Laboratory Measurements and Astronomical Search of the HSO Radical

Valerio Lattanzi

CAS@MPE
Garching (Germany)

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Authors

- Cristina Puzzarini & Gabriele Cazzoli

  (Dip. Chimica "Giacomo Ciamician" Università di Bologna)

- Jürgen Gauss & Till Kirsch

  (Institut für Physikalische Chemie, Universität Mainz)

- José Cernicharo & Belén Tercero

  (Grupo de Astrofísica Molecular, ICMM–CSIC)

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- Many sulfur (single S) species detected in the interstellar gas
- From diatomic up to CH_3CH_2SH
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- ***Location and chemical form of missing sulfur***

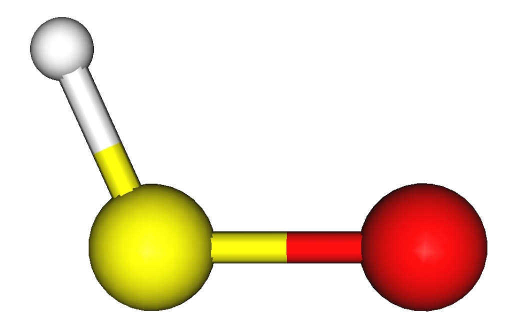
Motivations

- Large abundance of triatomic S, O, and H species
- Especially in high–mass star-forming regions
- Key intermediates in the atmospheric oxidation of H_2S to H_2SO_4
- Prominent role in catalytic cycles of stratospheric ozone depletion

- First experimental evidence of HSO by Schurath et al. (1977)
  - low-resolution chemiluminescence visible spectra
- High-resolution spectroscopy by Endo et al. (1981)
  - HSO and DSO
  - hydrogen hyperfine coupling constant

HSO – Experiment

- A'' electronic ground state (Endo et al. 1981)
- $\mu_a = 2.20$ D (Webster et al. 1982)

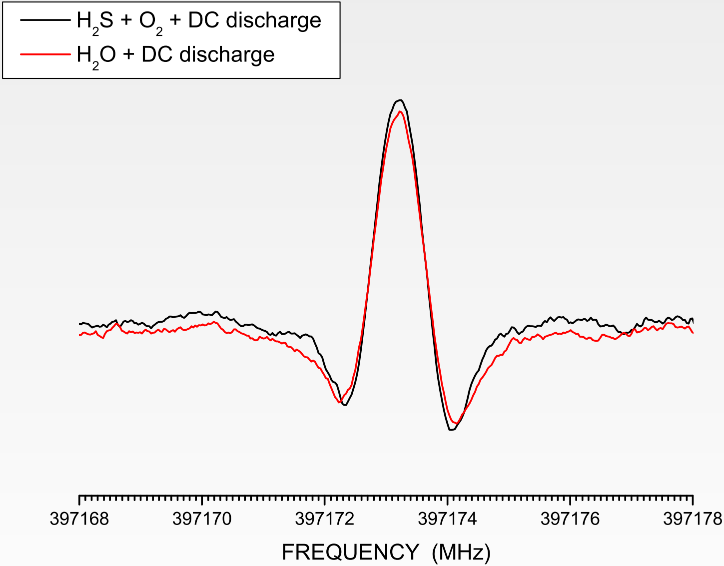


HSO – Experiment

- Measured in the 194 GHz – 1.2 THz range
- Free–space cell, 3m long, single–pass arrangement
- Cryogenic InSb and Schottky diode detectors
- Room temperature measurements

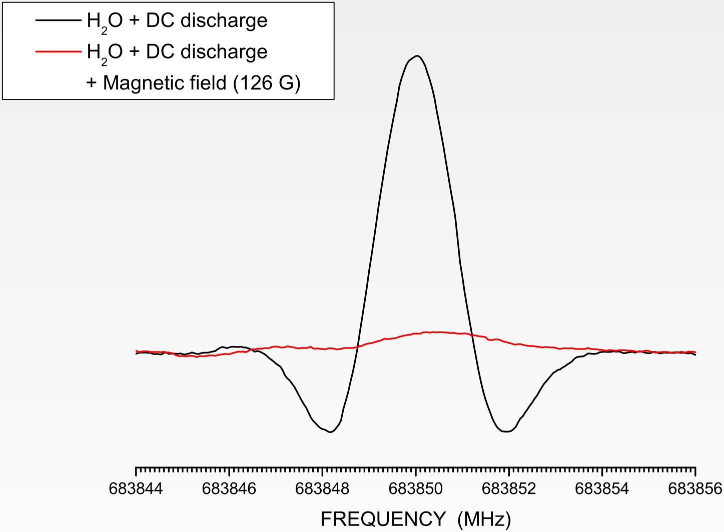
- Sulfur is very sticky! – Similar results with two settings:
  1. DC discharge ($\sim$ 10–40 mA) of H_2S and O_2 (1:2) total pressure < 20 mTorr
  2. DC discharge ($\sim$ 35–50 mA) of $\sim$ 40 mTorr of H_2O cleaner experiment

HSO – Experiment



HSO – Experiment

- Confirmation by means of magnetic field



Computations

$$H = H_{rot} + H_{S-N} + H_{hfs}$$

- All computations made with CFOUR
- A_e, B_e, and C_e at the CBS+CV+fT+fQ level
- Vibrational corrections at the CCSD(T)/cc-pCVQZ level
- Quartic and sextic at the CCSD(T)/cc-pCVQZ level
- Electronic and nuclear Spin-Rotation at the CCSD(T)/cc-pCV5Z level
- Isotropic and anisotropic hyperfine coupling constants at the aug-cc-pCV5Z level

Results – Rotational Constants

Parameter	This work		Previous
	Experiment	Theory	
A_0 (MHz)	299483.90(12)	300316.2	299484.68(14)
B_0 (MHz)	20502.7847(10)	20527.6	20502.7823(83)
C_0 (MHz)	19135.6989(10)	19160.0	19135.7168(83)
D_N (kHz)	29.4675(13)	28.61	29.64(11)
D_{NK} (kHz)	904.18(11)	882.33	903.41(40)
D_K (MHz)	26.24(11)	25.99	[27.2]
d_1 (kHz)	-2.02504(43)	-1.86	-1.926(65)
d_2 (kHz)	-0.35187(30)	-0.29	-0.527(52)
H_N (mHz)	-28.42(75)	-29.07	
H_{NK} (Hz)	2.779(88)	2.28	
H_{KN} (Hz)	144.7(43)	126.26	
H_K (kHz)	[6.43]	6.43	
$h_1 \times 10^2$ (mHz)	[-8.32]	-8.32	
h_2 (mHz)	[3.69]	3.69	
h_3 (mHz)	1.10(22)	0.725	
L_{JK} (mHz)	-11.4(32)		

Results – Spin rotation and Hyperfine interactions

Parameter	This work		Previous
	Experiment	Theory	
ϵ_{aa} (MHz)	-10366.15(10)	-10979.0(-10940.5)	-10366.17(16)
ϵ_{bb} (MHz)	-426.633(17)	-439.4(-438.9)	-426.683(31)
ϵ_{cc} (MHz)	0.191(21)	2.82(3.29)	0.210(48)
$\widetilde{\epsilon}_{ab}$ (MHz)	377.971(16)	404.8(403.3)	377.81(80)
ϵ_{aa}^{NK} ^{e} (MHz)			0.047(12)
ϵ_{aa}^{K} ^{e} (MHz)	2.979(10)		3.023(35)
ϵ_{bb}^{NK} ^{e} (MHz)	-0.001676(32)		
ϵ_{bb}^{K} ^{e} (MHz)	0.0638(36)		
ϵ_{cc}^{NK} ^{e} (kHz)	-0.114(30)		
a_F(H) (MHz)	-35.72(50)	-35.94(-34.58)	-35.98(42)
T_{aa}(H) (MHz)	-11.932(86)	-12.38(-13.25)	-11.883(71)
T_{bb}(H) (MHz)	10.45(14)	10.71(11.25)	10.41(11)
T_{ab}(H) (MHz)	[-7.53]^{f}	-7.56(-7.53)	[-7.8]^{f}
C_{aa}(H) (kHz)		-20.18(-21.56)	
C_{bb}(H) (kHz)		2.51(2.51)	
C_{cc}(H) (kHz)		-1.52(-1.59)	

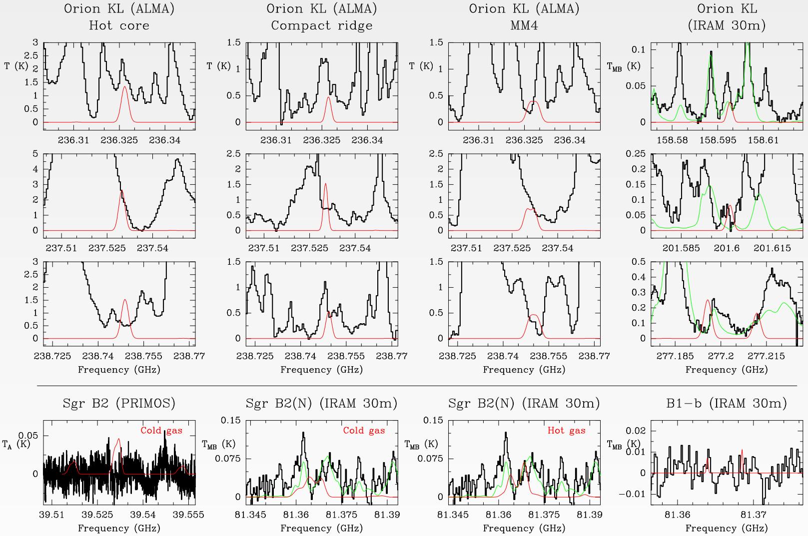
Astronomical observations

Source	Coordinates [J2000.0]	HPBW [″]	Frequencies [GHz]
Orion KL (IRAM 30m)	α=$5^{\mathrm{h}}35^{\mathrm{m}}14\overset{\mathrm{s}}{.}5$ δ=$-05^\circ22'30\overset{\prime\prime}{.}0$	30-8	80-307
Orion KL (ALMA SV) Hot core	α=$05^{\mathrm{h}}35^{\mathrm{m}}14\overset{\mathrm{s}}{.}5$ δ=$-05^\circ22'32\overset{\prime\prime}{.}5$	$\sim$1.9$\times$1.4	213.7-246.7
Orion KL (ALMA SV) Compact ridge	α=$05^{\mathrm{h}}35^{\mathrm{m}}14\overset{\mathrm{s}}{.}1$ δ=$-05^\circ22'36\overset{\prime\prime}{.}9$	$\sim$1.9$\times$1.4	213.7-246.7
Orion KL (ALMA SV) MM4	α=$05^{\mathrm{h}}35^{\mathrm{m}}14\overset{\mathrm{s}}{.}2$ δ=$-05^\circ22'31\overset{\prime\prime}{.}1$	$\sim$1.9$\times$1.4	213.7-246.7
Sgr B2(N) Cold gas	(IRAM 30m) α=$17^{\mathrm{h}}47^{\mathrm{m}}20\overset{\mathrm{s}}{.}0$ δ=$-28^\circ22'19\overset{\prime\prime}{.}0$	30-21	80-115.5
	(GBT 100m) α=$17^{\mathrm{h}}47^{\mathrm{m}}19\overset{\mathrm{s}}{.}8$ δ=$-28^\circ22'17\overset{\prime\prime}{.}0$	80-15	7-50
Sgr B2(N) (IRAM 30m) Hot gas	α=$17^{\mathrm{h}}47^{\mathrm{m}}20\overset{\mathrm{s}}{.}0$ δ=$-28^\circ22'19\overset{\prime\prime}{.}0$	30-21	80-115.5
B1-b (IRAM 30m)	α=$03^{\mathrm{h}}33^{\mathrm{m}}20\overset{\mathrm{s}}{.}0$ δ=$31^\circ07'34\overset{\prime\prime}{.}0$	30-21	80-115.5

Astronomical observations

Source	$v_{\rm LSR}$ (km s^{-1})	$\Delta v_{\rm FWHM}$ (km s^{-1})	$d_{\rm sou}$ ($''$)	$T_{\rm rot}$ (K)	N(HSO) $\times 10^{14}$ (cm^{-2})
Orion KL (IRAM 30m)	8	3	5	150	$\leq$(2.0$\pm$0.6)
Orion KL (ALMA SV) Hot core	8	3	3	150	$\leq$(4$\pm$1)
Orion KL (ALMA SV) Compact ridge	7.5	2	3	100	$\leq$(1.0$\pm$0.3)
Orion KL (ALMA SV) MM4	3	3	3	150	$\leq$(1.0$\pm$0.3)
	5	8	3	150	$\leq$(1.0$\pm$0.3)
Sgr B2(N) Cold gas	64	9	60	14	$\leq$(1.0$\pm$0.3)
	75	12	60	14	$\leq$(1.0$\pm$0.3)
Sgr B2(N) (IRAM 30m) Hot gas	64	8	3	150	$\leq$(700$\pm$200)
	73	8	3	150	$\leq$(100$\pm$30)
	52	14	3	150	$\leq$(100$\pm$30)
B1-b (IRAM 30m)	6.7	0.7	60	12	$\leq$(0.010$\pm$0.003)

HSO – Astronomical Spectra



Conclusions

- New THz measurements for HSO radical
- Excellent test for quantum chemical calculations
- Deep search in astronomical sources
- No radioastronomical detection (so far)
  - HSO has not been included in chemical models
  - $CH_3S + O$ might produce HSO
  - $\Rightarrow$ yield of HSO might be too low for detection

- S-chemistry in space is very active and intriguing
- Extending astrochemical models to new S-species
- Laboratory work on new sulfur molecules (ions? radicals?)