Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting information to:

Speciation of adsorbed CO_2 on metal oxides by a new 2-dimensional approach: 2D Infrared Inversion Spectroscopy (2D IRIS)

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This section details the procedure used to obtain the energy distribution functions from the experimental isotherms. Being merely similar for both types of isotherms, the method is detailed for the more general case of spectroscopic isotherms. In essence, the method is a straightforward extension of the method proposed by Wilson[1] to a 2-dimensional case.

The spectroscopic isotherm (absorbances vs. pressure) is expressed as:

$$a(\nu,p) = \int_{g_{min}}^{g_{max}} \theta(p,g) f(\nu,g)\, dg \qquad (1)$$

where $a(\nu,p)$ is the absorbance at wavenumber ν and pressure p, g is the reduced Gibbs free energy of adsorption ($g = -\ln K = \Delta_{ads}G/RT$), and $\theta(p,g)$ is the functional dependence which is expected to hold between pressure and the coverage of surface sites. For a Langmuir isotherm:

$$\theta(p,g) = 1/(e^{g} + p/p^{\circ}) \qquad (2)$$

$f(\nu,g)$ is the function describing the energy distribution of the adsorption sites leading to adsorbed species absorbing at wavenumber ν :

$$f(\nu,g)dg = N(g)\epsilon(\nu,g)/A \qquad (3)$$

where $N(g)$ is the number of sites leading to a reduced Gibbs free energy of adsorption between g and $g+dg$, $\epsilon(\nu,g)$ is the absorption coefficient of the corresponding adsorbed species and A the geometric surface of the pellet.

In order to discretize Eqn (1), the spectroscopic isotherm $a(\nu,p)$, the kernel function $\theta(p,g)$ and the energy distribution function $f(\nu,g)$ are represented by matrixes which elements are given by :

$$\begin{aligned} a_{ij} &= a(\nu_i,p_j) \qquad i = 1,\dots,m\ ;\ j = 1,\dots,n \\ \theta_{jk} &= \theta(p_j,g_k) \qquad k = 1,\dots,q \\ f_{ki} &= f(\nu_i,g_k) \end{aligned} \qquad (4)$$

The q g_k values are linearly spaced in the interval $[g_{min}, g_{max}]$:

$$\begin{aligned} g_k &= g_{min} + (k-1)\Delta g \\ \text{with } \Delta g &= (g_{max} - g_{min})/(q-1) \end{aligned} \qquad (5)$$

The left-hand side integral of Eq (1) is approximated by a numerical quadrature, consisting in approximating the integral by the weighted sum of the values of the function under integral:

$$\int_{g_{min}}^{g_{max}} \theta(p,g) f(\nu,g)\, dg \approx \sum_{k=1}^{q} w_k \theta_{jk} f_{ki} \qquad (6)$$

where the weighting coefficients w_k are given by :

$$w_k = \begin{cases} \Delta g, & 2 \le k \le q-1 \\ \Delta g/2, & k = 1, q. \end{cases} \qquad (7)$$

Discretization of equation (1) thus results in the following system of linear algebraic equations :

$$a_{ij} = \sum_{k=1}^{q} w_k \theta_{jk} f_{ki} \qquad (8)$$

Denoting :

$$\Theta_{jk} = w_k \theta_{jk} \qquad (9)$$

the following matrix equation is obtained :

$$\mathbf{a} = \mathbf{\Theta}\,\mathbf{f} \qquad (10)$$

Denoting $\mathbf{a_i}$ and $\mathbf{f_i}$ the vectors of absorbance values a_{ij} and energy distribution function values f_{ki} at the wavenumber ν_i, this linear system could be solved with respect to $\mathbf{f}$ by minimizing the residuals using a least-squares method, i.e. by minimizing:

$$\begin{aligned} \phi_{LS}(\mathbf{f}) &= \sum_i \|\mathbf{\Theta}\,\mathbf{f}_i - \mathbf{a}_i\|^2 \\ &= \sum_i (\mathbf{\Theta}\,\mathbf{f}_i - \mathbf{a}_i)^T (\mathbf{\Theta}\,\mathbf{f}_i - \mathbf{a}_i) \end{aligned} \qquad (11)$$

with the additional constraint that $\mathbf{f}$ is positive ($f_{ki} \ge 0$), see Eqn 3.

However, because of the smoothness of the kernel $\mathbf{\Theta}$, which varies slowly with g_k, this is a numerically ill-posed problem: the optimum solutions $\mathbf{f}_i$ are unstable with respect to slight variations in the experimental data $\mathbf{a}_i$ and may present spurious oscillations.[2, 3] The usual procedure to tackle such problems is the Tikhonov regularization and consists in enforcing the smoothness of the solution by adding a weighted constraint to the objective function to be minimized:[4]

$$\phi_{reg}(\mathbf{f}) = \phi_{LS}(\mathbf{f}) + \lambda\, S(\mathbf{f}) \qquad (12)$$

where λ is the regularization parameter ($\lambda \geq 0$) which controls the level of smoothing to be applied and *S*(**f**) is a measure of the smoothness of **f** in the energy dimension. Common choices for *S*(**f**) are the norm of **f** or the norm of its second derivative with respect to g. In the present case, both criteria led to similar solutions and the latter criterion was chosen by approximating the second derivative by finite differences and its norm was calculated by the numerical quadrature:

$$S(\mathbf{f}) = \|\partial^2\mathbf{f}/\partial g^2\|^2 \approx \sum_i^{q+1}\sum_{k=0} \left(f_{(k-1)i} - 2f_{ki} + f_{(k+1)i}\right)^2 \Delta g/(\Delta g)^4 \qquad (13)$$

where $f_{(-1)i} = f_{0i} = f_{qi} = f_{(q+1)i} = 0$. This choice enforces the solution to be smoothed towards zero values at g_{min} and g_{max} which is appropriate for a distribution function. With this choice, Eqn (13) can be expressed as a matrix equation:

$$S(\mathbf{f}) = \sum_i \mathbf{f}_i^T \mathbf{S}\, \mathbf{f}_i \qquad (14)$$

where $\mathbf{S}$ is the symmetric matrix defined by:

$$\mathbf{S} = \frac{1}{(\Delta g)^3}\begin{pmatrix} 6 & -4 & 1 & 0 & \cdots & 0 & 0 \\ -4 & 6 & -4 & 1 & \cdots & 0 & 0 \\ 1 & -4 & 6 & -4 & \cdots & 0 & 0 \\ 0 & 1 & -4 & 6 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \cdots & 6 & -4 \\ 0 & 0 & 0 & 0 & \cdots & -4 & 6 \end{pmatrix}$$

Using equations (11) and (14), equation (12) becomes:

$$\phi_{reg}(\mathbf{f}) = \sum_i (\mathbf{\Theta}\,\mathbf{f}_i - \mathbf{a}_i)^T(\mathbf{\Theta}\,\mathbf{f}_i - \mathbf{a}_i) + \lambda\, \mathbf{f}_\mathbf{i}^T\mathbf{S}\mathbf{f}_\mathbf{i} \qquad (15)$$

After expansion of and dropping the constant term, the problem of minimizing $\phi_{reg}[\mathbf{f}]$ amounts to solve the m quadratic programming (QP) problems**:**

$$\Phi_{\mathrm{reg}}[\mathbf{f}_i] = \mathbf{f}_i{}^T(\mathbf{\Theta}^T\mathbf{\Theta} + \lambda\mathbf{S})\mathbf{f}_i - 2\mathbf{a}_i^T\mathbf{\Theta}\mathbf{f}_i \qquad (16)$$

with the non-negativity constraint, which can be solved by most of numerical computational packages under its standard form, i.e. minimize:

$$\Phi_{reg}(\mathbf{f}_i) = \frac{1}{2}\mathbf{f}_\mathbf{i}^T\mathbf{Q}\mathbf{f}_\mathbf{i} + \mathbf{c}^T\,\mathbf{f}_i \qquad (17)$$

With $\mathbf{Q} = 2\mathbf{\Theta}^T\mathbf{\Theta} + 2\lambda\mathbf{S}$ and $\mathbf{c} = -2\mathbf{\Theta}^T\mathbf{a}_i$ subject to the constraint $\mathbf{f}_i \geq 0$.

For the present study, the numerical calculations were carried out with Matlab 7.10.0 using the *quadprog* routine to solve the quadratic programming problem (Eqn. 17).

The inversion of the gravimetric isotherm was carried out using the same procedure, with the exception that **a** (mass changes) and **f** (distribution function) are vectors.

1 J. D. Wilson, *Journal of Materials Science,* 1982, **27**, 3911-3924.
2 J. Mroczka and D. Szczuczynski, *Metrology and Measurement Systems,* 2009, **XVI**, 333-357.
3 S. I. Kabanikhin, *Inverse and Ill-posed Problems. Theory and Applications*, De Gruyter, 2011.
4 A. N. Tikhonov and V. Y. Arsenin, *Solutions for Ill-Posed Problems*, Winston & Sons, Washington DC, 1977.