UV irradiation-induced structural transformation in phosphosilicate glass

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Abstract

Raman spectra of optical fibers with core of P_2O_5–SiO_2 glass with P_2O_5 concentrations about 4, 9 and 12 mol%, manufactured using modified chemical vapor deposition (MCVD) technology were investigated. Significant changes of the spectra were observed after UV irradiation by KrF excimer laser (244 nm, 1 kJ cm^{-2}). An interpretation of the photostructural changes is proposed based on quantum chemical calculation of phosphorus-related centers. © 1999 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

Phosphorus is a dopant in high-purity silica glass used for fiber optics. It forms an optimal refraction index profile in fiber and modifies the viscosities of core and cladding of the fiber [1]. Phosphosilicate-core fibers have been used to develop Raman lasers [2]. Since phosphosilicate glass is photosensitive under UV irradiation near 190 nm [3], refractive index gratings can be formed immediately in these fibers [2]. The phosphosilicate glasses doped with rare-earth elements are considered to be a potential material for optical amplifiers, converters and sources of visible and near IR radiation [4].

The extent of knowledge of the structure and optical properties of P_2O_5–SiO_2 glasses is much less than about SiO_2 and P_2O_5 glasses. In Ref. [5]

the Raman spectra of glassy P_2O_5 (v-P_2O_5) were interpreted as due to phosphorus atoms forming three single bonds with three bridging oxygen atoms and one double bond with one nonbridging oxygen atom in a three-dimensional atomic network. IR absorption [6] and Raman scattering [7] have been measured in phosphosilicate glasses with various P_2O_5 concentrations.

Vitreous P_2O_5 is assumed to consist of O=PO_3 tetrahedra bound by their three vertices into three-dimensional atomic network with O=P and P—O bond lengths being 0.143 and 0.158 nm, respectively [8] (notice that the double- and single-bond lengths vary from 0.140 to 0.151 nm and from 0.157 to 0.160 nm, respectively in known crystalline forms of phosphorus oxide and molecules [9,10]). It seems reasonable to assume, as in Ref. [6], that in phosphosilicate glass the phosphorus atoms also form just such tetrahedra bound either with each other or with SiO_4 tetrahedra. Anyway, a typical feature of vibrational spectra of phosphorus oxide glasses is a vibrational band caused

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by stretching of the O=P double bonds in the O=PO$_3$ tetrahedra (1390 cm^{-1} in v-P$_2$O$_5$ and 1320 cm^{-1} in phosphosilicate glasses) [5–7]. Thus, the pentavalent fourfold coordinated phosphorus atoms, O=PO$_3$, are typical for these glasses. Though there is no direct experimental evidence of other forms of phosphorus in phosphosilicate glass, it is reasonable to assume that the phosphorus atoms could occur in the glass also as pentavalent fivefold coordinated atoms, PO$_5$, and as trivalent threefold coordinated atoms, PO$_3$. Besides it is conceivable that fourfold coordinated phosphorus atoms, PO$_4$, may replace silicon atoms in the regular silica glass host. Obviously, the charge states +1 and perhaps −1 of these centers are stable (if any) in v-SiO$_2$. The oxygen atoms bound with the phosphorus atom form bridging linkages either with silicon atoms or with other phosphorus atoms.

In Ref. [11] during investigation of photosensitivity of optical fibers with core of germanosilicate glass containing about 2 mol% of P$_2$O$_5$, the Raman scattering band near 1320 cm^{-1} was found to disappear after UV irradiation of the fiber. This change indicates that the structure around phosphorus atoms in glass does change. The Raman scattering in the 1320 cm^{-1} band in optical fibers with core of phosphosilicate glass not containing germanium decreases in amplitude after UV irradiations in these fibers as well. In this paper we present the results of such research and their interpretation on the basis of quantum-chemical calculation of phosphorus centers in the phosphosilicate glass with approach successfully used in modelling structure and electronic properties of silica and germanosilicate glasses [13,14].

2. Experimental results

We investigated optical fibers with phosphosilicate core and pure silica glass cladding manufactured using modified chemical vapor deposition (MCVD) technology. The glass in the core of the fibers contained about 4, 9 and 12 mol% of P$_2$O$_5$. Specimens of the fibers were irradiated by exposure to KrF excimer laser UV radiation (244 nm) with total fluence about 1 kJ cm^{-2} with the beam normal to the axis of the fiber.

The Raman scattering spectra of 514.5 nm light of an Ar laser (Spectra Physics' Stabilite 2000) in the fibers were measured using triple spectrograph (Jobin Ivon's T64000) with spectral resolution about 2 cm^{-1} and accuracy of evaluation of vibrational bands better than 1 cm^{-1} (see Ref. [11] for details).

The UV irradiation was found to result in a decrease of Raman scattering in four bands near 1320, 1150, 680 and 530 cm^{-1}, and to two new Raman bands arising near 1060 and 890 cm^{-1}. These photoinduced changes were stable at room temperature, at least for several weeks. As an example Fig. 1 shows the initial Raman spectra of 9 mol%-P$_2$O$_5$ core and 4 mol%-P$_2$O$_5$ core fibers, the spectrum of an irradiated 9 mol%-P$_2$O$_5$ core fiber, and the difference of the irradiated and the nonirradiated 9 mol%-P$_2$O$_5$ core fibers. As evident from Fig. 1, 1320 cm^{-1} Raman scattering in the irradiated 9 mol%-P$_2$O$_5$ core fiber is similar to that
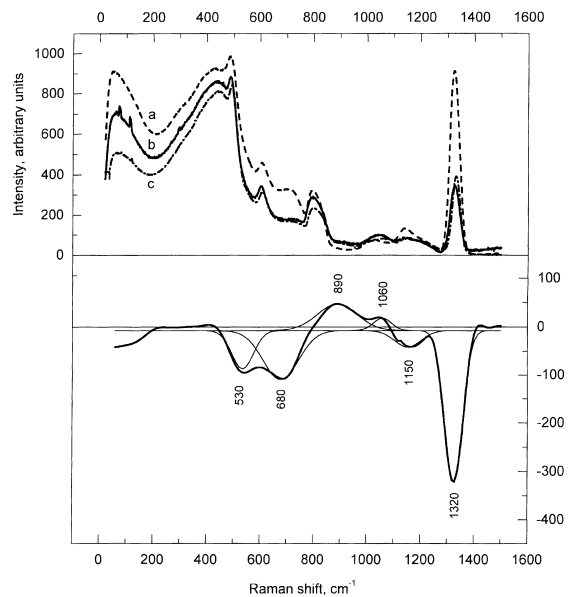

Fig. 1. Raman spectra of fibers with core of phosphosilicate glass. Upper graph: experimental spectra (spectral resolution about 2 cm^{-1}) (a) 9 mol%-P$_2$O$_5$ core fiber before UV irradiation, (b) 9 mol%-P$_2$O$_5$ core fiber after UV irradiation, (c) nonirradiated 4 mol%-P$_2$O$_5$ core fiber. Lower graph: difference of (b) and (a) spectra. The thin lines represent a Gaussian approximation of the peaks.

in the nonirradiated fiber with a concentration less by one half of P_2O_5, the 4 mol%-P_2O_5 core fiber.

3. Calculation method and cluster model

Some theoretical work has been done recently on the vibrational properties of phosphorus glasses. In Ref. [12] the structure of P_2O_5 glass is studied by ab initio method in STO-3G and 3-21G basis using the GAUSSIAN-80 program and by CNDO/2 method for small clusters. However no calculations of large clusters or using more reliable quantum-chemical methods have been performed, to our knowledge.

In the present paper only the centers formed by pentavalent phosphorus atoms, namely the centers with single phosphorus atom, $O=P(O-Si)_3$ and $P(O-Si)_5$ and centers with two phosphorus atoms, $O=P-O-P=O$ and $(Si-O)_4P-O-P$ $(O-Si)_4$, are studied using the cluster model similar to one used in our previous works for silica glass (see, for example, Refs. [13,14]).

To model the $O=P(O-Si)_3$ center we used the cluster with single $O=PO_3$ tetrahedron bound by common oxygen atoms with three SiO_4 tetrahedra and to study mutual transformation of the $O=P(O-Si)_3$ and $P(O-Si)_5$ centers we used the same cluster with the $(H_3Si-O)_3$ $Si-O-Si(O-SiH_3)_3$ fragment simulating $\equiv Si-O-Si\equiv$ linkage placed near the $O=P(O-Si)_3$ center (Fig. 2). For modeling the $P(O-Si)_5$ center the cluster with the central phosphorus atom bound by bridging oxygen atoms with five SiO_4 tetrahedra was used (Fig. 3). To model the $O=P-O-P=O$ center the cluster with two $O=PO_3$ tetrahedra bound together by common oxygen atom, each of the tetrahedra bound by common oxygen atoms with two SiO_4 tetrahedra was used, and to study mutual transformation of the $O=P-O-P=O$ and $(Si-O)_4$ $P-O-P$ $(O-Si)_4$ centers the same cluster with two $H_3Si-O-SiH_3$ fragments simulating $\equiv Si-O-Si\equiv$ linkages was used (Fig. 4). In all the clusters the dangling bonds of the outer silicon atoms were saturated with hydrogen atoms to eliminate influence of surface states formed by these bonds on electronic structure of the clusters.
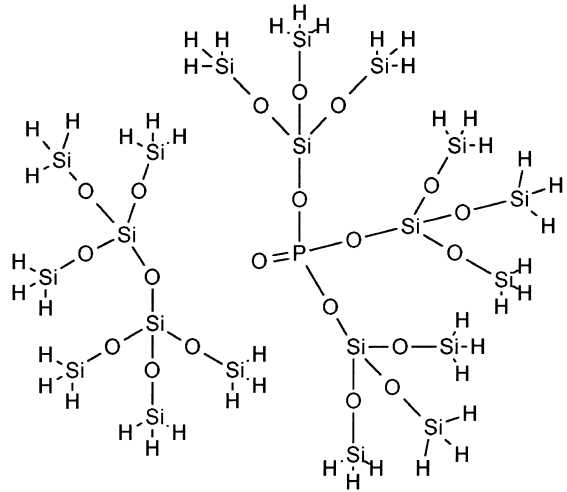

Fig. 2. Cluster used to study mutual transformation of the $O=P(O-Si)_3$ and $P(O-Si)_5$ centers.
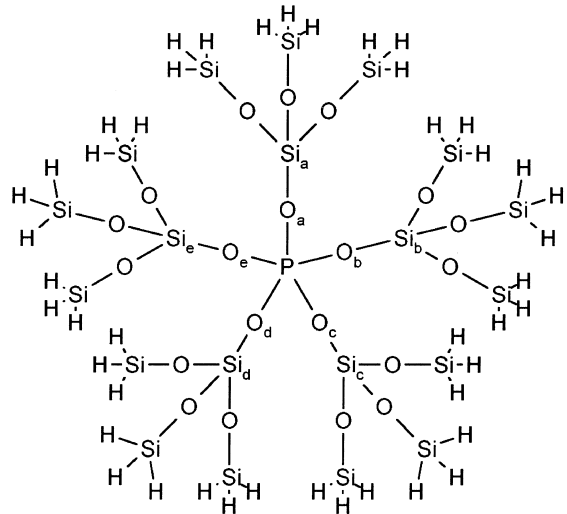

Fig. 3. Cluster used to model the $P(O-Si)_5$ center.

All calculations were performed using semiempirical quantum-chemical methods, MNDO and PM3, with the help of the MOPAC 93 program package [15].

Initially we took bond lengths and valence angles in clusters equal to average lengths and angles typical for silica glass and molecules containing phosphorus and oxygen atoms, then *all coordinates of all atoms of each cluster* were optimized by
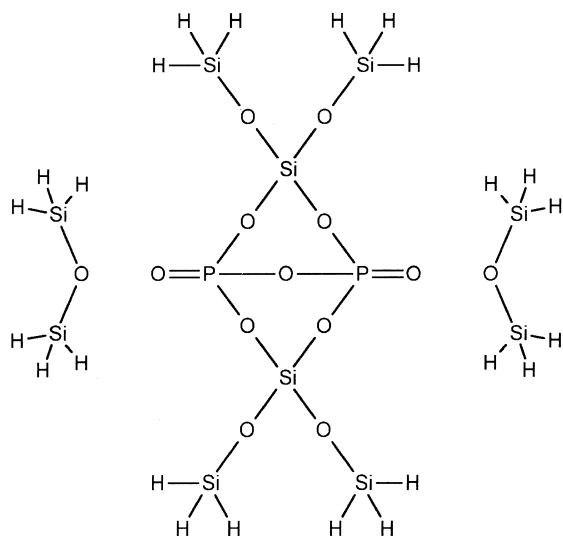
Fig. 4. Cluster used to study mutual transformation of the O=P—O—P=O and $(Si—O)_4P—O—P(O—Si)_4$ centers.

PM3 method. The configurations obtained were used as initial data for all further calculations using both PM3 and MNDO methods. In the latter case the outer silicon atoms were fixed in their positions obtained by PM3 and coordinates of all other atoms were optimized by MNDO. The necessity of such procedure was caused by well-known lack of the MNDO method, systematic overestimation of valence angles of oxygen linkages, while the PM3 method is free of this shortcoming. Such an approach allowed us, on the one hand, to obtain reasonable ≡Si—O—Si≡ angles (in average about 150° compared with the mean angle in v-SiO$_2$, about 144°), and on the other hand, to optimize the cluster geometry well enough to study vibrational properties of the clusters.

Geometry, formation energy, and vibrational properties of all the centers were calculated using the PM3 method (however it should be noted that results of MNDO calculations differ insignificantly), and electronic structure and optical properties were calculated by MNDO method with the help of the MOPAC 93 package. Energies of excited electronic states and oscillator strengths of optical transitions were calculated by single-reference configurations interaction (CI) method with 10 electrons in 10 orbitals and all possible configu-

rations (about 64 000) taken into account. In each CI calculation 256 states were obtained and all excited states with energies less than 10 eV were considered.

To eliminate influence of the outer hydrogen atoms on the vibrational spectra we assumed masses of all these atoms to be very large ($\sim 10^5$ a.u.) to freeze their motions. However the artificial freezing of the outer hydrogen atoms resulted in excessive localization of vibrations with participation of the silicon atoms of the SiH$_3$ groups and vibrations with participation of the bridging oxygen atoms bound with these silicon atoms. To reduce such a localization we calculated the vibration spectra for a sequence of masses of the outer silicon atoms in the range from 28 to 45 a.u. and then averaged them. By such an approach we managed to describe the basic features of vibrational spectra of silica and germania glasses, in particular, areas of the vibrational spectrum where the vibrations are accompanied, practically, only by movement of bridging oxygen atoms, namely, in SiO$_2$

(a) vibrational density of states peak near ≈400 cm^{-1};

(b) smaller maximum of the density of states near ≈600 cm^{-1};

(c) the density of states peak >1000 cm^{-1}

and in GeO$_2$

(a) vibrational density of states peak near ≈300 cm^{-1};

(b) smaller maxima of the vibrational density of states in the range from 450 to 500 cm^{-1};

(c) the density of states peak >900 cm^{-1}.

In both cases the vibrational states in the two oxides are identical which is explained by the qualitatively similar structure of their atomic hosts. The type (a) vibrations include displacement of bridging oxygen atoms in direction perpendicular to planes of ≡Si—O—Si≡ or ≡Ge—O—Ge≡ linkages; the (b) and (c) type vibrations are caused by displacement of bridging oxygen atoms in planes of these linkages, in the first case mainly perpendicular to the Si—Si or Ge—Ge line and in the second case mainly parallel to this line. Obviously, only the type (c) vibrations are accompanied by change of the Si—O (Ge—O) bond lengths. It should be stressed that all these vibrations practi-

cally are not accompanied by movement of Si or Ge atoms, and hence do not include either distortions or translations of the SiO_4 or GeO_4 tetrahedra. On the other hand, vibrations < 400 cm^{-1} (SiO_2) or < 200 cm^{-1} (GeO_2) and in ranges from 600 to 800 cm^{-1} in SiO_2 or from 550 to 650 cm^{-1} in GeO_2 are accompanied by displacement of the SiO_4 or GeO_4 tetrahedra with rather small distortions of their form (vibrations at lower frequencies) or distortions of the tetrahedra, in other words change of O—Si—O or O—Ge—O angles (vibrations in the middle part of the spectrum). Identical classification of vibrational states was done previously in Refs. [16,17] where the vibrations of (a), (b) and (c) types are designated as R ('Rocking'), B ('bond Bending') and S ('bond Stretching'), respectively, and vibrations accompanied with movements of Si or Ge atoms are designated as C ('Central atom'), and in Ref. [18] where detailed molecular dynamics calculations were performed.

Results of our calculations of vibrational frequencies in clusters agree with experimental data with accuracy of about 10% (generally the calculated frequencies are too large).

We expect our approach to provide satisfactory results for phosphosilicate glass as well. For illustration purposes, instead of discrete vibrational spectra of clusters in what follows we present vibrational density of states curves calculated representing each frequency by a gaussian with width $\sigma \sim 20$ cm^{-1}.

4. Discussion

4.1. Raman spectra

Vibrational mode corresponding to the 1320 cm^{-1} band is undoubtedly stretching of the O=P double bond. Hence the reduction by more than 50 of the intensity of this band suggest that more than a half of the O=PO$_3$ tetrahedra are transformed under the UV irradiation into another structural form (or forms) which do not contain the double bonds.

We assume that it is reasonable that the O=PO$_3$ tetrahedra excited by UV irradiation interact with

the nearest ≡Si—O—Si≡ linkages transforming to the P(O—Si)$_5$ centers, coordination of the phosphorus atom changing without change of its valence state. Since data available on phosphosilicate glass structure are not sufficient to verify this assumption and to interpret other results, we have performed quantum chemical calculation of centers formed by pentavalent phosphorus atoms, namely, the O=P(O—Si)$_3$ and P(O—Si)$_5$ centers with one atom of phosphorus and several complex centers containing P—O—P linkages, among them centers with two phosphorus atoms, either fourfold or fivefold coordinated, and the O=P(O—Si)$_3$ and P(O—Si)$_5$ centers with one or more silicon atoms substituted by phosphorus atoms.

4.2. Calculations

Equilibrium configurations. Calculated configurations of the O=P(O—Si)$_3$ and P(O—Si)$_5$ centers method are shown in Figs. 5 and 6, respectively. In the O=P(O—Si)$_3$ center the phosphorus atom forms normal bonds, P—O, with three oxygen atoms in three P—O—Si linkages (lengths of the normal P—O bonds are 0.155 nm, bond order approximately 0.8), and one double bond, O=P,
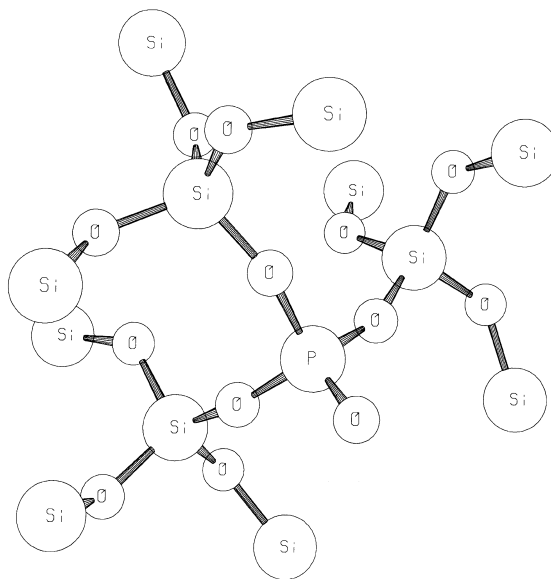

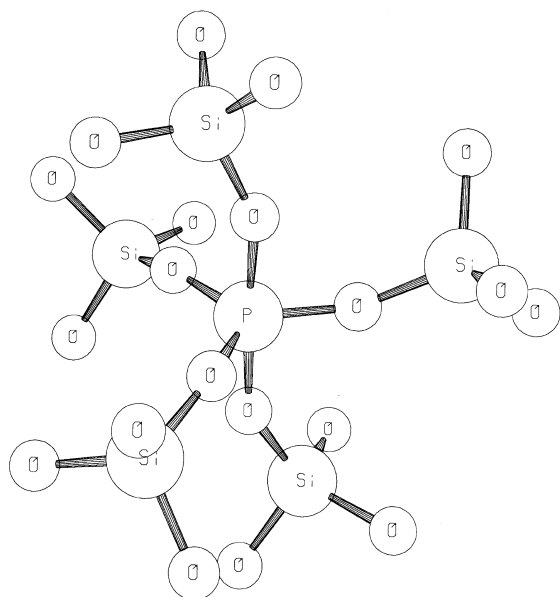Fig. 5. O=P(O—Si)$_3$ center (outer hydrogen atoms are not shown).

Fig. 6. P(O—Si)$_5$ center (outer groups of atoms, —SiH$_3$, are not shown).

Fig. 7. O=P–O–P=O center (outer hydrogen atoms are not shown).

Fig. 8. (Si—O)$_4$P—O—(O—Si)$_4$ center (outer hydrogen atoms are not shown).

(bond order about 1.3) with the fourth oxygen atom, bond length being 0.149 nm (C$_{3v}$ local symmetry). In the P(O—Si)$_5$ center the phosphorus atom forms normal bonds with five oxygen atoms in the P—O—Si linkages. However properties of these bonds and accordingly the linkages differ. Two oxygen atoms lie on a straight line with the phosphorus atom forming the third-order axis, O—P—O (lengths of the P—O bonds are 0.163 nm, bond order 0.7) and other three oxygen atoms lie in the plane perpendicular to this axis, all the O—P—O angles for these three atoms being 120°, P—O bond lengths being 0.158 nm, bond order about 0.8 (D$_{3h}$ local symmetry).

In Figs. 7 and 8 configurations of the O=P—O—P=O and (Si—O)$_4$P—O— P(O—Si)$_4$ centers are shown. As in the O=P(O—Si)$_3$ center, in the O=P—O—P=O center each of the phosphorus atoms forms three normal bonds with three oxygen atoms. Two of these oxygen atoms form P—O—Si linkages and the fourth atom forms the P—O—P linkage connecting the phosphorus atoms. Each of the phosphorus atoms forms as well one double bond, O=P, with the fourth atom of oxygen. Lengths of the P—O bonds are 0.156 and
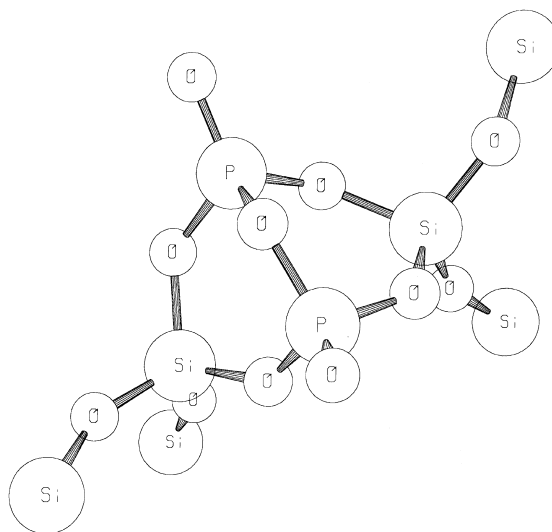
0.161 nm, bond orders are 0.8 and 0.7 in the P—O—Si and P—O—P linkages, respectively. Length of the O=P double bond, as in the O=P(O—Si)$_3$ center is equal to 0.148 nm, bond order about 1.3. In the (Si—O)$_4$P—O—P (O—Si)$_4$

center, similarly to the $P(O-Si)_5$ one, the phosphorus atoms form normal bonds with five oxygen atoms, so that each phosphorus atom is bound by P—O—P linkage with another phosphorus atom and by P—O—Si linkages with four silicon atoms. Neighborhood of the phosphorus atoms is similar to that described above for the $P(O-Si)_5$ center: two oxygen atoms lie on a straight line with each phosphorus atom forming the O—P—O third-order axes (lengths of the P—O bonds are 0.167 and 0.164 nm, bond orders 0.6 and 0.7 in the P—O—P and P—O—Si linkages, respectively) and other three oxygen atoms lie in a plane perpendicular to this axis, all O—P—O angles for these three atoms being 120°, lengths of P—O bonds being 0.159 nm and bond order about 0.8. So in the O=P—O—P=O and $(Si-O)_4P-O-P$ $(O-Si)_4$ centers the symmetry of the close neighborhood of each of the phosphorus atoms turn out to be the same as in the $O=P(O-Si)_3$ and $P(O-Si)_5$ centers (C_{3v} and D_{3h}, respectively).

Transition states. To understand possibility of mutual transformation of the $O=P(O-Si)_3$ and $P(O-Si)_5$ centers one needs the cluster total energies for equilibrium configurations of these centers (with the formation energy of the fragments simulating the additional ≡Si—O—Si≡ linkage taken into account) and the total energy of the cluster for the transition state between the $O=P(O-Si)_3$ and $P(O-Si)_5$ configurations, the saddle point on the total energy surface of the cluster. The transition state was optimized with the help of procedures incorporated in the MOPAC 93 package. The calculation showed that the $P(O-Si)_5$ center to be energetically more favorable, approximately by 0.4 eV and the activation energy of the reaction of transformation of the $O=P(O-Si)_3$ center to the $P(O-Si)_5$ one (calculated as a difference between total energies of the cluster for the transition state configuration and for the $O=P(O-Si)_3$ center configuration) is about 0.3 eV (Fig. 9). Configuration of the central part of the cluster in the transition state is shown in Fig. 10 where the forming bonds, P—O and Si—O, and the disappearing bond, Si—O, are emphasized. Hence *isolated* phosphorus atoms in silica glass would be expected to transform from the fourfold coordinated state with the double O=P bond to the

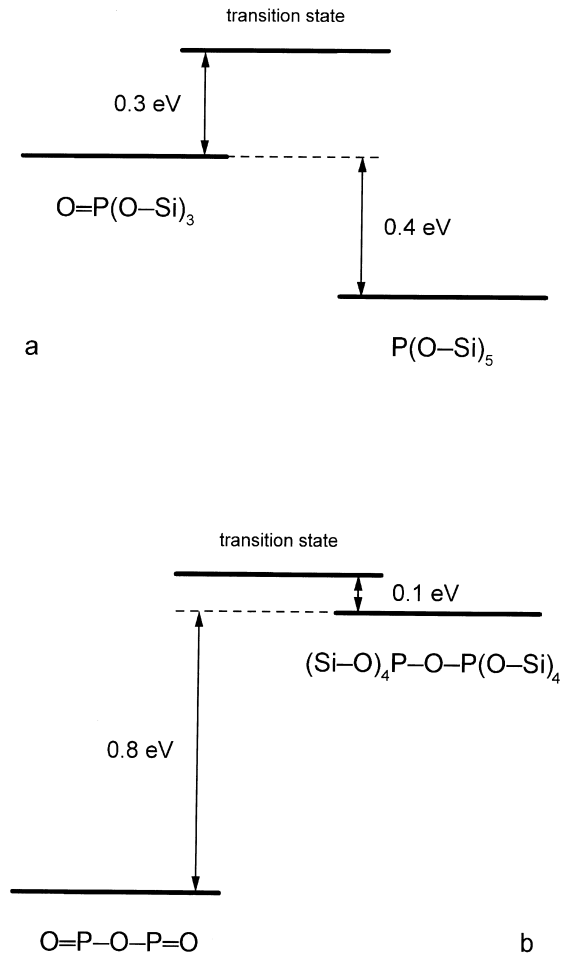Fig. 9. Relative energy of defects and transition states: (a) $O=P(O-Si)_3 + ≡Si-O-Si≡ ↔ P(O-Si)_5$; (b) $O≡P-O-P≡O +2 ≡Si-O-Si≡ ↔ (Si-O)_4P-O-P (O-Si)_4$.

fivefold coordinated form in which all the bonds are single, in accordance with the reaction $O=P(O-Si)_3 + ≡Si-O-Si≡ → P(O-Si)_5$. In what follows we show that the optical absorption of the $O=P(O-Si)_3$ center does result in excitation with energy sufficient to overcome the activation barrier. But, certainly, such a transformation is possible only if there is ≡Si—O—Si≡ linkage close enough to the O=P bond: initial distance between phosphorus atom and bridging oxygen atom is found to be not more than 0.25 nm, so only certain part of the $O=P(O-Si)_3$ centers can transform to the $P(O-Si)_5$ ones.
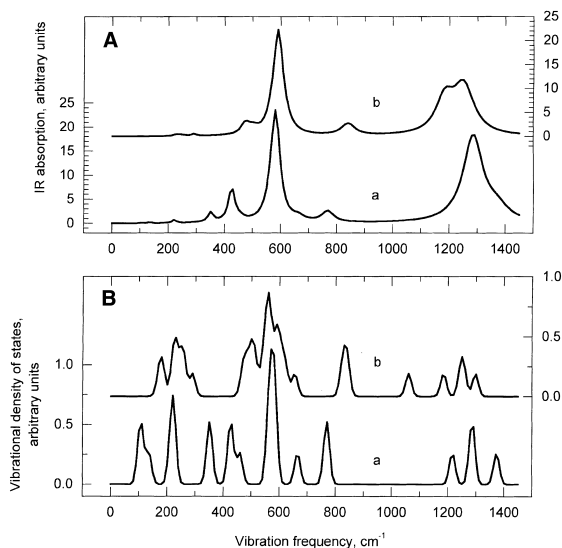
Fig. 10. The transition state between $O{=}P(O{-}Si)_3$ and $P(O{-}Si)_5$ configurations (outer groups of atoms, $-O{-}SiH_3$, are not shown). Forming bonds, $P{-}O$ and $Si{-}O$, are shown in gray, disappearing bond, $Si{-}O$, is shown by dashed lines.

On the other hand, calculation of the $O{=}P{-}O{-}P{=}O$ and $(Si{-}O)_4P{-}O{-}P$ $(O{-}Si)_4$ centers and corresponding transition state showed the $O{=}P{-}O{-}P{=}O$ center to be energetically more favorable (approximately by 0.8 eV). The same results obtained for clusters similar to those used for calculations of the $O{=}P(O{-}Si)_3$ and $P(O{-}Si)_5$ centers but with the silicon atoms bound by bridging oxygen atoms with the phosphorus atom substituted with phosphorus atoms (in other words, with the central phosphorus atom surrounded *only* by $P{-}O{-}P$ linkages instead of $P{-}O{-}Si$ linkages). So we found that in the phosphorus centers containing the $P{-}O{-}P$ linkages the configurations with the $O{=}P$ double bond are more favorable. This case is most likely realized in phosphosilicate glasses. For all the phosphorus centers with some or all of the $P{-}O{-}Si$ linkages substituted by the $P{-}O{-}P$ ones, the energy barriers of the reactions of destruction of the $P(O{-}Si)_5$ centers do not exceed 0.1 eV in the calculation (Fig. 9). However this energy is less than that of the cluster approach.

In the next section the optical absorption of all these centers (in which the phosphorus atoms are not isolated in $v{-}SiO_2$ host) is shown to lead to excitation with energy sufficient for one or both phosphorus atoms to transform to the fivefold coordinated configuration. The transformation results in disappearance of the centers with the double $O{=}P$ bond. However since the energy barriers of the reverse reactions are of the same order, the centers with the fivefold coordinated phosphorus atoms containing $P{-}O{-}P$ linkages may transform back to the centers with the double bond under thermal excitation. Unfortunately, accuracy of the cluster model gives no way to estimate the temperature of back transition.

Optical absorption. The $O{=}P(O{-}Si)_3$ center gives rise to singlet-to-singlet optical absorption near 4.7 eV (265 nm) with oscillator strength of the order of 10^{-2}. The energy of corresponding singlet-to-triplet transitions is equal to 4.3 eV (290 nm). These excitations correspond to transfer of electronic density from nonbonding p_π orbitals of the nonbridging oxygen atom bound by the double bond with the phosphorus atom mainly to the s orbital of the phosphorus atom. External electrostatic field with strength of the order of 10^7 V cm or more turns out to change the transition energies by ~ 0.2 eV. So the absorption band of the $O{=}P(O{-}Si)_3$ centers in phosphosilicate glass should be inhomogeneously broadened.

The states of the $O{=}P{-}O{-}P{=}O$ center are formed of states of two mutually interacting $O{=}P(O{-}Si)_3]$ centers, so, approximately, each state of the $O{=}P(O{-}Si)_3$ center corresponds to a pair of states of the $O{=}P{-}O{-}P{=}O$ center formed by symmetrical and antisymmetrical combinations of the formers, respectively. There is singlet-to-singlet optical absorption in the $O{=}P{-}O{-}P{=}O$ center near 5.2 eV (235 nm) with oscillator strength of the order of 10^{-2}. The energy of the corresponding singlet-to-triplet transition is equal to 4.7 eV (265 nm).

All the lowest electronic excitations in the $P(O{-}Si)_5$ center correspond to transfer of electronic density from nonbonding p_π states of oxygen atoms (in other words from the $v{-}SiO_2$ valence band edge) to empty levels of the center. So the oscillator strengths are small ($<10^{-3}$) and the

transition energies exceed 7.0 eV for both singlet-to-singlet and singlet-to-triplet transitions.

As in the O=P—O—P=O center, the localized states of the $(Si—O)_4P—O—P (O—Si)_4$ center are formed by states of two mutually interacting $P(O—Si)_5$ centers, and hence a pair of states (symmetrical and antisymmetrical ones) corresponds in the $(Si—O)_4P—O—P (O—Si)_4$ center to each state of the $P(O—Si)_5$ center. The $(Si—O)_4$ $P—O—P (O—Si)_4$ center gives rise to singlet-to-singlet absorption near 5.9 eV (210 nm) with an oscillator strength of the order of 10^{-3}. The energy of corresponding singlet-to-triplet transition is equal to 5.7 eV (215 nm).

Vibrations. Fig. 11 shows vibrational density of states of the cluster and IR absorption ($\sim$ Im $1/\varepsilon$) for the O=$P(O—Si)_3$ and $P(O—Si)_5$ centers, Fig. 12 represents the same for the O=P—O—P=O and $(Si—O)_4P—O—P (O—Si)_4$ centers.

In the high-frequency part of the vibrational spectra of the O=$P(O—Si)_3$ and $P(O—Si)_5$ phosphorus centers it is possible to identify several vibrations corresponding to normal vibrations of the O=PF_3 and PF_5 molecules marked previously in Refs. [5–7], namely, in the O=$P(O—Si)_3$ center (C_{3v} local symmetry):
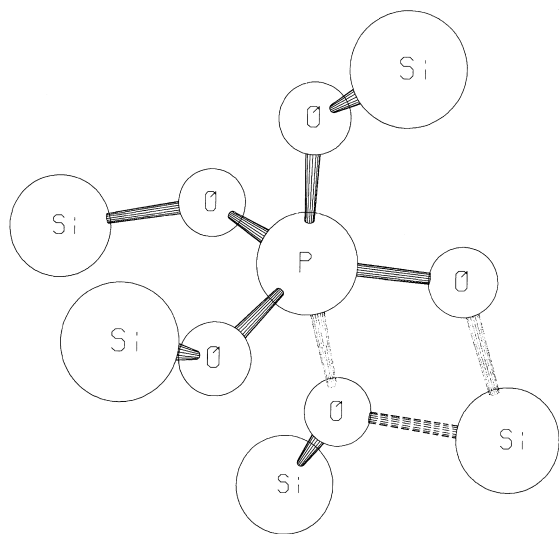

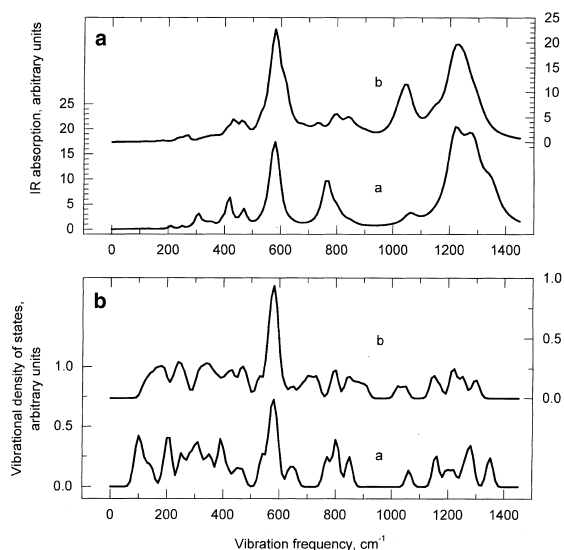Fig. 11. Vibrational spectra (A) of (a) O=$P(O—Si)_3$ and (b) $P(O—Si)_5$ centers.

Fig. 12. a. Vibrational spectra of (a) O=P—O—P=O and (b) $(Si—O)_4P—O—P (O—Si)_4$ centers. b. Calculated vibrational density of states of (a) P_2O_5 and (b) Phosphosilicate vibrational density of states, B, for the two cases shown in A.

A_1: 1370 cm^{-1}, stretching of the O=P double bond;

E: 1280 cm^{-1}, displacement of the oxygen atom in two or three P—O—Si linkages parallel to the Si—P line accompanied by stretching of the P—O and Si—O normal bonds;

A_1: 1215 cm^{-1}, stretching of the O=P double bond with simultaneous displacement of the oxygen atoms in three P—O—Si linkages parallel to the Si—P line and stretching of the P—O and Si—O normal bonds (complete-symmetry 'breathing' mode),

and in the $P(O—Si)_5$ center (D_{3h} local symmetry):

A_1': 1300 cm^{-1}, complete-symmetry breathing vibration with stretching both long and short P—O bonds;

E': 1250 cm^{-1}, stretching of the P—O short bonds;

A_2'': 1180 cm^{-1}, antisymmetrical stretching of both P—O long bonds;

A_1': 1060 cm^{-1}, symmetrical stretching of both P—O long bonds.

Frequencies of the A_1 and A_1' breathing vibrations increase compared with the O=PF_3 and PF_5 molecules. The reason is that the P—O—Si linkages

prevent displacement of the oxygen atoms along P—O bonds, which is obviously larger in the P(O—Si)$_5$ center.

The local symmetry of the O=P(O—Si)$_3$ and P(O—Si)$_5$ centers is broken by the neighboring atoms. This disruption yields numerous new normal vibrations, with frequencies <870 cm^{-1} in both centers, which are not classified in terms of the local symmetry. All these vibrations are caused by deformations of the P—O—Si linkages and adjacent ≡Si—O—Si≡ linkages. In connection with results of our experiment, vibrations of the O≡P(O—Si)$_3$ center in the ranges 680–690 and 470–500 cm^{-1} should be noticed. These are caused by A$_1$ and E deformations of the O=PO$_3$ tetrahedra practically not accompanied with stretching of the O—P or O=P bonds (bond-bending vibrations). In Refs. [6,7] the bands near 650 cm^{-1} (IR) or 710 cm^{-1} (Raman scattering) are ascribed to bond-bending vibrations of the O=P—O fragments in the O=PO$_3$ tetrahedra and the band near 475 cm^{-1} (IR) or 520 cm^{-1} (Raman scattering) to bond-bending vibrations of the O—P—O fragments in these tetrahedra. The results of our calculation and experiment completely confirm this interpretation.

Vibrations of the P(O—Si)$_5$ center in the range 800–870 cm^{-1} are caused by rotational movement of PO$_5$ groups accompanied by bond-bending deformations of the P—O—Si linkages with very small change of both O—P bond lengths and O—P—O angles.

Classification of vibrations of the O=P—O—P=O and (Si—O)$_4$P—O—P (O—Si)$_4$ centers in terms of local symmetry is inconvenient because their symmetry is broken by neighboring atoms. Qualitatively, in the O=P—O—P=O center there are vibrational modes

1345 and 1355 cm^{-1}, simultaneous stretching of the O=P double bonds at both phosphorus atoms, symmetrical and antisymmetrical modes respectively;

1290 and 1280 cm^{-1}, displacement of the oxygen atoms in two of three P—O—Si linkages parallel to the Si—P line accompanied by stretching of the P—O and Si—O normal bonds, symmetrical and antisymmetrical modes respectively;

1190 and 1155 cm^{-1}, stretching of the P—O—P linkage accompanied by stretching of the O=P double bonds of both phosphorus atoms simultaneously, symmetrical and antisymmetrical modes respectively;

1060 cm^{-1}, displacement of the oxygen atom in the P—O—P linkage parallel to the P—P line accompanied by stretching of the P—O normal bonds;

845–850 cm^{-1}, displacement of the oxygen atom in the P—O—P linkage parallel to the P—P line accompanied by simultaneous bending of the O=P—O fragments;

800–810 cm^{-1}, various vibrational modes accompanied by simultaneous bending of the P—O—P linkages and O=P—O fragments;

535 cm^{-1} (bond-rocking type vibration of the P—O—P linkage,

and in the (Si—O)$_4$P—O—P(O —Si)$_4$ center

1210–1245 cm^{-1}, stretching of the short P—O bonds;

1020–1150 cm^{-1}, stretching of both long P—O bonds accompanied by the various contributions of stretching of the neighboring P—O—Si linkages;

907 cm^{-1}, displacement of the oxygen atom in the P—O—P linkage parallel to the P—P line accompanied by stretching of the P—O bonds;

840–890 cm^{-1}, rotational movement of one or both groups of atoms, PO$_5$, accompanied by bond-bending deformations of the P—O—P and P—O—Si of linkages practically without change of the O—P bond lengths or O—P—O angles in the rotating group;

645 cm^{-1}, bond-rocking type vibration of the P—O—P linkage.

Our calculation confirm, qualitatively, main conclusions of Refs. [6,7] concerning the high-frequency vibrations in IR absorption spectrum of phosphosilicate glass. Namely, in Refs. [6,7] vibrational bands near 1150 cm^{-1} (IR) or 1200 cm^{-1} (Raman scattering), 950 cm^{-1} (IR) or 1120 cm^{-1} (Raman scattering) and 780 cm^{-1} (IR) or 800 cm^{-1} (Raman scattering) are ascribed to stretching of P—O—P linkages. Our calculation confirms this interpretation. Besides, vibration bands near 475 cm^{-1} or 520 cm^{-1} (535 cm^{-1} in our calculation) can be caused not only by bending of O—P—O

fragments in the $O=PO_3$ tetrahedra as it is assumed in Refs. [6,7] and confirmed by our results, but also by rocking of P—O—P linkages in the $O=P—O—P=O$ centers.

4.3. Comparison of experimental Raman data with calculations

Results of the calculation confirm our assumption on the mechanism of photoinduced changes in phosphosilicate glass as transformation of part of the $O=P(O—Si)_3$ centers in the $P(O—Si)_5$ centers. So, the experimentally observed reduction of the Raman band near 1320 cm^{-1} (P=O double bond stretching) unambiguously indicates that the $O=P$ double bond concentrations, in other words concentration of the $O=PO_3$ tetrahedra, decreases. According to the calculation such reduction should be accompanied by decrease of intensity of other vibrations of these tetrahedra in the ranges 1280–1210, 680–690, 470–500 cm^{-1}. With the estimated accuracy of executed vibrational frequencies taken into account there is agreement with experimental data 1150, 680 and 530 cm^{-1}. If the $O=PO_3$ tetrahedra do turn in PO_5 pentahedra, new vibrations should appear in the ranges 1250–1300, 1060–1180 and 800–870 cm^{-1}. Partial (in view of calculation accuracy) overlapping of first vibrational range with high-frequency vibrations of the $O=PO_3$ tetrahedra does not allow conclusions about this frequency range. However the other two frequencies agree with the experimental values, 1060 and 890 cm^{-1}, within the calculation accuracy.

5. Conclusions

In conclusion,
- intensive 244 nm-UV irradiation of phosphosilicate glass by KrF laser results in decreasing of Raman scattering bands near 1320, 1150, 680 and 540 cm^{-1} and in two new bands arising simultaneously near 1060 and 890 cm^{-1};
- reduction of Raman scattering band at 1320 cm^{-1} is caused by correspondent reduction of $O=PO_3$ tetrahedra concentration;

- the quantum chemical calculation relates the reduction of $O=PO_3$ tetrahedra concentration with transformation of a part of the $O=P(O—Si)_3$ centers to the $P(O—Si)_5$ centers and to explain the changes of Raman spectrum observed in our experiment just by such rearrangement of the atomic network of the glass;
- the results of calculations of phosphorus centers are in good agreement (about $\pm 5\%$) with available data on vibrational properties of phosphosilicate glass [6,7].
- transformation of $O=P(O—Si)_3$ centers to $P(O—Si)_5$ centers under UV irradiation should result in photobleaching of broad absorption band near 4.7 eV (265 nm). Experimental observation of both the absorption band and its UV photobleaching in phosphosilicate glass is of obvious interest.

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