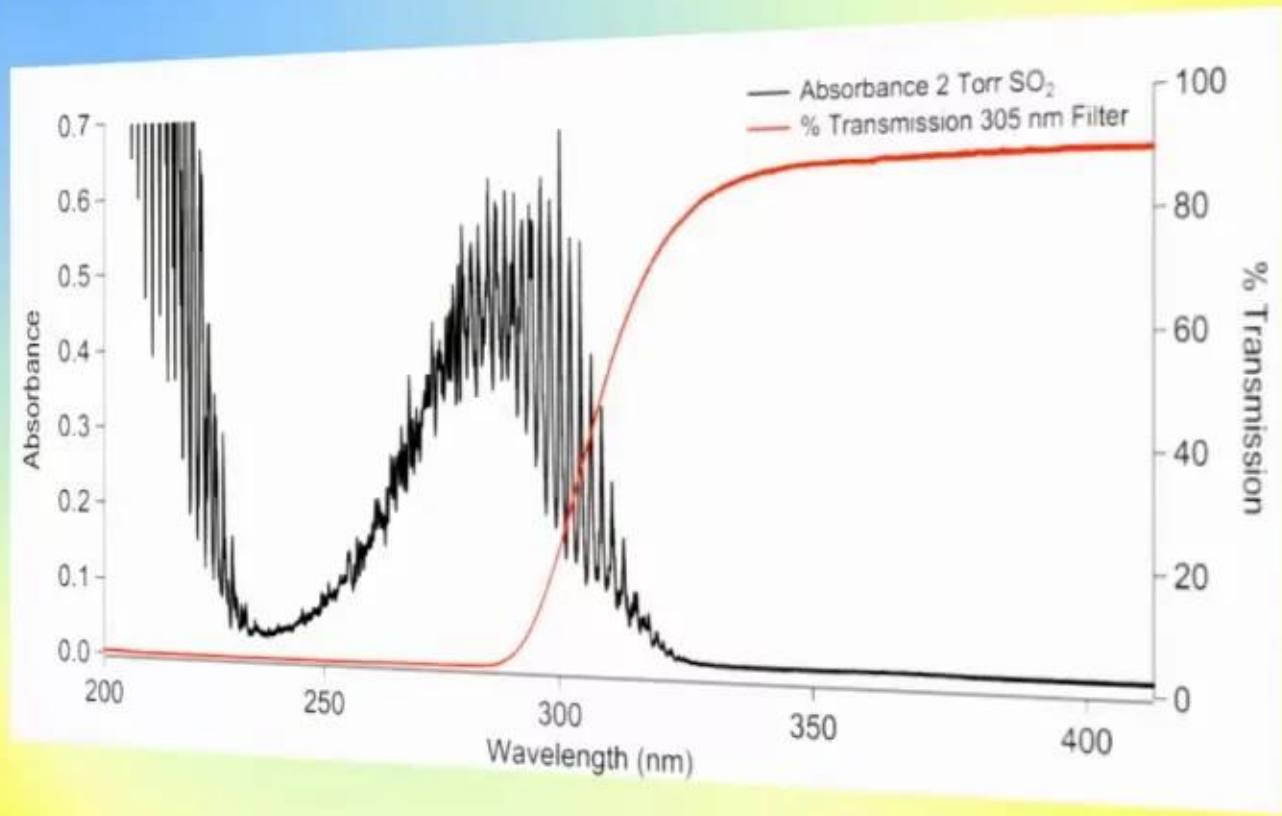
Current Experimental Results



1
00:00:12,930 --> 00:00:10,110
chemistry and so first off really why do

2
00:00:15,570 --> 00:00:12,940
we even care about sulfur and so

3
00:00:20,010 --> 00:00:15,580
particularly sulfur compounds are found

4
00:00:21,690 --> 00:00:20,020
throughout Earth's atmosphere and down

5
00:00:24,240 --> 00:00:21,700
in the lower troposphere they mostly get

6
00:00:26,640 --> 00:00:24,250
rained out through because they're

7
00:00:28,800 --> 00:00:26,650
particularly good at being dissolved in

8
00:00:30,860 --> 00:00:28,810
the rain but up in the upper

9
00:00:33,869 --> 00:00:30,870
stratosphere we see this increase in so2

10
00:00:35,940 --> 00:00:33,879
and this is really important because

11
00:00:38,160 --> 00:00:35,950
these are a major source of aerosol

12
00:00:41,759 --> 00:00:38,170
particularly up in the stratosphere and

13
00:00:44,099 --> 00:00:41,769

so what happens is that sulfur gets

14
00:00:47,220 --> 00:00:44,109
oxidized to form sulfuric acid which

15
00:00:49,709 --> 00:00:47,230
thing can then seed aerosol and that

16
00:00:51,599 --> 00:00:49,719
aerosol does a particularly great job of

17
00:00:53,399 --> 00:00:51,609
scattering light and so it becomes

18
00:00:55,610 --> 00:00:53,409
really important when we're looking at

19
00:00:58,889 --> 00:00:55,620
climates and trying to understand

20
00:01:02,000 --> 00:00:58,899
different processes that are driving the

21
00:01:04,170 --> 00:01:02,010
temperature on a planet and so

22
00:01:08,010 --> 00:01:04,180
traditionally the idea with so2

23
00:01:12,450 --> 00:01:08,020
chemistry is the so2 reacts with o H to

24
00:01:14,789 --> 00:01:12,460
make this HS o 3 and that HS o 3

25
00:01:19,200 --> 00:01:14,799
immediately finds itself running into

26
00:01:21,480 --> 00:01:19,210
oxygen to make H 0 2 plus s 0 3 and then

27
00:01:23,520 --> 00:01:21,490
that s 03 through a water catalyzed

28
00:01:25,649 --> 00:01:23,530
reaction will form sulfuric acid and

29
00:01:27,149 --> 00:01:25,659
ultimately leads to these aerosol

30
00:01:30,029 --> 00:01:27,159
particles with through these small

31
00:01:33,060 --> 00:01:30,039
liquid or solid suspended particles in

32
00:01:35,340 --> 00:01:33,070
the atmosphere so I guess really the

33
00:01:37,170 --> 00:01:35,350
question is what's the problem and the

34
00:01:39,480 --> 00:01:37,180
problem is sulfur compounds have been

35
00:01:43,620 --> 00:01:39,490
observed throughout our solar system not

36
00:01:46,170 --> 00:01:43,630
just on earth in particularly there on

37
00:01:48,359 --> 00:01:46,180
Venus where we have these sulfuric acid

38
00:01:51,719 --> 00:01:48,369

clouds from 50 to 70 kilometers through

39
00:01:54,209 --> 00:01:51,729
the atmosphere but once you get above

40
00:01:56,099 --> 00:01:54,219
those clouds starting about 90

41
00:02:00,870 --> 00:01:56,109
kilometers there's this massive increase

42
00:02:02,819 --> 00:02:00,880
in so2 concentration and these increases

43
00:02:05,190 --> 00:02:02,829
in so2 really exceed any model

44
00:02:08,279 --> 00:02:05,200
predictions by orders of magnitude two

45
00:02:09,660 --> 00:02:08,289
or three orders of magnitude and so what

46
00:02:11,790 --> 00:02:09,670
this really is suggesting it there's

47
00:02:13,979 --> 00:02:11,800
some sort of chemical source of so2 in

48
00:02:16,949 --> 00:02:13,989
the middle atmosphere of Venus that we

49
00:02:19,470 --> 00:02:16,959
don't know about and interestingly

50
00:02:20,670 --> 00:02:19,480
enough this area has very

51
00:02:22,890 --> 00:02:20,680
similar conditions to Earth's

52
00:02:24,990 --> 00:02:22,900
stratosphere in miso sphere so similar

53
00:02:26,869 --> 00:02:25,000
temperatures pressures and water content

54
00:02:32,970 --> 00:02:26,879
is specifically what I'm talking about

55
00:02:35,220 --> 00:02:32,980
and so initially one suggested fix for

56
00:02:38,369 --> 00:02:35,230
this is some work that was done in the

57
00:02:41,400 --> 00:02:38,379
Vita group about 15 years ago I'm

58
00:02:45,180 --> 00:02:41,410
specifically looking at ir overtone

59
00:02:47,789 --> 00:02:45,190
stretches or overtone o-h stretches and

60
00:02:50,399 --> 00:02:47,799
the through this overtone you could put

61
00:02:54,420 --> 00:02:50,409
enough energy in to drive the fatah

62
00:02:57,240 --> 00:02:54,430
lysis of sulfuric acid to form wha water

63
00:03:02,400 --> 00:02:57,250

in s 03 and that s 03 can rapidly photo

64
00:03:05,369 --> 00:03:02,410
lies under standard UV conditions and so

65
00:03:07,559 --> 00:03:05,379
the idea behind this is that you put in

66
00:03:09,479 --> 00:03:07,569
your eye our photon you get this oh h

67
00:03:11,849 --> 00:03:09,489
stretch going and that hydrogen starts

68
00:03:15,180 --> 00:03:11,859
hopping around the molecule jumping from

69
00:03:17,910 --> 00:03:15,190
oxygen to oxygen and eventually it finds

70
00:03:20,160 --> 00:03:17,920
its way to the other oxygen that has a

71
00:03:22,710 --> 00:03:20,170
hydrogen and we get out water plus s 03

72
00:03:24,089 --> 00:03:22,720
this is a very fast process so high up

73
00:03:26,370 --> 00:03:24,099
in the atmosphere in these lower

74
00:03:33,390 --> 00:03:26,380
pressures it can actually out-compete

75
00:03:35,460 --> 00:03:33,400
the collisional deactivation and so a

76
00:03:37,140 --> 00:03:35,470
lot of work was done to actually go and

77
00:03:39,300 --> 00:03:37,150
measure these overtone stretches these

78
00:03:42,809 --> 00:03:39,310
going from V equals zero to four and

79
00:03:44,879 --> 00:03:42,819
five transitions and so you can see

80
00:03:48,000 --> 00:03:44,889
these happen in the red so in the

81
00:03:49,710 --> 00:03:48,010
visible this is particularly important

82
00:03:51,990 --> 00:03:49,720
because UV photons required for

83
00:03:53,580 --> 00:03:52,000
photolysis of sulfuric acid simply

84
00:03:56,550 --> 00:03:53,590
aren't available in the atmosphere

85
00:03:58,470 --> 00:03:56,560
they're filtered out via other

86
00:04:01,020 --> 00:03:58,480
absorption processes higher up in the

87
00:04:06,770 --> 00:04:01,030
atmosphere in Venus it's the co2 doing

88
00:04:09,030 --> 00:04:06,780

it and then interestingly enough these

89
00:04:12,240 --> 00:04:09,040
transitions do provide enough energy to

90
00:04:14,909 --> 00:04:12,250
get over this barrier about 40 kcal per

91
00:04:17,939 --> 00:04:14,919
mole to then go to this s 03 plus water

92
00:04:20,400 --> 00:04:17,949
and this does a really great job of

93
00:04:23,310 --> 00:04:20,410
explaining the so2 vertical profile on

94
00:04:25,379 --> 00:04:23,320
earth unfortunately it's still not good

95
00:04:27,529 --> 00:04:25,389
enough for Venus so even when this is

96
00:04:30,630 --> 00:04:27,539
included in the Venus models we are

97
00:04:32,370 --> 00:04:30,640
still in order or to an order of

98
00:04:35,180 --> 00:04:32,380
magnitude or two below

99
00:04:38,640 --> 00:04:35,190
so2 concentrations that are observed and

100
00:04:40,860 --> 00:04:38,650
so our thought was are there any other

101
00:04:44,520 --> 00:04:40,870
reservoirs for so2 anything else that

102
00:04:46,710 --> 00:04:44,530
could be hiding so2 and so what we are

103
00:04:51,050 --> 00:04:46,720
interested in is looking at sulfurous

104
00:04:54,600 --> 00:04:51,060
acid this h2s 03 and the idea is that

105
00:04:58,820 --> 00:04:54,610
through water a water catalyzed reaction

106
00:05:01,800 --> 00:04:58,830
this could go to s 0 2 plus water and

107
00:05:04,560 --> 00:05:01,810
unlike sulfuric acid sulfurous acid is

108
00:05:06,990 --> 00:05:04,570
energetically the unfavored product it's

109
00:05:08,820 --> 00:05:07,000
actually downhill to go to s 0 2 plus

110
00:05:11,070 --> 00:05:08,830
water and so it's actually really hard

111
00:05:12,870 --> 00:05:11,080
to observe this in the gas phase and

112
00:05:17,790 --> 00:05:12,880
actually hasn't ever been observed in

113
00:05:19,020 --> 00:05:17,800

the gas phase before and so you can see

114
00:05:21,030 --> 00:05:19,030
if you start with the sulfurous acid

115
00:05:22,590 --> 00:05:21,040
it's downhill to these products but you

116
00:05:24,690 --> 00:05:22,600
do have to go through this barrier so

117
00:05:27,090 --> 00:05:24,700
it's possible that with this higher

118
00:05:30,750 --> 00:05:27,100
barrier that there could be this so2 or

119
00:05:39,279 --> 00:05:30,760
this H to so3 product hiding in the

120
00:05:49,689 --> 00:05:47,139
I have a big picture no okay so what's

121
00:05:51,489 --> 00:05:49,699
interesting is we want to know how do

122
00:05:54,279 --> 00:05:51,499
you get sulfurous acid and how do you

123
00:05:56,559 --> 00:05:54,289
get up that hill to make that and so

124
00:05:59,499 --> 00:05:56,569
interestingly enough so2 has this strong

125
00:06:01,989 --> 00:05:59,509
absorption from 250 to 300 and 10 10

126
00:06:04,149 --> 00:06:01,999
nanometers in the atmosphere that's not

127
00:06:07,510 --> 00:06:04,159
filtered out in our atmosphere or and

128
00:06:10,119 --> 00:06:07,520
Venus's and so the idea is that you can

129
00:06:12,549 --> 00:06:10,129
excite from the ground state into this

130
00:06:15,159 --> 00:06:12,559
singlet excited state and then you

131
00:06:17,230 --> 00:06:15,169
internally convert you walk your way

132
00:06:19,689 --> 00:06:17,240
down and you find eventually you can get

133
00:06:23,049 --> 00:06:19,699
this internal conversion to a triplet

134
00:06:26,139 --> 00:06:23,059
state and so the direct process that

135
00:06:28,749 --> 00:06:26,149
goes here is forbidden but you can so2

136
00:06:30,909 --> 00:06:28,759
does make its way here it's known to

137
00:06:32,889 --> 00:06:30,919
react with organics to make sulfates and

138
00:06:41,079 --> 00:06:32,899

so the idea is that it can react with

139
00:06:42,369 --> 00:06:41,089
water to make h2s 03 and so we decided

140
00:06:45,549 --> 00:06:42,379
to do some experiments trying to

141
00:06:47,860 --> 00:06:45,559
actually make this sulfurous acid and so

142
00:06:50,499 --> 00:06:47,870
here i show that transition and what we

143
00:06:54,189 --> 00:06:50,509
use is a filter to cut out anything

144
00:06:57,730 --> 00:06:54,199
below about 300 nanometers specifically

145
00:06:59,439 --> 00:06:57,740
to avoid exciting this deeper UV

146
00:07:01,209 --> 00:06:59,449
absorption which can actually lead to

147
00:07:04,029 --> 00:07:01,219
Fatah lysis of so2 and drive other

148
00:07:08,320 --> 00:07:04,039
chemistry that we aren't interested in

149
00:07:10,959 --> 00:07:08,330
right now and so what we used is we have

150
00:07:14,199 --> 00:07:10,969
this simple glass cell with quartz

151
00:07:16,779 --> 00:07:14,209
windows and we used a this filter to cut

152
00:07:20,820 --> 00:07:16,789
out the higher energy UV light but let

153
00:07:24,040 --> 00:07:20,830
through all of this UVA light really and

154
00:07:29,739 --> 00:07:24,050
then we used a green laser to monitor

155
00:07:31,359 --> 00:07:29,749
the aerosol content in our cell and so

156
00:07:34,329 --> 00:07:31,369
interestingly enough when we turn on the

157
00:07:36,820 --> 00:07:34,339
light we immediately start generating

158
00:07:38,350 --> 00:07:36,830
aerosol it's not a secret that there's

159
00:07:40,269 --> 00:07:38,360
something going on it's not something

160
00:07:45,820 --> 00:07:40,279
you can't see you can visibly see this

161
00:07:47,860 --> 00:07:45,830
aerosol formation and so looking at the

162
00:07:50,050 --> 00:07:47,870
controls we wanted to make sure that

163
00:07:52,089 --> 00:07:50,060

this wasn't something that just shows up

164
00:07:52,690 --> 00:07:52,099
all the time and so if you start with

165
00:07:55,210 --> 00:07:52,700
just

166
00:07:58,210 --> 00:07:55,220
water we don't really see any changes or

167
00:08:01,300 --> 00:07:58,220
if we just use so2 we don't see anything

168
00:08:03,190 --> 00:08:01,310
going on but whenever we use a mixture

169
00:08:07,030 --> 00:08:03,200
of the two we immediately see this

170
00:08:08,680 --> 00:08:07,040
aerosol formation this decrease and so

171
00:08:10,870 --> 00:08:08,690
we're looking at this laser going

172
00:08:12,340 --> 00:08:10,880
through and you can immediately actually

173
00:08:14,950 --> 00:08:12,350
see the laser going through you can

174
00:08:17,320 --> 00:08:14,960
watch the particles move through it and

175
00:08:19,210 --> 00:08:17,330
so this is really exciting this is

176
00:08:21,040 --> 00:08:19,220
really some new results coming out of

177
00:08:23,980 --> 00:08:21,050
our group but what we think we're doing

178
00:08:29,020 --> 00:08:23,990
is actually making this so2 or this h2s

179
00:08:30,490 --> 00:08:29,030
03 and so I'd like to acknowledge the

180
00:08:31,740 --> 00:08:30,500
other members of the vitae group who've

181
00:08:35,170 --> 00:08:31,750
helped me with some of this work

182
00:08:37,420 --> 00:08:35,180
particularly a Katie Platt who is now a

183
00:08:40,390 --> 00:08:37,430
professor see you as well as jamie

184
00:08:42,520 --> 00:08:40,400
donaldson who is the collaborator doing

185
00:08:44,130 --> 00:08:42,530
a lot of the work on the theory end of

186
00:08:47,320 --> 00:08:44,140
this looking at the triplet state

187
00:08:48,760 --> 00:08:47,330
reactions of so2 um as well as our

188
00:09:01,150 --> 00:08:48,770

funding and thank you guys for your time

189
00:09:02,620 --> 00:09:01,160
have any questions for Jay all right in

190
00:09:05,530 --> 00:09:02,630
that case I will use my prerogative and

191
00:09:08,190 --> 00:09:05,540
ask question on my own so how would you

192
00:09:10,890 --> 00:09:08,200
go about confirming that it is h 2 sot

193
00:09:14,710 --> 00:09:10,900
one of the things we want to do is maybe

194
00:09:17,440 --> 00:09:14,720
use a mass spectrometer as well as i'm

195
00:09:19,810 --> 00:09:17,450
working and we just got our cavity ring

196
00:09:23,710 --> 00:09:19,820
down experiment up and going so i could

197
00:09:25,870 --> 00:09:23,720
actually use the this red cavity ring

198
00:09:28,120 --> 00:09:25,880
down to look at the o H stretches and

199
00:09:30,430 --> 00:09:28,130
actually confirm that i'm not making

200
00:09:31,810 --> 00:09:30,440
sulfuric acid because it is possible

201
00:09:34,840 --> 00:09:31,820
there are other rats that would take us

202
00:09:38,050 --> 00:09:34,850
to sulfuric acid we've been careful to

203
00:09:39,750 --> 00:09:38,060
try and remove all H so we pump the sell

204
00:09:41,680 --> 00:09:39,760
out overnight to remove everything

205
00:09:43,300 --> 00:09:41,690
unfortunately if we try and put an o H

206
00:09:45,700 --> 00:09:43,310
scavenger in the cell it turns out that

207
00:09:47,770 --> 00:09:45,710
the triplet state so2 really likes to

208
00:09:50,740 --> 00:09:47,780
react with that o H scavenger and

209
00:09:52,060 --> 00:09:50,750
generates even more impressive clouds so

210
00:09:57,910 --> 00:09:52,070
that's actually something that will be

211
00:09:59,350 --> 00:09:57,920
looking into next as well thank you any

212
00:10:01,600 --> 00:09:59,360
other questions everyone looks like

213
00:10:06,590 --> 00:10:01,610

they're about to applaud yeah but we got

214
00:10:12,960 --> 00:10:09,300
maybe I missed this but do you know what

215
00:10:19,020 --> 00:10:12,970
the reaction efficiency or what percent

216
00:10:21,900 --> 00:10:19,030
of sulfur gets transferred converted the

217
00:10:23,460 --> 00:10:21,910
HS 03 the h2s are three yeah we don't

218
00:10:24,810 --> 00:10:23,470
yet so that's the next thing that I'm

219
00:10:26,430 --> 00:10:24,820
really working on is actually getting

220
00:10:28,440 --> 00:10:26,440
the kinetics down for these sorts of

221
00:10:30,060 --> 00:10:28,450
reactions so that we can actually feed

222
00:10:32,940 --> 00:10:30,070
these back into the models and see

223
00:10:34,650 --> 00:10:32,950
what's going on there okay and I just

224
00:10:36,360 --> 00:10:34,660
another quick question maybe you haven't

225
00:10:39,120 --> 00:10:36,370
thought about this but you know if the

226
00:10:41,970 --> 00:10:39,130
sulfur isotope fractionation would be

227
00:10:43,650 --> 00:10:41,980
mass dependent during this process um so

228
00:10:45,990 --> 00:10:43,660
that's the other exciting thing as we

229
00:10:47,700 --> 00:10:46,000
suspect that it will be and because that

230
00:10:51,030 --> 00:10:47,710
internal conversion is dependent on the

231
00:10:53,430 --> 00:10:51,040
masses and that internal conversion is

232
00:10:55,350 --> 00:10:53,440
related to those vibrations and so

233
00:10:57,870 --> 00:10:55,360
that's another thing especially with

234
00:11:00,180 --> 00:10:57,880
that oh h scavenger that we use we want