namic information.

We are currently investigating the application of the present method to higher-dimensionality systems. The minus signs and resulting cancellations ordinarily associated with Fermi statistics do arise for two or more space dimensions. However, a major part of the cancellation will automatically be taken into account by our breakup method, so that we expect our approach to be applicable. Our Monte Carlo algorithm will remain local in more dimensions so that the time required for the calculation will be comparable to that for a boson Monte Carlo calculation. In 1 + 1 dimensions, there are many interesting models in condensed-matter physics involving electron-electron and electron-phonon interactions, as well as in high-energy physics with fermion and gauge field degrees of freedom, some of which are presently under investigation.

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Vibrational Overtone Absorption in Solid Hydrogen

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The first measurements of the second-overtone absorption spectrum of solid n-H_2 are reported. The observed frequencies and line strengths are not predicted from the known high-pressure gas data, but the trend is consistent with similar data for the fundamental band. The observation of this very weak optical absorption provides important data for reexamination and extension of theoretical treatment of this important molecular solid.

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Overtone spectra of fundamental vibrational modes in condensed phases of large molecules such as benzene,[1,2] methane,[3,4] and ethylene[5] have been extensively studied. The strength of overtone absorption in these molecules arises from the single-molecule properties and the effects of collisions (or pressure) are seen only as the modification of band positions and bandwidths. Hydrogen, on the other hand, whose forbidden fundamental vibrational frequency lies in the 4150-cm^{-1} region, shows only very weak overtone spectra in the low-pressure region.[6] McKellar and Welsh[7] have summarized the high-pressure gas data for the second and third harmonics of H_2 and have shown that in the pressure region of ~30–40 amagat and at $T \approx 80$ K a description based on binary collisions reasonably explains the observed absorption strengths. Further, the single- (isolated) molecule frequencies accurately describe their spectra.

We report a study of second and third harmonics of solid H_2 in the 8000- and 12 000-cm^{-1} regions, respectively. Solid H_2 is a molecular solid in which the rotational quantum number, J, remains a good quantum number for the H_2 molecules.[8] Further, because of the small mass of H_2, molecular solid H_2 exhibits large zero-point motion. Dipole moments induced in pairs of neighboring H_2 molecules by intermolecular forces lead to infrared absorption on vibrational overtones of H_2

molecules reminiscent of the high-pressure H_2 gas case studied extensively for vibrational overtone absorptions. However, in the solid phase the overtone spectra are very narrow compared with the broad features seen in high-pressure gas-phase data and hence it is easy to assign their positions accurately. Our transition frequencies for the second overtone vibrational absorption band in the solid are lower than the calculated free-molecule values. The intermolecular forces on molecules in the solid are expected to result in a slight lowering of the frequencies as compared to the isolated-molecule values. However, no calculations exist at the present time for the second overtone. Further, electric quadrupole-quadrupole interaction theory has been quite successful[7] in predicting the relative strengths of the various components of overtone absorption spectra in high-pressure H_2. We are not aware of similar calculations for solid H_2. These new experimental data have only become possible now because of the advent[9] of pulsed laser piezoelectric transducer (PULPIT) optoacoustic (OA) spectroscopy. At low temperatures it is ideally suited for the study of very weak absorption spectra of condensed-phase materials. Our results provide important data (in addition to the absorption data for the fundamental[10] vibrational band and the microwave absorption[11] data of solid H_2) on the overtone absorption in solid H_2 which can be used for improving our insights into this simplest of the molecular solids.

The experimental setup for PULPIT optoacoustic spectroscopy has been described in detail in Ref. 3 and by Patel and Tam[12] and Nelson and Patel.[13] It consisted of a tunable dye laser pumped with the second harmonic of a neodymium: yttrium aluminum garnet laser, which provided tunable fundamental radiation in the 550- to 750-nm region. First- and second-order stimulated Raman scattering (SRS) in a high-pressure H_2 cell was used to shift the frequency of fundamental dye laser radiation down to the 700-nm to 1.6-μm region. Typical pulse energies of >1 mJ, with a pulse width of ~8 ns and a pulse repetition rate of 10 Hz, were available.[13] Solid H_2 was studied with a slightly modified OA cell (path length of ~8 mm) described previously.[3] A piezoelectric transducer, described earlier,[12] was used to detect the OA signal. With use of a Janis Varitemp Dewar the cell could be cooled down to ~1.2 K. (The present studies are, however, carried out at 13 K to avoid problems arising from cracking of solid H_2 in the cell. A new cell is being designed. Details of cell construction and lower-temperature data will be published later.) Hydrogen was condensed directly into the cell and solidified by lowering the cell temperature to less than 14 K. Earlier studies of liquid methane (94 K) and ethylene (113 K) in similar OA cells have shown that low-temperature PULPIT optoacoustic spectroscopy can be easily carried out[3,5,13] to absorption coefficients $\lesssim 5 \times 10^{-6}$ cm^{-1}. The pulsed-laser radiation was gently focused to a beam diameter $2R \approx 1$ mm within the OA cell. The laser frequency, ν (linewidth and pulse-to-pulse stability of ~0.5 cm^{-1}), was monitored by comparison with Ne atomic emission lines.

The voltage $V_{\mathrm{OA}}(\nu)$ generated in the piezoelectric transducer due to an impinging acoustic pulse caused by nonradiative relaxation of the absorption of optical pulse of energy, $E(\nu)$, is related to the optical absorption coefficient, $\alpha(\nu)$, of the material through the relation[14]

$$\frac{V_{\mathrm{OA}}(\nu)}{E(\nu)} = K_a \frac{\beta v_a^{\,2}}{C_p}\left(\frac{Z_{\mathrm{abs}}}{Z_{\mathrm{abs}}+Z_{\mathrm{pzt}}}\right)\alpha(\nu), \qquad (1)$$

where β, v_a, and C_p are the volumetric expansion coefficient, sound velocity, and specific heat of the optical absorber; Z_{abs} and Z_{pzt} are the acoustic impedances of the absorber and the piezoelectric transducer; and K_a is a constant determined by the specific OA cell geometry. This expression has been shown to be applicable[14] when the laser pulse width τ_p is shorter than the acoustic transit time, R/v_a, across the cylindrical excited region in the absorber and further when the response time τ_r of the piezoelectric transducer is longer than the laser pulse width. In the present case $\tau_p \approx 8$ ns, $\tau_r \approx 1$ μs, and $\tau_a \approx 100$ ns. Notice that there is *no* optical frequency dependence in any of the factors on the right-hand side of Eq. (1) except in $\alpha(\nu)$. Thus, the calibration[12] from a known absorber can be transferred to an unknown absorber through the appropriate changes in β, v_a, and C_p, to obtain $\alpha(\nu)$ from the measured normalized OA signal, $V_{\mathrm{OA}}(\nu)/E(\nu)$.

Figure 1 shows a normalized PULPIT optoacoustic signal as a function of laser frequency for solid H_2 at 13 K. We have used the I Stokes-shifted dye-laser radiation (Rh 610 and DCM dyes) from 11 600 to 12 900 cm^{-1}. A number of absorption peaks are seen whose linewidths are typically 8–12 cm^{-1}. The integration time used for the spectrum was ~0.5 s per resolution element and the pulse energy was ~0.5 mJ. The

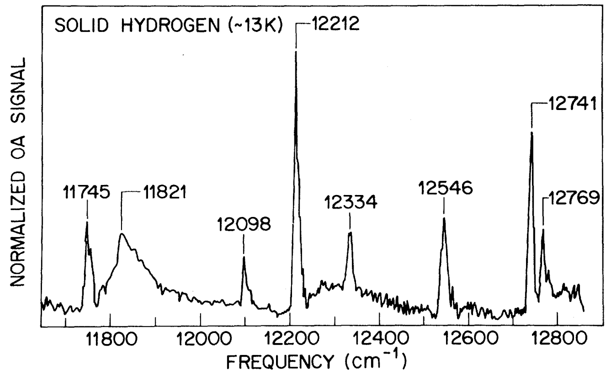

FIG. 1. Normalized PULPIT optoacoustic signal arising from the 0→ 3 vibrational overtone absorption in solid *n* hydrogen.

pulse-to-pulse amplitude fluctuation for the I Stokes-shifted radiation was ~±50% which is responsible for the noise seen in Fig. 1 at the two ends of the scan. Table I shows the frequencies of the observed lines, together with the suggested identifications of the lines and the positions calculated with use of isolated-molecule transition frequencies.[15] Also shown are the expected collision-induced quadrupole strengths[7] for these transitions for high-pressure H_2 gas at $T\approx 85$ K. Several observations can be made. The first is that in solid H_2 only one single transition is observed with the rest being double transitions. Single transitions are defined as those in which the collision-induced absorption (although collision induction is strictly a misnomer for solid H_2, but the mechanism is the same, namely the distortion[7] of the electron charge distribution due to long-range anisotropic quadrupole interaction or due to a short-range isotropic overlap interaction) of a photon leads to a true harmonic excitation of a *single* H_2 molecule. Examples of such single transitions for the $0\rightarrow 3$ band would be $S_3(0)$, $Q_3(0)$, $Q_3(1)\ldots$, etc. The double transitions, on the other hand, would involve, during the absorption of a single photon, excitation of a *pair* of molecules, e.g., the $0\rightarrow 3$ band would consist of excitations like $(0\rightarrow 2)+(0\rightarrow 1)$. Examples of such double transitions are $S_2(1)+Q_1(0)$, $Q_2(1)+Q_1(1)$, and so on. (Notice the extensive studies of rotational spectra in solid H_2 in the microwave region[11] arising from transitions between split rotational levels of nearest-neighbor o-H_2 pairs. Further, low-frequency excitations of isolated $J=1$ H_2 pairs have been observed in

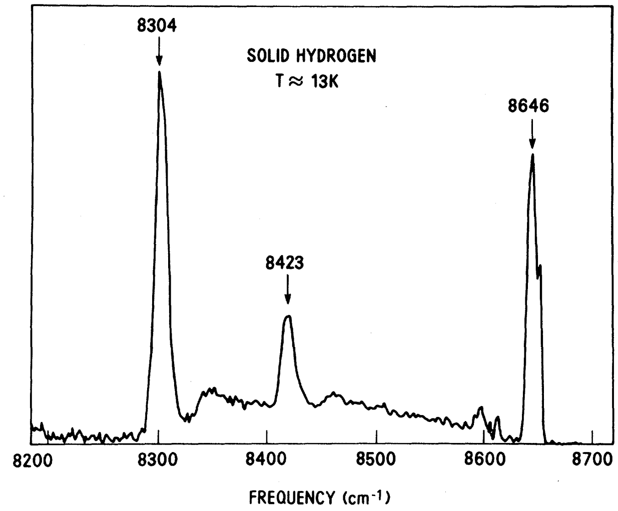

FIG. 2. Normalized PULPIT optoacoustic signal arising from the 0→2 vibrational overtone absorption in solid *n* hydrogen.

TABLE I. Second-overtone absorption spectrum of solid hydrogen.

Observed frequency (cm⁻¹)	Intensity (rel. units)	Identification	Isolated molecule frequency[a] (cm⁻¹)	High-pressure-gas calculated strength[b]
11 745	1.35	$Q_3(1)$	11 765	S
12 098	0.85	$Q_3(1)+S_0(0)$	12 121	W
12 212	3.9	$Q_2(1)+Q_1(1)$	12 231	M
12 334	1.2	$Q_3(1)+S_0(1)$	12 361	M
12 546	1.46	$S_2(0)+Q_1(1)$	12 563	M
12 741	2.7	$S_2(1)+Q_1(1)$	12 765	S
12 769	1.2	$Q_2(1)+S_1(1)$	12 788	M

[a] From Foltz, Rank, and Wiggins (Ref. 15).

[b] Qualitative data from McKellar and Welsh (Ref. 7).

TABLE II. First overtone absorption spectrum of solid hydrogen.

Observed frequency (cm^{-1})	Intensity (rel. units)	Identification	Isolated calculated frequency[a] (solid, cm^{-1})	Molecule frequency[b] (cm^{-1})	High-pressure-gas calculated strength[c]
8304	4.8	$Q_1(0)+Q_1(0)$	8306	8311	S
8423	1.3	$Q_2(0)+S_0(0)$		8431	W
8646	3.8	$Q_2(1)+S_0(0)$		8653	M

[a] From Van Kranendonk (Ref. 8).

[b] From Foltz, Rank, and Wiggins (Ref. 15).

[c] Qualitative data from McKellar and Welsh (Ref. 7).

Raman scattering.[16]) The earlier high-pressure gas data[7] showed that the single and double transitions were of comparable strengths, as expected from theoretical arguments involving quadrupole induction during a binary collision. The weakness of single transitions with the appearance of mostly double transitions indicates the inadequacy of earlier theoretical treatments. (At present we have no evidence of observation of triple transitions in the $0 \rightarrow 3$ band which would require simultaneous excitation of three molecules and would point to the need for ternary induction.) Secondly, the frequencies calculated for the transition with use of isolated-molecular transition frequencies which so well fit the high-pressure gas-absorption data do not describe the solid-state H_2 line positions. The differences between the observed and calculated line positions are 21 ± 4 cm^{-1} and are much larger than the estimated experimental uncertainty of ± 2 cm^{-1}. These observations are qualitatively consistent with the observed and calculated values[8] for lower harmonics of solid H_2. No calculations are available for higher overtones, and thus our experimental results should provide an incentive for extension of the earlier calculations to higher harmonics.

Figure 2 shows the data on the second harmonic of solid H_2 studied with II Stokes SRS of Rh610 and Rh590 dyes. Again, the noise seen is primarily from the $\pm 100\%$ pulse-to-pulse fluctuation of the laser energy. Several absorption peaks with linewidths of ~10 cm^{-1} are seen. Allin *et al.* have reported[17] similar structure for the first-overtone spectrum of solid H_2. Data from Fig. 2 are summarized in Table II along with single-molecule transition frequencies,[15] identifications, and the high-pressure gas calculation strengths[7] together with one solid-H_2 calculation. Unlike Allin *et al.*,[17] we observe no single transitions at strengths of a factor of 20 less than those for the double transitions.

In conclusion, we have reported the first optical absorption spectra of the third harmonic of the fundamental vibration of H_2 molecules in solid H_2 at $T < 14$ K. The difference seen in measured solid-H_2 overtone absorption frequencies and the calculated isolated-molecule values can be qualitatively understood in the framework of solid-state interactions. The relative strengths of the various components of the overtone absorption band provide rich data for detailed checks on theories. Our data indicate a need for an extension of the theoretical description of quadrupole induction in binary interaction which has served well for understanding the high-pressure gas-phase data. From the present studies we expect to be able to report similar measurements of yet higher overtones of solid H_2, i.e., third and fourth overtones at ~15 600 and ~19 000 cm^{-1}, respectively. These overtones have never been observed in laboratory spectra in any phase of H_2 because of their extreme weakness, and are of importance for understanding the ground-based planetary optical astronomy spectra[18] of Uranus, Neptune, etc.

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