

Detection of electron-vibrational transitions in the spectrum of Raman scattering of light by adsorbed xenon atoms

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The bands attributable to electron-vibrational transitions have been observed in the spectrum of Raman scattering of an argon laser beam by xenon atoms that were adsorbed by a highly developed porous-glass surface. In the Stokes region the most intense band is at 1800 cm^{-1} and in the anti-Stokes region the most intense band is at 2200 cm^{-1} . The width of the bands is $300\text{--}400\text{ cm}^{-1}$.

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The adsorption of a gas on the surface of a condensed body generally results in a change in the spectral properties of the gas, which characterizes the interaction of the adsorbate with the surface.

Studies of the Raman spectra of the adsorbed atoms, for which Raman scattering is absent in the gaseous phase, are of special interest. In this case the lines of Raman scattering by adsorbed atoms are produced only by their interaction with the adsorbent. We have observed Raman scattering of light by the vibrations of xenon atoms adsorbed in a porous glass.¹

In this paper we report the observation of other lines of Raman scattering (RS) by xenon atoms in this porous structure, which are produced by electron-vibrational transitions.

In the experiment we used an LG-68 argon laser and a DFS-24 spectrophotometer designed for studying RS. The experimental apparatus, the method of cleaning the porous-glass specimen, and its filling with xenon have been described elsewhere.¹ The diameter of the pores of the sample is 80 \AA , and their relative volume is 0.2.

The RS study was carried out at wavelengths of 514.5, 496.5, and 488.0 nm; the radiation power was $\sim 200\text{ mW}$. The structure of the scattering spectra is identical for light of all three wavelengths.

The scattering spectrum of the porous glass sample before its filling with xenon is shown in Fig. 1a. The broad scattering band in the 500- to 600-nm region, which is caused by the luminescence of foreign impurities in the pores, is typical for many transparent porous materials. The weak RS bands, which are characteristic of ordinary and porous glasses and which are normally observed against the background of this luminescence, have not been observed under the conditions of our experiment. We have observed intense RS bands of adsorbed xenon (lying outside the region in which the RS bands of the glass appear) after the porous sample was filled with xenon (Fig. 1b).

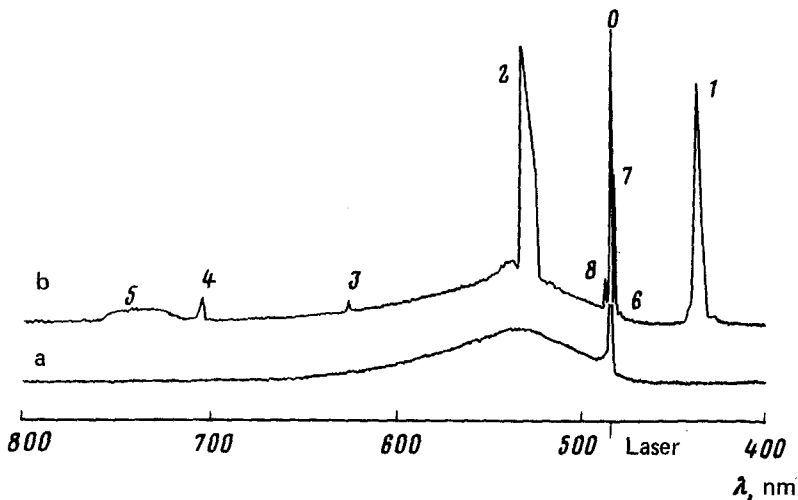


FIG. 1. Scattering spectra of (a) porous glass and (b) xenon adsorbed in porous glass. The resolution is 7 cm^{-1} , the time constant is 2 sec, the recording speed is 66.7 \AA/min , and the laser wavelength is 488.0 nm .

The intensity of strong RS bands, which depends linearly on the intensity of laser radiation in the range of 10 to 200 mW, is $\sim 10^{-6}$ of the intensity of scattering at the laser frequency.

The peaks 7 and 8 lying in the $80\text{-}100\text{-cm}^{-1}$ interval are the anti-Stokes and Stokes components of RS by the vibrations of xenon atoms in the adsorption potential well, and peak 6 is the anti-Stokes overtone of these vibrations¹; we also observed the Stokes overtone. The intensity of these peaks is twice as large for irradiation with the 514.5-nm light than for irradiation with 488.0-nm light of the same power; the intensity of bands 1-5 is a factor of 3 greater.

The bands 1-5 have a complicated structure (Fig. 2 shows the spectrograms of bands 1-4 traced at slow speeds); they also have individual characteristic details: well-defined maxima and sharp boundaries. We assume that the broad bands 1 and 2 are a superposition of separate, narrower bands and we can identify the boundary bands. It turned out that the frequencies of the maxima and of the band limits are in good agreement with the frequencies of transitions between excited levels of xenon atoms. These transitions are as follows:

$$\begin{aligned}
 5d [3/2]_2^{\circ} &\rightarrow 6p [5/2]_2 \quad (2203,4 \text{ cm}^{-1}) \\
 6p [3/2]_2 &\rightarrow 6s [1/2]_1^{\circ} \quad (2030,5 \text{ cm}^{-1}) \\
 6p [5/2]_2 &\rightarrow 5d [1/2]_1^{\circ} \quad (1864,3 \text{ cm}^{-1}) \\
 6s [1/2]_0 &\rightarrow 6p [5/2]_2 \quad (1923,5 \text{ cm}^{-1}) \\
 8p [3/2]_2 &\rightarrow 8s [3/2]_2^{\circ} \quad (1566,4 \text{ cm}^{-1}) \\
 7p [1/2]_1 &\rightarrow 8p [1/2]_0 \quad (4629,4 \text{ cm}^{-1}) \\
 7p [1/2]_1 &\rightarrow 9p [1/2]_0 \quad (6360,3 \text{ cm}^{-1})
 \end{aligned}$$

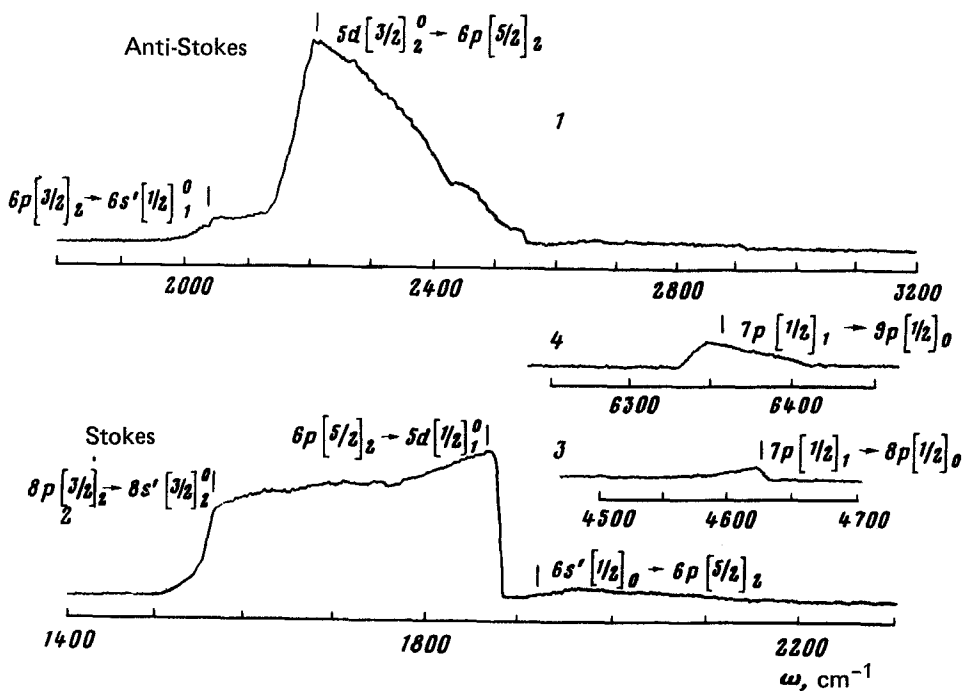


FIG. 2. Scattering spectrum of adsorbed xenon. The resolution is 2 cm⁻¹, the time constant is 4 sec, the recording speed is 15 cm⁻¹/min, and the laser wavelength is 488.0 nm. (The band numbers correspond to those indicated on the composite spectrum in Fig. 1.)

(Tables of spectral lines² were used to determine the levels.) Many transitions lie within the broad bands 1 and 2 and on their tails, but they are poorly resolved spectrally. It can be stated with certainty that the observed scattering spectrum is the spectrum of RS by electron-vibrational transitions of adsorbed xenon atoms.

We point out some features of the observed scattering. Raman transitions occur among the lower excited levels of xenon, which are separated a large distance from the ground level (~ 10 eV). Raman transitions from the $6s'$, $6p [1/2]_1$, and $6p [5/2]_2$ levels due to irradiation with 514.5-nm light and from the $6s'$ and $6p [1/2]_1$ levels due to irradiation with 488.0-nm light occur via the excitation of high pre-ionized levels, and transitions from the higher levels occur via ionization (the ionization threshold of xenon is 97 834.4 cm⁻¹). Raman transitions observed in an anti-Stokes RS are missing in a Stokes RS, and vice versa, i.e., if there is a transition between two levels, then it occurs only in one direction. When the laser radiation is allowed to stimulate one point of the sample for a long period, the intensity of the anti-Stokes bands decreases; the spectrum can be reconstructed by shifting the beam to a new section of the sample.

The Raman transitions in adsorbed xenon cannot be explained by multiphoton absorption: the intensity of the laser beam is low (~ 100 W/cm²), and there are no levels in xenon that are resonant to the argon-laser radiation. There is only one level

$5d[5/2]_2^0$ ($81\,929.1\text{ cm}^{-1}$) which has an energy close to four quanta of the 488.0-nm radiation ($81\,969.6\text{ cm}^{-1}$); this level, however, does not appear in the RS, and there are no transitions from it. In addition, the similarity of the RS spectra of light of different frequencies indicates that there are no resonances.

It must be assumed that the adsorbed xenon atoms are in an excited state or acquire energy at the moment of adsorption. In addition, the distribution of excitation is nonuniform in the electron levels, and there is an inversion in the population of individual levels. It is interesting that the largest peak in the anti-Stokes RS (its Stokes analog is missing) corresponds to the transition at which intense lasing occurs in the He-Xe laser. The action of the laser beam causes a redistribution of adsorbed xenon atoms among the energy levels. Determination of the mechanism of xenon excitation on the surface requires a detailed study of the adsorption of inert gases.

1. N. V. Karlov, A. N. Orlov, Yu. N. Petrov, A. M. Prokhorov, and M. A. Yakubova, *Pis'ma Zh. Eksp. Teor. Fiz.* **34**, 13 (1981) [*JETP Lett.* **34**, (to be published)].
2. A. R. Striganov and N. V. Sventitskii, *Tablitsy spektral'nykh liniĭ* (Tables of Spectral Lines), Atomizdat, Moscow, 1966.

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