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An influence of HCl and water co-adsorption at ice surfaces on HCl uptake

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Abstract. A mechanism of HCl and water co-adsorption at ice surface is studied within a simple two-component model, treated in the mean field approximation. It is shown that a realistic choice of the HCl-water interaction (about the hydrogen bond strength) leads to a remarkable increase of HCL uptake in comparison to the case when HCl is adsorbed alone. Based on the model we are able to recover the experimental results for HCl on ice at stratospheric conditions.

Вплив коадсорбції HCl і води на поверхні льоду на покриття HCl

В.І.Капко, Е.В.Вакарін, М.Ф.Головко

Анотація. Механізм коадсорбції HCl і води на поверхні льоду вивчено в рамках простої двокомпонентної моделі в наближенні середнього поля. Показано, що реалістичний вибір енергії взаємодії HCl-вода, яка за порядком величини співмірна з енергією водневого зв'язку, веде до значного зростання покриття льоду хлороводнем (HCl) в порівнянні з випадком, коли HCl адсорбується окремо. На основі даної моделі ми можемо пояснити експериментальні дані по покриттю льоду HCl в стратосферних умовах.

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1. Introduction

It is widely believed that the ozone layer in the stratosphere protects all living organisms from solar radiation. Therefore the ozone hole attracted so much attention of scientists since its discovery. The important stage of the destruction of ozone is adsorption of breakdown products of chlorofluorocarbons (HCl, HClO and so on) on the ice surface of the polar stratospheric clouds. These clouds form over Antarctic on 10-20 km altitudes during winter when temperature drops below 190 K [1]. The object of intensive studies are the heterogeneous reactions (those that occur on surface) which produce chlorine radicals as well as the high HCl uptake (0.1-16.2 monolayers). The last fact can not be explained by the simple deposition mechanism [2] that predicts the surface coverage $\theta \approx 4 * 10^{-8}$ to $1 * 10^{-8}$ for submonolayer regime in a broad range of stratospheric conditions (temperature $T \approx 190\ K$ and pressure $p_{HCl} \approx 10^{-7} - 10^{-8}$ Torr).

In order to understate how so high adsorption level of HCl can happen several theoretical approaches have been introduced. They are mainly based on computer simulation [3–5] and the mean field approximation (MFA) [6–8]. One model [3] considers of H_2O and HCl co-adsorption with encapsulation of HCl molecules during the process of ice growth. Other model [4] takes into account a quasi-liquid film on ice surface what leads to increase of coordination for adsorbed HCl molecules by H_2O molecules and increase of HCl adsorption.

In work [6] it has been shown that the adsorption of HCl molecules on ice surface can cause its melting at low temperatures relevant to polar stratosphere. Increasing of adsorption due to the surface heterogeneity (O-, OH-sites and point-like defects) was studied in papers [5,7]. In [7] an analytical theory for HCl adsorption on ice was developed based on a random lattice gas model within MFA. Taking into account the defect sites and changing their binding energy and concentration in reasonable limits this theory reproduced the experimental data for the adsorption energy and for the coverage in a submonolayer regime. A role of ice corrugation in increasing HCl coverage was studied in [8], where has been suggested that the surface steps create new adsorption sites and have a larger binding energy compared to the flat area.

In the present paper we use a two-component lattice gas model within MFA to explore the co-adsorption of HCl and H_2O on ice surface. As it was mentioned above similar process has been examined by computer simulation [3]. In contrast to it we consider only submonolayer regime and develop an analytical theory what operates with general characteristics of HCl-ice interface (like lattice symmetry and binding energy). Our theory recovers the experimental results for the coverage of HCl in reasonable limits of pair interaction energy and the coverage of H_2O molecules.

2. Theory

We consider an idealized model of ice surface made with adsorbing sites on a planar honeycomb lattice. For the sake of simplicity all these sites are assumed to be equal and rigid fixed in their positions. Thereby we neglect the influence of surface heterogeneity and the dynamic nature of the ice surface on the HCl adsorption. These both effects lead to increase of adsorption and were studied by us before [6,7].

An interaction of two-component gas with the surface is described by the lattice gas Hamiltonian:

$$\begin{aligned} H = {} & \frac{1}{2} W_{AA} \sum_{ij} t_i^A t_j^A (1 - t_i^w)(1 - t_j^w) + W_{Aw} \sum_{ij} t_i^A t_j^w (1 - t_i^w) * \\ & (1 - t_j^A) + \frac{1}{2} W_{ww} \sum_{ij} t_i^w t_j^w (1 - t_i^A)(1 - t_j^A) - \\ & (\mu_A + \epsilon_A) \sum_i t_i^A (1 - t_i^w) - (\mu_w + \epsilon_w) \sum_i t_i^w (1 - t_j^A), \end{aligned} \tag{1}$$

where subscript A corresponds to HCl molecule and w to H_2O one. W_{xy} is the pair interaction between two adsorbed molecules, μ_x is their chemical potential and ϵ_x is their binding energy.

The state of the i - adsorbing site is described by the set of its occupation numbers $t_i^A = 0, 1$ and $t_i^w = 0, 1$. Multiple occupancy of a site is forbidden and only nearest neighbor interactions are taken into account. So there are only three states: $t_i^A = 0$ and $t_i^w = 0$ (free state), $t_i^A = 1$ and $t_i^w = 0$, or $t_i^A = 0$ and $t_i^w = 1$ (occupied states).

Of course, our approach leaves aside most of microscopic details of the real system. But the model contains the essential physical characteristics of the system (like the lattice symmetry and binding energy of different components) and can be solved analytically.

The free energy per site in the mean field approximation (MFA) for the occupation numbers is given by

$$\begin{aligned} \frac{\beta F}{V} = {} & -\frac{1}{2} q\beta W_{AA} \Theta_A^2 - \frac{1}{2} q\beta W_{ww} \Theta_w^2 - q\beta W_{Aw} \Theta_A \Theta_w - \\ & \ln [1 + \exp(\beta\mu_A + \beta\epsilon_A - q\beta W_{AA} \Theta_A - q\beta W_{Aw} \Theta_w) + \end{aligned}$$

$$\exp(\beta\mu_w + \beta\epsilon_w - q\beta W_{Aw}\Theta_A - q\beta W_{ww}\Theta_w)] \,, \tag{2}$$

where θ_A and θ_w are the HCl and H_2O surface coverages and q=3 is the co-ordination number of the lattice. β is the inverse temperature. Then the free energy is minimized with respect to the surface coverages θ_A and θ_w. This minimum corresponds to the conditions

$$\begin{aligned} \frac{\partial}{\partial\Theta_A}\left(\frac{\beta F}{N}\right) &= 0, \\ \frac{\partial}{\partial\Theta_A}\left(\frac{\beta F}{N}\right) &= 0. \end{aligned} \tag{3}$$

Performing the indicated above differentiation we obtain the following equations:

$$\begin{aligned} \beta\mu_A + \beta\epsilon_A &= q\beta W_{AA}\Theta_A + q\beta W_{Aw}\Theta_w + \ln\left[\frac{\Theta_A}{1-\Theta_A-\Theta_w}\right], \\ \beta\mu_w + \beta\epsilon_w &= q\beta W_{Aw}\Theta_A + q\beta W_{ww}\Theta_w + \ln\left[\frac{\Theta_w}{1-\Theta_A-\Theta_w}\right]. \end{aligned} \tag{4}$$

If we neglect the pair interaction setting $W_{AA} = W_{Aw} = W_{ww} = 0$ our treatment is exact (there is no restriction due to the MFA). Then the expressions (4) can be solved with respect to Θ_A and Θ_w:

$$\begin{aligned} \Theta_A &= \frac{\exp(\beta(\mu_A+\epsilon_A))}{1+\exp(\beta(\mu_A+\epsilon_A))+\exp(\beta(\mu_w+\epsilon_w))}, \\ \Theta_w &= \frac{\exp(\beta(\mu_w+\epsilon_w))}{1+\exp(\beta(\mu_A+\epsilon_A))+\exp(\beta(\mu_w+\epsilon_w))}. \end{aligned} \tag{5}$$

In the one-component case ($\Theta_w = 0$) we recover the standard Langmuiriar isotherm $\Theta_A = \exp(\beta(\mu_A+\epsilon_A))/\left(1+\exp(\beta(\mu_A+\epsilon_A))\right)$.

3. Results and discussion

At a glance one could obtain the isotherm of adsorption both H_2O and HCl molecules from solution of of system of equations (4). But there are two problems on this way. First one arises from the dynamic nature of ice-vapour interface. We must take into account that the surface coverage of H_2O molecules changes during the process of ice growth. After one layer has been built the filling of another one will start. Therefore the H_2O surface coverage can not be evaluated from equations (4).

Other problem is connected with the fact that the adsorbed molecules interact each other direct as well as through gas particles. As a result the interaction energy differs from one obtained by quantum chemistry calculations. From obvious reason we assume the binding energy of H_2O and the water-water interaction are approximatly equal to energy of hydrogen bond (about 20 kJ/mol). We fix $\epsilon_A = 20$ kJ/mol because this value is close to the cluster dissociation energy for HCl − H_2O complex at T=200 K calculated in [9]. Such high value of W_{ww} leads to a significant hysteresis loop for water molecules, which corresponds to the standard Van der Waals picture of phase transitions. Unfortunately, we have not any good estimations for parameters W_{AA} and W_{Aw}. But the parameter W_{AA} is less important then the last one due to the low concentration of HCl molecules in stratosphere. All parameters W_{xy} have negative sign because molecules attract at such distances. In the absence of theoretical estimations of energy of interaction between HCl and H_2O we assume that $-W_{Aw} > -W_{AA}$ and $-W_{Aw} < -W_{ww}$.

The surface coverage of HCl molecules is displayed in Fig. 1 as func-

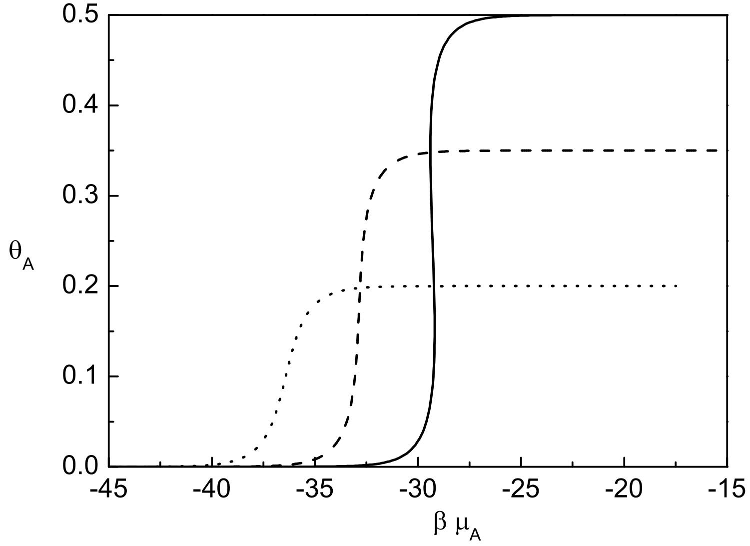

Figure 1. Surface coverage of HCl as function of the dimensionless chemical potential of HCl and different values of coverage of H_2O. Solid line correspondes to $\theta_w = 0.5$, dashed one correspondes to $\theta_w = 0.65$ and dotted one correspondes to $\theta_w = 0.8$.

tion of its dimensionless chemical potential and the surface coverage of H_2O molecules. We made calculations at fixed θ_w and $W_{AA} = -5$ kJ/mol and $W_{wA} = -15$ kJ/mol. Solid, dashed and dotted lines correspond to θ_w=0.5, 0.65 and 0.8, respectively. All the curves have similar shapes. One observes a large jump in the adsorption isotherms at some threshold of chemical potential μ_A^0. Adsorption of HCl is neglected if $\mu_A < \mu_A^0$ and molecules HCl fill almost all free adsorbing sites if $\mu_A > \mu_A^0$. The threshold value of chemical potential strogly dependents upon the coverage of H_2O molecules and can be approximately evaluated by formula

$$\beta\mu_A^0 = -\beta\epsilon_A + \frac{1}{2}q\beta W_{AA} + q\beta\left(W_{Aw} - \frac{1}{2}W_{AA}\right)\Theta_w, \qquad (6)$$

which was obtained from the first equation (4) and condition, $\theta_A = 1 - \theta_A - \theta_w$ which vanish the logarithm in the right side of the first equation (4). The threshold value of chemical potential decreases with increasing of θ_w if $-W_{AA} < -2\,W_{Aw}$. One can see from Fig. 1 that at $\theta_w = 0.65$ $\beta\mu_A^0 \approx -34$ which corresponds to chemical potential of HCl at stratospherical conditions, what can be established using the ideal gas equation of state.

On other hand fig. 1 demonstrates a hysteresis loop in the coverage of HCl which arises with decreasing of θ_w. The condition of its emergence can be easy obtained with differentiation of the first equation (4) with respect to θ_A:

$$\theta_w < 1 + \frac{4}{q\beta W_{AA}}. \qquad (7)$$

At $W_{AA} = -5$ kJ/mol the hysteresis loop exists if $\theta_w < 0.58$.

Dependence of the adsorption isotherm of HCl upon the interaction of HCl – H_2O is shown in fig. 2. We fix $\beta\mu_A = -34$ and calculate the HCl coverage at different values of θ_w. All adsorbtion isotherms exhibit a step-like dependence on W_{Aw}. This is precisely the situation described above. The adsorption of HCl occurs only if the H_2O – HCl interaction is less then some threshold value, which decreases with decreasing of the coverage of H_2O.

4. Conclusion

A mechanism of co-adsorption of H_2O and HCl on ice is investigated within a simple and analytically tractable two-component model based on the mean field approximation. Thermal fluctuations, which are neglected in the treatment, do not seem to play an important role in this phenomenon.

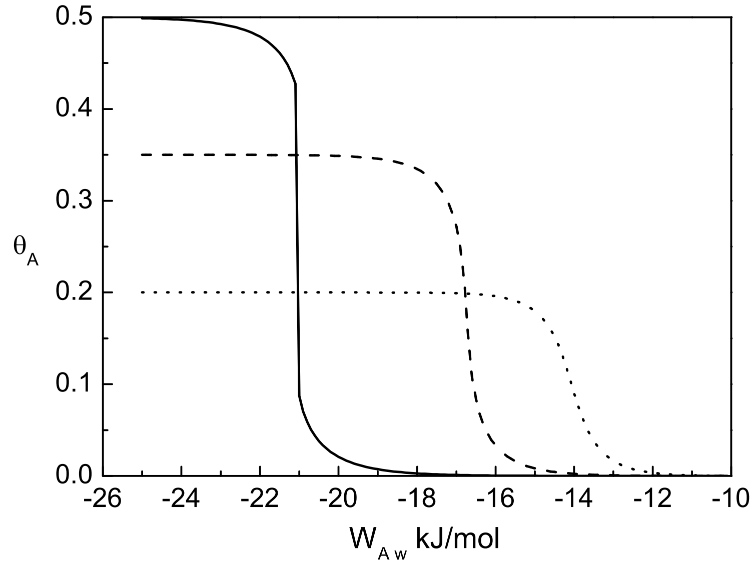

Figure 2. Surface coverage of HCl as function of the interaction energy between adsorbated molecules HCl and H_2O. The meaning of lines and values of coverage of H_2O are the same as in the previous figure.

The main conclusion of this study is that the H_2O – HCl interaction may cause the strong increase (in a few order of magnitude) in the HCl coverage. At stratospheric conditions it happens if the H_2O coverage exceed some threshold value, which varies from $\theta_w^0 = 0.65$ to $\theta_w^0 = 0.8$. The results presented here are obtained with physically reasonable assumption about the interaction between adsorbated molecules H_2O and HCl, which was made in the absence of theoretical estimations.

The calculations have been performed for a planar and homogenous lattice. Inclusion of effects of the surface heterogeneity and the corrugation which were introduce in our previous studies [7,8] will reduce value of θ_w^0.

5. Acknowledgments

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