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Brute force determination of the optimum pore sizes for CO<sub>2</sub> uptake<sup>†</sup>L. Scott Blankenship,<sup>a\*</sup> Nawaf Albeladi,<sup>ab‡</sup> Thria Alkhaldi,<sup>ac‡</sup> Asma Madkhali,<sup>ad‡</sup> and Robert Mokaya<sup>a</sup>

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Porosity, and in particular pore size is the one of the most important considerations in the development of porous carbons for CO<sub>2</sub> capture. Current methods for determining the optimum pore size for adsorption of CO<sub>2</sub> either make very broad assumptions (in computational studies), or are not sufficiently thorough (in experimental studies). Herein we present a brute force, first principles method for determining the range of pore sizes,  $\Omega$ , best suited to adsorption of a given sorptive at a range of pressures. This is then used to determine  $\Omega$  for CO<sub>2</sub> in a broad pressure range according to N<sub>2</sub> porosimetry. The analysis is then extended to other porosimetric sorptives and combinations thereof to assess their efficacy in determining  $\Omega$  for CO<sub>2</sub>.

## 1 Introduction

Porous carbons have been extensively investigated for their potential use in gas storage and/or capture applications, in particular related to energy storage applications including for alternative fuels such as H<sub>2</sub> and CH<sub>4</sub> or for CO<sub>2</sub> capture.<sup>1–9</sup> A material's capacity for a particular sorptive is known to be related to the porosity of the material, and in particular the pore width plays an important role.<sup>5,10–21</sup> Pore entrances for sorption of some gas at a given pressure and temperature must be large enough for the molecule in question can diffuse into it. This lower limit to the so-called pore size range is not necessarily solely determined by the size of the molecule; for example while N<sub>2</sub> has a nominal kinetic diameter ( $d_k$ ) of 3.60 Å, it has been observed that at -196 °C in biochars this molecule diffuses extremely slowly into pores of width 4 Å.<sup>22–24</sup> On the other hand, adsorption can be improved by optimising the interactions between parallel pore walls and adsorptive molecules. That is, when the distance between pore walls is sufficiently small adsorbed molecules are affected by physical attraction to both walls, which increases the heat of adsorption and thus the retention of molecules within the pores.<sup>25,26</sup> This

is particularly significant at low pressures where the adsorbate-adsorbent interactions dominate.<sup>13,15,27–34</sup> It follows therefore, that there is a range of optimum pore sizes for adsorption of any given molecule at some pressure and temperature.

There have been several attempts to determine the optimum pore size for given sorptives under some conditions. In general, the approach to this has been to either identify the 'ideal' pore size, i.e. a single width such as 6 Å for H<sub>2</sub> with slight variations depending on temperature and pressure.<sup>12,28</sup> An alternative method is to propose larger regions, i.e. an optimum pore size range (herein referred to as  $\Omega$ );<sup>15,35,36</sup> for H<sub>2</sub> it has been reported that ultramicropores, i.e. pores of width <7 Å are ideal.<sup>20,31</sup> These regions or single widths are determined *via* purely computational methods or from experimentally determined uptakes and pore size distributions (PSDs). Computational methods attempt to determine the uptake of the sorptive in an idealised sorbent with pores of a single width *via* DFT or GCMC methods.<sup>5,12,37</sup> Whereas experimental data can be used to performing linear regressions of uptake at a given pressure against pore volume in a certain range (usually all pores below some maximum).<sup>11,13,15,17,35,38</sup> By the latter method, Presser *et al* determined (N=24) that at 1.0 bar, pores in activated carbons of width <8 Å are most strongly associated with gravimetric CO<sub>2</sub> uptake, while this reduced to 5 Å for uptake at 0.1 bar. Pores larger than 10 Å, as well as the oft-used parameter of average pore size were shown to be poor predictors of uptake at these low pressures.<sup>13</sup> Average pore size can however be useful when compared against so-called uptake density (uptake per unit surface area). For example, Masika *et al* found that uptake density of H<sub>2</sub> (1 bar, -196 °C) reduced drastically as average pore width increased from 10 to 20 Å.<sup>16</sup>

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<sup>†</sup> Electronic Supplementary Information (ESI) available: [Supplementary figures and tables; raw (.aif) isotherms; PSD and modelling analysis summaries as .csv; and raw outputs of  $D_v$ ,  $D_\pi$ , and  $D_c$  for each DataSet (.csv)]. See DOI: 00.0000/00000000.

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Current experimental approaches to determining  $\Omega$  are limited in that they typically only consider a small set of possible  $\Omega$ s, which is informed by theoretical data, and only at one or two pressures. Furthermore, the lower limit of the  $\Omega$  is not typically varied – the assumption being that pores larger than the diameter of the sorptive will always be strong contributors to sorptive uptake under all conditions. As for computational studies, not only is the use of materials having a single pore width unrealistic for amorphous porous carbon, it is difficult to account for factors such as surface chemical and energetic heterogeneity and variation in pore geometry. Thus we present the python Porosity Uptake Correlator (pyPUC); a combined, iterative experimental and computational approach to  $\Omega$  determination. Regressions are performed using experimental data between all possible  $\Omega$ s at a large range of pressures and used to determine the  $\Omega$  at each pressure. Both the range and increment of the possible  $\Omega$ s and pressures can be easily adjusted to give an extremely fine level of detail. As a demonstration, pyPUC is applied to the determination of  $\Omega$  for CO<sub>2</sub> uptake in amorphous carbons at 25 °C where porosity is determined from N<sub>2</sub> sorption isotherms obtained at -196 °C. The relative efficacy of H<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> (-196 °C) isothermal porosimetry as well as dual fit N<sub>2</sub>/H<sub>2</sub> and O<sub>2</sub>/H<sub>2</sub> analyses is then assessed for their ability to predict  $\Omega$  for CO<sub>2</sub> in highly ultramicroporous carbons.

## 2 Methods

### 2.1 pyPUC

The pyPUC software requires both uptake isotherms ( $v$ ) for the adsorptive in question, and cumulative PSDs ( $\pi$ ) for a set of porous samples. Firstly, a model isotherm is fit to each experimental isotherm in  $v$  using the pyGAPS adsorption isotherm processing framework, via the modelling package initially developed in pyIAST.<sup>39,40</sup> These model isotherms are converted to point isotherms according to some user-defined pressure range and increment. Thus, discrete loadings are determined for all samples at identical pressures, and is stored in the so-called loading DataFrame ( $D_v$ ).

Next, from  $\pi$  the apparent pore volume ( $V$ ) or surface area ( $S$ ) of each sample between the minimum and maximum pore width ( $w_{min}$  and  $w_{max}$ , respectively) is determined via;

$$V = V(w_{max}) - V(w_{min}), \quad (1)$$

$$S = S(w_{max}) - S(w_{min})$$

This is repeated across all pairs of  $w_{max}$  and  $w_{min}$  prescribed by the user, thus generating a parameter DataFrame ( $D_\pi$ ). The number of parameters calculated  $N_\pi$  is thus related to the number of pore widths defined in the calculation  $N_w$  by;

$$N_\pi = \frac{1}{2} \frac{N_w!}{(N_w - 2)!} \quad (2)$$

Thereafter, linear regressions are determined between every row of  $D_v$  and  $D_\pi$  to give the correlation DataFrame ( $D_c$ ), i.e.  $D_c$  shows how well each pore width range in  $D_\pi$  correlates to the loading of the sorptive on the sample at each pressure in  $D_v$ . Each row of  $D_c$  contains the Pearson coefficient ( $r^2$ ), slope ( $m$ ) and in-

tercept ( $c$ ) of the regression. Finally, the best correlation at each pressure is found simply through the maximum  $r^2$  value<sup>41</sup> for a given pressure after the exclusion of regressions giving a negative slope. Thus, the  $\Omega$  associated with uptake of the sorptive at each pressure is given.

### 2.2 Carbon synthesis

Carbons were synthesised by pyrolysis of various biomasses and synthetic polymers either alone or with the aid of a porogen. In all cases they were washed after synthesis to remove any non-carbonaceous matter. Synthetic summaries are provided in for DataSet 1 (33 samples) and DataSet 2 (12 samples) in tables S1.1 and S2.1 respectively.

### 2.3 Isotherm measurement and processing

All raw experimental isotherms measured as described below are available in the electronic supplementary information as human- and machine-readable .aif files.<sup>42</sup> N<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub> isotherms for determination of PSDs were measured at -196 °C on a Micromeritics 3flex porosimeter at pressures up to  $P_0$  for N<sub>2</sub> and O<sub>2</sub> and 1013 mbar for H<sub>2</sub>. PSDs were determined using the appropriate SAIEUS software with the 2D-NLDFT heterogeneous surface kernel(s), in order to adequately account for chemical and energetic heterogeneity. Within SAIEUS it is possible to select an appropriate fitting parameter,  $\lambda$ <sup>43–45</sup> which controls the roughness of the PSD.  $\lambda$  was selected to provide the most realistic differential PSD based on known properties of carbons, and in all cases was between 2.5 and 5.0 and kept constant for carbons derived from the same precursor (see tables S1.1 and S2.1). Isotherms and derived PSDs can be found in figures S1.6-S1.10 and S2.4-S2.12.

Gravimetric CO<sub>2</sub> uptakes were measured on gravimetric analysers provided by Hiden; either the Xemis analyser at 25 °C (0-40 bar) or the IGA at 18 °C (0-20 bar) for DataSet 1 and 2 respectively. Fits were attempted with Langmuir,<sup>46,47</sup> Double Site Langmuir (DSL<sub>Langmuir</sub>),<sup>47</sup> Triple Site Langmuir (TSL<sub>Langmuir</sub>),<sup>47</sup> Guggenheim-Anderson-de Boer (GAB),<sup>48–50</sup> Freundlich,<sup>51</sup> Dubinin-Raduschkevich (DR)<sup>52</sup> and Toth<sup>53</sup> theoretical isotherms using pyGAPS (see section 2.1). The best fit was then selected by minimum root mean square error (RMSE). CO<sub>2</sub> isotherms as well as their best fits and details thereof can be found in figures S1.1-S1.5 and S2.1-S2.3

## 3 Results and Discussion

### 3.1 From N<sub>2</sub> isotherms only

We first present the use of pyPUC to determine  $\Omega$  according to porosity derived from isotherms of the "traditional" porosimetric molecule, N<sub>2</sub>. This is to establish the validity of this brute force method and to compare results derived in this way to those reported in the literature. A set of 33 carbon samples were used in this section.

#### 3.1.1 DataFrame preparation.

The 33 activated carbons and biochars used in the initial analysis have varied PSDs in the range 3.6-100 Å (by pore volume)

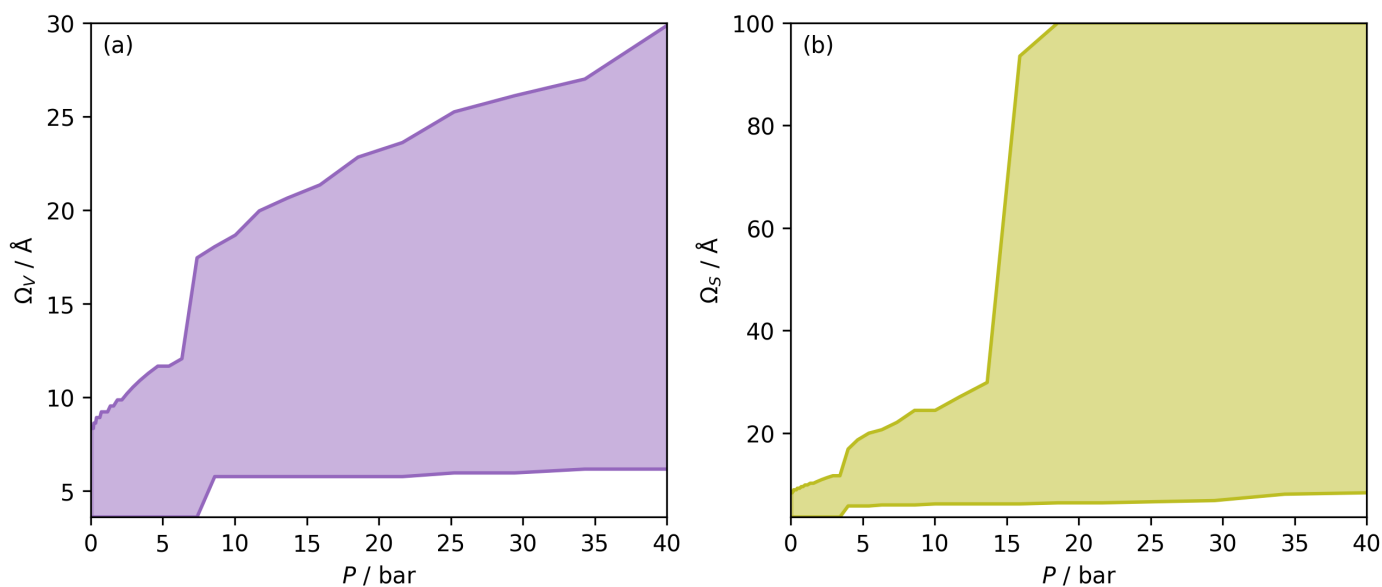


Fig. 1 :  $\Omega_V$  (a) and  $\Omega_S$  (b) at each pressure, i.e. optimum  $w_{max}$  and  $w_{min}$  plotted against pressure. The shaded area is thus the  $\Omega$  in each case.

according to fits to  $N_2$  isotherms with the 2D-NLDFT heterogeneous surface kernel (see figures S1.6-S1.10). It was possible to fit model isotherms to the experimental  $CO_2$  isotherms in the full range 0.10-40 bar with a maximum root mean square error (RMSE) of 0.168 (figure S1.1-S1.5), although fits were slightly poorer for some isotherms at low pressures, notably *aP-2800*, *aP-2900* and *aP-3700* (figure S1.1(b2, b3, b5), respectively). It should be noted, that while a wide range of model fits were attempted, only DSLangmuir, TSLangmuir and Toth models provided the best fits to the experimental isotherms. DSLangmuir was by far the most common best fit, while Toth was only used for two samples. The model isotherms were output as 40 points in the range 0.1-40 bar defined using a base-10 logarithmic increment between points to give  $D_v$ . Similarly,  $D_\pi$  was calculated using a base-10 logarithmic increment to give 100  $w$  values between 3.6 and 100  $\text{\AA}$ . Determination of  $D_c$  therefore required 198 000 linear regressions, which were used to determine the  $\Omega$  at each of the 40 pressures defined in  $D_v$  in terms of  $V$  and  $S$  i.e.  $\Omega_V$  and  $\Omega_S$  respectively. A more detailed calculation, using a  $D_\pi$  of 500 values between 3.6 and 500  $\text{\AA}$  was also performed in order to ascertain the effect of increasing level of detail on the calculated  $\Omega$ . This calculation took almost 7 days each for  $\Omega_V$  and  $\Omega_S$  compared to the original calculation which was completed within 24 h and results are not significantly different. As such this data was not used as the basis of the study. A comparison can be seen in figure S1.11.

### 3.1.2 The optimum pore size region, $\Omega$ .

Figure 1 shows  $\Omega_V$  (a) and  $\Omega_S$  (b) in the pressure range studied. As expected, in both cases the range of  $\Omega$  broadens with increasing pressure. This shows the positive effect on high pressure  $CO_2$  uptake of hierarchical PSDs. It is also notable that for both  $V$  and  $S$  while  $w_{max}$  increases almost constantly, there are basically only two values for  $w_{min}$ , starting at 3.6  $\text{\AA}$  and then increasing to

around 7.0  $\text{\AA}$  at some pressure. In other words, there is a pressure range in which ultramicropores are strongly associated with  $CO_2$  uptake. This range is up to 7.4 and 3.4 bar for  $V$  and  $S$ , respectively.<sup>§</sup> At 0.10 bar,  $w_{max}$  is approximately 8  $\text{\AA}$  and increases to 17 and 11  $\text{\AA}$  for  $V$  and  $S$ , respectively once  $\Omega$  begins to exclude the ultramicropores. That is, with increasing pressure supermicropores have an increasing influence on  $CO_2$  uptake. The fact that the pressure range wherein  $w_{min}$  is 3.6  $\text{\AA}$  is much smaller for  $S$  relative to  $V$  may be a result of reduced influence of London interactions between the carbon surface and the sorptive as pressure increases. Increased pressure means that multilayer adsorption, and thus interactions between  $CO_2$  molecules becomes more dominant.

Once  $\Omega$  begins to exclude ultramicropores, there is a sharp increase in  $w_{max}$ . As a result,  $\Omega_S$  includes both supermicropores and small mesopores after 6 bar. Conversely,  $\Omega_V$  remains strictly in the supermicropore region until 13 bar. Again, this seems to be a result of an indication of the difference in the how surface area vs pore volume improve adsorption of  $CO_2$ . That is smaller pores result in improved sorptive-sorptive interactions, while larger pores provide more surface for  $CO_2$  to interact with. This is further exhibited by the large increase in  $w_{max}$  up to 100  $\text{\AA}$  for  $\Omega_S$  at 16 bar which does not exist for  $\Omega_V$ . Of course, this upper limit for  $\Omega_S$  is not real but represents the upper limit of  $w_{max}$  established in the determination of  $D_\pi$ . Nevertheless, these results may inform design of porous carbons for different applications; for example a carbon with high porosity below 8.0  $\text{\AA}$  is best suited for low pressure capture of  $CO_2$ , whereas carbons for so-called pressure-swing adsorption (PSA) should have hierarchical micro-mesoporous PSDs with minimal porosity below 8.0  $\text{\AA}$ . This confirms previous reports.<sup>13,15,27,54,55</sup>

<sup>§</sup> In the more detailed calculation (see figure S1.11) this limit is found to be slightly lower.

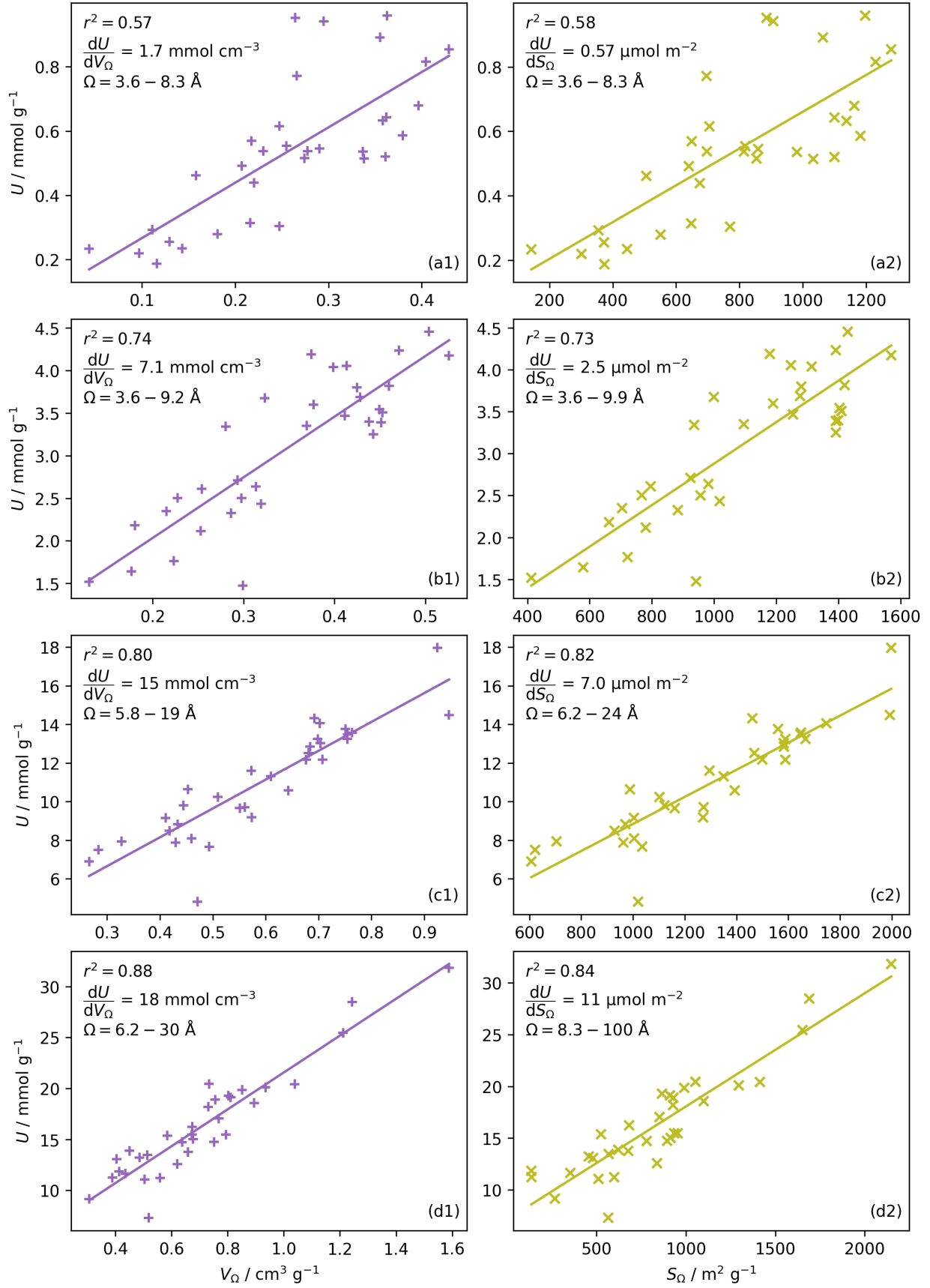


Fig. 2 : CO<sub>2</sub> uptake,  $U$  vs pore volume,  $V_{\Omega}$  (column a) and surface area,  $S_{\Omega}$  column (b) in  $\Omega$ , at 0.10 (row 1), 1.0 (row 2), 10 (row 3), and 40 (row 4) bar.

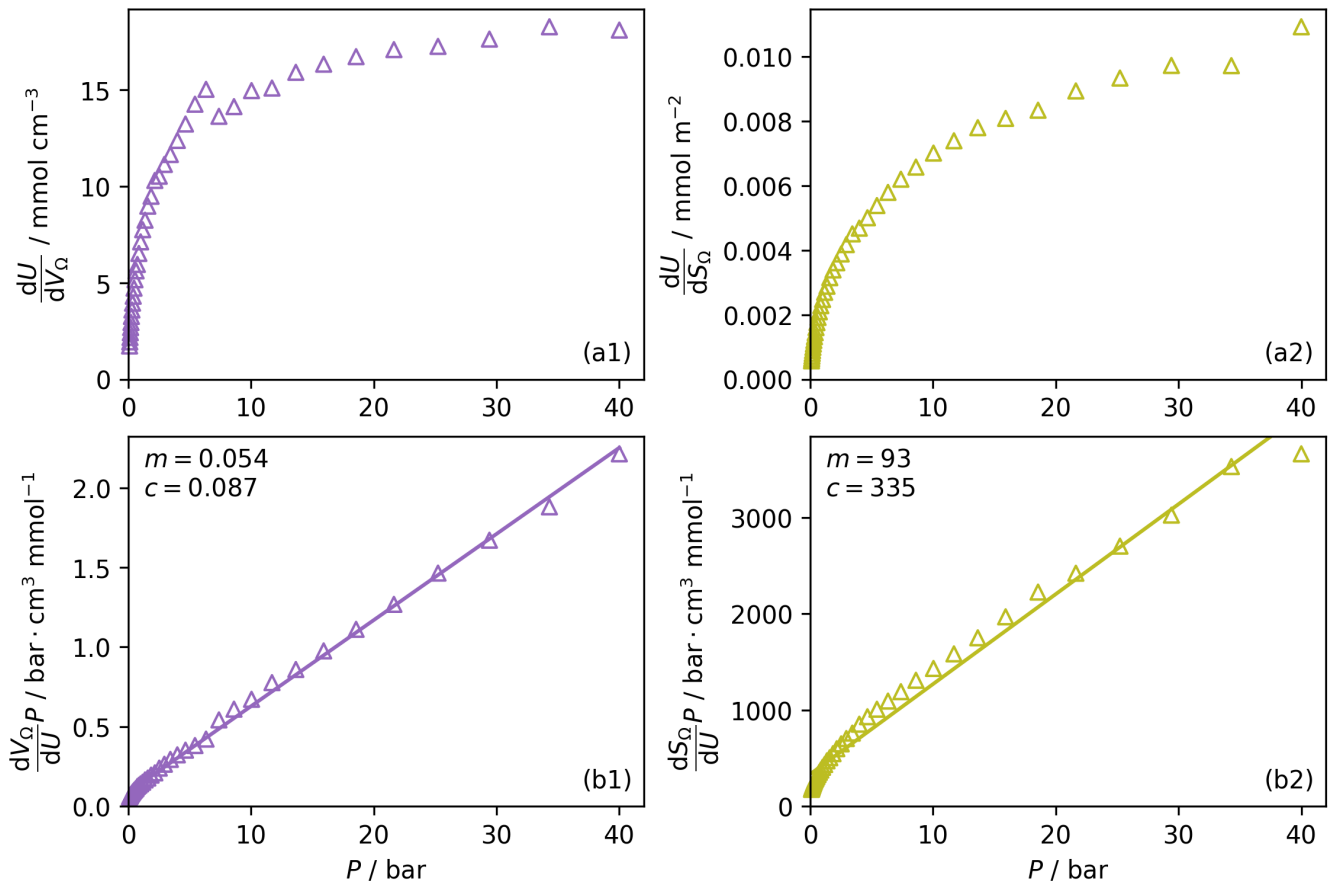


Fig. 3 : Change in  $\frac{dU}{dV_{\Omega}}$  (a1) and  $\frac{dU}{dS_{\Omega}}$  (a2) with  $P$ , and in a linearised form (b1) and (b2).

### 3.1.3 Relative strength of correlations.

Figure 1, however does not tell the full story as it presents each of the  $\Omega$ s as equal. That is, there is no consideration of relative Pearson coefficients ( $r^2$ ), which is presented in figure 2. While positive correlations were established for each pressure in question,  $r^2$  ranges from 0.57 at 0.10 bar (figure 2 (a1)) to 0.88 at 40 bar (figure 2 (a4)). Indeed,  $r^2$  steadily improves with increasing pressure and this trend is shared both for the volume and surface area of pores within  $\Omega$ , i.e.  $V_{\Omega}$  and  $S_{\Omega}$  respectively. The relatively poor fit at low pressure may be a result of the imprecision of PSDs derived from  $N_2$  isotherms in the ultramicropore region.<sup>22,24,34</sup> In addition, as mentioned before fitting of models to  $CO_2$  isotherms to  $P < 1.0$  bar was in some cases less successful than for higher pressures thus there may be inaccuracies in the determined gravimetric uptake at such pressures.

### 3.1.4 Effect of increasing pressure on influence of $\Omega$ on $CO_2$ uptake.

Figure 2 also shows the approximate relationship between uptake at the pressure ( $U$ ) in question and pore volume or surface area within the  $\Omega$  in the form  $\frac{dU}{dV_{\Omega}}$  or  $\frac{dU}{dS_{\Omega}}$ , as derived from the linear regression. It is thus possible to predict the effect of increasing pore volume within the  $\Omega$  on  $CO_2$  uptake at that pressure, i.e. increasing volume of pores of width 3.6-8.3 Å by 1  $cm^3 g^{-1}$

ought to result in an increase in uptake of 1.7  $mmol g^{-1} CO_2$  at 0.1 bar, whereas the same increase in pore volume in the range 6.2-30 Å (approximately the supermicropore and small mesopore region) results in an improvements in  $CO_2$  uptake at 40 bar of 18  $mmol g^{-1}$ . If we examine slopes of fits in figure 2, (column b), a similar pattern appears, with an increase in surface area of 1000  $m^2 g^{-1}$  in pores between 3.6 and 8.3 Å corresponding to a meager 0.57  $mmol g^{-1}$  improvement in  $CO_2$  uptake compared with an increase in uptake of 11  $mmol g^{-1}$  at 40 bar when surface area in pores of width 8.3-100 Å increases by the same amount.

Furthermore, a clear positive, semi-logarithmic trend is observed between  $\frac{dU}{dV_{\Omega}}$  and  $P$ , i.e. it takes the form of a gas adsorption isotherm (see figure 3). A similar transform to that used in determination of a Langmuir isotherm<sup>46</sup> demonstrates a strong relationship of the form;

$$\frac{dU}{dV_{\Omega}} = \frac{P}{mP + c} \quad (3)$$

where the slope  $m$  is 0.054  $cm^3 mmol^{-1}$  with an  $r^2$  of 0.997. The intercept,  $c$  does not have any physical significance as it ought to be a multiple of  $CO_2$  uptake at 0 bar, and thus should be zero. Its non-zero value is likely a reflection of the relatively high uncertainty in the relationship between  $U$  and  $V$  at pressures below 1

bar. A similarly strong fit ( $r^2 = 0.980$ ) can be observed for  $\frac{dU}{dS_\Omega}$  by the same treatment as in equation 3, where  $m = 93 \text{ m}^2 \text{ mmol}^{-1}$ . However the relationship between  $\frac{dU}{dS_\Omega}P$  and  $P$  is not exactly linear. Nevertheless, it is clear that with increasing pressure, improvements in  $\Omega_V$  or  $\Omega_S$  correspond to rapid improvements in  $U$  at low pressures, but these improvements diminish at higher pressures. This is likely a result of a reduction in enthalpy of adsorption with increasing adsorbate loading.

### 3.1.5 Association of arbitrary pore-size regions with uptake.

While sections 3.1.2, 3.1.3, and 3.1.4 discuss  $\Omega$ , i.e. the absolute best pore size for  $\text{CO}_2$  uptake at a given pressure (according to our methods), experimentally targeting porosity of amorphous porous carbons within such precise limits (e.g.  $3.6\text{-}9.2 \text{ \AA}$  at 1 bar) is unlikely to be practicable. Besides, these limits are 'fuzzy', in that the next best pore size region to  $\Omega$  typically has a similar  $r^2$  value at the pressure in question. It is useful therefore to examine the dependence of  $r^2$  as determined in the  $D_c$  on pressure within specific pore size regions, as shown in figure 4. For brevity, these results are discussed and displayed in terms of pore volume only. The traditional division of nanopores separates micropores into so-called ultramicropores ( $<7 \text{ \AA}$ ) and supermicropores ( $7\text{-}20 \text{ \AA}$ ). As shown in figure 4(a1) ultramicropores are not particularly strongly associated with  $\text{CO}_2$  uptake at any pressure, although  $r^2$  does improve at low pressures - in contrast to previous reports.<sup>13,15</sup> On the other hand, supermicroporosity does appear to correlate fairly strongly ( $0.6 < r^2 < 0.8$ ) with uptake at pressures between 10 and 40 bar. This analysis also shows that mesoporosity does not show any particularly strong relationship with a carbon's ability to capture  $\text{CO}_2$  at any pressure below 40 bar - the maximum  $r^2$  is only 0.52. That is not to say that mesopores are not important for high pressure  $\text{CO}_2$  adsorption, indeed as discussed in 3.1.2, both  $\Omega_V$  and  $\Omega_S$  at 40 bar include small mesopores, in addition to supermicropores, with  $r^2$  of 0.88 and 0.84, respectively.

In section 3.1.2 and figure 1 we see that at lower pressures  $\Omega$  is approximately  $3.6\text{-}10 \text{ \AA}$ . Therefore, a reasonable alternative to the traditional subdivision of micropores at  $7 \text{ \AA}$  could be at  $10 \text{ \AA}$ . As shown in figure 4(a2), pores of width  $<10 \text{ \AA}$  do indeed show improved correlation with  $\text{CO}_2$  uptake at relatively low pressures with  $r^2$  reaching 0.79 at 2.9 bar. Conversely the larger subdivision, i.e. between 10 and  $20 \text{ \AA}$  does not show improvements relative to the supermicropore designation, and has much poorer correlations at high pressures. Expanding this pore size region to include all pores above  $10 \text{ \AA}$  does not significantly improve  $r^2$  values in the pressure range used in this study. In other words it appears that pore size regions to target for high (10-40 bar) and medium ( $<10$  bar) pressure uptake overlap, with the former being pores above  $7 \text{ \AA}$ , and the latter below  $10 \text{ \AA}$ . Low pressures ( $<1$  bar) require even smaller pores of widths less than  $8\text{-}9 \text{ \AA}$  (see figures 1 and 2(a1-2, b1-2)).

Figure 4(b1 and b2) show the effect of a broadening pore size region on the relationship between  $r^2$  and  $P$ , with a fixed lower limit of  $3.6$  and  $7.0 \text{ \AA}$  respectively. These lower limits correspond to the two values of  $w_{min}$  mentioned in 3.1.2. In both cases

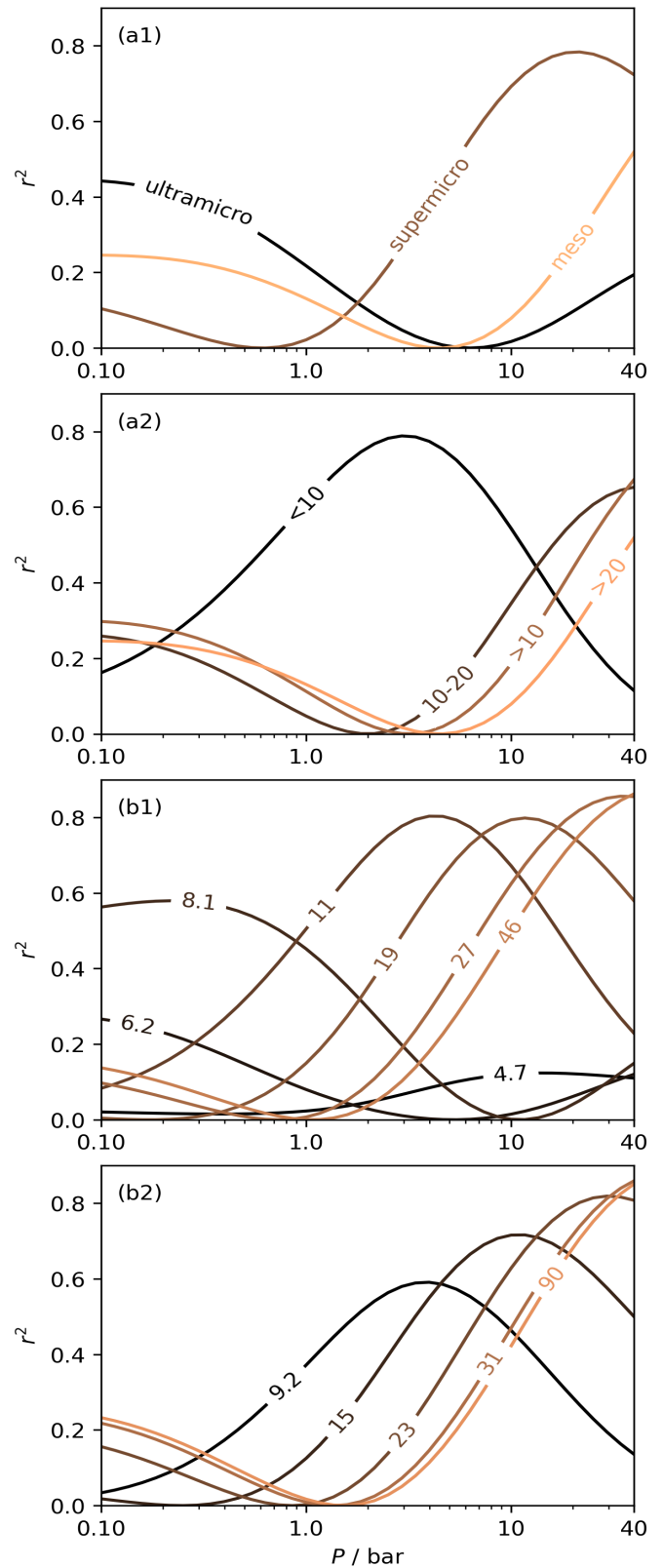


Fig. 4 : Dependence of  $r^2$  on pressure within different pore size regions by pore volume, i.e. ultramicropores, supermicropores and mesopores (a1); pores of width  $<10$ ,  $10\text{-}20$ , and  $>20 \text{ \AA}$  (a2); increasing  $w_{max}$  with a fixed  $w_{min}$  of  $3.6$  (b1) and  $7.0 \text{ \AA}$  (b2).



small increases in  $w_{max}$  have a strong effect on the pressure at which correlation is strongest for the pore size region. However at higher values of  $w_{max}$ , this discrepancy is reduced. For example pores of width 7.0-31 and 7.0-90 Å have their strongest association ( $r^2 \approx 0.85$ ) with CO<sub>2</sub> uptake at 40 bar. This corresponds roughly to  $\Omega_V$  at 40 bar (figure 2(d1)) and shows that at high pressures larger pores may not significantly effect adsorption of CO<sub>2</sub>. It is interesting to note that very narrow pore size ranges i.e. 3.6-4.7 and 3.6-6.2 Å (figure 4(b1)) do not show any significant relationship to CO<sub>2</sub> uptake, in fact  $r^2$  never exceeds 0.27 for either of these pore size regions, so any variation in  $r^2$  here is essentially meaningless. That is, there appears to be a lower limit to pore size that positively effects uptake at pressures of 0.10 bar and greater which is around 8.1 Å.

### 3.2 Highly ultramicroporous carbons

We recently reported on relative improvements in precision of PSD determination by use of dual fits to O<sub>2</sub> and H<sub>2</sub> isotherms relative to N<sub>2</sub> and H<sub>2</sub>.<sup>34</sup> This was particularly relevant to so-called biochars and carbons activated with small amounts of porogen, both having a high proportion of ultramicropores. The rationale being that N<sub>2</sub>'s poor diffusion into ultramicropores meant that PSDs, especially at the smaller end of the micropore region, are imprecise. In addition, when NLDFT kernels were fit to N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub> isotherms individually there were notable discrepancies in derived PSDs, which were more evident for the more ultramicroporous carbons.<sup>34</sup> In the previous section it was noted that the Pearson coefficient for  $\Omega$  was very low at low pressures, which may be a result of imprecise PSDs for DataSet 1 in the ultramicropore region. It is useful therefore to examine the relative results of  $\Omega$  determination using PSDs from single N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub> isotherms as well as from dual kernel fitting. The following sections examine PSDs from these sorptives and combinations thereof in the determination of optimum porosity in the 12 carbons in DataSet 2. Synthetic details for these samples can be found in table S2.1.

#### 3.2.1 Analysis using PSDs from single isotherm H<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> fits.

CO<sub>2</sub> uptake isotherms, their fits, and PSDs from the three sorptives can be found in figures S2.1-S2.3 and S2.4-S2.6. A comparison of  $\Omega_V$  derived using each of the three isotherms (i.e.  $\Omega_V^{sorpive}$ ) in question in the pressure range 0.10-20 bar can be found in figure 5.<sup>¶</sup> It is clear that no single sorptive is providing a reasonable  $\Omega_V$  for DataSet 2 throughout the prescribed pressure range. In particular,  $\Omega_V$  from N<sub>2</sub> ( $\Omega_V^{N_2}$ ) isotherms (figure 5(a1)) gives the unreasonable conclusion that up to 2.1 bar  $\Omega_V^{N_2}$  is constant at around 5.8-6.3 Å. This is both a surprisingly narrow range, and it is unlikely that there would be effectively no broadening of  $\Omega_V^{N_2}$  with increasing  $P$  up to this point. Similarly, after 2.1 bar  $\Omega_V^{O_2}$  (figure 5(a2)) drops to a very narrow, relatively constant range (approximately 10-11 Å). This may simply be an effect of the minimal improvements in CO<sub>2</sub> for these carbons above 2 bar (see figures

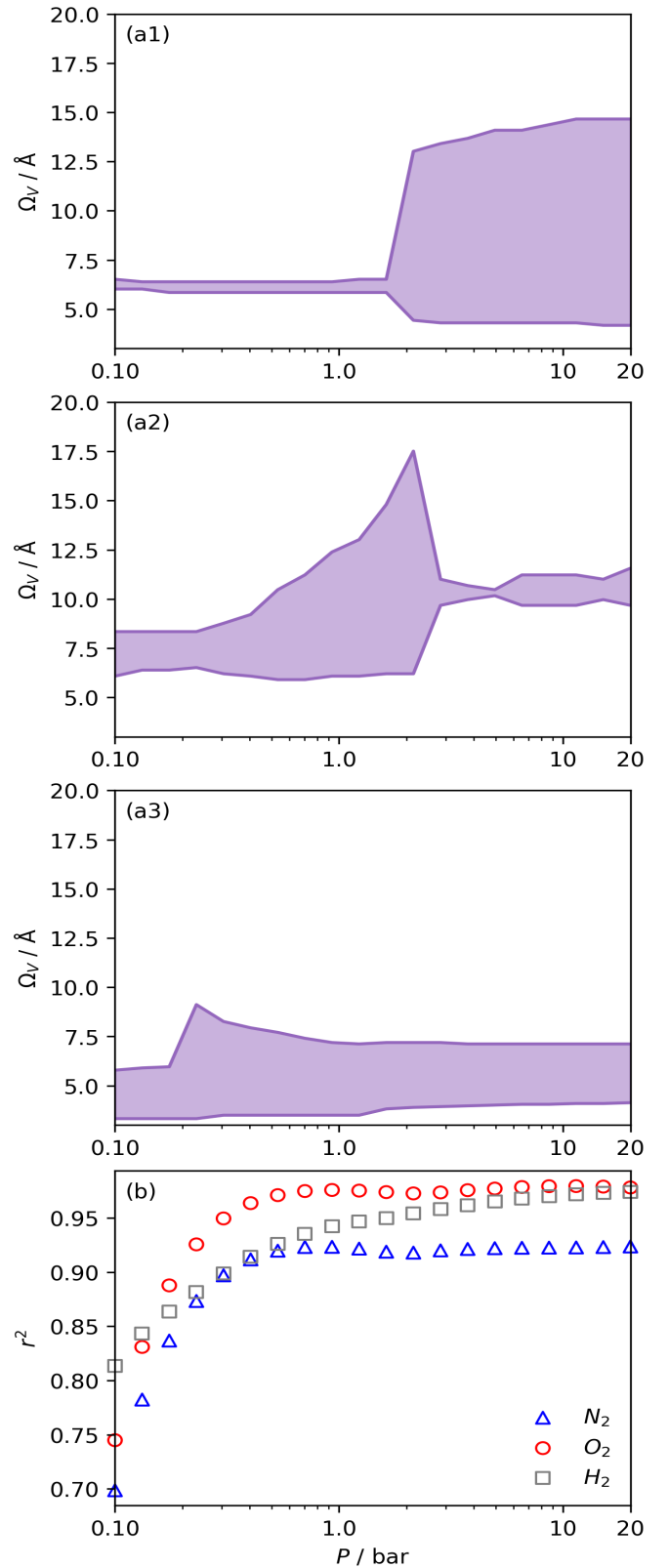


Fig. 5 :  $\Omega_V$  calculated from DataSet 2 using PSDs derived from N<sub>2</sub> (a1), O<sub>2</sub> (a2), and H<sub>2</sub> (a3) isotherms as well as corresponding  $r^2$  values (b).

<sup>¶</sup>Results for  $\Omega_V^{sorpive}$  are sufficiently similar to not require a separate discussion here. A comparison is displayed in figure S2.13.

S2.1-S2.3), which is attributable to the very minimal porosity of these carbons in the supermicropore and mesopore regions (see figures S2.4-S2.6).<sup>34</sup> As such discussions of these analyses are best limited to uptakes at  $P < 2$  bar.

For analyses using both  $O_2$  and  $H_2$  there is a broadening in  $\Omega_V$  with increasing  $P$  at relatively low pressures which is not present according to  $N_2$  analysis. In addition, as shown in figure 5(b),  $r^2$  is lower at all pressures for correlations derived using  $\Omega_V^{N_2}$  data compared to  $\Omega_V^{O_2}$  and  $\Omega_V^{H_2}$ . While  $\Omega_V^{O_2}$  data shows the best correlations in general,  $r^2$  from  $\Omega_V^{H_2}$  data is greater at 0.10 and 0.13 bar. In other words, for this set of carbons, porosity accessible to  $CO_2$  is best determined using  $H_2$  isotherms up to 0.13 bar, and thereafter (up to around 2 bar) using  $O_2$  isotherms. This follows from the standpoint of  $H_2$  having access to - and thus predicting the presence of - pores of widths as small as 3.0 Å, while the lower limit for  $O_2$  is 3.6 Å. Thus the contribution of pores of widths less than 3.6 Å to low pressure  $CO_2$  uptake can only be accounted for using  $H_2$  porosimetry, yielding  $\Omega_V^{H_2} = 3.3\text{-}5.9$  Å. At 0.17 bar and above, pores above 6.0 Å appear to become more heavily utilised for  $CO_2$  adsorption according to relative magnitudes of  $r^2$ . The upper limit of porosity measurable by  $H_2$  at  $-196^\circ\text{C}$  is unknown, however it is usually said to be between 8.0-10 Å.<sup>22,24</sup> This explains why results for  $\Omega_V^{H_2}$  become less reasonable at pressures above 0.3 bar;  $H_2$  porosimetry is unsuitable for prediction of  $CO_2$  uptake at these pressures. Indeed, in determination of PSDs for from  $H_2$  isotherms,  $w_{max}$  was set to 10 Å.

Figure 6 presents further information on the relative efficacy of the three sorptives in measuring pores of widths below some limit ( $w_{max}$ ), and the relationship between pores of these widths and  $CO_2$  uptake between 0.10 and 2.0 bar. It is striking that when  $w_{max}$  is set at 5.0 or 6.0 Å, only  $H_2$  porosimetry provides reasonable correlations ( $r^2 > 0.60$ ) at any pressure. Indeed, in the case of  $O_2$  (see figure 6(b))  $r^2$  is zero at all pressures and thus cannot be displayed within the figure. Strong correlations only begin to be shown when  $w_{max}$  is set to 10. PSDs derived from  $O_2$  isotherms do show porosity in the ultramicropore region, thus it may be concluded that the ultramicropores accessible to  $O_2$  are not important for  $CO_2$  uptake, while those ultramicropores accessible to  $H_2$  do contribute to  $CO_2$  uptake. The latter statement can be accounted for by the fact  $H_2$  has access to pores undetectable by  $O_2$ . Similar rationale can be applied to the plot for  $N_2$  (figure 6(a)). When  $w_{max}$  is increased past 10 Å,  $r^2$  vs  $P$  plots become very similar in the case of calculations made using both  $N_2$  and  $O_2$  derived PSDs. This indicates that there is little measurable improvement in  $CO_2$  adsorption by broadening the PSD past 10 Å, however this may simply be a result of the relatively narrow PSDs present in these samples.

In summary, examination of  $D_c$  for DataSet 2 with each of the three porosimetric sorptives shows that low pressure ( $<2.0$  bar)  $CO_2$  uptake is improved by increasing volume in pores below 10 Å. In addition,  $N_2$  is consistently outperformed by  $O_2$  and/or  $H_2$  at measuring porosity appropriate for  $CO_2$  uptake. However, while porosity as determined by  $O_2$  improves  $CO_2$  uptake at pressures above 0.13 bar,  $H_2$  is needed to determine optimum porosity for uptake at ultra-low pressures. It is therefore logical to consider

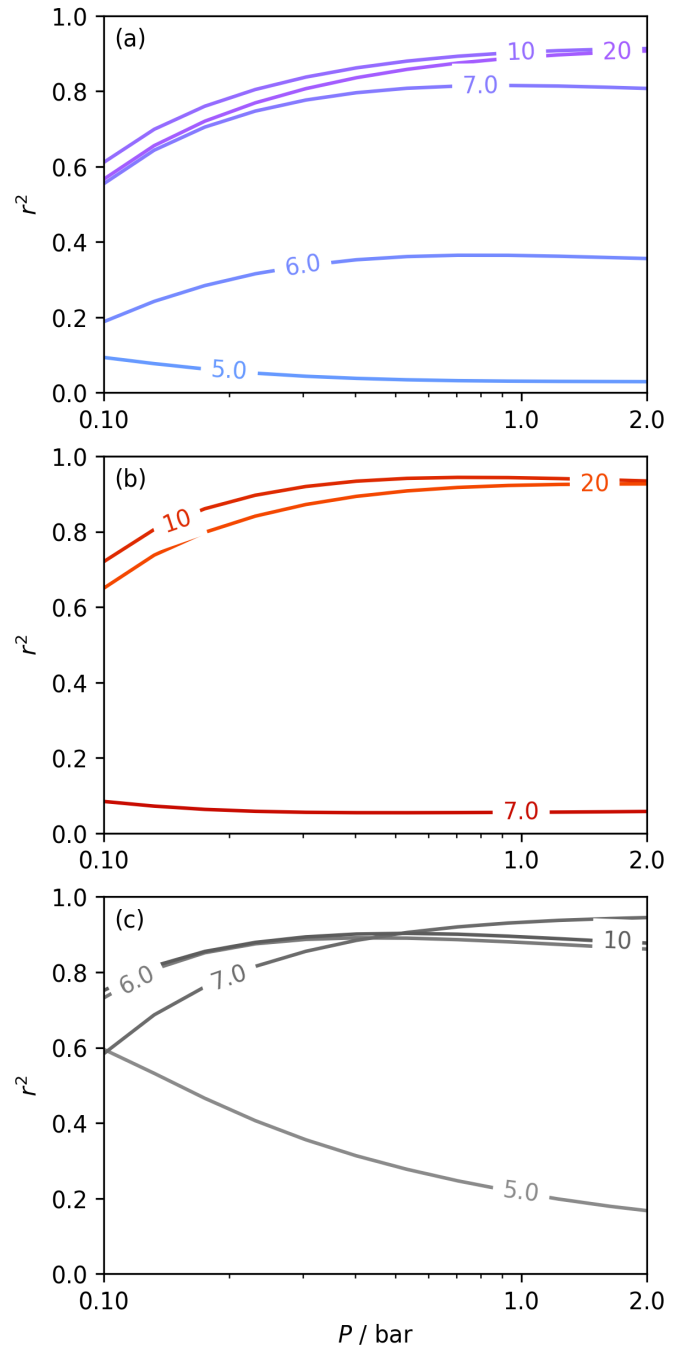


Fig. 6 : Comparison of dependence of  $r^2$  on pressure with increasing  $w_{max}$  as determined using PSDs from  $N_2$  (a),  $O_2$  (b), and  $H_2$  (c) isotherms.

PSDs as determined via dual isotherm analysis as a way to extend the range of pressures at which optimum pore size for  $CO_2$  can be accurately determined.

### 3.2.2 Analysis using PSDs from dual isotherm $N_2/H_2$ and $O_2/H_2$ fits.

Fitting the 2D-NLDFT heterogeneous surface kernel to  $H_2$  simultaneously with  $N_2$  or  $O_2$  allows the calculation of the range of the PSD in the range 3.0-500 Å. Thus, using these dual-fit PSDs in the calculation of  $D_c$  and  $\Omega$  should allow for consideration of the



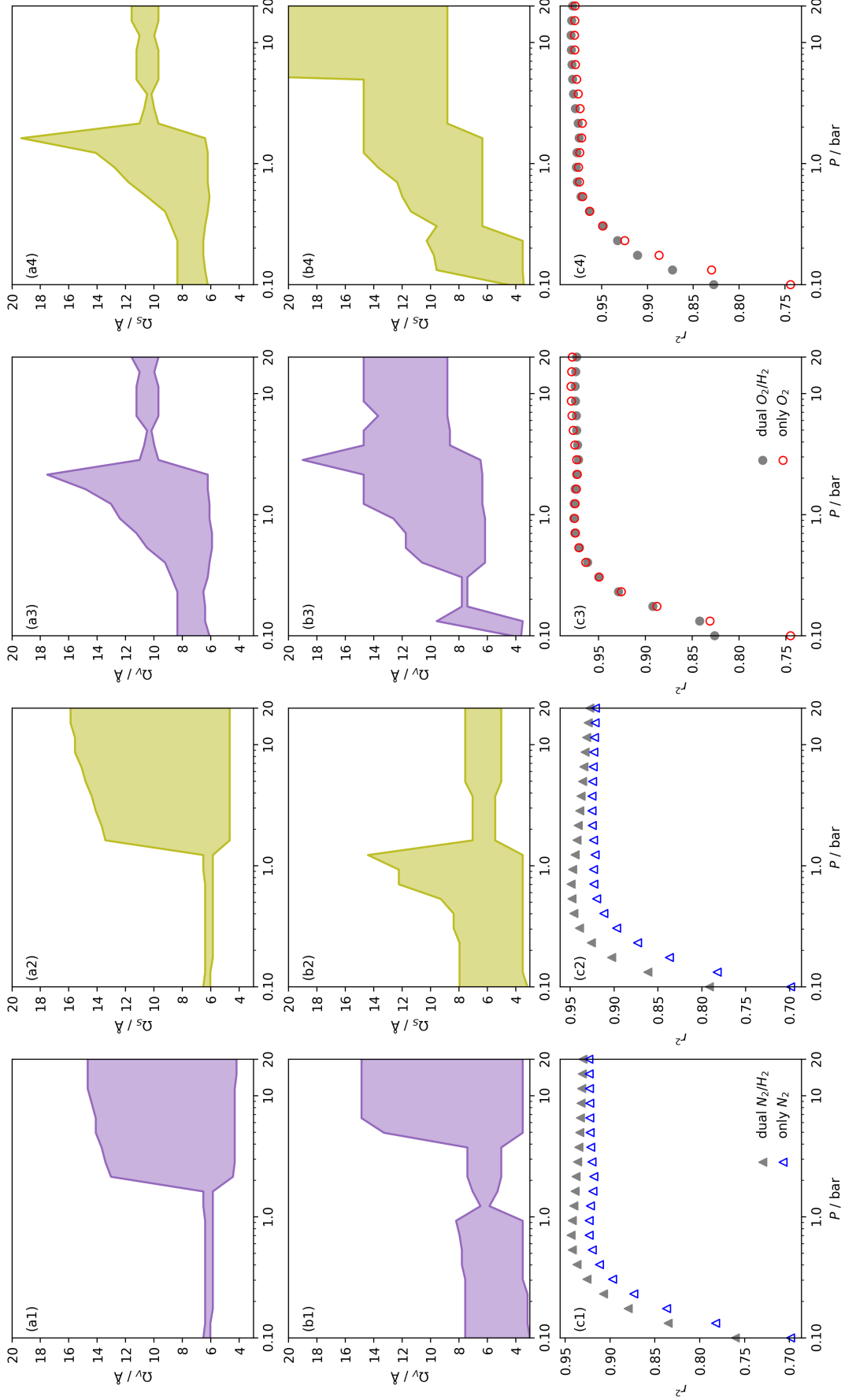


Fig. 7 : Comparison of  $\Omega_V$  (a1, b1, a3, b3) and  $\Omega_S$  (a2, b2, a4, b4) as determined by  $N_2$  (a1, a2),  $O_2$  (a3, a4) and dual  $N_2/H_2$  (b1, b2) and  $O_2/H_2$  (b3, b4) porosimetry. Row (c) contains comparisons of  $r^2$  with  $P$  for the two  $\Omega$  plots directly above.

affinity of all pores in this range for CO<sub>2</sub> in the defined pressure range. Figure 7 compares  $\Omega_V$  and  $\Omega_S$  from single isotherm (N<sub>2</sub> and O<sub>2</sub>) fits to those obtained by dual fitting with H<sub>2</sub>. In all cases, the  $\Omega$  vs  $P$  plot for the dual fit (Figure 7(b1-4)) appears more reasonable than the corresponding plot for single fit (Figure 7(a1-4)), especially when  $P < 1.0$  bar. In the case of  $\Omega_V^{N_2/H_2}$  the improvement over single fit is principally in that the breadth of pore sizes (approx. 3.0-8.0 Å) in  $\Omega_V^{N_2/H_2}$  below 1.0 bar is much more realistic than for  $\Omega_V^{N_2}$ . There is however no broadening within this region with increasing pressure, unlike for  $\Omega_S^{N_2/H_2}$  which may be a result of the nature of adsorbate-adsorbent relative to adsorbate-adsorbate interactions as highlighted in section 3.1.2. In addition to the relationship between  $\Omega$  and  $P$  being more realistic in terms of both surface area and pore volume, the  $r^2$  is consistently better for both  $\Omega_V^{N_2/H_2}$  (c1) and  $\Omega_S^{N_2/H_2}$  (c2) than their single-isotherm PSD counterparts. That is to say, that extending the range of accurate, measurable porosity well into the ultramicropore region yields improved certainty in the determination of optimum porosity for CO<sub>2</sub> uptake.

$r^2$  values for  $\Omega_V^{O_2/H_2}$  and  $\Omega_S^{O_2/H_2}$  only shows noticeable improvements at pressures below 0.30 bar compared to their single isotherm counterparts (figure 7(c3-4)). This again indicates the importance of porosity penetrable by H<sub>2</sub> alone in the adsorption of CO<sub>2</sub> at low pressures. For  $\Omega_V^{O_2/H_2}$  (figure 7(b3)) this corresponds to a significantly smaller range at low pressures, with pores in the range 3.6-4.2 Å being most associated with CO<sub>2</sub> uptake at 0.10 bar, compared to 6.1-8.3 Å for  $\Omega_V^{O_2}$  (a3). Broadening in  $\Omega_V^{O_2/H_2}$  is also briefly apparent as  $P$  increases to 0.13 bar, but falls to an unrealistically narrow range again quickly. On the other hand  $\Omega_S^{O_2/H_2}$  (figure 7(b4)) gives the most physically reasonable result as it broadens consistently with increasing  $P$ . Furthermore, we see three distinct values of  $w_{min}$  of 3.5, 6.3, and 8.8 Å. The latter two values reflect the results shown in figure 1, indicating that the use of dual O<sub>2</sub>/H<sub>2</sub> isotherms gives information on the pressures at which the influence of the smallest of ultramicropores on CO<sub>2</sub> uptake is greatest, that is below 0.30 bar.

The utility of dual isotherm porosimetry with H<sub>2</sub> as one of the probes in CO<sub>2</sub> porosity uptake correlations is further emphasised on examination of the dependency of  $r^2$  on  $P$  with broadening PSDs (see figure 8). In the case of the corresponding plots for single isotherm fits (figure 6) H<sub>2</sub> was the only probe molecule that provided strong correlations where  $w_{max}$  is 5.0 or 6.0 Å. While dual N<sub>2</sub>/H<sub>2</sub> porosimetry (figure 8(a)) provides some improvements for these narrow pore width ranges compared to single isotherm N<sub>2</sub> (figure 6(a)), the most significant improvements are for O<sub>2</sub>/H<sub>2</sub> relative to O<sub>2</sub>. Indeed, for all values of  $w_{max}$  between 5.0 and 7.0 Å there are reasonable  $r^2$  values ( $>0.50$ ) (figure 8(b)) at some pressure, with  $w_{max} = 5.0$  Å showing the greatest improvement relative to the its single isotherm counterpart. In fact, the plot for 5.0 Å shows improvement even relative to its corresponding plot from single isotherm H<sub>2</sub> porosimetry (figure 6(c)), as  $r^2$  does not fall below 0.50 at pressures below 5.0 bar. In other words, while H<sub>2</sub> porosimetry shows that pores of width less than 5.0 Å have a reasonable association with CO<sub>2</sub> uptake at 0.10 bar only, combined O<sub>2</sub>/H<sub>2</sub> porosimetry shows that this continues to

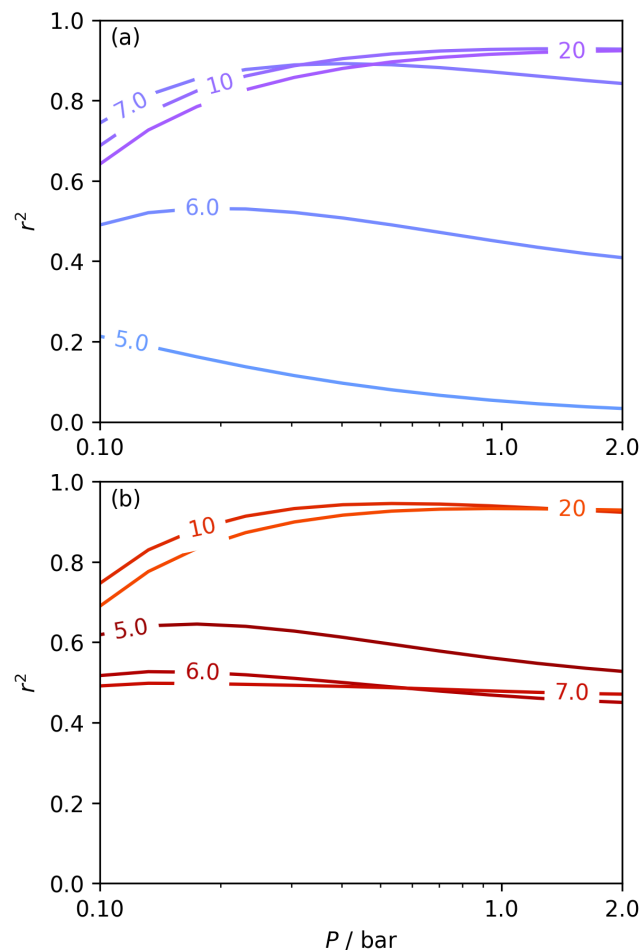


Fig. 8 : Comparison of dependence of  $r^2$  on pressure with increasing  $w_{max}$  as determined using PSDs from dual N<sub>2</sub>/H<sub>2</sub> (a) and O<sub>2</sub>/H<sub>2</sub> (b) isotherms.

much higher pressures.

It appears therefore that dual O<sub>2</sub>/H<sub>2</sub> porosimetry may give a more nuanced and reasonable picture of porosity relevant to CO<sub>2</sub> uptake within samples in DataSet 2 as compared to both dual N<sub>2</sub>/H<sub>2</sub> analysis as well as PSDs from single sorptives. In particular, if we compare results from O<sub>2</sub>/H<sub>2</sub> analysis to the traditional N<sub>2</sub> analysis it is interesting that the presence of micropores of width  $<5.0$  Å according to the former figure 8(b)) are at least as important as micropores in general according to the latter for CO<sub>2</sub> uptake at very low pressures (see figures 8(b) and 6(a), respectively). While more investigation is necessary to determine the precise reasons for the differences in results given by dual isotherm O<sub>2</sub>/H<sub>2</sub> and the other methods measurement of the porosity most relevant to CO<sub>2</sub> uptake in highly ultramicroporous carbons, it remains clear that both the certainty of these results from the former and their correspondence with accepted theory of gas adsorption in pores is better.

## 4 Conclusions

pyPUC shows promise in its ability to thoroughly and definitively elucidate the relationship between porosity within some pore size

range, and uptake of a gas at some pressure. We have examined its utility in determining the optimum pore size region in terms of pore volume or surface area ( $\Omega_V$  or  $\Omega_S$ ) for CO<sub>2</sub> capture in carbons between 0.10 and 40 bar. More than broadly confirming reports by previous experimental and theoretical studies, this work gives a much higher level of precision concerning the relationship between  $\Omega$  and  $P$ . Furthermore, it is possible to approximately predict the increase in CO<sub>2</sub> uptake achieved by increasing porosity within the  $\Omega$ . Apart from optimum pore sizes ranges, we also find the relationship between pores within arbitrary width ranges on CO<sub>2</sub> uptake.

In addition this method allows facile, comprehensive comparison of such results using different isothermal porosimetric methods for PSD determination. This is particularly relevant to highly ultramicroporous carbons, wherein the utility of N<sub>2</sub> has been called into question. Here, we show that dual isotherm analysis, and in particular O<sub>2</sub>/H<sub>2</sub> analysis improves our predictions of CO<sub>2</sub> uptake especially at very low pressures.

The pyPUC method can be easily expanded to be used for calculations related to the uptake of other sorptives, under different conditions, and with other variables (e.g. surface chemistry) accounted for. Results from our methods may help improve the design of porous materials for a wide range of adsorption applications.

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## Author Contributions

**L. Scott Blankenship:** Conceptualization, Methodology, Software, Formal Analysis, Data Curation, Investigation, Writing – Original Draft, Visualization

**Nawaf Albeladi:** Investigation

**Thria Alkhaldi:** Investigation

**Asma Madkhali:** Investigation

**Robert Mokaya:** Validation, Resources, Writing – Review & Editing, Funding acquisition

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Notes and references

- 1 M. Sevilla and R. Mokaya, *Energy & Environmental Science*, 2014, **7**, 1250–1280.

- 2 T. C. Drage, J. M. Blackman, C. Pevida and C. E. Snape, *Energy & Fuels*, 2009, **23**, 2790–2796.
- 3 M. G. Plaza, S. Garcia, F. Rubiera, J. J. Pis and C. Pevida, *Chemical Engineering Journal*, 2010, **163**, 41–47.
- 4 A. Altwala and R. Mokaya, *Energy & Environmental Science*, 2020, **13**, 2967–2978.
- 5 S. Biloé, V. Goetz and A. Guillot, *Carbon*, 2002, **40**, 1295–1308.
- 6 M. Beckner and A. Dailly, *Applied Energy*, 2016, **162**, 506–514.
- 7 J. Juan-Juan, J. Marco-Lozar, F. Suárez-García, D. Cazorla-Amorós and A. Linares-Solano, *Carbon*, 2010, **48**, 2906–2909.
- 8 K.-S. Lin, A. K. Adhikari, K.-C. Chang, C.-L. Chiang and C.-H. Wang, *Journal of Nanoscience and Nanotechnology*, 2014, **14**, 2700–2708.
- 9 Q. Zhao, F. Wu, K. Xie, R. Singh, J. Zhao, P. Xiao and P. A. Webley, *Chemical Engineering Journal*, 2018, **336**, 659–668.
- 10 J. Alcaniz-Monge, M. A. de la Casa-Lillo, D. Cazorla-Amorós and A. Linares-Solano, *Carbon*, 1997, **35**, 291–297.
- 11 D. Lozano-Castello, D. Cazorla-Amorós, A. Linares-Solano and D. F. Quinn, *Carbon*, 2002, **40**, 989–1002.
- 12 I. Cabria, M. J. López and J. A. Alonso, *Carbon*, 2007, **45**, 2649–2658.
- 13 V. Presser, J. McDonough, S.-H. Yeon and Y. Gogotsi, *Energy & Environmental Science*, 2011, **4**, 3059–3066.
- 14 W. Zhao, V. Fierro, C. Zlotea, E. Aylon, M. Izquierdo, M. Lacroche and A. Celzard, *International Journal of Hydrogen Energy*, 2011, **36**, 11746–11751.
- 15 M. Sevilla, J. B. Parra and A. B. Fuertes, *ACS Applied Materials & Interfaces*, 2013, **5**, 6360–6368.
- 16 E. Masika and R. Mokaya, *The Journal of Physical Chemistry C*, 2012, **116**, 25734–25740.
- 17 Z. Geng, C. Zhang, D. Wang, X. Zhou and M. Cai, *Journal of Energy Chemistry*, 2015, **24**, 1–8.
- 18 B. Adeniran and R. Mokaya, *Chemistry of Materials*, 2016, **28**, 994–1001.
- 19 Y.-K. Choi and S.-J. Park, *Bulletin of the Korean Chemical Society*, 2016, **37**, 830–834.
- 20 G. Sethia and A. Sayari, *Carbon*, 2016, **99**, 289–294.
- 21 T. K. Das, S. Banerjee, P. Sharma, V. Sudarsan and P. U. Sastry, *International Journal of Hydrogen Energy*, 2018, **43**, 8385–8394.
- 22 J. Jagiello, J. Kenvin, A. Celzard and V. Fierro, *Carbon*, 2019, **144**, 206–215.
- 23 D. Grau-Marin, J. Silvestre-Albero, E. O. Jardim, J. Jagiello, W. R. Betz and L. E. Peña, *Carbon*, 2020, **157**, 495–505.
- 24 J. Jagiello, J. Kenvin, C. O. Ania, J. B. Parra, A. Celzard and V. Fierro, *Carbon*, 2020, **160**, 164–175.
- 25 D. H. Everett and J. C. Powl, *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, 1976, **72**, 619–636.
- 26 J. Jagiello and M. Thommes, International Conference on Carbon for Energy Storage and Environment Protection, 2005.

- 27 N. P. Wickramaratne and M. Jaroniec, *Journal of Materials Chemistry A*, 2013, **1**, 112–116.
- 28 M. De la Casa-Lillo, F. Lamari-Darkrim, D. Cazorla-Amoros and A. Linares-Solano, *The Journal of Physical Chemistry B*, 2002, **106**, 10930–10934.
- 29 K. R. Matranga, A. Stella, A. L. Myers and E. D. Glandt, *Separation Science and Technology*, 1992, **27**, 1825–1836.
- 30 S. Reljic, E. Jardim, C. Cuadrado-Collados, M. Bayona, M. Martinez-Escandell, J. Silvestre-Albero and F. Rodríguez-Reinoso, in *CO 2 Adsorption in Activated Carbon Materials*, 2021, pp. 139–152.
- 31 N. Texier-Mandoki, J. Dentzer, T. Piquero, S. Saadallah, P. David and C. Vix-Guterl, *Carbon*, 2004, **42**, 2744–2747.
- 32 Z. Tan and K. E. Gubbins, *Journal of Physical Chemistry*, 1990, **94**, 6061–6069.
- 33 C. M. Simon, J. Kim, D. A. Gomez-Gualdrón, J. S. Camp, Y. G. Chung, R. L. Martin, R. Mercado, M. W. Deem, D. Gunter and M. Haranczyk, *Energy & Environmental Science*, 2015, **8**, 1190–1199.
- 34 L. S. Blankenship, J. Jagiello and R. Mokaya, *Available at SSRN 3946228*, 2022.
- 35 J. Li, B. Michalkiewicz, J. Min, C. Ma, X. Chen, J. Gong, E. Mi-jowska and T. Tang, *Chemical Engineering Journal*, 2019, **360**, 250–259.
- 36 S.-Y. Lee and S.-J. Park, *Journal of Colloid and Interface science*, 2013, **389**, 230–235.
- 37 S. Hlushak, *Physical Chemistry Chemical Physics*, 2018, **20**, 872–888.
- 38 G. Sethia and A. Sayari, *Carbon*, 2015, **93**, 68–80.
- 39 P. Iacomì and P. L. Llewellyn, *Adsorption*, 2019, **25**, 1533–1542.
- 40 C. M. Simon, B. Smit and M. Haranczyk, *Computer Physics Communications*, 2016, **200**, 364–380.
- 41 K. Pearson, *Proceedings of the Royal Society of London*, 1895, **58**, 240–242.
- 42 J. D. Evans, V. Bon, I. Senkovska and S. Kaskel, *Langmuir*, 2021, **37**, 4222–4226.
- 43 P. C. Hansen, *SIAM review*, 1992, **34**, 561–580.
- 44 P. C. Hansen and D. P. O’Leary, *SIAM Journal on Scientific Computing*, 1993, **14**, 1487–1503.
- 45 P. Hansen, in *The L-curve and its use in the numerical treatment of inverse problems*, ed. P. Johnston, WIT Press, Southampton, 2001, pp. 119–142.
- 46 I. Langmuir, *Journal of the American Chemical Society*, 1916, **38**, 2221–2295.
- 47 I. Langmuir, *Journal of the American Chemical society*, 1918, **40**, 1361–1403.
- 48 E. A. Guggenheim, *Applications of Statistical Mechanics*, Oxford Clarendon Press, 1966.
- 49 R. B. Anderson, *Journal of the American Chemical Society*, 1946, **68**, 686–691.
- 50 J. H. de Boer, *The Dynamical Character of Adsorption*, Oxford Clarendon Press, 1953, vol. 76.
- 51 H. Freundlich, *Zeitschrift für Physikalische Chemie*, 1907, **57**, 385–470.
- 52 B. Bering, M. Dubinin and V. Serpinsky, *Journal of Colloid and Interface Science*, 1966, **21**, 378–393.
- 53 J. Tóth, *Journal of Colloid and Interface Science*, 1994, **163**, 299–302.
- 54 M. E. Casco, M. Martínez-Escandell, J. Silvestre-Albero and F. Rodríguez-Reinoso, *Carbon*, 2014, **67**, 230–235.
- 55 M. Sevilla, A. S. M. Al-Jumaily, A. B. Fuertes and R. Mokaya, *ACS Applied Materials & Interfaces*, 2018, **10**, 1623–1633.