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# Measuring elemental abundance ratios in protoplanetary disks at millimeter wavelengths

D. Fedele<sup>1</sup> and C. Favre<sup>2</sup>

<sup>1</sup> Istituto Nazionale di Astrofisica, Osservatorio Astrofisico di Arcetri, L.go E. Fermi 5, 50126 Firenze, Italy  
e-mail: fedele@arcetri.astro.it

<sup>2</sup> Univ. Grenoble Alpes, CNRS, IPAG, 38000 Grenoble, France  
e-mail: cecile.favre@univ-grenoble-alpes.fr

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## ABSTRACT

Over million years of evolution, gas dust and ice in protoplanetary disks can be chemically reprocessed. There is evidence that the gas-phase carbon and oxygen abundances are subsolar in disks belonging to nearby star forming regions. These findings have a major impact on the composition of the primary atmosphere of giant planets (but it may also be valid for super-Earths and sub-Neptunes) as they accrete their gaseous envelopes from the surrounding material in the disk. In this study, we performed a thermochemical modeling analysis with the aim of testing how reliable and robust are the estimates of elemental abundance ratios based on (sub)millimeter observations of molecular lines. We created a grid of disk models for the following different elemental abundance ratios: C/O, N/O, and S/O, and we computed the line flux of a set of carbon-nitrogen and sulphur-bearing species, namely CN, HCN, NO, C<sub>2</sub>H, c-C<sub>3</sub>H<sub>2</sub>, H<sub>2</sub>CO, HC<sub>3</sub>N, CH<sub>3</sub>CN, CS, SO, H<sub>2</sub>S, and H<sub>2</sub>CS, which have been detected with present (sub)millimeter facilities such as ALMA and NOEMA. We find that the line fluxes, once normalized to the flux of the <sup>13</sup>CO *J* = 2–1 line, are sensitive to the elemental abundance ratios. On the other hand, the stellar and disk physical parameters have only a minor effect on the line flux ratios. Our results demonstrate that a simultaneous analysis of multiple molecular transitions is a valid approach to constrain the elemental abundance ratio in protoplanetary disks.

**Key words.** astrochemistry – protoplanetary disks

## 1. Introduction

Planets inherit their chemical composition from the protoplanetary disk in which they form. Because of thermal and chemical reprocessing, the relative abundance of different species within a disk can differ from the values of the natal molecular cloud. There is, in fact, evidence of nonsolar abundance of gas-phase carbon in some protoplanetary disks: TW Hya (e.g., Bergin et al. 2013; Favre et al. 2013; Kama et al. 2016), GM Aur (McClure et al. 2016), DM Tau (McClure et al. 2016) and HD 100546 (Kama et al. 2016). Compared to the solar abundance of C/H =  $2.69 \times 10^{-4}$  (Asplund et al. 2009), these systems appear to have subsolar carbon abundance. In particular, TW Hya and GM Aur show a substantial deficit by nearly 2 orders of magnitude. These results are based on the detection of deuterated hydrogen (HD) emission with the *Herschel* Space Observatory (see e.g., Bergin et al. 2013; Kama et al. 2020), which allows us to derive robust constraints on overall gas mass of disks. Further indications of the under abundance of gas-phase carbon in disks come from recent ALMA observations of multiple CO isotopologues, which reveal a surprisingly low CO abundance in the disk population of the Lupus star forming region (e.g., Ansdell et al. 2016; Miotello et al. 2017; Zhang et al. 2020).

The elemental abundance ratios within a disk is relevant for the composition of the primary gaseous atmosphere of giant planets. Several authors have investigated how the distribution of ices and volatiles in disks affect the final composition of planets. Growing attention is given to the gas-phase elemental abundance ratio of carbon-to-oxygen (hereafter C/O) in disks (e.g., Öberg et al. 2011; Piso et al. 2015; Mordasini et al. 2016;

Espinoza et al. 2017; Madhusudhan et al. 2017; Cridland et al. 2019). In this regard, there is evidence of disk-to-disk scatter of the gas-phase C/O abundance ratios (e.g., Semenov et al. 2018; Cleeves et al. 2018).

This paper presents a modeling analysis that aims to test the possibility of measuring the global values of the elemental abundance ratios C/O, N/O, and S/O in disks by means of (sub)millimeter observations of molecular transitions. The model details are given in Sect. 2, and the results of the grid are presented and discussed in Sects. 3 and 4, respectively. Conclusions are given in Sect. 5.

## 2. DALI thermochemical disk models

This work is based on simulations performed with the DALI thermo-chemical code of disks (Bruderer et al. 2012). DALI takes the stellar spectrum and the disk density structure as input. The code computes the dust temperature and radiation field strength by solving the dust continuum radiative transfer. In this work, the time-dependent thermochemistry is evaluated taking a typical age of  $10^6$  yr. The dust-continuum and line-emission maps are finally estimated through ray tracing. The collisional rates are taken from the LAMDA database (Schöier et al. 2005). The chemical network used in this work is based on the UMIST database (Woodall et al. 2007) and it is made of 167 species and 2138 reactions. The calculation starts with atomic abundances (with all molecular abundances set to zero) including nine elements (H, He, C, N, O, S, Mg, Si, Fe). The list of reactions includes (besides gas phase reactions): H<sub>2</sub> formation on

**Table 1.** Input physical parameters.

Parameter	Value	Description
$M_*$ [ $M_\odot$ ]	0.9	Stellar mass
$T_{\text{eff}}$ [K]	3250	Stellar temperature
$L_*$ [ $L_\odot$ ]	<b>1.5</b> ; 5; 10	Stellar luminosity
$L_X$ [erg s $^{-1}$ ]	<b>10<sup>29</sup></b> ; 10 <sup>30</sup> ; 10 <sup>31</sup>	Stellar X-rays luminosity
$R_{\text{in}}$ [au]	0.15	Inner disk radius
$R_{\text{out}}$ [au]	300.0	Outer disk radius
$\gamma$	0.2	$\Sigma(r)$ power-law exponent
$\Sigma_c$	1.0	$\Sigma(r)$ at $R = R_c$
$R_c$ [au]	120.0	Tapering disk radius
$h_c$	0.08; <b>0.13</b> ; 0.15	Disk scale height at $R_c$
$\psi$	0.0; <b>0.1</b> ; 0.2	Disk flaring exponent
$\Delta_{\text{gd}}$	5; <b>10</b> ; 50	Gas-to-dust mass ratio
$p$	3.5	Dust power-law exponent
$a_{\text{min}}$ [ $\mu\text{m}$ ]	0.001; <b>0.005</b> ; 0.01	Minimum grain size
$\chi$	<b>0.2</b> , 0.4, 0.6	Dust settling
$f_{\text{large}}$	0.55, <b>0.85</b> , 0.95	Large grains mass fraction

**Notes.** The values in boldface refer to the reference setup used for the model grid.

grains, freeze-out of molecules on grains, hydrogenation of ices, photodesorption, photodissociation, X-rays, cosmic-ray induced reactions, and PAH exchange charge reactions.

### 2.1. Disk physical structure

The gas surface density adopted here is described by a power-law radial profile with an exponential cut-off:

$$\Sigma_{\text{gas}}(R) = \Sigma_c \left(\frac{R}{R_c}\right)^{-\gamma} \exp\left[-\left(\frac{R}{R_c}\right)^{2-\gamma}\right], \quad (1)$$

where  $R_c$  is the cut-off radius and  $\Sigma_c$  the gas surface density at  $R = R_c$ . The dust surface density is  $\Sigma_{\text{gas}}/\Delta_{\text{gd}}$ , with  $\Delta_{\text{gd}}$  the gas-to-dust mass ratio. In the vertical direction, the gas density is parameterized by a Gaussian distribution with scale height  $h (= H/R)$  as follows:

$$h = h_c \left(\frac{R}{R_c}\right)^\psi, \quad (2)$$

where  $h_c$  is the gas scale height at  $R = R_c$ , and  $\psi$  the degree of flaring. Two populations of dust grains are included: small (size: 0.005–1  $\mu\text{m}$ ) and large (0.005–1000  $\mu\text{m}$ ), with a power-law size distribution and mass absorption cross sections as in [Andrews et al. \(2011\)](#). The small grains follow the same vertical distribution of the gas with scale height  $h$ , while the large grains have a reduced height  $\chi h$  ( $\chi < 1$ ) to account for the settling at the disk midplane. The dust surface density is  $\Sigma_{\text{dust}}(1 - f_{\text{large}})$  and  $\Sigma_{\text{dust}} f_{\text{large}}$  for the small and large grains, respectively. The adopted values are given in [Table 1](#).

### 2.2. Model grid

A grid of models was created for different initial abundances of N, O, and S relative to H while keeping the carbon abundance fixed to  $C/H = 1.35 \times 10^{-4}$ . [Table 2](#) reports the list of models with the initial abundances and the corresponding elemental abundance ratios C/O, C/N, N/O, and S/O. The initial abundances of the other elements are fixed and equal to:  $\text{He}/H = 7.59 \times 10^{-2}$ ,

**Table 2.** Grid of DALI chemical models.

ID #	N/H $\times 10^{-5}$	O/H $\times 10^{-4}$	C/O	N/O
1a	0.21	28.8	0.047	$7.4 \times 10^{-4}$
1b	0.21	2.88	0.469	$7.4 \times 10^{-3}$
1c	0.21	1.35	1.000	$1.6 \times 10^{-2}$
1d	0.21	0.86	1.562	$2.5 \times 10^{-2}$
2a	2.14	28.8	0.047	$7.4 \times 10^{-3}$
2b	2.14	2.88	0.469	$7.4 \times 10^{-2}$
2c	2.14	1.35	1.000	$1.6 \times 10^{-2}$
2d	2.14	0.86	1.562	$2.5 \times 10^{-2}$
3a	21.4	28.8	0.047	$7.4 \times 10^{-2}$
3b	21.4	2.88	0.469	$7.4 \times 10^{-1}$
3c	21.4	1.35	1.000	1.585
3d	21.4	0.86	1.562	2.477
	S/H $\times 10^{-8}$	O/H $\times 10^{-4}$	S/O	
2b-a	0.19	2.88	$6.6 \times 10^{-6}$	
2b	1.91	2.88	$6.6 \times 10^{-5}$	
2b-b	19.1	2.88	$6.6 \times 10^{-4}$	
2b-c	191.0	2.88	$6.6 \times 10^{-3}$	

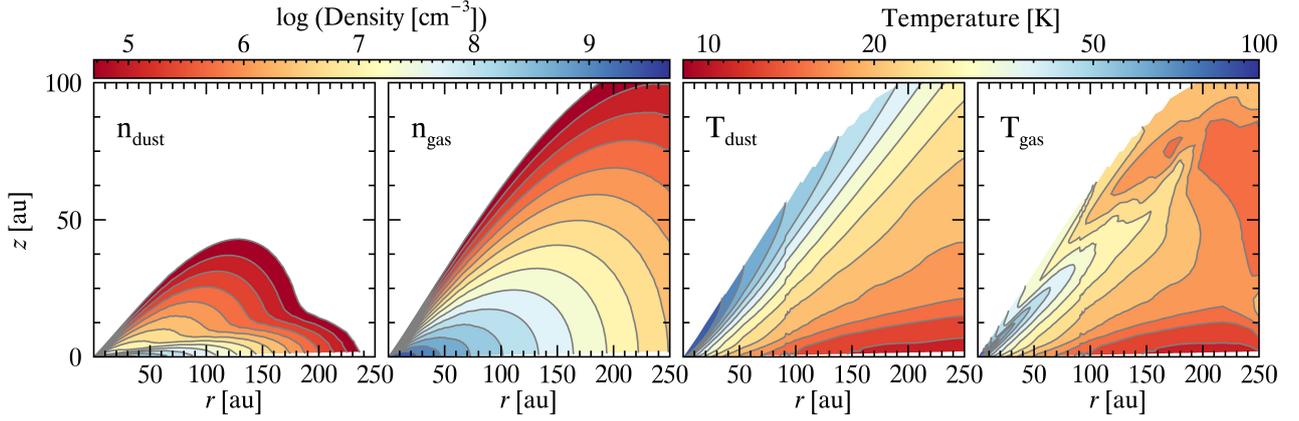
**Notes.** Each model starts with atomic abundances and is run in time-dependent mode with a stopping time of  $10^6$  yr.

$\text{Mg}/H = 4.17 \times 10^{-7}$ ,  $\text{Si}/H = 7.94 \times 10^{-6}$ ,  $\text{Fe}/H = 4.27 \times 10^{-7}$ . Four different values of oxygen abundances have been explored in order to investigate a wide range of C/O, from 0.046 to 1.562. Multiple sets of models have been created with the same ranges of C/O but for three abundances of nitrogen with the C/N spanning a range of 0.63 to 63.8. A subset of models for different sulfur abundances was computed.

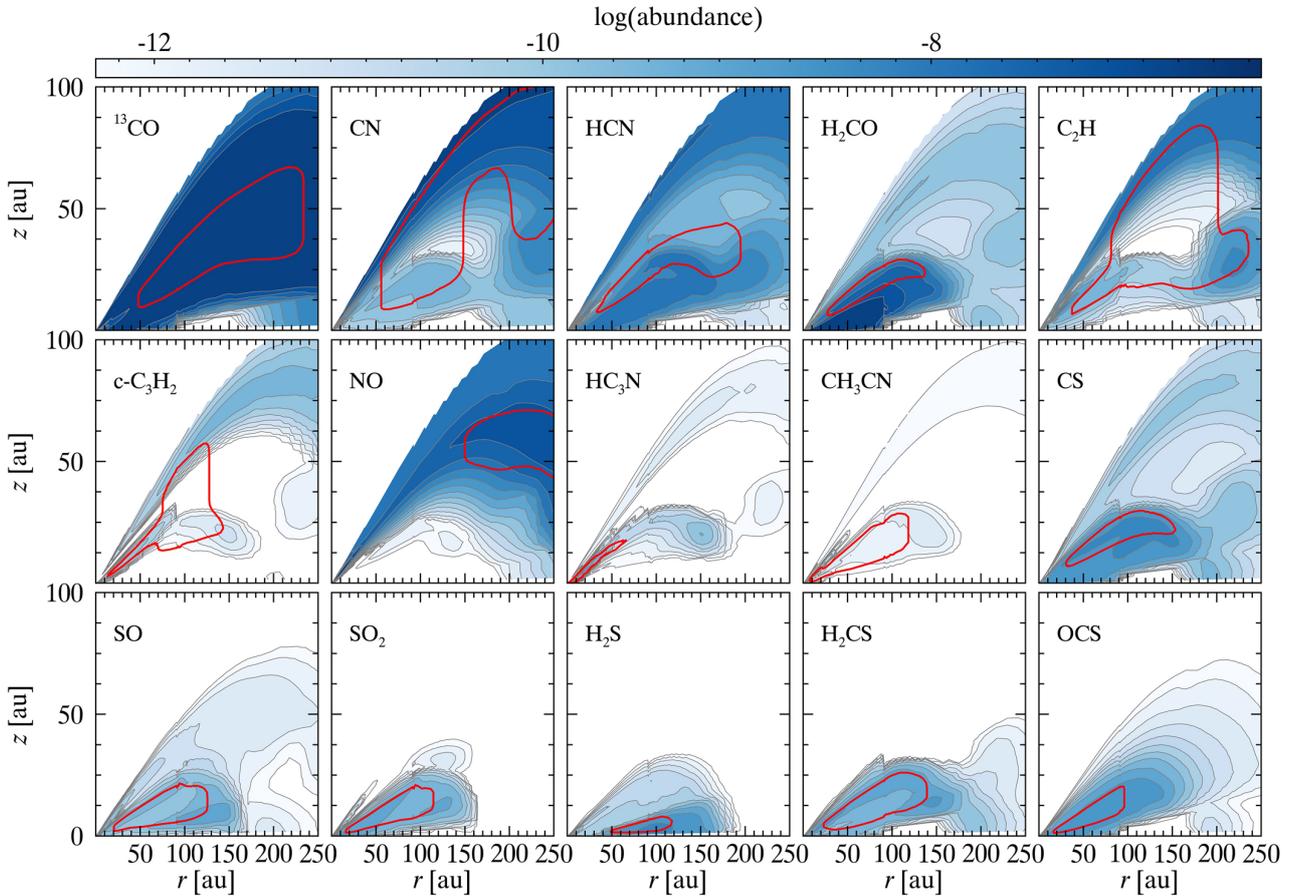
The input physical parameters of the reference model are listed in [Table 1](#) (values in boldface). Additional models have been created to analyze the response of the molecular transitions to the input physical structure for a given set of elemental abundances. Among the others, the parameters that influence the line intensities are the disk-flaring and scale height, the gas-to-dust mass ratio, and the dust properties (minimum grain size and dust settling, e.g., [Fedele et al. 2016](#)). Indeed,  $\psi$  and  $h_c$  control the gas temperature (hence line excitation and intensity), while the dust properties affect the opacity. The incident X-ray luminosity and total stellar luminosity are also investigated here. For each of these parameters, three different values are being examined here ([Table 1](#)).

In this work, we selected a set of carbon-, nitrogen- and sulphur-bearing species previously detected in disks at millimeter wavelengths with, for example, ALMA and NOEMA: CN, HCN, NO,  $\text{C}_2\text{H}$ ,  $c\text{-C}_3\text{H}_2$ ,  $\text{H}_2\text{CO}$ ,  $\text{HC}_3\text{N}$ ,  $\text{CH}_3\text{CN}$ , CS, SO,  $\text{H}_2\text{S}$ , and  $\text{H}_2\text{CS}$  (e.g., [Dutrey et al. 1996](#); [Qi et al. 2008, 2013](#); [Henning et al. 2010](#); [Chapillon et al. 2012](#); [Guilloteau et al. 2013](#); [Öberg et al. 2015](#); [Loomis et al. 2018](#); [Bergin et al. 2016](#); [Bergner et al. 2018](#); [Phuong et al. 2018](#); [Podio et al. 2019](#); [Le Gal et al. 2019a](#)). To our knowledge, NO has not been detected in protoplanetary disks yet, while it was detected in protostellar envelopes and shocks (e.g., [Codella et al. 2018](#)).

The density and temperature structures for the reference model are shown in [Fig. 1](#). [Figure 2](#) shows the abundance structures of the molecules studied here (initial elemental abundance



**Fig. 1.** Physical structure of the DALI reference model (boldface values in Table 1) showing the density and temperature structure of dust and gas.



**Fig. 2.** Abundance structure of the molecules studied in this paper for the reference model (boldface values in Table 1 and initial elemental abundances as in model 2b in Table 2). The (red) solid line indicates the layer including 75% of the emission for the transitions listed in Table 3.

as in model 2b of Table 2) along with the emitting layer of the transitions of Table 3.

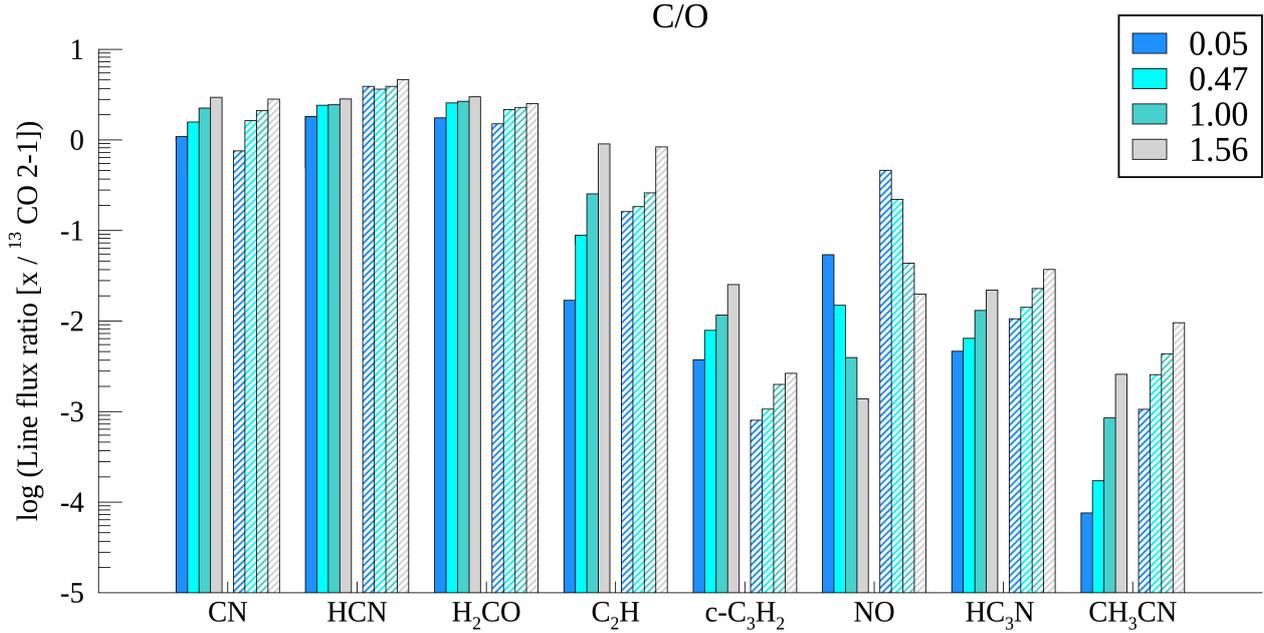
### 3. Results

Disk-integrated line fluxes are computed for a selection of commonly detected molecular transitions (Table 3). The lines are selected with the aim of minimizing the frequency settings with ALMA. In particular, all these transitions can be observed with three frequency settings (two in band six and one in band seven). In all cases, the disk inclination is fixed at  $30^\circ$  and the distance is set to 100 pc. The flux of the individual transitions is sensitive

to the excitation conditions and molecular abundances. To first order, the  $^{13}\text{CO } J = 2-1$  transition is a proxy of the temperature gradient of the disk. Thus, with the aim of normalizing the effect of the temperature structure on the line excitation, we divide all the line fluxes by the flux of the  $^{13}\text{CO } J = 2-1$  line. As a consequence, the changes in the line flux ratios reflect the intrinsic variation of the molecular abundances.

#### 3.1. Line flux ratios versus elemental abundance ratios

The line flux ratios are shown in Fig. 3 as a function of the initial C/O abundance ratio and for two different values of the initial



**Fig. 3.** Line flux ratios as a function of the initial C/O ratio for the transitions listed in Table 3. In all cases, the abundances of carbon, nitrogen, and sulfur are fixed at  $1.35 \times 10^{-4}$ ,  $2.14 \times 10^{-5}$  and  $1.91 \times 10^{-8}$ , respectively (model ID 2a, 2b, 2c, and 2d from Table 2).

**Table 3.** Molecular transitions analyzed here.

Species	Transition	$E_u$ [K]	$\nu$ [Gz]
$^{13}\text{CO}$	2–1	15.87	220.39868
CN	3–2	32.66	340.24777
HCN	4–3	42.53	354.50547
$\text{H}_2\text{CO}$	$3_{0,3}-2_{0,2}$	62.50	218.21000
$\text{C}_2\text{H}$	$J = \frac{7}{2} - \frac{5}{2}, F = 4 - 3$	25.15	262.00426
$\text{c-C}_3\text{H}_2$	$6_{1,6}-5_{0,5}$	38.61	217.82215
$\text{HC}_3\text{N}$	27–26	165.04	245.60632
$\text{CH}_3\text{CN}$	$12_2-11_2$	97.44	220.73027
CS	5–4	35.30	244.93556
SO	$7_8-6_7$	81.20	340.71415
NO	$J = \frac{7}{2} - \frac{5}{2}, F = \frac{9}{2} - \frac{7}{2}$	36.13	351.04352
OCS	18–17	99.81	218.90335
$\text{SO}_2$	$5_{3,3}-4_{2,2}$	35.90	351.25722
$\text{H}_2\text{S}$	$2_{2,0}-2_{1,1}$	84.00	216.71044
$\text{H}_2\text{CS}$	$7_{16}-6_{15}$	60.0	244.04850

**Notes.** The collisional rates are taken from the LAMDA database (Schöier et al. 2005; <https://home.strw.leidenuniv.nl/~moldata/>). Note in particular that the  $\text{C}_2\text{H}$  rates have been recently updated with those from Dagdigan (2018) for collisional partners ortho and para  $\text{H}_2$ .

abundance of nitrogen: filled bars are the models with low nitrogen abundance (model IDs: 1a, 1b, 1c, and 1d in Table 2), while the dashed bars show the high nitrogen abundance case (model IDs 3a, 3b, 3c, and 3d in Table 2). Further models are presented in the appendix. All the species show a positive trend with the initial C/O abundance ratio. The only exception is NO, whose line-flux ratio decreases with increasing C/O. Among the others, NO,  $\text{C}_2\text{H}$ ,  $\text{c-C}_3\text{H}_2$ ,  $\text{HC}_3\text{N}$ , and  $\text{CH}_3\text{CN}$  are the most sensitive species to the gas-phase C/O abundance ratio, with the flux ratio increasing by 1–2 orders of magnitude.

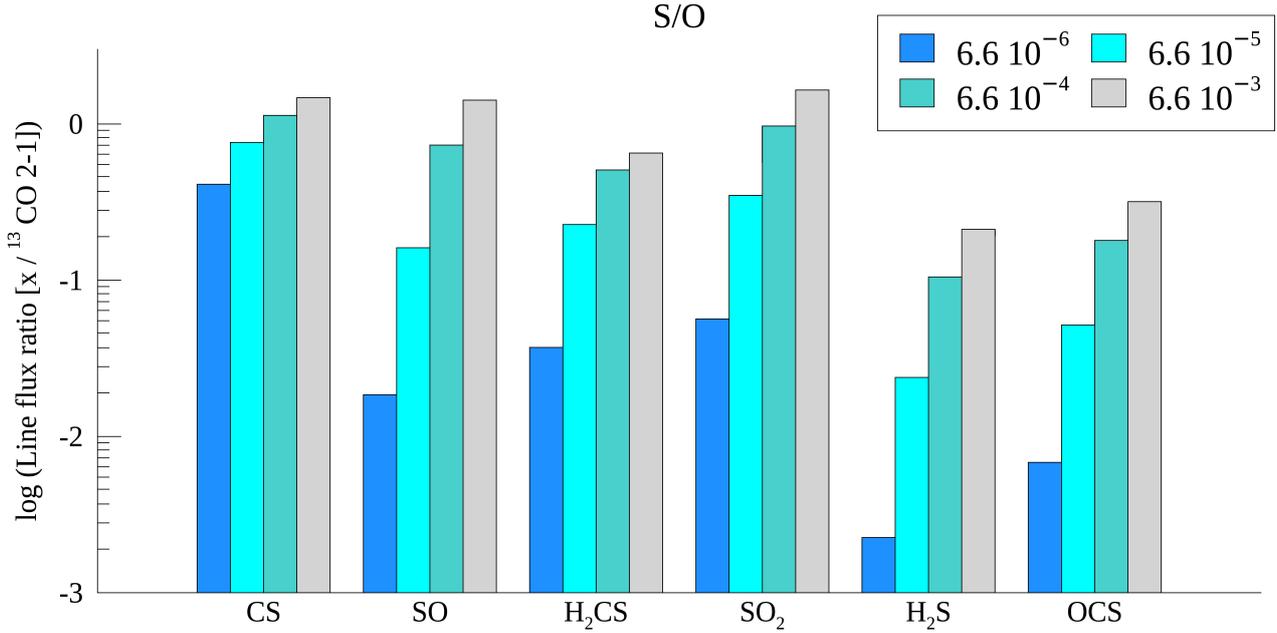
The models with the high nitrogen abundance show the same trends with regard to the C/O value. Increasing the

nitrogen abundance has the effect of increasing the flux ratios of HCN, NO,  $\text{HC}_3\text{N}$ , and  $\text{CH}_3\text{CN}$ . Interestingly, the ratio  $\text{CN}/^{13}\text{CO}$  does not change substantially. Notably, the  $\text{c-C}_3\text{H}_2/^{13}\text{CO}$  ratio decreases drastically compared to the low-nitrogen case.

Figure 4 shows the behavior of sulphur-bearing species as a function of the initial S/O abundance ratio. In this case, the nitrogen, carbon, and oxygen abundances are fixed (model IDs 2b, 4b, 5b). We note that initial sulphur abundance is varied by two orders of magnitude to account for the low detection rate of sulphur species in disks (e.g., Semenov et al. 2018). The flux ratio of SO and  $\text{H}_2\text{S}$  varies by almost the same amount.

### 3.2. Line fluxes versus stellar-disk physical parameters

The line-flux ratios presented above can also be sensitive to the stellar and disk physical parameters that alter the temperature and density structures, hence the excitation conditions. The results of the physics model grid are shown in Fig. 5. In all cases, the initial elemental abundances are fixed in the same way as in the reference model (model ID 2b in Table 2). A first immediate result is that the flux ratios of some species remain almost unaltered in all cases: this is the case of CN, HCN,  $\text{H}_2\text{CO}$ , CS, and  $\text{H}_2\text{CS}$ . On the other hand, variations by a factor of a few are predicted for the other species. The effect of the individual parameters are described as follows: (i) Stellar luminosity ( $L_*$ ) – the flux ratio of  $\text{HC}_3\text{N}$  and  $\text{CH}_3\text{CN}$  increases by a factor of a few when the luminosity goes from 1.5 to  $10 L_\odot$ ; (ii) stellar X-ray luminosity ( $L_X$ ) – varying  $L_X$  by two orders of magnitude induces only minor changes in the line-flux ratios,  $\text{SO}_2$  and OCS decrease substantially for large  $L_X$  values, on the contrary,  $\text{H}_2\text{S}$  and  $\text{c-C}_3\text{H}_2$  slightly increase with increasing  $L_X$ ; (iii) gas-to-dust mass ratio ( $\Delta_{\text{gd}}$ ) – variations by a factor of a few are predicted for  $\text{C}_2\text{H}$  (decreasing with increasing  $\Delta_{\text{gd}}$ ),  $\text{HC}_3\text{N}$ , and  $\text{CH}_3\text{CN}$  (increasing with  $\Delta_{\text{gd}}$ ); (iv) disk scale height ( $h_c$ ) – increasing  $h_c$  lead to higher flux ratios for  $\text{C}_3\text{H}_2$ ,  $\text{HC}_3\text{N}$ , and  $\text{CH}_3\text{CN}$ ; (v) disk flaring ( $\psi$ ) – minor changes are predicted for  $\text{c-C}_3\text{H}_2$ , whose line-flux ratio increases slightly with  $\psi$ , no substantial changes are expected



**Fig. 4.** Line flux ratios of sulphur-bearing species as a function of the initial S/O abundance ratio (Table 2, ID 2b-a, 2b, 2b-c, 2b-d). In this case, only the sulphur-bearing species are shown.

for the other transitions; (vi) minimum grain size ( $a_{\min}$ ) – varying  $a_{\min}$  from  $0.001 \mu\text{m}$  to  $0.01 \mu\text{m}$ , it has no impact on the line-flux ratios; (vii) dust settling ( $\chi$ ) – minor changes are predicted for some sulphur-bearing species, as well as for  $\text{CH}_3\text{CN}$ ; (viii) large grain mass fraction ( $f_{\text{large}}$ ) – increasing the mass fraction of the large grain population from 55 to 95% has the effect of lowering the line-flux ratio of several species by a factor of a few. On the contrary, NO,  $\text{HC}_3\text{N}$ , and  $\text{CH}_3\text{CN}$  show an opposite trend.

#### 4. Discussion

For a detailed description of the molecular composition of protoplanetary disks, we invite the reader to read the seminal papers of, for example, Aikawa et al. (2002), Semenov & Wiebe (2011), Henning & Semenov (2013), Walsh et al. (2015), Guilloteau et al. (2016), Agúndez et al. (2018), Le Gal et al. (2019a). This section aims instead to discuss the chemical routes that lead to the chemical enrichment as a function of the elemental abundance ratios. The following discussion is based on reactions taken from the UMIST chemical network (Woodall et al. 2007) (see Sect. 2).

An interesting finding of our modeling (see Sect. 3) is that the initial C/O value simultaneously influences several species, that emit within different layers of the disk. The higher abundance of the hydrocarbons  $\text{C}_2\text{H}$  and  $c\text{-C}_3\text{H}_2$  with C/O is a direct consequence of the enhanced carbon chemistry (Bergin et al. 2016). Indeed, inside a protoplanetary disk there are multiple paths for the formation of  $\text{C}_2\text{H}$  starting from neutral atomic and molecular carbon. The formation routes starting with atomic carbon are described in Bergin et al. (2016) and Bergner et al. (2019) and are not repeated here. A third important route is:



We also note that  $\text{C}_2\text{H}^+$  can further react to form  $\text{C}_2\text{H}_2^+$ :



Similarly, the gas-phase formation of  $c\text{-C}_3\text{H}_2$  in disks proceeds from the  $\text{C}_3\text{H}^+$ :



Although reaction (10) is about an order of magnitude slower than reaction (9), it might still influence the production of  $\text{C}_3\text{H}^+$ .

In turn, the higher content of hydrocarbons trigger the production of the nitriles. The formation of  $\text{HC}_3\text{N}$  is indeed strictly linked to  $\text{C}_2\text{H}$  as the main reactions are:



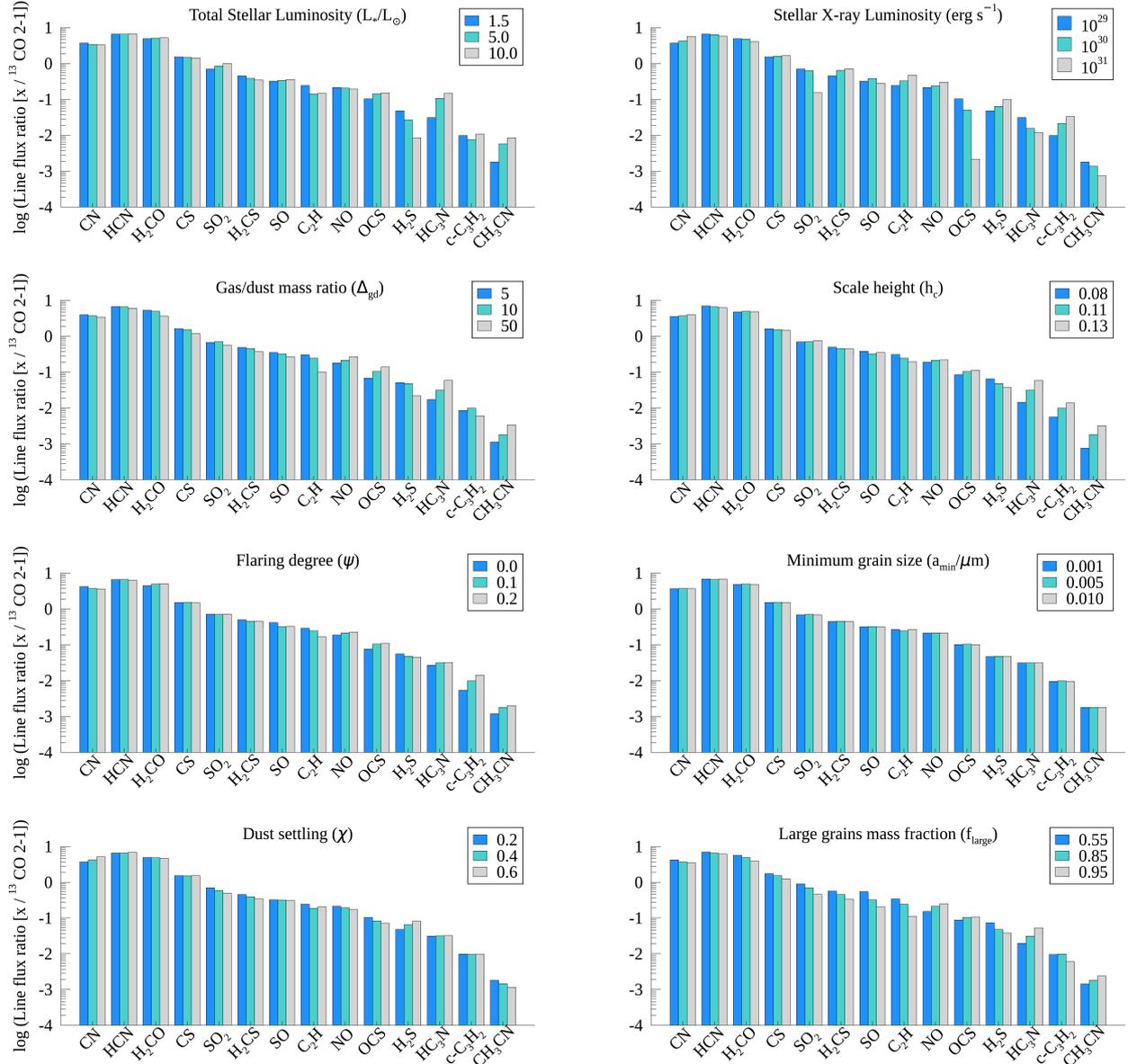
while that of the methyl cyanide  $\text{CH}_3\text{CN}$  proceeds primarily from:



and potentially (but less probably) from:



Thus, the formation of both  $\text{HC}_3\text{N}$  and  $\text{CH}_3\text{CN}$  (strictly linked to the presence of hydrocarbons) requires free atomic or molecular carbon to be triggered. This likely explains the positive trend of the line-flux ratios of the nitriles transitions with C/O.



**Fig. 5.** Line flux ratios for different stellar and disk physical properties (see Table 1 for definitions). In all cases, the initial elemental abundances are fixed as in model run 2b in Table 2.

However, the situation is the opposite for NO, which is destroyed by atomic carbon and hydrocarbons:



The trend of the nitriles with the initial nitrogen abundance can be easily understood. An interesting result is the behavior of  $\text{C}_2\text{H}$  and  $c\text{-C}_3\text{H}_2$  with  $\text{N}/\text{H}$  (and  $\text{N}/\text{O}$ ): in the first case, the line-flux ratio increases slightly with the nitrogen abundance, and this is due to the formation of  $\text{C}_2\text{H}_2^+$  (precursor of  $\text{C}_2\text{H}$ ) via reaction (7). On the other hand,  $c\text{-C}_3\text{H}_2$  is destroyed (among others) by the reaction with atomic nitrogen (reaction (16)) to form  $\text{HC}_3\text{N}$  (depending on the location in the disk).

Finally, the behavior of the sulphur-bearing species with  $\text{S}/\text{O}$  is easily understood, as their abundance increases with increasing abundance of sulphur. Among the species studied,  $\text{SO}$  and  $\text{H}_2\text{S}$  are more sensitive to the global sulphur abundance compared to  $\text{CS}$  and  $\text{H}_2\text{CS}$ . The low detection rate of  $\text{SO}$  and  $\text{H}_2\text{S}$  (e.g., Booth et al. 2018; Semenov et al. 2018) and the detection of  $\text{CS}$  and  $\text{H}_2\text{CS}$  (e.g., Le Gal et al. 2019b) hints at a low gas-phase abundance of sulphur in disks, with sulphur being primarily locked in refractory elements (e.g., Kama et al. 2019). In this regard, it is interesting to note that the direct comparison of  $\text{H}_2\text{CO}$  and  $\text{H}_2\text{CS}$  can provide direct information on the  $\text{S}/\text{O}$  abundance ratio in disks as the main formation route of both species share the same parent molecule, the radical  $\text{CH}_3$ :



From the discussion above, it is clearly evident that the simultaneous analysis of multiple molecular transitions is a powerful tool to constrain the elemental abundance ratios in

protoplanetary disks. A proper selection of molecular lines is further important to breaking the degeneracy between the elemental abundances and physical parameters. For example, the line-flux ratios of  $c\text{-C}_3\text{H}_2$ ,  $\text{HC}_3\text{N}$  and  $\text{CH}_3\text{CN}$  increases with increasing  $C/O$  ratio, but also with the disk scale height ( $h_c$ ); therefore, one could not distinguish between the two. This is not the case for  $\text{C}_2\text{H}$ ,  $\text{CN}$ ,  $\text{HCN}$ , and  $\text{H}_2\text{CO}$ , for example, which do not substantially vary with  $h_c$ . We also note that the situation is similar for the flaring degree.

### Considerations about dynamical processes

The results presented in this paper are based on a static disk model. Viscous accretion, inward migration of pebbles, and vertical mixing may induce a variation of the elemental abundance ratios (e.g., [Piso et al. 2015](#); [Öberg & Bergin 2016](#); [Booth et al. 2017](#); [Krijt et al. 2018](#)). As a consequence, the molecular abundances and the line fluxes also vary accordingly. The significance of radial and vertical mixing depends on several factors such as the viscosity, the ionization rate (for viscous accretion), the degree of turbulence (for the vertical mixing), and the coupling of gas and dust (radial drift). We note in particular, that large ( $\geq 1$  mm) dust grains can be easily trapped in local pressure maxima (e.g., [Pinilla et al. 2012](#); [Zhu & Stone 2014](#)), slowing down the inward migration or ice-coated pebbles.

Nevertheless, the molecular transitions investigated in this paper are mostly sensitive to the cold gas reservoir in the outer disk. The molecular content of the inner disk region (spatial scales  $\leq 10$  au) can be traced via infrared spectroscopy, which is sensitive to warm and hot gas. In particular, future observations with e.g., JWST will also allow us to detect several species highly sensitive to the  $C/O$  ratio (e.g.,  $\text{C}_2\text{H}_2$ ,  $\text{CH}_3$ ,  $\text{CH}_4$ ,  $\text{C}_3\text{H}_4$ ,  $\text{C}_6\text{H}_6$ ), enabling us to constrain the molecular richness and the elemental abundance ratio. A direct comparison between infrared and millimeter molecular transitions can thus provide information about the radial distribution of the elemental abundance ratios.

## 5. Conclusions

The results presented in this paper demonstrate that the gas-phase elemental abundance ratio of  $C/O$ ,  $N/O$ , and  $S/O$  in protoplanetary disks can be constrained by means of line-flux ratios of multiple molecular transitions. The stellar and disk physical properties appear to only slightly change the flux ratios studied here, and only some species are affected. This further demonstrates that the flux of the  $^{13}\text{CO } J = 2-1$  line is indeed a good proxy of the physical conditions in disks. Nevertheless, our study strongly suggests the need to simultaneously compare the flux ratios of multiple species to discern between physical properties and elemental abundances.

The advent of broad-band correlators in (sub)millimeter interferometry offers a unique opportunity to carry out simultaneous observations of multiple species. This allows us to perform a statistical investigation of the chemical composition of disks and to determine the elemental abundance ratios. Such a study is important to make the link between the atmospheric composition of planets and the primordial composition of protoplanetary disks.

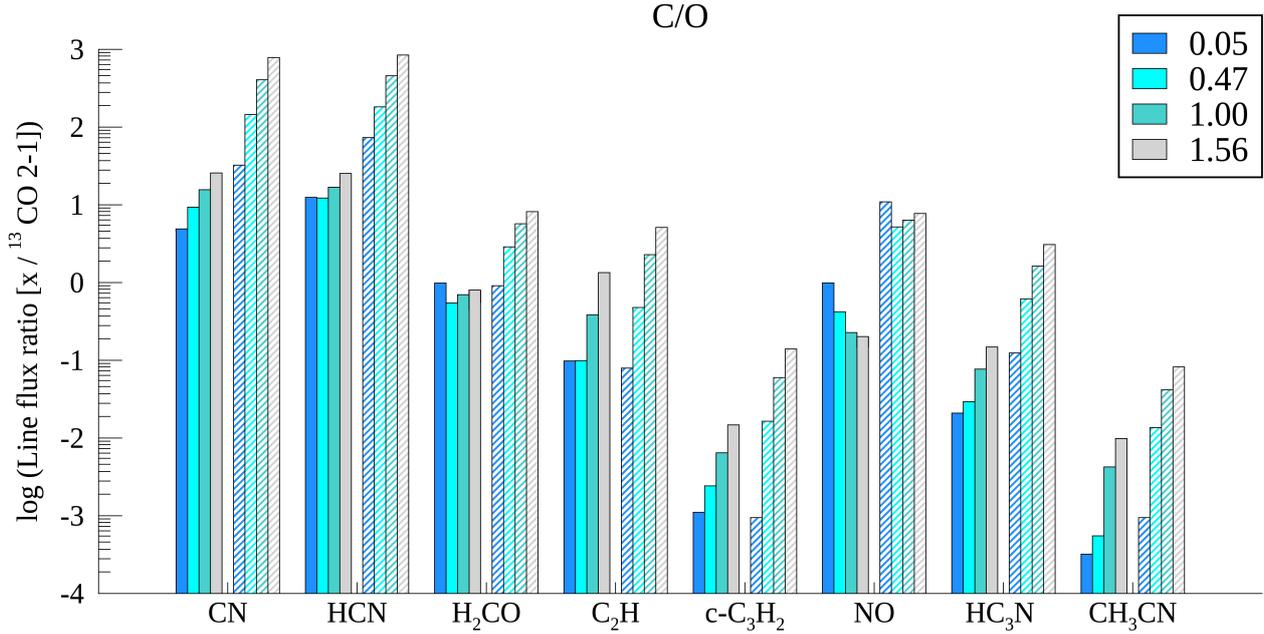
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## Appendix A: Model with carbon depletion



**Fig. A.1.** Same as Fig. 3 for  $C/H = 1.35 \times 10^{-5}$  (filled bars) and  $1.35 \times 10^{-6}$  (dashed bars) (see Table A.1).

A direct link may exist between the depletion of different elements in disks. This depends on their volatility with nitrogen, carbon, oxygen, and sulphur, forming a sequential path from the most to the least volatile element that we can observe. While there is evidence of depletion of C, N, and O in disks, as of today there is no evidence of depletion of nitrogen (e.g., [Cleeves et al. 2018](#)). We thus performed further DALI models fixing the nitrogen abundance and lowering the elemental abundance of carbon (Table A.1). The results are shown in Fig. A.1. Overall, the line-flux ratios show similar trends as in Fig. 3. Notably, the transitions of the nitrogen-bearing species are now much stronger than  $^{13}\text{CO } J = 2-1$ .

**Table A.1.** Further DALI chemical models for two different values of the carbon abundance.

ID #	N/H $\times 10^{-5}$	O/H $\times 10^{-4}$	C/O	N/O
$C = 1.35 \times 10^{-5}$				
#	N/H $\times 10^{-5}$	O/H $\times 10^{-4}$	C/O	N/O
4a	2.14	28.8	0.047	$7.4 \times 10^{-4}$
4b	2.14	2.88	0.469	$7.4 \times 10^{-3}$
4c	2.14	1.35	1.000	$1.6 \times 10^{-2}$
4d	2.14	0.86	1.562	$2.5 \times 10^{-2}$
$C = 1.35 \times 10^{-6}$				
#	N/H $\times 10^{-5}$	O/H $\times 10^{-4}$	C/O	N/O
5a	2.14	28.8	0.047	$7.4 \times 10^{-4}$
5b	2.14	2.88	0.469	$7.4 \times 10^{-3}$
5c	2.14	1.35	1.000	$1.6 \times 10^{-2}$
5d	2.14	0.86	1.562	$2.5 \times 10^{-2}$