

Supporting Information

Cation-dependent increase of the polarizability of CO adsorbed on Pt electrodes

Ghulam Hussain,^{†a,b} Laura Pérez-Martínez,^{†a} Jia-Bo Le,^{†c} Marco Papisizza,^a Gema Cabello,^{a,d} Jun Cheng^c and Angel Cuesta^{*c}

^a School of Natural and Computing Sciences, University of Aberdeen, Aberdeen AB24 3UE, Scotland, UK

^b Curtin Institute for Functional Molecules and Interfaces, School of Molecular and Life Sciences, Curtin University, GPO Box U1987, Perth, 6845, WA, Australia

^c State Key Laboratory of Physical Chemistry of Solid Surfaces, *i*ChEM, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

^d School of Medicine, Medical Sciences and Nutrition, University of Aberdeen, Foresterhill, Aberdeen AB25 2ZD, Scotland, UK

[†]These authors contributed equally to this work.

*Corresponding author: chengjun@xmu.edu.cn; angel.cuestaciscar@abdn.ac.uk

1. Deviation from linearity of the dependence of the CO_L stretching frequency on the electrode potential

While in the potential region where the dependence of the CO_L stretching on the electrode potential is linear, the spectra of CO_{ad} on Pt display all its typical signature, with a CO_L band much more intense than that corresponding to CO_B (Figs. 1b and S1a), in the case of the alkaline- and alkaline-earth metal cations the relative intensity of the CO_L and CO_B bands starts changing around -0.30 V and, at the most negative potentials, the intensities of the CO_L and CO_B bands are similar (Figs. 1b and S1a). This is accompanied by a faster shift of the CO_L frequency with potential below -0.30 V (Fig. 2a) which results in a non-linear dependence of the CO_L stretching on the electrode potential. This effect could be due either to (i) the electrochemical reduction of CO_{ad}, which would lead to a decrease in CO coverage, or (ii) a site interconversion triggered by the polarisation of the CO adlayer. Option (i) can be discarded, because the same effect has been observed, also only in the case of alkaline-metal cations, in non-aqueous electrolytes[1] (please note that reduction of CO is a proton electron transfer, and water is an excellent proton donor/acceptor). Furthermore, the change in the

relative intensity of the CO_L and CO_B bands occurs at a potential approximately 1.50 V more negative than the pzc both in aqueous (this work) and non-aqueous[1] electrolytes.

Like Roth and Weaver,[1] we attribute the change in intensity of the CO_L and CO_B bands to a population interconversion between the corresponding adsorption sites, triggered by the cation induced polarisation of CO_{ad}. This is similar to the well-known shift of CO coordination from terminal to bridging geometries in some dissolved polynuclear carbonyls induced by dissolved Lewis acids.[2–4] Polarisation of CO_{ad} by accumulation of cations at the electric double layer must involve the accumulation of electronic density on the O atom, which must happen through a population of the antibonding 2π* orbital. This will occur through back-bonding from the metal, which is known to strengthen the metal-C bond, weaken the C-O bond, and favour a bridge-bonded adsorption geometry.[5–8] This site interconversion also explains the faster change of CO_L stretching frequency at the most negative potentials in the presence of alkaline- and alkaline-earth metal cations, because as the distance between CO_L molecules within the adlayer increases due to the site interconversion, the degree of dipole-dipole coupling between them will decrease, leading to an additional decrease in the CO_L stretching frequency.

2. Calculation of the ratio between charge number and hydrodynamic radius from the cation's limiting ionic conductivity

The limiting ionic conductivity of an ion is given by $\lambda = zuF$, where z is the charge number, u is the ionic mobility and $F = N_A e$ is Faraday's constant, with N_A Avogadro's number and e the elementary charge. The ionic mobility is defined as the ratio between the drift speed, s , at which an ion moves through an electrolyte solution when a potential difference is applied between two electrodes immersed in the electrolyte, and the electric field, E , experienced by

the ion. *I.e.*, $u = \frac{s}{E}$. Since $s = \frac{zeE}{6\pi\eta r_H}$, with η the viscosity of water and r_H the hydrodynamic

radius of the ion, it follows that $u = \frac{ze}{6\pi\eta r_H}$. From which $\lambda = \frac{z^2 e^2 N_A}{6\pi\eta r_H}$ and, therefore:

$$\frac{z}{r_H} = \frac{\lambda}{z e^2 N_A} \quad \text{Eq. S4}$$

SUPPLEMENTARY TABLES AND FIGURES

Table S1. Change of the CO_L stretching frequency with potential ($\frac{d\bar{\nu}}{d\Delta\phi}$), double-layer capacitance (C_T), ratio between the limiting ionic conductivity and the cation's charge number ($\frac{\lambda}{z}$) and ratio between the charge number and the cation's hydrodynamic radius ($\frac{z}{r_H}$) for all the cations used in this work.

	$\frac{d\bar{\nu}}{d\Delta\phi} / \text{cm}^{-1} \text{V}^{-1}$	$C_T / \mu\text{F cm}^{-2}$	$\frac{\lambda}{z} / \text{mS m}^2 \text{mol}^{-1}$	$10^3 \frac{z}{r_H} / \text{pm}^{-1}$
[N(C ₄ H ₉) ₄] ⁺	15.06 ± 0.54	4.60 ± 0.01	1.95 ^[a]	2.12
[N(C ₃ H ₇) ₄] ⁺	20.41 ± 0.68	6.04 ± 0.08	3.06 ^[b]	3.32
[N(C ₂ H ₅) ₄] ⁺	28.91 ± 0.17	8.63 ± 0.06	3.26 ^[c]	3.54
H ⁺	30.31 ± 0.18	11.13 ± 0.08	N/A	N/A
Li ⁺	30.76 ± 0.60	10.64 ± 0.04	3.87 ^[c]	4.20
[N(CH ₃) ₄] ⁺	31.47 ± 0.43	10.41 ± 0.01	4.49 ^[c]	4.88
Na ⁺	31.47 ± 0.49	11.95 ± 0.14	5.01 ^[c]	5.44
NH ₄ ⁺	32.00 ± 2.02	13.35 ± 0.14	7.35 ^[c]	7.99
Sr ²⁺	32.69 ± 0.24	11.63 ± 0.08	5.945 ^[c]	6.46
Mg ²⁺	33.20 ± 0.06	11.71 ± 0.07	5.30 ^[c]	5.76
Ca ²⁺	33.74 ± 0.47	11.18 ± 0.08	5.95 ^[c]	6.46
Cs ⁺	34.08 ± 1.90	14.25 ± 0.04	7.72 ^[c]	8.38
K ⁺	35.66 ± 0.88	13.46 ± 0.13	7.35 ^[c]	7.99
Rb ⁺	36.33 ± 0.60	14.47 ± 0.08	7.78 ^[c]	8.45

[a] From[9]; [b] This work; [c] From [10]

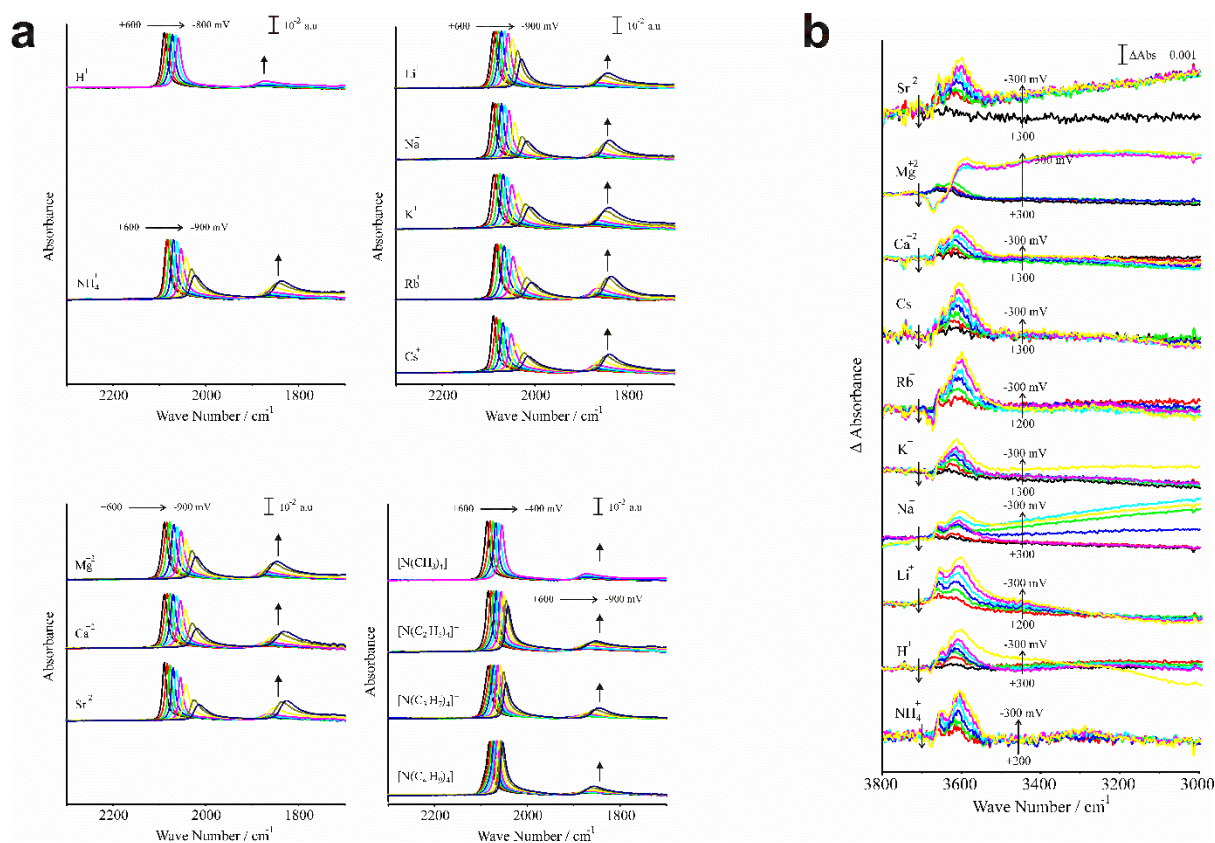


Figure S1. a, ATR-SEIRA spectra of a saturated CO adlayer on a Pt electrode in electrolytes containing either H⁺, NH₄⁺, Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Mg²⁺, Ca²⁺, TMA⁺, TEA⁺, TPA⁺ or TBA⁺. The cations have been grouped by cation type in four panels, the top-left pane; showing H⁺ and NH₄⁺, the top-right panel showing the alkaline-metal cations, the bottom-left panel the alkaline-earth cations, and the bottom-right panel showing the tetraalkylammonium cations. The spectra are show at potential intervals of 200 mV for the sake of clarity and were calculated using the spectrum of the CO-free Pt surface at the open-circuit potential as background. **b**, ATR-SEIRA spectra in the region corresponding to the O-H stretching of water. The background spectrum was that corresponding to the CO-covered Pt electrode at 0.4 V vs. SHE.

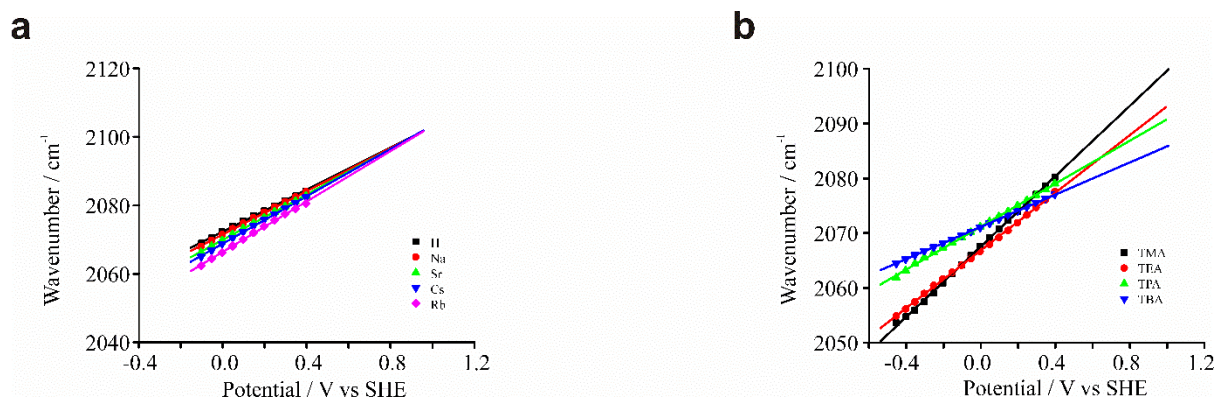


Figure S2. a, Plots of the CO_L stretching frequency as a function of the electrode potential in the potential region between -0.1 and 0.4 V vs. SHE for H⁺, Na⁺, Sr²⁺, Cs⁺, Rb⁺, and best fit to the experimental data for each of the cations. Only five cations are shown for the sake of clarity. **b,** Plots of the CO_L stretching frequency as a function of the electrode potential in the potential region between -0.45 and 0.4 V vs. SHE for TMA⁺, TEA⁺, TPA⁺ and TBA⁺, and best fit to the experimental data for each of the cations.

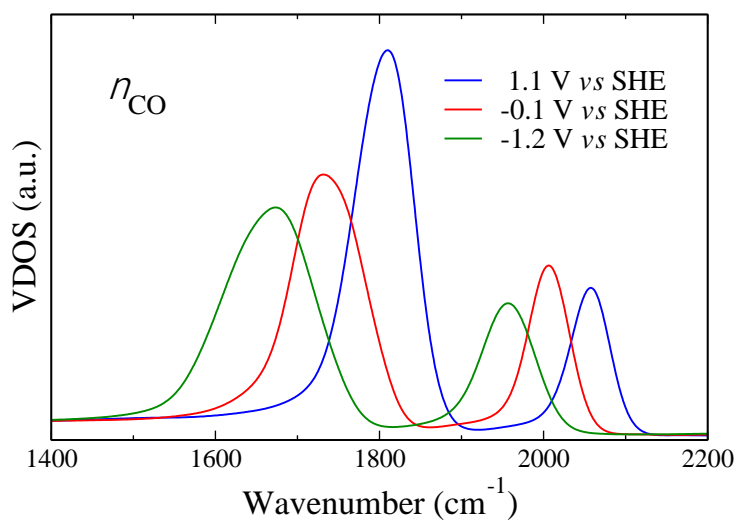


Figure S3: The vibrational density of states spectra of CO at -1.1, -0.1 and -1.2 V vs SHE.

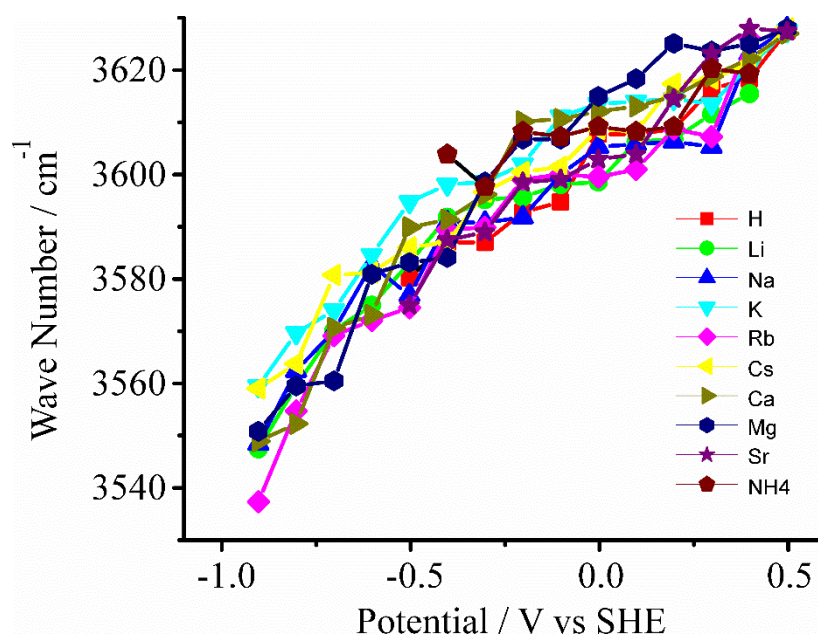


Figure S4. Dependence of the frequency of the band around 3600 cm^{-1} , corresponding to the O-H stretching of water molecules in the cations' solvation shell, on the electrode potential.

REFERENCES

- [1] J.D. Roth, M.J. Weaver, Role of double-layer cation on the potential-dependent stretching frequencies and binding geometries of carbon monoxide at platinum-nonaqueous interfaces, *Langmuir*. 8 (1992) 1451–1458. doi:10.1021/la00041a034.
- [2] A. Alich, N.J. Nelson, D. Strobe, D.F. Shriver, Solution infrared study of carbon- and oxygen-bonded carbon monoxide. Interaction of bridging carbonyl ligands with aluminum alkyls, *Inorg. Chem.* 11 (1972) 2976–2983. doi:10.1021/ic50118a022.
- [3] D.F. Shriver, Basicity and reactivity of metal carbonyls, *J. Organomet. Chem.* 94 (1975) 259–271. doi:10.1016/S0022-328X(00)88721-5.
- [4] H.-N. Adams, G. Fachinetti, J. Strähle, Distribution of Terminal and Bridging CO-Groups in an Anionic Carbonylmethyl Cluster as a Result of Ion-Pair Formation. Crystal and Molecular Structure of $\text{LiCo}_3(\text{CO})_{10}\cdot\text{i-Pr}_2\text{O}$, *Angew. Chemie Int. Ed. English*. 19 (1980) 404–405. doi:10.1002/anie.198004041.
- [5] W. Tornquist, F. Guillaume, G.L. Griffin, Vibrational behavior of carbon monoxide adsorbed on platinum in nonacidic electrolytes, *Langmuir*. 3 (1987) 477–483. doi:10.1021/la00076a007.
- [6] S.L. Yau, X. Gao, S.C. Chang, B.C. Schardt, M.J. Weaver, Atomic-resolution scanning tunneling microscopy and infrared spectroscopy as combined in situ probes of electrochemical adlayer structure: carbon monoxide on rhodium (111), *J. Am. Chem. Soc.* 113 (1991) 6049–6056. doi:10.1021/ja00016a018.
- [7] K.J. Uram, L. Ng, J.T. Yates, Electrostatic effects between adsorbed species—the K ... Co interaction on Ni(111) as studied by infrared reflection-absorption spectroscopy, *Surf. Sci.* 177 (1986) 253–277. doi:10.1016/0039-6028(86)90138-X.
- [8] A. Cuesta, C. Gutiérrez, Study by Fourier Transform Infrared Spectroscopy of the Adsorption of Carbon Monoxide on a Nickel Electrode at pH 3–14, *Langmuir*. 14 (1998) 3397–3404. doi:10.1021/la9706274.
- [9] L. Coury, A Review of Parameters Describing Electrolyte Solutions, *Curr. Sep.* 18 (1999) 91–

96. <http://www.currentseparations.com/issues/18-3/cs18-3c.pdf> (accessed April 2, 2019).
- [10] P.W. Atkins, J. De Paula, Atkins' Physical Chemistry, 8th ed., Oxford University Press, n.d.