Physical adsorption in porous glasses

Volodymyr Ovechko, Andriy Dmytruk, Valentyna Mygashko

Radiophysical Faculty, Kyiv National Taras Shevchenko University, Academician Glushkov Prosp., 6, Kyiv, 03127, Ukraine.

We have presented the results of our investigation concerning adsorption in porous glass (PG). Chemical adsorption of gas molecules is due to indicator substances which were deposited from solution on the surface of pores. Physical adsorption of organic molecules is due to OH-adsorption centres which are always arranged on the surface of PG at room temperature. Adsorption processes were investigated with infrared spectroscopy.

Keywords: porous glass, physical adsorption, vibration spectroscopy.

1. Introduction

The base of PG matrix is composed of oxide-silicon tetrahedrons SiO_4 ($d \cong 0.16$ nm, $\varphi = 109°$). Amorphous matrix consists of tetrahedrons that have random orientation. The most stable orientation corresponds to the longest distance between Si atoms. This is the orientation in which neighbouring tetrahedrons have one common oxygen atom. On the surface of PG there are two types of Si–atoms: single qualifier tie Si–O and double one $Si <^O_O$. After the interaction with H_2O molecules these ties form hydroxyl groups: single Si–OH and geminal $Si <^O_O$. In the first case a distance betwen hydroxyl groups is about 5 Å, in the second one about 2.5 Å. The latter is suitable to form H bonds. IR spectra [1], [2] and NMR data [3] confirm this model of adsorption centers on the surface of PG.

2. Oscillator model of physical adsorption

It is necessary to consider more closely the way molecule forms bonds with OH-center in PG. The energy of physical adsorption is much lover than chemical bounding of OH groups with PG matrix. Molecular complex can be represented as two relatively independent parts which are bonded by weak Van der Waals forces. The energy of nonpeculiar Van der Waals interactions involves orientation, induction and dispersion potentials [4]. Common properties of these interactions are their electromagnetic origin and identical dependences of energy on intermolecular distance. Taking into consideration the additive property of Van der Waals energy and its correlation nature,

we can write potential energy of complex adsorbate molecule–adsorbent complex (for short adsorbate–adsorbent) in harmonic approximation

$$U(q_1; q_2; q_3...q_n; \theta_{12}; \theta_{1i}; \theta_{2i}) = k_{11}q_1^2 + \sum_{i \geq 3} k_{ii}q_1^2 + k_{12}(q_1 - q_2)^2 \tag{1}$$

$$+ \sum_{i \geq 3} k_{1i}(q_1 - q_i\cos\theta_{1i})^2 + \sum_{i \geq 3} k_{2i}(q_i\cos\theta_{2i} - q_2)^2$$

where q_1, q_2, q_i – stretching coordinates of OH group, adsorbate–adsorbent and adsorbent, respectively, k_{ij} – force constants, and $\theta_{12} = (\overline{q_1}, \overline{q_2})$, $\theta_{1i} = (\overline{q_1}, \overline{q_i})$, $\theta_{2i} = (\overline{q_2}, \overline{q_i})$.

We place $\theta_{12} = 0°$ in Eq. (1) because this value corresponds to the maximum of interaction [5]. Then we have to average Eq. (1) over θ_{1i}, θ_{2i} angles because Van der Waals forces are not directional as in case of chemical ones. Then

$$\langle U \rangle = q_1^2\left(k_{11} + \sum_{i \geq 3} k_{1i} + k_{12}\right) + q_2^2\left(k_{12} + \sum_{i \geq 3} k_{2i}\right) + \sum_{i \geq 3} q_i^2\left(k_{ii} + \frac{1}{2}k_{1i} + \frac{1}{2}k_{2i}\right).$$

It may be deduced from the last formula that the molecule–adsorbent interaction results in force constants reduction and formation of a new oscillator. The harmonic approximation potential and kinetic energy have standard expressions:

$$U(q_j) = \frac{1}{2}\sum_j A_j q_j^2, \tag{2}$$

$$T(\dot{q}_j) = \frac{1}{2}\sum_j C_j \dot{q}_j^2, \tag{3}$$

$$A_1 = 2\left(k_{11} + \sum_{i \geq 3} k_{1i} + k_{12}\right), \tag{4}$$

$$A_2 = 2\left(k_{12} + \sum_{i \geq 3} k_{2i}\right), \tag{5}$$

$$A_j = 2\left(k_{jj} + \frac{1}{2}k_{1j} + \frac{1}{2}k_{2j}\right), \quad j \geq 3 \tag{6}$$

where C_j are kinematic constants.

Relations (2)–(6) can be simplified if we assume that the force constants of this intermolecular interaction are much lower than the ones inside the molecule. Then we can write the approximate formulae for frequency shifts for the adsorbent $\Delta\omega_1$, adsorbate molecules $\Delta\omega_{2j}$ and normal vibration of the adsorbate–adsorbent complex ω_2

$$\Delta\omega_1 = \omega_1 - \omega_{01} = \omega_{01} \frac{k_{12} + \sum k_{1i}}{2k_{11}}, \tag{7}$$

$$\Delta\omega_j = \omega_j - \omega_{0j} = \omega_{0j} \frac{k_{1j} + \sum k_{2j}}{4k_{jj}}, \tag{8}$$

$$\omega_2 = \left[\frac{2}{C_{22}} \left(k_{12} + \sum_{j \geq 3} k_{2j} \right) \right]^{1/2} \tag{9}$$

where ω_{01}, ω_{0j} are eigenfrequencies of the adsorbent centers and molecules in free states, and

$$\omega_{01} = \sqrt{\frac{2k_{11}}{C_{11}}}, \qquad \omega_{0j} = \sqrt{\frac{2k_{jj}}{C_{jj}}}.$$

From Eqs. (7)–(9) and equilibrium condition $k_{12} + \sum k_{2i} = 2\sum k_{1i}$ one can get

$$\omega_2 = \left[\frac{1}{C_{22}} \left(\frac{\Delta\omega_1}{\omega_{01}} 2k_{11} + 4\sum_{j \geq 3} \frac{\Delta\omega_j}{\omega_{0j}} k_{jj} \right) \right]^{1/2}. \tag{10}$$

The last formula can be written as a function of frequencies and kinematic constants

$$\omega_2 = \left[2\frac{C_{11}}{C_{22}} \left(\frac{1}{2}\Delta\omega_1\omega_{01} + \sum_{j \geq 3} \Delta\omega_j\omega_{0j} \right) \right]^{1/2}. \tag{11}$$

This formula shows the eigenfrequency ω_2 of the complex.

Let us suppose that oscillator ω_2 can be represented by Morse potential with the unharmonic coefficient χ_2. Then dissociation potential

$$D_e = \varepsilon_V^{max} - \varepsilon_0 = \frac{\hbar\omega_2}{4\chi_2} (1 - \chi_2)^2. \tag{12}$$

This value can be presented as potential of adsorption.

3. Experimental

Theoretical value of D_e for an ammonia molecule was calculated taking into consideration two stretch modes for NH_3 ($\omega_{03} = 3444$ cm^{-1}, $\omega_{04} = 3337$ cm^{-1}) and measured spectral shifts ($\Delta\omega_3 = 34$ cm^{-1}, $\Delta\omega_4 = 30$ cm^{-1}, $\Delta\omega_1 = 675$ cm^{-1}) – see the Figure. The substitution of these data into Eq. (11) gives value $\omega_2 = 418$ cm^{-1}. We consider $C_{11}/C_{22} = 17$, $\omega_{01} = 3750$ cm^{-1} in this calculation. Substitution of ω_2 into
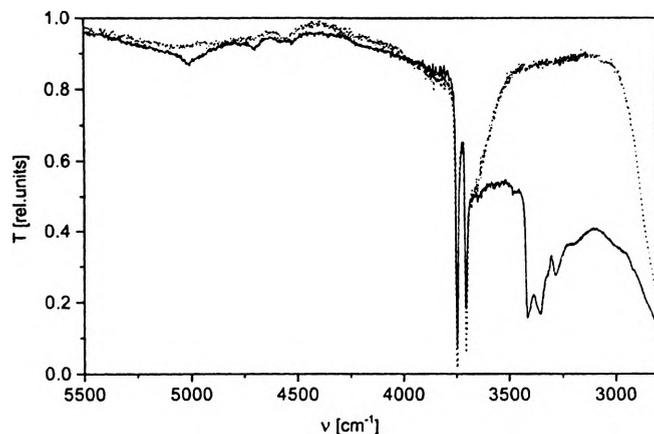
Figure. Panoramic absorption spectrum of adsorbed ammonia (——) and clear PG (-----).

Eq. (12), assuming $\chi = 0.022$ for H nucleus, leads to the dissociation potential (or adsorptive energy) $D_e = 4560$ cm^{-1} = 54.6 kJ/moll. One can compare this value with the reported ones (52 kJ/moll [5]). A qualitative agreement between the theory and experiment is a reasonable one.

4. Summary

The physical adsorption of molecules NH_3 on the surface of PG was studied by means of IR spectroscopy in order to state connection between frequency shifts of normal vibration modes and stretch frequency of molecule–adsorbent bond. Oscillator model of physical adsorption, which takes anharmonicity of vibration of molecule–adsorbent bond into account, enables to make theoretical estimation of adsorption energy. The energy of adsorption was found in good agreement with known microcalorimetry data for NH_3 molecule.

References

[1] OVECHKO V.S, DMYTRUK A.M, MYGASHKO V.P, MULENKO S.A., Vib. Spectrosc. **22** (2000), 87.
[2] BOLIS V., BUSCO C., BORDIGA S., UGLIENGO P., LAMBERTI C., ZECCHINA A., Appl. Surf. Sci. **196** (2002), 56.
[3] KISELEV V., KOZLOV S., ZOTEEV A., *Basic of Physics of Solid State Surface*, Moscow Univ. Print, 1999 (in Russian).
[4] HOBZA P., ZAHRADNIK R., *Intermolecular Complexes*, Academia, Prague 1988, p. 376.
[5] ROGGERO I., CIVALLERI B., UGLIENGO P., Chem. Phys. Lett. **341** (2001), 625.