00:07:42,230 --> 00:07:39,039
are corresponding to the n1 and the n2

184
00:07:44,950 --> 00:07:42,240
components on the nitro uh the neutral

185
00:07:47,670 --> 00:07:44,960
histidine molecules while these smaller

186
00:07:49,670 --> 00:07:47,680
peaks out here the m3 and the n4 peaks

187
00:07:52,550 --> 00:07:49,680
correspond to nitrogen with on this

188
00:07:54,550 --> 00:07:52,560

wider ionic species

189
00:07:56,629 --> 00:07:54,560
um

190
00:07:58,390 --> 00:07:56,639
it turns out that these winter ionic

191
00:08:00,550 --> 00:07:58,400
species are important because

192
00:08:03,430 --> 00:08:00,560
depending on the thickness of our sample

193
00:08:05,830 --> 00:08:03,440
uh you you see more or less abundances

194
00:08:08,230 --> 00:08:05,840
of those of those winter ionic species

195
00:08:10,150 --> 00:08:08,240
um and so it turns out that for a thin

196
00:08:13,510 --> 00:08:10,160
film or a monolayer film sort of

197
00:08:15,670 --> 00:08:13,520
corresponding to this uh 0.3 nanometer

198
00:08:17,350 --> 00:08:15,680
thickness where the the n3 and the n4

199
00:08:18,710 --> 00:08:17,360
components of the switter ions are

200
00:08:20,950 --> 00:08:18,720
hardly there

201
00:08:23,670 --> 00:08:20,960
um you get more strongly interaction

202
00:08:26,390 --> 00:08:23,680
interactions with the molecules in the

203
00:08:29,189 --> 00:08:26,400
surface whereas with the thicker samples

204
00:08:30,390 --> 00:08:29,199
uh those those interactions aren't quite

205
00:08:31,670 --> 00:08:30,400
as strong

206
00:08:33,750 --> 00:08:31,680
so that the presence of multiple

207
00:08:35,990 --> 00:08:33,760
monolayers can weaken the molecular

208
00:08:37,269 --> 00:08:36,000
interactions between the the molecules

209
00:08:40,230 --> 00:08:37,279
and the surface

210
00:08:43,909 --> 00:08:40,240
potentially enhancing any measurement of

211
00:08:45,829 --> 00:08:43,919
this spindle dichroism in fact

212
00:08:48,790 --> 00:08:45,839
when we look at the

213
00:08:51,750 --> 00:08:48,800

abundance or the area of those peaks as

214
00:08:54,630 --> 00:08:51,760
a function of a radiation fluence or the

215
00:08:56,949 --> 00:08:54,640
cumulative electron fluence that these

216
00:08:58,870 --> 00:08:56,959
molecular films have been exposed to

217
00:09:00,710 --> 00:08:58,880
we see that they are well fit by

218
00:09:06,870 --> 00:09:00,720
exponential decays

219
00:09:09,910 --> 00:09:06,880
used to give us uh cross sections

220
00:09:12,710 --> 00:09:09,920
for the damage or what is the the damage

221
00:09:14,710 --> 00:09:12,720
cross-section for these molecules with

222
00:09:16,150 --> 00:09:14,720
the spin polarized electrons

223
00:09:17,829 --> 00:09:16,160
and so again it turns out that the

224
00:09:19,509 --> 00:09:17,839
thicker samples because there's more

225
00:09:20,949 --> 00:09:19,519
molecules there and they're less

226
00:09:22,790 --> 00:09:20,959
strongly interacting with the surface

227
00:09:25,190 --> 00:09:22,800
they give better and more precise

228
00:09:28,070 --> 00:09:25,200
exponential fits which ultimately give

229
00:09:29,990 --> 00:09:28,080
us better statistics and then we also

230
00:09:32,150 --> 00:09:30,000
see that it's pretty clear that the

231
00:09:33,750 --> 00:09:32,160
zwitter ionic species both in the thick

232
00:09:36,230 --> 00:09:33,760
and in the thinner samples those

233
00:09:40,550 --> 00:09:36,240
vitorianic species are damaged more

234
00:09:42,470 --> 00:09:40,560
readily than are the the neutral species

235
00:09:45,750 --> 00:09:42,480
so when we take measurements of these

236
00:09:48,150 --> 00:09:45,760
damaged cross sections uh at multiple

237
00:09:51,590 --> 00:09:48,160
different spots on the same sample so

238
00:09:54,150 --> 00:09:51,600

same deposition different spot uh we

239
00:09:56,790 --> 00:09:54,160
take about fifth 10 to 15 different

240
00:09:57,990 --> 00:09:56,800
spots in both of the magnetization

241
00:10:00,710 --> 00:09:58,000
conditions

242
00:10:03,030 --> 00:10:00,720
and then do a statistical comparison for

243
00:10:05,350 --> 00:10:03,040
those cross sections measured

244
00:10:07,190 --> 00:10:05,360
in both magnetization conditions and

245
00:10:08,550 --> 00:10:07,200
look for statistical significantly

246
00:10:11,030 --> 00:10:08,560
differences

247
00:10:12,870 --> 00:10:11,040
between those two populations

248
00:10:14,630 --> 00:10:12,880
and what we see that in fact the total

249
00:10:16,470 --> 00:10:14,640
cross-section and

250
00:10:18,870 --> 00:10:16,480
the cross-sections for this wider ionic

251
00:10:21,590 --> 00:10:18,880
species so strong evidence of spin

252
00:10:24,630 --> 00:10:21,600
dichroism so that the dependence that of

253
00:10:28,470 --> 00:10:24,640
the damage on that electron helicity

254
00:10:30,790 --> 00:10:28,480
for these l histidine molecules um if we

255
00:10:32,710 --> 00:10:30,800
assume that the the reverse is true for

256
00:10:35,190 --> 00:10:32,720
the d-histidine molecules which can be

257
00:10:37,590 --> 00:10:35,200
expected from previous measurements uh

258
00:10:39,910 --> 00:10:37,600
we get that if we had a racemic mixture

259
00:10:42,230 --> 00:10:39,920
of l-histidine on the surface

260
00:10:44,230 --> 00:10:42,240
we would produce actually a 17

261
00:10:45,430 --> 00:10:44,240
enantiomeric excess

262
00:10:47,509 --> 00:10:45,440
when only

263
00:10:49,670 --> 00:10:47,519

forty percent of the original molecular

264
00:10:52,069 --> 00:10:49,680
population remains uh so these are

265
00:10:54,790 --> 00:10:52,079
pretty strong effects of of this uh spin

266
00:10:57,110 --> 00:10:54,800
dichroism that we're showing here

267
00:11:00,230 --> 00:10:57,120
uh so in conclusion we've shown that uh

268
00:11:02,069 --> 00:11:00,240
elk hyrule lumentomeric excesses

269
00:11:04,470 --> 00:11:02,079
have been identified in many pretty much

270
00:11:06,710 --> 00:11:04,480
meteorites and uh although many

271
00:11:07,829 --> 00:11:06,720
mechanisms exist to explain these

272
00:11:09,990 --> 00:11:07,839
excesses

273
00:11:13,910 --> 00:11:10,000
uh ultimately the the cause of the

274
00:11:16,150 --> 00:11:13,920
symmetry breaking between y l versus d

275
00:11:18,389 --> 00:11:16,160
remains an open question

276
00:11:19,750 --> 00:11:18,399
um these experiments have shown that

277
00:11:21,590 --> 00:11:19,760
their strong and anti-selective

278
00:11:23,910 --> 00:11:21,600
preferences measured

279
00:11:26,470 --> 00:11:23,920
for spin polarized electrons ejected

280
00:11:28,790 --> 00:11:26,480
from a magnetized substrate

281
00:11:31,350 --> 00:11:28,800
in their interactions with deposited uh

282
00:11:33,350 --> 00:11:31,360
l-histidine amino acids uh it sort of

283
00:11:35,030 --> 00:11:33,360
remains to be seen how the spin

284
00:11:36,949 --> 00:11:35,040
polarized electron

285
00:11:39,350 --> 00:11:36,959
um

286
00:11:41,829 --> 00:11:39,360
molecule these spin polarized electrons

287
00:11:43,030 --> 00:11:41,839
can create these enantiomeric excesses

288
00:11:45,590 --> 00:11:43,040

are within different molecular

289
00:11:48,630 --> 00:11:45,600
populations um

290
00:11:51,190 --> 00:11:48,640
and and this is largely an unexplored

291
00:11:53,829 --> 00:11:51,200
mechanism uh within the field so with

292
00:11:55,350 --> 00:11:53,839
that i'd like to uh thank uh the the

293
00:11:58,150 --> 00:11:55,360
people who helped me out with this work

294
00:12:00,310 --> 00:11:58,160
uh tom and cermane georgia tech and

295
00:12:02,790 --> 00:12:00,320
richard at argonne as well as our

296
00:12:04,870 --> 00:12:02,800
funding from the doe and nasa post

297
00:12:07,030 --> 00:12:04,880
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