# Thermodynamic study of $C_2H_2$ thin films adsorbed on graphite (0001)

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Thermodynamic properties of  $C_2H_2$  thin films adsorbed on (0001) surfaces of an exfoliated graphite substrate have been investigated by means of volumetric adsorption isotherms technique. A complete isotherm of  $C_2H_2$  adsorbed on graphite shows five steps with different height. Such steps represent a transition from a (2D) dilute phase to a (2D) dense one. For each step, a set of adsorption isotherms is measured. Clapeyron equations P:f(1/T) are then determined and thermodynamic quantities are calculated and compared to the literature available ones. The second step is divided into two sharp steps at a given range of temperature which means that the condensed matter undergoes two phase transitions. The nature of such phases is discussed in light of thermodynamic quantities. The molecules orientation in the suggested structures seems to be governed by quadrupole-quadrupole interaction. Recent neutron diffraction measurements support thermodynamic conclusions.

Keywords: Volumetric adsorption isotherms, Bi-dimensional phase, Commensurate structure

## **1** Introduction

Experimental studies of two-dimensional phases adsorbed on uniform substrates have begun with Tomy and Duval<sup>1</sup>. Since then, a multitude of substrates have been used such as graphite<sup>2</sup>, Lamellar halides<sup>3</sup>, MgO (Ref.4), ZnO (Ref. 5) and zeolites (Ref. 6). Original properties have been pointed and generally, dependent on the adsorbate-substrate system.

The adsorption of acetylene on different substrates<sup>7-12</sup>, have been studied. The  $C_2H_2$  is a simple molecule of quasi-linear geometry, with its large quadrupolar moment Q=7.2 DÅ<sup>-1</sup> and it is a suitable molecule to probe electrostatic interaction when adsorbed on ionic surfaces<sup>7,11,12</sup>. Quadrupole-quadrupole interaction is also an important contribution to the adsorption energy. It would play a decisive role to establish the structure of bi-dimensional (2D) condensed phases.

The interesting environmental and interstellar problems using plane soot and polycyclic hydrocarbon as substrates, have been studied. Graphite can be considered as a model of speck of carbonic dust in interstellar environment<sup>13</sup>. At least three groups have been interested to the adsorption of  $C_2H_2$  on graphite<sup>8,9,14</sup>. The published results are important but incomplete since they deal with a

peculiar point of the subject. An elaborate lecture of the various papers reveals contradictions. The obvious one is that related to the (2D) critical temperature since two groups<sup>8,9</sup> have published values which differ by more than 30 K. This point has been resolved in a previous letter<sup>15</sup>.

In the present paper, labelled I, a detailed experimental thermodynamic study of  $C_2H_2$  adsorbed on exfoliated graphite (0001) surfaces, has been presented. Thermodynamic values, derived from volumetric adsorption isotherms, are compared to available literature ones. Critical discussion is conducted.

In paper II, the structural results have been presented. In fact, neutron diffraction spectra have been recorded for coverage  $0.7 \le \theta \le 1.23$  layers. At least, two (2D) solids S<sub>1</sub> and S<sub>2</sub> have been determined. An intermediate solid S<sub>12</sub>, is identified as a mixture of S<sub>1</sub> and S<sub>2</sub>. At a constant temperature, as coverage increases, the (2D) solid undergoes a series of (2D) structures which is found to be in good agreement with thermodynamic results. Taking partial disorder transition in bulk solid phases,  $T_{\alpha\beta} \approx 132$  K, the vapour pressure has been measured and the corresponding Clapeyron lines have been used in the present work to calculate the thermodynamic quantities.

## **2** Experimental Details

A conventional volumetric apparatus has been used to measure the adsorption isotherms and described many times before<sup>15</sup>. The temperature of the adsorption cell is measured by using Xe vapour pressure thermometer The substrate is a sample of 44 mg of exfoliated graphite having a specific surface area<sup>16</sup> of  $35m^2g^{-1}$ . The C<sub>2</sub>H<sub>2</sub> gas, purchased from l'Air Liquide, has a nominal purity of 99.6%, the only notable impurity being nitrogen. It is trapped in a cold finger at liquid nitrogen temperature, the gas contained in a bulk of 1ℓ and pumped out of it the volatile impurities. This operation is repeated until the pressure over the trapped gas becomes negligible.

## **3 Results and Discussion**

Thermodynamic properties of acetylene thin films adsorbed on exfoliated graphite (0001) surface have been investigated by volumetric adsorption isotherms. A complete isotherm measured at T=130 K shows at least five vertical steps with different height (Fig. 1). Each step corresponds to first order phase transition between two bi-dimensional (2D) adsorbed phases.



Fig. 1 — A complete adsorption isotherm of C<sub>2</sub>H<sub>2</sub> on exfoliated graphite (0001) surfaces at *T*=130.05 K

The first transition from a (2D) dilute phase to a (2D) dense one is not represented on the isotherm since it occurs at lower pressure which is not accessible at the temperature of the isotherm and has been studied<sup>9</sup> at higher temperature T>130 K. The two first transitions are associated to the first layer condensation of C<sub>2</sub>H<sub>2</sub> on graphite whereas the transitions labelled 3 to 5 correspond to the C<sub>2</sub>H<sub>2</sub> second layer formation. Such interpretation is based on adsorbed quantity which is about 0.39 cm<sup>3</sup> STP per monolayer.

### 3.1 First Layer

The first two transitions are attributed to the first layer condensation. Figure 2 shows a set of adsorption isotherms of  $C_2H_2$  corresponding to the first transition. For the second transition, the measured isotherms are shown in Fig. 3. At temperatures



Fig. 2 — Adsorption isotherms of  $C_2H_2$  on exfoliated graphite surfaces (first phase transition) a: 147.72 K, b: 153.26 K, c: 156.27 K, d: 159.06 K and e: 161.50 K



Fig. 3 — Adsorption isotherms of  $C_2H_2$  on exfoliated graphite surfaces (at T  $\geq$ 132.00K two phase transitions are observed) a: 129.51 K, b: 132.25 K, c: 133.18 K, d: 134.39 K, e: 135.37 K, f: 136.43 K and g: 137.33 K

T>  $T_{\alpha\beta} \approx 132$  K, the transition temperature of the order-partially disorder bulk solid phase, the second transition is divided in two sharp transitions suggesting two successive phase transitions. Such transitions can be interpreted as a commensurateincommensurate phase transition or as a fusion of the bi-dimensional solid (solid-liquid). When the adsorbed phase presents commensurability with the substrate surface only along one direction, semicommensurate phase, it can undergo a series of phase transitions as the coverage increases. The final interpretation will be given in light of neutron diffraction spectra measured, respectively at corresponding coverage but preliminary conclusions can be deduced from thermodynamic quantities extracted from adsorption isotherms and presented in Table 1. The coefficients  $A_n$  and  $B_n$  of the Clapeyron lines equations,  $\log P_n(\operatorname{torr}) = \{-[A_n/T(K)] + B_n\}$  where n is the adsorbed layer order, are also given in Table 1.

Enthalpy excess, entropy excess, free energy excess and isosteric heat of adsorption, summarized in Table 1, are calculated by application of Larher formalism<sup>16</sup>. The constants  $A_{\infty}$  and  $B_{\infty}$  of the vapour pressure variation as a function of temperature are determined in two domains of temperature, respectively  $T \le T_{\alpha\beta}$  and  $T \ge T_{\alpha\beta}$ . The corresponding Clapeyron equations are:

$$\log P_{\infty}(\text{torr}) = -\frac{1239.84}{T(K)} + 9.592 \quad \text{for } T \le T_{\alpha\beta} \quad \dots(1)$$

$$\log P_{\infty}(\text{torr}) = -\frac{1174.30}{T(K)} + 9.103 \quad \text{for } T_{\alpha\beta} < T < T_{t}(3\text{D})$$
...(2)

where  $T_t(3D)$  is the fusion temperature of the bulk solid phase.

Eq. (1) or (2) was used depending on the temperature of the measured isotherms.

Table 1 reveals important results:

- Firstly, the thermodynamic values of the first transition and the second transition at  $T \leq T_{\alpha\beta}$  (labeled 2) compare well with the literature ones<sup>9</sup>. And the difference in  $\Delta S_{(1)}$  can be explained by the fact that the first transition is not measured in the same range of temperature as in Ref. 9.
- Secondly, at lower temperature  $T \leq T_{\alpha\beta}$ , the (2D) phase condensed at the top of the second transition is stable due to its entropic term  $-T.\Delta S(2)$  since  $\Delta H(2)$  is positive. When the temperature exceeded  $T_{\alpha\beta}$  the condensed phase undergoes two different structures. For both structures, the measured excess of entropy  $\Delta S_{21}$  and  $\Delta S_{22}$  are negative excluding then positional and/or orientational disorder of the adsorbed molecules. Furthermore, the structures of the adsorbed phases are commensurate/semicommensurate with the (0001) surface of the exfoliated graphite. This conclusion is supported by neutron diffraction measurements where it has been shown that the two (2D) solid phases are commensurate with the (0001) surface of graphite substrate.
- One can suppose that the two steps observed at  $T \ge T_{\alpha\beta}$  may appear at  $T \le T_{\alpha\beta}$  but their pressure formation cannot be resolved with our gauge. By extrapolation of the corresponding Clapeyron equations, we can calculate their values at T=129 K,  $P_{21} \approx 6.8 \ 10^{-2}$  torr and  $P_{22} \approx 7.7. \ 10^{-2}$  torr, which differ by less than 1%. So at lower temperature, the two steps align indicating then only one phase transition.

Table 1 presents the isosteric heat of adsorption  $Q_{st}(n)$  which is the sum of two terms: the first one  $Q_{\perp}$  is the energy of perpendicular interaction between adsorbed molecules and the surface of the graphite and the second one  $Q_{\parallel}$  is the energy of the lateral interaction between adsorbed molecules. If we do the crude assumption that  $Q_{\perp}$  is not drastically changed

Table 1 — Enthalpy excess, entropy excess, free energy excess and isosteric heat of adsorption, calculated by application of Larher formalism<sup>16</sup>, are summarized

| T range                  | Transition<br>order | A(n)     | B(n)   | < T(K) > | $\Delta H$ (cal/mol) | $\Delta S$ (cal/mol/K) | $\Delta F$ (cal/mol) | Qst<br>(kcal/mol) |
|--------------------------|---------------------|----------|--------|----------|----------------------|------------------------|----------------------|-------------------|
| $T \ge T_{\alpha\beta}$  | 1                   | 1271.44  | 8.048  | 150.00   | -444.41              | 4.827                  | -1168.40             | 5.816             |
|                          | 1 <sup>9</sup>      |          |        | 127.00   | -785.00              | 2.1                    | -1051.70             | 6.40              |
| $T \leq T_{\alpha\beta}$ | 2                   | 1189.432 | 8.200  | 130.39   | 230.65               | 6.370                  | -560                 | 5.441             |
|                          | $2^{9}$             | 1193.87  | 8.229  | 120      | 146                  | 5.7                    | -538                 | 5.461             |
| $T \ge T_{\alpha\beta}$  | $2_1$               | 1678.851 | 11.846 | 139.46   | -2309.67             | -12.55                 | -559.44              | 7.608             |
|                          | $2_{2}$             | 1756.947 | 12.510 | 137.41   | -2666.01             | -15.59                 | -523.79              | 8.038             |

| Table 2 — Thermodynamic values corresponding to the first adsorbed phase of acetylene on different substrates are summarized. |                                     |                      |                        |                      |             |  |  |
|---|-------------------------------------|----------------------|------------------------|----------------------|-------------|--|--|
| Substrat  | <i><t< i="">(K)<i>&gt;</i></t<></i> | $\Delta H$ (cal/mol) | $\Delta S$ (cal/mol/K) | $\Delta F$ (cal/mol) | Reference   |  |  |
| Graphite  | 145-155                             | -445                 | 4.8                    | -1168.5              | Our results |  |  |
| NiCl <sub>2</sub>   | 149-158                             | 720                  | 6.9                    | -339.1               | 13          |  |  |
| FeCl <sub>2</sub>   | 146-160                             | 903                  | 7.4                    | -229.2               | 13          |  |  |
| CdCl <sub>2</sub>   | 150 - 159                           | 958                  | 7.6                    | -216.2               | 13          |  |  |
| $MnI_2$   | 155 – 163                           | 902                  | 7.8                    | -338.2               | 13          |  |  |
| $CdI_2$   | 147 – 155                           | -120                 | 1.6                    | -261.6               | 13          |  |  |
| CaI <sub>2</sub>  | 152 – 159                           | 512                  | 4.7                    | -218.8               | 13          |  |  |

within the monolayer coverage, the increase in  $Q_{st}(n)$ ;  $Q_{21}=7.608$  kcal/mol and  $Q_{22}=8.038$  kcal/mol; can be attributed to the lateral interaction  $Q_{\parallel}$ .

In this two phases, the position and orientation of the adsorbed molecules optimize the lateral interaction increasing then  $Q_{\parallel}$ . Especially, the quadripole-quadripole electrostatic interaction orients molecules in *T* configuration.Thermodynamic values corresponding to the first adsorbed phase of acetylene on different substrates are summarized in Table 2. The lower value of  $\Delta F$ =- 1168.5cal/mol indicates that the condensed phase presents the best stability when adsorbed on graphite.

The excess of enthalpy  $\Delta H$  has a negative value when calculated on graphite and CdI<sub>2</sub>. This can be partially explained by the parameters of the lattice of the adsorption sites which are very close at the surface of the two substrates, 4.26Å for graphite and 4.24Å for CdI<sub>2</sub>. So we can qualitatively suggest the same structure for the (2D) phase condensed respectively on graphite and CdI<sub>2</sub>. For the rest of substrates, this quantity is positive, so the first condensed phase is stable do to its entropic factor  $-T\Delta S$ .

### 3.2 Second Layer

The three transitions corresponding to the second layer formation are shown in Fig. 4.

The shown isotherms are measured in desorption mode and caution has been taken to reach equilibrium pressure. The hysteresis phenomenon has been observed in the second layer domain formation. Such phenomenon has been mentioned by Menaucourt *et al*<sup>9</sup> what they interpret as a substrate distortion especially at the contact lines of the (0001) graphite planes which are not completely disconnected. Independently, we think that such effect can be correlated with the molecules reorganization in the first layer when supplementary matter is added to form the second layer.



Fig. 4 — Adsorption isotherms of  $C_2H_2$  on exfoliated graphite surfaces (we can clearly show the 3<sup>rd</sup>, 4<sup>th</sup> and 5<sup>th</sup> transitions) a: 128.20 K, b: 130.05 K, c: 132.50 K, d: 134.77 K, e: 137.13 K, f: 140.00 K and g: 141.78 K

Peters *et al*<sup>8</sup>. reported three isotherms corresponding to the 2<sup>nd</sup> layer condensation. The steps expressing the 3<sup>rd</sup>, 4<sup>th</sup> and 5<sup>th</sup> transitions are not well defined. So the thermodynamic values we deduce from their isotherms present large incertitude than those deduced from our measured isotherms. While the isotherms reported by Menaucourt are measured in the same range of temperature as those of Peters, the thermodynamic quantities corresponding to the 3<sup>rd</sup> and 4<sup>th</sup> transitions and deduced from Menaucourt data disagree with those of Peters, but are in good agreement with our values.

Thermodynamic quantities calculated using Eqs (1) and (2) of the vapour pressure as a function of temperature are summarized in Table 3. The values determined from the isotherms<sup>8</sup> and those calculated from the Clapeyron equations<sup>9</sup> are also reported to make comparison easier. At  $T \leq T_{\alpha\beta}$ , it is concluded that our values are found to be in agreement with those of Menaucourt<sup>9</sup>. Whereas at  $T \geq T_{\alpha\beta}$ , our calculated thermodynamic quantities corresponding to the 4<sup>th</sup> and 5<sup>th</sup> transitions are in agreement with those

Table 3 — For the three transitions observed during the second layer condensation, thermodynamic quantities calculated using equations (1) and (2) of the vapor pressure as a function of temperature are summarized. The values determined from the isotherms given by Peters<sup>8</sup> and those calculated from the Clapeyron equations given by Menaucourt<sup>9</sup> are also reported to make comparison easier

| Т                        | Transition<br>order | A(n)     | B(n)   | < <i>T</i> (K)> | $\Delta H$ (cal/mol) | $\Delta S$ (cal/mol/K) | $\Delta F$ (cal/mol) | <i>Q</i> st<br>(kcal/mol) |
|--------------------------|---------------------|----------|--------|-----------------|----------------------|------------------------|----------------------|---------------------------|
|                          | 3                   | 1246.694 | 9.528  | 152.72          | -331.20              | -1.944                 | -34.31               | 5.703                     |
|                          | 4                   | 1244.379 | 9.535  | 139.22          | -320.61              | -1.76                  | -45.06               | 5.693                     |
| $T \ge T_{\alpha\beta}$  | 5                   | 1223.803 | 9.437  | 137.00          | -226.47              | -1.528                 | -17.12               | 5.558                     |
|                          | $4^{8}$             | 1326.644 | 10.168 | 110.51          | -397.12              | -2.635                 | -105.89              | 6.069                     |
|                          | 5 <sup>8</sup>      | 1264.258 | 9.715  | 110.51          | -111.71              | -0.562                 | -49.52               | 5.784                     |
|                          | 3                   | 1235.664 | 9.455  | 130.25          | 19.10                | 0.626                  | -62.53               | 5.653                     |
| $T \leq T_{\alpha\beta}$ | 4                   | 1221.04  | 9.368  | 130.25          | 85.98                | 1.025                  | -47.50               | 5.586                     |
|                          | 3 <sup>9</sup>      | 1230.79  | 9.38   | 111             | 41.40                | 0.97                   | -66                  | 5.630                     |
|                          | 4 <sup>9</sup>      | 1204.73  | 9.207  | 111             | 35.11                | 1.76                   | -160.40              | 5.511                     |

of Peters<sup>8</sup>. This latest agreement is less expected since the isotherms of Peters and from which thermodynamic values are calculated and measured at lower temperature. The values deduced<sup>8</sup> are less accurate than those of Menaucourt<sup>9</sup>. The reason is that long time is needed to reach the thermodynamic equilibrium when recompressed exfoliated graphite is used as a substrate instead of non recompressed one. The bi-dimensional critical temperature  $T_C(2D)$  determined when studying the first layer of C<sub>2</sub>H<sub>2</sub> adsorbed on graphite was in agreement with that determined by Menaucourt<sup>3</sup> rather than that of Peters<sup>2</sup>.

## **4** Conclusions

The thermodynamic properties of acetylene  $[C_2H_2]$ adsorbed on the (0001) surfaces of an exfoliated graphite substrate have been investigated by volumetric adsorption isotherms. The measured isotherms show the condensation of two layers. Each layer undergoes a succession of phase transitions. The condensed phases have been thermodynamically characterized and the determined thermodynamic quantities were compared to available literature ones. It has been inferred that the structure of the monolayer condensed film depends both on the temperature and on the coverage. The lower values of the entropy are direct indication of a located adsorption.

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