Molar Entropy and Enthalpy of CO Adsorbed in Zeolites as Derived from VTIR Data: Role of Intermolecular Modes

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Detailed analysis of recently reported variable-temperature IR (VTIR) spectra of carbon monoxide adsorbed in alkaline zeolites shows how, not only the corresponding values of standard adsorption enthalpy (ΔH^0) and entropy (ΔS^0) can be obtained, but also the thermodynamic values of molar entropy and enthalpy which characterize the adsorbed gas phase. In addition, it is shown that the so obtained molar entropy data can lead to new insights into soft molecular modes, which would be hardly accessible by conventional IR spectroscopic techniques.

1. Introduction

Carbon monoxide is a probe molecule very often used to investigate cationic adsorption sites in zeolites (and metal oxides) by infrared spectroscopy.[1–8] A main reason to choose CO for that purpose comes from the fact that, when used at a small dose, the main gas–solid interaction process taking place is the coordination of CO (through the C atom) to a single cation, thus forming a monocarbonyl ($M^+\cdots CO$) species, which can easily be monitored by the corresponding hypsochromic shift of the C–O stretching mode, from the 2143 cm^{-1} value shown in the free gas phase. Exceptions are:

i) The simultaneous interaction of the probe molecule with two neighboring cationic centers, observed sometimes when dealing with zeolites that have a small Si : Al ratio;[9,10]
ii) The formation of a small proportion of isocarbonyl species, which show the CO molecule interacting through the oxygen atom with the cation ($M^+\cdots OC$);[11]
iii) Possible redox processes that can take place when the adsorbents show exposed transition metal ions (*e.g.*, supported NiO).[12]

Crystallinity of their aluminosilicate framework and regular layout of their internal channels (and cages) endow zeolites with a regular distribution of charge balancing cations, which can form arrays of all equal and non-mutually-interacting adsorption sites, thus facilitating the use of the Langmuir model for studying gas adsorption thermodynamics.[13] For such a purpose, classical infrared spectroscopy (IR) can give valuable structural information, derived from analysis of the wavenumber shifts undergone by vibrational modes of the adsorbed molecule; but determination of the gas-solid interaction energy is out of reach, unless some other complementary technique is also used.[14,15] However, for Langmuir type adsorption, a method has been designed in the recent past, envisaging the recording of IR spectra of an adsorbed species at different temperatures, while simultaneously measuring the temperature and equilibrium pressure. This procedure has been termed VTIR (Variable-Temperature IR) spectroscopy.[16,17] As briefly reported below, application of basic thermodynamics to a set of VTIR data gives access to the fundamental quantities for the (Langmuirian) adsorption process, *i.e.* both ΔH^0 and ΔS^0. Over the years, several cases have been studied, so that some more general considerations are now possible. Herein, an extension of those studies to include determination of the molar enthalpy and entropy of the adsorbed gas is proposed and discussed.

An outline of the VTIR spectroscopic method is reported below.

Referring to CO adsorption on single-cation adsorption sites of alkaline zeolites, let Eq. (1) below represent the adsorption equilibrium:

$$Z{-}M^+_{(s)} + CO_{(g)} \leftrightarrows Z{-}M^+ \cdots CO \quad (1)$$

where $Z{-}M^+$ stands for the adsorption site and $Z{-}M^+\cdots CO$ is the adsorption complex. From here onwards, the Z representing the zeolite framework will be dropped for simplicity.

Throughout the text, the zeolite adsorption site will be considered to remain fixed, and all changes will be attributed to the adsorbed molecule alone. Such an assumption would be erroneous for Li-containing systems, being the corresponding cation mass comparable to that of the atoms constituting the CO molecule; hence Li-containing systems are not considered herein.

If adsorption follows the Langmuir model, the characteristic C–O stretching frequency of adsorbed CO will remain constant along the series of measurements. Moreover, the integrated

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intensity of that IR absorption band should be proportional to surface coverage, θ, according to the Lambert-Beer law, and therefore it gives information on the activity (in the thermodynamic sense) of both the adsorbed species and the empty adsorption sites. Simultaneously, the equilibrium pressure, p, gives the activity of the gas phase. Hence, by measuring IR absorbance and equilibrium pressure at any given temperature, the equilibrium constant, K, of the adsorption process (at that temperature) can be determined.

The variation of K with temperature, T, is related to the standard adsorption enthalpy, ΔH^0, and entropy, ΔS^0, through the well-known van't Hoff equation:

$$K(T) = exp(-\Delta H^0/RT)\ exp(\Delta S^0/R) \tag{2}$$

Combination of Eqn. (2) with the Langmuir Eqn. (3) leads to Eqn. (4) below:

$$\theta = K(T)p/[1 + K(T)p] \tag{3}$$

$$ln\ \{\theta/[(1\ -\ \theta)p]\} = (-\Delta H^0/RT) + (\Delta S^0/R) \tag{4}$$

Assuming that the standard change in specific heat upon adsorption, ΔC_p^0, is negligible over the range of adopted temperatures, both ΔH^0 and ΔS^0 become temperature independent. Such crucial assumption is made throughout this paper: its validity is discussed at the end.

Alternatively, Eqn. (4) can be written as,

$$ln\ \{A/[(A_M\ -\ A)p]\} = (-\Delta H^0/RT) + (\Delta S^0/R) \tag{5}$$

where A is the actual IR absorbance being measured and A_M stands for the maximum absorbance, which corresponds to $\theta = 1$. Note that A_M is usually not know *a priori* and enters the calculation as a parameter to be determined. After measuring (relative) IR absorption as a function of T and p over a temperature range, Eq. (5) provides direct access to the values of ΔH^0 and ΔS^0 that characterize the gas adsorption process.

A detailed discussion about the potential and limitations of the VTIR method can be found elsewhere.[18] Nevertheless, there is a critical point worthy of comment herein. It is well known[19] that the use of the van't Hoff equation to derive ΔH^0 and ΔS^0 can give rise to spurious correlations when the range of temperature covered is small. To avoid this problem, VTIR spectra should be recorded over a sufficiently wide temperature range. That notwithstanding, it is also true that the obtained values of ΔH^0 and ΔS^0 have to be referred to the average temperature, T_m, of the experimental measurements, and to that purpose a too large temperature range would be inconvenient. An abridged description of how the VTIR method can be implemented is reported below.

2. Results and Discussion

To illustrate the method and corresponding results, the case of CO adsorbed on K-FER was chosen, because such a system exhibits three types of adsorption sites that the VTIR method can deal with independently. Preparation of the sample from ammonium ferrierite and sample characterization were described elsewhere.[20] A home-made IR cell,[21] which allowed *in situ* sample activation, gas dosage and IR spectroscopy to be carried out was used.

After recording the background zeolite spectrum at liquid-nitrogen temperature, on a self-supported wafer previously outgassed at 650 K for 3 h, the cell was dosed with CO, closed, and allowed to warm up, while a series of transmission IR spectra were recorded within the 170–230 K range, along with the corresponding sample temperature and CO equilibrium pressure inside the cell. Transmission IR spectra were recorded at 2 cm^{-1} resolution on a Bruker IFS66 spectrometer, accumulating 64 scans for each run. The results are shown in Figure 1. Main IR absorption bands are seen at 2163, 2148 and 2116 cm^{-1}; the much weaker band peaking at 2276 cm^{-1} will be considered later on.

Detailed DFT (Density Functional Theory) calculations, using a periodic model of the zeolite framework,[20] have shown that the 2163 cm^{-1} band comes from the C–O stretching mode of CO molecules interacting through the C atom with a single K^+ ion, while the 2148 cm^{-1} band is due to the C–O stretching mode of CO molecules bridging two nearby K^+ ions, and, thus, forming $K^+\cdots CO\cdots K^+$ adsorption complexes (on dual-cation sites). The much weaker IR absorption band peaking at 2116 cm^{-1} corresponds to a small fraction of CO molecules interacting with a single K^+ adsorption-site through their O atom.[11,21]

After computer resolution and integration of the IR absorption bands peaking at 2163 cm^{-1}, the van't Hoff plot of the left-hand side of Eq. (5) against the reciprocal of the

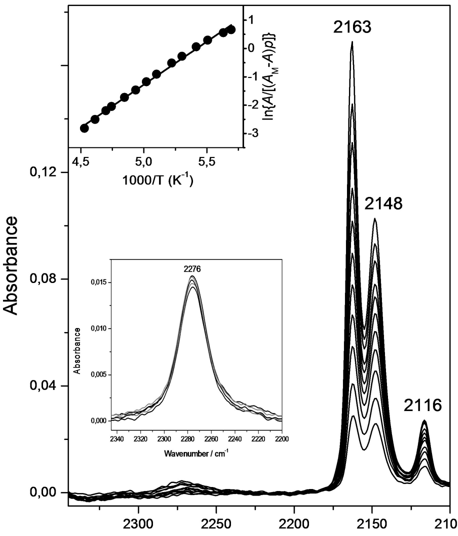


Figure 1. VTIR spectra (zeolite blank subtracted) of CO adsorbed on K-FER (Si:Al = 27.5:1). From top to bottom, temperature goes from 176 to 223 K; and equilibrium pressure from 0.16 to 0.85 mbar. The top inset shows the van't Hoff plot obtained for the adsorption complex giving the IR absorption band at 2163 cm^{-1}. The lower inset shows a magnification of the weak IR absorption band peaking at 2276 cm^{-1}.

Table 1. Some relevant features of CO/zeolite systems, as obtained by means of VTIR spectroscopy: stretching frequency of the adsorbed CO molecule ($\nu_{(CO)}$, cm^{-1}); temperature range (T_{range}, K) and average temperature (T_m, K) of the VTIR measurements; standard adsorption enthalpy ($-\Delta H^0$, kJ mol^{-1}) and entropy ($-\Delta S^0$, J mol^{-1} K^{-1}) change. Calculated values of enthalpy and entropy of the adsorbed phase (h^0_{ads}, kJ mol^{-1}; s^0_{ads}, J mol^{-1}K^{-1}). Calculated values of enthalpy and entropy of the adsorbed phase at the common temperature $T^* = 230$ K ($h_{ads}{}^*$, kJ mol^{-1}; $s_{ads}{}^*$, J mol^{-1}K^{-1}).

Zeolite	Na-ZSM-5	Na-FER	Na-Y	K-ZSM-5	K-FER
$\nu_{(CO)}$ (cm^{-1})	2178	2175	2172	2164	2163
T_{range} (K)	233–278	207–274	155–212	187–242	176–223
T_m (K)	255.5	240.5	183.5	214.5	199.5
$-\Delta H^0$ (kJ mol^{-1})	33.5	30.5	27.0	28.2	25.0
$-\Delta S^0$ (J mol^{-1} K^{-1})	99	95	97	98	83
h^0_{ads} (kJ mol^{-1})	-26.1 ± 0.6	-23.5 ± 1.0	-21.7 ± 0.8	-22.0 ± 0.8	-19.2 ± 0.7
$h_{ads}{}^*$ (kJ mol^{-1})	-27.1	-23.9	-19.9	-21.4	-18.0
s^0_{ads} (J mol^{-1} K^{-1})	94 ± 2.5	96 ± 3.8	86 ± 4.2	90 ± 3.5	103 ± 3.2
$s_{ads}{}^*$ (J mol^{-1} K^{-1})	90	94	95	93	109

temperature depicted in Figure 1 was obtained. From this linear plot, the standard adsorption enthalpy was determined to be $\Delta H^0 = -25$ kJ mol^{-1}, while for the corresponding entropy change the value $\Delta S^0 = -83$ J mol^{-1} K^{-1} was obtained (referred to a standard state at 1 bar).

Table 1 summarizes the above values of ΔH^0 and ΔS^0 for CO adsorption on K-FER (single cation site) as well as the corresponding data reported in the literature[23] for CO adsorption in several other alkaline zeolites. Also reported in Table 1 is the C–O stretching frequency of the adsorbed molecule, the temperature range covered by the experimental measurements, the average temperature T_m, and the standard changes in both enthalpy ($\Delta H^0 = h^0_{ads} - h^0_{gas}$) and entropy ($\Delta S^0 = s^0_{ads} - s^0_{gas}$), obtained using the VTIR method. The reference pressure is 1 bar in all cases. For temperature the reference is T_m, which has a specific value for each case. Other quantities are defined below.

ΔH^0 values span the range from -25.0 kJ mol^{-1} (K-FER) to -33.5 kJ mol^{-1} (Na-ZSM-5). The estimated error limits within which ΔH^0 and ΔS^0 were determined were of about ± 1 kJ mol^{-1} and ± 5 J mol^{-1} K^{-1}, respectively. In general terms, the higher the absolute value of the standard enthalpy change, the higher the corresponding change in entropy. Thus showing a compensation effect between the two terms entering the standard change in Gibbs energy, widely discussed in the literature for many other weakly interacting systems.[24]

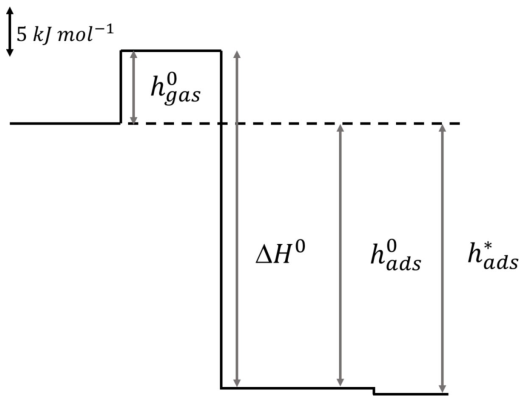
The cases discussed herein are particularly interesting for two reasons. On the one hand, the temperature range of the measurements extends at least over 40 K, and frequently over 60 K: thus, the VTIR method is not biased by a small temperature range, as can happen in other cases. On the other, configurational terms of entropy have already been accounted for when assuming Langmuir-type adsorption; and data reported concern ideal ensembles for both, the gas and the adsorbed phase.

So far, we have dealt with the thermodynamics of the adsorption process, but the same experimental data can be used to describe the adsorbed phase. Thus, the enthalpy of the standard gas phase can be added to ΔH^0 to yield h^0_{ads}, the molar enthalpy of the adsorbed phase. Note that for a condensed phase, such as that formed by localized adsorption, enthalpy and energy necessarily coincide. We will, however, keep the notation in terms of enthalpy. For CO, such gas phase data are not readily available below ambient temperature, but we can have recourse to simple statistical thermodynamics (equipartition principle) according to which for CO (as well as for other diatomic molecules) one has,

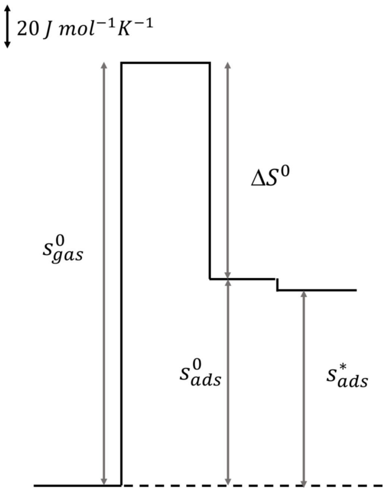
$$h^0_{gas} = h^0_{trans} + h^0_{rot} + pV = \frac{7}{2}RT_m \tag{6}$$

where R is the gas constant ($R = 8.314$ J mol^{-1} K^{-1}) and the C–O stretching mode is considered to be not excited, as done all along this paper.

Values of h^0_{ads} are reported in Table 1, and they result to be negative. Scheme 1 illustrates why. Use of Eqn. (6), which takes into account all active degrees of freedom of the CO gas molecule, means that the reference state for the CO species is one mole of immobile molecules, characterized by zero enthalpy. Bringing the gas to the temperature T_m imparts to the system a moderate increase in enthalpy: adsorption, *i.e.*, the process depicted in Eqn. (1) is exothermic and overcomes the thermal enthalpy, so that the final level is below zero. The opposite will happen with entropy, as illustrated in Scheme 2, and explained below. The values of h^0_{ads} and s^0_{ads} may be considered as being the enthalpy (and entropy) of formation of the M···CO adduct at the temperature T_m.



Scheme 1. Enthalpy (energy) levels for the adsorption of CO. The example concerns Na-ZSM-5.



Scheme 2. Entropy levels for CO adsorption. The example concerns

The uncertainty introduced by the choice of T_m as representative of the standard temperature was evaluated as $\frac{7}{2}R\delta T$, where δT is the difference between $T_{h,}$ the highest temperature of the measurement, and T_m. The uncertainty is reported in the same column of Table 1 as a relative error of h^0_{ads}. It amounts to about 1 %, which is acceptable.

Besides h^0_{ads}, Table 1 shows the corresponding values of the molar entropy of the adsorbed phase, s^0_{ads}, which was calculated as the sum of ΔS^0 and s^0_{gas}, the value of the molar entropy of the gas phase at the same temperature and (standard) pressure. Again, tabulated values of s^0_{gas} are not readily available below ambient temperature, so that recourse was made to simple statistical thermodynamics. The Sackur-Tetrode formula was used for translational degrees of freedom (Eqn. 8 below). Regarding rotational entropy, when dealing with diatomic molecules, difficulties arise only for hydrogen at low temperatures. For other diatomic molecules, excellent approximations exist (Eqn. 9).

In summary:

$$s^0_{gas} = s^0_{rot} + s^0_{trans} \tag{7}$$

where

$$s^0_{trans} = R\left[-1.16 + \left(\frac{5}{2}\right)lnT_m + \left(\frac{3}{2}\right)\ln(m_{CO})\right] \tag{8}$$

and

$$s^0_{rot} = R[lnT_m + 1 - \ln\Theta_r] \tag{9}$$

Where the rotational temperature Θ_r for CO is only 2.77 K. In practice:

$$s^0_{gas} = R\ [3.85 + 3.5\ \ln\ T_m] \tag{10}$$

Note that Eqn. (10) gives the correct tabulated value at the standard temperature of 298 K.[25]

Scheme 2 illustrates the case of entropy in the same way as done above for enthalpy. The increase in thermal entropy is substantial, and not compensated by the change in entropy due to adsorption, so that values of s^0_{ads} correctly result to be positive, because residual degrees of freedom are present in the adsorbed molecule. s^0_{ads} can be considered as being the entropy of formation at the adsorbed phase, according to Eqn. (1), having as standard states one mole of sites and motionless molecules at temperature T_m. The uncertainty on s^0_{ads} was evaluated, similarly to what done above for h^0_{ads}, amounting to $\frac{7}{2}Rln(T_h/T_m)$. The resulting values are reported in Table 1 and are seen to be smaller than 5 % of the corresponding s^0_{ads} value.

The set of data concerning h^0_{ads} and s^0_{ads}, reported in Table 1, refers to different temperatures (T_m). It has to be noted that, at a difference with ΔH^0 and ΔS^0, which were assumed to be temperature independent, the enthalpy and entropy content of both the gas and the adsorbed phase do depend on temperature. In other words, whereas ΔC^0_p can be assumed to be negligible, the two terms making it up are not. Bringing the values of h^0_{ads} and s^0_{ads} to a common temperature requires knowledge of the specific heat of the adsorbed phase. This problem is further examined below. For the moment, we shall comment data shown in Table 1 keeping such an observation in mind.

The entropy of the adsorbed phase is related to the vibrational modes of the adsorbed species. The number of normal modes of adsorbed CO is established by observing that the cationic center M^+ can be considered as motionless, on account of its large mass (as compared to those of C and O) and its anchorage to the zeolite framework structure. It can thus act as the reference for a system of coordinates. The location of both C and O atoms require three coordinates each. This gives rise to a total of six modes: two of them are stretching modes (basically C–O and M–C), two frustrated translations (FT) and two frustrated rotations (FR), or librations. We shall refer to this ensemble of modes (excepting the C–O stretch) as "intermolecular" or "soft" modes.

For other diatomic molecules, the reasoning is the same. An illustration of the normal modes for molecular hydrogen on $M{-}B_{12}C_6N_6$ (M = Li, Na, Mg, Ca, and Sc) was given by Wang and Chen.[26]

The C–O stretching mode does not contribute to entropy in the temperature range explored, being too high in frequency. The other modes lye at a range of low frequencies not attained by usual IR instruments, and reached with difficulty even with sophisticated techniques such as synchrotron radiation or neutron diffraction. A possibility, explored below, is the detection of combination bands involving the fundamental C–O stretch and soft modes.

The role of the M–C stretch will now be considered. Were it described by a harmonic potential, the corresponding molar entropy would be given by Eqn. (11), for frequency ν at the temperature T:

$$F(\nu, T) = s_\nu = R\ [\frac{x}{e^x - 1} - \ln(1 - e^{-x})] \tag{11}$$

where x stands for $h\nu/kT$. For clarity, Figure 2 reports a plot of such a function.

In freely vibrating diatomic molecules, the potential is more faithfully described by a Morse potential, or even by combinations of Morse functions. For a molecule adsorbed on a "flat" surface like that, *e.g.*, of MgO (100), a Morse oscillator is probably more apt to describe the motion perpendicular to the surface itself, the depth of the potential well corresponding basically to the adsorption enthalpy. This was shown long ago in the theoretical study of the adsorption of one single atom of He on the regular surfaces of solid Kr.[27]

In zeolites, however, due to the pore walls, a confinement effect[28] is operative and may be substantial. Accordingly, the potential well is steep on both sides, and hence necessarily sort of symmetric. Nachtigallova et al.[29] have indeed shown recently that the electric field at the adsorption site, inside a zeolite cavity, can be factorized into an "effect from the bottom" and an "effect from the top".

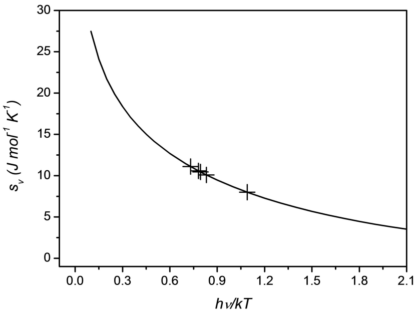


Figure 2. Plot of s_v as a function of the ratio ν/T. The symbols correspond to the cases reported in Table 2.

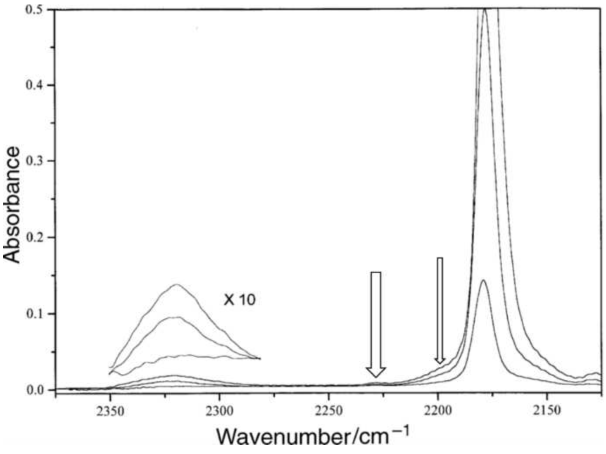


Figure 3. IR spectra of CO adsorbed on Na-ZSM-5. Arrows show combination bands between ν(C–O) and FR modes.

The cation-CO stretching mode of CO adsorbed on several alkaline zeolites has been measured by Areán *et al.*[30] (who studied a whole series going from Na^+ to Cs^+) as being the difference between the observed combination mode $\nu(C-O)+\nu(M-C)$ and the stretching $\nu(C-O)$ mode itself. The frequency of the cation-carbon (M–C) mode resulted to be basically the same for any given cation, irrespective of the zeolite being considered.

Two examples of the combination bands observed are reported in Figure 1 and in Figure 3. The latter reports IR spectra of CO adsorbed at 77 K on Na-ZSM-5, showing a weak and broad band centered at 2319 cm^{-1}. This band was ascribed to a combination mode $[\nu_{(C\text{-}O)}+\nu_{(Na\text{-}C)}]$,[30] which leads to the value of 141 cm^{-1} for the cation-carbon stretching mode, $\nu_{(Na\text{-}C)}$. The combination band is slightly asymmetric, showing an ill-defined shoulder at higher frequencies. The corresponding region of the IR spectra of CO adsorbed on K-FER (Figure 1) shows that, in this case, the combination band $[\nu_{(C\text{-}O)}+\nu_{(K\text{-}C)}]$ is nearly symmetric, and no distinctive components can be discerned.

Data for the five available Na- and K-containing zeolites are reported in Table 2. The cation-carbon vibrational frequencies for the three Na-containing zeolites are very close to each other, as are the two pertaining to K-containing zeolites, in agreement with the general observation that this frequency strictly depends on the cation. Table 2 also reports for clarity the data for the enthalpy of the adsorbed phase, already shown in Table 1. It is seen that, in contrast with the strict constancy of ν(M–C) within each family, the value of h^0_{ads} varies appreciably. This observation rules out any possibility of describing the M–C motion by a Morse function, in agreement with the fact that a Morse behavior would require the M–C distance to increase freely, which is not possible in a confined system.

The absence of components in the spectra in Figure 3 and their symmetry suggest a nearly harmonic nature of the M–C motion. The contribution to entropy of the M–C stretch has thus been evaluated by means of Eqn. (11). The values of the parameter $x = h\nu/kT_m$ corresponding to the five cases available are shown in Figure 2. It results that the contribution of the M-C

Table 2. Some relevant features of the CO/zeolite systems for which the cation-CO stretching mode has been measured by Arean *et al.*[30] calculated values of enthalpy and entropy of the adsorbed phase (h^0_{ads}, kJ mol^{-1}; s^0_{ads}, J mol^{-1}K^{-1}), frequency of the cation-CO stretching mode ($\nu(M-C)$, cm^{-1}); average temperature (T_m, K) of the VTIR measurements; entropy of the intermolecular mode ($s^0(M-C)$, J mol^{-1}K^{-1}), average entropy value of the soft modes (s'_{av}, J mol^{-1}K^{-1}), average frequency of the of the soft modes (ν_{av}, cm^{-1}).

Zeolite	Na-ZSM-5	Na-FER	Na-Y	K-ZSM-5	K-FER
h^0_{ads} (kJ mol^{-1})	−26.1	−23.5	−21.7	−22.0	−19.2
ν (M–C) (cm^{-1})	141	139	139	109	108
T_m (K)	255.5	240.5	183.5	214.5	199.5
s^0_{ads} (J mol^{-1} K^{-1})	94	96	86	90	103
s^0 $(M-C)$ (J mol^{-1} K^{-1})	10	10	8	10	11
s'_{av} (J mol^{-1} K^{-1})	21	21.5	19.5	20	23
ν_{av} (cm^{-1})	44	42	32	37	36

stretching mode $s^0(M-C)$ to the overall entropy of the adsorbed phase is about 10%, *i.e.* the major part of s^0_{ads} is due to frustrated translational and rotational modes.

In principle, should the energy levels of all modes of adsorbed CO be available, both the ground state and the excited states, one could compare directly calculated and measured values of entropy. In the absence of such an ideal situation, one is compelled to assume harmonicity of all motions. For instance, in the paper by Wang and Chen,[26] the same Eqn. (6) is applied to all modes without any evidence of their harmonic nature.

The term $s^0(M-C)$ has been subtracted from s^0_{ads}, so to be left with the contribution to entropy of the two FT and two FR modes. Further, the gross assumption has been made that all remaining soft modes contribute equally to entropy, in order to estimate an average value $s^{'}_{av}$:

$$s^{'}_{av} = (s^0_{ads} - F[\nu(M-C)])/4 \tag{12}$$

Corresponding values are reported in Table 2.

Eqn. (12) has been used to determine what values of x correspond to the listed value of $s^{'}_{av}$, although, again, the harmonic nature of related motions is not granted. From this, a value for the average frequency of soft modes ν_{av} was calculated (Table 2). The obtained values are in the range 30–50 cm^{-1}, which appears to be quite reasonable. Leaving aside for the moment the case of Na–Y, the values of ν_{av} for Na are higher than the values for K, which again is to be expected. This has prompted us to re-examine the spectra of the five systems in Table 2 at frequencies some 40 cm^{-1} above the C–O stretching mode of adsorbed CO. Such work of examining the regions between $\nu(C-O)$ and the combination band [$\nu_{(C\text{-}O)}$ + FT] (or [$\nu_{(C\text{-}O)}$ + FT]) is very delicate and ill fated, for the following reasons.

First, any combination band is intrinsically weak, being related to non-quadratic terms in the overall vibrational potential. Second, soft FT or FR modes themselves are likely to be anharmonic, so that transitions $n \diamond n+1$ with different initial quantum number may fall at different frequencies, with possible smearing out of the signal. Lastly, for FT or FR modes the change in CO dipole moment is probably small, *i.e.* the transition is again intrinsically weak. Nonetheless, out of five, in one case (Na-ZSM-5), a feature not described in the literature was noted, *i.e.* a very weak band at 2228 cm^{-1}. Figure 3 illustrates this finding. The rotational contour of CO gas present in the cell causes the wiggles seen below the 2178 cm^{-1} band at relatively high pressures, of no real interest. The band falling 50 cm^{-1} above the C–O stretch is readily related to a combination band between $\nu(C-O)$ and the frequency of a frustrated mode. Let us assume, rather arbitrarily, this to be a frustrated rotation, FR.

Let us note that, because of the symmetry of the zeolite site one can assume that the two (in principle different) FR (or FT) modes have the same frequency. We can use again the approach expressed by Eqn. (12), *i.e.* subtract from $s^{'}_{ads}$ the contributions of two FR modes, assumed to be equal and falling both at 50 cm^{-1}, and divide by two, assuming again that the two FT modes have the same frequency. The result is the entropy related to a single FT mode:

$$s^{'}_{FT} = [s^{'}_{ads} - 2\,F[\nu(FR)]]/2 \tag{13}$$

The entropy at 255.5 K for a harmonic motion with frequency 50 cm^{-1} is 18 J K^{-1}mol^{-1}. This implies that the entropy for one FT mode is 24 J K^{-1}mol^{-1}; which corresponds to a frequency, at the same temperature, of 26 cm^{-1}.

Indeed, a band is seen at a frequency $2204 = 2178 + 26$ cm^{-1} as a shoulder to the main band. Because of the closeness to the intense mode at 2178 cm^{-1} this band has not been identified since the very beginning as a "soft" mode: the indication is, however, rather clear. As a whole, the (vibrational) entropy of CO adsorbed on Na-ZSM-5 is evaluated to be due: 0% to C–O stretch; 10% to M–C stretch; 40% to FR (presumed) and 50% to FT (presumed) modes.

The availability of (approximate) values for the frequencies of soft modes enables one to estimate the specific heat c_{vib} of the adsorbed molecules. Always within the harmonic approach, each active mode contributes to c_{vib} according to Eqn. (14):

$$\frac{c_{vib}}{R} = \exp(-x)^{*}[x/(1-\exp(-x))]^2 \tag{14}$$

FT and FR modes appear to be fully excited, thus contributing to c_{vib}practically with one R unit each. The M–C stretch contributes with some 0.7 R unit. In summary, it results $c_{vib} \approx 4.7\,R$. Being the specific heat of the gas 7/2 R, the difference is about one R unit. Note that, surprisingly, c_{vib} for the adsorbed phase is larger than for the free gas phase.

This estimated value of Δc_p allows us to ascertain the validity of the assumption, fundamental to the whole treatment, of the constancy of both ΔH^0 and ΔS^0. In the range of temperatures reported in Table 1, the Δc_p value being $\approx +1.0\,R$, and the temperature range being typically *ca.* 60 K, ΔH^0 varies by *ca.* 0.5 kJ mol^{-1} and ΔS^0 by *ca.* 1.5 J mol^{-1}K^{-1}. This conclusion is in excellent agreement with the assumption made.

Going back to Table 1, it is now possible to bring all the data to a common temperature, T^*. This has been assumed, somewhat arbitrarily, as 230 K, which is nearly the average of the five values for T_m in Table 1. Corrections to be applied are simply given by:

$$h^0_{ads}(T^*) = h^0_{ads}(T_m) + c_v\,(T^* - T_m) \tag{15}$$

and

$$s^0_{ads}(T^*) = s^0_{ads}\,(T_m) + c_v\,\ln\,(T^*/T_m) \tag{16}$$

Results are reported in Table 1 as $h_{ads}{}^*$ and $s_{ads}{}^*$. Scheme 1 and 2 illustrate the decrease in both enthalpy and entropy observed when T_m is $< T^*$.

It has been reported in the literature[31] that for adsorption on metal oxides ΔH^0 correlates with the stretching frequency of adsorbed CO. Figure 4 shows a similar correlation between $h_{ads}{}^*$ and ν_{CO} for the cases studied herein.

The molar enthalpy is seen to be linearly correlated to the C–O frequency, the intercept at vanishing interaction energy corresponding correctly to the value of the free molecule in the gas phase (2143 cm^{-1}). The consequence is that one can write a simple proportionality between $h_{ads}{}^*$ and the frequency shift:

$$h_{ads}{}^* \approx a\,[\nu(\mathrm{C}-\mathrm{O}) - 2143] \tag{17}$$

being $a = 0.71 \pm 0.10$ kJ cm mol^{-1}.

The existence of such a simple relationship is due to the non-sophisticated nature of the cation-CO interaction, which is basically electrostatic, and to the moderate range of interaction enthalpies being considered. For stronger interactions, deviations from linearity may occur, as suggested from available ΔH^0 versus ν correlations.[31]

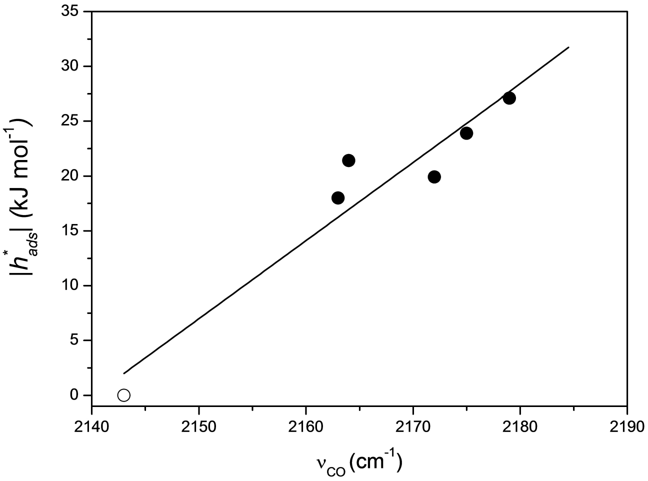


Figure 4. Correlation between the enthalpy of the adsorbed phase (absolute value of $h_{ads}{}^*$) at T = 230 K and the C–O stretching frequency for the set of zeolites listed in Table 1. Full symbols refer to cation exchanged zeolites; the empty symbol to the free CO molecule.

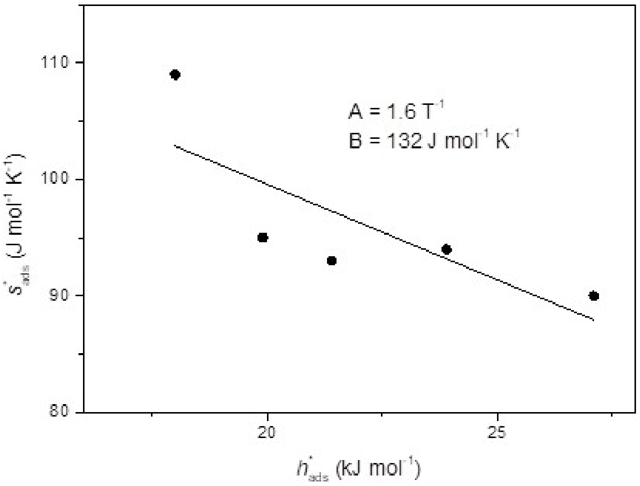


Figure 5. Correlation between entropy and enthalpy of the adsorbed phase ($s_{ads}{}^*$ vs. – $h_{ads}{}^*$) for the studied set of CO/zeolite systems.

Figure 5 explores the correlation between $h_{ads}{}^*$ and $s_{ads}{}^*$. Whereas several plots illustrating the compensation effect of the enthalpic and entropic term *in the adsorption process* are available, the correlation in Figure 5, though straightforward, is apparently new and worth of consideration.

Indeed, $H - S$ compensation effects in both equilibrium and kinetic processes have been observed and discussed since decades and have been found to have, sometimes, a non-linear behavior: as a whole, non-linearity in not unexpected, although the reasons are still unclear and explanations are controversial.[32] However, as far as results reported in Figure 5 are concerned, it is quite evident that the more tightly bound the molecule, the less free to move. The entropy of the adsorbed ideal phase, due to the low frequency vibrational modes, arising from the loss of translational and rotational modes of the gas-phase molecule, depends as a whole on the enthalpy of formation of the adduct. A linear equation of the type:

$$s^*_{ads} = A\,h^*_{ads} + B \tag{18}$$

is found to describe reasonably well the plot in Figure 5, where A results to be 1.6 ± 0.1 T^{-1} and B = 132 J mol^{-1} K^{-1}, in the limited range of cases explored. For stronger interaction energies, the entropy of the adsorbed phase is expected to decrease, because the molecule becomes more strongly bonded to the adsorption site.

3. Conclusions

Detailed analysis of available VTIR data for CO adsorption in zeolites allows one to gain access to the thermodynamic quantities characterizing the adsorbed phase, $h^{\,0}_{ads}$ and $s^{\,0}_{ads}$, respectively. The correctness of the values so obtained is suggested, on the one hand, by the proportionality between $h^{\,0}_{ads}$ and the frequency shift of the C–O stretching mode, and, on the other, by detailed analysis of $s^{\,0}_{ads}$.

Simple statistical thermodynamics, based on the knowledge of three combination modes, observed in the IR spectra of Na-ZSM-5, two of them relatively easy to discern (the $\nu(C-O) + \nu(M-C)$ and presumably the $\nu(C-O) + \nu(FR)$), and a third one buried at the foot of the intense $\nu(C-O)$ mode, shows that the value obtained for the entropy of the adsorbed phase is entirely compatible with those three modes. The use made of the harmonic oscillator model, and related equations, for $\nu(M-C)$ is justified by the presence of a confinement effect, which rules out any possible similarity with the Morse oscillator; and it is not unlikely that the harmonic approximation works also for the other soft modes.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: thermodynamic values · adsorption enthalpy · zeolites · IR spectroscopy · soft molecular modes.

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