Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 148 (2015) 271–279

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Effect of resonance dipole–dipole interaction on spectra of adsorbed SF_6 molecules

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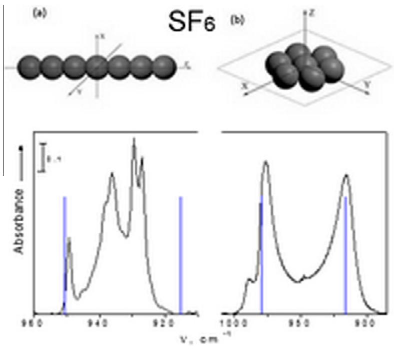
HIGHLIGHTS

- Spectra of adsorbed SF_6 depend on the mutual arrangement of interacting molecules.
- Adsorbed molecules form an one-dimensional (1D) and two-dimensional (2D) systems.
- The dynamic interaction (RDDI) is manifested as the doublet spectral band structure.
- Components correspond to transversal and longitudinal vibrations of dipole moment.
- Maximal RDD splitting between components for 1D chains is smaller than for 2D flat.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 January 2015
Received in revised form 1 April 2015
Accepted 5 April 2015
Available online 11 April 2015

Keywords:
Dipole–dipole interaction
Dynamic interaction
SF_6
Adsorption
ZnO
Silicalite

ABSTRACT

Adsorption of SF_6 on zinc oxide and on silicalite-1 was investigated by a combination of IR spectroscopy with the calculations of spectra by means of a modernized model, developed previously for liquids. Comparison of the experimental spectra and the results of modeling shows that the complex band shapes in spectra of adsorbed molecules with extremely high absorbance are due to the strong resonance dipole–dipole interaction (RDDI) rather that the surface heterogeneity or the presence of specific surface sites. Perfect agreement between calculated and observed spectra was found for ZnO, while some dissimilarity in band intensities for silicalite-1 was attributed to complicated geometry of molecular arrangement in the channels.

Introduction

Lateral interactions, studied in detail by IR spectroscopy for CO adsorbed on metals [1,2] and oxides [3–5], affect greatly the adsorption and catalytic properties of solid surfaces. The method of isotopic dilution enables us to distinguish two kinds of interactions: static effect and the dynamic interaction, referred also as resonance dipole–dipole interaction (RDDI) or dipole coupling. The former influences the energy of adsorption and the observed strength of surface sites and often determines the geometry of adsorbed layer. It can be attractive and lead to 2D islands formation [2], or repulsive, then it prevents occupation of the nearest neighboring sites and promotes the formation of domains with

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http://dx.doi.org/10.1016/j.saa.2015.04.002
1386-1425/

ordered structures on the low-index faces of crystals [6]. The latter kind of interaction, the RDDI, does not change chemical or most of physical characteristics of the adsorbed layer, but it modifies the positions, shapes and widths of absorption bands in the spectra of surface species. If the frequencies of adsorbed probe molecules are used as a measure of the strength of surface sites, whose concentration is reflected in the band intensities, RDDI distorts this information. It accounts also for the vibrational energy exchange in the adsorbed layers and cannot be neglected when considering the dynamics of resonance excitation or the energy dissipation processes.

The theory of RDDI in adsorbed layers was first developed by Hammaker et al. [7] to explain the spectra of CO adsorbed on Pt. They considered a layer of regularly arranged dipoles, included the energy of interaction into the Hamiltonian and obtained the solution of vibrational problem, which explained the frequency shift to higher wavenumbers. But to achieve the quantitative agreement the model had to be modified by taking into account the image dipoles induced by the surrounding molecules under the metal surface [8] and interaction of the molecule with its own image [9], as well as the increase of vibrational polarizability of adsorbed molecules [10]. For oxides the observed dynamic shift was also greater than that one predicted by the model [11], despite the decrease of α_v corresponding to lowered integrated adsorption coefficient [12]. This means that the role of the surface is not restricted to fixation of mutual arrangement of molecules at the surface, but the solid itself participates in the interaction, enhancing it.

Up to now, the dynamic interaction has been observed mostly for CO molecules somehow oriented with respect to the flat surface of crystals. It was shown, however, that complex band shapes in the spectra of such symmetric molecules as SF_6 and CF_4 in liquid or dissolved state can be explained by RDDI [13–16]. These molecules have extremely high integrated absorption coefficient of the asymmetric stretching vibration ν_3, and one could anticipate the manifestations of RDDI in adsorbed state. Adsorption of SF_6 on graphite was investigated by Hess et al. [17] at 80–170 K. In their model molecules were considered as dipoles oriented normally to the surface. Only one band was observed in the spectrum, shifted from band position in gas phase to higher wavenumbers, the frequency shift being enhanced due to the conductivity of graphite.

The aim of this work was to find out the manifestations of the RDDI in the spectra of SF_6 adsorbed on the surface of oxide adsorbents with different geometry of the surface and to provide a new insight into the structural aspects of studied systems, comparing the observed spectra with those calculated by means of a model previously developed for liquids and modernized here for molecules adsorbed at interfaces. Two systems were chosen in this study: zinc oxide and silicalite-1. ZnO has a wurtzite-type structure with predominating flat plots of $(10\bar{1}0)$ faces, where the cations and anions are arranged in a rectangular 2D lattice. Unlike it, the surface of silicalite silica modification with ZSM-5 structure is presented by a framework of channels with maximal diameter of 6.3 Å. As far as the size of SF_6 molecule is 5.13 Å [18], the adsorbed molecules can fill the silicalite channels forming a sort of 1D chains. Thus, two variants of mutual arrangement of SF_6 molecules depending on the kind of adsorbent will be considered: (i) 2D structure of adsorbed layer on the flat surface, and (ii) 1D chain-like structure that had to reproduce the filling of silicalite channels with the adsorbed molecules. For comparison, spectra of solid films of SF_6 on cell windows were also obtained. The latter can be considered as three-dimensional (3D) system of interacting molecules.

Experimental and calculation procedures

Experimental measurements

Batches of ZnO or SiO_2 (silicalite-1) powders for spectral studies were pressed into thin pellets (17–30 and 2–10 mg cm^{-2}, respectively). The samples were preliminarily heated in vacuum (residual pressure $< 10^4$ Torr) for 1 h inside the IR cell, described elsewhere [19], at 723 or 773 K for ZnO and at 773 K for SiO_2. After thermal activation of the samples the cell was cooled by liquid nitrogen and 0.2–0.3 Torr of He gas was let into the sample compartment to improve thermal contact between the pellet and the coolable part of the cell.

After recording the initial spectrum of the cold sample a dose of SF_6 was introduced into the cell and was frozen upon the cold walls of it. Then liquid nitrogen was removed and the temperature of the inner part was raised until the bands of adsorbed SF_6 arose and grew, and the pressure increase indicated that the excess of adsorbate appeared in the gas phase. The cell was then cooled again and a series of IR spectra was recorded at different coverage of the samples at 77 K. For that, the sample was moved upwards to the warmer part of the cell for progressively increasing time and temperature. The desorbing molecules were trapped upon the cold walls and spectra of samples placed back between the windows showed the changes following the desorption.

For the quantitative estimations of surface coverages the amount of gas brought into contact with the sample was preliminarily measured in a special calibrated small volume. Alternatively, the pressure increase caused by desorption on moving the sample from the cold inner part of the cell to the quartz tube kept at ambient temperature was measured. Unfortunately, both the methods, successively applied for CO, were found not good enough for SF_6. In fact, after the bands of adsorbed SF_6 reached their maximum intensity on temperature increase up to about 130–140 K, further heating led to their decrease due to desorption evidenced by the appearance of the bands of gaseous adsorbate. Attempts to cool the cell quickly so that to fix the maximum coverage also resulted in the substantial decrease of the bands of adsorbed SF_6. Apparently, certain part of adsorbed molecules became trapped again on the cold walls of the cell. So, when using the former method we have to suppose that at certain temperature most of molecules are adsorbed, and cannot be sure that some part of them does not remain still trapped somewhere. Thus the coverage, measured in such a way, should be considered as the upper estimate of it. The latter method is not much better, since as soon as the temperature in the cell is high enough, so that the pressure of desorbed gas is less than the saturating vapor pressure of SF_6, a great deal of adsorbate is already desorbed and the band of the remaining adsorbed species is superimposed with the strong absorption of gaseous molecules. These difficulties are the consequence of the low adsorption energy that in the case of SF_6 does not differ much from the heat of condensation.

During the experiments equilibrium gas pressure inside the cell was measured with Edwards Barocel 600 pressure gauges. One, for pressure range 0–10 Torr with the accuracy of 0.001 Torr was connected directly with the sample-containing central part of the cell. Another one for pressures up to 1000 Torr and accuracy 0.1 torr was placed in a separate dosing volume. For temperature measurements a thermocouple inserted into the coolant compartment close to the sample holder was used. FTIR spectra were recorded typically with 2 cm^{-1} resolution for ZnO and 1 cm^{-1} for silicalite, using a Nicolet 710 spectrometer with a coolable MCT detector. 128 scans were accumulated for each spectrum.