

Segregation of O₂ and CO on the surface of dust grains determines the desorption energy of O₂



J. A. Noble, S. Diana and F. Dulieu

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ABSTRACT

The thermal desorption of O₂ and CO from a submonolayer mixture is greatly affected by the composition of the initial surface population. We have performed thermally programmed desorption (TPD) experiments on various submonolayer mixtures of O₂ and CO. Pure O₂ and CO exhibit almost the same desorption behaviour, but their desorption differs strongly when mixed. Pure O₂ is slightly less volatile than CO, while in mixtures, O₂ desorbs earlier than CO. We analyse our data using a desorption law linking competition for binding sites with desorption, based on the assumption that the binding energy distribution of both molecules is the same. We apply Fermi–Dirac statistics in order to calculate the adsorption site population distribution, and derive the desorbing fluxes. Despite its simplicity, the model reproduces the observed desorption profiles, indicating that competition for adsorption sites is the reason for lower temperature O₂ desorption. CO molecules push-out or ‘dislodge’ O₂ molecules from the most favourable binding sites, ultimately forcing their early desorption. It is crucial to consider the surface coverage of dust grains in any description of desorption. Competition for access to binding sites results in some important discrepancies between similar kinds of molecules, such as CO and O₂. This is an important phenomenon to be investigated in order to develop a better understanding of the apparently selective depletion observed in dark molecular clouds.

EXPERIMENTS AND ASCERTAINMENTS

All experiments were performed using the FORMOLISM set-up (e.g. Congiu et al. 2012). A non-porous, compact ASW ice sample (~50 ML) is grown by gas phase deposition on to a gold mirror held at 110 K. We deposit molecules on the ASW sample held at 18 K using one triply pumped molecular beam of, alternately, O₂ or CO (at a flux of about 3×10^{12} mol cm⁻² s⁻¹). After deposition of both molecules, the sample temperature is ramped linearly at 10 K min⁻¹.

Figure 1 shows the desorption of various submonolayer mixtures of O₂ (dashed lines) and CO (solid lines). Each colour corresponds to one experiment, and in each experiment the total surface coverage was kept below the monolayer. The first important point to note is that, when we consider the whole subset of submonolayer desorption experiments, we observe an inversion in the desorption order of O₂ and CO compared to the multilayer. In the multilayer regime, CO desorbs first, whereas in the submonolayer regime, O₂ desorbs first. We can also observe that, for CO, the common tail above 40 K is present, almost unperturbed compared to pure CO desorption experiments. This means that CO follows a filling behaviour desorption and seems to be unaffected by the presence of O₂. The global trend is that the O₂ molecules seems to desorb earlier, and before the CO molecules. More specifically, it appears that the more CO is co-adsorbed on the surface, the earlier the O₂ molecules desorb from the surface.

DESORPTION MODELLING INCLUDING SURFACE SEGREGATION MECHANISMS

O₂ molecules are clearly pushed to less favourable surface adsorption sites by the presence of CO molecules, ultimately resulting in the earlier desorption of O₂ during heating. It is important to note that the molecules of the two species rearrange their positions on the surface, but none are directly ejected into the gas phase during the process. This ‘dislodging’ mechanism, where molecules of one chemical species displace another on the surface, has been already encountered in the case of D₂ and H₂ mixtures (Dulieu et al. 2005), and has been discussed in an astrophysical context by Kristensen et al. (2011). A desorption model was developed in these studies, capable of reproducing the distortion in the TPD spectra of mixtures. It was even applied to the desorption of ortho and para D₂ from porous water (Amiaud et al. 2008), allowing the measurement of a tiny (1.4 meV) difference in the binding energy of the two states. In the present study, we will apply basically the same model to the submonolayer data presented above.

For our experiments we need a model that includes both (i) a binding energy distribution, but also (ii) a redistribution factor for the two molecules, since they obviously behave differently. Here, we assume that the substrate is unchanged during the desorption and is comprised of adsorption sites equally attainable for all of the molecules. Both molecular species are in direct competition to populate the binding sites.

The binding sites are described by a binding energy distribution, approximated as a Gaussian function. We also assume that the adsorbate is spread over the binding sites following the Fermi–Dirac statistical equilibrium. Figure 2 shows the total binding energy distribution of CO (blue), with distributions for 0.2 ML of CO at T = 10 (black) and T = 35 K (red). The red arrow indicates the energy of maximum desorption at T = 35 K.

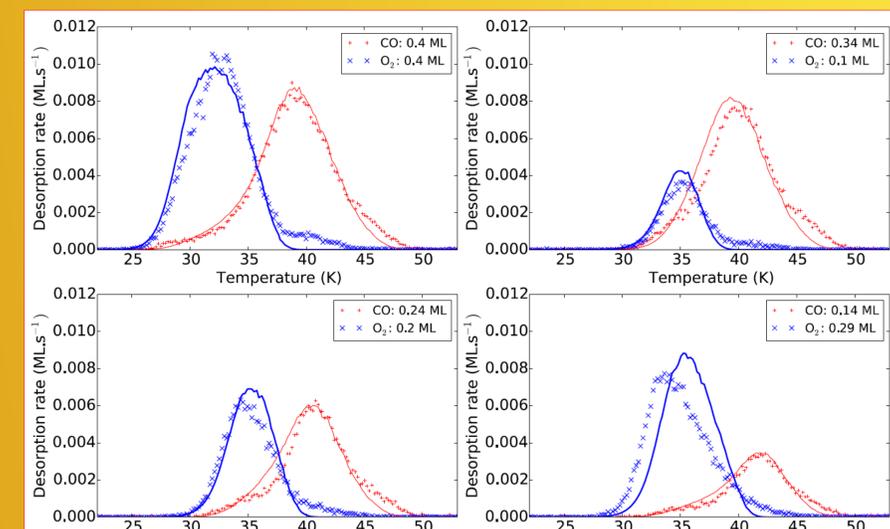


Figure 3 shows four of the seven submonolayer CO/O₂ mixtures that have been fitted simultaneously. The solid lines represent the model whereas the crosses correspond to the experimental data. We have only adjusted the two E_0 parameters (the median binding energy of each adsorbate) and used a common adjusted energy spread to ensure the minimum number of free parameters when testing the method. The results of the fitting procedure are very good. All the CO curves (in red) are nicely reproduced, and the O₂ desorption curves (in blue), although not perfectly reproduced, are very predictive.

The very good quality of the fit is the verification of our hypothesis that the competition for adsorption sites is the main physical source of the differentiated desorption of CO and O₂. Moreover, this behaviour can be modelled using Fermi–Dirac statistics applied to the distributions of adsorbate binding energies. The detail in the shape of the distribution does not play a very important role and, therefore, even if the surface is changed, the observed trend of the earlier desorption of O₂ should remain true.

CONCLUSION

Contrary to what happens in the multilayer regime, O₂ and CO co-adsorbed on an amorphous surface show very different desorption behaviour when mixed than when adsorbed separately. CO molecules dislodge O₂ molecules thanks to a slightly higher affinity with the surface. Although the binding energy distribution, centred at 1100 K, is only shifted by 85 K, this small difference is enough to provoke a strong reduction of the binding energy of O₂ in the presence of CO. It is possible to model this behaviour with a distribution of the adsorbates in the different available binding sites defined using the Fermi–Dirac statistical repartition law.

