Supplementary Information

New data on photochemistry of the interstellar molecule: HNCS. Identification of the S...HCN complex.

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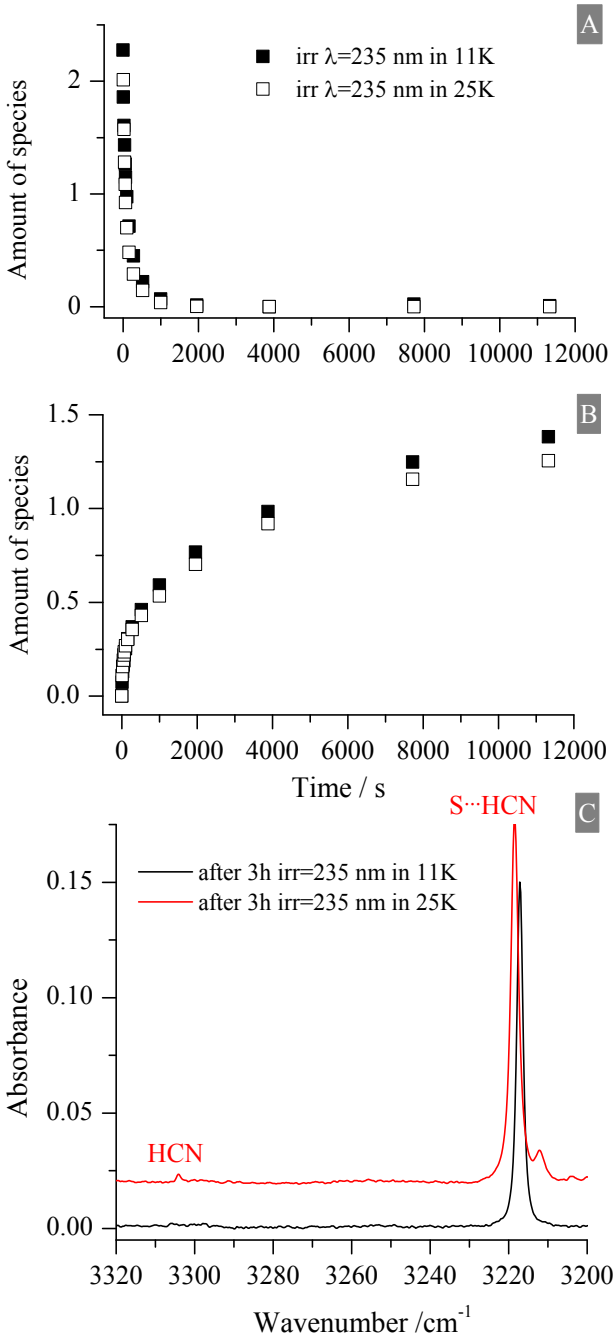

Fig S1 The ν CH stretching region of the HNCS/Ar spectra obtained after irradiation at 235 nm at 11K and 25K.

Table S1. Energetic parameters and abundances of CHNS isomers calculated at MP2 and DFT levels with 6-311++G(3df,3pd) basis set.

Isomer	MP2			B3LYP			B2PLYP(D3)		
	ΔE_{ZPE}	ΔG	%	ΔE_{ZPE}	ΔG	%	ΔE_{ZPE}	ΔG	%
HNCS	0.00	0.00	100.00	0.00	0.00	100.00	0.00	0.00	100.00
HSCN	14.58	30.27	0.00	33.25	47.05	0.00	41.84	39.78	0.00
HSNC	152.43	171.19	0.00	145.81	165.47	0.00	167.95	165.33	0.00
HCNS	125.41	145.29	0.00	132.52	159.17	0.00	144.47	157.62	0.00
HCSN	474.53	458.39	0.00	491.81	514.69	0.00	480.53	479.04	0.00
HNSC	484.62	503.96	0.00	501.64	519.76	0.00	506.36	503.50	0.00
c-C(H)NS	200.67	201.45	0.00	212.17	213.03	0.00	210.32	207.75	0.00
c-S(H)CN	231.09	252.07	0.00	221.76	246.42	0.00	249.89	246.76	0.00
c-N(H)CS	323.91	330.81	0.00	311.96	320.48	0.00	326.93	323.70	0.00

Table. S2. Experimental wavenumbers (cm^{-1}) of the HNCS, HSCN and HSNC isomers isolated in argon and nitrogen matrices. See also M. Wierzejewska and Z. Mielke, *Chem. Phys. Lett.*, 2001, **349**, 227 and M. Wierzejewska and R. Wieczorek, *Chem. Phys.* 2003, **287**, 169.

HNCS			HSCN			HSNC		
Ar matrix	**N_2 matrix**	**Mode**	**Ar matrix**	**N_2 matrix**	**Mode**	**Ar matrix**	**N_2 matrix**	**Mode**
3508.5	3497.0 3487.5	ν NH	2581.0	2581.0 2580.0	ν SH			
1981.5	1996.5 1990.5	ν CN	2182.5	2182.0	ν CN	2064.0	2065.5	ν NC
850.0	847.0	ν CS	959.5	966.0 961.0	δHSC			
578.0		δNCS						
465.5	473.0	δNCS						
987.0		comb.						

Table S3. Calculated harmonic (unscaled) wavenumbers of the S···HNC and S···HCN complexes at UMP2 and UB3LYP level with 6-311++G(3df,3pd).

UMP2[1]				UB3LYP				Mode
S···HNC		S···HCN		S···HNC		S···HCN		
ν	Δν	ν	Δν	ν	Δν	ν	Δν	
3666 (948)	-186	3409 (248)	-56	3618 (1007)	-111	3372 (273)	-12	ν CH
2018 (10)	-10	2035 (3)	+4	2101 (32)	+73	2192 (273)	+9	ν CN
589 (96)	+124	740 (29)	+36	530 (103)	+2	791 (28)	0	δ CH
580 (84)	+115	738(27)	+34	530 (106)	+2	790 (29)	-1	δ CH

[1]calculated wavenumbers (intensities) of the HNC and HCN monomers are equal to 3852 (258), 2028 (34), 465 (125) and 3465 (78), 2031 (0), 704 (72) (MP2) and 3729 (255), 2083 (72), 528 (131) and 3384 (67), 2183 (2), 791 (37) (B3LYP), respectively

Table S4. BSSE and ZPE corrected interaction energies (kJ/mol), interatomic distances (Å) and electron density parameters of the intermolecular bond critical points (au) computed at the MP2 and B3LYP/6-311++G(3df,3pd) level.

Complex	ΔE_{MP2}	Interatomic distance S···H	AIM parameters	
			$\rho(r)$	$\nabla^2\rho(r)$
S···HCN	-6.88	2.828	0.0100	0.0280
S···HNC	-10.25	2.513	0.0167	0.0414
H_2S···HCN	-6.95	2.749	0.0100	0.0270
H_2S···HNC	-10.60	2.450	0.0170	0.0412

Complex	ΔE_{B3LYP}	Interatomic distance S···H	AIM parameters	
			$\rho(r)$	$\nabla 2\rho(r)$
S···HCN	-1.06	2.819	0.0088	0.0230
S···HNC	-8.52	2.519	0.0152	0.0364
H_2S···HCN	-0.54	2.760	0.0098	0.0253
H_2S···HNC	-7.39	2.473	0.0166	0.0384