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Intrinsic surface phonons in amorphous silica

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We have detected intrinsic surface phonons in amorphous silica by performing Raman scattering and infrared-reflectivity measurements on samples of porous Vycor glass. Qualitative agreement of our experimental spectra with theoretical calculations provides an identification of the surface features in terms of microscopic atomic motions. We find a sharp Raman-active peak at 980 cm^{-1} associated with the stretching vibration of a hydroxyl group against the surface silicon atom to which it is bonded. The corresponding wagging motion of the hydroxyl group appears in the infrared spectrum as a sharp feature at 380 cm^{-1}. Both the appearance of these surface features as sharp peaks in the spectra and their relative amplitudes in the Raman and infrared spectra can be explained only if the sympathetic vibrations of underlying substrate layers are taken into account. Experimental confirmation of our assignment is provided by the effects of deuteration and adsorbed ammonia molecules on the Raman-active surface modes. Our experiment is the first in which the perturbations of these surface modes due to adsorbed molecules are studied. In our examination of the effects of water adsorption on the Raman spectrum of porous Vycor, we have observed a decrease in the intensity of the bulk "defect" mode near 600 cm^{-1} with increasing water coverage. We also present evidence that the intense scattering background observed in Raman experiments on silica and other oxide surfaces is primarily an intrinsic electronic surface effect.

I. INTRODUCTION

The recent widespread interest in surface physics has been concentrated primarily on the electronic and static structural properties of solid surfaces. Less emphasis has been placed on surface vibrational properties due to the extreme difficulty of studying them experimentally. However, the study of the vibrational excitations of the atoms near a solid surface is important for a complete understanding of both the atomic structure of the surface as well as its interactions with adsorbed molecules.

Surface vibrational spectroscopy is extremely difficult due to the minute percentage of surface atoms in a solid sample, the small cross sections, and resulting long penetration depths of traditional vibrational probes. Visible light and neutrons interact weakly with matter and are therefore inherently less surface sensitive than probes of electronic structure such as x-rays, ultraviolet photons, and electrons, which can have extremely small penetration depths. Thus bulk effects dominate and may overwhelm the signal in experiments intended to measure surface vibrations. As an example, in even the most advantageous configuration for an absorption-reflection experiment, the maximum contribution from an adsorbed monolayer of molecules is typically 1% of the total signal.[1] There are two methods of circumventing this problem. The first is to develop new vibrational probes which are more surface sensitive, and the second is to alter the sample or the experimental arrangement so that a traditional probe encounters more surface.

In the last decade, the development of high-resolution inelastic low-energy-electron scattering, a highly-surface-sensitive technique, has allowed the detection of vibrations on atomically clean and adsorbate-covered single-crystal surfaces.[2] Electron-energy-loss experiments are sensitive to essentially the same surface vibrational modes as infrared-reflectivity measurements[3] and can conveniently cover a larger spectral range than is easily accessible with infrared experiments. However, optical techniques, despite their lower surface sensitivity, have a crucial potential advantage over electron scattering in that the surface is not restricted to ultrahigh-vacuum conditions. In an optical experiment, for example, surface reactions can be studied both in conditions of ultrahigh vacuum and at the high pressures at which most heterogeneous catalysis occurs. Optical surface studies are possible as well in high magnetic or electric fields where electron spectroscopy is inadequate. It is evident that optical spectroscopy will continue to play an important role in the study of vibrations on surfaces.

Optical surface vibrational spectroscopy has been primarily used to measure the frequency shifts of infrared or Raman bands of adsorbed molecules in spectral regions where a high surface area substrate is transparant to the light.[4,5] In some cases multiple reflection-absorption spectroscopy can be used,[6] in which the adsorbed layer is sampled many times by the light beam as it bounces back and forth between two flat reflecting substrate surfaces. There have also been a number of recent developments in the detection of the vibrations of thin layers of molecules on metal surfaces using Raman[7] and single reflection infrared absorption spectroscopy.[18] For the most part these experiments have been concerned solely with the detection of weak signals due to adsorbed molecules.

In the present experiment, we have concentrated on the vibrational spectrum of the adsorbent. We have studied the Raman and infrared spectra of intrinsic surface phonons of amorphous silica and investigated their interactions with adsorbed molecules using Raman scattering. We performed the measurements on a porous substrate with a large internal surface area in order to increase the surface signal relative to that of the bulk. The experiment is one of a very few which have studied high-frequency intrinsic surface phonons of any material.

We have chosen porous Vycor glass as a substrate for a number of important reasons. First, the enormous internal surface area of the glass assures a large surface atom to bulk atom ratio. Approximately 10% of the atoms sampled by the light as it traverses the material are *surface* atoms. Second, the smallest dimension of the pores in porous Vycor is large on an atomic scale, but small compared to the wavelength of visible light. As a result elastic scattering of the light is minimized while the internal pore surfaces are accessible to small molecules and the local environment of an adsorbed molecule is that of a two-dimensional surface. Third, despite the large surface area and high porosity of porous Vycor, it is not only more transparent to visible light but is more easily handled than powders or gels of comparable surface area. Finally, porous Vycor has been used for nearly 30 years as a substrate for infrared-absorption studies of the spectra of adsorbate molecules[4] and therefore its surface is moderately well characterized as an adsorbent. Recently Raman scattering experiments have been performed on porous Vycor substrates.[5,8] In these experiments spectra of adsorbate molecules have been studied exclusively. Although Buechler and Turkevich[8] published the Raman spectrum of porous Vycor, they also concentrated on the spectra of adsorbates and did not examine the perturbations of the intrinsic phonons of the glass due to adsorbed molecules. As a result, the intrinsic surface features were not studied in their experiment.

Until recently both Raman and infrared experiments on silica adsorbants have been plagued by dirt effects such as oil contamination from diffusion pumps and have been performed in low-vacuum conditions where water contamination is likely to be present.[5] Our experiment was performed with the sample enclosed in an ultrahigh-vacuum system in order to minimize surface contamination.

The vibrations of bulk amorphous substances have recently aroused great interest. Hopefully, this experiment will encourage interest in the surface vibrations of amorphous as well as crystalline materials.

II. EXPERIMENTAL APPARATUS AND TECHNIQUES

A. Description of the substrate: Porous Vycor

Porous Vycor glass (Corning code 7930) is manufactured from a phase-separated borosilicate glass. The boron-rich phase, initially comprising about 30% of the volume, is leached out to form a network of 40-Å-diam pores throughout the sample. Nordberg[9] gives a detailed description of the manufacturing process. Watson[10] describes a number of methods which have been used to determine the pore size distribution in porous Vycor. Electron microscope studies[11] have shown that the glassy matrix of porous Vycor resembles a randomly packed collection of distorted silica spheres of about 300-Å diam. For our purposes, we need only know that the smallest dimension of the voids is large on an atomic scale, and that virtually all of the internal surface area is accessible to small molecules as determined by chemical methods.[4] It is also interesting to note that the pores are multiply connected in a three-dimensional manner.[12] Studies have shown that the surface of Vycor is energetically heterogeneous[13] with isoteric heats of adsorption decreasing by nearly 25% as the coverage is increased to saturation. This is thought[14] to be due to both the presence of surface hydroxyl groups existing in a number of different configurations which are active sites for adsorption as well as less active siloxane bridge sites. Boron impurity sites on the surface have also been shown to take part in adsorption.[15] The composition of the glass matrix of porous Vycor is by weight 96% SiO_2, 3% B_2O_3, 0.03% NaO, 0.2% Al_2O_3, and trace R_2O_3, where R can be of a number of heavy-metal impurities.[16] In an ion microprobe study, we detected no change in the ratio of boron to silicon atoms near the flat faces of a porous Vycor sample. By contrast, the impurity content of Suprasil l,[17] a synthetic fused silica prepared by burning $SiCl_4$ in an oxyhydrogen flame, is less than 1 ppm.

B. Sample-cleaning procedure

The following cleaning procedure was devised for the porous Vycor samples. This treatment was found to reduce the intense background in the Raman scattering spectrum of off the shelf samples by about six orders of magnitude, thus making the Raman scattering from intrinsic phonons of the glass visible. Each sample as received from the manufacturer was boiled repeatedly in 30% solutions of hydrogen peroxide for several hours, then rinsed in deionized distilled water and placed in a clean quartz tube inside an oven. The sample was heated to 600 °C in high-purity oxygen gas at a pressure of about 800 Torr flowing at 0.5 liter/min for periods ranging from 10 h to two weeks. Extreme care was taken so that no air or organic contaminants could come into contact with the sample. The sample was then cooled to room temperature in flowing high-purity nitrogen gas and transferred in a nitrogen atmosphere to the cell which had been previously backfilled with nitrogen gas. The equilibration time for water-vapor adsorption into the samples is about 1 h and the diffusion time of nitrogen gas is approximately 1 min. Thus we believe that transfer of the sample from the oven to the cell in a closed bag filled with nitrogen gas, a procedure which took approximately 0.5 min, did not substantially contaminate the sample. The cell was immediately evacuated with a sorption pump and ion pump to a pressure of 10^{-8} Torr before Raman scattering measurements began. No increase of pressure was apparent when the laser beam was put through the sample.

C. Vacuum system

In order to minimize surface contamination, the experiments were performed with the sample enclosed in a small table-top stainless-steel ultrahigh-vacuum system with a base pressure of 5×10^{-10} Torr. Adsorption isotherms were measured volumetrically by admitting doses of gas into a calibrated volume at room temperature, measuring the pressure of the gas with a capacitance manometer, and then expanding the gas into the cell. Molecules which were "missing" from the system were assumed to be adsorbed on the sample. This is a good approximation as the total surface area of the cell and reference volume is about three orders of magnitude smaller than that of the sample. Total estimated errors in the measurement of the number of molecules on the sample are ±3%, due in large part to temperature drifts during the measurements. Equilibration times for adsorption on the sample ranged from one to three hours. All of the adsorption measurements were performed during Raman scattering runs, with about 400 mW of laser power through the sample. The equilibrium temperature of the region of the sample illuminated by the laser beam in vacuum was 150 ± 10 °C, determined by the ratio of the Stokes to anti-Stokes scattering of the 608-cm^{-1} peak in the Raman spectrum. The sample temperature dropped to about 30 °C at the edges.

D. Raman scattering measurements

The samples of porous Vycor were obtained from Corning Glass Works in the form of flat plates. All faces of the samples had been polished prior to leaching. A sharp razor blade was used to break the samples. The finished samples were approximately $\frac{1}{16}\times\frac{1}{2}\times\frac{3}{4}$ in., with a volume of about 0.3 cm^3, and weighed about 0.5 g. The laser beam entered the "polished" end face of the sample for the Raman measurements and traversed it lengthwise. In order to minimize the intense stray light, the scattered light was collected from the large face of the sample at an angle of 90° from the incident beam. The 5145-Å line of a cw Spectra Physics model 165 argon-ion laser was used as the light source and a Spex 1401 double monochrometer with gratings blazed at 5000 Å was used to analyze the scattered light. The instrumental full width at half height used was 4 cm^{-1}. The light was detected with a cooled ITT FW130 photomultiplier tube and conventional photon counting electronics. The counting interval used was 10 sec and the spectra were swept at a rate of 5 cm^{-1}/min. The signal-to-noise ratio at this integration time was limited by shot noise due to the intense broadband background scattering from the porous Vycor samples: a typical signal-to-noise ratio for the surface phonon peaks is 20–30. Due to the spatial inhomogeneity of the samples caused by the leaching process during manufacture, the laser beam spread out horizontally in the samples. As the spreading of the beam and thus the laser power density was greatly modified by variations of the input laser beam angle as small as 10^{-3} rad, which could occur over the length of a single trace of a spectrum, each spectrum required internal calibration. For this reason the low-frequency bulk SiO_2 phonon spectrum of each sample was taken both at the beginning and end of each high-frequency trace and the spectra were normalized to the height of the 800-cm^{-1} bulk band. The repeatability in normalized peak heights from trace to trace is within 4%.

Polarized spectra were obtained and are discussed in Ref. 48. Accurate depolarization ratios were difficult to obtain for porous Vycor because of the spatial inhomogeneity of the sample and the uncertainties due to background subtraction. The spatial inhomogeneity of the porous Vycor caused an additional depolarization of the bulk SiO_2 bands compared to that in Suprasil.[48]

E. Intrared-reflectivity measurements

The infrared-reflectivity measurements were performed with a Digilab FTS14 Fourier-transform spectrometer. A reflection jig was designed[20] to accept the light scattering cell which could be sealed off with all metal valves and transported to the infrared spectrometer. Thus infrared-reflectivity and Raman scattering measurements were made on the same sample. The reflectivity of a large flat face of a sample was measured at approximately 10° incidence through a KRS-5 window on the sample cell, tilted by a small angle with respect to the sample face to avoid spurious reflections from the window at the detector. The reflectivity measurements were normalized to a freshly evaporated gold mirror (~1000 Å thick) placed in the sample holder in the same manner as the sample inside the cell. Because of the sharp spectral cutoff of the KRS-5 window, it was impossible to obtain spectra below 250 cm^{-1}. The instrumental spectral width was 8 cm^{-1} in all traces. Identical spectra were obtained for Suprasil samples both in position inside and outside the cell. As the direct reflectivity of the porous Vycor samples is less than 1%, care was taken to subtract the reflected background light due to scattering in the cell and reflections of the incident infrared beam from the window.

F. Background subtraction from the Raman and infrared spectra

The elastic scattering (Rayleigh scattering and stray reflected light in the scattering cell) from porous Vycor is approximately 150 times more intense than that from Suprasil, which is turn is about 50 times larger than the Rayleigh scattering from air at 1 atm pressure and 25 °C. The elastic peak in Vycor is eight orders of magnitude more intense than the peak heights of the SiO_2 bulk phonons. The background in the Vycor Raman spectrum due to the high-frequency tails of the elastic peak is comparable in intensity to the Raman scattering at 50 cm^{-1}. Each trace of the spectrum was corrected for this background in the following manner: The instrumental line shape of the spectrometer was measured by directing through the collection optics the elastically scattered light from a clean roughened metal surface positioned in place of the sample. The intensity of the Vycor elastic peak was measured at the beginning of each Raman trace with identical collection optics. The high-frequency tails of the instrumental profile were scaled by the peak height ratio and subtracted from the Raman spectrum. The total error in the resulting spectrum due to this subtraction procedure in the frequency region from 30 to 100 cm^{-1} is estimated to be less than 15%. Above 100 cm^{-1} this error estimate is reduced to 5%, due to the rapid falloff of the instrumental tails. Traces taken on clean Vycor samples agree to well within this quoted absolute error. The elastic background is negligible above 300 cm^{-1}.

At high frequency, there is a broad flat background in the Raman spectrum of porous Vycor, which we believe to be attributed to a combination of an intrinsic surface effect and bulk impurity fluorescence, as discussed in Sec. VI. The line shape of this broad background was approximated by a smooth curve, and fit to the spectrum near 1700-cm^{-1} Stokes shift where Raman scattering from the phonons of the glass is negligible. The spectral line shape of the background was obtained by subtracting two Vycor traces, one with a larger background than the other. This estimate is in good agreement with the smoothed line shape obtained by requiring the ratios of intensities of the SiO_2 bulk phonons to match those of Suprasil. In addition, it was discovered that porous Vycor spectra in which this background was several orders of magnitude larger than the Raman scattering from the phonons matched the line shape obtained by either of the other methods after multiplying by a constant factor. Figure 1 shows the spectral line shapes and relative intensities of the two backgrounds in the Raman spectrum for a typical porous Vycor sample which has undergone the cleaning procedure outlined.

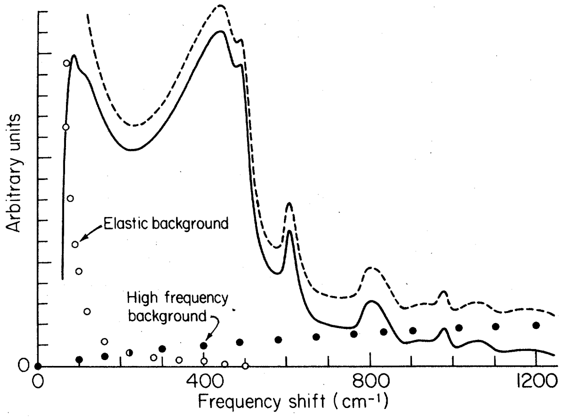

FIG. 1. Contributions to the background in the Raman spectrum of porous Vycor. The upper trace (dashed line) is the observed Raman spectrum and the lower (solid line) is the corrected spectrum with background subtracted. The dots show the relative intensities of the two backgrounds described in the text.

The background in the infrared-reflectivity spectrum is due mainly to reflections from the KRS-5 cell window. It was measured before each experimental run by taking several thousand scans of the Fourier-transform interferometer with the sample removed from the cell, then smoothed and subtracted point by point from the spectra of both the sample and gold mirror. Although the background spectrum was essentially flat, this procedure was necessary as the background could be as large as the signal from the Vycor, and was a particular problem in the frequency region below 500 cm^{-1}. The background subtraction is the major cause for the quoted error bars for the absolute reflectivity spectrum.

III. THEORETICAL MODEL FOR INTRINSIC SURFACE PHONONS OF AMORPHOUS SILICA

In this section we will first review briefly the present understanding of the structure and vibrational excitations of bulk amorphous silica, and then discuss theoretical calculations and physical expectations for vibrations on the surface of this material.

A. Vibrational excitations of bulk amorphous silica

The generally accepted structural model for bulk amorphous silica is one in which near perfect SiO_4 tetrahedral units are connected together at bridging oxygens into a continuous random network, as proposed by Zachariasen.[21] The short-range bonding order of amorphous silica manifests itself by the presence of relatively sharp high-frequency features in the phonon density of states.[22] X-ray diffractions studies[23] show that long-range order is destroyed by Si–O–Si bond-angle variations which can be as large as 20° from the average angle of 144°, as well as dihedral angle variations which disorient neighboring tetrahedra by random rotations about the connecting Si–O bond axis. Bonding coordination changes or unsatisfied broken bonds are relatively low in concentration and are considered defects in a perfect vitreous network. The vibrational spectra of amorphous silica are for the most part understood in the framework of this model of a tetrahedrally bonded solid, although there are still uncertainties[24] as to whether the tetrahedra are connected in a completely random fashion.

Working from a continuous random network model for amorphous silica constructed of several hundred atoms in a tetrahedral bonding arrangement, Bell and Dean[25] carried out numerical calculations of the vibrational density of states which are in moderately good agreement with that obtained from neutron scattering experiments.[26] The phonon density of states for the material is

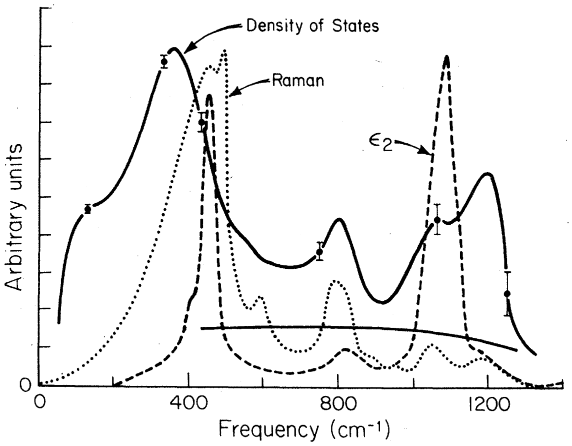

FIG. 2. Phonon density of states compared to the infrared and Raman spectra of bulk amorphous silica. The phonon density of states (solid line) was obtained with neutron scattering (from Ref. 26). The lower solid line shows the estimated two-phonon contribution to the density of states, and the error bars are representative for the neutron scattering data. The imaginary part of the dielectric constant, ϵ_2, (dashed line), and the reduced polarized Raman spectrum (dotted line) are those of Suprasil. The vertical scales are arbitrary. The peaks near 450, 800, and 1100 cm^{-1} can be described as the normal modes of an Si_2O molecular unit.

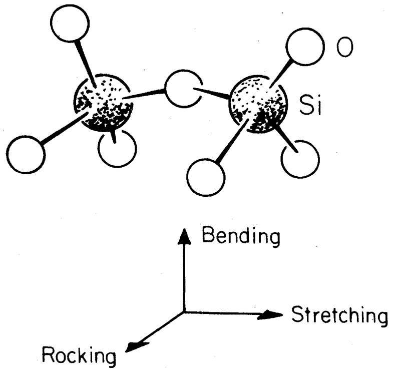

FIG. 3. Normal vibrations of an Si_2O molecular unit in bulk amorphous silica. Two adjacent SiO_2 units are shown connected by a bridging oxygen atom. The axes point along the directions in which the oxygen moves in the bond bending, stretching, and rocking normal modes of the Si_2O "molecule." These normal modes correspond to peaks in the spectra. Here the bond bending axis is parallel to the bisector of the Si–O–Si angle; the bond stretching axis is perpendicular to this bisector, but still in the Si–O–Si plane; the bond rocking direction (which is orthogonal to the other axes) is normal to the Si–O–Si plane (from Bell and Dean, Ref. 25).

shown in Fig. 2. Laughlin and Joannopoulos[27] recently demonstrated, using a Bethe lattice as a model, that the peaks at 450 cm^{-1}, 800 cm^{-1}, and 1050 cm^{-1} in the vibrational density of states correspond to bond rocking, bond bending, and bond stretching normal modes of an Si_2O molecule in accordance with Bell and Dean's original classification scheme. These normal modes are depicted in Fig. 3. Laughlin and Joannopoulos and Gaskell and Johnson[24] have shown that the Si–O–Si bond-angle variations in the amorphous network are the major cause of broadening of these peaks.

In a crystalline material the constraint of wave-vector conservation allows only discrete zone-center phonons to interact with light and thus sharp lines appear in the first-order infrared absorption and Raman spectra. In the absence of long-range order this constraint is relaxed and any phonon can be optically active.[28] This results in continuous first-order spectra for amorphous materials. These spectra display features due to structure in the one-phonon density of states as well as matrix element effects due to the interaction of local bonding arrangements with the light. Figure 2 compares the Raman and infrared spectra with the vibrational density of states for pure bulk amorphous silica. This material exhibits a complicated combination of "moleculelike" and density-of-states continuum effects.[22] The low-frequency Raman spectrum is a continuum which is approximately proportional to the vibrational density of states.[28] The higher-frequency peaks in the Raman and infrared spectra and the peak at 450 cm^{-1} in the infrared exhibit strong variations in their coupling to light. These peaks can be attributed to localized bond bending and bond stretching modes.[29] The peak at 1200 cm^{-1} in the Raman spectrum has been shown to correspond to a peak in the dielectric loss function $1/\epsilon$ and thus has been attributed[30] to a longitudinal mode split off in frequency from the transverse mode at 1060 cm^{-1} due to the slightly ionic behavior of the Si–O bonds. While the longitudinal and transverse nature of vibrations in an amorphous substance is not obvious in terms of atomic motions, the macroscopic electric polarization fields accompanying these vibrations must play a role in this frequency splitting. The sharp peaks at 490 cm^{-1} and 606 cm^{-1} in the Raman spectrum have been attributed[31] to bonding defects in the network as they have been shown to increase in intensity after neutron bombardment.[31,32] An alternative explanation[30] for the 490-cm^{-1} mode is that it is a longitudinal counterpart of the broad peak at 450 cm^{-1}. The microscopic origin of neither of these sharp peaks in the Raman spectrum has been determined and the question is a matter of recent controversy.[33]

B. Surface vibrations of vitreous silica

In a first approximation, the surface of vitreous silica contains unsatisfied silicon and oxygen bonds. The high-frequency vibrations of these dangling bonds are expected to be spatially localized due to the molecular-type bonding of the underlying bulk. A good model for a localized unsaturated bond on an amorphous surface is to connect the surface atom to a Bethe lattice.[19,34] The Bethe lattice appropriate for silicon dioxide has been discussed in detail by Laughlin and Joannopoulos.[27] They have performed numerical phonon density-of-states calculations for the SiO_2 Bethe lattice terminated either with a silicon atom or an oxygen atom, and find a number of sharp surface features. The amplitudes of the surface modes extend several layers deep into the bulk and therefore these vibrations, though spatially localized, can not be visualized as the surface atom vibrating against an infinitely massive substrate. Since surface reconstruction or differences in force constants at the surface bonds were not taken into account, the frequencies of the modes in the Bethe lattice calculations are not expected to be precise. These calculations give a good qualitative feel for the relative frequency position of the features in the density of states.

For the silicon terminated surface, they find a sharp surface state at 450 cm^{-1} at the upper edge of the bulk band. This corresponds to the vibration of the surface silicon atom normal to the surface in the cage of the three oxygens to which it is bonded. There is also an increase in the density of states around 100 cm^{-1} which is caused by the high-frequency surface acousticlike vibrations. These vibrations are acousticlike in that they are at such low frequencies that neighboring surface atoms must vibrate in phase.

At the oxygen terminated surface, they find a sharp surface state at 850 cm^{-1} associated with the bond stretching motion of the surface oxygen atom, a low-frequency band of surface states peaking at 300 cm^{-1} associated with the wagging motion of this atom, and again, there is an enhancement of the low-frequency density of states due to surface acousticlike vibrations. Si–O bond stretching and wagging features at 850 and 350 cm^{-1} were also found by Bell and Dean[25] in their bulk density-of-states calculations when they allowed the nonbridging oxygens in their model to vibrate freely.

As a result of numerous infrared-absorption and chemical reaction studies,[4,14] it is well known that the surface of silica is covered with hydroxyl groups whose concentration depends on the prior heat treatment of the glass. For heat treatments below 300 °C it is believed[14] that every surface silicon dangling bond is saturated with an OH group in one of three configurations: a single noninteracting "free" OH group; geminal OH groups, where two hydroxyls are attached to the same surface silicon; and in a configuration where two OH groups on neighboring silicons are hydrogen bonded to each other. As the temperature of heat treatment is raised, the number of surface hydroxyl groups decreases and the relative concentrations of the three configurations change; however, the variations are somewhat sample dependent. These hydroxyls are very tightly bound on the surface, some remaining at temperatures above 1000 °C. The oxygen terminated surface of Laughlin and Joannopoulos with the oxygen replaced by a hydroxyl group should be a good model for the noninteracting hydroxyl groups on the actual silica surface, and thus we compare our experimental spectra with their model calculations for the oxygen terminated surface. For geminal OH groups, the Si–O stretch mode in their calculations splits into two peaks separated by about 100 cm^{-1}, and the wagging mode splits into two peaks with about half that separation. We see strong peaks in our experimental spectra that are associated with noninteracting Si–OH stretching and wagging modes, but do not see clear evidence for hydroxyls in a geminal configuration.

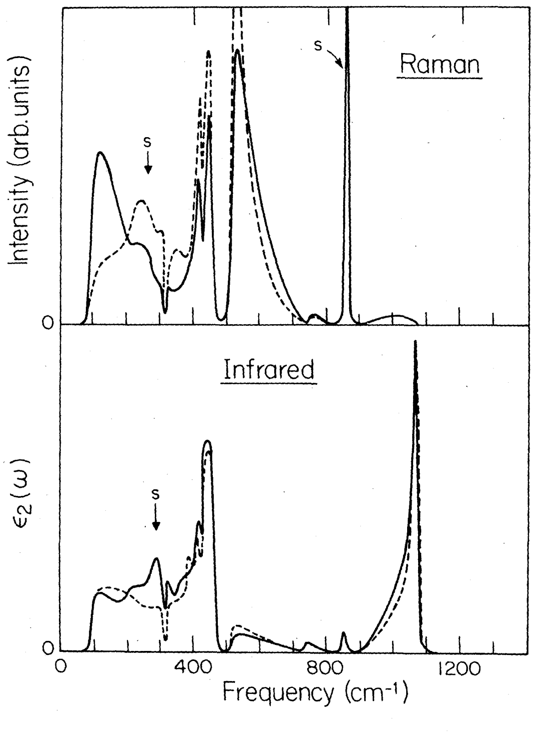

FIG. 4. Theoretical Raman and infrared spectra for the oxygen-terminated silica surface. Cluster–Bethe-lattice calculations of the spectra are shown for the silica surface (solid line) and bulk (dashed line). The arrows designate surface induced features in the spectra (from Laughlin and Joannopoulos, Ref. 19).

Laughlin and Joannopoulos have calculated Raman and infrared spectra for the surface using matrix elements appropriate for quartz by assuming that a small cluster of atoms near the surface interacts with the light. Kleinman and Spitzer's[35] dynamic effective charges were used for the infrared, and the polarizability was considered to change only with Si–O bond stretching for the Raman effect. Their calculated spectra for the oxygen (free hydroxyl) terminated surface are shown in Fig. 4. The Si–O stretch mode at 850 cm^{-1} in their calculations is strongly Raman active but not active in the infrared, while the wagging mode at about 300 cm^{-1} shows the opposite tendency. This can be understood from the fact that only bond stretching is Raman active in their model, and that the oscillating dipole moment of the oxygen vibrating normal to the surface is nearly cancelled by the sympathetic motion of the substrate beneath. There is also a shift to lower frequency of the surface Raman spectrum compared to that of the bulk due to the acoustic surface modes. This is not evident in the infrared.

IV. EXPERIMENTAL RESULTS: INTRINSIC SURFACE PHONONS OF THE CLEAN SURFACE

In this section we compare the experimental spectra of bulk pure amorphous silica with those of clean porous Vycor. We find that certain modes in the porous Vycor spectra exhibit similar characteristics to the surface phonons of the oxygen terminated Bethe lattice. We demonstrate that those modes are not caused by bulk impurities in Vycor. They are shifted in frequency by surface deuteration. In the following section we show that they are strongly affected by adsorbed molecules.

A. Bulk impurity effects on the Raman and infrared spectra of porous Vycor

Figure 5 contrasts the low-frequency Raman and infrared-reflectivity spectra of clean porous Vycor with those of Suprasil. The Raman intensity of the bulk SiO_2 bands is proportional to the density of the two samples and the spectra have been normalized to be equal at 440 cm^{-1}. The background has not been subtracted from the Vycor spectrum. The Raman spectrum of porous Vycor is similar to that obtained by Buechler and Turkevitch.[9] The Vycor infrared-reflection spectrum is the first to be obtained in the intrinsic phonon region. Both the low intensity and the frequency shifts of the bulk bands in the Vycor reflectivity spectrum with respect to that of Suprasil are explained by the low density of the Vycor samples. As the reflectance is determined by both the real and imaginary parts of the dielectric constant, the peaks in the reflectance are "pulled" more to higher frequency in the more dense sample. The peaks in the imaginary part of the dielectric constant for the SiO_2 bulk modes coincide for the two samples. As we will demonstrate, the features marked by "*s*" in the porous Vycor spectra are due to intrinsic surface phonons of silica. We attribute the sharp mode in the Raman spectrum at 980 cm^{-1} to the Si-OH stretching mode and the peak at 380 cm^{-1} in the infrared to the corresponding wagging peak. The O–H vibrations associated with these features are observed as peaks near 3700 cm^{-1} and will be discussed later. A shift of intensity in the Raman spectrum of porous Vycor is also apparent near 300 cm^{-1}. This could be due to the "acoustic" surface modes of Laughlin and Joannopoulos.[34]

We observe an increase in intensity of the mode near 600 cm^{-1} marked *d* in the porous Vycor Raman spectrum which we attribute to an increase in the number of structural defects in the silica near the surfaces of the internal pores as a result of the leaching process. Further discussion of this mode in Vycor will be reserved for Sec. VI. The origin of the broad background in the porous Vycor Raman spectrum will be discussed in Sec. VII.

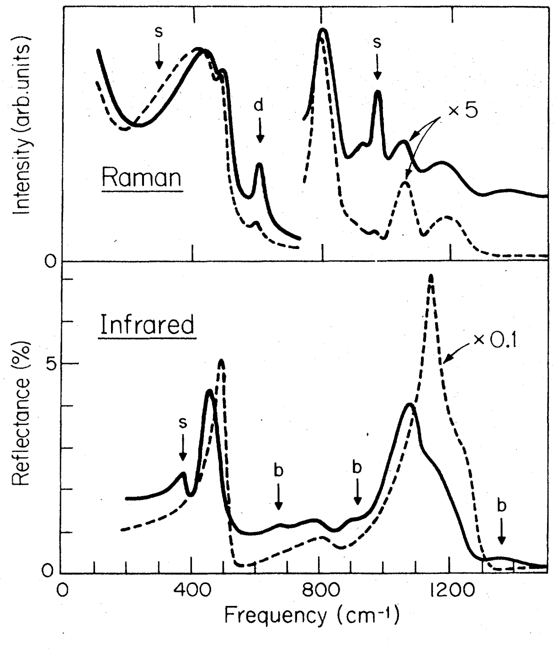

FIG. 5. Experimental spectra for porous Vycor and Suprasil. The experimental spectra for porous Vycor (solid line) and Suprasil (dashed line) are shown in the low-frequency region. Top: The Raman intensities have been normalized to 1 at 450 cm^{-1}. Bottom: The absolute infrared reflectance is shown for the two samples. Typical error bars are less than the line thickness for the traces with the exception of the far-ir (< 450 cm^{-1}) region in the reflectance measurements, where they are ± 0.3%. The arrows designate important changes in the spectra as discussed in the text.

The features marked *b* in the figure are due to boron impurities in Vycor. Infrared active modes at 670, 930, and 1380 cm^{-1} have been observed[36] in low-boron-content borosilicate glasses as well as in condensed Vycor.[37] These modes can be attributed to bond rocking, bending, and stretching modes of a B–O–Si bridging structure.[38] The modes at 930 and 1380 cm^{-1} are also visible in the Raman spectrum of porous Vycor. In Fig. 6 we display for comparison the Raman spectra of preleached Vycor, porous Vycor, condensed Vycor, and Suprasil. The three different forms of Vycor are results of steps in the manufacturing process of condensed Vycor glass (Corning code 7900) as described by Nordberg.[9] There are several important observations to be made about these spectra. First, the surface peak at 980 cm^{-1} does not appear in the nonporous forms of Vycor. These have comparable impurity contents to porous Vycor other than the existence of the B_2O_3 phase in preleached Vycor. The absence of this mode in

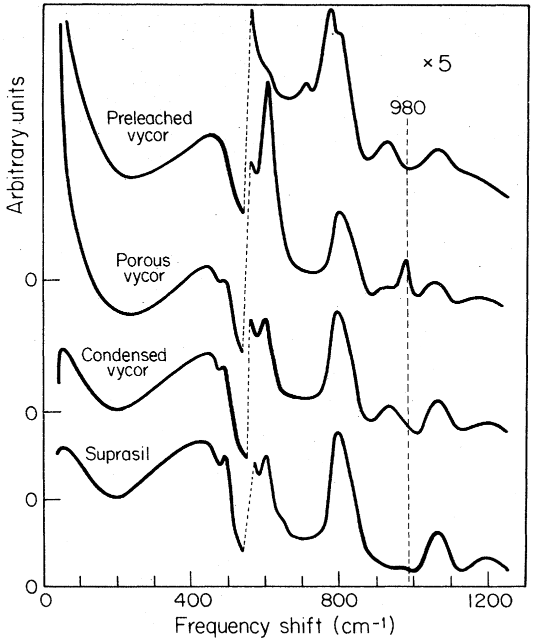

FIG. 6. Raman spectra of preleached, porous, and condensed Vycor compared to the spectrum of Suprasil. The intensities of the spectra at 450 cm^{-1} have been normalized to be equal and the zero has been shifted for each trace. The surface peak 980 cm^{-1} in the porous Vycor spectrum is absent in the nonporous Vycors. Impurity effects on the spectra are discussed in the text.

the preleached and condensed Vycors thus demonstrates this mode is not an impurity effect. Likewise, the corresponding wagging surface mode at 380 cm^{-1} does not appear in the far-infrared-absorption spectrum of condensed Vycor.[37] Second, the mode at 930 cm^{-1} due to boron-oxygen-silicon linkages, which has previously been identified in the infrared, appears in all three forms of Vycor. Third, there is a similar flat background in all three Vycor traces which extends far into the red (–4000-cm^{-1} shift) which may be due in part to heavy-metal-impurity fluorescence. More discussion on this point is in Sec. VII. The sharp peak near 800 cm^{-1} in the preleached Vycor spectrum has been observed in the Raman spectrum of borate glass and is a vitreous B_2O_3 mode.[39] This peak does not appear in the leached Vycors as the B_2O_3 phase has almost completely been removed in the leaching process. There is a small peak at 970 cm^{-1} in the Suprasil spectrum which is due to *bulk* Si–OH stretch. As we will demonstrate in Sec. V, the 980-cm^{-1} peak in the porous Vycor spectrum is affected by adsorbed molecules and we believe that it is primarily a *surface* Si–OH stretch.

B. Discussion of the spectra in the low frequency region

Figure 7 compares the reduced Stokes Raman spectrum of porous Vycor and Suprasil as well as the imaginary part of the dielectric constant, ϵ_2, for these two materials. The dielectric constant was obtained by a Kramers-Kronig analysis[20] of the infrared-reflectivity spectrum for each material. The reduced Raman spectrum[28,40] is given by the expression

$$I(\nu)\frac{\nu}{n(\nu,T)+1}\left(\frac{\nu_0}{\nu_0-\nu}\right)^4 ,$$

where ν is the Stokes shift from the exciting frequency ν_0, $n(\nu,T)$ is the Bose population factor at sample temperature T, and $I(\nu)$ is the observed spectrum with background subtracted. The temperatures used for reduction of the data were measured by the Stokes–anti-Stokes ratio as discussed in Sec. II. They are 105 ± 5 °C and 150 ± 10 °C for the nonporous and porous samples, respectively, for 400-mW input laser power in a spot of 50-μm diam. Both the Raman spectra and ϵ_2 for the samples have been normalized to be equal at the 450-cm^{-1} bulk band. The normalization factors used were 1.5 for the Raman spectra, and 8.5 for ϵ_2. The reason for this discrepancy is the decrease of density in the porous samples near the edges where the infrared-reflectivity data were taken. A penetration depths for light of several microns is typical in this frequency region. Thus different portions of the Vycor samples, and thus most likely different surface to bulk ratios, were studied in the two experiments, and the absolute Raman and infrared intensities of the surface modes can not be directly compared. As a flat face of the sample is needed for reflectivity measurements, the only way to circumvent this problem would be to perform infrared absorption and Raman measurements on a very thin Vycor sample.

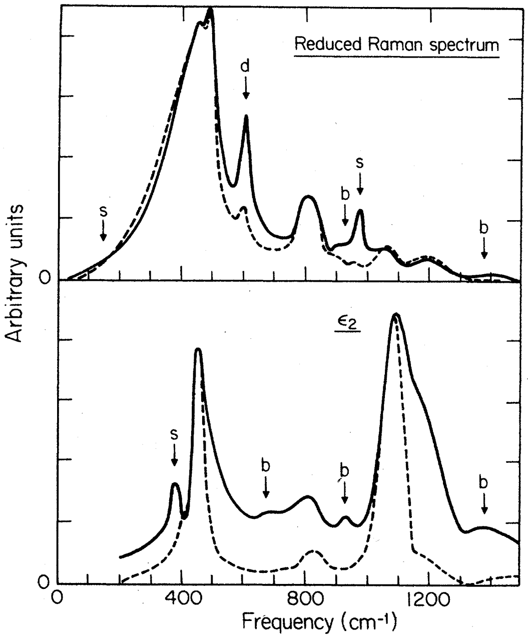

FIG. 7. Reduced experimental infrared and Raman VV polarized spectra for porous Vycor (solid line) and Suprasil (dashed line). Both spectra have been normalized to be equal at 450 cm^{-1}. The features marked with *s* are surface derived. The features marked with *b* are due to boron impurities in porous Vycor. The peak marked *d* is due to bulk bonding defects.

The shift of intensity near 150 cm^{-1} in the Raman spectrum of porous Vycor with respect to that of Suprasil as seen in Fig. 7 is also found with respect to the reduced condensed Vycor spectrum. This implies that the shift is neither an impurity nor temperature-related effect, but may be due to the acousticlike surface phonons previously mentioned. Note that the low-frequency region of the reduced spectra is deemphasized by the multiplicative frequency factor. At frequencies below 150 cm^{-1}, we find an increase of about 20% in the porous spectrum compared to the nonporous. In this region, however, the absolute error due to background subtraction is estimated to be about 15%. The decrease of intensity in the porous spectrum about 150 cm^{-1} is well within the error estimates.

The modes marked by b in the figure are due to boron impurities as discussed previously. There is a continuous infrared absorption in porous Vycor which is not present in Suprasil and cannot be accounted for by errors due to subtraction of spurious background reflections. The SiO_2 bulk bands at 450 and 1050 cm^{-1} are also wider in porous Vycor than those of Suprasil. Both of these features in the Vycor infrared spectrum could possibly be due to surface or disorder-induced absorption.

It has been suggested[41] that the 970-cm^{-1} peak in the Raman spectrum of *bulk* vitreous silica is an Si–OH stretching vibration of isolated hydroxyl defect sites. Recently this identification has been confirmed[42] by deuteration of the bulk hydroxyls and correlation with the high-frequency O–H stretching mode intensity. We observe a small shoulder near 400 cm^{-1} in the infrared spectrum of Suprasil which we identify as the *bulk* counterpart of the *surface* Si–OH wagging mode at 380 cm^{-1} in the porous Vycor spectrum. Apparently this shoulder has not been previously reported.

We find that the 980-cm^{-1} surface Si–OH stretching peak in the Vycor Raman spectrum is approximately 20 times larger in integrated intensity than the corresponding bulk feature in the Suprasil spectrum. The ratio of integrated intensity for the 380-cm^{-1} surface Si–OH wagging peak and the bulk 400-cm^{-1} shoulder is consistent with the above ratio for the stretching modes but necessarily much more inaccurate. If the matrix elements do not appreciably differ for the surface and bulk Si–OH stretch modes, and also the ratio of the hydroxyl density to the integrated intensity of this peak is similar in the two samples, an estimate for the number of surface hydroxyl groups can be made if the OH content of the Suprasil is known. By measuring the absorption of our Suprasil sample at 2.2 μm,[43] we determined its hydroxyl content to be $(3.3 \pm 0.5) \times 10^{19}/\text{cm}^3$. This gives a Vycor surface hydroxyl density equal to

$$d^{\text{OH}}_{\text{Vycor}} \approx d^{\text{OH}}_{\text{Suprasil}} \times \alpha \times 20 \,,$$

or $(4.6 \pm 2) \times 10^{20}/\text{cm}^3$. Here α is the normalization factor for the spectra, approximately equal to the density ratio (0.7) of the two samples. This hydroxyl density is in good agreement with a more accurate measurement which we obtain with ammonia adsorption and also with published values in the literature, as discussed in Sec. V. Hartwig[44] suggests that the value of the extinction coefficient quoted in Ref. 43 may be too small by about 20%. This is also in better agreement with our results, but within the error bars for our infrared-absorption measurements on Suprasil.

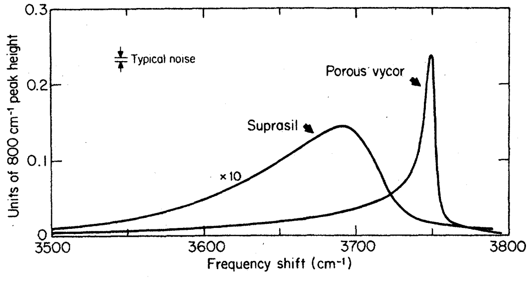

FIG. 8. O-H stretching peak in the Stokes Raman spectrum of porous Vycor and Suprasil. Note the scale change on the Suprasil peak. The porous Vycor peak is due to surface hydroxyls, while that of Suprasil is due to hydroxyls in the bulk silica network.

C. High-frequency region of the Raman spectrum and the effects of deuteration on the surface modes

The feature due to the O–H stretching mode in the porous Vycor Raman spectrum at 3750 cm^{-1} is radically different from that in bulk silica. It is significantly narrower, about an order of magnitude more intense, and shifted to higher frequency by 60 cm^{-1} compared to its bulk counterpart in the Suprasil spectrum. It is this OH stretching mode which has been studied so widely in infrared-absorption experiments on silica gel and porous Vycor. The OH stretching modes in the Raman spectra of porous Vycor and Suprasil, scaled to the 800-cm^{-1} bulk band height for each sample, are shown in Fig. 8. The background in the Vycor trace at high frequency can be approximated by a sloping straight line and has been subtracted from the spectrum. It is difficult to estimate the extent of the systematic error in the long low-frequency tail of the Vycor OH peak due to this subtraction procedure. The total integrated intensity of the OH feature differs by a factor of 4 in the two samples.

The OH stretching mode in the Raman spectrum of bulk silica has undergone detailed spectral analysis.[45,46] It is believed[45] that both the asymmetry and width of the band can be explained by the existence of a number of separate hydroxyl species located in different environments in the bulk network. It has also been suggested[46] that hydrogen bonding in different environments could spread the eigenfrequencies of a single bulk OH unit. In a similar fashion, the sharp absorption peak which occurs at 3548 cm^{-1} in the infrared spectra of silica surfaces has been attributed[14] to isolated surface hydroxyls, while the broad low-frequency portion of the band has been associated with mutually hydrogen bonded surface OH groups. We find that the sharp peak at 3750 cm^{-1} in the Raman spectrum of porous Vycor is affected by the adsorption of ammonia on the surface and is definitely a surface feature. The asymmetry of the peak is due mainly to the existence of a broad peak centered near 3700 cm^{-1} which is less affected by adsorbed ammonia. The resemblance of the spectral shape of this low-frequency peak in Vycor to the Suprasil band suggests that it is associated either with bulk hydroxyls or surface hydroxyls which are mutually hydrogen bonded and are not affected by ammonia adsorption.

A 30% deuterated surface was obtained by boiling a porous Vycor sample repeatedly for several hours in 98-vol% D_2O before the normal heat treatment at 600 °C in oxygen. The OD stretching peak occurs at 2765 cm^{-1} in the Raman spectrum as compared to 2763 cm^{-1} in the infrared spectrum.[47] The OD peak in our Raman spectrum exhibits less asymmetry at low frequency than the OH peak and is slightly narrower, as shown in Fig. 9. The figure also compares the low-frequency spectra for the normal hydroxylated and partially deuterated samples. The Si–OH surface peak at 980 cm^{-1} is reduced in intensity in the spectrum of the deuterated sample by about 30%, while the region of the spectrum near 950 cm^{-1} is filled in. If the Si–OH stretching mode is assumed harmonic, the band will shift on deuteration by the ratio $(17/18)^{1/2}$ due to the increased mass of the deuteroxyl group to a frequency of 952.4 cm^{-1}. The Raman spectrum for the deuterated sample is consistent with a peak of the same width and about half the intensity of the 980-cm^{-1} peak located at this frequency. The bulk Si–OH stretching mode has been observed[42] to decrease in frequency by this ratio from 969 cm^{-1} to 941 cm^{-1}, which is in good agreement with the shift of the surface peak. The interaction of the deuterated surface with ammonia, discussed in Sec. V, indicates clearly that there is a surface OD peak in the region near 950 cm^{-1}.

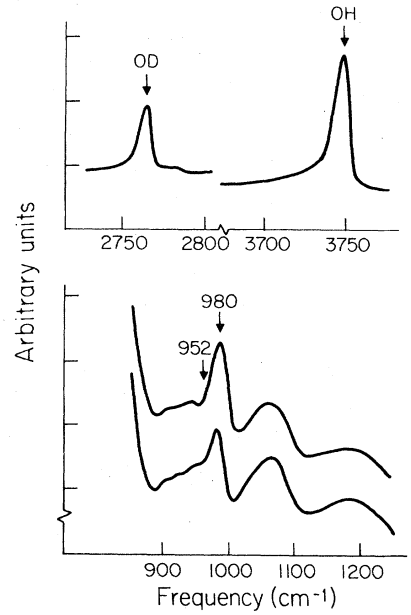

FIG. 9. Effects of deuteration on the Raman spectrum of porous Vycor. Top: An O–D stretching peak appears at 2765 cm^{-1} in the high-frequency region of the spectrum of a 30% deuterated surface. Bottom: The low-frequency region of the spectrum is compared for a normal surface (upper curve) and the 30% deuterated surface (lower curve). The spectral response of the collection optics has been taken into account. In the spectrum of the partially deuterated surface, the 980-cm^{-1} Si–OH peak is reduced in intensity and the region around 950 cm^{-1} fills in due to the addition of Si–OD stretching vibrations at 952 cm^{-1}.

V. INTERACTION OF THE SURFACE PHONONS WITH ADSORBED AMMONIA MOLECULES

In this section, we experimentally verify the identification of the Raman-active 980-cm^{-1} and 3750-cm^{-1} modes as surface derived by studying their interactions with adsorbed ammonia molecules.

The ammonia molecule was chosen as an adsorbate in the Raman experiment for a number of important reasons: The NH_3-SiO_2 system has been extensively studied with infrared-absorption experiments[4,14] in the 3-μm wavelength region. It is known from these experiments that NH_3 interacts strongly and almost exclusively with the hydroxyl groups on the silica surface. Therefore the molecule is well suited for probing the Raman-active surface Si–OH stretching mode of the glass. The ammonia molecule is small, simple, and has strong Raman bands which do not overlap in frequency with the surface phonons. Another extremely important consideration is the fact that we find that adsorbed ammonia does not affect the background in the Raman spectrum. The large increase in scattering background upon exposure to hydrocarbons has been a major problem in Raman studies of silica and other oxide surfaces.[5] For example, Buechler and Turkevich[8] reported a tenfold increase in the background intensity several hours after initial exposure of porous Vycor to benzene vapor. This background became so intense that it soon overwhelmed all Raman scattering from the adsorbed benzene, as well as the much weaker bands of the bulk silica. No previously reported Raman experiments have studied the effect of adsorbates on the silica surface vibrations, possibly for this reason. Because the background was unaffected by the ammonia even after periods of exposure of a few weeks, we were able to study not only the spectrum of ammonia molecules perturbed by the nearby surface, but also the perturbations on the surface phonons brought about by the molecules. Our Raman experiment spans the frequency range from about 100 cm^{-1} to over 4000 cm^{-1}, a larger range than is easily obtainable with typical infrared spectrometers. We measured the number of molecules adsorbed on the sample concurrently with the Raman experiment and thus monitored the often subtle changes in the spectrum as a function of known coverage. Our measurements of the total number of molecules on the sample are accurate to ±3%. The intensity of the Raman scattering in each trace was internally calibrated to the height of the 800-cm^{-1} bulk silica peak which was found unchanged to within 4% due to adsorbates. The low-frequency spectrum was measured both before and after the high-frequency region of each spectral trace. The background was subtracted from each trace in the same manner as for the spectral traces on the pristine sample. The normalized peak heights of the bulk SiO_2 bands were constant to within 6% in the resulting subtracted traces. Thus we are able to measure the alterations of peak height of the surface bands resulting from adsorbate molecules to this accuracy. Our measurements of the frequencies of the band centers are reproducible to ±1 cm^{-1}.

We have also studied the effects of water adsorption on the Raman spectrum. In agreement with infrared experiments,[14] we find very subtle changes in the surface modes. The effect of water on the defect mode is discussed in Sec. VI. Also, water was found to affect the background in the Raman spectrum. A detailed discussion of the water adsorption experiment is given in Ref. 48.

A. High-frequency region and 3750-cm^{-1} surface O-H stretching mode

A number of infrared-absorption experiments performed in the 3-μm region have revealed that ammonia reacts with the surface hydroxyl groups by the formation of hydrogen bonds.[14] This is manifested in the infrared spectrum by a decrease in the sharp "free" OH absorption band at 3748 cm^{-1} and the appearance of an extremely intense and broad absorption around 3100 cm^{-1} caused by the hydrogen bonded surface hydroxyl groups. The width and intensity of this band have been attributed[49] to extremely polarizable hydrogen bonds coupled with the stochastic electric fields which exist on the surface. The absorption bands of the ammonia appear on top of this intense continuum which extends from about 2000–4000 cm^{-1}.

In the high-frequency Raman spectrum, shown

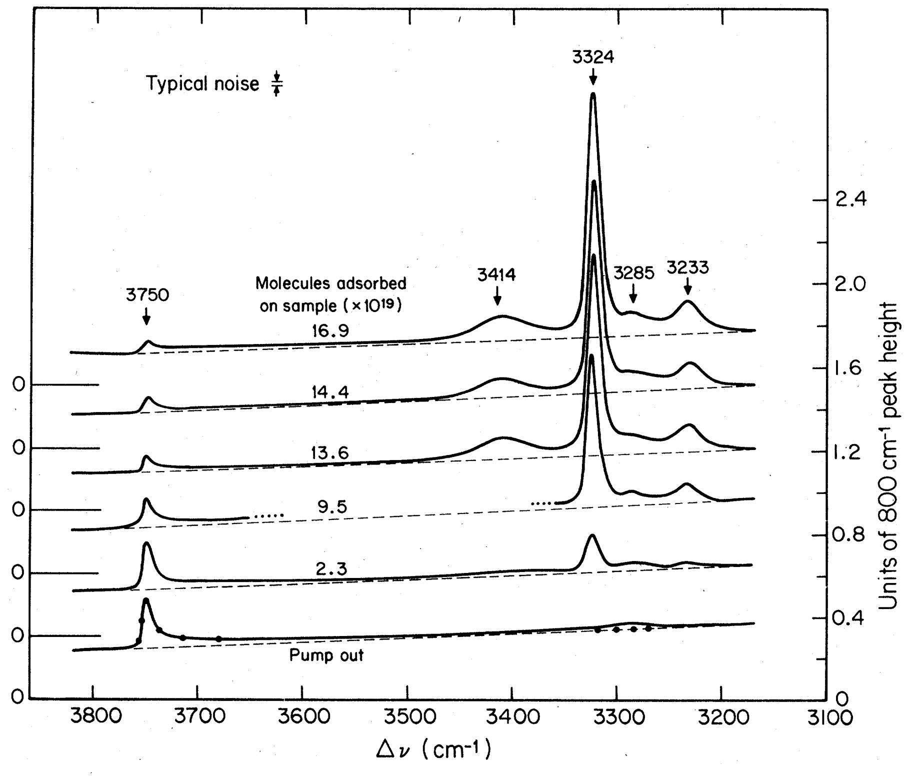

FIG. 10. High-frequency region of the Raman spectrum of porous Vycor as ammonia is adsorbed on the surface. Each trace has been normalized to the height of the 800-cm^{-1} bulk silica peak. The background estimate for each trace is shown by a dashed line. The dots in the lowest trace represent the spectrum for the clean sample. The surface O–H stretching peak at 3750 cm^{-1} decreases as the group of lines near 3300 cm^{-1} grows in intensity due to adsorbed ammonia.

in Fig. 10, we observe a linear decrease in the O–H stretching peak at 3750 cm^{-1} with ammonia coverage as a collection of NH_3 lines grow in intensity around 3300 cm^{-1}. Raman scattering from the perturbed hydroxyl groups is not apparent. The reduction of Raman intensity is characteristic of hydrogen bonded systems.[50] This is an advantage in the Raman experiment as we can study the adsorbed ammonia spectrum without interference from this continuum or the substrate bands. The positions of the adsorbed ammonia peaks in the Raman spectrum agree well with the infrared measurements[14] on porous Vycor. The ammonia lines will be discussed in a separate paper.[51]

The background in the Raman spectrum in this frequency region can be accurately approximated by a sloping straight line as depicted in the figure. The background does not change until near monolayer coverage when we begin to observe a weak broad band similar to the infrared absorption band due to hydrogen bonded OH previously mentioned. As this broad band disappears on evacuation of the samples, it is most likely caused by the same mechanism which produces the infrared continuum. A similar broad but weak continuous Raman scattering has been attributed[52] to extremely polarizable hydrogen bonds in aqueous acid solutions.

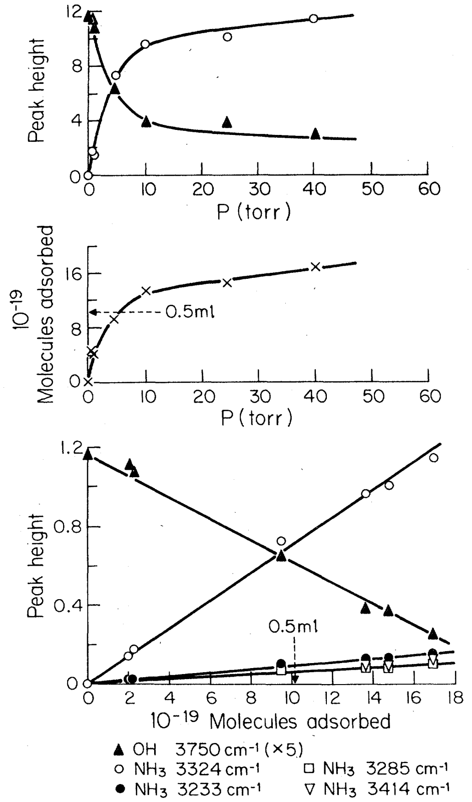

FIG. 11. Normalized peak heights in the high-frequency Raman spectrum as a function of ammonia pressure (top graph) and the measured isotherm for ammonia adsorption (center graph) on the hydroxylated surface. Bottom graph: Normalized peak heights in the high-frequency Raman spectrum as a function of ammonia coverage for the hydroxylated surface. A monolayer is defined as the total number of OH groups on the surface.

Figure 11 shows the normalized heights of various high-frequency peaks in the Raman spectrum plotted as a function of surrounding ammonia gas pressure and ammonia coverage along with the adsorption isotherm measured during the scans of the Raman spectrum. At low coverage, the ammonia peak heights increase linearly with coverage to within measurement error. The surface O–H stretching peak at 3750 cm^{-1} decreases in height linearly with coverage. It completely disappears when the sample is exposed to 700 Torr of ammonia pressure. The width of the sharp O–H peak does not change appreciably with coverage. The slight decrease in frequency of this peak with increasing coverage apparent in the figure is caused by the relative insensitivity of the low-frequency tail of the O–H stretching mode to ammonia adsorption. Infrared measurements[14] have also demonstrated that the low-frequency portion of the OH absorption band is unaffected by ammonia, while the sharp "free" OH band at 3748 cm^{-1} exhibits a linear decrease with increasing coverage. The inverse proportionality of the OH peak intensity to ammonia coverage, along with the narrow width of the adsorbed ammonia bands in the Raman spectrum [full width at half-maximum (FWHM) of 13 ± 1 cm^{-1}, instrumental FWHM of 4 cm^{-1}] suggest that most of the adsorbed NH_3 molecules are hydrogen bonded to the free surface OH groups, which have a range of binding energies. Van der Waals binding to the surface (physisorption) is unlikely at these high temperatures. Upon evacuation, the intense ammonia lines disappear and the original intensity of the 3750-cm^{-1} peak is restored, as shown by the lowest curve in Fig. 10. Thus the small percentage of strongly chemisorbed ammonia which we observe[48,51] takes place on surface sites other than isolated OH.

As the O–H stretching vibration shifts in frequency by about 600 cm^{-1} after hydrogen bonding to ammonia,[14] we can assume that the contribution of all hydrogen bonded hydroxyl groups is removed from the 3750-cm^{-1} peak in the Raman spectrum. Assuming a one to one correspondence between the number of adsorbed ammonia molecules and occupied OH sites, we obtain an upper estimate for the total number of "free" surface OH of $(7.1 \pm 1) \times 10^{20}$ OH/cm^3 or $(4.4 \pm 1) \times 10^{20}$ OH/g. These val-

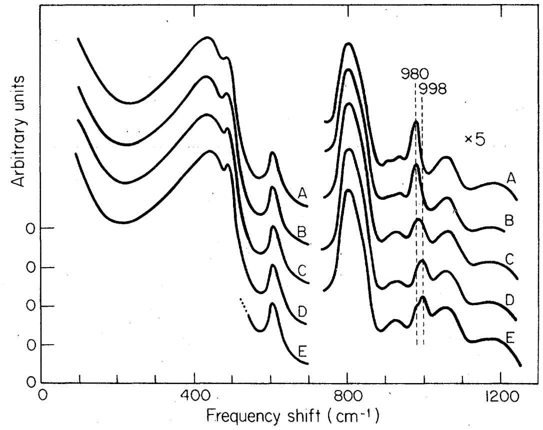

FIG. 12. Effect of adsorbed ammonia on the low-frequency Raman spectrum. The Stokes Raman spectrum of porous Vycor with background subtracted in the low-frequency region is shown as increasing amounts of ammonia are adsorbed on the sample: Curve *A*—clean sample, *B*—2.0×10^{19} molecules, *C*—9.5×10^{19} molecules, *D*—13.6×10^{19} molecules, *E*—16.7×10^{19} molecules. The dashed lines show the frequency shift of the 980-cm^{-1} surface peak due to interaction with the adsorbed molecules.

ues are consistent with the intensity ratios of the 980-cm^{-1} Si–OH stretching modes of porous Vycor and Suprasil obtained in Sec. IV. Assuming a surface area of 200 m^2/g for the sample, we obtain a surface density of ~2.2 OH/(100 Å^2), in excellent agreement with values in the literature[4,14] for silica surfaces pretreated at 600 °C. For our purposes we will define a monolayer capacity to be the total number of OH groups on the surface.

B. Low-frequency region: 980-cm^{-1} surface Si-OH stretching mode

Along with the drastic changes in the 3750-cm^{-1} O–H stretching mode as ammonia is adsorbed on porous Vycor, we observe a very interesting but more subtle alteration of the 980-cm^{-1} peak. Figure 12 shows the low-frequency portion of the Raman spectrum of porous Vycor with increasing ammonia coverage. What at first resembles a broadening of the surface peak is actually a frequency shift from 980 to 998 cm^{-1} of each isolated Si–OH surface vibration as an NH_3 molecule interacts with the OH group. The 2% increase in frequency of this mode may be caused by the increase in polarity of the silicon–oxygen bond resulting from the formation of the hydrogen bond with the ammonia molecule. In the accepted[14] configuration for this hydrogen bond the hydroxyl group acts as the donor with the lone pair electrons of the nitrogen as the acceptor. In the lowest trace in the figure, the 980-cm^{-1} peak remains as a shoulder on the shifted peak. At this coverage about $\frac{1}{5}$ of the original O–H stretching peak intensity (and therefore about this fraction of unaffected silanol groups) remains. A good qualitative fit to the surface Si–OH stretching peak can be obtained by the addition of two Gaussian peaks separated in frequency by 18 cm^{-1}, scaled to the 3750-cm^{-1} surface O–H peak height and having full widths of about 20 and 25 cm^{-1} for the lower- and higher-frequency peaks, respectively. This evidence, along with the observed isotope shift of the 980-cm^{-1} mode upon deuteration, establishes a direct connection between the 3750- and 980-cm^{-1} modes, and that they are both surface derived.

Figure 13 shows the low-frequency region of the Raman spectrum of the deuterated surface as NH_3 is adsorbed. After the first addition of ammonia there is a sharp decrease in intensity in the region around 950 cm^{-1} and a corresponding increase in the height of the 980-cm^{-1} peak. This is consistent with the removal of Si-OD groups at 952 cm^{-1} and the addition of new Si-OH groups due to surface hydrogen exchange which is also observed[48,51] in the high-frequency region of the spectrum. After the initial removal of Si-OD stretching mode intensity, the spectral changes with NH_3 adsorption follow those of the pure hy-

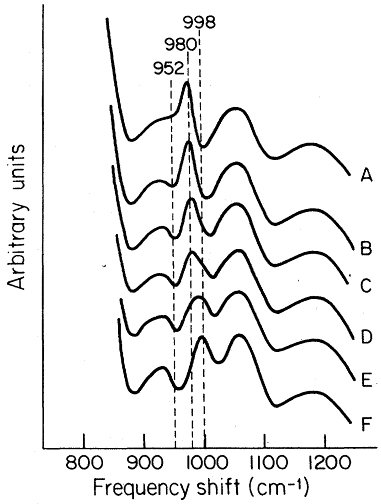

FIG. 13. Effects of adsorbed ammonia of the low-frequency spectrum of the partially deuterated surface. Curve *A*—clean sample, Curve *B*—3.5×10^{19} molecules adsorbed on sample, Curve *C*—6.8×10^{19} molecules, Curve *D*—8.3×10^{19} molecules, Curve *E*—10.3×10^{19} molecules, and Curve *F*—17.2×10^{19} molecules. The dashed lines at 952, 980, and 998 cm^{-1} mark the frequencies of the Si–OD stretching mode, the Si–OH stretching mode, and the perturbed Si–OH stretching mode due to the formation of hydrogen bonds with adsorbed ammonia. The spectra have been vertically shifted for clarity.

droxylated surface exactly. Again the 980-cm^{-1} peak decreases in intensity in proportion to the coverage and a peak at 998 cm^{-1} appears due to hydrogen bonded silanols. There is no apparent alteration of this peak due to adsorbed heavy ammonia. In the experimental run shown in Fig. 13, the 980-cm^{-1} peak has almost vanished at the highest coverage and it is thus evident that there are two overlapping peaks in this region at lower coverages. When the sample is evacuated, the surface Si–OH stretch peak shifts back to 980 cm^{-1} and increases in intensity by approximately 30% over its original height on the pristine surface in accordance with the increase in the number of OH groups on the surface as determined by a proportional increase in the 3750-cm^{-1} peak and complete disapperance of the 2765-cm^{-1} OD stretching peak.[18,51]

Neither the defect mode near 600 cm^{-1} nor the bulk silica bands are affected by ammonia adsorption. We notice an enhancement in the Raman spectrum below 100 cm^{-1} which increases with ammonia coverage, disappears upon evacuation, and does not follow the instrumental line shape. Near monolayer coverage the enhancement observed at 50 cm^{-1} is about a factor of 2 over the Raman bands of silica. It is similar to that observed by Pernoll *et al.*[52] in the very-low-frequency Raman spectra of aqueous acid and salt solutions, which they attribute to extremely polarizable hydrogen bonds. This type of hydrogen bond is believed[49] to exist in the ammonia-silica system and is considered the origin of the intense infrared continuum at high frequencies. Therefore the enhancement which we see at low frequencies in our Raman spectrum may be due to the low-frequency vibrations of surface hydrogen bonds with large Raman cross sections caused by their high polarizability.

VI. DEFECT MODE NEAR 600 cm^{-1}

The sharp peak near 600 cm^{-1} in the Raman spectrum, marked by *d* in Figs. 5 and 7, is attributed to bonding defects in the perfect network of bulk amorphous silica as it has been observed[53] to increase with neutron bombardment and increasing fictive (glass transition) temperature.[54,55] The 608-cm^{-1} peak in the clean porous Vycor spectrum is approximately five times larger in integrated intensity when normalized to the bulk silica band at 450 cm^{-1}, than the corresponding peak at 606 cm^{-1} in the Suprasil spectrum. Due to the leaching process in the manufacture of porous Vycor, it would not be surprising to find bulk defects near the surface of the internal pores, and this is most likely the cause of the increased intensity over that in Suprasil. As shown in Fig. 6, the defect peak is extremely small in the spectrum of preleached Vycor, and is reduced to the size of that in Suprasil in the condensed Vycor spectrum due to annealing at the high temperature used in the contraction.

We observe a $(33 \pm 5)\%$ decrease in the 608-cm^{-1} peak height in porous Vycor with an estimated 3.5×10^{20} water molecules adsorbed on the sample. The decrease of this peak is approximately linear with coverage as shown in Fig. 14. A similar decrease in the intensity of the 606-cm^{-1} defect peak in Suprasil with increasing *bulk* OH content was found by Stolen and Walrafen.[54] However, Galeener *et al.*[55] attribute their observed decrease in the Suprasil defect mode with OH content solely to the fact that material of higher OH content reaches equilibrium faster and therefore has a lower fictive temperature than material of lower OH content. The fact that the peak decreases in intensity in porous Vycor is in contradiction to their assertion and demonstrates that the defect responsible for the peak is apparently directly affected by water.

The microscopic origin of the defect responsible for the sharp peak in the Raman spectrum is a subject of recent controversy. Bates *et al.*[53] have suggested that the defect is related to a dangling silicon bond in the network. Galeener *et al.*[55] attribute the peak to a vibration of a nonbridging oxygen-dangling silicon complex. Both of these proposed structures contain a localized dangling silicon bond in the bulk network which can be modeled by the silicon-terminated Bethe lattice calculations of Laughlin and Joannopoulos.[19] In these calculations, the mode associated with the vibration of the terminating silicon atom normal to the cage of the three oxygens to which it is bonded occurs at the higher-frequency edge of the 450-cm^{-1} bulk SiO_2 band and thus occurs at about the frequency of the defect mode. However, they find this dangling silicon vibration to be in-

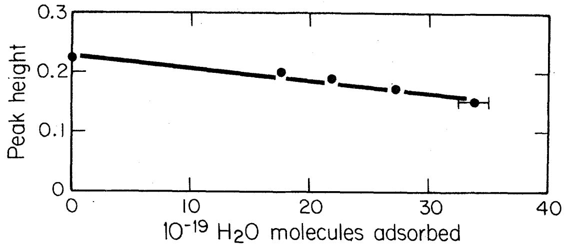

FIG. 14. Height of the 608-cm^{-1} defect peak in the Raman spectrum of porous Vycor normalized to the SiO_2 450-cm^{-1} peak in each trace, plotted as a function of the number of water molecules adsorbed on the sample. The width of the peak remained constant within measurement accuracy. The error bars for the graph are the size of the symbols, and the line is a guide to the eye.

frared active and Raman inactive, and thus the Bethe lattice model shows the opposite tendency of the actual defect mode which is only visible in the Raman spectrum.

As we have subjected our porous Vycor samples to treatment in oxygen at 600 °C, it is unlikely that dangling silicon bonds remain near the surface where the bonding defect structures most likely exist. An alternative explanation for the nature of this defect, suggested by Laughlin and Joannopoulos,[19,34] is a silicon-silicon bond. This complex would have a Si–Si stretching vibration near the frequency of the dangling silicon defect but, due to the approximate symmetry of the configuration, this vibration is expected to be Raman active. Galeener *et al.*[55] have shown that an analogous mode in the Raman spectrum of vitreous GeO_2 does not increase in intensity in germanium-rich samples of the glass, and therefore disagree with the assignment of the defect mode in SiO_2 to Si–Si bonds. The exact nature of the microscopic structure responsible for this defect remains a mystery. The effect of water on this mode in our spectra could be due either to the formation of new bonds in the network or simply to a reduction in the polarizability of the structure due to the presence of nearby water molecules. It may be an important clue for understanding the origin of this sharp mode in the Raman spectrum of bulk amorphous silica.

VII. BACKGROUND IN THE RAMAN SPECTRUM OF POROUS VYCOR

The intense scattering background which we observe in the Raman spectrum of porous Vycor is similar to that found in Raman experiments from other oxide surfaces. Egerton and Hardin[5] review the properties of this intense background scattering found in a number of Raman experiments on silicas, silica aluminas, aluminas, and zeolites. The scattering background is so strong in off-the-shelf samples that the Raman bands of the adsorbent are not observed. It has been attributed[5,8] to fluorescence from adsorbed hydrocarbon impurities such as diffusion pump oil which are subsequently decomposed and polymerized by the laser beam on the sample surface.

We have studied the spectrum of the Raman

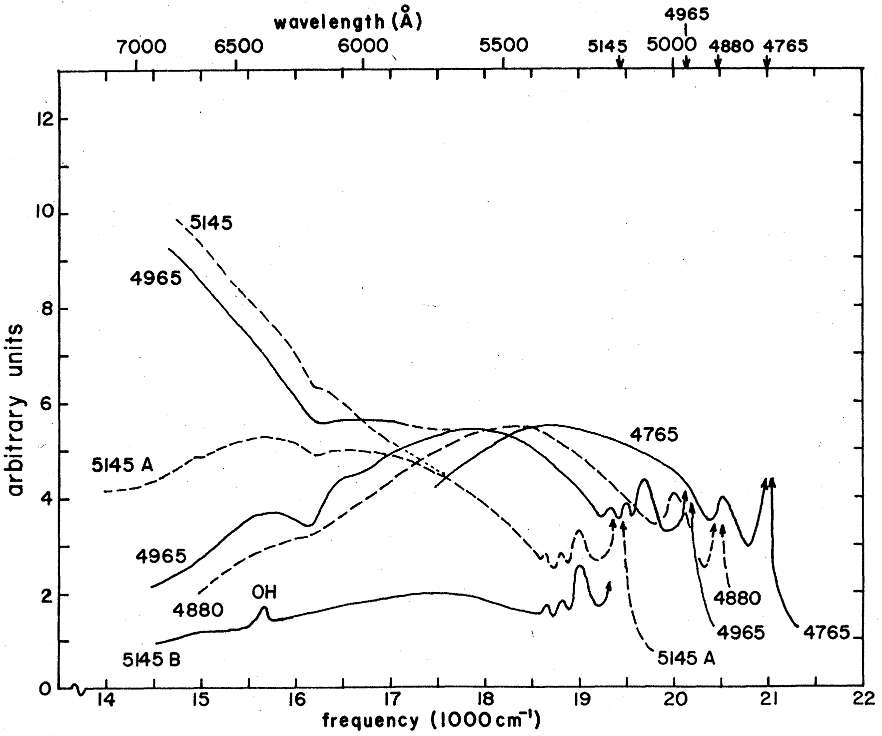

FIG. 15. Background in the Raman spectrum of porous Vycor excited by the argon laser lines at 4765, 4880, 4965, and 5145 Å. The spectra are normalized so that the SiO_2 Raman peak Stokes shifted by 450 cm^{-1} from the exciting line is the same intensity in all the traces. The spectra are shown on an absolute frequency scale. The anti-Stokes spectrum is shown for several of the traces. The traces labeled 4765, 4880, 4965, and 5145*A* are the spectra of a clean Vycor sample prepared in the manner discussed in the text. The trace labeled 5145*B* was taken immediately after the sample was exposed to water vapor. The curves labeled 5145 and 4965 in the upper left represent the high-frequency portion of the background taken with these exciting lines after heating the sample to 300° C in vacuum. They are reduced in scale by a factor of 30. The phonon bands are not visible in these two traces.

background in a number of porous Vycor samples subjected to several different cleaning procedures and transferred in a nitrogen atmosphere to our all stainless-steel ion and sorption pumped ultrahigh-vacuum system with minimal chance of hydrocarbon contamination. We believe that the background in our samples is a surface phenomenon, but that it is not due to fluorescence from polymerized hydrocarbons. In this we agree with Careri *et al.*,[56] who rule out hydrocarbon contaminants as the cause of the background in silica on the basis of the striking universal nature of the background on a number of oxide surfaces and their results on the background scattering in alumina.

The overall shape of the background spectrum, particularly at small Stokes shifts near the exciting laser line, is remarkably similar from sample to sample and on a single sample when subjected to different cleaning procedures. However, the intensity of the background can be affected drastically by various surface treatments, discussed in detail in Ref. 48.

We find that the background scattering in our samples consists of two distinct overlapping features as shown in Fig. 15. We observe a broad Raman-like band shifted by about 3000-cm^{-1} Stokes shift from the exciting line. The anti-Stokes spectrum is roughly consistent with a Boltzmann factor. In addition to this Raman-like band we observe another broad feature peaking near 15 500 cm^{-1} (6350 Å) which is independent of the exciting line and thus exhibits a typical fluorescent behavior.

We find that the spectrum exhibits a complex "bleaching" behavior when the laser beam is first directed through the sample; the intensity of the scattering monitored at a single frequency decreases rapidly in the first few minutes and then levels off in a few hours with a near-exponential behavior to an equilibrium level about $\frac{2}{3}$ of the original intensity. The "bleaching" effect seems to exist at all regions of the spectrum, but the overlap of the two broad bands is a complicating factor. After bleaching has equilibrated with the laser beam in the sample, the intensity of the spectrum is linearly proportional to laser power both at small and large Stokes shifts from the laser line. The background undergoes a restoration of intensity in a few days after the laser beam is removed from the sample.

The background in the spectrum of an off-the-shelf sample which had been boiled repeatedly in several 30% hydrogen peroxide solutions, rinsed in triple distilled water, and dried at 150 °C in vacuum was so large that it completely obscured the Raman scattering from the $\mathrm{SiO_2}$ phonons. Subsequent heating of the sample to 300 °C in vacuum in the sample cell irreversibly increased the amplitude of the scattering. The background intensity monitored at a Stokes shift of 1600 cm^{-1} from 5145 Å was monotonic with increasing temperature and remained at the level corresponding to the highest temperature attained upon cooling of the sample. When an entire spectrum was taken after cooling from 300 °C, the high-frequency "fluorescent" band had increased immensely in magnitude, by a factor of at least 10^2–10^3, as shown by the upper traces in Fig. 15, while there was a smaller effect on the lower-frequency "Raman" band. The approximate tenfold increase of the amplitude of the background in this low-frequency region could be due to the overlap of the tails of the high-frequency component.

On the other hand, after the hydrogen peroxide treatment, heating the samples at 500 °C in flowing ultrahigh-purity nitrogen gas resulted in a spectrum in which the $\mathrm{SiO_2}$ Raman bands were detectable, corresponding to an approximate reduction of 10^4–10^5 in the background level compared to samples dried in vacuum at 300 °C. The overall shape of the background particularly at low frequencies remained similar to that of the off-the-shelf samples. When ultrahigh purity oxygen gas was substituted for nitrogen in the same cleaning procedure, there was an additional reduction of background level by about a factor of 50. The background levels attained in this manner differed slightly from sample to sample but could not be reduced further than a level comparable to the low-frequency background found in nonporous Vycors (Fig. 6). This may be an indication that a small portion of the original background intensity in the porous Vycor spectrum is caused by bulk fluorescent impurities. However, when the samples were boiled in 12-vol% HCl and rinsed in a solution of 30-vol% $\mathrm{HNO_3}$, a procedure suggested[16] for removing trace metal impurities from the surfaces of the internal pores, the background level was not reduced over that of the off-the-shelf samples with the cleaning procedures described above.

That the background is primarily a surface effect is apparent from its behavior when the sample is exposed to gasses. Exposure to oxygen gas at temperatures about 500 °C for several hours reduces its intensity by several orders of magnitude but does not effect the shape of the Raman-like band. Subsequent exposure at room temperature to dry nitrogen or ammonia gas does not appreciably alter its resultant intensity. However, if the sample is dried by heating in nitrogen gas at 500 °C, room-temperature exposure to pressures of ~1 Torr of either high-purity oxygen or nitrogen gasses immediately *increases* the background intensity monitored at a single frequency near 18 000 cm^{-1} by as much as 50%. This intensity increase is *reversible*, the background returning to its original intensity after opening of the evacuation valve within about 30 sec for N_2 and about 5 min for O_2. These time scales are too fast for this to be a thermal effect, and thus the restoration of background intensity seems to be governed by the diffusion time out of the sample. On the other hand, exposure to air or to water vapor at room temperature has a completely different effect on the background. We observe an immediate fourfold reduction of intensity of the entire background after several minutes exposure of the sample to 20 Torr of water vapor. At first, we note a decrease in intensity of the background with increasing water coverage on the sample. After several days with the laser beam in the sample, however, the background nearly returns to its prewater adsorption intensity.

Careri *et al.*[56] attribute the background which they observe on alumina surfaces to water molecules which are tightly hydrogen bonded to the surface. In particular they observe a broad peak similar in shape to the Vycor "Raman" peak which exhibits a constant Stokes shift centered at about 3000 cm^{-1} independent of exciting frequency as well as a slow broad fluorescent band peaking near 16 000 cm^{-1} (6250 Å) 150 μsec after excitation. They report the observation of a complex bleaching phenomenon and a large increase in background intensity several weeks after exposure of a clean sample to water vapor. Heating in vacuum at temperatures above 400 °C reduced the intensity of the background of their scattering by several orders of magnitude, but not the overall band shape.

The similarity between our results and those obtained by Careri *et al.* on the considerably more intense background scattering from alumina surfaces is certainly striking, and suggests a similar if not common origin. The background in our porous Vycor samples is for the most part a surface effect. The large Stokes shift (~0.4 eV) and width of the Raman-like band as well as its large intensity before oxygen treatment above 500 °C (~10^4 times larger in integrated intensity than the Raman bands of silica) suggests that this band may be due to a resonant electronic Raman effect from a broadened surface electronic state. The "fluorescent" band may also be due to similar surface states. The two background bands in silica seem to be interrelated in a complex manner which could be studied more thoroughly in a time resolved experiment. Candidates for surface states which exist on all oxide surfaces are dangling or strained surface oxygen bonds which bring electronic states from the predominantly oxygenlike valence band up into the band gap. It is interesting that the reduction of the background intensity of Careri *et al.* in alumina with temperature treatment is correlated with the removal of OH groups from oxide surfaces.[14] This suggests that electronic states of the hydroxyl groups may be responsible for the background and would explain the effect of water adsorption on the surfaces. The reversible effect on the background in porous Vycor caused by exposure to gasses at low temperatures could be explained by an increase in polarizability of the surface states due to Van der Waals interactions with the surrounding gas molecules. Heating in vacuum or nitrogen gas must alter the populations of a number of energy levels as well as remove OH groups from the surface. The bleaching behavior must include photodepopulation processes. However, the apparent necessity for high-temperature oxygen treatment of silica samples in order to reduce the background suggests that cation dangling bond states may be responsible for at least some of this background.

VIII. CONCLUSIONS AND SUMMARY

In summary, we have detected intrinsic surface phonons in amorphous silica by performing Raman scattering and infrared-reflectivity measurements on an extremely porous sample. The experiments were performed with the sample in an ultrahigh-vacuum system in order to minimize surface contamination. We have demonstrated that the features in our spectra which we attribute to surface modes are not found in the spectrum of nonporous forms of Vycor and are thus not due to impurities. We have identified them as surface features by observing their perturbations due to adsorbed molecules.

In particular, we observe a shift in intensity in the Raman spectrum of porous Vycor due to low-frequency surface vibrations as well as three features in the Raman and infrared spectra which are due to the presence of hydroxyl groups bonded to surface silicon atoms. The O–H stretching mode at 3750 cm^{-1} has long been studied in infrared-absorption experiments. Ours is the first Raman scattering experiment in which the perturbations of this mode due to adsorbates are observed. The modes associated with Si–OH stretching and wagging occur at 980 and 380 cm^{-1}, respectively. They have not been previously identified. The role of the underlying substrate in these low-frequency vibrations is much larger than in the high-frequency O–H stretching mode, due to the fact that the masses of the surface atoms and force constants of the surface silicon-oxygen bond are very close to those of the bulk. The Bethe-lattice calculations of Laughlin and Joannopoulos for the silica surface terminated with oxygen are in good qualitative agreement with our experimental results. These calculations, which take into account the infinite amorphous substrate, explain the relative intensities of the modes in the Raman and infrared spectra and the reason behind the occurrence of these surface features as relatively sharp peaks. We have studied the effects of deuteration and adsorbed ammonia on the Si–OH stretching mode in the Raman spectrum. Deuterating the surface hydroxyl groups shifts the frequency of this mode by the factor $\sqrt{17/18}$ in accordance with the increase mass of the deuteroxyl group. Ammonia adsorbs specifically on the isolated surface hydroxyl groups by the formation of hydrogen bonds. The 980-cm^{-1} Si–OH stretching vibration of each localized hydroxyl group shifts to 998 cm^{-1} upon hydrogen bonding to ammonia. At the same time the 3750-cm^{-1} O–H stretching vibration of the localized hydrogen bonded hydroxyl disappears from the Raman spectrum.

The adsorption of water on the surface caused subtle changes in the surface modes and also caused a decrease in the intensity of the sharp mode near 600 cm^{-1} in the Raman spectrum of porous Vycor which is associated with bonding defects in bulk amorphous silica. This mode is not affected by adsorbed ammonia. Neither the exact microscopic origin of this defect mode nor the effect of water on the mode is understood.

The intense background in the Raman spectrum of porous Vycor was studied under a number of experimental conditions. It was concluded that the primary origin of this background is possibly a combination of resonance Raman scattering and fluorescence due to intrinsic surface electronic states. We do not believe the background, similar to that observed in other Raman scattering experiments on oxide surfaces, is due to hydrocarbon contaminants in the pores. This origin has been suggested for the background in a number of different Raman studies of surfaces.

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