

# Electrostatically Mediated Specific Adsorption of Small Molecules in Metallo-Organic Frameworks

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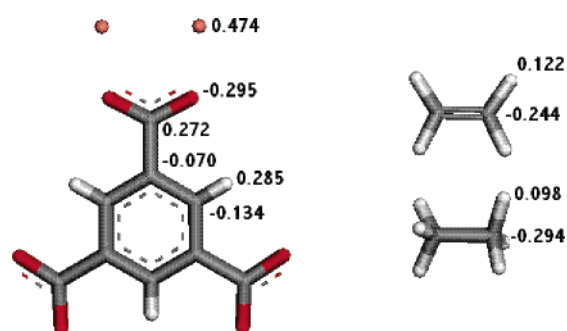
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We investigate the interaction of ethylene and ethane with a Cu–tricarboxylate complex and show that at low loadings the lighter molecule has a higher binding energy as a result of an increased interaction with the framework Cu and stronger hydrogen bonding with the basic framework oxygens. This leads to selective adsorption of ethylene by a factor of about 2 at low pressure, which is overcome by the stronger van der Waals interaction of ethane at high loadings, explaining recent literature data. The results suggest the possibility of separation of light hydrocarbons at low pressures or in trace amounts.

Metallo-organic frameworks (MOFs) form an exciting class of novel materials now receiving much attention<sup>1–6</sup> because of their potential for gas storage<sup>7,8</sup> and separation.<sup>9</sup> While such potential has been related to their attractive structural properties, the role of H-bonds and other electrostatic interactions in affecting selective adsorption in such materials is unrecognized. The recent reports of unconventional H-bonding between surface oxygens and CH groups of chemisorbed complexes<sup>10</sup> and of acetylene with basic framework oxygens of a Cu<sub>2</sub>(pydc)<sub>2</sub>(pyz) MOF<sup>4</sup> auger well for this possibility. If present for other physisorbed molecules, such interactions can be exploited in separation of trace hydrocarbons.

Separation of ethane and ethylene is the holy grail of adsorption, where conventional molecular sieving is difficult because of their very similar molecular dimensions. In recent studies,<sup>9</sup> however, the highly porous MOF [Cu<sub>3</sub>(BTC)<sub>2</sub>(H<sub>2</sub>O)<sub>x</sub>] has been found to show differing sorption properties for ethane and ethylene, with the latter being preferentially adsorbed by a factor of about 2 at low pressures. At higher pressures the difference lessens. Here we investigate the origin of these differences and demonstrate that they are attributable to electrostatic interactions between the small molecules and framework charges, including H-bonding with framework oxygens, opening the door for exploitation of this effect in low-pressure separation.

Quantum mechanical calculations were performed on the structure using the DMol3 program.<sup>11</sup> The HCTH/407 functional<sup>12</sup> was chosen, which is a flexible form of gradient-corrected functional fitted to a training set of molecules. This is reported to predict a much improved thermochemistry for a wide range of systems and is an updated version of a functional that has successfully predicted the binding energies of hydrogen-bonded systems.<sup>13</sup> Similarly, a double numerical basis set plus a polarization on the hydrogen atoms was used which is essential to include hydrogen bonds. A Mulliken population analysis was performed to obtain atomic charges. The size of the structure precluded performing the calculation for the whole unit cell, which contains 624 atoms, so several representative portions of the structure containing approximately 70 atoms each were simulated. The results for each of the six types of atoms were



**Figure 1.** Calculated charges for framework and small molecules. The isolated atoms are Cu ions.

**TABLE 1: Calculated and Experimental Effective Quadrupole Moments (e Å<sup>2</sup>)**

	calculated	experimental <sup>a</sup>
C <sub>2</sub> H <sub>6</sub>	0.515	0.09–0.67
C <sub>2</sub> H <sub>4</sub>	0.636	0.63–0.81

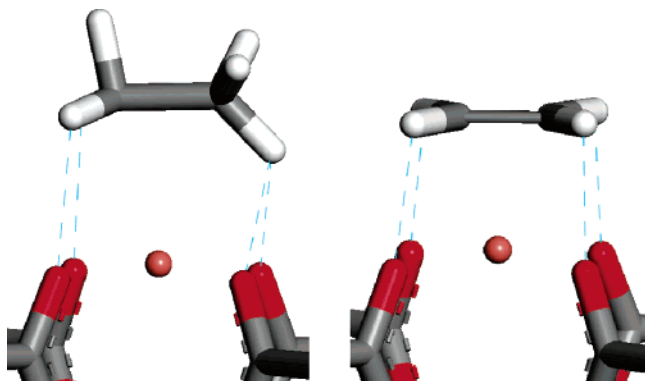
<sup>a</sup> Data from ref 14.

averaged over the three structures simulated. Further details are available in the Supporting Information accompanying this paper. A full quantum mechanical calculation for each of the small molecules could be performed using the same choices of functional and basis set.

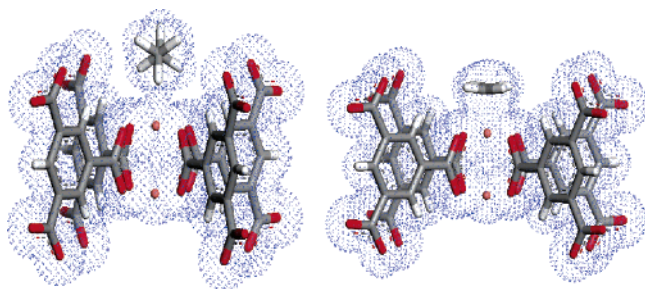
The calculated charges are shown in Figure 1. The validity of the charges on the small molecules was verified by comparison of the calculated quadrupole moment with the range of experimental values from the literature,<sup>14</sup> as shown in Table 1. Our predicted values lie within the experimental range (which are quite broad) and rank in the correct order.

The energy of the system of the framework and a small molecule was then minimized using the Discover program,<sup>15</sup> using the charges calculated by DMol3 and van der Waals (vdW) parameters from the built-in Compass force field. This procedure was adopted as a full quantum mechanical minimization was not possible due to the size of the structure. The lattice was held fixed, and the small molecules were allowed movement, in both position and conformation. Although grand canonical Monte Carlo simulation with a more accurate force field is perhaps preferable to using the Discover program with

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**Figure 2.** Minimized positions of ethane (left) and ethylene (right) in the framework. The dashed lines indicate the positions of hydrogen bonds. The Cu ion is indicated by the isolated ball.

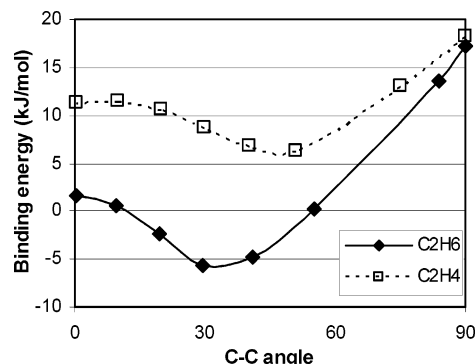


**Figure 3.** Isosurfaces of total charge density  $0.1 \text{ e}/\text{\AA}^3$  for portions of minimized structures (ethane left, ethylene right).

the Compass force field, in this initial study we were interested predominantly in the energetic *differences* between the two similarly sized molecules adsorbed in the host lattice. In particular, differences in the electrostatic interactions and H-bonding, using charges independently obtained from the quantum calculations, will be an important indicator of any separation potential.

Figure 2 shows the minimized positions of an ethane and ethylene molecule. The dashed lines in the figure show hydrogen bonding (calculated on the basis of the distance between H and O atoms being  $<2.5 \text{ \AA}$ ). In both cases, the small molecule minimized to a position close to four framework oxygen atoms surrounding a copper ion. In this position, the ethylene molecule can form four symmetric hydrogen bonds to the four oxygen atoms, with a H-bond distance of  $2.16 \text{ \AA}$ . In comparison, the ethane molecule, while also forming four hydrogen bonds, has a less symmetric arrangement. The H-bonding is still with the four oxygen atoms surrounding a copper ion, but in this case two of the oxygens make a bond with the same hydrogen, so only three hydrogen atoms are involved. The average bond lengths are also higher at about  $2.4 \text{ \AA}$ . The C–H...O angle is  $134^\circ$  for ethane and  $96^\circ$  for ethylene, which are within the accepted range for weak hydrogen bonding.<sup>16</sup> Hydrogen bonding will thus play a part in the sorption of the small molecules, and the shorter H-bond length for ethylene suggests that this molecule may be selectively adsorbed.

Previous authors<sup>9</sup> have speculated that the adsorption properties are related to an interaction between the double bond in the ethylene molecule with the partially charged copper atoms in the framework. Figure 3 shows total self-consistent charge density plots for the two minimized configurations, calculated by DMol3 on the small part of the structure illustrated. The isosurfaces shown correspond to a charge density of  $0.1 \text{ e}/\text{\AA}^3$  in both cases and clearly show that a stronger interaction is present for ethylene. This factor will supplement the increased



**Figure 4.** Binding energy as a function of C–C angle in a small molecule relative to the perpendicular to the closest part of the framework;  $90^\circ$  corresponds to the orientations shown in Figure 2.

hydrogen-bonding seen in ethylene and so will also contribute to an increased adsorption of the smaller molecule. The relative importance of these two factors is discussed further below.

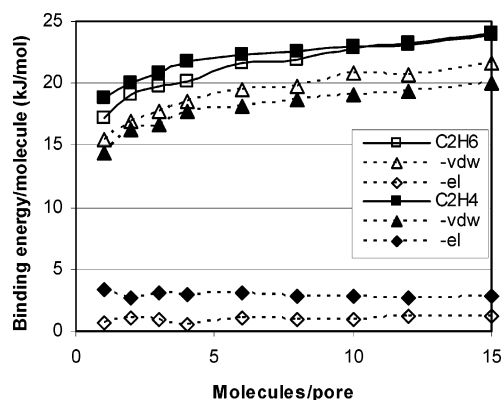
The lowest energy configurations are as shown in Figure 2, with the C–C bond of the small molecule lying parallel to the closest point of the framework with which hydrogen bonds are being formed. In order to check that this was indeed the most stable position, the binding energy was calculated as a function of small molecule orientation. Figure 4 shows this change of binding energy as the C–C bond was forced to be oriented at varying angles to the perpendicular to the closest part of the framework (a line running through the two closest Cu ions). This confirms that Figure 2 shows the most stable structures (corresponding to  $90^\circ$  in Figure 4) but also that there is a meta-stable binding orientation with the C–C bond rotated perpendicular to this (or parallel to the line running through the two closest Cu ions).

To quantify the difference in the behavior of the two small molecules, the binding energy was compared for the minimized structures for both molecules. The difference between the binding energies was found to be  $1.6 \text{ kJ mol}^{-1}$ . At  $22^\circ \text{C}$  this corresponds to a variation of 1.9 in the Boltzmann factor, in agreement with the observed differences in the adsorption<sup>9</sup> of a factor of about 2.

A full calculation of binding energy using DMol3 was only possible using a portion of the framework and one small molecule involving those atoms shown in Figure 3. These gave a difference in binding energy of  $2.1 \text{ kJ mol}^{-1}$ , which corresponds to a Boltzmann factor of 2.3. This is in good agreement with the calculation using the Discover program. While the absolute binding energies differed from the Discover calculation, partly because only a portion of the framework could be considered using DMol3, the energy difference is similar, suggesting that the trends observed in our force field calculation give useful insights.

Figure 5 shows the effect on the binding energies (calculated via the force field approach) expressed per molecule, as more molecules were added to the unit cell. As more molecules are added, the binding energy per molecule increases as interactions between the small molecules increase, and at higher loadings the difference between the two molecules becomes negligible.

Also shown in Figure 5 are the electrostatic and van der Waals contributions to the binding energy. Though the parameters for the van der Waals and the electrostatic interactions have been obtained from different approaches, and so the absolute values of the binding energies obtained may be inexact, a qualitative comparison between the behaviors of the two small molecules will still be valid. The electrostatic component for  $\text{C}_2\text{H}_4$  is



**Figure 5.** Binding energy per molecule for multiple ethane and ethylene molecules in the large pore of the framework. Total binding energy ( $\square$ ) and van der Waals (vdw) and electrostatic (el) contributions are shown.

greater than that for  $C_2H_6$ , which is to be expected if H-bonding and the electrostatic interaction with Cu plays a more important role in ethylene. The relative contributions of different parts of the system to the overall electrostatic interaction were determined and show that for ethylene the H-bond contribution is about 1.5 times greater than the copper ion interaction, while the latter contribution was relatively insignificant for ethane. Thus, while supporting the earlier speculation<sup>9</sup> of importance of interactions of  $C_2H_4$  with Cu, the results also indicate the importance of the H-bond. Further, Figure 5 also shows that the overall trend of increasing binding energy with loading comes from the van der Waals component.

To compare these results with the sorption data presented by Wang et al.,<sup>9</sup> we note that a single molecule in the unit cell corresponds to a loading of  $0.52 \text{ mol kg}^{-1}$ . Thus, the loading at which the difference between ethane and ethylene disappears is at a load of ten molecules or  $5.2 \text{ mol kg}^{-1}$ , which is similar to the loading observed experimentally when the behavior of ethane and ethylene become similar. This suggests that the use of these metallo-organic frameworks for separation of small molecules will be more practical at low pressures. At higher pressures (i.e., higher loadings) the stronger fluid–fluid interactions for  $C_2H_6$  overcomes the difference in the electrostatic part of the binding energies. Thus, while the force field used in the present calculations may be approximate, it is clear that the difference in binding energies is related to the electrostatic part, leading to specific adsorption at low loading.

We note here that at about the same time as the original submission of this paper a very recent computational study by Yang and Zhong<sup>17</sup> appeared reporting the importance of electrostatic effects in separation of gaseous mixtures of  $CO_2$ ,  $CH_4$ , and  $C_2H_6$  using the same Cu–BTC framework considered here. In this interesting study, the authors show that the electrostatic interactions of carbon dioxide with the framework

led to moderate enhancement in its adsorption and suggest that such effects can enhance separation in MOFs. However, the ethane molecule was considered to have only vdW interactions, with no electrostatic charges in their work, as also for methane. The present study, considering the electrostatic charges on both ethylene and ethane, highlights the difference between the electrostatic interactions more comprehensively, including the H-bonding (cf. Figure 2) as well as the interaction of the ethylene with the Cu ion (cf. Figure 3), which were absent under the modeling assumptions of Yang and Zhong.<sup>17</sup> Thus, we show that even differences in electrostatic interaction between very similar charged molecules can lead to selective adsorption.

In summary, we have shown that electrostatic interactions, including H-bonding with basic surface oxygens, can lead to selective adsorption of light hydrocarbons at low pressure, an effect that may be exploited in separation or other processes.

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**Supporting Information Available:** A description of the representative portions of the framework selected for DFT calculations and the method whereby charges were obtained. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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