CORRECTION

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Correction: Surface heterogeneity and inhomogeneous broadening of vibrational line profiles

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Correction for 'Surface heterogeneity and inhomogeneous broadening of vibrational line profiles' by Skandar Taj *et al.*, *Phys. Chem. Chem. Phys.*, 2017, **19**, 7990–7995.

Ref. 1 considered the profile of the $C \equiv O$ stretching vibration for carbon monoxide (CO) adsorbed in sub-monolayer quantities on amorphous silica ($aSiO_2$) and on porous amorphous solid water (p-ASW). The paper presented the hypothesis that the $C \equiv O$ stretching frequency is sensitive to the interaction experienced by the CO on the surface and that this heterogeneity can be recovered from temperature programmed desorption (TPD) analysis. In the paper, we reported TPD inversion for CO on $aSiO_2$ from which we derived the relevant probability distribution $P(E_{des})$ reflecting the interaction of CO with the $aSiO_2$. The data for p-ASW were taken from work by Kay and colleagues as cited in the paper. Simulations of the heterogeneously broadened line profiles in both cases were then presented and discussed.

We wish to highlight that the published $P(E_{des})$ in Fig. 4 of ref. 1 was actually that for the p-ASW surface and not the $aSiO_2$ surface as implied by the figure caption. This clearly necessitates correction. Fig. 1 below presents the correct figure. On further review of the work, we found that an early version of the $P(E_{des})$ curve for CO on $aSiO_2$ had been used to derive Fig. 5A and B and to populate Table 2. Fig. 2A and B and Table 1 present the corrected figures and table.
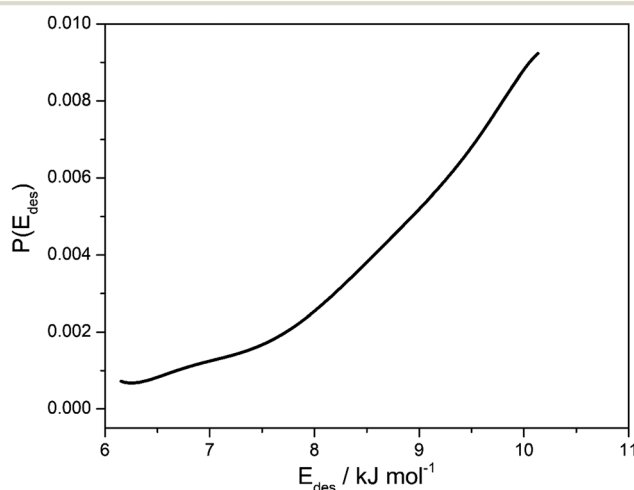

Fig. 1 $P(E_{des})$ versus E_{des} as derived from sub-monolayer TPD of CO from our $aSiO_2$ substrate.

For ballistic deposition of CO on the $aSiO_2$ surface, there is no impact at all on the outcome of our simulations. Ballistic deposition cannot explain the line profile observed (Fig. 2A). In the case of the adsorb and diffuse mechanism, the corrected $P(E_{des})$ distribution produces a somewhat better fit (Fig. 2B) and at a slightly smaller linewidth than reported in our paper. This has the effect of further emphasising the linewidth difference between the $C \equiv O$ vibration on $aSiO_2$ and on p-ASW in a manner consistent with our argument that the presence of the underlying pseudo-continuous absorption due to the water libration + bend

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vibrational combination mode provides an additional pathway to relax the C≡O vibration that reduces the lifetime and hence increases the linewidth on the p-ASW surface.
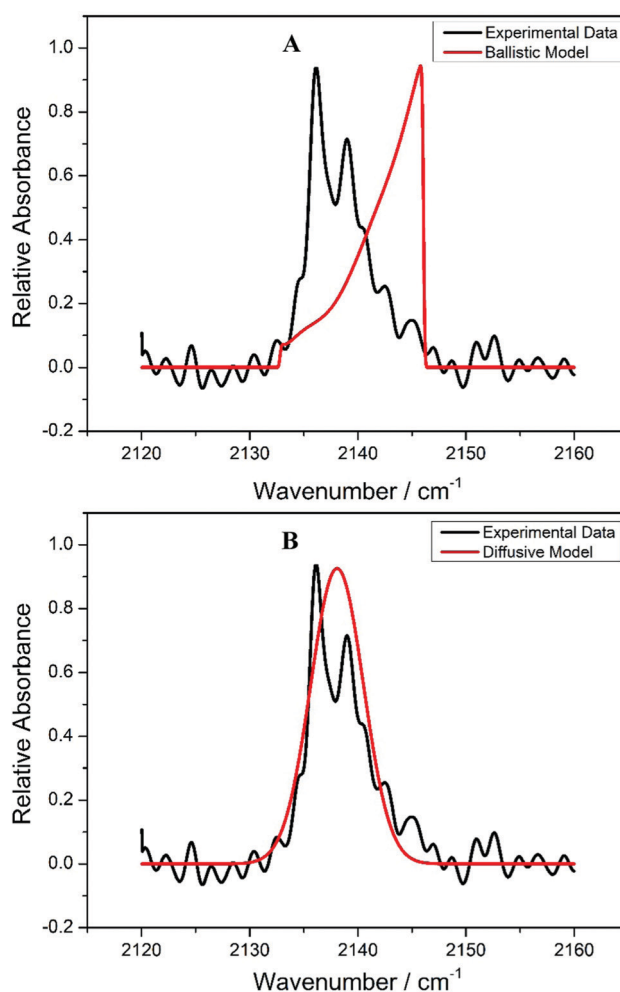
Fig. 2   Comparison of the experimental (black line) and modelled (red line) data for CO on aSiO$_2$. The experimental data is of 0.6 ML CO at 18 K and exhibits a FWHM of 4.7 cm^{-1}. (A) Shows the simulated line profile for an instrument-limited linewidth when CO is ballistically deposited with a FWHM of 4.7 cm^{-1}. (B) Shows how a better fit is obtained when CO is free to diffuse using the inverse Boltzmann weighted distribution of E_{des} and leads to a best-fit FWHM of 5.7 cm^{-1}. A point to note is the substructure in the experimental line profiles which is due to overlapping features from gas-phase water in the optics purge gas outside of the UHV chamber.

Table 1   Comparison of the best-fit parameters, ν_0 and δ, and of the corresponding FWHM for the modelled and experimental CO vibrational line profiles on aSiO$_2$ and p-ASW

	ν_0/cm^{-1} (± 0.5)	δ/cm^{-1} (± 0.2)	Model FWHM/cm^{-1} (± 0.5)	Exp. FWHM/cm^{-1} (± 0.1)
CO on aSiO$_2$	2102.5	2.4	5.7	4.7
CO on p-ASW (ballistic)	2108.0	2.6	5.9	5.6
CO on p-ASW (diffusive)	2089.0	3.2	7.6	8.0

The Royal Society of Chemistry apologises for these errors and any consequent inconvenience to authors and readers.

References

1 S. Taj, D. Baird, A. Rosu-Finsen and M. R. S. McCoustra, Surface heterogeneity and inhomogeneous broadening of vibrational line profiles, *Phys. Chem. Chem. Phys.*, 2017, **19**, 7990–7995, DOI: 10.1039/c6cp07530d.