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Adsorbate-induced distortion of solid surfaces. Application to HCl on ice at stratospheric conditions

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It is shown that the adsorption of HCl molecules at the surface of ice increases, if the HCl binding energy increases with the distortion amplitude of the oxygen sites of ice. At the same time, the adsorption stimulates an increase of the Lindemann parameter for the ice lattice, driving its melting at temperatures ($T = 190$ K) relevant to the polar stratosphere. Similar effects take place when the lateral interaction between HCl molecules becomes more attractive due to the coupling through the ice lattice.

Key words: *adsorption of HCl on ice, two-dimensional lattice gas, lattice distortion, surface melting*

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1. Introduction

Adsorption of HCl on ice is believed to be one of the preliminary steps, involved into the ozone depletion over the Antarctic [1]. The exceptional importance of the problem has initiated extensive theoretical [2–5] and experimental [7–11] investigations in this field. One of the most important points is the mechanism for chlorine accumulation through the HCl ionization upon adsorption on ice. Semiempirical calculations suggest [12] that at least four to six water molecules are needed to ionize HCl, while the natural coordination of the honeycomb lattice (ice Ih) at the surface is three. It should be stressed that the solvation mechanism is strongly correlated with the mechanism of HCl adsorption.

Several theoretical approaches were developed to explore this phenomenon. One of them [3] takes into account the dynamic nature of ice-vapour interface. In the course of water and HCl co-adsorption the latter can be encapsulated during the process of ice growth. However, the collision frequency (partial pressure) of water molecules with the ice surface should be high enough to account for the formation of the solvation shell before HCl has time to desorb.

Another model [4] assumes that the ionization is assisted by a quasi-liquid layer which exists on the surface of ice, providing in this way an appropriate coordination for adsorbed HCl molecules. Nevertheless, the nature of the quasi-liquid layer at stratospherically relevant conditions (low temperatures, $T \approx 200$ K and pressures, $p_{\mathrm{HCl}} \approx 10^{-7} - 10^{-6}$ Torr) remains to be investigated.

The nonideality of the ice surface was examined as a source of increasing adsorption. For instance, the defect-assisted adsorption [5] is consistent with the encapsulation scenario. However, our preliminary estimation [6] implies that point-like defects (like vacancies) do not give a significant increase of the binding energy. To recover the experimentally measured adsorption energy (46 kJ/mole), one has to assume a binding energy of about 60–80 kJ/mole at the defect sites, depending on their concentration. This suggests the investigation of more extended defects (like cracks or pores).

Moreover, recent experiments [7–9] give a convincing evidence that adsorbate-induced effects should be considered in order to make a link between all the aspects concerning the HCl-ice interface. In particular, we have already demonstrated that in the quite general case (when the cohesion energy of a crystal is comparable to the adsorbate-substrate or adsorbate-adsorbate interactions), the adsorbate-substrate coupling may lead to a distortion [13] or restructuring [14] of the substrate lattice. In addition, it was shown that the adsorption may facilitate a local melting [15] and roughening [16] of the substrate, such that the corresponding disordering temperatures are much lower than those for a clean surface. Since both the HCl-ice binding energy and the ice cohesion energy are of the order of the hydrogen bond strength (≈ 20 kJ/mole), we expect these effects to be especially pronounced.

In this paper, based on previous experience, we argue that the adsorbate-induced effects may lead to the formation of quasi-liquid droplets [15], involving a local distortion (or even melting) of the ice lattice supplemented by the condensation of HCl molecules around the distorted domains. We take into account the dynamic nature of the ice surface, that is, the lattice sites are allowed to displace from their equilibrium positions, distorting in this way an ideal lattice arrangement. Then the binding energy of HCl at a given site should depend on the distortion amplitude. Dynamical effects are discussed within the harmonic approximation, which is known [17] to be quite reliable for the bulk ice-Ih. Application of these simple models together with order of magnitude estimations, based on experimental data, demonstrate that the formation of quasi-liquid droplets can be realized at stratospherically relevant conditions. Nevertheless, the distortion alone does not explain experimental results regarding coverage and adsorption energy. For that reason, our approach should be modified to include a solvation mechanism.

2. Single-site approach

The surface of ice is modelled as a planar honeycomb lattice of N adsorbing sites whose equilibrium positions are given by the set $\{\mathbf{R}_i^0\}$. More precisely, we associate the lattice with the arrangement of oxygen atoms. The lattice is taken as non-rigid, that is the sites are allowed to deviate from their equilibrium positions (for instance, due to vibration at non-zero temperatures, or dynamic distortion). We consider the displacements $\mathbf{u}_i = \mathbf{R}_i - \mathbf{R}_i^0$, where $\mathbf{R}_i$ is a vector specifying the site location. To provide an adequate lattice dynamics calculation we have to take into account the random heterogeneity of the force constants [18]. As we only focus on certain dynamic aspects, it is sufficient to consider a single-site approach, capable of recovering the mean square displacements with a reasonable choice of the effective rigidity coefficient. Thus the surface of ice is described by the effective Hamiltonian

$$H_I = \frac{\gamma}{2} \sum_i \mathbf{u}_i^2 \,, \tag{1}$$

where γ is the rigidity coefficient determining the mean square displacement (or the lattice distortion)

$$\delta_0^2 = \langle \sum_i \mathbf{u}_i^2 \rangle / N = kT/\gamma. \tag{2}$$

Here $\langle ... \rangle$ denotes thermodynamic averaging. This Gaussian form can be taken as a mean-field limit of the harmonic approximation [17] used for the description of the lattice dynamics of ice. By introducing such an approach we underestimate the pair correlations and neglect the heterogeneity [18] in the force constants. Nevertheless, our model gives a reasonably good agreement with the lattice dynamics calculations. In particular, at $T = 190$ K, the mean square displacement for the ice bulk is [19] $\delta_0^2 = 0.0083$ Å^2, which is consistent with experimental data. To recover this value (using equation (2)) we have to assume $\gamma = 1.97$ eV/Å^2, which is in the range between the weaker (1.1 eV/Å^2) and the stronger (2.1 eV/Å^2) intermolecular stretching force constants [19] used in the lattice dynamics calculations of the ice-Ih bulk.

The lattice is in contact with a fluid of HCl that occupies the half-space above the surface. An HCl molecule is modelled as a hard sphere with a point-like sticky site, that may bind with the lattice sites. Therefore, the interaction of HCl molecules with the surface is described by the lattice gas Hamiltonian

$$H = \frac{W}{2} \sum_{ij} t_i t_j - \sum_i (\mu + \epsilon_0 + \epsilon(\mathbf{u}_i)) t_i, \tag{3}$$

where W is the pair interaction between the two adsorbed nearest neighbour HCl molecules and μ is their chemical potential. The set of occupation numbers $t_i = 0, 1$ controls the distribution of adsorbates at the lattice sites. As it was shown in our earlier works [13,14], such a Hamiltonian can be obtained, by integrating out the fluid bulk. In this way, W and $\mu + \epsilon_0 + \epsilon(\mathbf{u}_i)$ are related to the mean force potential and the density profile in the fluid, respectively. The binding energy ϵ_0 corresponds to a lattice "frozen" at equilibrium (rigid lattice). This case corresponds to the conditions studied by Kroes and Clary [2]. In addition, we have a term, $\epsilon(\mathbf{u}_i)$, which depends on the lattice distortion.

$$\epsilon(\mathbf{u}_i) = \frac{\epsilon}{2}\mathbf{u}_i^2 + \dots . \tag{4}$$

The expansion above implies that $\epsilon(\mathbf{u}_i)$ is an isotropic function. To proceed further we have to decide on whether $\epsilon(\mathbf{u}_i)$ increases or decreases with $\mathbf{u}_i$. A recent theoretical study [20], which allowed HCl to vibrate, gave an adsorption energy (roughly, the average binding energy) of 25 kJ/mole, which is about 6 kJ/mole larger than that for a rigid HCl model. We may expect a similar increase, if the lattice of ice is not rigid. Also, we argue that ϵ_0 does not correspond to a maximum, because of the quite limited ability of the Cl atom to interact with the surface. A distortion of the oxygen lattice may distort the HCl-ice hydrogen bonds, reducing the distance between a Cl atom and the surface and allowing for a larger binding energy. Based on this, we assume $\epsilon > 0$. Of course, such a mechanism cannot give an unlimited gain in the binding energy. If the distortion is too strong, then it may break the hydrogen bonds between HCl and ice. This can be reproduced by taking additional terms in the expansion (4). Instead of doing so, we retain the quadratic approximation, keeping in mind its restricted validity ($|\mathbf{u}_i| \leqslant u_{\max}$). On the other hand, we have to keep $\epsilon < \gamma$, in order to avoid instabilities because of the Gaussian approximation of the lattice displacements. The free energy, in the mean field approximation (MFA) for the occupation numbers, is given by

$$\Phi = \frac{\beta F}{N} = \frac{\beta F_I^0}{N} - \frac{3\beta W\Theta^2}{2} - \ln\left(1 + \frac{1}{1-\epsilon/\gamma}\mathrm{e}^{\beta(\mu+\epsilon_0-3W\Theta)}\right), \tag{5}$$

where F_I^0 is the lattice free energy at zero coverage and $\beta = 1/kT$. Minimizing Φ with respect to Θ, we obtain the equilibrium coverage

$$\Theta = \frac{1}{N}\sum_i \langle t_i \rangle = \frac{\frac{1}{1-\epsilon/\gamma}\mathrm{e}^{\beta(\mu+\epsilon_0-3W\Theta)}}{1 + \frac{1}{1-\epsilon/\gamma}\mathrm{e}^{\beta(\mu+\epsilon_0-3W\Theta)}}. \tag{6}$$

For a rigid lattice ($\epsilon = 0$, $\epsilon_0 = 20$ kJ/mole) and at stratospherically relevant conditions ($p_{\mathrm{HCl}} = 10^{-7}$ Torr, $T = 190$ K) equation (6) gives $\Theta = 4.3 \cdot 10^{-8}$, which is exactly of the same order of magnitude as in the simulation [2]. It is clear that Θ increases as $\epsilon/\gamma \to 1$, since the effective binding energy

$$E = \epsilon_0 + kT \ln\left[1/(1-\epsilon/\gamma)\right] \tag{7}$$

grows with ϵ/γ. This gives a shift of the adsorption isotherm towards lower pressures (see figure 1). This, in turn, gives a larger adsorption energy than that corresponding to a rigid lattice. To demonstrate this we rearrange equation (6) to the conventional form [21], involving the free energy of adsorption ΔG

$$\mathrm{e}^{-\beta\Delta G} = \mathrm{e}^{\beta(E-3W\Theta)}\frac{\Theta}{1-\Theta}. \tag{8}$$

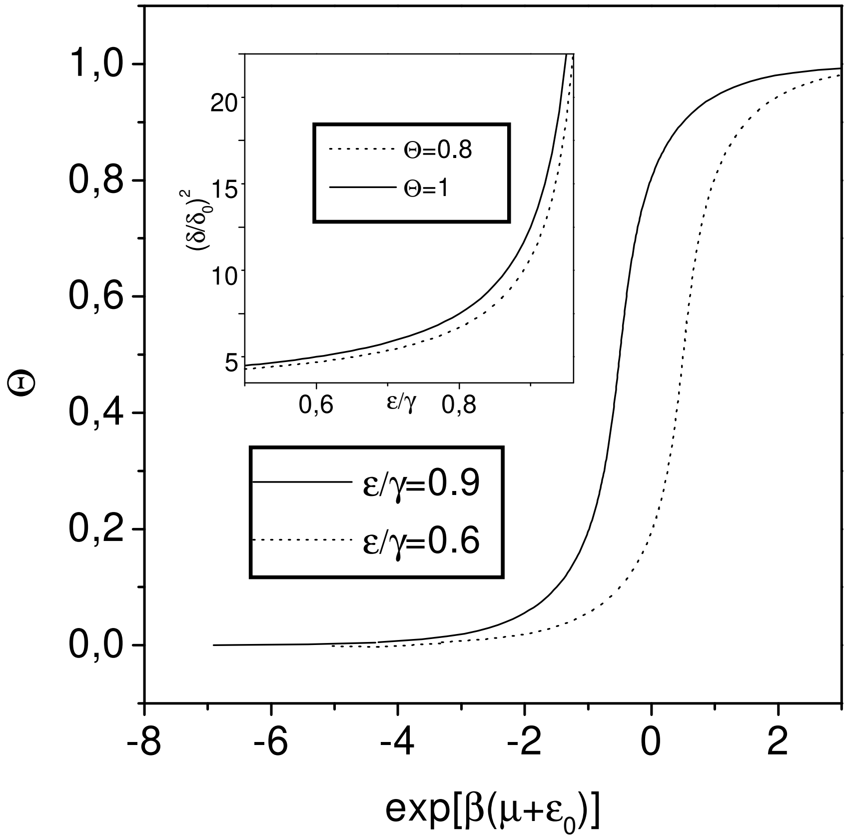

Figure 1. Coverage, calculated at $W = 0$, as a function of the dimensionless pressure $P = \exp[\beta(\mu + \epsilon_0)]$ (single-site approach). Relative mean square displacement $(\delta/\delta_0)^2$ as a function of ϵ/γ is shown in the inset. Stratospheric conditions ($T = 190$ K, $p_{\mathrm{HCl}} = 10^{-7} - 10^{6}$ Torr, $\epsilon_0 = 20$ kJ/mole) correspond to $P = 4.3 \cdot (10^{-8} - 10^{-7})$.

The so-called standard value ΔG_0 (calculated at $\Theta = 1/2$) is then proportional to the binding energy $\Delta G_0 = -E + 3W/2$. If we neglect the lateral interaction W between HCl molecules, then E is a measure of the adsorption free energy. The distortion implies an increase in the coverage up to $\Theta = 4 \cdot 10^{-6}$ (at $\epsilon/\gamma = 0.99$), which is still too far from the experimental results $\Theta \approx 0.4 - 0.8$.

Taking a derivative of Φ with respect to γ and using the result (2) for δ_0^2, we obtain the coverage-dependent mean square displacement of the lattice

$$\delta^2 = \delta_0^2 \left[1 + \frac{\epsilon/\gamma}{1 - \epsilon/\gamma} \Theta \right] \tag{9}$$

increases with increasing ϵ (the inset in figure 1). The mean square displacement is closely related to the Lindemann parameter $L = \sqrt{\delta^2}/d$, which is a semiempirical measure of melting. Recall that the Lindemann criterium states that a crystal melts when $L \approx 0.1$, where d is the equilibrium lattice spacing. The equilibrium spacing in the bulk ice is $d = 2.76$ Å (at $T = 190$ K). Thus, to match the Lindemann criterium, we must have $\delta = 0.276$ Å. Returning to equation (9) we see that this is the case when $\delta/\delta_0 = 3.03$. The latter occurs when $\epsilon/\gamma = 0.91$ and $\epsilon/\gamma = 0.89$ for $\Theta = 0.8$ and $\Theta = 1$, respectively. Therefore, if the gain in the binding energy ϵ becomes comparable with the rigidity coefficient γ, then the ice surface is driven towards melting (provided that we know how to explain $\Theta \approx 1$). It is instructive to calculate the molar energy excess ΔE due to the lattice distortion

$$\Delta E = \langle E - \epsilon_0 \rangle = \frac{\epsilon}{2} N_{\mathrm{A}} \delta^2. \tag{10}$$

For $\epsilon = 1.95$ eV/Å^2 and $\delta = 0.276$ Å we obtain $\Delta E = 7.23$ kJ/mole. Then the total energy $E \approx 28$ kJ/mole, which is far below the experimental data (46 kJ/mole). Our estimation is closer to the result [20] (25 kJ/mole), obtained when the HCl molecules were allowed to vibrate. Based on this we may conclude that the distortion energy is not enough to explain experimental values for both coverage and adsorption energy. Nevertheless, this does not mean that the distortive mechanism should be abandoned. Simply, the adsorbate-induced distortion is not the only effect. If the mean square displacements of oxygen sites become large enough, then an adsorbed HCl molecule is found in a quasi-liquid environment [4] that may facilitate its dissociation. The latter is beyond the scope of our simple model. However, the model does explain how such distorted (or quasi-liquid) domains may appear at stratospherically relevant conditions.

3. Dynamic effects

In the previous section we neglected the pair correlations. For that reason we were not able to determine the extent of the distorted domains. It is known [22] that an indirect (through the substrate) interaction between the adsorbates is inversely proportional to the substrate shear modulus. Therefore, pair-wise effects should become quite important with increasing distortion. We keep the same model for the lattice and HCl molecules, but now the ice Hamiltonian is given by the following harmonic approximation

$$H_I = \sum_{ij} D_{ij} (\mathbf{u}_i - \mathbf{u}_j)^2, \tag{11}$$

where D_{ij} is the force constant (or elastic) matrix. The HCl-HCl pair interaction is represented by the expansion

$$W(\mathbf{R}_i, \mathbf{R}_j) = W + \Delta_{ij} (\mathbf{u}_i - \mathbf{u}_j)^2 + \ldots, \tag{12}$$

where W is the pair interaction between two HCl molecules, adsorbed at the equilibrium positions of the ice lattice. The second term corresponds to the interaction,which is mediated by the lattice distortion. For simplicity, we drop the linear term, by assuming that the equilibrium lattice spacing is close to an extremum of $W(|\mathbf{R}_i - \mathbf{R}_j|)$, such that, Δ_{ij} represents the curvature of the HCl mean force potential, calculated at distances of the order of the equilibrium lattice spacing. Therefore, the adsorption of HCl is described by the lattice gas model

$$H = \sum_{ij} [W + \Delta_{ij} (\mathbf{u}_i - \mathbf{u}_j)^2] t_i t_j \,, -(\mu + \epsilon_0) \sum_i t_i \tag{13}$$

in which the lateral HCl interaction is coupled to the lattice distortion. As we are interested in estimating the difference due to this additional interaction, it is reasonable to apply a perturbative technique, developed in our previous studies [15,16]. Choosing a system with $\Delta_{ij} = 0$ as reference and performing a summation over $\{t_i\}$ we obtain the following effective Hamiltonian for the displacements

$$H_{\rm ef} = \sum_{ij}[D_{ij} + \chi_{ij}\Delta_{ij}](\mathbf{u}_i - \mathbf{u}_j)^2, \tag{14}$$

where $\chi_{ij} = \langle t_i t_j\rangle - \langle t_i\rangle\langle t_j\rangle \approx \xi^2 \exp(-R_{ij}/\xi)$ is the adsorbate correlation function and ξ is the correlation length. It is now clear that the range of the adsorbate-induced perturbation is of an order of the adsorbate correlation length. The latter determines an average size of the distorted domains, as mentioned in the previous section. The Hamiltonian (14) allows us, at least in principle, to explore all the lattice dynamic aspects. Instead of doing so, we restrict ourselves by an order of magnitude estimation to determine the conditions under which quasi-liquid droplets may be formed. Clearly, everything depends on the symmetry of the D_{ij} and Δ_{ij} matrices and on the magnitude of their elements. Also, the range and symmetry of χ_{ij} plays a role. If the HCl gas is correlated at distances much larger than the lattice spacing, then the correlation function may be replaced by a number proportional to ξ^2. Fourier transformation allows one to diagonalize the Hamiltonian (14). This gives a dispersion law. At small wave vectors $\mathbf{k}$, the frequency splits according to the splitting of the dynamic matrix

$$D(\mathbf{k}) + \xi^2\Delta(\mathbf{k}) \rightarrow \Omega(\mathbf{k}) = \omega_0(\mathbf{k}) + \xi^2\omega_1(\mathbf{k}), \tag{15}$$

where $\omega_0(\mathbf{k})$ is the frequency spectrum of the pure ice lattice, while $\xi^2\omega_1(\mathbf{k})$ gives the shift due to the adsorbate-induced effects. To estimate the mean square displacement δ^2 we use the so-called flat spectrum approximation $\Omega(k) = \Omega \propto D + \xi^2\Delta$, in which the collective frequency $\Omega(k)$ for a given mode is replaced by an effective one-body frequency Ω. Then we obtain

$$\delta^2 = \frac{\delta_0^2}{1 + \xi^2\Delta/D}. \tag{16}$$

It is seen that δ^2 increases with ξ^2 when Δ is negative. Then we are restricted to $\xi^2\Delta/D < 1$ in order to keep the stability of $H_{\rm ef}$. Therefore, the surface of ice is strongly distorted when the HCl-HCl interaction becomes more attractive due to the coupling through the ice substrate. Conditions at which an indirect interaction between the adsorbates is attractive are extensively discussed in [22]. Note, however, that $W(\mathbf{R}_i, \mathbf{R}_j)$ is a mean force potential for HCl, so that an additional attraction through the gas phase may exist [13,14]. However, the distortion is not monotonic with the coverage, since $\xi^2 \propto \Theta(1-\Theta)$. The maximum is at $\Theta = 1/2$, that is, when the strongest density fluctuations in the adsorbate take place [15].

Using the same perturbative technique we calculate the coverage

$$\Theta = \frac{\mathrm{e}^{\beta(\mu+\epsilon_0)}\mathrm{e}^{-3\beta[W+\Delta\delta^2]\Theta}}{1 + \mathrm{e}^{\beta(\mu+\epsilon_0)}\mathrm{e}^{-3\beta[W+\Delta\delta^2]\Theta}}, \tag{17}$$

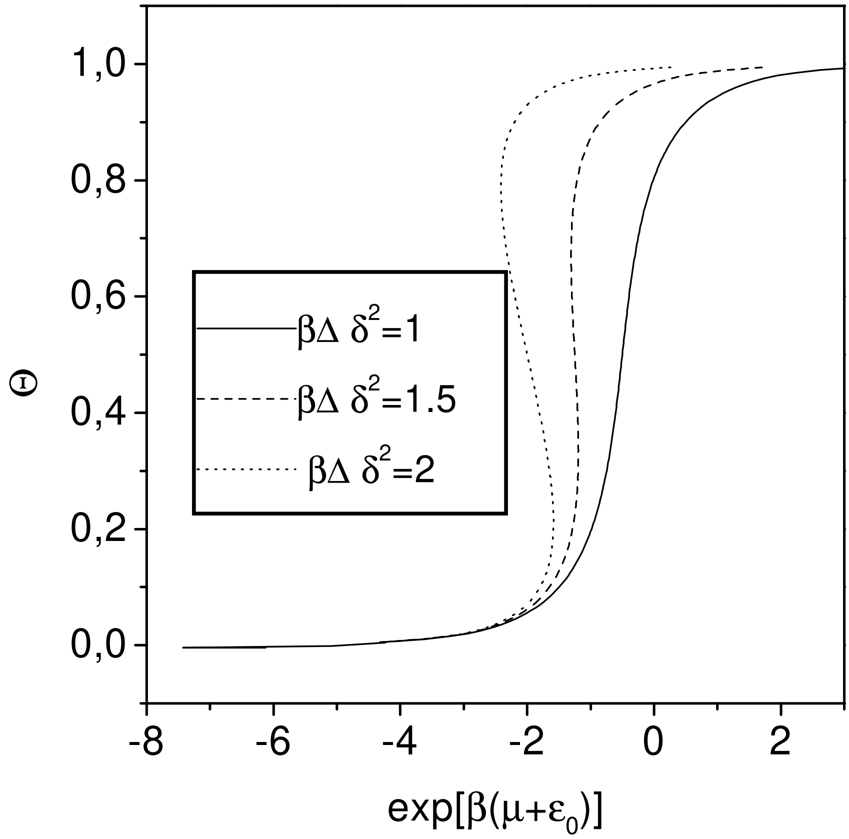

Figure 2. Coverage, calculated at $W = 0$, as a function of the dimensionless pressure $P = \exp[\beta(\mu + \epsilon_0)]$ (pair approach) at different $\beta\Delta\delta^2$. Other parameters are the same as for the previous figure.

where we have replaced δ_0^2 by δ^2 in order to correct our approximate treatment. As is seen in the figure 2, the coverage increases with increasing distortion, provided that $\Delta < 0$. The adsorption isotherms exhibit a liquid-gas coexistence when the interaction parameter $\beta\Delta\delta^2$ increases. This implies a droplet formation for the adsorbate around the distorted lattice domains. To observe this effect at stratospheric conditions ($P = \mathrm{e}^{\beta(\mu+\epsilon_0)} = 4 \cdot 10^{-8}$) we have to accept an unphysically large distortion. Nevertheless, we were able to obtain a reasonably high coverage out of the critical regime. For instance, $\Theta = 1/2$ can be achieved if $N_{\mathrm{A}}\Delta\delta^2 \approx 4.74$ kJ/mole. For a distortion amplitude $\delta = 0.276$ Å, satisfying the Lindemann criterium, this corresponds to $\Delta = 2.4$ eV/Å^2 (that is $\Delta \approx D$). The total binding energy (25 kJ/mole) is still below the experimental value. As is discussed above, we have to incorporate a solvation mechanism in order to remove this discrepancy.

4. Conclusion

In this paper an adsorbate-induced mechanism of the ice lattice distortion is suggested. It is shown that the adsorption of HCl molecules at the surface of ice increases, if either the HCl binding energy or the HCl-HCl attraction increase with increasing distortion amplitude for the oxygen sites of ice. Simultaneously, the adsorption stimulates an increase of the Lindemann parameter for the ice lattice, driving its local melting at temperatures ($T = 190$ K) relevant to the polar stratosphere. This may cause the ionization of HCl, since the local coordination of HCl-water complexes increases with the lattice distortion. The range of the distorted domains is shown to be comparable with the adsorbate correlation length. The coverage varies from $\Theta \approx 10^{-6}$ to $\Theta \approx 1/2$ for a realistic choice of the parameters. The adsorption energy is estimated to be about 28 kJ/mole, that is, below the experimental results. This discrepancy is attributed to the neglect of HCl solvation upon adsorption.

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Адсорбційно індуковане спотворення поверхні твердого тіла. Застосування до адсорбції HCl на льоді при стратосферних умовах

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Показано, що адсорбція молекул HCl на поверхню льоду зростає, якщо зростає енергія зв'язку молекул HCl при збільшенні амплітуди спотворення кисневих вузлів льоду. В той же час адсорбція стимулює зростання параметра Ліндемана для гратки льоду, приводячи до її плавлення при температурах ($T = 190$ K), відповідних до полярної стратосфери. Подібні ефекти спостерігаються, коли латеральна взаємодія між молекулами HCl стає більш притягальною внаслідок з'єднання через гратку льоду.

Ключові слова: *адсорбція HCl на льоді, двовимірний гратковий газ, спотворення гратки, поверхневе плавлення*

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