

Overtone Absorption and Raman Spectra of H₂ and D₂ in Silica Optical Fibers

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We have recorded quantitative optical absorption and Raman spectra of H₂ and D₂ diffused into silica optical fibers at a pressure of 500 atm. The absorption spectra recorded were fundamental through the third overtone for H₂ (0.6 through 2.5 μm) and the first through fourth overtone for D₂ (0.7 through 1.7 μm). The observed spectra show fine structure similar to what has been seen in gas-phase Raman spectra. By considering all our absorption and Raman spectra for both H₂ and D₂, including temperature dependence and anharmonicities, and comparing the spectra to gas-phase Raman spectra, we have made unambiguous assignments for all observed spectral lines. As a result of these assignments, we conclude that H₂ and D₂ are trapped singly in interstitial sites in silica and are free to rotate. The absorption spectra provide information on the added loss due to H₂ saturation of silica optical fibers. For example, extrapolating the experimental results to the case of a fiber saturated under 1 atm of H₂, the added loss due to the intense first overtone Q-branch line is 14 dB/km at 1.2445 μm and 0.14 dB/km at 1.30 μm . High loss due to the fundamental absorption of H₂ occurs beyond 1.5 μm ; at 1.55 μm it is 0.8 dB/km for 1 atm of H₂. There is, however, a transmission window in H₂-saturated fibers between 1.32 and 1.45 μm .

I. INTRODUCTION

During a study of the Raman gain properties of molecular hydrogen (H₂) diffused into silica fiber, it was found that H₂ in silica is infrared active with a broad absorption spectrum in a wavelength region extending from 2.4 μm into the visible. The report of this work showed

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a portion of the first overtone spectrum between 1.0 and 1.4 μm (a region of interest for fiber optical transmission), along with tentative spectroscopic assignments.¹ This H_2 optical absorption in fibers subsequently was found to be of practical importance to lightwave communications with the observation of *in situ* generation of H_2 in optical fiber cables due to electrolysis.²⁻⁴ Also, the recent literature contains calibrated first-overtone loss spectra for silica fibers containing H_2 under about 1-atm pressure, as well as spectral assignments for the fundamental and first-overtone regions.^{1,3,5,6} We show here that all of the reported assignments are at least partially incorrect.

To obtain sufficient information for unambiguous assignment of all observed absorption lines, we have observed the absorption spectra of silica fibers impregnated with H_2 or D_2 at pressures that (1) are sufficiently high (500 atm) to produce gas concentrations in the fibers close to their saturation limits in silica, and (2) are larger by a factor of 50 than the highest pressures reported in other recent experiments.⁴ The observations include calibrated fundamental and first- through third-overtone spectra for H_2 , first- through fourth-overtone spectra for D_2 , and spontaneous Raman spectra for both H_2 and D_2 . The assignments made possible by measurements of these spectra also indicate that the "guest" molecules are trapped singly in the silica and are free to rotate.

II. EXPERIMENTS

In the experiments we employed several-hundred-meter lengths of multimode silica fiber with a 50- μm core and 125- μm outer diameter. The core contained a graded concentration of GeO_2 (about 14 percent GeO_2 at the center) and a small amount of P_2O_5 . One fiber was subjected to H_2 at 500-atm pressure at room temperature for 30 days. We calculated the concentration of dissolved H_2 using the Langmuir adsorption model, with data adjusted to 25°C.⁷ The resulting concentration of H_2 in the fiber was 5.6×10^{20} molecules/ cm^3 , which is about 500 times the reported concentration at 1 atm. We treated similar fiber with D_2 in the same way. In addition, we treated a 10m length of single-mode fiber in H_2 under the same conditions for five days. After treatment the fiber was removed from the pressure vessel and its spectra were measured at ambient atmospheric pressure. Between measurements the fibers were stored in liquid nitrogen to eliminate out-diffusion. The absorption spectra of all samples were obtained using a tungsten-lamp source and a 3/4-meter monochromator; all were normalized to the spectrum of an equal length of untreated fiber, and all were fully resolved. We chose absorption path lengths to ensure that the measured absorptions were within the dynamic range of the instrumentation. Raman spectra were obtained on the same mono-

chromator with a krypton-ion laser at 647.1-nm as the excitation source. The spectra were taken at room temperature and 77K.

III. RESULTS AND DISCUSSION

In the gas phase, direct absorption of infrared radiation is a rigorously forbidden process for homonuclear diatomic molecules, such as H_2 and D_2 , due to their lack of a transition dipole moment.⁸ The high symmetry of H_2 and D_2 dissolved in silica is reduced by the silica matrix surrounding the dissolved molecule, leading to induction of a transition dipole moment and absorption of infrared radiation resonant with molecular transition frequencies. Figure 1a shows the mea-

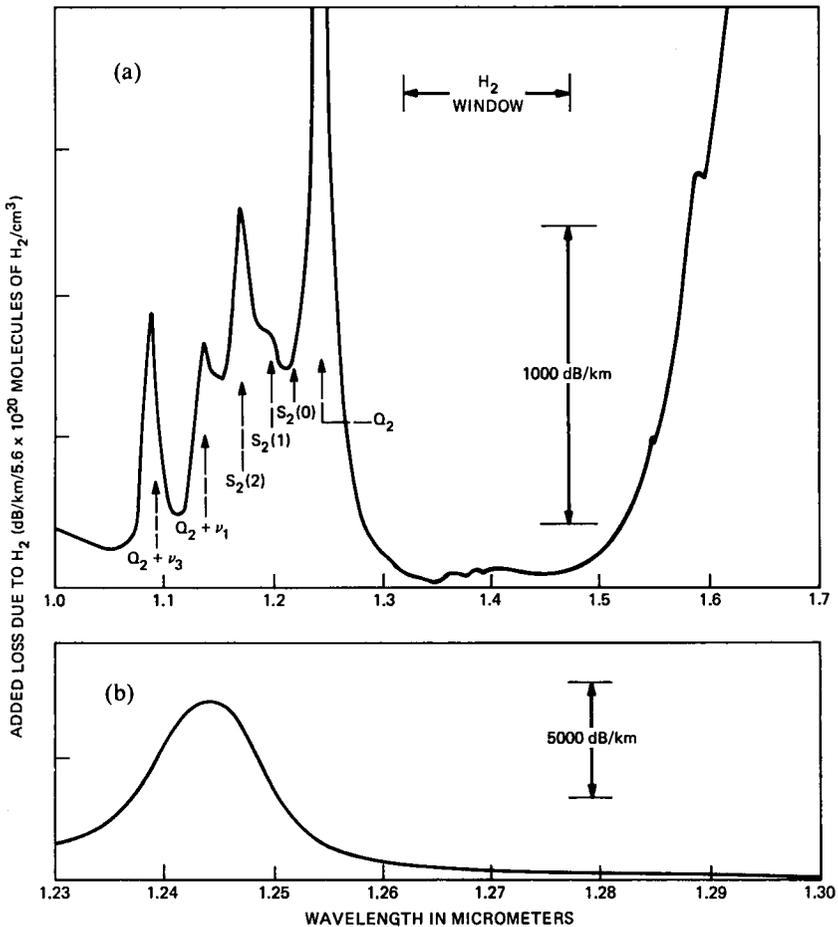


Fig. 1—First-overtone loss spectrum at room temperature of H_2 in silica fiber: (a) Entire spectrum of the first overtone, measured in a 10m single-mode fiber; ν_1 and ν_3 are silica vibrations;⁹ (b) Expanded view of the most intense band, the Q branch, measured on 2.3m of multimode fiber.

sured H_2 loss spectrum between 1.0 and 1.6 μm for the single-mode fiber. Figure 1b shows the main absorption band, i.e., the Q branch of the first-overtone transition, measured at high resolution in the multimode fiber. Figures 2 and 3 show the second and third H_2 -overtone absorption regions, respectively, for the multimode fiber. We also recorded spectra for the fundamental absorption region of H_2 and the first- through fourth-overtone regions of D_2 , as well as Raman spectra for H_2 and D_2 . HD was seen as an impurity in the D_2 spectra.

The spectra shown in Figs. 1 through 3 have the general features observed in all the absorption spectra. The strongest feature is identified as the Q-branch transition. Table I shows transition energies, wavelengths, and attenuation coefficients (measured for 500-atm treatment pressure, and reduced to 1 atm) for the observed Q branches of H_2 , D_2 , and HD. The spacing between successive vibrational levels (Q-branch spacing) decreases due to anharmonicity. Table I also shows the measured high-pressure attenuation coefficients and the derived 1-atm values. Note the large ratios of the H_2 and D_2 absorption strengths. We observed other weaker lines, and assigned these to vibration-rotation transitions, S(J) and O(J) lines (for a general description of the H_2 spectral lines see Ref. 8), or to combination absorptions with the silica tetrahedral modes ν_1 (800 cm^{-1}) and ν_3 (1100 cm^{-1}).⁹ Figure 4 shows a correlation diagram of the Raman,

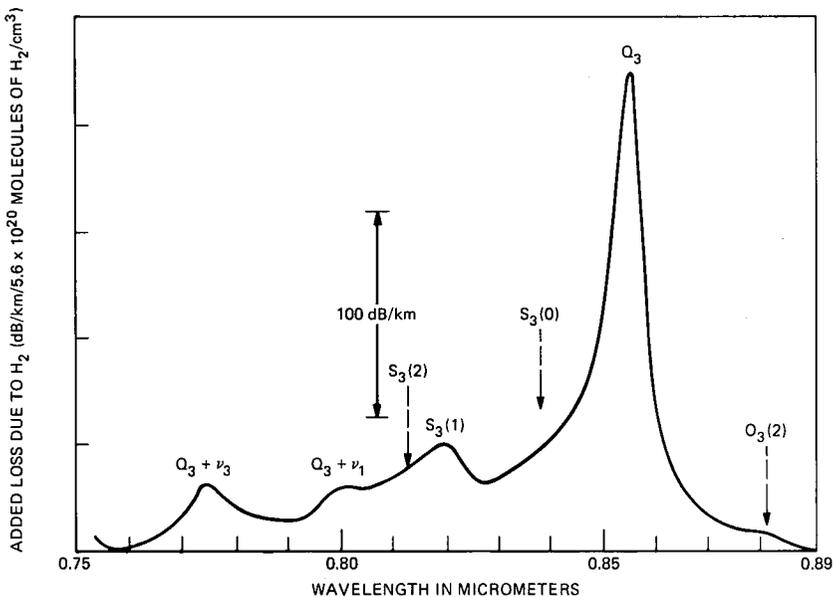


Fig. 2—Second-overtone spectrum of H_2 at room temperature measured on 13m of multimode fiber.

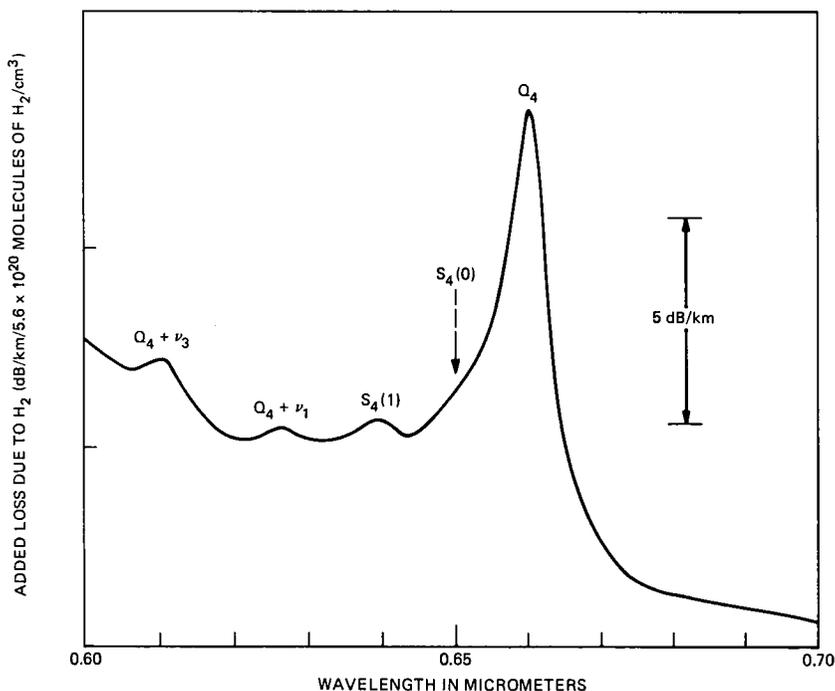


Fig. 3—Third-overtone spectrum of H_2 at room temperature measured on 450m of multimode fiber.

fundamental, and overtone lines for H_2 , all relative to the Q-branch lines. If we reference the observed lines to the appropriate Q-branch transition, the consistency of the fine structure in each vibrational transition becomes apparent. This procedure also eliminates the energy shifts due to vibrational anharmonicity. Figure 5 shows similar results for the Raman and first four overtone lines of D_2 , as well as gas-phase Raman lines¹⁰ and the positions of the silica tetrahedral modes.⁹

The assignment of the S(J) and O(J) vibration-rotation lines is based on three factors:

1. The closer spacing and greater number of these lines in the D_2 spectra compared to the H_2 spectra, in accord with general expectations for the H-D isotope shifts.⁸
2. The excellent quantitative agreement between the rotational spacings observed in the fiber spectra for H_2 and D_2 compared to the spacings in the corresponding gas-phase spectra.
3. The relative intensities of the lines and the variation of relative intensities with temperature. [At 295K, the most intense rotational lines are S(1) for H_2 and S(2) for D_2 . At 77K, the most intense lines are S(0) and S(1) for H_2 and S(0) for D_2 .]

Table I—Observed Q-branch transition energies, $\bar{\nu}$, wavelengths, λ , and attenuation coefficients, α , HD room temperature data

H ₂					
	$\bar{\nu}$ (cm ⁻¹)	λ (μ m)	α (dB/km)		Intensity (arb)
			(a)	(b)	
Fundamental	4139	2.4159	4×10^5	800	—
1st Overtone	8035	1.2445	7100	14	—
2nd Overtone	11693	0.8552	260	0.52	—
3rd Overtone	15156	0.6598	13	0.026	—
4th Overtone					
D ₂					
Fundamental	2975	3.361	—	—	—
1st Overtone	5828	1.716	2100	4.2	—
2nd Overtone	8565	1.1675	26	0.052	—
3rd Overtone	11198	0.8930	3.1	6.2×10^{-3}	—
4th Overtone	13699	0.7300	0.19	3.8×10^{-4}	—
HD					
Fundamental	3605	2.774	—	—	—
1st Overtone	7067	1.415	—	—	220
2nd Overtone	10293	0.9715	—	—	1
3rd Overtone	—	—	—	—	—
4th Overtone	—	—	—	—	—

(a) Measured coefficient for 500 atm, gas concentration = 5.6×10^{20} molecules/cm³.
 (b) Derived coefficient for 1 atm, gas concentration = 1.1×10^{18} molecules/cm³.

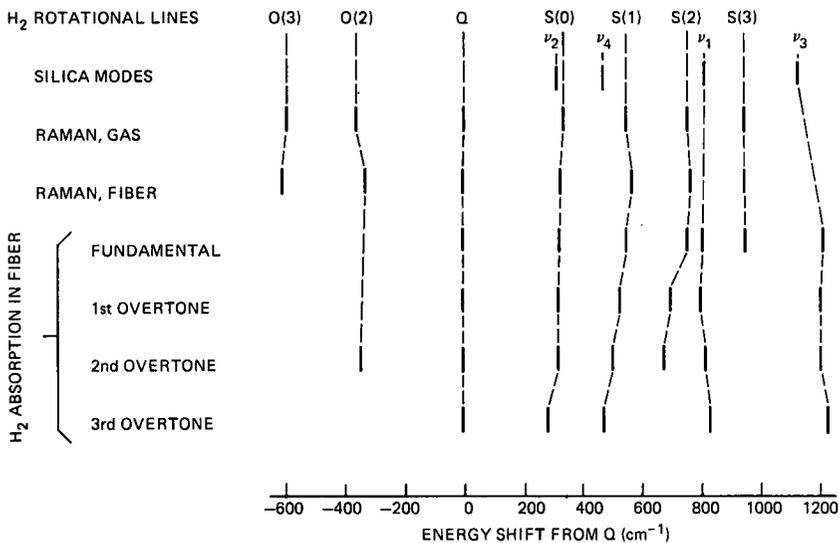


Fig. 4—Correlation diagram of Raman and fundamental and overtone absorption spectra of H₂ in silica. Frequencies are measured with respect to the Q-branch frequency. The gas-phase H₂ rotational structure¹⁰ and silica tetrahedral vibrations⁹ are shown.

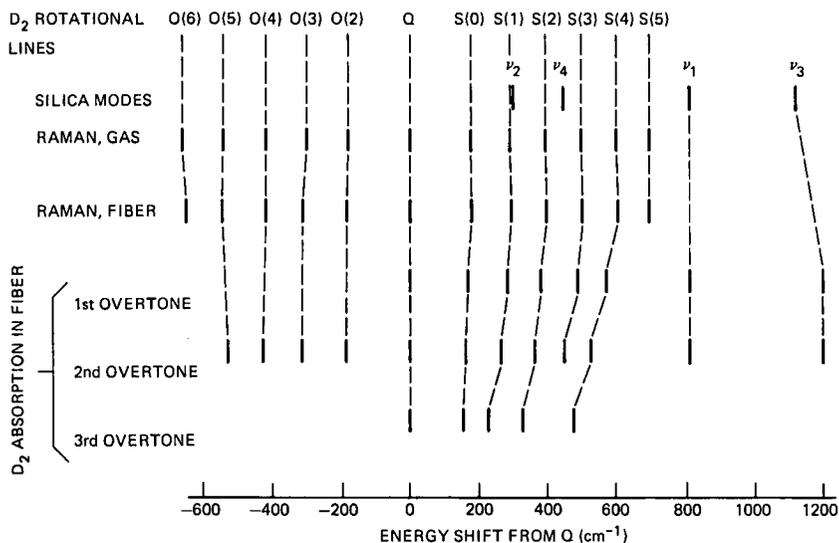


Fig. 5—Correlation diagram of Raman and overtone absorption spectra of D_2 in silica. Frequencies are measured with respect to the Q branch. The gas-phase D_2 rotational structure¹⁰ and silica tetrahedral vibrations⁹ are shown.

In contrast, the combination lines with the silica ν_1 and ν_3 modes show none of these effects; the separation from Q is the same in both the H_2 and D_2 spectra, and the intensities relative to Q and each other are independent of temperature. Even the fine details of Figs. 4 and 5 support the above interpretation. The $S(J)$ lines shift closer to Q for the higher-overtone absorptions, as expected, due to rotation-vibration coupling for a nonrigid rotor.⁸ In contrast, the lines due to combination with the silica modes show no such shift.

Previous workers have observed many of the lines in the first-overtone spectrum reported here, but have made incorrect assignments, either assuming that all lines were due to combinations with silica modes,⁶ which would indicate that the H_2 and D_2 did not rotate, or otherwise incorrectly identifying some of the transitions.^{3,5} In a Raman study of H_2 and D_2 in bulk silica glass, Hartwig and Vitko observed the $S(J)$ lines and thus concluded that the dissolved species rotated in interstitial sites in the glass.¹¹

The full set of spectra that we have recorded, of which only a portion is shown here, contains a wealth of detailed information concerning the nature of H_2 and D_2 dissolved in silica. In a subsequent publication we shall present the complete spectra, a complete set of assignments for all the absorption and Raman spectra, and full analyses of the spectra. Table II identifies the lines of most importance for lightwave communication, those due to H_2 between 1.0 and 1.7 μm .

Table II—Observed transitions between 1.0 and 1.7 μm due to H_2 dissolved in a silica optical fiber

$\lambda(\mu\text{m})$	Transition	Spectral Origin
1.696	$S_1(1) + \nu_3$	Fundamental
1.642	$S_1(2) + \nu_3$	Fundamental
1.590	$S_1(3) + \nu_3$	Fundamental
1.550	$Q_1 + 2\nu_3$	Fundamental
1.2445	Q_2	First overtone
1.197	$S_2(0)$	First overtone
1.1682	$S_2(1)$	First overtone
1.1455	$S_2(2)$	First overtone
1.1320	$Q_2 + \nu_1$	First overtone
1.0825	$Q_2 + \nu_3$	First overtone

The present work shows that H_2 , even when dissolved close to saturation in silica, is still free to rotate. In contrast, when N_2 is diffused into a silica fiber, only a single band is observed in the Raman spectrum, and contributions from molecular rotation are absent (although it is possible that these are not observed due to the small concentration of N_2).¹² We also note confirmation of the fact that there is only a single gas molecule per site,⁷ since no lines due to double excitations are observed, despite the very high gas concentration.

For H_2 the strongest component of the first overtone, Q_2 , is very intense, about 7000 dB/km/ 5.6×10^{20} molecules/ cm^3 , but also very narrow. The absorption strength is about 70 dB/km/ 5.6×10^{20} molecules/ cm^3 at 1.30 μm . These values correspond to 14 dB/km at 1.2445 μm , and 0.14 dB/km at 1.30 μm , for the H_2 concentration equivalent to 1 atm. Other reported values for the attenuation coefficient are considerably lower^{2,4,6,13} for the Q branch but are in good agreement^{2,4,6} at 1.30 μm . We believe this discrepancy in the peak attenuation coefficient of the Q branch is due to saturation that occurred in the other measurements of the intense Q-branch absorption. The absorption in the 1.5 to 1.6- μm portion of the spectrum is very large and increases rapidly with wavelength. The loss in this region is due to wings of the extremely intense fundamental absorption near 2.4 μm , which, like the overtones, is asymmetric and more intense toward shorter wavelengths. At 1.55 μm the absorption due to the wing of the fundamental absorption seen in Fig. 1a is about 400 dB/km/ 5.6×10^{20} molecule/ cm^3 or 0.8 dB/km at 1 atm equivalent. Finally, we note that, even in the presence of H_2 , there is a transmission window in silica from about 1.32 μm to about 1.45 μm , which might permit use of a hydrogen-contaminated fiber as a communications medium at a wavelength of approximately 1.4 μm . However, since this is the wavelength at which absorption in silica fibers due to OH contamination occurs,

such use would require the manufacture of fibers with negligible OH concentration. (No additional OH formation in silica due to H₂ has been observed below about 100°C.)¹⁴

In summary, we have recorded and analyzed both absorption spectra up to the fourth overtone, and Raman spectra for fibers saturated with either H₂ or D₂ at 500 atm. The spectral lines have been completely assigned to vibration-rotation transitions of H₂ (D₂) and combination vibrational transitions with only the ν_1 and ν_3 silica tetrahedral modes. The H₂ (D₂) molecule is trapped singly and is free to rotate.

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