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Chemistry on hot astrochemical dust surfaces: Sulfur in AGB outflows

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Abstract. Astrochemical models treat dust surfaces as ice covered. We investigate the effects of implementing increased bare dust binding energies of CO and S-bearing species on the chemistry in the outflows of asymptotic giant branch (AGB) stars. We demonstrate the potential for improving agreement with observations in the outflow of IK Tau.

Increasing the binding energies to measured and computationally derived values in high mass-loss AGB outflows increased the production of daughter species. Switching from a high binding energy on bare dust to weaker binding to ice, the gas phase abundance increased at a radius in agreement with observations of IK Tau, suggesting that displacement of bound species could contribute to this observational puzzle. Using a strong binding to bare dust, a gas phase increase was not observed, however parent species concentrations had to be increased by around a factor of four to explain observed concentrations.

Keywords. Surface Binding, Kinetics, AGB Outflows, Sulfur

1. Introduction

Chemistry on hot, bare dust surfaces affects the chemical constituents of a variety of astrochemical environments, from the outflows of stars on the Asymptotic Giant Branch (AGB), through the InterStellar Medium (ISM) to ProtoPlanetary Disks (PPDs). Some binding and reaction processes on ice surfaces have been studied Cuppen *et al.* (2017), but chemistry on bare dust is poorly constrained by experiment Penteado *et al.* (2017).

Most stellar dust is formed in the outflows of Asymptotic Giant Branch (AGB) stars Zhukovska & Henning (2013), where temperatures from 10s to 1000s K, interstellar radiation, and gas concentrations from 10 to 10^{13} cm^{-3} produce bare dust surfaces Van de Sande *et al.* (2019). There is widespread interest in new oxidation pathways to CO_2 and SO_2 Gobrecht *et al.* (2016), chemical routes to Complex Organic Molecules (COMs) from e.g. acetylene Millar (2016), and modelling concentrations of observed species in the outflows of AGB stars Danilovich *et al.* (2020).

Chemical kinetic models designed to investigate processes in these environments typically use chemical networks of many reactions to consume a relatively small number of "parent" species, which have initial concentrations constrained by observations, and produce "daughter" species McElroy *et al.* (2013).

Here we report on development of a technique to treat the binding of gas phase CO and sulfur bearing species to bare dust in a chemical model of AGB outflows. We examine the impact of bare dust binding energies, E_{bind}, on gas phase (observable) composition in outflows with generic initial parent species abundance (Carbon or Oxygen rich outflows)

Table 1. Physical parameters used in model outflows.

Physical Parameters	Carbon-Rich	Oxygen-Rich	IK Tau
Mass-loss rate, $M_\odot$ / yr^{-1}	1×10^{-5}	1×10^{-5}	5×10^{-6}
Stellar Temperature, T* / K	2000	2000	2100
Outflow velocity, ν_∞ / km s^{-1}	10	10	17.5
Stellar Radius, R* / cm	5×10^{13}	5×10^{13}	2×10^{13}
Drift velocity, ν_{drift} / km s^{-1}	15	15	10
Dust temperature, T$_{dust,*}$ / K	1950	1110	1110
Exponent of T, ϵ [a]	0.7	0.7	0.7
Exponent of T$_{dust}$(r)/dust temperature profile, s [b]	0.9	1.3	1.3

[a] See equation 2.1, [b] See equation 2.2.

Table 2. Grid of chemical models calculated.

Outflow	Species	E$_{bind}$ treatment
C-rich	CO	Range from 855 to 10,300 K
C-rich	SO	Switch from 1,800 to 15,000 K
O-rich	SO	Switch from 1,800 to 15,000 K
IK Tau	SO, CO, SiO, SiS, CS, H$_2$S, SO$_2$, HS	Switch from ice to dust[a]
IK Tau	SO, CO, SiO, SiS, CS, H$_2$S, SO$_2$, HS	Separate dust bound species

[a] See Section 3, Table 3 for values.

and for oxygen rich AGB star IK Tau, where we attempt to explain the observed radial concentration profiles of SO and SO$_2$.

2. Methods

To identify targets for laboratory investigation of binding energies, electronic structure calculations with hybrid density functional/Hartree-Fock theory with the B3LYP functional and the 6-311+G(2d,p) basis set were used to estimate the binding energies of a range of species to a model Fe$_2$SiO$_4$ molecule and a cluster of 12 H$_2$O molecules, as proxies for astrochemical dust and ice surfaces, respectively. This is a relatively flexible basis set with both diffuse and polarisation functions. A CO or sulfur bearing molecule was allowed to relax into a cluster with the model surface and the reduction in energy of the system taken to be the binding energy.

The estimated binding energies were then implemented in an existing chemical kinetics model AGB outflows (Van de Sande *et al.* 2019). Tables 1 to 2 list the physical parameters and the grid of models calculated. All model runs used initial and final radii of 10^{15} and 10^{18} cm, respectively and a gas temperature, T, defined by equation 2.1:

$$T(r) = T_* \left(\frac{r}{R_*} \right)^{-\epsilon}$$ (2.1)

where, T_* and R_* are the stellar temperature and radius, respectively, and ϵ is a dimensionless power law exponent. The dust temperature is then determined by the energy balance between gas and dust, given by equation 2.2:

$$T_{dust}(r) = T_{dust*} \left(\frac{2r}{R_*} \right)^{-\frac{2}{(4+s)}}$$ (2.2)

where T_{dust*} is the stellar temperature determined from fits to radiative transfer modelling, and s describes the wavelength dependency of the dust opacity. Parent species concentrations were set as in Van de Sande & Millar (2022). The "C-rich" and "O-rich" model conditions used here represent generic initial parent species concentrations (Van de Sande, Walsh, & Millar 2021), but with high mass loss rates to maximise dust-gas interactions.

Table 3. Calculated binding energies of CO and S bearing species on Fe-silicate, as a model of bare dust, and ice surfaces.

Species	Binding energy on Fe-silicate kJ mol^{-1}	on H$_2$O Ice kJ mol^{-1}
SO	124	13
CO	86	7
SiO	245	41
SiS	116	43
CS	157	17
H$_2$S	74	20
SO$_2$	83	39
HS	218	21

As a first approximation, the binding energies for CO and SO in the chemical network were adjusted to those estimated by electronic structure calculations. This assumes that all dust in the outflow is bare, the opposite extreme case to previous work where all dust is implicitly assumed to be covered by ice (Van de Sande *et al.* 2019). To improve upon this, a switch in binding energy was implemented when more than two monolayers of ice were present on the dust. This approximates displacement of material strongly bound to the dust surface by the bulk ice species (mostly H$_2$O). Finally, material bound to bare dust was treated as a separate, non-interacting species, which could only form from gas uptake and be destroyed by thermal or photo-desorption. This represents the assumption that material bound to the bare dust surface can become trapped underneath layers of ice. If a significant effect is observed, this study can indicate the likely effect of each of these scenarios, without the involved process of implementing a full treatment such as a layered ice model.

3. Results and Discussion

Table 3 shows the results of the electronic structure calculations of binding energies. Binding to dust was always found to be significantly stronger than binding to H$_2$O ice, in the case of SO, CO, CS, and HS with E$_{bind}$ larger by a factor of as much as 10. This suggests that implementation of binding to bare dust in chemical kinetic networks could have a significant effect on observable species.

3.1. *Bare dust in generic outflows*

In this case the binding energy used in previous work (Van de Sande *et al.* 2019) is increased to account for a bare dust surface. Increased binding energy for the parent CO leads to a longer lifetime and higher concentration on the dust surface, which allows reactions on the surface to compete with other routes to chemical synthesis. This results in competitive chemical pathways to surface bound and gas phase product daughter species. Figure 1 shows the effect on surface and gas phase parent CO and daughter CO$_2$ for a high mass-loss rate C-rich outflow. As the parent binding energy increases, the surface and gas phase concentrations of the CO$_2$ daughter increase, with a relatively small (< 1 %) impact on the parent concentration. Whilst in this case the gas phase CO$_2$ daughter concentration remains low, this does demonstrate that a treatment of binding to bare dust can alter the balance of competitive chemical pathways to more daughter species, e.g. including oxidation of CO under C-rich conditions.

A similar effect was found for the oxidation of SO to SO$_2$, both in C-rich and O-rich outflows, with gas phase SO$_2$ increasing by more than two orders of magnitude. This again demonstrates an altered balance of competing chemical pathways, and suggests that dust surfaces might be able to act as reservoirs for chemical species of increasing chemical complexity.
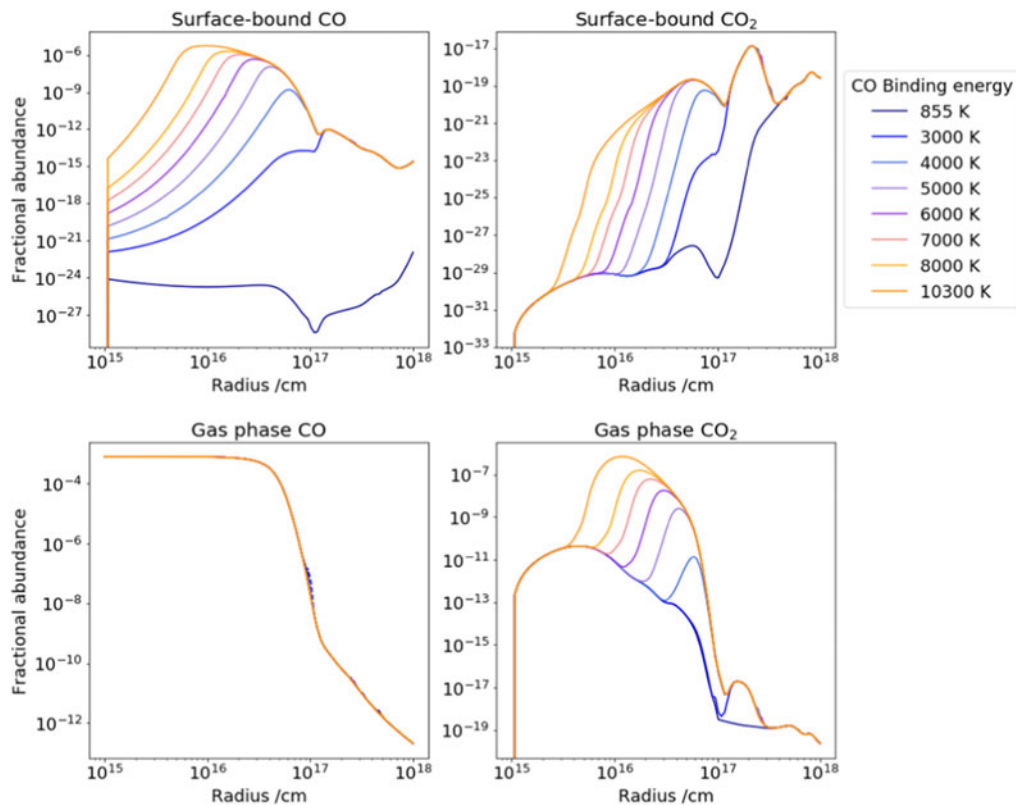
Figure 1. The fractional abundance of surface-bound CO, surface-bound CO_2, gas phase CO and gas-phase CO_2 against radius with various binding energies of CO for a generic C-rich stellar outflow.

3.2. *Binding energy switch in IK Tau*

Switching the binding energy from a value representing binding to bare dust to one which represents binding to ice once two ice monolayers have formed on the surface approximates displacement of material strongly bound to the dust surface by the bulk ice species. This could lead to an increased gas phase concentration such as observed at around 10^{16} cm radius in the outflow of IK Tau (Danilovich *et al.* 2020). Figure 2 shows the effect on SO and SO_2 of implementing such a switch for IK Tau. In the relatively low radiation field less than 10^{16} cm from the star, SO and other species are able to accumulate on the dust surface, leading to a depletion of the initial parent abundance. When the surface becomes coated and the binding energy of the sulfur species switches to the lower ice-surface value, the temperature is still sufficiently high ($>$100 K) for thermal desorption to release the SO into the gas phase. This could be a mechanistic explanation for some puzzling observations, although other mechanisms which allow increased UV radiation field have also been proposed (Danilovich *et al.* 2020).

As shown in Figure 3, treating the bare dust-bound material as a separate species leads to a rather similar gas-phase abundance profile to the assumption of ice only binding, though the concentrations of all species in Table 3 were found to decrease by a factor of approximately four. This suggests that dust could act as a significant chemical reservoir. In the case of these species in the outflow of IK Tau, photo-desorption removes the ice layer in the outer reaches of the outflow. However for species which chemisorb strongly to the surface (essentially becoming part of the dust) material may remain bound to the
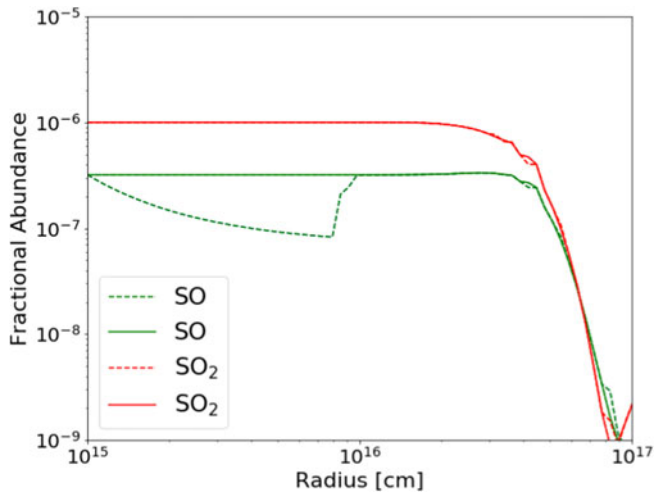
Figure 2. The fractional abundance of SO (green, initial concentration 3×10^{-7}) and SO$_2$ (red, initial concentration 1×10^{-6}) when using a binding energy switch at two monolayers ice coverage (dashed lines) compared to assuming an ice surface binding energy for IK Tau.
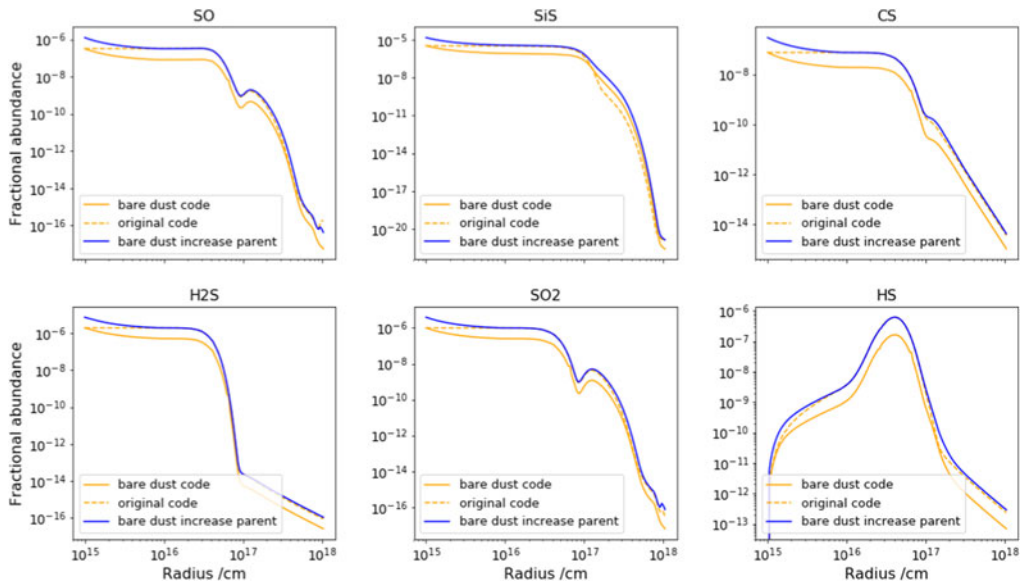

Figure 3. The gas-phase fractional abundance of sulfur species in the simulated outflow of IK Tau.

surface until its supply to the ISM. If reaction occurs in the warmer part of the outflow, complex products could remain bound to the dust, protected by layers of ice, and be carried to other astrochemical environments.

Measurement of binding to bare dust, rather than ice covered surfaces, using relevant laboratory techniques would be required to constrain the potential impact of bare dust in astrochemical environments. Stable species such as CO, CO$_2$ and SO$_2$ seem good candidates for initial investigations, since there are open questions in the literature where these species are relevant. For more reactive and hazardous compounds which are difficult to handle in the laboratory, computational methods to constrain binding energies may also be appropriate.

4. Conclusions

We have presented an initial assessment of the impact of treating binding to bare dust surfaces in the outflows of AGB stars. Different chemical routes were found to be competitive in the oxidation of CO and SO to CO_2 and SO_2 in both C-rich and O-rich high mass-loss rate AGB outflows. The implications of binding to bare dust were also investigated under several different assumptions for IK Tau. An SO abundance profile similar to observations, with an increase towards the end of the outflow, could be produced by assuming that ice which forms on the surface is able to displace other material, which then binds less strongly to the ice. If bare dust-bound species were treated as strongly bound to the surface, remaining protected by the ice, this allowed initial parent concentrations of sulfur species to be increased by a factor of four, suggesting that bare dust surfaces can act as significant chemical reservoirs.

Acknowledgements

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