ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 6, pp. 1002–1003. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © V.B. Kopylov, K.A. Aleksandrov, E.V. Sergeev, 2007, published in Zhurnal Obshchei Khimii, 2007, Vol. 77, No. 6, pp. 910–911.

Influence of Silicon Coordination Surrounding on the Chemical Structure of Oxides

V. B. Kopylov, K. A. Aleksandrov, and E. V. Sergeev

Herzen Russian State Pedagogical University,
nab. r. Moiki 48b, St. Petersburg, 191186 Russia
e-mail: vladimir_kopylov@mail.ru

Received January 20, 2007

Abstract — A comparative analysis of structural features of SiO_2 polymorphic modifications was made by Raman, and high-resolution electronic spectroscopy. It was found that the presence of isolated Si–O, Si–Si, and O–O oscillators in the ground and electronically excited states is a characteristic feature of all the structures involving silicon atoms in oxygen tetrahedral coordination surrounding. It was shown that the increase in the silicon coordination number to six (stishovite) leads to a decrease in the extent of formation of electronically excited states due to removal of barriers to the relaxation of excitation energies. This conclusion is confirmed by the low-frequency shift of the fundamental absorption and by the disappearance of the high-frequency anomaly (Si–O) and characteristic lines of Si–Si oscillators.
DOI: 10.1134/S1070363207060072

The concept of orbital-deficient electronic interactions, hypervalent bonds [1], which rules out the efficient participation of extravalent *nd* orbitals of the central atom, corresponds in the best way to the electron-excessive character of *p*-element compounds, including oxides. The problem of the participation of these orbitals in bonding with ligands for atoms of main group elements was not solved unambiguously until recently. However, the modern viewpoint on the role of *nd* orbitals considers their participation to be negligible in most cases [1]. It concerns complexes of main group elements in the ground state. It is assumed that the participation of *nd* orbitals of the central atom in molecular orbitals can result from the interaction of the nonexcited configuration with electronically excited configurations in which *nd* orbitals are considerably populated [1]. This agrees with one of the concepts considering silica as an essentially distorted crystal in which a great number of ≡Si–O– bonds are broken [2]. However, this effect on the states of bonds was not found in SiO_2, which is one of the systems most important for scientific and technical practice.

The aim of this study was to determine the spectrum of bond states, including electronically excited states, in a series of samples of silicon oxides essentially differing crystal-chemically, including differences in the coordination polyhedra. In this study we used highly sensitive instruments of electronic spectroscopy (SF-56), including diffuse reflection spectroscopy (SF-26 with a PDO-5 diffuse reflection device), and various kinds of vibration spectroscopy: traditional, high-resolution (~0.01 cm^{-1}) IR (IKS-25M), Fourier (Chromex, the United States; Shimadzu-8400S), and Raman (Chromex Wisard 1200, the United States) spectroscopy. We studied the spectra of high-purity dispersed SiO_2: Aerosil (of grades A-300, A-175, and A-120), silica gel (KSK-2.5 grade), quartz glass and synthetic single-crystalline quartz wafers, coesite, and stishovite [3]. To obtain vibration spectra, dispersed samples were deposited on a thin film (polyethylene terephthalate, cellulose, and mica, L ~5 μm). The controlled surface density was 1–2 mg cm^{-2}. The spectra of samples were selected by digital compensation of the background signal.

A comparative analysis of the vibration spectra of amorphous and crystalline SiO_2 modifications, recorded at 298 K, shows that the characteristic feature of all the structures with oxygen tetrahedral surrounding of silicon is the presence of a high-frequency anormaly (~1230 cm^{-1}) corresponding to the ground state of isolated Si–O oscillators [4]. Transitions to electronically excited states of the monoxide are observed at 600–800 cm^{-1} [5]. The presence of intensive vibration transitions of isolated Si–Si oscillators in the ground ($^3\Sigma_g^+$, 505 cm^{-1}) and electronically excited states ($^3\Sigma_u^-$ 460 and 275 cm^{-1}) [5], along with the presence of molecular oxygen species, confirms the following scheme of redox processes: $n[SiO_2] \rightleftarrows n[SiO] + nO \rightleftarrows Si_n + O_{2n}$. The electronic transitions

(absorption bands) in the ranges 280–250 and 430–470 nm suggest the presence of local exciton-type electronic states. An increase in the silicon coordination number to six (stishovite) essentially changes the spectral pattern, with disappearance of the high-frequency anormaly and of characteristic lines of Si–Si bonds. The fundamental absorption band of Si–O–Si stretching vibrations, ν_{as} 1100 cm^{-1}, is shifted toward lower frequencies to 949–885 and 769–560 cm^{-1}, which is indicative of a decrease in the force constant of ≡Si–O–Si≡ bonds and suggests the contribution of highly excited states of isolated Si–O fragments [667 cm^{-1}, $^1\Sigma^+$; 949 cm^{-1}, $^3\Sigma^{(+)}$] with the excitation energy reaching 4–5 eV [5]. This fact is apparently responsible for the metastability of the stishovite structure. Examination of the molecular orbital schemes of the silicon–oxygen tetrahedron and octahedron constructed with the participation of 3*d* orbitals [6] shows that the electronic structure of the tetrahedron ($t_1^{nonbond}$, $3t_2$, e, $2a_1$) is characterized by a significant contribution of the d_π–p_π bonding. It increases the order of bonds and hampers the rotational, about the bond axes, relaxation of various excitations, including the excitation resulting from configuration interaction. In the octahedron, for which the set of nonbonding and bonding levels ($t_{1g}^{nonbond}$, $t_{2u}^{nonbond}$, $2t_{1u}$, $2t_{2g}$, e_g, and $2a_{1g}$) considerably exceeds that in the tetrahedron, σ bonds involving six electron pairs (sp^3d^2) predominate. Thus, the experiment and the electronic structure analysis show in conformity that the increase in the silicon coordination number in the oxide structure reduces the extent of formation of electronically excited states, apparently due to the absence of barriers on the way of nonradiating relaxation of the excitation energy and, as a consequence, due to the stabilization of ≡Si–O– bonds. Thus, the concept that silica has a strongly distorted structure with a large number of broken bonds is confirmed.

REFERENCES

1. Korol'kov, D.V., *Elektronnoe stroenie i svoistva soedinenii neperekhodnykh elementov* (Electronic Structure and Properties of Compounds of Main Group Elements), St. Petersburg: Khimiya, 1992.
2. Lisichkin, G.V., Kudryavtsev, G.V., Serdan, A.A., Staroverov, C.M., and Yuffa, A.Ya., *Modifitsirovannye kremnezemy v sorbtsii, katalize i khromatografii* (Modified Silica in Sorption, Catalysis, and Chromatography), Moscow: Khimiya, 1986.
3. Feltz, A., *Amorphe und glasartige anorganische Festkörper,* Berlin: Akademie, 1983.
4. Kopylov, V.B. and Pushkar', I.V., *Zh. Obshch. Khim.,* 2006, vol. 76, no. 10, p. 1597.
5. Huber, K.P. and Herzberg, G., *Constants of Diatomic Molecules,* Ottawa: Litton Educational, 1979.
6. Marfunin, A.S., *Vvedenie v fiziku mineralov* (Introduction to the Physics of Minerals), Moscow: Nedra, 1974.