Probing the diffuse interstellar medium with observations of selected diatomic molecules:

recent results from observations of ArH^+ and SH

David Neufeld

Johns Hopkins University

SOFIA Teletalk May 6, 2015

A dozen diatomic hydrides have now been detected in diffuse molecular clouds

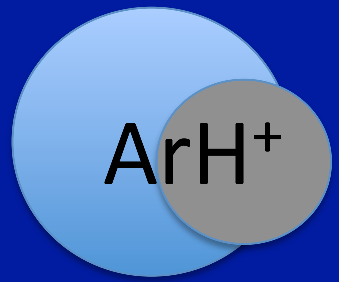
5 ions: CH^+, OH^+, SH^+, HCl^+, ArH^+

6 or 7 neutrals: CH, NH, OH, HF, SiH (tentative), SH, HCl

Orange → detected in past five years

Simple formation mechanisms → carefully interpreted, they provide unique information of general astrophysical interest

Today's teletalk will consider the cases of ArH^+ (observed with *Herschel*/HIFI) and SH (observed with SOFIA/GREAT)



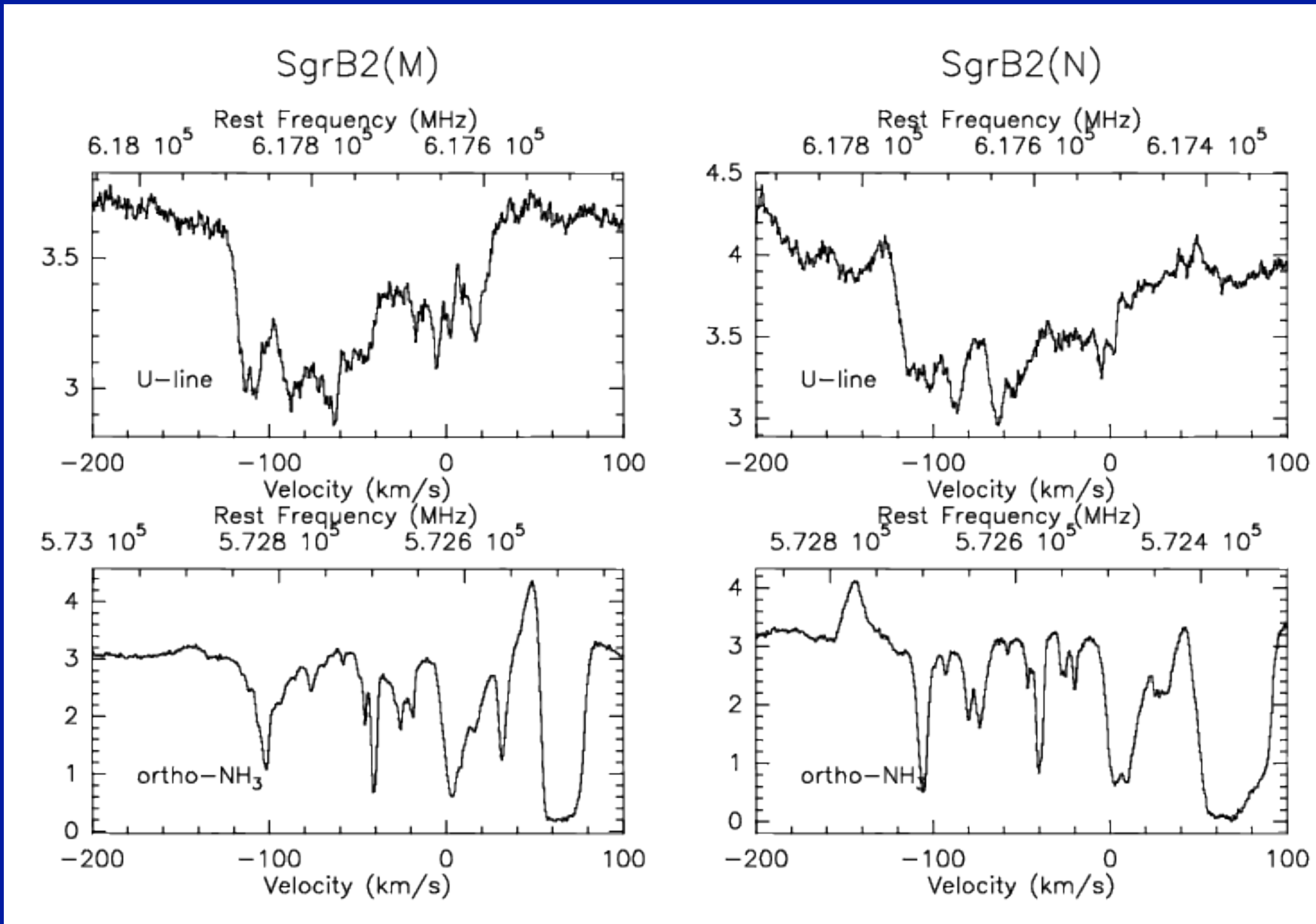
Argonium: the first known interstellar molecule containing a noble gas atom

David Neufeld

P. Schilke, D. A. Neufeld, H. S. P. Müller, et al., A&A 566, A29 (2014)

An unidentified line at 617.5 GHz

- Early Herschel observations with the HIFI instrument (High Resolution Spectrometer) revealed an unidentified absorption feature
  - First observed towards Sgr B2



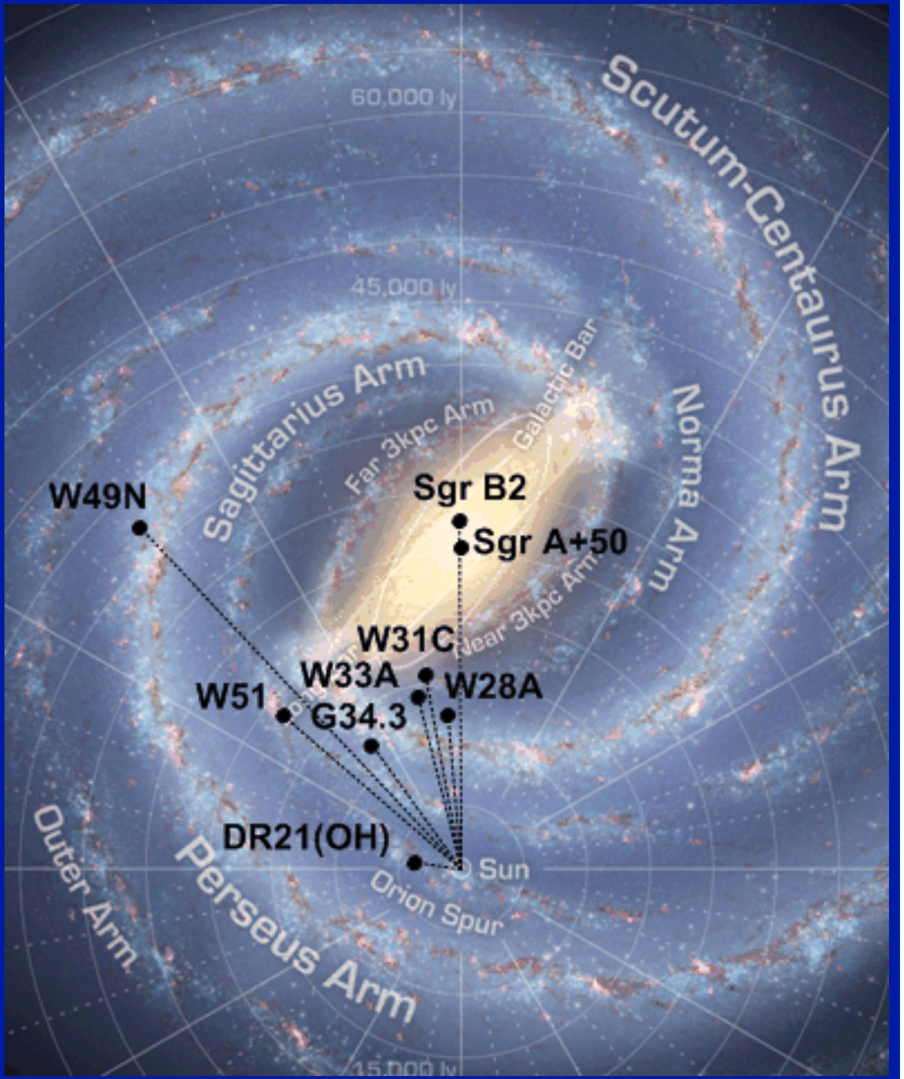
Müller et al. (2013) – using data provided by P. Schilke

An unidentified line at 617.5 GHz

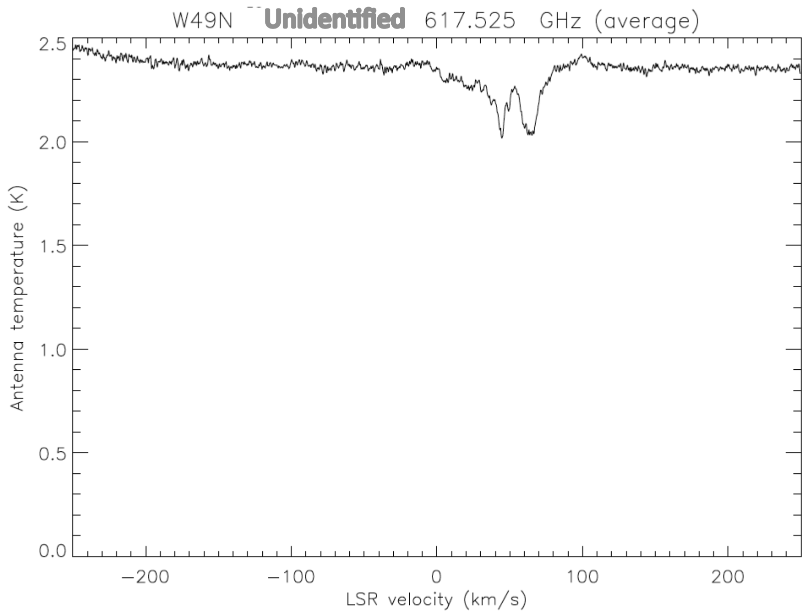
- Early Herschel observations with the HIFI instrument (High Resolution Spectrometer) revealed an unidentified absorption feature
  - First observed towards Sgr B2
  - Also detected towards other bright submillimeter continuum sources

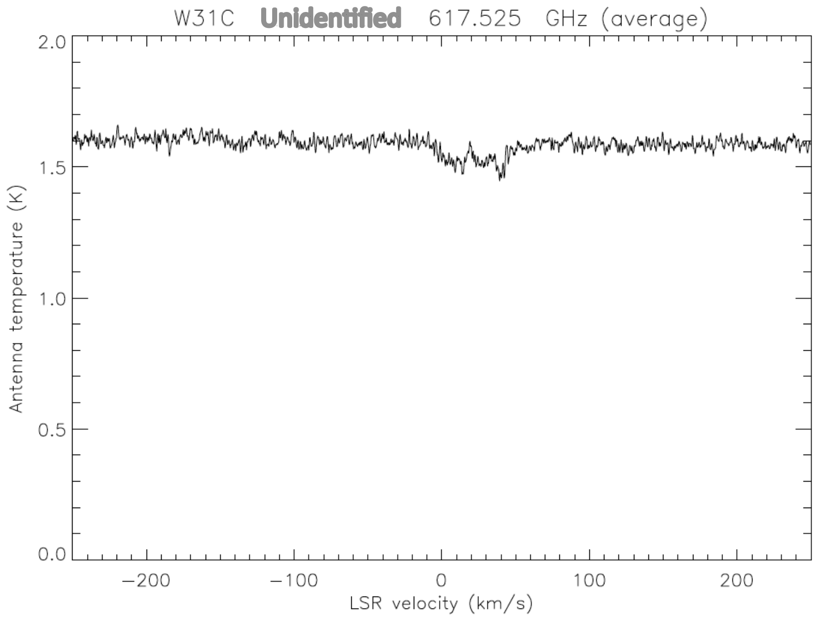
Absorption line observations

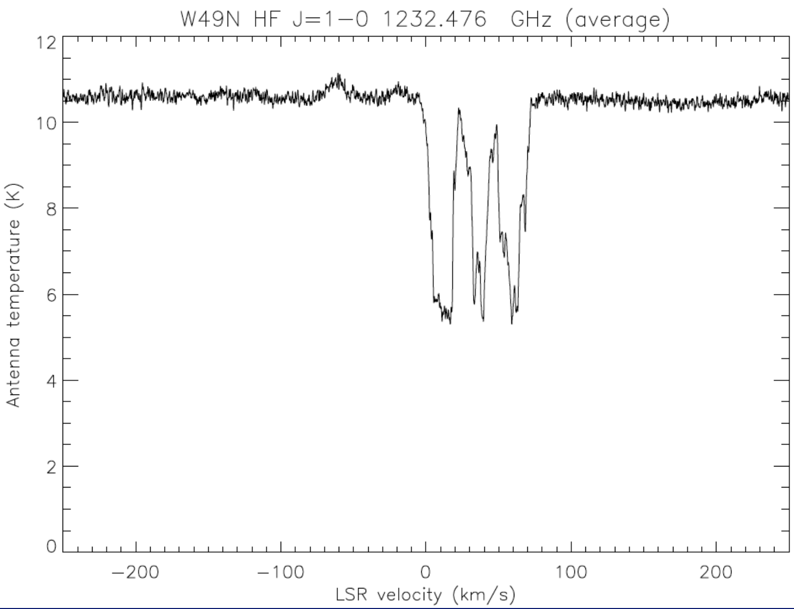
- We can use a very luminous region of massive star formation as a background THz source
- This allows us to search for absorption by gas in foreground material

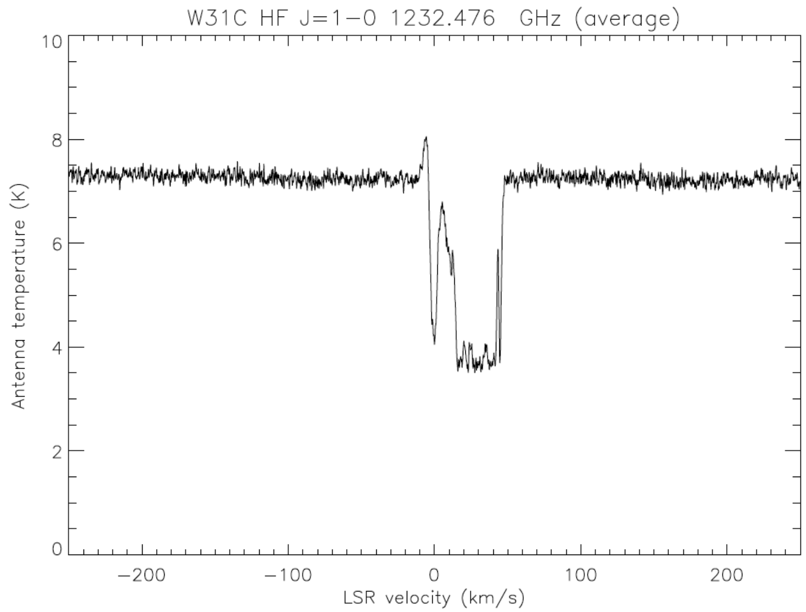


Spectra toward W49N and W31C









An unidentified line at 617.5 GHz

- Early Herschel observations with the HIFI instrument (High Resolution Spectrometer) revealed an unidentified absorption feature
  - First observed towards Sgr B2
  - Also detected towards other bright submillimeter continuum sources
  - Present only in foreground clouds along the sight-line and not in the regions of high-mass star-formation used as a background "lamp"

An unidentified line at 617.5 GHz

- Discussed extensively at the Herschel First Results meeting in Noordwijk in 2010
- On the programs that detected it (HEXOS and PRISMAS) we had top spectroscopists as team members: they had no idea what it could be

It is thus, to the best of our knowledge, the first submillimeter Diffuse Interstellar Band (DIB). The feature may be caused by an atomic or molecular species, possibly in a metastable electronic state. If a rotational transition should cause the absorption then it contains probably at most two hydrogen atoms, two heavy atoms, and possibly not more than three atoms altogether. We do not exclude the possibility that the feature may be caused by a vibration-rotation transition of a fairly large molecule – Müller et al. (2013)

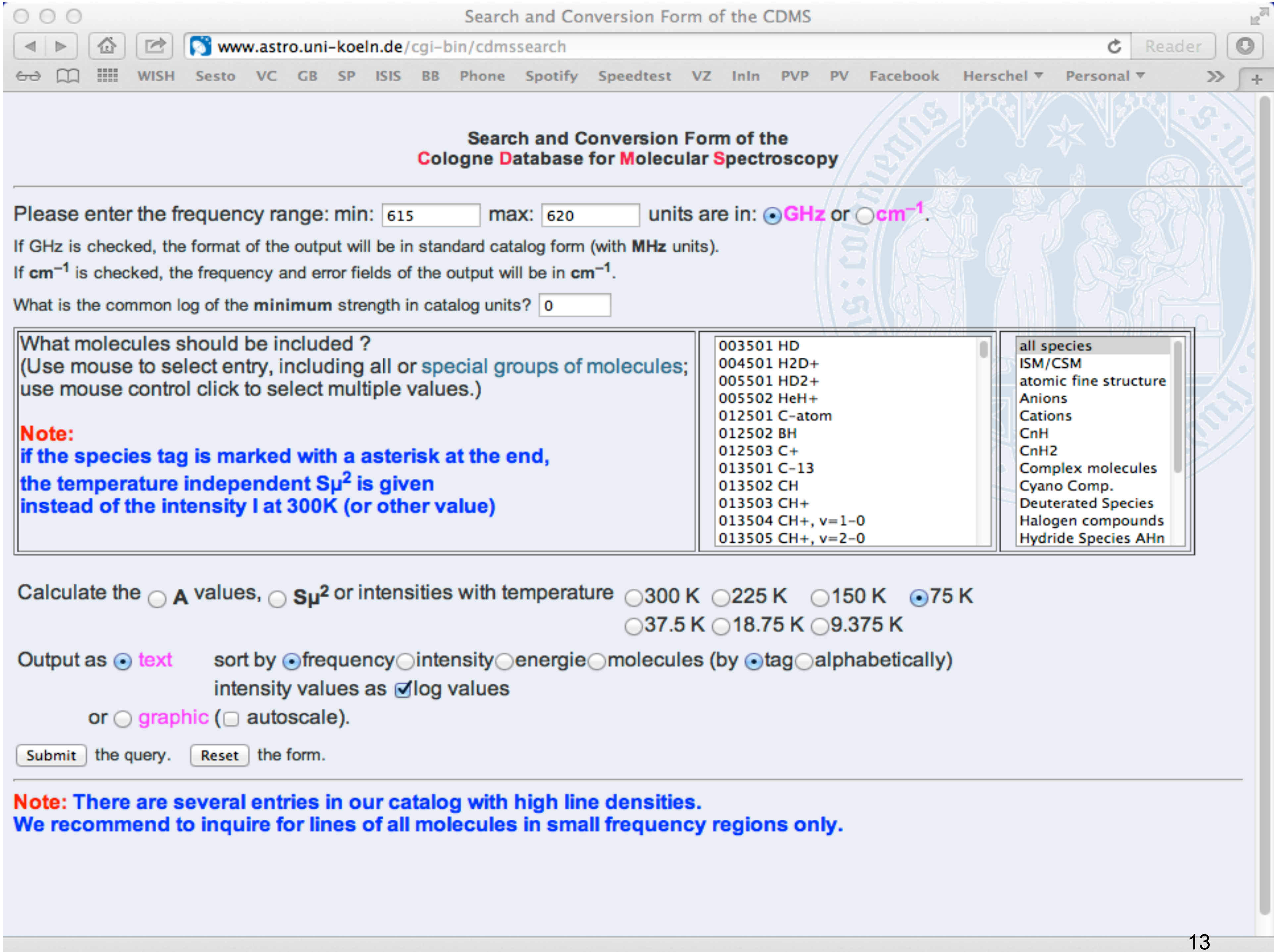
An unidentified line at 617.5 GHz

- Two years ago, again in Noordwijk.....

- Mike Barlow from the MESS team reports the detection of two emission lines from the Crab Nebula, at frequencies of 617.5 and 1235 GHz
  - Low spectral resolution observations using SPIRE
  - Identifies them at $^{36}ArH^+$ J=1-0 and J=2-1

How did we (HEXOS/PRISMAS) miss this?

- Let’s do a quick search of one of the online catalogs (the Cologne Database for Molecular Spectroscopy, maintained by HEXOS team member Holger Müller)



Search and Conversion Form of the CDMS

www.astro.uni-koeln.de/cgi-bin/cdmssearch

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Search and Conversion Form of the
Cologne Database for Molecular Spectroscopy

Please enter the frequency range: min: 615 max: 620 units are in: (•) GHz or ( ) cm^{-1}.

If GHz is checked, the format of the output will be in standard catalog form (with **MHz** units).

If **cm^{-1}** is checked, the frequency and error fields of the output will be in **cm^{-1}**.

What is the common log of the **minimum** strength in catalog units? 0

What molecules should be included ?
(Use mouse to select entry, including all or special groups of molecules; use mouse control click to select multiple values.)

Note:
if the species tag is marked with a asterisk at the end, the temperature independent $S\mu^2$ is given instead of the intensity I at 300K (or other value)

003501 HD
004501 H2D+
005501 HD2+
005502 HeH+
012501 C-atom
012502 BH
012503 C+
013501 C-13
013502 CH
013503 CH+
013504 CH+, v=1-0
013505 CH+, v=2-0

all species
ISM/CSM
atomic fine structure
Anions
Cations
CnH
CnH2
Complex molecules
Cyano Comp.
Deuterated Species
Halogen compounds
Hydride Species AHn

Calculate the ( ) **A** values, ( ) **$S\mu^2$** or intensities with temperature ( ) 300 K ( ) 225 K ( ) 150 K (•) 75 K ( ) 37.5 K ( ) 18.75 K ( ) 9.375 K

Output as (•) text sort by (•) frequency ( ) intensity ( ) energie ( ) molecules (by (•) tag ( ) alphabetically)
intensity values as [x] log values
or ( ) graphic ([ ] autoscale).

Submit the query. Reset the form.

Note: There are several entries in our catalog with high line densities.
We recommend to inquire for lines of all molecules in small frequency regions only.

www.astro.uni-koeln.de/cgi-bin/cdmssearch

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(For units and further details on the catalog entries see the **General** section.)

```
 frequency | uncert.   | intens.  |  | E.lower  |  | tag  |   | quantum nos:  up-low |   molecule

 615858.1345     0.0502    0.86299 2    0.0000   3  41504 101 1             0            ArH+
 616153.5500      0.837     1.1228 3  749.435   45  32504 999 22 -7 16   1 22 -6 17  1   *CH3OH, vt=0,1
 616556.2870      0.258     0.7252 3  656.900   47  32504 999 23 +8 16   0 24 +7 18  0   *CH3OH, vt=0,1
 616721.7340      0.129     0.4458 3  539.064   37  32504 999 18 +9 10   0 19 +8 12  0   *CH3OH, vt=0,1
 616750.0160       0.03    0.52402 2   72.0122153 -30509 101 8              7            N2D+
 616979.9840       0.05     0.5645 3   13.556    9 -32504 999  4 -2  3   0  3 -1  3  0   *CH3OH, vt=0,1
 617525.2256     0.1512    0.86628 2    0.0000   3  37502 101 1             0            Ar-36-H+
 617568.4120      0.702      1.114 3  714.130   43  32504 999 21 -7 15   1 21 -6 16  1   *CH3OH, vt=0,1
 618051.0900      0.024     1.0196 3  133.902   27  33502 999 13  1 12 -0 12  1 11 -0   *C-13-H3OH, vt=0,1
 618716.6070      0.034     0.3535 3  181.656   23  32504 999 11  5  7 +0 12  4  8 +0   *CH3OH, vt=0,1
 618717.9370      0.034     0.3535 3  181.656   23  32504 999 11  5  6 -0 12  4  9 -0   *CH3OH, vt=0,1
 618803.9630      0.587     1.1027 3  680.423   41  32504 999 20 -7 14   1 20 -6 15  1   *CH3OH, vt=0,1
 619074.5410       0.03     0.0762 3   91.244   15  32504 999  7 +4  3   0  8 +3  5  0   *CH3OH, vt=0,1
 619300.4281      0.035    0.71355 2   82.6415  19 -32505 101 9             8             DCO-18+
 619787.9760      1.197     1.2485 3  556.848   53  33502 999 26  2 25 -0 26  1 26 +0   *C-13-H3OH, vt=0,1
 619873.3500      0.491     1.0889 3  648.314   39  32504 999 19 -7 13   1 19 -6 14  1   *CH3OH, vt=0,1
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618717.9370	0.034	0.3535	3	181.656	23	32504	999	11 5 6 -0 12 4 9 -0	*CH3OH, vt=0,1
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- Until July 2012, erroneous frequencies had been entered for $^{36}ArH^+$

Ar-36-H+

www.astro.uni-koeln.de/cgi-bin/cdmsinfo?file=e037502.cat

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$^{36}ArH^+$

Argon hydride cation, $^1\Sigma^+$, ^{36}Ar isotopic species

Species tag	037502
Version	1*
Date of Entry	Sep. 2007
Contributor	H. S. P. Müller

Pure rotational as well as rovibrational data of several isotopic species of ArH^+ have been fit simultaneously.
The J = 1 – 0 transition frequency was reported in
(1) K. B. Laughlin, G. A. Blake, R. C. Cohen, D. C. Hovde, and R. J. Saykally, 1987, *Phys. Rev. Lett.*, **58**, 996.
Additional lines up to J = 7 – 6 were taken from
(2) J. M. Brown, D. A. Jennings, M. Vanek, L. R. Zink, and K. Evenson, 1988, *J. Mol. Spectrosc.* **128**, 587.

The J = 1 – 0 transition frequencies of three ArD^+ isotopic species involving ^{40}Ar, ^{36}Ar, and ^{38}Ar, were published by
(3) W. C. Bowman, G. M. Plummer, E. Herbst, and F. C. De Lucia, 1983, *J. Chem. Phys.* **79**, 2093;
the reported uncertainties for the ^{40}Ar and ^{36}Ar species have been increased somewhat.

High-J pure rotational transition frequencies of ArD^+ were taken from
H. Odashima, A. Kozato, F. Matsushima, S. Tsunekawa, and K. Takagi, 1999, *J. Mol. Spectrosc.* **195**, 356.

High-J pure rotational transitions of ArH^+ up to high vibrational states were detected in the lower infrared region by
(5) D. J. Liu, W. C. Ho, and T. Oka, 1987, *J. Chem. Phys.* **87**, 2442.

Rovibrational transitions of ArH^+ were recorded by
(6) J. W. Brault and S. P. Davis, 1982, *Physica Scripta* **25**, 268.

Additional high-v transitions as well as transitions of ArD^+ were reported by
(7) J. W. C. Johns, 1984, *J. Mol. Spectrosc.* **106**, 124.

Infrared data for $^{36}ArH^+$ and $^{38}ArH^+$ was provided by
(8) R. R. Filueira and C. E. Blom, 1988, *J. Mol. Spectrosc.* **127**, 279.
There is great consistency among essentially all experimental data. Therefore, it may well be that ion drift effects on the reported frequencies are small. Nevertheless, all predictions should be viewed with some caution, especially if the calculated uncertainties exceed 2 MHz by far.

There are no experimental transitions frequencies for $^{36}ArH^+$; reliable predictions can be derived from the available species.

Note: July 2012: the rest frequencies provided for $^{36}ArH^+$ actually refered the the first excited vibrational state. This has now been corrected. Version number and date have been retained. Thanks to Al Wooten for pointinmg this out.
The dipole moment was assumed to agree with that of the main species, see e041504.cat.
The partition function takes into account all vibrational states used in the fit. Non-zero contributions of individual vibrational states to the partition function are given in parentheses.

Lines Listed	27
Frequency / GHz	< 15246
Max. J	27
log STR0	-15.0
log STR1	-15.0
Isotope Corr.	-2.473
Egy / (cm^{-1})	0.0
μ_a / D	2.177
μ_b / D	
μ_c / D	
A	
B	308799.9
C	
Q(1000.)	70.1261 (68.3714, 1.7024, 0.0504, 0.0018, 0.0001)
Q(500.0)	34.2326 (34.2122, 0.0204)
Q(300.0)	20.6293 (20.6293, 0.0001)
Q(225.0)	15.5478 (15.5478)
Q(150.0)	10.4739 (10.4739)
Q(75.00)	5.4108 (5.4108)
Q(37.50)	2.8930 (2.8930)
Q(18.75)	1.6617 (1.6617)
Q(9.375)	1.1275 (1.1275)
detected in ISM/CSM	no

$^{36}ArH^+$

Argon hydride cation, $^1\Sigma^+$, ^{36}Ar isotopic species

Species tag	037502
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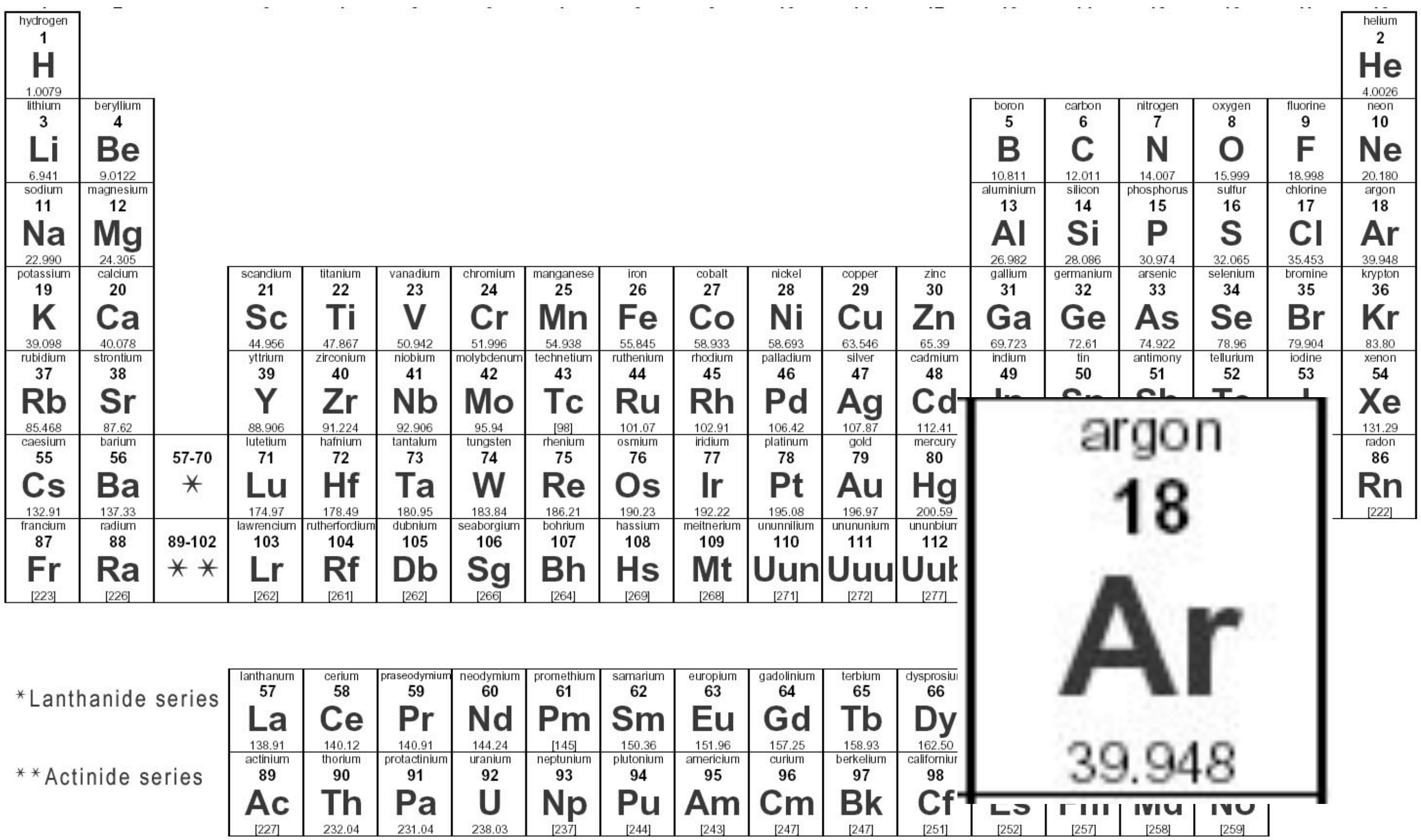
- Until July 2012, erroneous frequencies had been entered for $^{36}ArH^{+}$
- Any chemist knows the atomic weight of argon is ~ 40 and ^{40}Ar is the dominant isotope

hydrogen 1 **H** 1.0079																		helium 2 **He** 4.0026
lithium 3 **Li** 6.941	beryllium 4 **Be** 9.0122												boron 5 **B** 10.811	carbon 6 **C** 12.011	nitrogen 7 **N** 14.007	oxygen 8 **O** 15.999	fluorine 9 **F** 18.998	neon 10 **Ne** 20.180
sodium 11 **Na** 22.990	magnesium 12 **Mg** 24.305												aluminium 13 **Al** 26.982	silicon 14 **Si** 28.086	phosphorus 15 **P** 30.974	sulfur 16 **S** 32.065	chlorine 17 **Cl** 35.453	argon 18 **Ar** 39.948
potassium 19 **K** 39.098	calcium 20 **Ca** 40.078		scandium 21 **Sc** 44.956	titanium 22 **Ti** 47.867	vanadium 23 **V** 50.942	chromium 24 **Cr** 51.996	manganese 25 **Mn** 54.938	iron 26 **Fe** 55.845	cobalt 27 **Co** 58.933	nickel 28 **Ni** 58.693	copper 29 **Cu** 63.546	zinc 30 **Zn** 65.39	gallium 31 **Ga** 69.723	germanium 32 **Ge** 72.61	arsenic 33 **As** 74.922	selenium 34 **Se** 78.96	bromine 35 **Br** 79.904	krypton 36 **Kr** 83.80
rubidium 37 **Rb** 85.468	strontium 38 **Sr** 87.62		yttrium 39 **Y** 88.906	zirconium 40 **Zr** 91.224	niobium 41 **Nb** 92.906	molybdenum 42 **Mo** 95.94	technetium 43 **Tc** [98]	ruthenium 44 **Ru** 101.07	rhodium 45 **Rh** 102.91	palladium 46 **Pd** 106.42	silver 47 **Ag** 107.87	cadmium 48 **Cd** 112.41	indium 49 **In** 114.82	tin 50 **Sn** 118.71	antimony 51 **Sb** 121.76	tellurium 52 **Te** 127.60	iodine 53 **I** 126.90	xenon 54 **Xe** 131.29
caesium 55 **Cs** 132.91	barium 56 **Ba** 137.33	57-70 *	lutetium 71 **Lu** 174.97	hafnium 72 **Hf** 178.49	tantalum 73 **Ta** 180.95	tungsten 74 **W** 183.84	rhenium 75 **Re** 186.21	osmium 76 **Os** 190.23	iridium 77 **Ir** 192.22	platinum 78 **Pt** 195.08	gold 79 **Au** 196.97	mercury 80 **Hg** 200.59	thallium 81 **Tl** 204.38	lead 82 **Pb** 207.2	bismuth 83 **Bi** 208.98	polonium 84 **Po** [209]	astatine 85 **At** [210]	radon 86 **Rn** [222]
francium 87 **Fr** [223]	radium 88 **Ra** [226]	89-102 **	lawrencium 103 **Lr** [262]	rutherfordium 104 **Rf** [261]	dubnium 105 **Db** [262]	seaborgium 106 **Sg** [266]	bohrium 107 **Bh** [264]	hassium 108 **Hs** [269]	meitnerium 109 **Mt** [268]	ununnilium 110 **Uun** [271]	unununium 111 **Uuu** [272]	ununbium 112 **Uub** [277]		ununquadium 114 **Uuq** [289]				

*Lanthanide series	lanthanum 57 **La** 138.91	cerium 58 **Ce** 140.12	praseodymium 59 **Pr** 140.91	neodymium 60 **Nd** 144.24	promethium 61 **Pm** [145]	samarium 62 **Sm** 150.36	europium 63 **Eu** 151.96	gadolinium 64 **Gd** 157.25	terbium 65 **Tb** 158.93	dysprosium 66 **Dy** 162.50	holmium 67 **Ho** 164.93	erbium 68 **Er** 167.26	thulium 69 **Tm** 168.93	ytterbium 70 **Yb** 173.04
**Actinide series	actinium 89 **Ac** [227]	thorium 90 **Th** 232.04	protactinium 91 **Pa** 231.04	uranium 92 **U** 238.03	neptunium 93 **Np** [237]	plutonium 94 **Pu** [244]	americium 95 **Am** [243]	curium 96 **Cm** [247]	berkelium 97 **Bk** [247]	californium 98 **Cf** [251]	einsteinium 99 **Es** [252]	fermium 100 **Fm** [257]	mendelevium 101 **Md** [258]	nobelium 102 **No** [259]



IUPAC atomic weight: 39.948

Isotopic ratios

^{36}Ar: 0.33%

^{38}Ar: 0.06%

^{40}Ar: 99.6%

www.astro.uni-koeln.de/cgi-bin/cdmssearch

```
(For units and further details on the catalog entries see the General section.)
  frequency | uncert.  | intens.   | | E.lower |   | tag   |   | quantum nos:  up-low |   molecule

 615858.1345     0.0502    0.86299 2    0.0000   3  41504 101 1            0             ArH+
 616153.5500      0.837     1.1228 3  749.435   45  32504 999 22 -7 16   1 22 -6 17   1   *CH3OH, vt=0,1
 616556.2870      0.258     0.7252 3  656.900   47  32504 999 23 +8 16   0 24 +7 18   0   *CH3OH, vt=0,1
 616721.7340      0.129     0.4458 3  539.064   37  32504 999 18 +9 10   0 19 +8 12   0   *CH3OH, vt=0,1
 616750.0160       0.03    0.52402 2   72.0122153 -30509 101 8             7             N2D+
 616979.9840       0.05     0.5645 3   13.556    9 -32504 999  4 -2  3   0  3 -1  3   0   *CH3OH, vt=0,1
 617525.2256     0.1512    0.86628 2    0.0000   3  37502 101 1            0             Ar-36-H+
 617568.4120      0.702      1.114 3  714.130   43  32504 999 21 -7 15   1 21 -6 16   1   *CH3OH, vt=0,1
 618051.0900      0.024     1.0196 3  133.902   27  33502 999 13  1 12 -0 12  1 11 -0   *C-13-H3OH, vt=0,1
 618716.6070      0.034     0.3535 3  181.656   23  32504 999 11  5  7 +0 12  4  8 +0   *CH3OH, vt=0,1
 618717.9370      0.034     0.3535 3  181.656   23  32504 999 11  5  6 -0 12  4  9 -0   *CH3OH, vt=0,1
 618803.9630      0.587     1.1027 3  680.423   41  32504 999 20 -7 14   1 20 -6 15   1   *CH3OH, vt=0,1
 619074.5410       0.03     0.0762 3   91.244   15  32504 999  7 +4  3   0  8 +3  5   0   *CH3OH, vt=0,1
 619300.4281      0.035    0.71355 2   82.6415  19 -32505 101 9            8             DCO-18+
 619787.9760      1.197     1.2485 3  556.848   53  33502 999 26  2 25 -0 26  1 26 +0   *C-13-H3OH, vt=0,1
 619873.3500      0.491     1.0889 3  648.314   39  32504 999 19 -7 13   1 19 -6 14   1   *CH3OH, vt=0,1
```

We don't see $^{40}ArH^+$ at 615.858 GHz (simply designated ArH^+ in the catalog)

Isotopic ratios

^{36}Ar: 0.33%

^{38}Ar: 0.06%

^{40}Ar: 99.6%

Isotopic ratios

^{36}Ar: 0.33%

^{38}Ar: 0.06%

^{40}Ar: 99.6%

On Earth

Isotopic ratios

^{36}Ar: 0.33%

^{38}Ar: 0.06%

^{40}Ar: 99.6%

On Earth

But most argon in Earth's atmosphere comes from decay of ^{40}K in the crust

Isotopic ratios

^{36}Ar: 84.6%

^{38}Ar: 15.4%

^{40}Ar: 0.02%

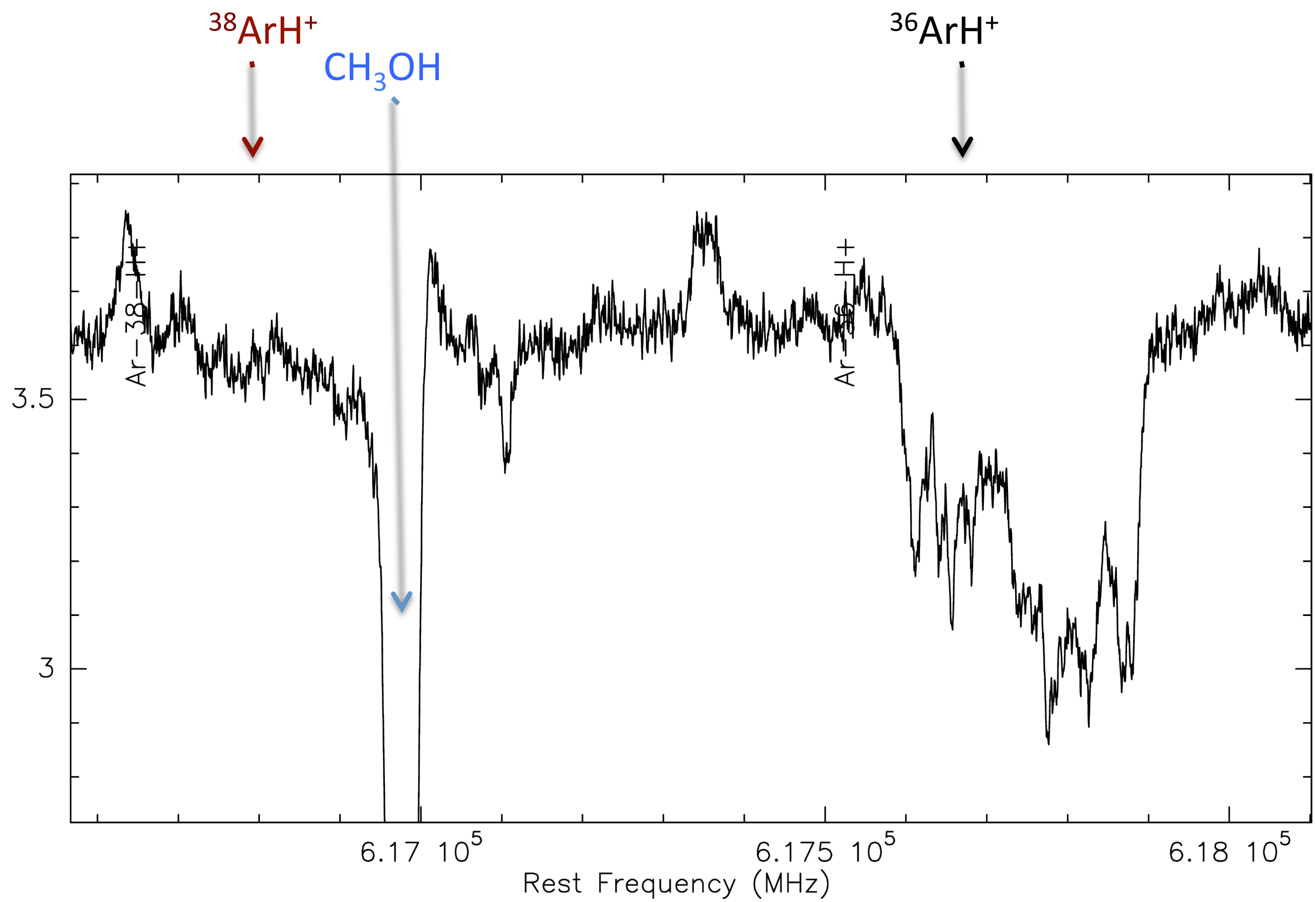
Solar system

But most argon in Earth's atmosphere comes from decay of ^{40}K in the crust

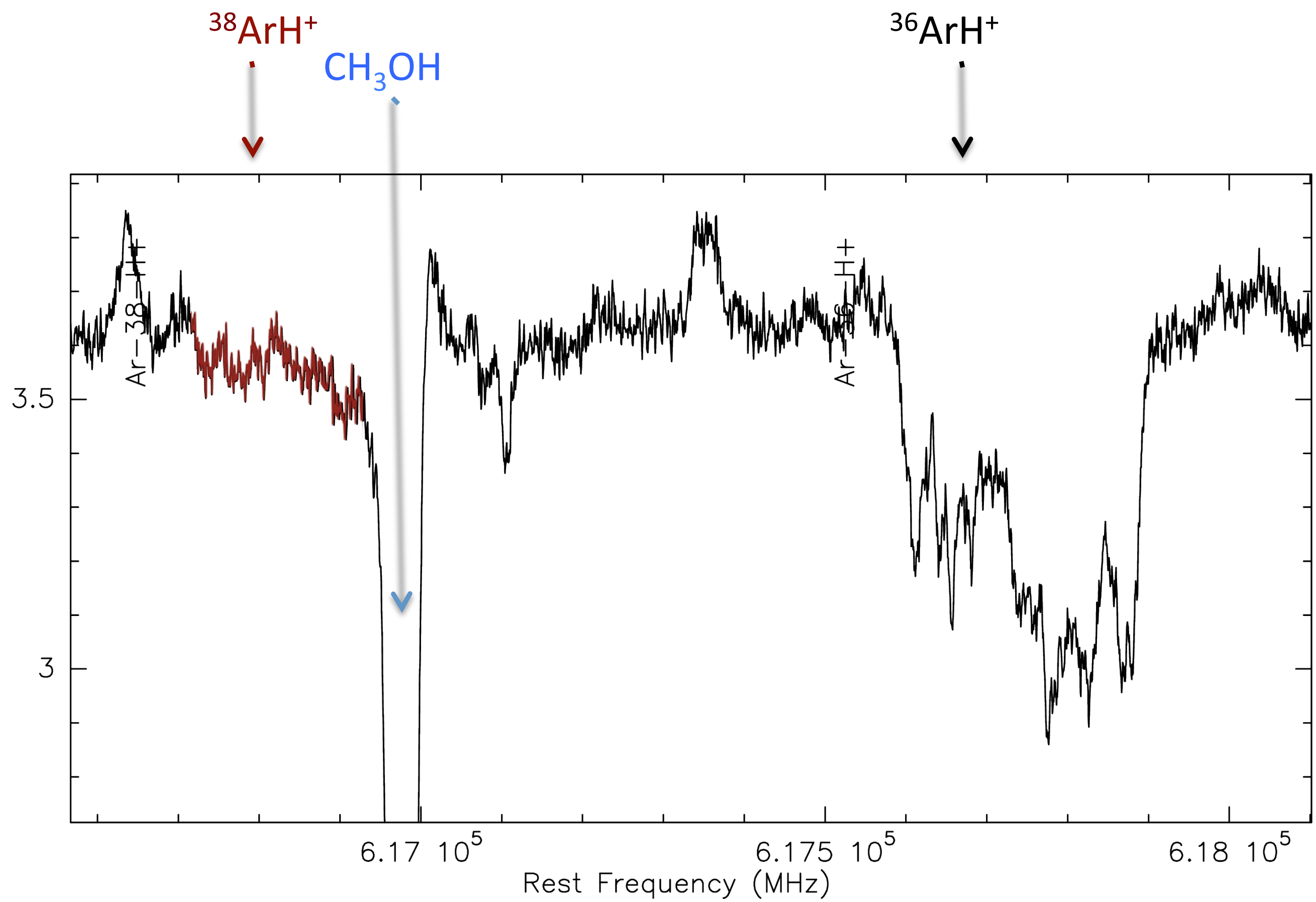
Is our 617.5 GHz absorption line really ArH^+?

- MESS identification is based on two emission lines: J = 1 – 0 and J = 2 – 1
- We only have J = 1 – 0 in diffuse clouds
- ArH^+ doesn't sound very plausible as a constituent of diffuse interstellar clouds
- Solar $^{38}Ar/^{36}Ar = 0.18$. We can look for $^{38}ArH^+$

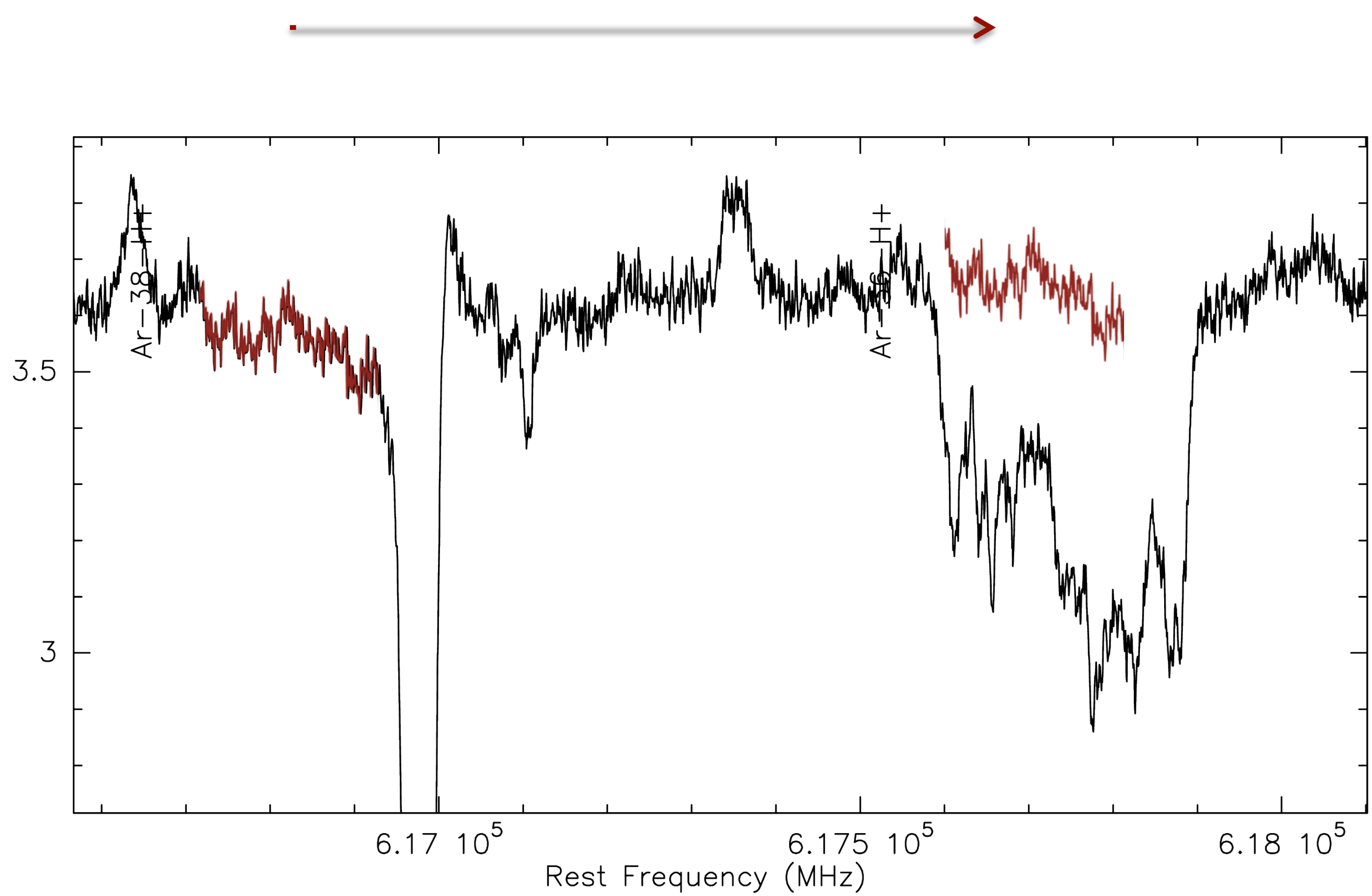
$^{38}ArH^+$ and $^{36}ArH^+$ in Sgr B2



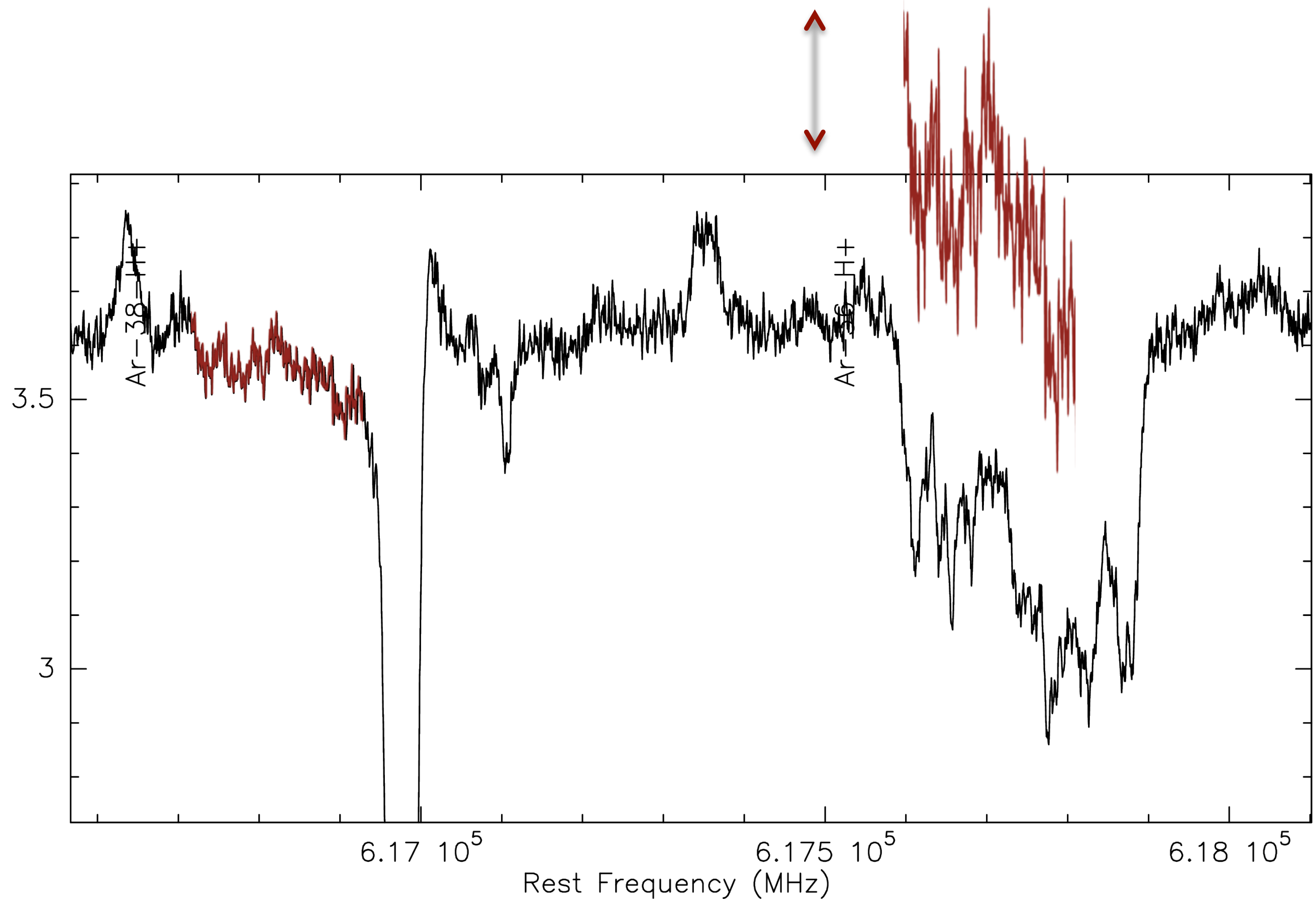
$^{38}ArH^+$ and $^{36}ArH^+$ in Sgr B2



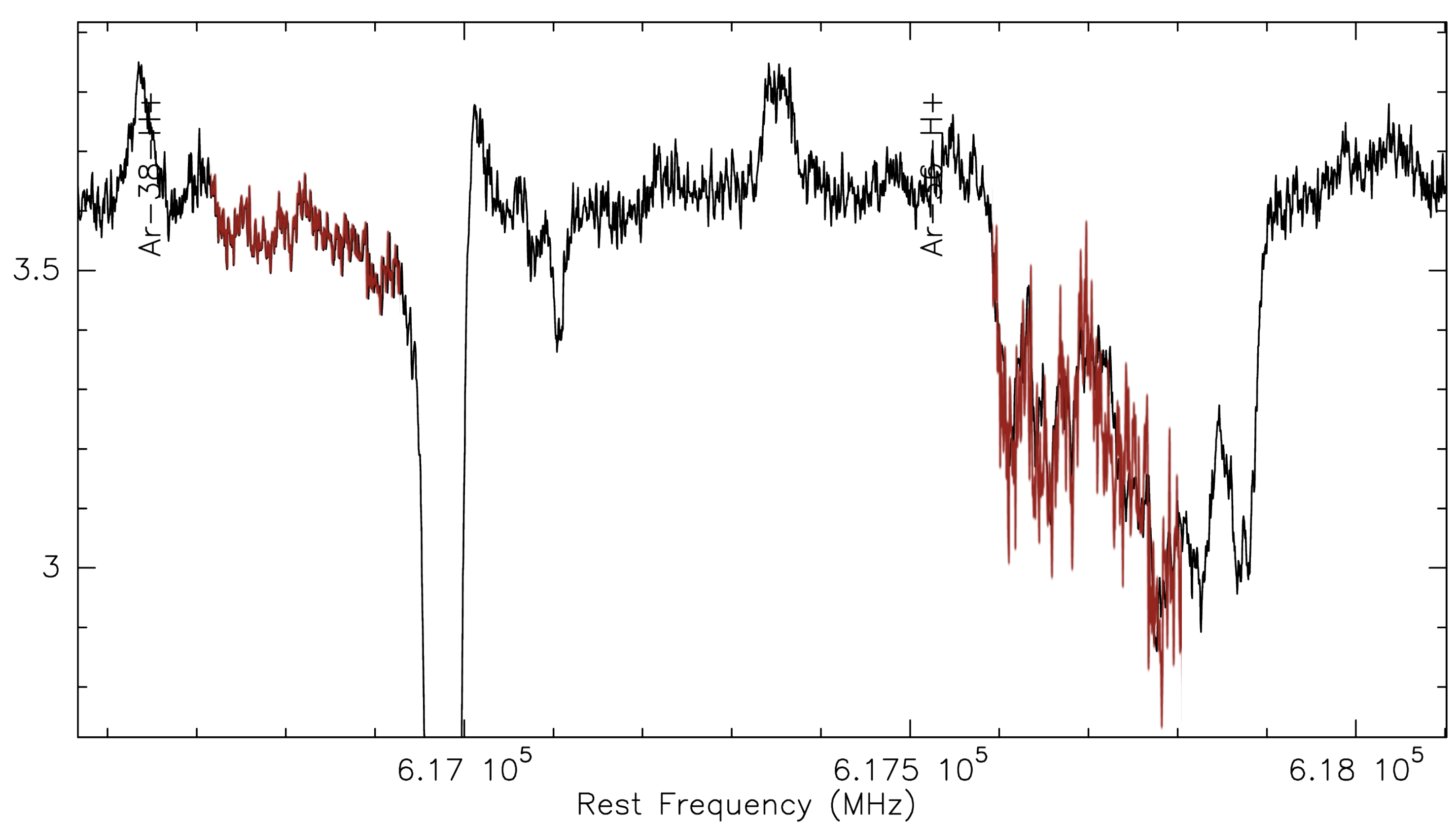
$^{38}ArH^+$ and $^{36}ArH^+$ in Sgr B2



$^{38}ArH^+$ and $^{36}ArH^+$ in Sgr B2



$^{38}ArH^+$ and $^{36}ArH^+$ in Sgr B2



ArH^+ is isoelectronic with HCl

J = 3

1876 GHz

J = 2

1251 GHz

J = 1

626 GHz

J = 0

HCl X $^1\Sigma$

ArH^+ is isoelectronic with HCl

J = 3

1851 GHz

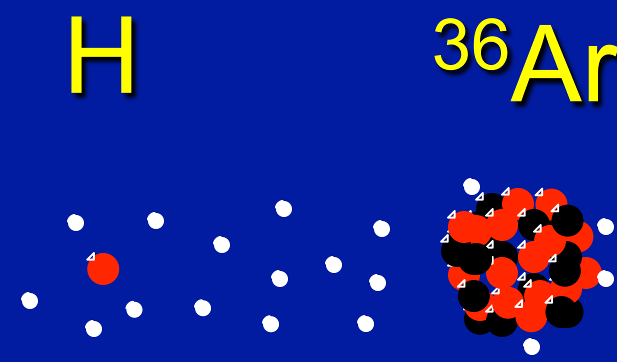
J = 2

1235 GHz

J = 1

617.5 GHz

J = 0



ArH^+ X $^1\Sigma$

How could ArH^+ be produced?

- In general, there are two main reactions that can produce a molecular ion XH^+
  - H-atom abstraction: $X^+ + H_2 \rightarrow XH^+ + H$
  - Proton transfer: $X + H_3^+ \rightarrow XH^+ + H_2$

But the basic thermochemistry looks very unfavorable

- Ionization potential of Ar = 15.76 eV
  - Greater than IP of H (13.61eV), so Ar is mainly neutral in atomic clouds
  - Relatively little Ar^+ available to produce argonium via $Ar^+ + H_2 \rightarrow ArH^+ + H$ reaction

- Proton affinity of Ar = 369 kJ mol^{-1}
  - Smaller than PA of H_2 (422 kJ mol^{-1}), so Ar does not react with H_3^+ at low temperature
  - Worse yet, ArH^+ will transfer a proton to H_2 (or O, C, CO……), resulting in its destruction

But a couple of silver linings....

- Ar^+ can be produced by direct cosmic ray ionization of Ar: the rate is 10 times that for H

- Once produced, Ar^+ does react rapidly with H_2 to produce argonium:

  $Ar^+ + H_2 \rightarrow ArH^+ + H$

But a couple of silver linings….

An important difference with Ne and He

Reaction of $Ne^+ + H_2$ yields $Ne + H + H^+$

Energetically possible, because ionization potential of Ne is 21.56 eV > IP(H) + $D_0(H_2)$ = 18.09 eV

Same thing with He, because IP (He) =24.58 eV

But for argon (IP = 15.76 eV), the only product channel is ArH^+

Even so, the equilibrium abundance of ArH^+ would be extremely small, except for two very unusual peculiarities of argonium

- The dissociative recombination rate is ususually small. For most diatomic molecular ions, $XH^+ + e \rightarrow X + H$ is very rapid, with a rate coefficient ~ 10^{-7} cm^3 s^{-1}
- For argonium, it's too small to measure

  $k < 10^{-9}$ cm^3 s^{-1}

Even so, the equilibrium abundance of ArH^+ would be extremely small, except for two very unusual peculiarities of argonium

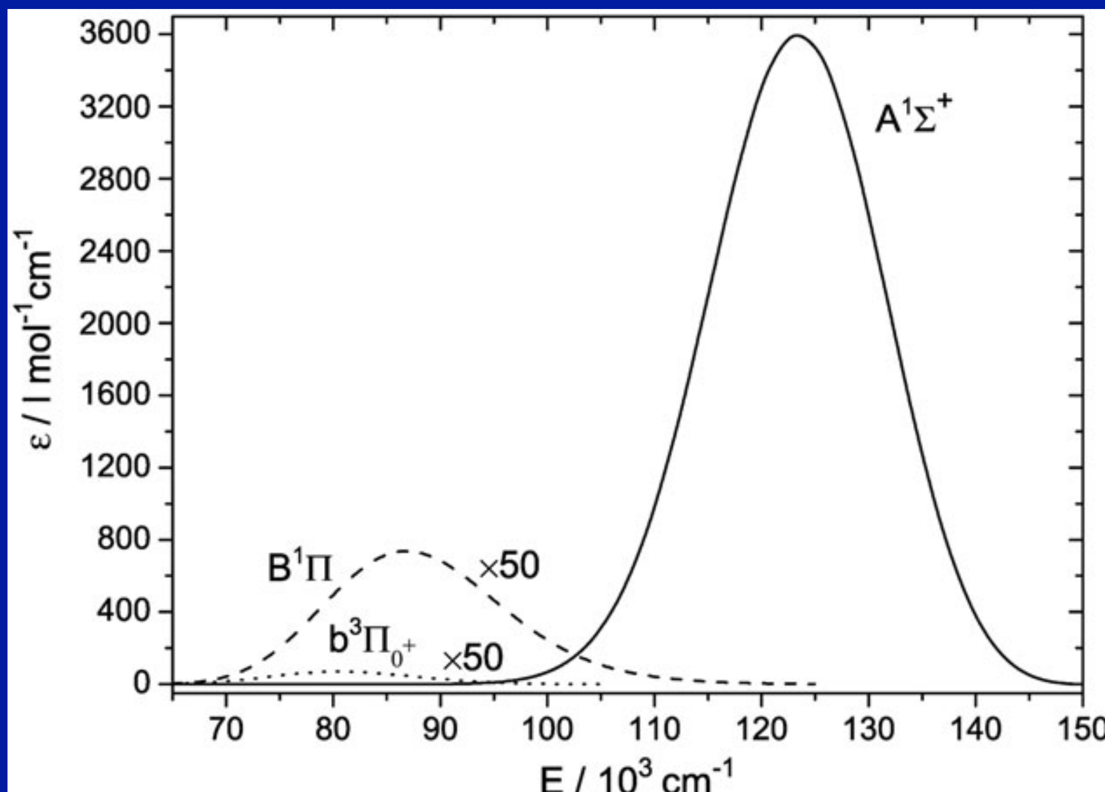
- The photodissociation rate is very small. For most diatomic molecules, the photodissociation rate is ~ $10^{-9}\ s^{-1}$
- For argonium, it is $1.1 \times 10^{-11}\ s^{-1}$

Photodissociation cross-section

Theoretical study of the ArH^+ photodissociation†

Aleksey B. Alekseyev,* Heinz–Peter Liebermann and Robert J. Buenker

Received 2nd May 2007, Accepted 20th June 2007
First published as an Advance Article on the web 24th July 2007
DOI: 10.1039/b706670h



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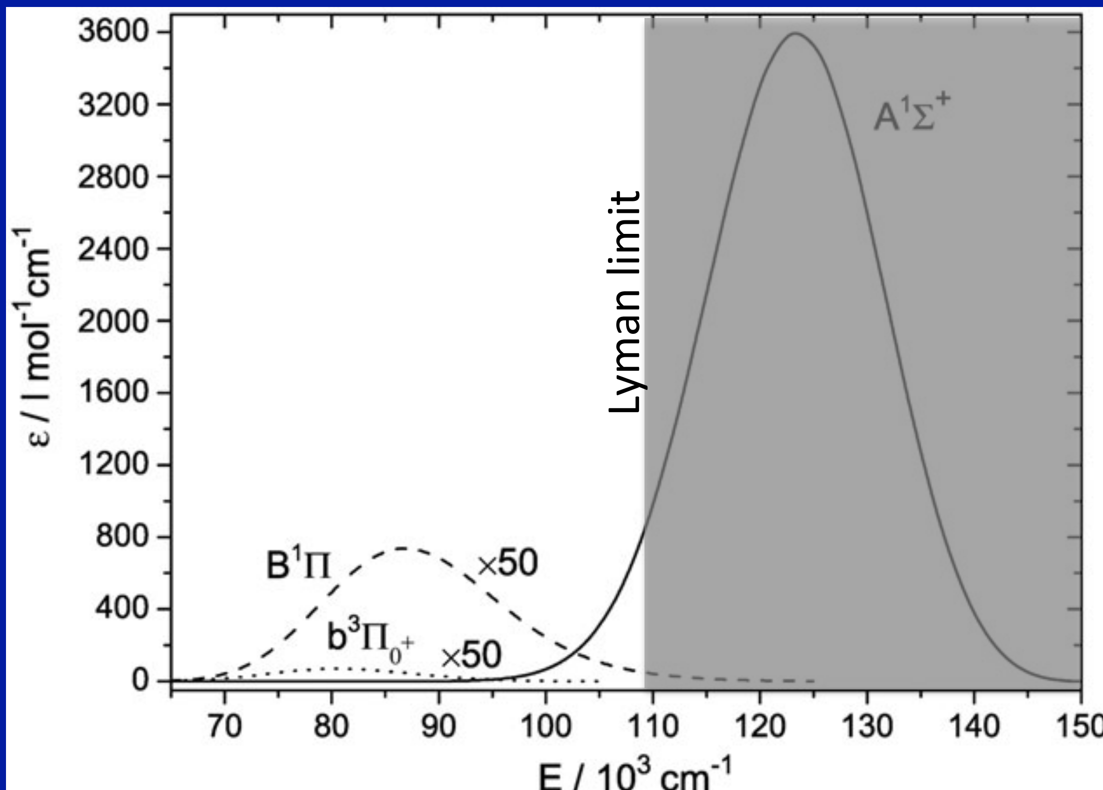
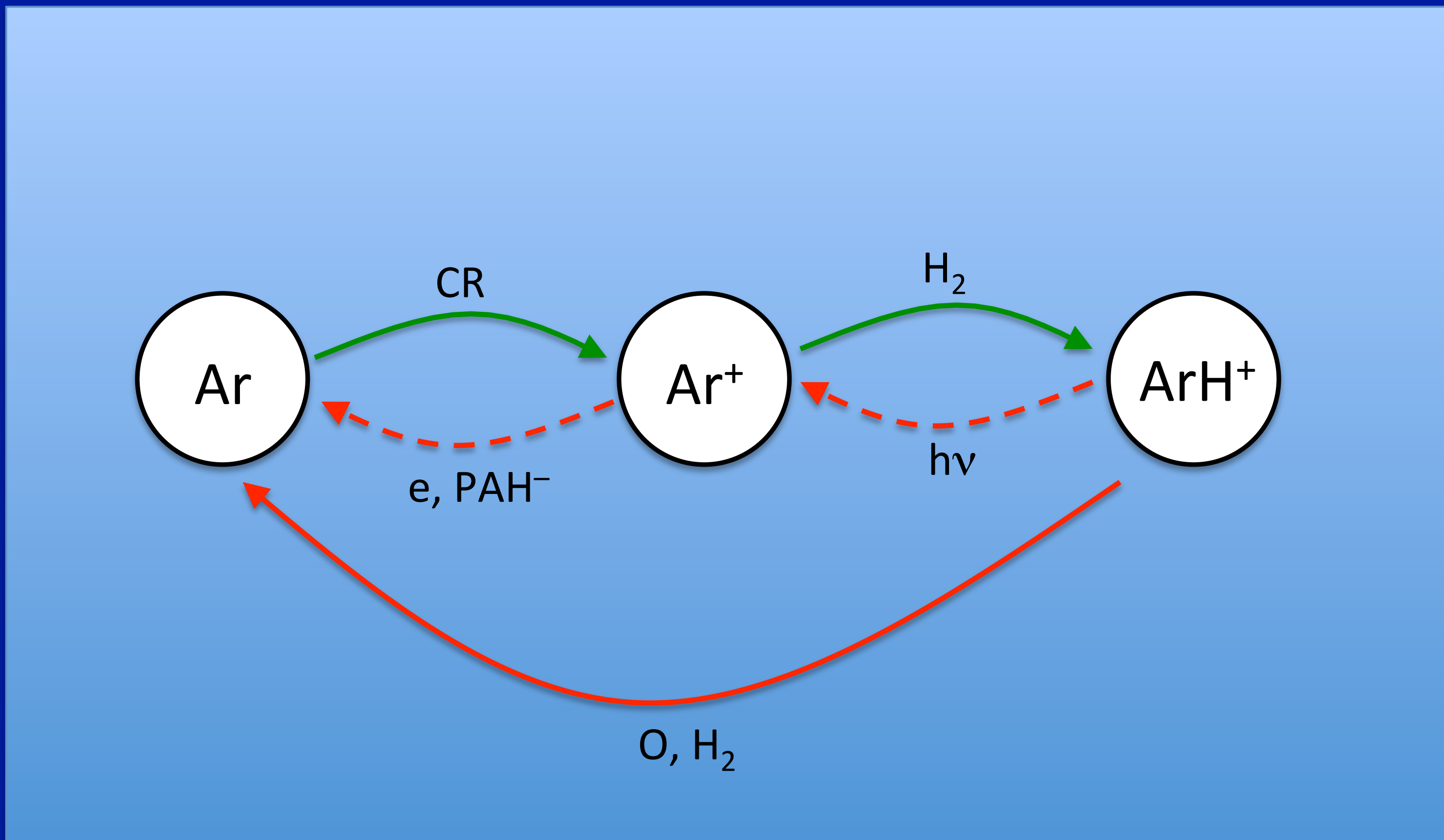
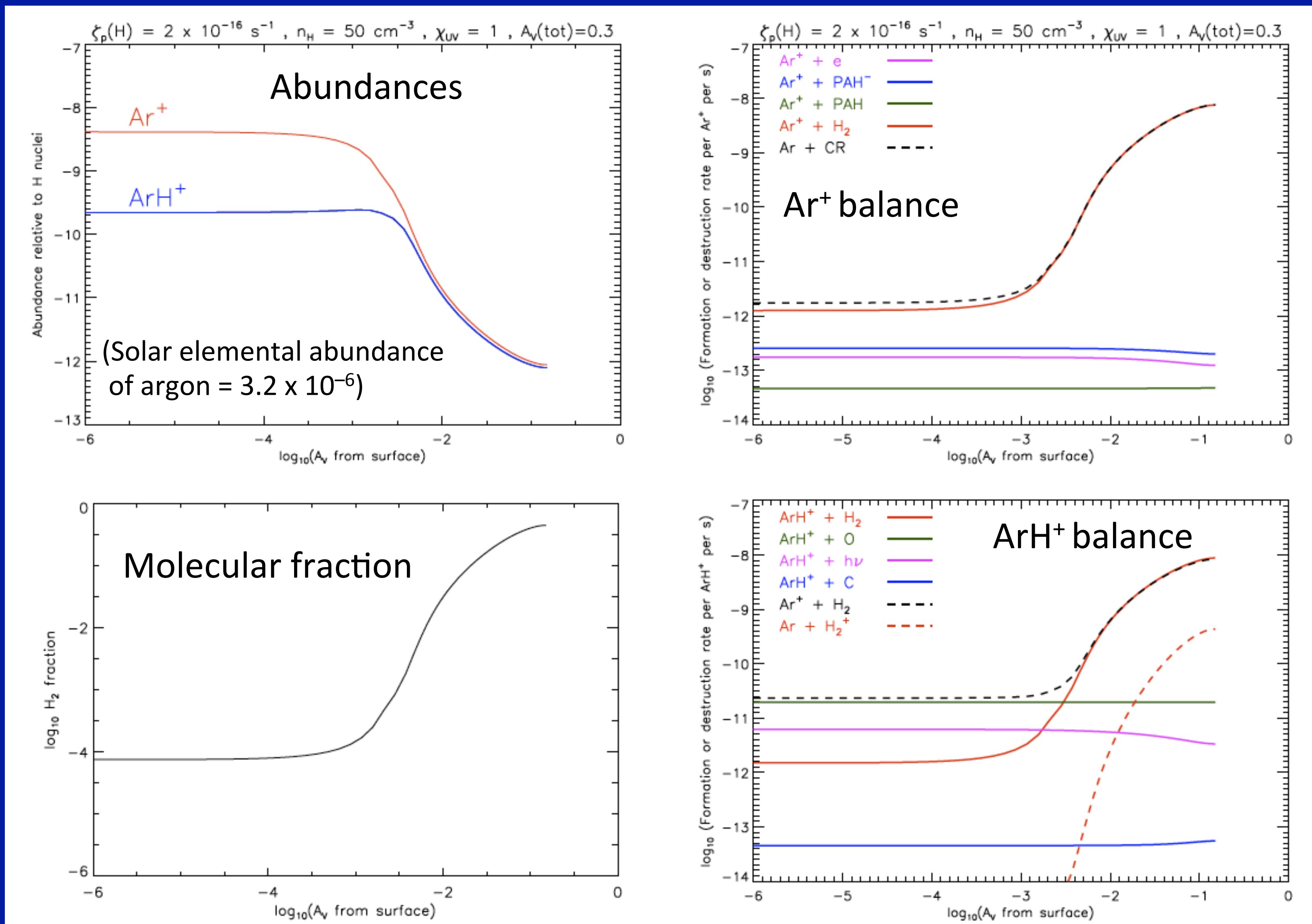


Argon chemistry

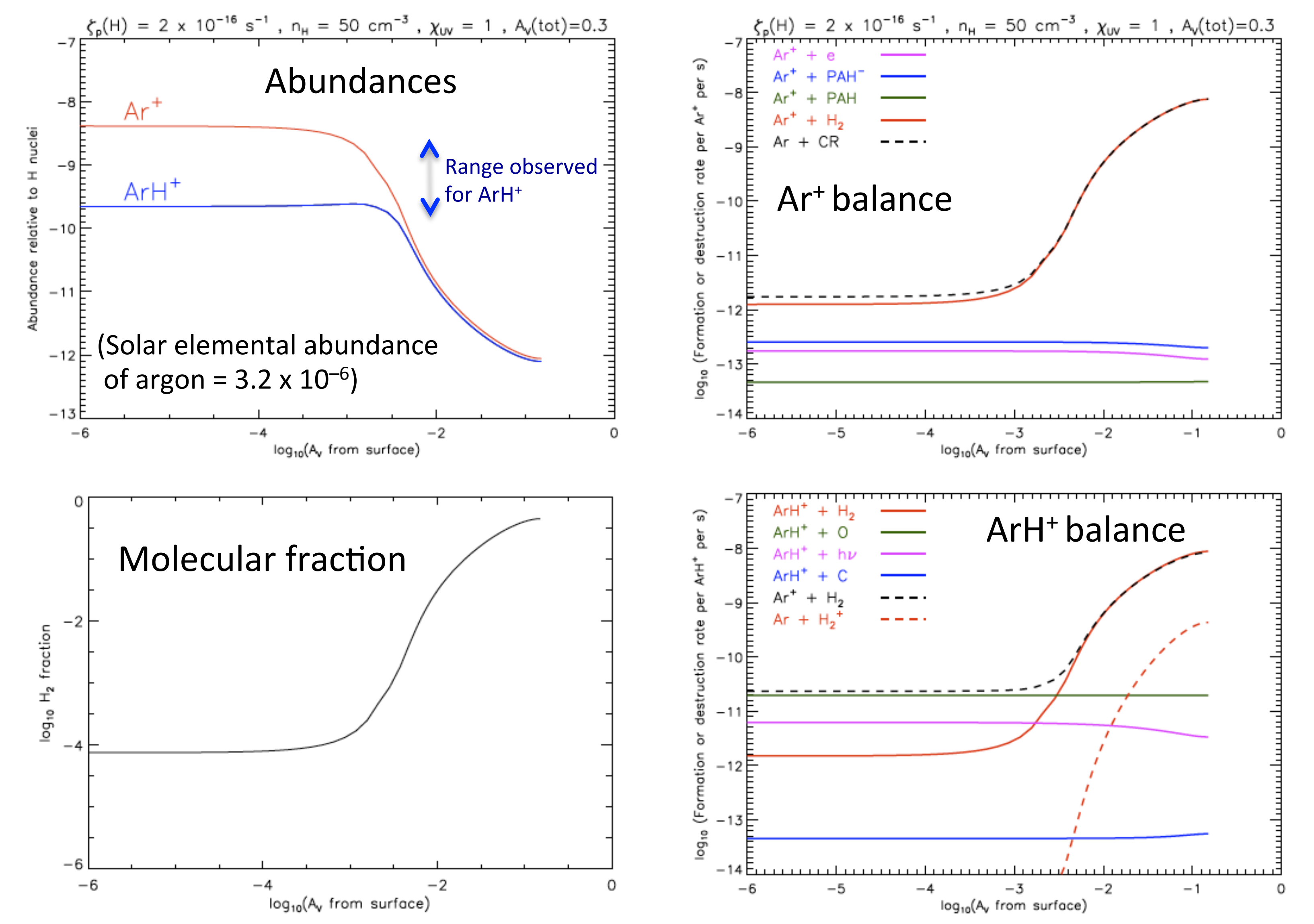


- If $n(H_2)/n_H > 10^{-5}$, almost every ionization of Ar leads to ArH^+
- Destruction of ArH^+ is usually dominated by reaction with O or H_2

Diffuse cloud model results
(with Mark Wolfire)



Diffuse cloud model results (with Mark Wolfire)



So what?

Is this just a interesting and rare curiosity, the sort of thing that is of great delight to a stamp collector, or might observations of ArH^+ serve a broader astrophysical purpose?

Not yet clear…..

Might be useful as a unique probe of gas with a very low molecular content

Argonium is "the molecule that abhors molecular clouds"

Also, measures the CR ionization rate (i.e. the cosmic ray density)

SOFIA/GREAT observations of the mercapto radical (SH) in diffuse molecular clouds

David Neufeld
(Johns Hopkins University)
and
M. Gerin, B. Godard,
E. Falgarone, E. Herbst,
G. Pineau des Forêts,
P. Schilke, P. Sonnentrucker,
U. Graf, R. Güsten
H. Wiesemeyer
and the GREAT team

arXiv:1502.05710

Interstellar hydrides

Individual hydrides and formed in relatively simple reaction networks and trace distinctive aspects of the interstellar environment

For example:

- OH^+ probes the cosmic ray ionization rate
- ArH^+ probes regions of very small H_2 fraction
- HF is a proxy for molecular hydrogen
- CH^+ and SH^+ probe warm regions – heated by shocks, or the dissipation of turbulence – where endothermic reactions (e.g. $C^+ + H_2 \rightarrow CH^+ + H$) are enhanced

Interstellar hydrides

- Prior to SOFIA, 5 or 6 neutral diatomic hydrides had been detected

CH (Swings & Rosenfeld 1937)	**NH** (Meyer & Roth 1991)	**OH** (Weinreb 1963)	**HF** (Neufeld et al. 1995)
SiH ? (Schilke et al. 2001)			**HCl** (Blake et al. 1985)

Interstellar hydrides

…along with four diatomic hydride cations (to which a fifth has recently been added)

CH^+ (Douglas & Herzberg 1941)	OH^+ (Gerin et al. & Wyrowski et al. 2010)		
	SH^+ (Benz et al. 2010)	HCl^+ (DeLuca et al. 2012)	ArH^+ (Barlow et al. 2013; Schilke et al. 2014)

The mercapto radical

- SH was conspicuously absent from the list of known interstellar hydrides

CH (Swings & Rosenfeld 1937)	**NH** (Meyer & Roth 1991)	**OH** (Weinreb 1963)	**HF** (Neufeld et al. 1995)
SiH ? (Schilke et al. 2001)		**What about SH ?**	**HCl** (Blake et al. 1985)

The mercapto radical

- Cold SH is unobservable from the ground

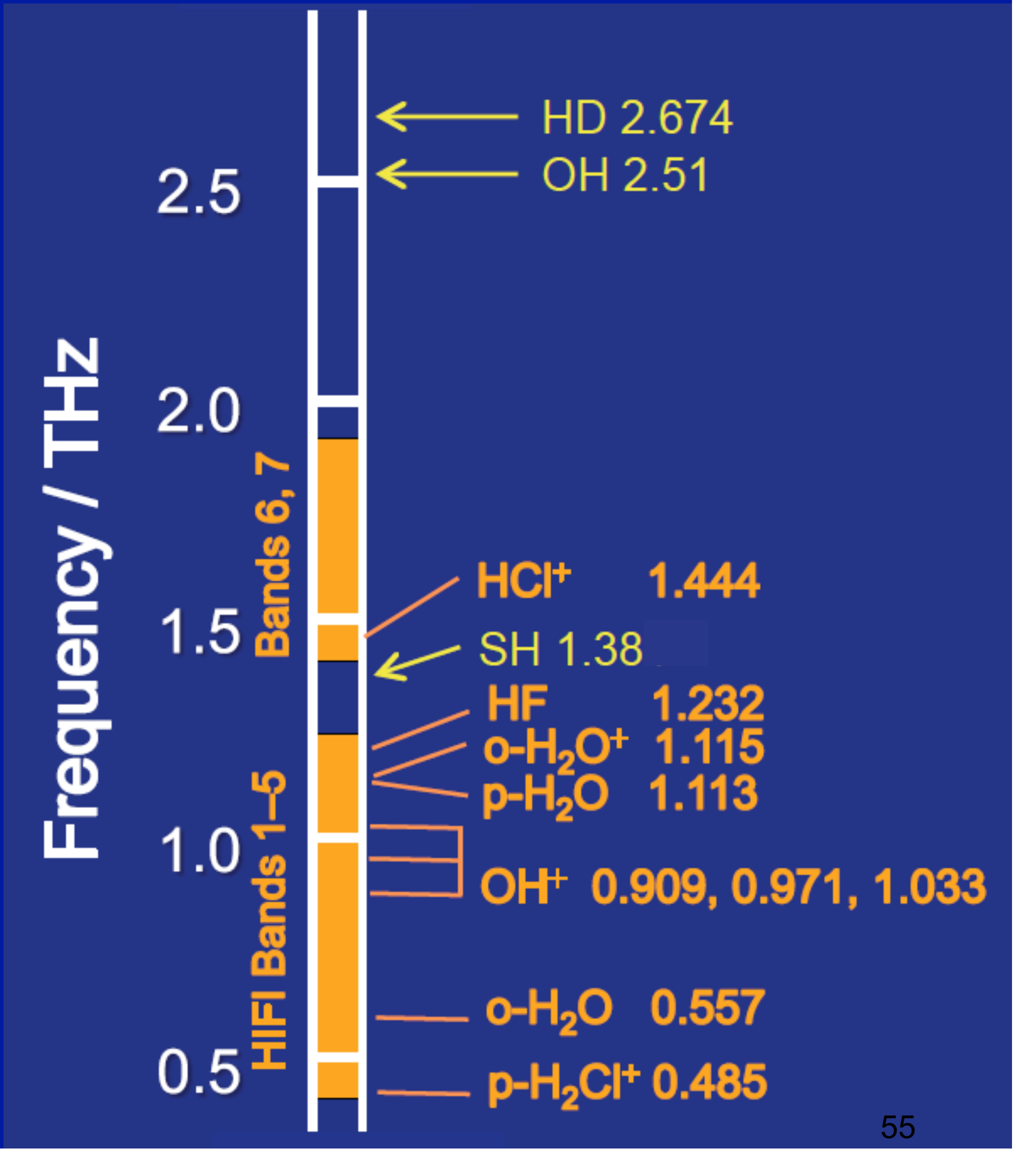
- The “ground state” rotational transition

  $^{2}\Pi_{3/2}$ J= 5/2 → 3/2 at 1.383 THz

  falls right in the gap between Bands 5 and 6 of *Herschel*’s HIFI spectrometer

The mercapto radical

- The GREAT (German REceiver for Astronomy at Terahertz frequencies) spectrometer on SOFIA has a receiver designed to cover this gap in *Herschel*/HIFI coverage (1250 – 1410 GHz)



The mercapto radical

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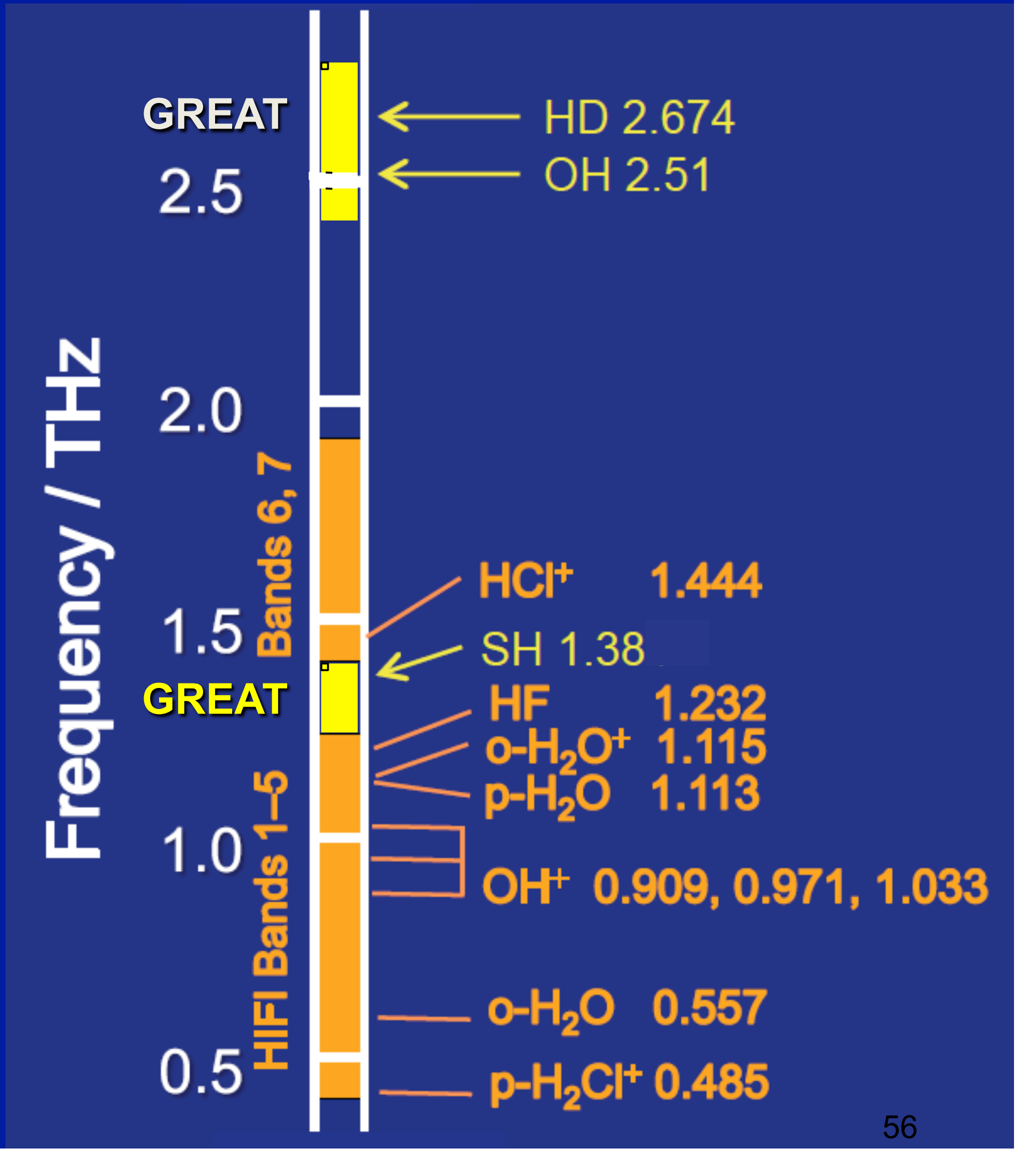
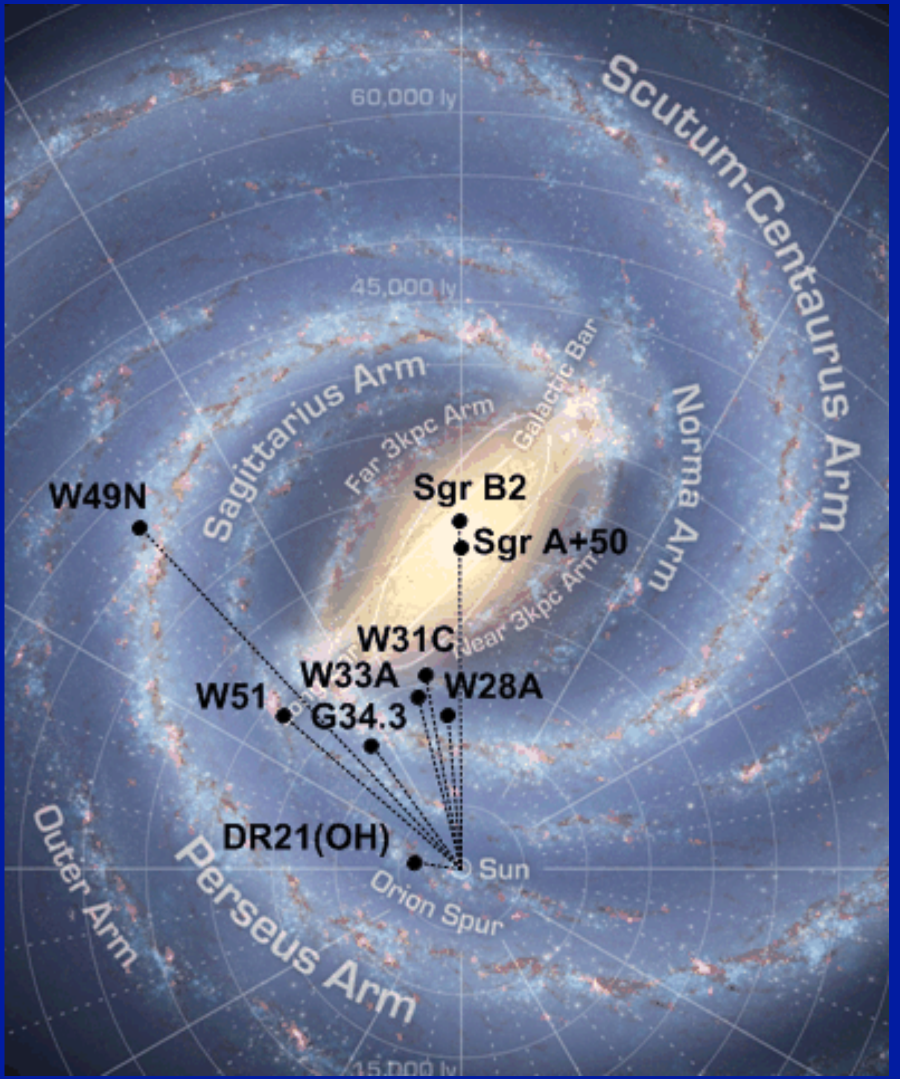
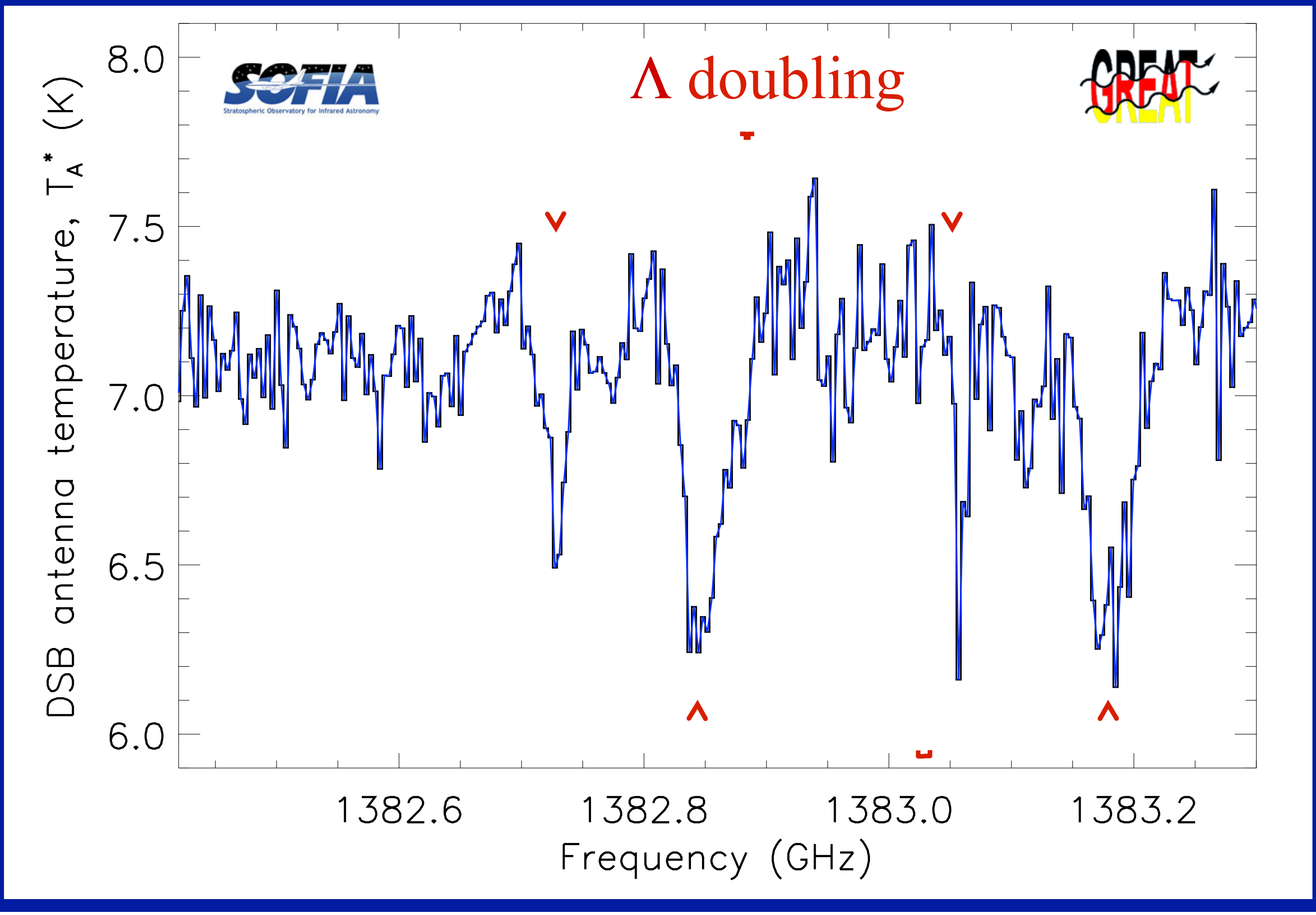


Search for SH in absorption toward W49N

- We used a very luminous region of massive star formation (W49N) as a background THz continuum source
- We searched for absorption by SH in foreground material
- This experiment was performed in a Basic Science ("General Investigator") program



Cycle 0: SH clearly detected in absorption toward W49N



Neufeld et al. 2012, A&A

Observations of SH performed toward four additional sources

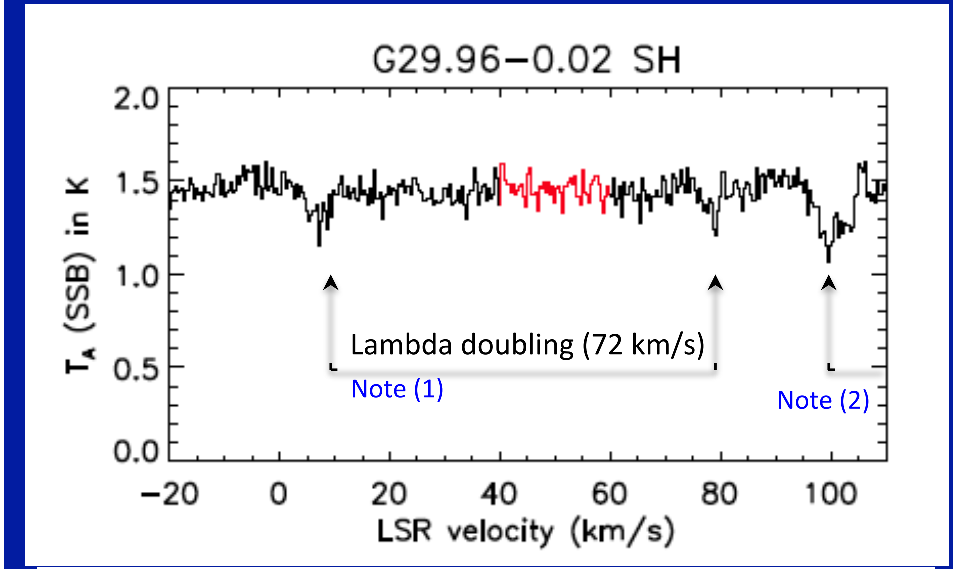
Following the first detection of interstellar SH toward W49N in Cycle 0, we observed diffuse clouds along the sight-lines to

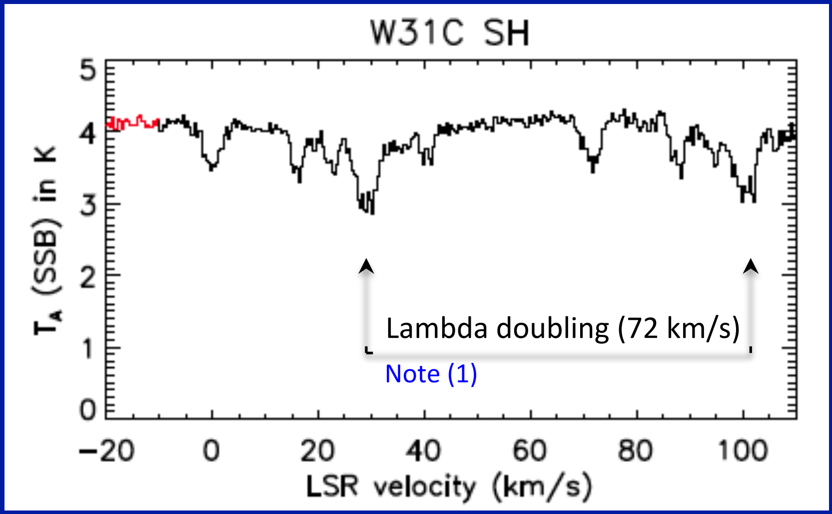
W31C*, G29.96–0.02*, G34.3+0.1*, W51**

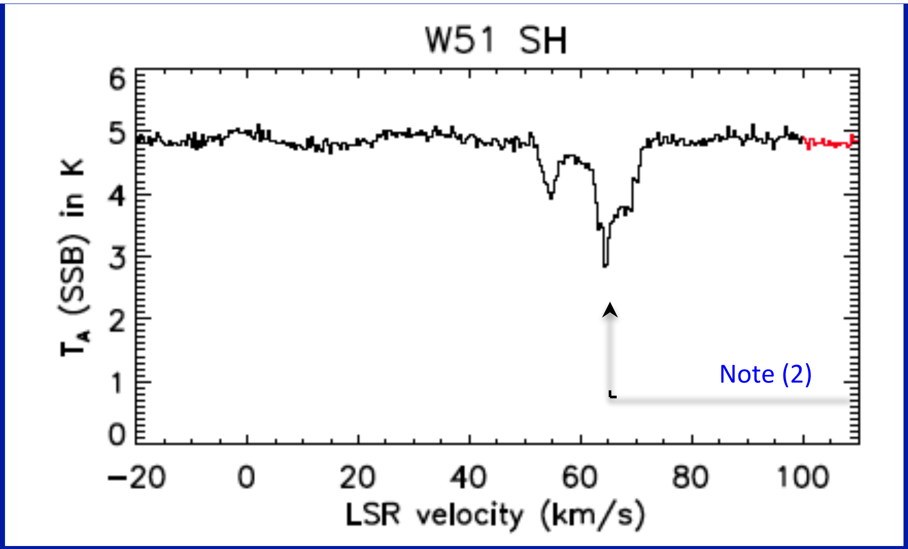
*July 2013 (Christchurch deployment)
**Nov 2013 (Palmdale deployment)

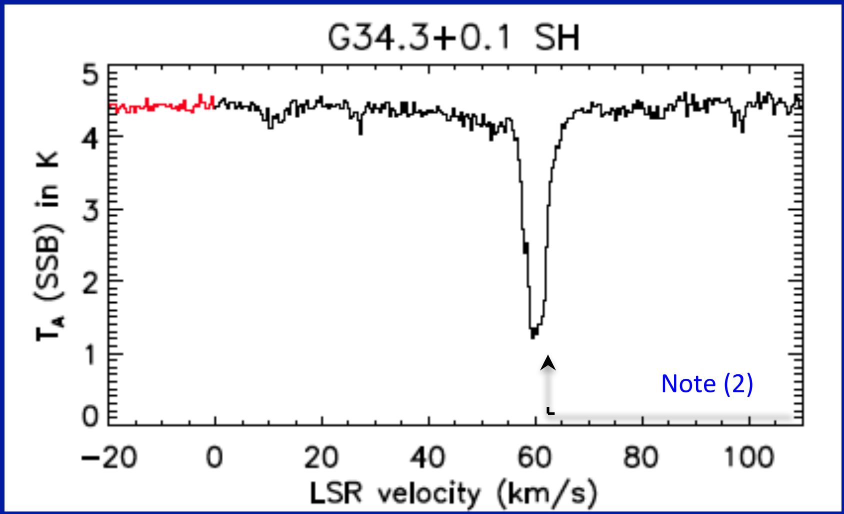
Motivation: SH is expected to trace regions where endothermic reactions can be driven by a "warm chemistry" in shocks or turbulent dissipation regions. Its abundance would be negligible in cold 80 K gas

Clear detections were obtained toward all four sources



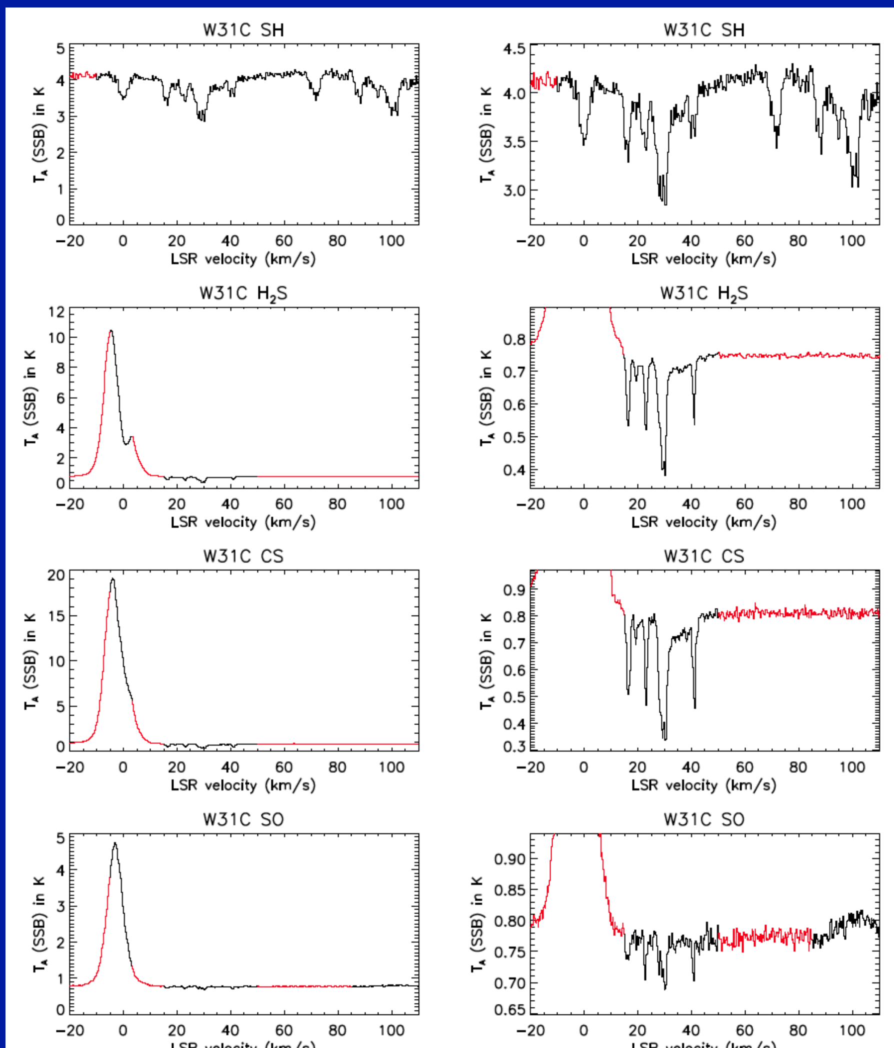




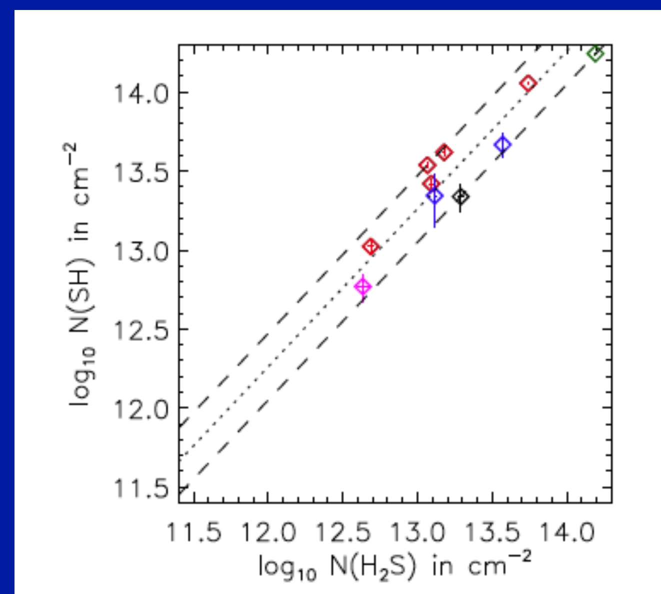


Notes (1) there is also a hyperfine splitting of 1 – 2 km/s
(2) the other doublet member lies beyond +120 km/s and is therefore not shown in this plot

Ancillary observations of H_2S, CS and SO were performed at the IRAM 30 m



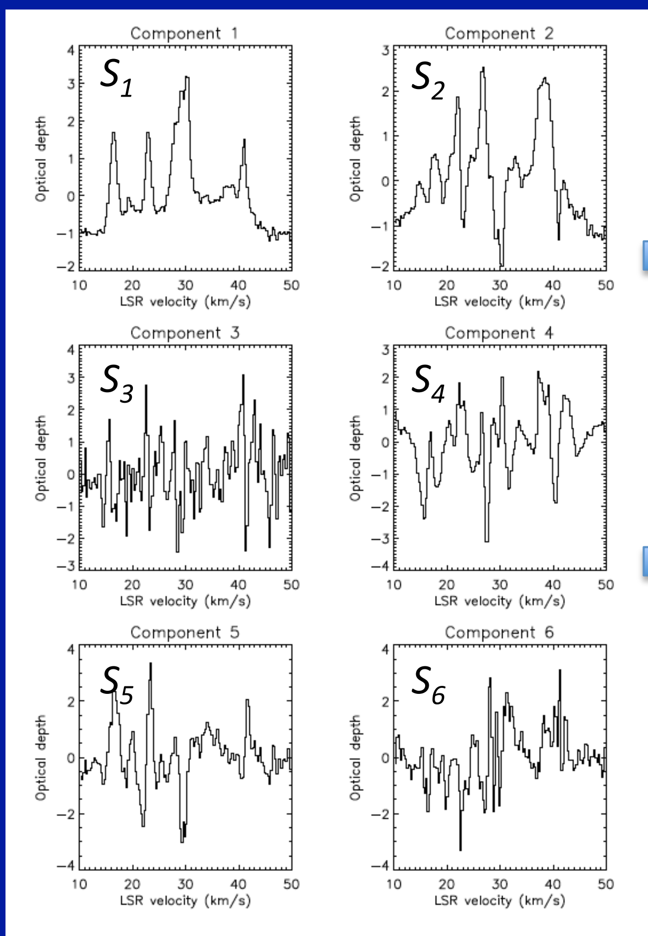
The absorption spectra are strikingly similar, with the column densities in the various absorption components being very well correlated. Example plot below shows N(SH) versus N(H_2S)



SH/H_2S ranges from 1.1 – 3.0 in ten foreground diffuse clouds detected toward five background sources

Principal component analysis

The optical depth spectra, shown by the black histograms on the right, are written as a linear combination of the six principal components shown at left. These six components are mutually orthogonal (uncorrelated) and listed in decreasing order of their contribution. The first two components are sufficient to yield a good fit to the data (red histogram on right) .



6 terms in Σ → black

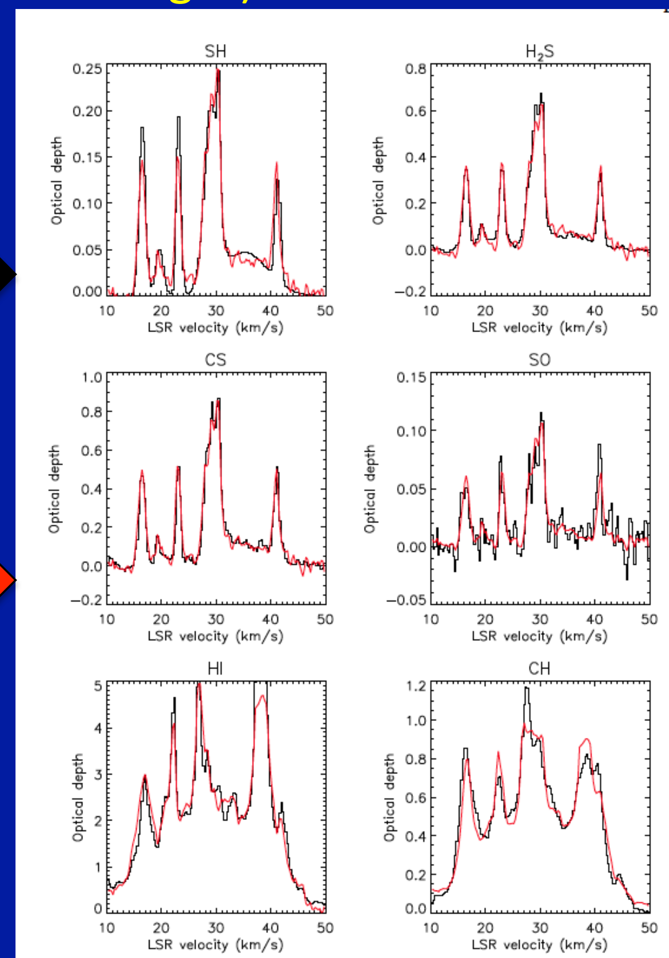
$$\tau_i(v) = a_i + b_i \sum_{j=1}^{6} C_{ij} S_j(v)$$

Gives an exact fit

2 terms in Σ → red

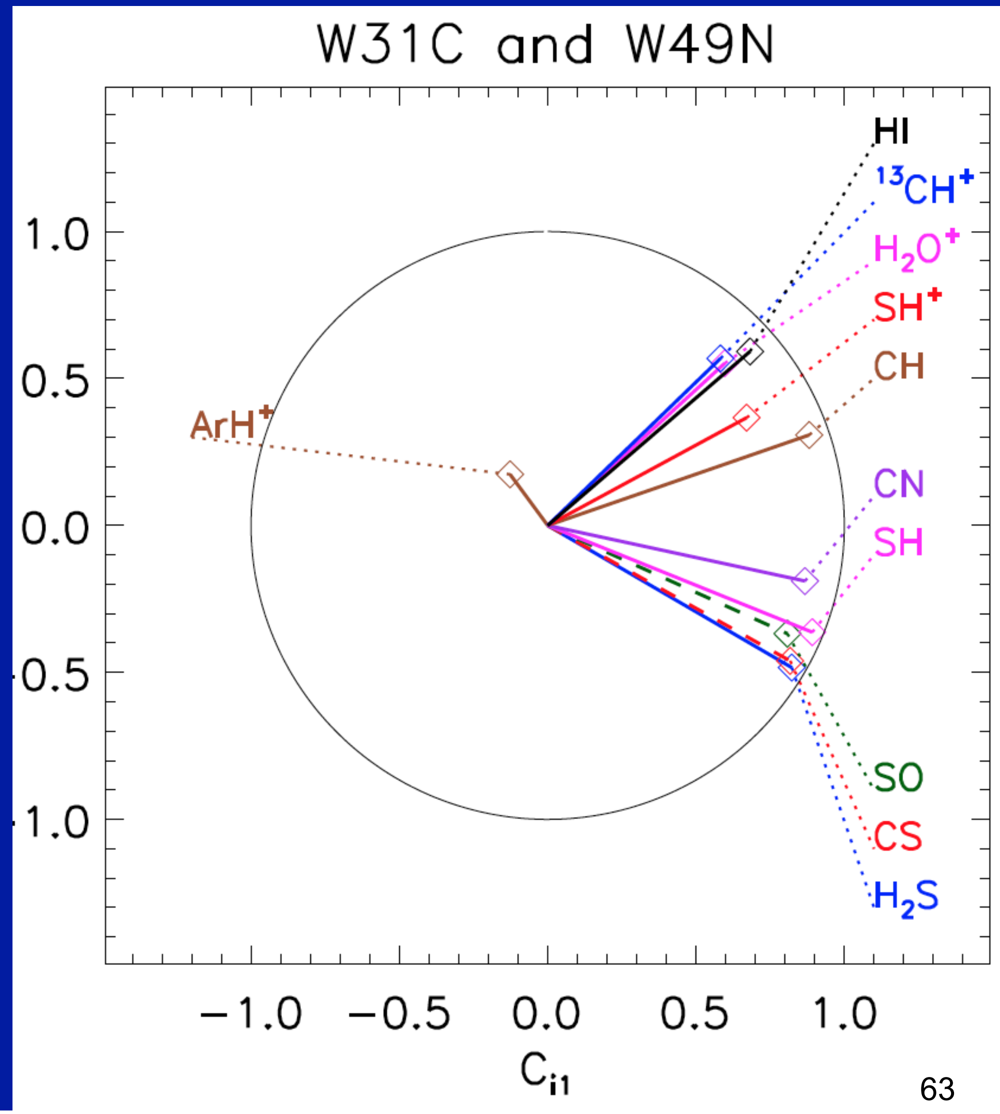
$$\tau_i(v) = a_i + b_i \sum_{j=1}^{2} C_{ij} S_j(v)$$

Good approximation



Principal component analysis

A plot of the first two coefficients, C_{i1} and C_{i2}, for each absorption line shows the similarities and differences graphically.



NOTES

(1) Except for ArH^+, all points lie close to unit circle, indicating that the first two components account for most of what is observed

➔ the correlation coefficient is roughly the cosine of the angle between any two vectors

(2) The position of the neutral sulphur-bearing molecules relative to H, CH and the other species may suggest that they are present mainly in material with a large molecular fraction (since HI traces atomic gas and CH traces H_2 in partially- or fully-molecular gas)

Molecular abundances

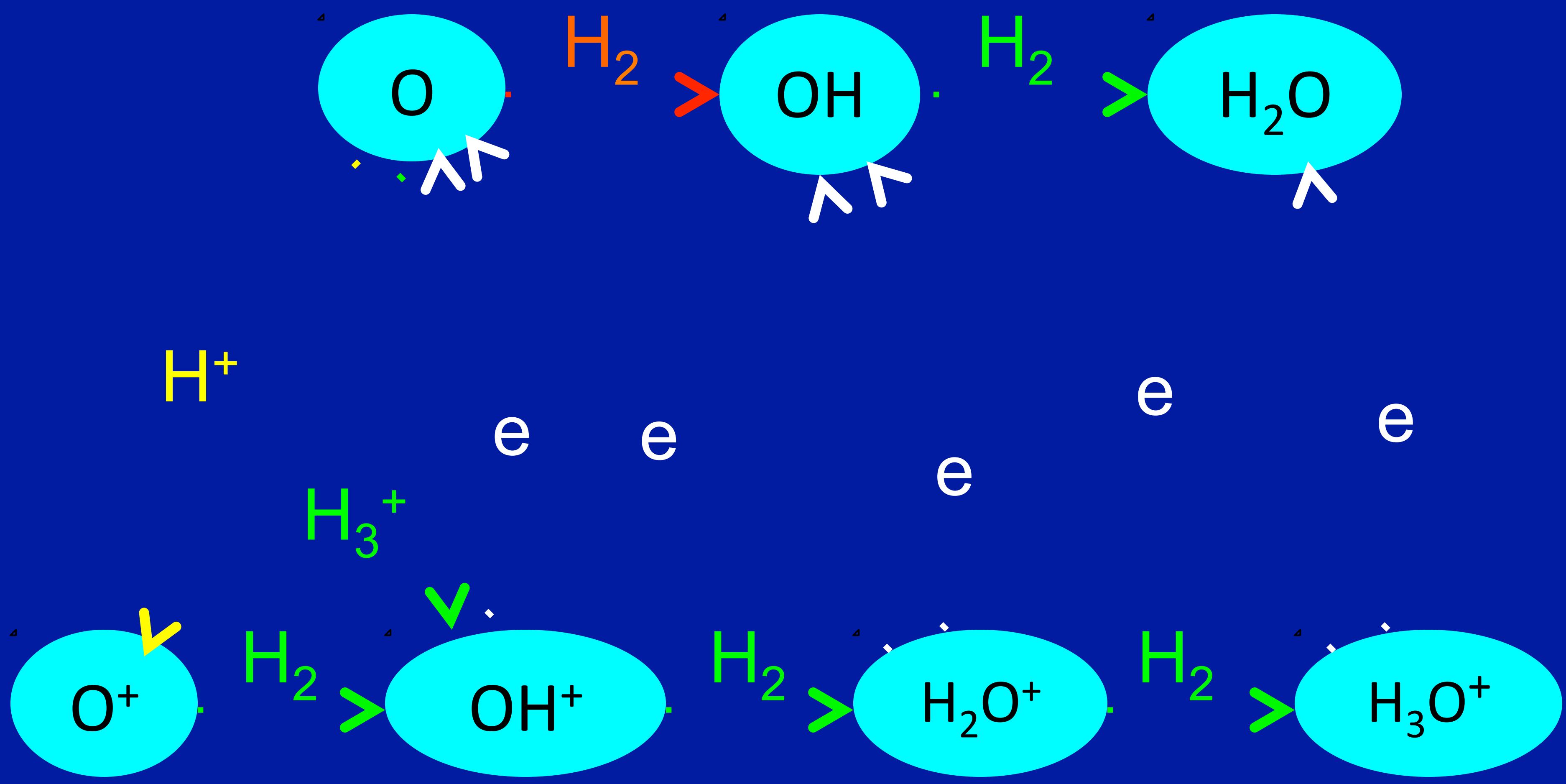
Table 5. Derived molecular abundances

Source	v_{LSR} (km s^{-1})	$N(H_2)^a$ (10^{21} cm^{-2})	$N(H)^b$ (10^{21} cm^{-2})	$N(SH)/N(H_2)^c$ $\times 10^9$	$N(H_2S)/N(H_2)$ $\times 10^9$	$N(CS)/N(H_2)$ $\times 10^9$	$N(SO)/N(H_2)$ $\times 10^9$
W49N	37 – 44	1.76	2.35	26.5	21.2	9.8	1.7
W49N	57 – 67	4.19	4.30	5.3	3.1	1.7	0.7
W31C	15 – 18	2.34	1.23	14.7	5.0	2.5	1.1
W31C	18 – 21	1.57	1.18	6.7	3.1	1.0	0.4
W31C	21 – 25	2.49	2.13	10.6	5.0	2.0	1.0
W31C	25 – 36	8.19	10.35	13.9	6.7	3.2	1.3
W31C	36 – 45	4.94	37.12	8.4	3.0	1.9	0.9
G34.3+0.1	25 – 30	1.07	3.72	5.5	4.0	1.3	$< 1.1\ (3\,\sigma)$
G29.96-0.02	5 – 10	1.43	1.11	15.3	13.6	5.1	1.1

SH accounts for only ~0.1% of S nuclei, but this is still much more than is expected in cold diffuse clouds

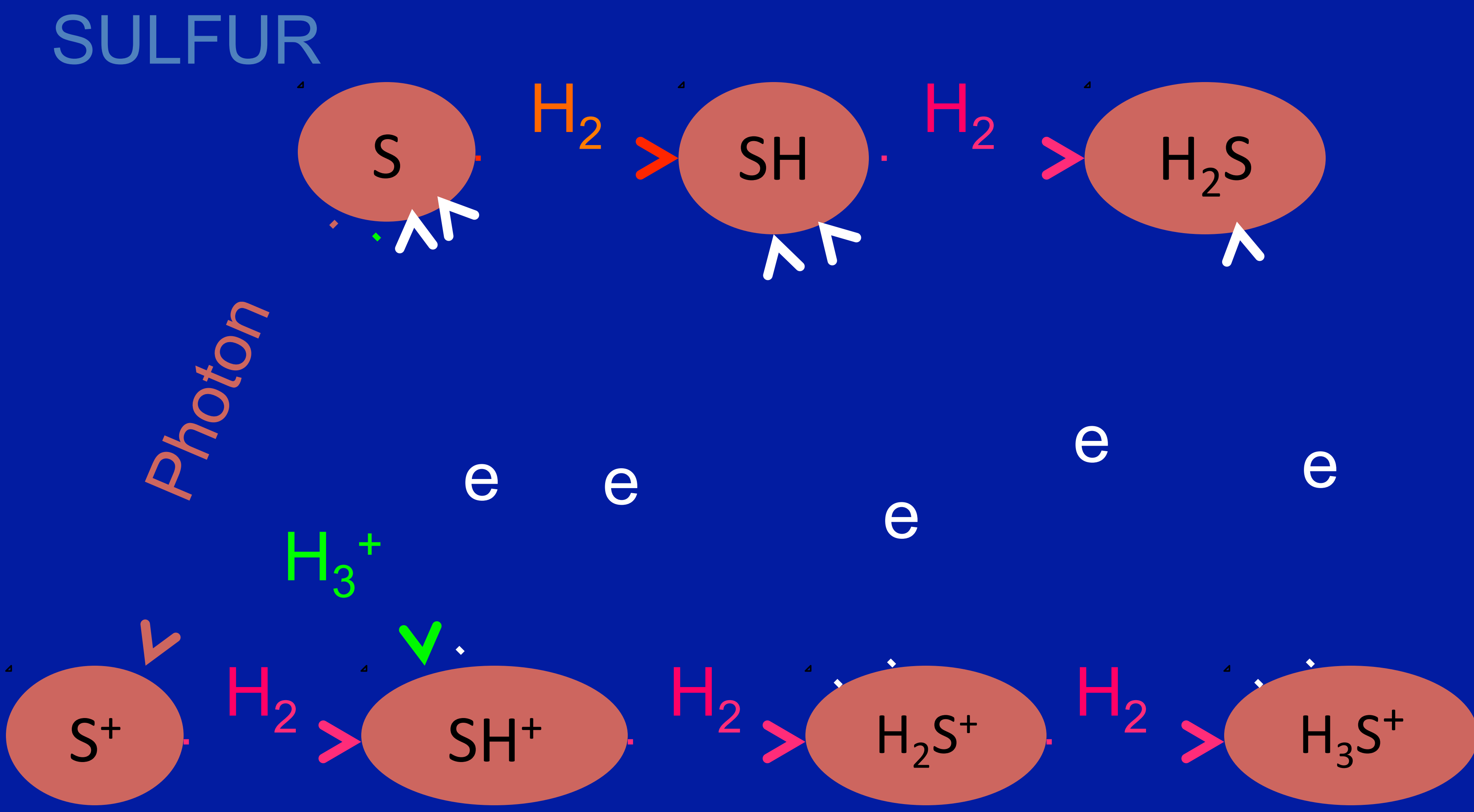
Underlying thermochemistry

OXYGEN



Green arrow=exothermic red=endothermic yellow=slightly endothermic

Underlying thermochemistry



Green arrow=exothermic red=endothermic yellow=slightly endothermic

Underlying thermochemistry

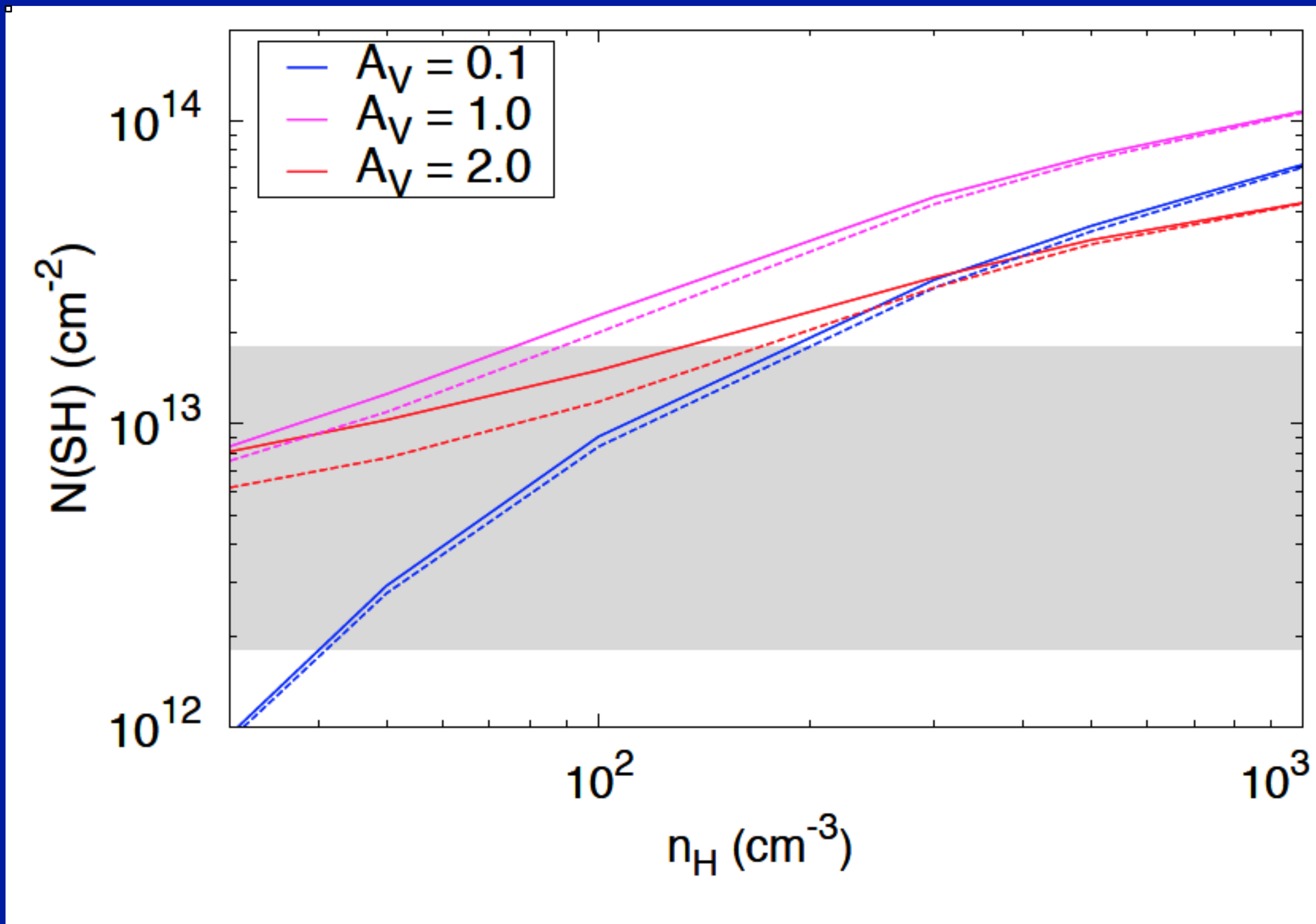
OH and H_2O can be produced via two pathways:

- Low temperature: ion-molecule reactions, then dissociative recombination of H_3O^+
- High temperature: neutral-neutral reactions

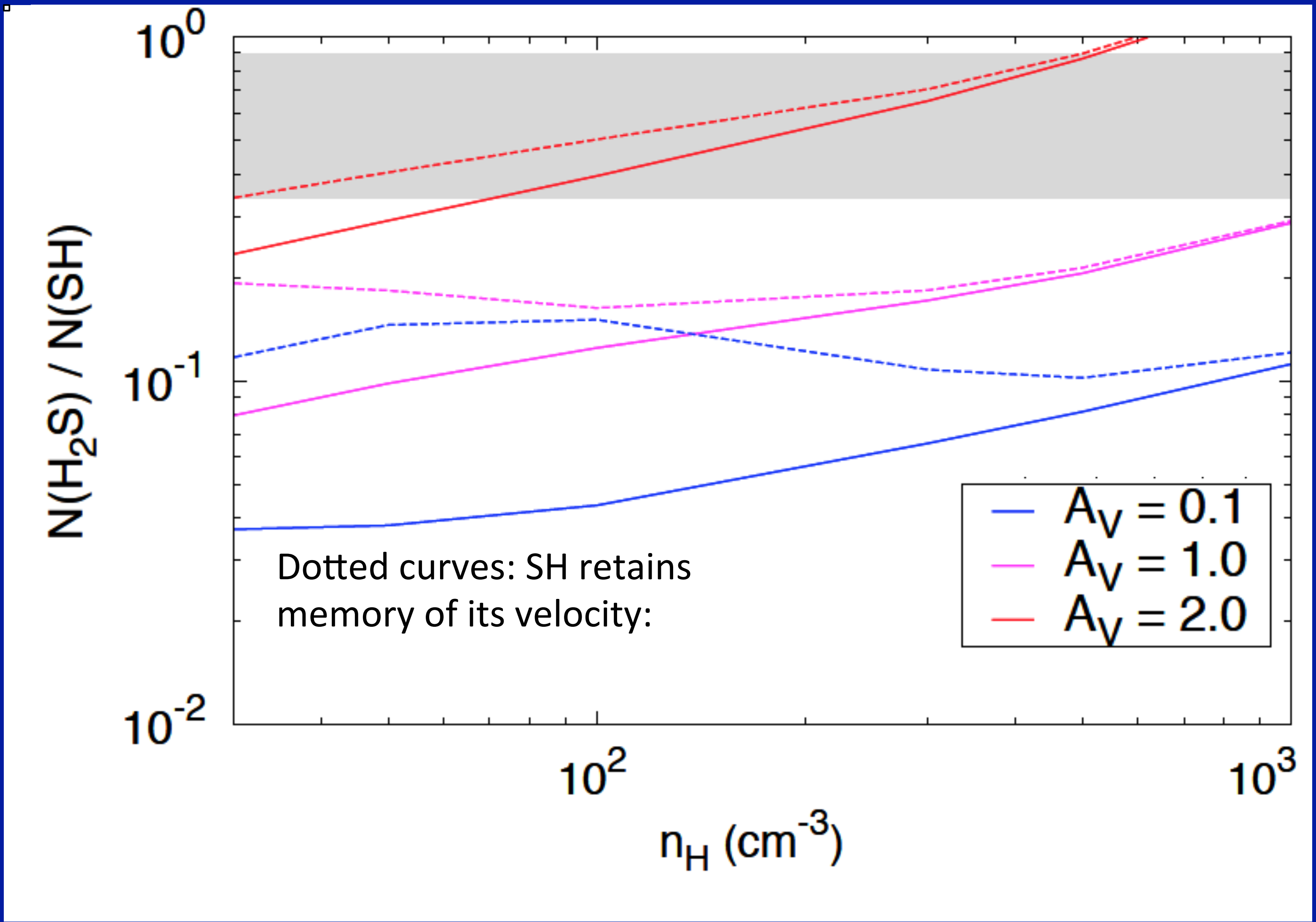
SH and H_2S are only produced at elevated temperatures:

- Their presence is evidence for shocks or turbulent dissipation regions

Shock model predictions:
SH column densities can be explained



Shock model predictions:
H_2S/SH is underpredicted



Future prospects for studies of interstellar hydrides with SOFIA

- GREAT continues to perform unique high-resolution spectroscopy, providing access to OH, OD, HD, p-H_2D^+ and SH in their ground states
- Lower frequency heterodyne spectroscopy ("downGREAT"?) would provide access to CH, ArH^+, HF, NH_3
- EXES now provides access to vibrational bands of hydrides

Summary

- SOFIA/GREAT introduces a powerful capability for heterodyne spectroscopy of interstellar hydrides at otherwise inaccessible frequencies

- It has discovered widespread absorption by interstellar SH in foreground diffuse clouds along the sight-lines to THz continuum sources

→ a key tracer of “warm chemistry”