Adsorption Isotherms of Low-Pressure H$_2$O on a Low-Temperature Surface Measured by a Quartz Crystal Microbalance

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1. INTRODUCTION

Chemical thrusters, the core devices used for attitude control and orbit maintenance of spacecraft, produce jets that will expand in the external environment and result in a plume. The low-pressure field known as vacuum plume during the operation. The gas-phase components in the plume, mainly including N$_2$, H$_2$O, CO, CO$_2$, and nitrates, are prone to be adsorbed on the low-temperature surface of the spacecraft and cause contamination effects, e.g., decreasing the sensitivity, breaking the thermal balance, and corroding the materials. These plume effects directly have an impact on the working status and service life of the spacecraft and even determine the success or failure of the space mission in severe cases. Therefore, it is essential to carry out the prediction of contaminant levels and influences.

Until now, though a lot of engineering experiments and contamination models have been performed and developed, respectively, most research results are not readily transferred to other spacecraft systems. Besides, there are few findings in the adsorption mechanism of typical pollutants in the plume on the spacecraft surface, especially for the low-pressure gas on the low-temperature surface. To accurately assess the contamination effects, it is significant to establish a general adsorption theory applicable to the plume pollutants.

The research on gas–solid surface interactions has started in the early 20th century, and a series of theoretical and empirical isotherm models have been proposed. Langmuir first advanced the treatment of monolayer adsorption by visualizing the equilibrium as a dynamic process and the isotherm model succeeded in fitting a variety of adsorption data. The Dubinin–Radushkevich model has been applied to express the adsorption mechanism with Gaussian energy distribution, and the Brunauer–Emmett–Teller (BET) model was theoretically derived to describe the multilayer adsorption by Brunauer, Emmett, and Teller. The universal model has provided a universal approach in predicting the adsorption isotherms, which can meaningfully capture the behaviors of all available isotherm types. The above isotherm models have made it feasible to describe the adsorption phenomenon in the formula, but the key constants of the models are still required to be determined by experiments under the plume condition.

In recent years, a quartz crystal microbalance (QCM) system has become an ideal tool to study adsorption as a gravimetric method on account of its high sensitivity and genuine relationship between mass and frequency. Tsionsky used the QCM for the study of adsorption from the gas phase onto a gold surface, determining the adsorption isotherms of several substances, including water at normal...
temperature. Venkatasubramanian experimentally investigated the CO₂, CH₄, and N₂ adsorption characteristics of two adsorbents at temperatures ranging from 30 to 70 °C and pressures ranging from 0.3 to 110 psi by the use of a QCM-based adsorption measurement apparatus. In addition, a number of studies focusing on the adsorption related to the polymers and the zeolite have been performed based on the QCM system. The above work has proved the feasibility of QCM to detect the subtle change in mass but indicated the lack of experimental data under the condition of low temperature and low pressure either.

In our preliminary work, an experimental system used for pressure and temperature control has been designed to study the adsorption of gas on the solid surface. The low-pressure CO₂ adsorption isotherms under nine different temperatures have been measured by QCM, and a multi-Langmuir isotherm model based on the data to describe the isotherms has been proposed, which is beneficial to analyze the adsorption process of CO₂ in the plume. For the purpose of providing support for the general adsorption theory, a more in-depth analysis of other gas-phase components of the plume should be carried out. In this study, the low-pressure adsorption isotherms of H₂O on gold-plated QCM have been experimentally measured at seven temperatures between 233 and 273 K. By means of the fitting, the key parameters of the classical models, including the Langmuir model, the Dubinin–Radushkevich model, the BET model, and the universal model, were determined, and the adsorption capacities indicated the occurrence of multilayer adsorption under the experimental condition. Not only have we analyzed the agreement between the isotherms and the multi-Langmuir model but compared the results with those of CO₂ as well. Based on the fitting results of the multi-Langmuir model, we have presented a new form suitable for describing H₂O isotherms and a simplified model that has a few variables. The simplified multi-Langmuir (SML) model can be conveniently applied to predict the adsorption of low-pressure H₂O on the low-temperature surface.

2. RESULTS AND DISCUSSION

In this study, low-pressure H₂O adsorption isotherms from 1 to 50 Pa were measured by a gold-plated QCM at seven temperatures from 233 to 273 K and the H₂O vapor was generated at room temperature during the experiment. It would take approximately 2 h for the QCM frequency to reach equilibrium at each pressure point.

2.1. Experimental Results and Accuracy. The accuracy of the QCM system has been justified in our previous work by (i) comparing the isotherms measured upon the single point measurement method and the continuous measurement method at six temperatures and (ii) comparing the adsorption and desorption isotherm measured by the continuous measurement method. The maximal error of the continuous measurement method based on the QCM system has been determined within ±(5–20)%, and a detailed analysis can be seen in ref. In this research, a repeated measurement has been carried out and the error of the obtained results is verified in this range.

The continuous measurement method has been adopted in our present work, and it consists of the following steps: (1) infuse the H₂O vapor into the pressure cell and complete the adsorption measurement when the pressure is p₁, (2) continue to infuse the H₂O vapor until the next pressure point p₂ was reached and then complete the measurement, and (3) after completing the measurement at the highest pressure pₙ, release H₂O from the pressure cell into the vacuum chamber. The H₂O isotherms at different temperatures measured by the continuous measurement method are plotted in Figure 1.

Figure 1. Adsorption isotherms of H₂O.

Focusing on the data obtained below 4 Pa, it can be seen that the adsorption amount increased rapidly with the change of the pressure and there is a significant linear correlation. When the pressure was between 4 and 10 Pa, the correlation was still positive but the increasing rate has slowed down a lot. After reaching 10 Pa, the deposition amount increased linearly with a lower slope as the pressure increased. In addition, it can be found at the end of both 233 and 243 K isotherms that the deposition amount is still increasing even without an increase in pressure, indicating that almost all of the gas of H₂O infused into the experimental cell has solidified on the low-temperature surface when the pressure was close to the saturated vapor pressure pₒ at the current wall temperature T.

2.2. Fitting Results of Classical Models. For the purpose of describing the adsorption process, it is essential to correlate the experimental data with the classical models that are applicable to the low-pressure region and have great performance in defining the isotherms. In this research, the Langmuir model, the Dubinin–Radushkevich model, the BET model, and the universal model were selected as the classical models to fit the experimental results.

The Langmuir model is considered valid in the low-pressure ranges and has been useful in interpreting lots of reported experimental data. The equation is given as:

\[
m = a₀ - \frac{b₁p}{1 + b₁p}
\]

where m is the mass amount deposited on the surface in ng·cm⁻², a₀ is the Langmuir adsorption capacity equal to the mass of full monolayer in ng·cm⁻², b₁ is the Langmuir affinity parameter in Pa⁻¹, and p is the steady-state pressure in Pa.

The Dubinin–Radushkevich model performs well near the saturation regions and the equation is given as:

\[
m = a₀ \exp \left[ -\frac{A}{E} \right] A = RT \ln(p/pₒ)
\]

where a₀ is the Dubinin–Radushkevich adsorption capacity equal to the total micropore volume in ng·cm⁻², A is the thermodynamical potential in J·mol⁻¹, E is the characteristic energy in J·mol⁻¹, R is the universal gas constant in J·mol⁻¹·K⁻¹.
Table 1. Critical Parameters of Classical Models

| Model                        | T/K | 233   | 243   | 248   | 253   | 258   | 263   | 273   |
|------------------------------|-----|-------|-------|-------|-------|-------|-------|-------|
| Langmuir model               |     |       |       |       |       |       |       |       |
| $a_i$/ng·cm$^{-2}$           | 5.56| 22.40 | 41.82 | 125.94| 217.93| 53.42 | 16.45 |       |
| $b_i$/Pa$^{-1}$              | 0.978| 0.968 | 0.969 | 0.972 | 0.972 | 0.948 | 0.962 | 0.899 |
| $R^2$                        | 0.098| 0.998 | 0.998 | 0.998 | 0.998 | 0.998 | 0.998 | 0.975 |
| Dubinin–Radushkevich model  |     |       |       |       |       |       |       |       |
| $a_i$/ng·cm$^{-2}$           | 1.269| 143.89| 122.80| 84.42 | 76.61 | 41.09 | 44.87 |       |
| $E$/J·mol$^{-1}$             | 5.56 | 22.40 | 41.82 | 125.94| 217.93| 53.42 | 16.45 |       |
| $R^2$                        | 0.099| 0.939 | 0.873 | 0.948 | 0.989 | 0.931 | 0.927 |       |
| BET model                    |     |       |       |       |       |       |       |       |
| $a_i$/ng·cm$^{-2}$           | 345.43| 232.78| 205.30| 139.57| 111.61| 50.73 | 26.11 |       |
| $c_i$/Pa$^{-1}$              | 0.15 | 0.24  | 0.19  | 0.18  | 0.20  | 0.15  | 0.23  |       |
| $R^2$                        | 0.992| 0.970 | 0.975 | 0.978 | 0.973 | 0.973 | 0.854 |       |
| universal model              |     |       |       |       |       |       |       |       |
| $a_i$/ng·cm$^{-2}$           | 345.43| 232.78| 205.30| 139.57| 111.61| 50.73 | 26.11 |       |
| $\alpha$                    | 0.89 | 0.34  | 0.23  | 0.34  | 0.30  | 0.24  | 0.39  |       |
| $e_o$/J·mol$^{-1}$           | 851.94| 1044.73| 1045.09| 2623.82| 3545.03| 4097.82| 7293.48|       |
| $m_1$/J·mol$^{-1}$           | 3975.134| 5709.21| 6068.89| 7635.30| 8745.66| 9257.29| 13186.90|       |
| $m_2$/J·mol$^{-1}$           | 1763.84| 1036.79| 785.53| 806.87| 275.86| 454.45|       |       |
| $R^2$                        | 0.998| 0.998 | 0.998 | 0.998 | 0.998 | 0.997 | 0.975 |       |

Figure 2. Comparison of the experimental data with the fitting isotherms.

K$^{-1}$, $T$ is the experimental temperature in K, and $p_0$ is the saturated vapor pressure in Pa.

The BET model has been widely used in the range of relative pressure from 0.05 to 0.35, and it is given as $^{31,32}$

$$m = a_i (p_0 - p)[1 + (\alpha - 1)p/p_0]^\beta$$

where $a_i$ is the BET adsorption capacity equal to the mass of the full monolayer in ng·cm$^{-2}$ and $\alpha$ is the BET affinity parameter in Pa$^{-1}$.

The universal model has been proposed in a unified approach that combined (i) the homotattic patch approximation (HPA), (ii) the revised Langmuir model, and (iii) the fractional probability factor for the distribution of site energy sets, so it can capture the isotherms of all types. For type-I to type-V isotherms, the equation can be given as $^{34,36}$

$$m = a_i \theta_i$$

$$\theta_i = \alpha \left( \frac{\exp \left( \frac{e_o}{R_i T} \right)}{1 + \exp \left( \frac{e_o}{R_i T} \right)} \right)^{RT/m_1}$$

$$+ (1 - \alpha) \left( \frac{\exp \left( \frac{e_o}{R_i T} \right)}{1 + \exp \left( \frac{e_o}{R_i T} \right)} \right)^{RT/m_2}$$

where $a_i$ is the available adsorption capacity in ng·cm$^{-2}$, $\theta_i$ is the total adsorption coverage of the surface, $\alpha$ is the probability factor, and $e_o$ and $m$ represent mean and deviation of an energy term, respectively; therefore, they have the same units, J·mol$^{-1}$.

To ensure that the correlation results can reflect the establishment process of adsorption, the effect of solidification when close to the saturated vapor pressure should be excluded. Therefore, taking into account the fact that there is a sharp rise in the deposition quality at the end of both the 233 K isotherm and the 243 K isotherm, only the minimum value at the corresponding pressure was utilized for fitting. Owing to the applicability of the BET model, the data whose relative pressure was in the range from 0.05 to 0.35 was selected when correlated with this model. After the curve fitting, the critical parameters of the above classical models are presented in Table 1.

The $R^2$ exported from the fitting process in Table 1 has indicated that there are good agreements between the data and the selected models at most temperatures. The comparison of the experimental data with the fitting isotherms at 258 and 263 K is chosen as examples shown in Figure 2.

According to the derived critical parameters and the comparison of the fitting isotherms, it can be found that there were great similarities in the fitting results of the Langmuir model and the Dubinin–Radushkevich model. The BET model is applicable for relative pressures higher than 0.05 and lower than 0.35, $^{31,32}$ and the fitting curve agrees well with the experimental data in this region. Additionally, the universal
model with $R^2$, which is most close to 1, has shown a significant consistency with the data points and almost captured all of the notable characteristics. Not only did the correlation results validate the reasonability of the experimental data but also gave a description of the adsorption from the perspectives of various models. Moreover, the trend of the isotherms has been delineated by the universal model so precisely that a superior prediction will be presented for the adsorption of low-pressure H$_2$O at the specific experimental temperature, and the general formula applicable to other temperatures will be hopefully researched in the further investigations.

It is worth noting that almost all of the parameters characterizing the adsorption capacity of each model (e.g., $a_{f1}$, $a_{f2}$, $a_{f0}$, and $a_{fU}$) have generally shown an excellent negative correlation with the temperature, which is a significant parameter affecting adsorption affinity. Besides, there should be a multilayer adsorption phenomenon, for these parameters are all higher than 28 ng·cm$^{-2}$, which is considered as the mass of full monolayer of H$_2$O.$^{54}$ However, there may exist a problem with the applicability of the above models at 273 K, for the $R^2$ values at this temperature of the above models are a little different compared with the others. Owing to the triple point of H$_2$O, which is about 273 K,$^{52}$ the adsorption process on the solid surface would become more complicated due to liquefaction and condensation. Hence, there will be a discrepancy in the experimental results when the data at 273 K are in comparison with those below it, and it is essential to exclude the relevant data to conduct further research.

2.3. Comparison with CO$_2$. In our previous work, a new multilayer adsorption model named the multi-Langmuir model has been developed to describe the adsorption process of CO$_2$ for the plume contamination effects. The equation is given as

$$m = a_M \frac{b_M p}{1 + b_M p}$$

where $a_M$ is the multi-Langmuir adsorption capacity in ng·cm$^{-2}$ and $b_M$ is the multi-Langmuir affinity parameter in Pa$^{-1}$.

The multi-Langmuir model has the same mathematical form as the Langmuir model, but there are differences in the physical meaning of the specific parameters. The semiempirical formulas of $a_M$ and $b_M$ were obtained based on the CO$_2$ adsorption results

$$a_M = a_0 \exp \left( \frac{E_d}{RT} \right)$$

$$b_M = \frac{\exp \left( E_d/RT \right) E_M}{P_0} = b_1 T + b_0$$

where $a_0$ is a fitted parameter related to the properties of the adsorbate and the adsorbent in ng·cm$^{-2}$, $E_d$ is the average adsorption energy in J·mol$^{-1}$, $E_M$ is defined as an energy parameter related to the adsorption heat in J·mol$^{-1}$, $b_1$ and $b_0$ are both fitted parameters in J·mol$^{-1}$·K$^{-1}$ and J·mol$^{-1}$, respectively.

Considering that the multi-Langmuir model is developed according to the adsorption data of CO$_2$, it is worth verifying its applicability to H$_2$O. The critical parameters of the multi-Langmuir model exported by the data no higher than 263 K are listed in Table 2. For the reason that the expressions are the same, the critical parameters of the multi-Langmuir model derived from experimental data are the same as those of the Langmuir model.

| $T$/K | $a_M$/ng·cm$^{-2}$ | $b_M$/Pa$^{-1}$ | $R^2$ |
|-------|-------------------|-----------------|--------|
| 233   | 345.43            | 0.15            | 0.992  |
| 243   | 232.78            | 0.24            | 0.970  |
| 248   | 205.30            | 0.19            | 0.975  |
| 253   | 139.57            | 0.18            | 0.978  |
| 258   | 111.61            | 0.20            | 0.973  |
| 263   | 50.73             | 0.15            | 0.973  |

Figure 3. Relationship between the saturation capacity $a_M$ and the temperature $T$ of H$_2$O compared with that of CO$_2$.

Figure 4. Relationship between the energy parameter $E_M$ and the temperature $T$ of H$_2$O compared with that of CO$_2$.  

To determine the accurate relationship of the parameters $a_M$ and $b_M$ relative to the temperature $T$, the $a_M$–$T$ curve and the $E_M$–$T$ curve are plotted in Figures 3 and 4, respectively. $E_M$ is the energy parameter calculated by the empirical expression of $b_M$ in the multi-Langmuir model as eq 7. The corresponding curves of CO$_2$ have also been plotted for comparison.

It is evident that the saturation adsorption amount $a_0$ of the H$_2$O experiment has a linear variation relationship with the wall temperature $T$, different from the exponential form determined by the CO$_2$ results, while there is a similarly strong linear relationship between $E_M$ and $T$ of H$_2$O as the phenomenon appeared in CO$_2$. Therefore, the multi-Langmuir model to describe the low-pressure adsorption process of H$_2$O on the low-temperature surface should be modified and given as follows

$$m = a_M \frac{b_M p}{1 + b_M p} = a_M \frac{p \exp \left( \frac{E_M}{RT} \right)}{1 + \frac{p \exp \left( \frac{E_M}{RT} \right)}{RT}}$$
where \( a_M = a_1 T + a_0 \) \( E_M = b_1 T + b_0 \) and the value of each constant is given in Table 3.

**Table 3. Value of Fitting Coefficients and Constant in H\(_2\)O’s Multi-Langmuir Model**

| \( \alpha_1 / \) | \( \alpha_0 / \) | \( b_1 / \) | \( b_0 / \) | \( R / \) |
|----------------|----------------|------------|------------|--------|
| ng-cm\(^{-2}\)  | ng-cm\(^{-2}\)  | kJ-mol\(^{-1}\) | kJ-mol\(^{-1}\) | J-mol\(^{-1}\)-K\(^{-1}\) |
| -9.565          | 2568.869       | 0.224      | -50.513    | 8.314  |

The H\(_2\)O’s multi-Langmuir model has presented a semi-empirical formula to plot more isotherms under other conditions so that it will be effective to predict the low-pressure H\(_2\)O adsorption results on the low-temperature surface in a continuous range. Moreover, this model can be justified by the universal model, whose general form can be expressed as:

\[
m = a_M T \sum_{j=1}^{M} \alpha_j \left[ \frac{\left( \frac{P}{P_0} \right) \exp \left( \frac{E_j}{RT} \right)}{1 + \left[ \frac{P}{P_0} \right] \exp \left( \frac{E_j}{RT} \right)} \right]_j
\]

(9)

Compared with the multi-Langmuir model shown in eq 8, although the universal model has an additional exponent and its term number is greater, the basic form of the two models is consistent. It can be suggested that the physical mechanism of the two models is similar and the application of the H\(_2\)O’s multi-Langmuir model is reasonable.

As for the adsorption characteristics of H\(_2\)O and CO\(_2\), the similarity and differences exist not only in the fitting results but also in the isotherms plotted in Figure 5.

By comparing the isothermals of H\(_2\)O measured in this work with those of CO\(_2\) measured in the previously published work,\(^{50}\) it shows that the overall trend of each isothermal looks analogous. The CO\(_2\) isotherms are typical type-I isotherms, while the H\(_2\)O isotherms have the characteristics of type-I and type-II isotherms. There exists fast growth in the deposition amount originally, but when the pressure is higher than 10 Pa, the deposition amount of H\(_2\)O increases with a slower rate and that of CO\(_2\) even keeps constant. While the H\(_2\)O isotherms have the characteristics of type-I and type-II isotherms. There exists fast growth in the deposition amount originally, but when the pressure is higher than 10 Pa, the deposition amount increases fast at first. However, the attraction force from the surface will diminish in intensity with increasing distance from the adsorbent,\(^{55,54}\) and this will result in a decrease in the increasing rate of the deposition quality when the pressure becomes higher. Besides, the adsorption process will transition to being dominated by the interaction between the molecules of the adsorbate, and the difference between the subsequent adsorption phenomenon of H\(_2\)O and CO\(_2\) will depend on the nature of the gas.

The triple-point temperature of H\(_2\)O is about 273 K,\(^{52}\) slightly higher than the experimental temperature. Hence, there is also condensation between H\(_2\)O molecules apart from the adsorption of H\(_2\)O on the surface, and the stable crystal structures will form to adsorb H\(_2\)O molecules continuously, as depicted in Figure 7.

**Figure 5.** Adsorption isotherms of H\(_2\)O compared with the published isotherms of CO\(_2\).

**Figure 6.** Schematic diagram of molecules’ interaction on the surface.

**Figure 7.** Schematic diagram of H\(_2\)O molecules’ adsorption and condensation on the surface.

In addition to that, the experimental pressure is closer to the saturated vapor pressure \( p_0 \) of H\(_2\)O, which will strengthen the condensation phenomenon. In terms of CO\(_2\), its triple-point temperature is about 216 K, relatively far lower than the wall temperature in the experiment, and its saturated vapor pressures at every experimental temperature are far higher than the experimental pressure.\(^{55}\) These characteristics prevented CO\(_2\) from noticeable condensation and formed a stable crystal structure. This is the reason why there is no more
capacity for more CO₂ molecules on the outer layer when the adsorption process is reaching a dynamic equilibrium.

2.4. Simplified Multi-Langmuir Model. The affinity parameter \( b_M \) of the H₂O’s multi-Langmuir model can be written as

\[
b_M = \frac{\exp[b_t/R + b_0/(RT)]}{p_0}
\]

The saturated vapor pressure \( p_0 \) has been given by the Clausius–Clapeyron equation⁶

\[
p_0 = \exp(c_i + c_0/T)
\]

where \( c_i \) and \( c_0 \) are both constants independent of temperature.

In eq 10, after substituting \( p_0 \) by eq 11, the equation of \( b_M \) will be written as

\[
b_M = \frac{\exp[b_t/R + b_0/(RT)]}{\exp(c_i + c_0/T)}
\]

Obviously, the numerator and denominator of \( b_M \) have a similar form, so it is understandable that the parameter \( b_M \) can degenerate into the constant \( b_M \) when the above constants are in certain ranges. If feasible, it will be significant to predict the adsorption of low-pressure H₂O on the low-temperature surface with fewer parameters. For the purpose of verifying the proposition, the original experimental data in Figure 1 has been normalized by the capacity of the corresponding temperature in Table 2, and the results are shown in Figure 8. The relative surface coverage \( \theta \) on the vertical axis represents the proportion of the adsorption mass relative to the multi-Langmuir adsorption capacity at corresponding temperatures.

Surprisingly, the normalized data at different temperatures have presented a good convergence and an overall trend of the normalized isotherms has appeared, which means that a general formula with an affinity constant can be derived to describe this phenomenon conveniently. Correlating the data with the H₂O’s multi-Langmuir model, the fitted curve is obtained in Figure 8, and the simplified equation named as the simplified multi-Langmuir model is as follows

\[
m = a_M \theta = (a_t + a_0) \frac{b_M p}{1 + b_M p}
\]

where the values of each coefficient and constant are given in Table 4.

As can be seen, the simplified multi-Langmuir model inherits the basic form of the multi-Langmuir model and adopts a specific constant \( b_M \), to represent the multi-Langmuir affinity parameter \( b_M \), which should be calculated from complex expressions. This results from the properties of H₂O and the special conditions under low temperatures and low pressures. Hence, the number of the required parameters has been reduced and the general formula of the simplified multi-Langmuir can also be utilized to estimate the adsorption of H₂O at other pressure or temperature within a certain range.

To validate the simplified multi-Langmuir model, the replotted isotherms depending upon the general formula are compared with the original experimental data at each specific temperature in Figure 9. As observed, the isotherms for prediction have reflected the main characteristics of the experimental data and are basically within an acceptable error range. It is obvious that the simplification has not affected the feasibility of the general formula and the simplified multi-Langmuir model has been justified to assess the adsorption of low-pressure H₂O on the low-temperature surface at other experimental conditions in the further application.

3. CONCLUSIONS

The low-pressure H₂O adsorption on the low-temperature surface was experimentally investigated by a QCM-based experimental system for the purpose of establishing the general adsorption theory of plume contamination. The isotherms, at temperatures ranging from 233 to 273 K and pressures ranging from 0 to 50 Pa, have been measured and are similar to type-I and type-II isotherms. The experimental data have been fitted with the selected classical adsorption models, and the critical parameters have been exported to describe the low-pressure adsorption by various models. Especially, the universal model has shown an excellent agreement with the data and a superior prediction has been given at the individual temperature point. Based on the experimental results under the conditions of low temperatures and low pressures, the multi-Langmuir model proposed in our preliminary work has been validated after simple correction, enabling to predict the low-pressure adsorption in certain ranges. If feasible, it will be significant to predict the adsorption of low-pressure H₂O on the low-temperature surface with fewer parameters. For the purpose of verifying the proposition, the original experimental data in Figure 1 has been normalized by the capacity of the corresponding temperature in Table 2, and the results are shown in Figure 8. The relative surface coverage \( \theta \) on the vertical axis represents the proportion of the adsorption mass relative to the multi-Langmuir adsorption capacity at corresponding temperatures.

![Figure 8. Comparison of normalized experimental data with the fitted curve.](image)

![Figure 9. Validation of the simplified multi-Langmuir model when compared with the experimental data.](image)

### Table 4. Value of Fitting Coefficients in H₂O’s Simplified Multi-Langmuir Model

| \( a_t/\text{ng cm}^{-2}\text{K}^{-1} \) | \( a_0/\text{ng cm}^{-2} \) | \( b_M/\text{Pa}^{-1} \) | \( R^2 \) |
|---|---|---|---|
| -9.565 | 2568.869 | 0.183 | 0.958 |
adsorption of gaseous plume pollutants on the low-temperature surface for a continuous range. The experimental results of H₂O have been compared with those of CO₂, and the reasons resulting in the similarity and differences have been explained. In addition, the simplified multi-Langmuir model with fewer variables has been proposed and validated, which can be utilized conveniently to estimate the adsorption results of H₂O in the temperature and pressure ranges we explored.

4. EXPERIMENTAL SECTION

To measure the low-pressure adsorption isotherms of H₂O, an adsorption experimental system has been designed in the vacuum plume effect system (PES) of Beihang University, which can obtain the high vacuity and stabilize the dynamic vacuum in the chamber not higher than 7.8 × 10⁻³ Pa. The adsorption experimental system, whose schematic diagram is shown in Figure 10, mainly consists of three subsystems: the pressure control system, the temperature control system, and the QCM system.

4.1. Pressure Control System. The pressure control system including (a)−(i) was designed for the purpose of providing water vapor and controlling the pressure in the experimental chamber from 1 to 100 Pa.

Having reached the ultrahigh vacuum condition by means of PES, we close solenoid valve (h), and open valve (d) so that liquid water tank (c) will be connected to pressure cell (b). Due to the nature of water that its boiling point is relatively low when exposed to a low-pressure environment, the liquid water in (c) will vaporize rapidly, generating water vapor in high purity. Through the infusion tube equipped with a CS5 mass flow controller (Beijing Measure Instrument Co., Ltd.), the vapor was injected slowly into the experimental chamber. Contemporarily, the pressure was monitored by a ZJ-51 vacuum gauge tube (Guoguang Electric Co., Ltd.) and a DL-3 thermocouple vacuum gauge (Department of Electronics, Peking University). After reaching the objective pressure, we close valve (d) and keep the pressure cell (b) sealed, so the pressure would remain constant to carry out the specific experiments. When all of the measurements have been finished, we open solenoid valve (h), and the gas in the experimental chamber will be pumped out by the pumps of PES.

4.2. Temperature Control System. The temperature control system, including (j)−(o) in Figure 10, was utilized to stabilize the temperature of QCM at a specific point in a range from 213 to 323 K. There are four parts in this subsystem, as shown in Figure 11: a cold source module, a primary temperature control module, a heat transfer unit, and an accurate temperature control module.

The cold source module operates with a YDZ-200 self-pressurized liquid nitrogen tank (Keyi Co., Ltd.), which provides an ample supply of liquid nitrogen to decrease the temperature of the cooling module and the heat transfer unit. At the same time, the heat transfer unit is also connected to the primary temperature control module (Beijing Westzh Technology Ltd.), whose heater band will work when the monitored temperature is lower than the objective value. Owing to the above three units, the QCM connected to the head of the transfer unit by hexagonal bolts will be affected by their heat transfer effects. To enhance the heat conduction performance, thermally conductive silicone was applied between the QCM housing and the heat transfer unit, stabilizing the temperature of QCM around the required temperature. Then, the accurate temperature control module will play a role in ensuring that the temperature remains stable at the objective point. The accuracy of the temperature control system was ±0.2 K.

4.3. QCM System. The quartz crystal microbalance (QCM) is a measurement device that can convert the mass change on the surface of the quartz crystal oscillator electrode into the frequency change of the electrical signal output based on a linear relationship. The change in mass per unit surface area, Δm, can be calculated from the change in frequency, Δf,

\[ Δm = -C'_mΔf \]  (14)

where \( C'_m \) is a constant depending on the property of the crystal.

In this experiment, the temperature-controlled QCM system with a gold-plated surface (Beijing Institute of Spacecraft Environment Engineering) was placed in the pressure cell to measure the low-pressure adsorption isotherms of H₂O. The \( C'_m \) equals 1.1 ng·cm⁻²·Hz⁻¹ according to the manufacturer’s instructions, i.e., the sensitivity of the QCM system in this
experiment is 1.1 ng·cm$^{-2}$ for a decrease in the frequency of 1 Hz.

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