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Mixed ortho-H_2 and para-H_2 clusters studied by vibrational coherent anti-Stokes Raman spectroscopy

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The search for macroscopic quantum effects, including superfluidity, in molecular hydrogen is mostly focused on its parahydrogen (p-H_2) nuclear spin modification because of weaker intermolecular interaction compared to orthohydrogen (o-H_2), both modifications being bosonic. In this work, mixed clusters of o-H_2 and p-H_2 containing $\sim 10^4$ molecules are prepared by supersonic expansion with helium and studied by vibrational coherent anti-Stokes Raman scattering (CARS) spectroscopy. At similar experimental conditions the neat p-H_2 clusters avoid freezing and remain fluid at 1–2 K, which is predicted to be the realm of their superfluid behavior [Phys. Rev. Lett. **101**, 205301 (2008)]. Dependence of the vibrational frequencies and intensities of the main CARS peaks due to o-H_2 and p-H_2 versus the ratio of the o-H_2 and p-H_2 concentrations in the expanding gas suggests that o-H_2 and p-H_2 molecules are uniformly mixed in the interior of the clusters. A weak spectral feature at 4157 cm^{-1} that appears independent of the concentration ratio is assigned to the outer shell of the clusters enriched with p-H_2 molecules. Although the phase of the mixed clusters could not be unambiguously identified, the shift of the vibrational frequencies with respect to the bulk solid is consistent with the liquid state of the clusters.

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I. INTRODUCTION

Superfluidity [1] is a fascinating macroscopic quantum effect that was first observed by Kapitza [2] and Allen and Misener [3] in liquid ^{4}He and explained by Landau [4,5]. Recent advancements in cold atoms physics led to demonstration of a close relationship between superfluidity and Bose-Einstein condensation [6,7]. Discovery of new quantum liquids obeying the superfluidity properties would open new possibilities for investigations in this area of physics.

Superfluidity in molecular hydrogen was first considered by Ginzburg and Sobyanin [8] and has been the topic of intensive research in the past decade in different systems, such as in clusters [9–13], on the surface [14,15], and in the bulk [16–20]. Hydrogen molecules may exist in two rather stable forms characterized by different mutual orientation of the nuclear spins [21]. At low temperatures the $I = 0$, *para*-hydrogen (p-H_2), and $I = 1$, *ortho*-hydrogen (o-H_2), species occupy molecular states with rotational quantum number of $J = 0$ and $J = 1$, respectively. Solidification of hydrogen at 13.8 K is the main obstacle in observing the superfluid transition at the predicted temperature of $\sim 1 - 2$ K [12,20]. Preparation of p-H_2 clusters in supersonic expansion has, so far, been the most successful method of circumventing freezing, and supercooling small amounts of hydrogen. Chromophore molecules embedded in such clusters revealed unhindered rotation [22,23] and translation [24] indicative of superfluid environment. Free rotation of the chromophore molecule, however, can be thought of as a manifestation of the missing rotational levels in the highly symmetric p-H_2 shell and concomitant weak coupling between the rotation of the chromophore molecule and the p-H_2 [25]. An alternative approach is to probe the hydrogen molecules themselves in search for superfluid transition. Raman spectroscopy of neat p-H_2 clusters [26,27] demonstrated their rapid freezing upon supersonic expansion. We found that dilution in He precools p-H_2 in an expansion prior to the onset of cluster formation, and allows formation of large ($\sim 10^4$ molecules) liquid p-H_2 clusters [28].

The o-H_2 molecules are bosons and can, in principle, have a superfluid transition as well as p-H_2. Usually it was not considered a feasible candidate because of stronger interaction between o-H_2 molecules than between p-H_2 molecules as well as because of the higher degeneracy of the o-H_2 species. The issue of o-H_2 freezing before it could reach a superfluid transition, therefore, would be more severe than in the case of p-H_2. Moreover, superfluid o-H_2 is predicted to be ferromagnetic [29]. In this work we present a vibrational Raman spectroscopic study of the mixed o-H_2/p-H_2 clusters that is primarily aimed at understanding the phase of these clusters at low temperature.

II. EXPERIMENT

The molecular beam/CARS experiments have been described previously [28]. The H_2 gas containing different

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fraction of the o-H_2 molecules was obtained upon dilution of the pure p-H_2 gas by normal hydrogen (n-H_2) gas. ^{4}He gas was then added to the mixture up to the desired pressure. In order to obtain p-H_2, n-H_2, which at room temperature contains 75% of o-H_2 and 25% of p-H_2, was liquefied and flown through a Fe_2O_3 catalyst at 14.5 K, where it was converted to p-H_2 with residual fraction of the o-H_2 molecules of $\sim 2 \times 10^{-4}$ [30]. The prepared o-H_2/p-H_2/He mixtures are characterized by two parameters: c_{ortho}, the fraction of o-H_2 in the total amount of hydrogen (p-H_2 and o-H_2), and X, the percentage of hydrogen (p-H_2 and o-H_2) in a mixture. The mixture was expanded into vacuum (1×10^{-4} mbar) from a cold pulsed nozzle with a 1 mm orifice diameter [31] operating at 20 Hz repetition rate. The nozzle temperature and the stagnation pressure were usually kept at $T_0 = 17$ K and $P_0 = 20$ bar, respectively. In addition, measurements have also been performed on the clusters obtained upon expansion of the corresponding mixtures of o-H_2 and p-H_2 without any dilution in He ($X = 100\%$) at $T_0 = 22$ K and $P_0 = 5$ bar.

Coherent anti-Stokes Raman scattering (CARS) spectroscopy in the folded box-CARS geometry [15,32] was used in this work to obtain the vibrational spectra of the H_2 clusters. Second harmonic output of the pulsed (6 ns) injection seeded Nd:YAG laser at 532 nm was used to form two CARS pump beams (5 mJ pulse energy in each) as well as to pump the tunable dye laser operating around 683 nm (3 mJ pulse energy), which was used to produce the CARS Stokes beam. The three laser beams were focused with a 50 cm focal length achromatic lens into a common spot 5 mm downstream from the nozzle along the expansion direction. Owing to the nonlinear character of the stimulated Raman scattering in the CARS process, the focal beam waist of about 30 μm × 30 μm × 1 mm yields the dominant fraction of the recorded intensity. The anti-Stokes beam at around 435 nm was separated from the pump and Stokes beams by an aperture, two Pellin-Broca prisms, and two interference band filters, and detected by a photomultiplier. The resolution of the CARS spectra is determined by the linewidth of the dye laser of ~ 0.3 cm^{-1}. The frequency readings in the spectra contain systematic errors of 0.2 cm^{-1} (1σ) originating from imperfect repeatability of the scanning mechanism in the laser.

III. RESULTS

CARS spectra of mixed o-H_2/p-H_2 clusters are shown in Fig. 1. The spectra were obtained upon the expansion of strongly diluted H_2 samples with $X = 0.5\%$. It was found in our previous work that, at this concentration, the obtained p-H_2 clusters do not freeze [28]. The spectra are shown as the square root of the measured CARS intensity and are, therefore, proportional to the absolute value of the sum of the third order resonance (CARS) and nonresonant (NR) susceptibilities $|\chi_{\text{CARS}} + \chi_{\text{NR}}|$. In the case of hydrogen clusters, the χ_{NR} is small as indicated by the negligible intensity of the baseline in the spectra. The spectra show the $Q_1(1)$ ($v' = 1, J' = 1 \leftarrow v'' = 0, J'' = 1$) and $Q_1(0)$ ($v' = 1, J' = 0 \leftarrow v'' = 0, J'' = 0$) vibrational transitions in o-H_2 and p-H_2 molecules, respectively. Different traces correspond to different content of o-H_2 in clusters, c_{ortho}, as indicated in Fig. 1. The line at 4161 cm^{-1} in Fig. 1 is assigned to the $Q_1(0)$ transition of the residual gaseous p-H_2 molecules in the beam. The two prominent features marked with solid lines in Fig. 1 are readily assigned to $Q_1(1)$ and $Q_1(0)$ transitions in the o-H_2 and p-H_2 molecules in clusters, respectively, labeled oClust and pClust.

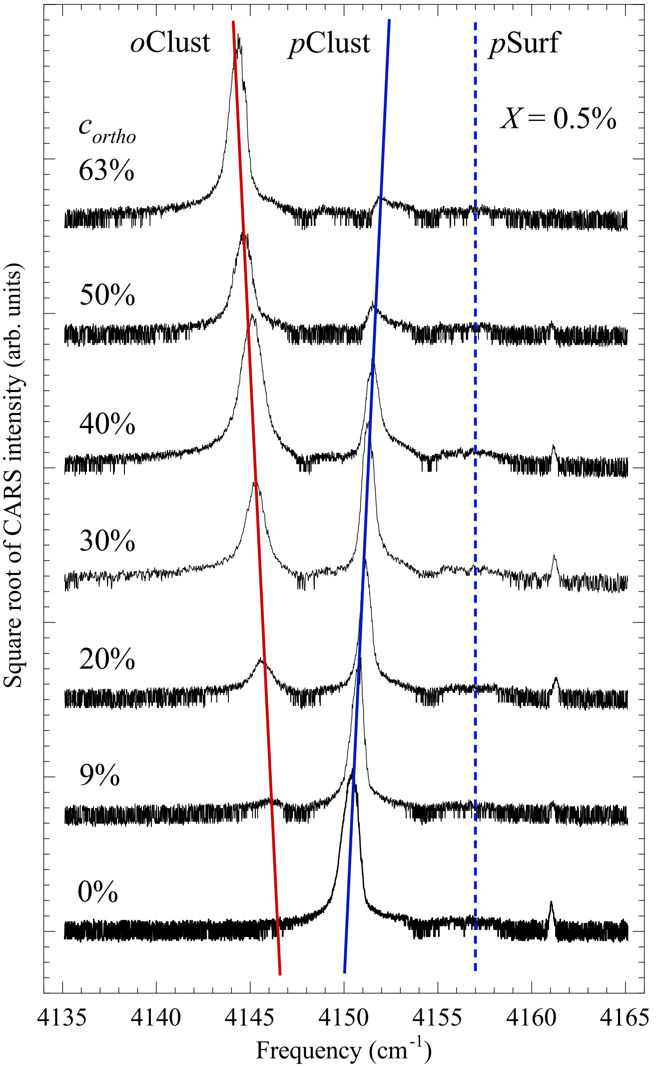

FIG. 1. Vibrational CARS spectra of the mixed o-H_2/p-H_2 clusters in ^{4}He. The content of o-H_2, c_{ortho}, is indicated for each trace. The dilution of hydrogen in He was constant at $X = 0.5\%$. Spectral bands marked with red (oClust) and blue (pClust) solid lines are due to the $Q_1(1)$ and $Q_1(0)$ transitions of the o-H_2 and p-H_2 molecules, respectively, in clusters. The line at 4161 cm^{-1} is due to free p-H_2 molecules in the beam. The vertical dashed line (pSurf) at $\sim$4157 cm^{-1} marks the broad ($\delta\nu = 3$–5 cm^{-1}) spectral feature that is tentatively assigned to the p-H_2 molecules residing on the surface of the mixed o-H_2/p-H_2 clusters.

The circles in Fig. 2 show the frequencies of the maxima of the lines pClust and oClust from Fig. 1 along with the frequencies of the corresponding transitions in bulk solid hydrogen [33], which are shown by solid lines. The frequencies of the main peaks in o-H_2/p-H_2 clusters that were obtained with hydrogen diluted in He are blueshifted with respect to those in bulk solid. For comparison, the squares in Fig. 2 show the frequencies of the $Q_1(0)$ and $Q_1(1)$ peaks obtained in this

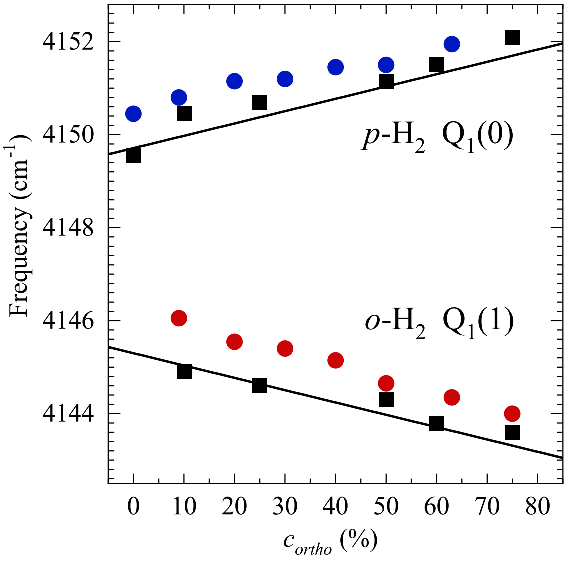

FIG. 2. Frequencies of the $Q_1(0)$ (upper part) and $Q_1(1)$ (lower part) transitions in mixed o-H_2/p-H_2 clusters versus the o-H_2 content. Circles: H_2 clusters formed in coexpansion with He—the frequencies of the *p*Clust and *o*Clust bands in Fig. 1. Squares: H_2 clusters formed upon expansion of neat H_2. Solid lines: fit of the data for bulk solid hydrogen [33]. The plotted frequencies are those of the maxima of the corresponding spectral bands, determined with the 0.2 cm^{-1} 1σ uncertainty. This choice is dictated by the apparent asymmetry of the bands in Fig. 1 and the concomitant ambiguity in determining their "center of mass" frequencies.

work upon expansion of neat hydrogen mixtures (i.e., without helium, $X = 100\%$), which are very close to those in the bulk solid. Therefore, we conclude that mixed o-H_2/p-H_2 clusters prepared without He are solid, as observed previously for neat p-H_2 clusters [28].

IV. DISCUSSION

Frequencies of the $Q_1(1)$ and $Q_1(0)$ transitions in Fig. 2 move apart with increasing c_{ortho} similarly to those in bulk solid hydrogen [33,34], but have systematic blueshift of $\sim$1 cm^{-1} at $X = 0.5\%$ as compared to the bulk measurements. The repulsion of the $Q_1(1)$ and $Q_1(0)$ bands upon increase of the o-H_2 content was assigned [35,36] to decrease of the number of p-H_2 nearest neighbors (NN) around the p-H_2 molecules and increase of the number of o-H_2 NN around the o-H_2 molecules. Interaction with the NN of the same kind gives rise to the reduction of the vibrational frequency. The appearance of the bands *o*Clust and *p*Clust is therefore consistent with a uniform mixture of the o-H_2 and p-H_2 molecules as in the bulk. The lack of phase separation into the o-H_2- and p-H_2-rich phases inside the clusters is in agreement with measured value of the excess enthalpy of mixing of o-H_2 and p-H_2 of $H_E = 1.6$ J/mol [37], which is much smaller than the average thermal energy at the estimated $T \approx 2$ K [28] of about 16 J/mol.

Figure 1 shows that even at $c_{\text{ortho}} = 50\%$ the *o*Clust peak is significantly more intense than the *p*Clust peak. In the mixed bulk solid hydrogen the Raman $Q_1(1)$ transition is known to be enhanced compared to the $Q_1(0)$ one [33,35,38]. The observed enhancement is again consistent with uniformly mixed clusters. In the bulk, the enhancement of the $Q_1(1)$ line $R = (I[Q_1(1)] \times c_{\text{para}})/(I[Q_1(0)] \times c_{\text{ortho}})$ was found to be $R = 2.7 \pm 0.8$ for the concentration range of $0.25 < c_{\text{para}} < 0.95$ [38]. The enhancement is accounted for by the coupling between the vibron collective modes (coherent collective vibration of hydrogen molecules characterized by k vector) of the o-H_2 and p-H_2 molecules in the solid, which leads to cophase contribution of p-H_2 vibron to o-H_2 vibron and the corresponding opposite-phase contribution of o-H_2 vibron to the p-H_2 vibron [38]. The frequency of the *o*Clust and *p*Clust peaks, as well as their intensity variation with c_{ortho} show that they originate from a mixed o-H_2/p-H_2 phase in clusters.

TABLE I. Integrated intensities of the three bands in Fig. 1. The band intensities are deduced from the square root of the CARS spectra and thus are proportional to the Raman cross sections of H_2 molecules in the environment of the o-H_2/p-H_2 clusters. The intensities are normalized by the total intensity of a Fig. 1 spectrum in the 4135–4160.5 cm^{-1} range, i.e., excluding the free p-H_2 transitions.

c_{ortho} (%)	*o*Clust	*p*Clust	*p*Surf
63	0.75	0	0.12
50	0.69	0.12	0.12
40	0.60	0.22	0.13
30	0.43	0.37	0.15
20	0.30	0.47	0.17
9	0.13	0.69	0.13
0	0	0.84	0.13

Besides the three well resolved peaks, *o*Clust, *p*Clust, and free hydrogen molecule peak, Fig. 1 shows some broad weak features. The band around 4157 cm^{-1} labeled in Fig. 1 as *p*Surf was previously detected in our experiments with pure p-H_2 clusters and was assigned to the molecules on the surface of the clusters [28]. The vibrational frequency of the H_2 molecules in clusters depends on the cluster size, N. Experiments and calculations [27,39] show that the shift of the vibrational frequency from that in free p-H_2 molecules is almost a linear function of the number N of p-H_2 molecules in cluster with $N = 1 - 10$ and reaches $\sim$3 cm^{-1} for $N = 10$. Calculations for larger clusters with $N = 33$ and 55 [27] revealed the slower dependence of the frequency shift on N. The measured [27] spectral feature at $\sim$4154 cm^{-1} was assigned to clusters with $N \approx 55$ based on the good agreement with the calculated vibrational shift of about -7 cm^{-1} [27].

The broader ($\delta\nu = 3 - 5$ cm^{-1}) band with the center at 4157 cm^{-1} is distinct from the bands *o*Clust and *p*Clust in that its frequency (Fig. 1) and relative intensity (Table I) remains virtually unchanged throughout the entire series of o-H_2 concentrations. One explanation could be that the *p*Surf band could be due to smaller p-H_2 clusters containing from 20 to 40 p-H_2 molecules. However, it is not clear why those neat small pH_2 clusters should be formed instead of mixed clusters. Note that the *p*Clust band is closely resembling a feature in the Raman spectra of large p-H_2 cluster spectra measured by Tejeda *et al.* [27]. Based on these observations, we concluded that the *p*Surf band has its origin in large clusters including neat p-H_2 and mixed clusters. In clusters, the coordination of the surface molecules, C_S, is lower than in the volume, C_V, which must contribute to smaller vibrational shift of the

TABLE II. Frequency of the $Q_1(0)$ line of p-H_2 in different states.

State	ν (cm^{-1})	Frequency shift (cm^{-1})
Gas[a]	4161.2	0
Liquid, $T = 26.4$ K[b]	4153.4	−7.8
Liquid, $T = 14.3$ K[b]	4151.3	−9.9
Liquid, extrapolated to $T = 0$ K[b]	4150.4	−10.8
In large p-H_2 clusters[c]	4150.4	−10.8
Solid, $T = 5$ K[b]	4149.7	−11.5

[a] Data from Ref. [42].

[b] Data from Ref. [43].

[c] Measured in this work and in Ref. [28] with p-H_2 diluted in He.

surface molecules. The fraction of the surface molecules is given by [40]

$$\frac{N_S}{N_S + N_V} = \frac{4}{(N_S + N_V)^{1/3}}. \tag{1}$$

The average ratio of the intensity of the pSurf band to the integrated intensity of the spectrum (Table I) is 0.137. The fractional intensity of the pSurf band $N_S/(N_S + N_V) = 0.137$ gives $N = N_S + N_V = 2.5 \times 10^4$ H_2 molecules, similar to what was estimated for neat p-H_2 clusters using the $c_{ortho} = 0$ spectrum [28]. As we discuss above, it has been established that in mixed o-H_2/p-H_2 solids the frequency and intensity of the $Q_1(1)$ and $Q_1(0)$ Raman transitions show strong dependence on the o-H_2: p-H_2 concentration ratio due to the NN interaction between the two hydrogen species [35,36,38]. The fact that pSurf band does not shift significantly as a function of c_{ortho} as is the case with the oClust and pClust indicates that this band comes from some homogeneous phase, such as p-H_2 molecules on the surface of the large clusters. This assignment is also supported by the fact that the fractional intensity of the pSurf band is independent of c_{ortho}.

The relevant data on the frequency of the $Q_1(0)$ transition in neat p-H_2 are presented in Table II. The positions of the main peaks $Q_1(0)$ and $Q_1(1)$ in the spectra as obtained in coexpansion with He gas and in the spectra of neat hydrogen clusters for different concentrations c_{ortho} follow the linear trends observed in bulk solid hydrogen [33] as it is seen in Fig. 2. As discussed previously [28], using H_2 gas diluted in He may lead to faster cooling of H_2 and reaching lower temperatures than upon expansion of the neat hydrogen gas. On the other hand, the experiments with neat He expansion [31,41] at $P_0 = 20$ bar and $T_0 = 17$ K show the formation of He droplets containing $\sim 10^4$ atoms. Therefore, it is conceivable that hydrogen clusters are embedded in He droplets and have low temperature of $T < 2$ K [28].

The solidification of hydrogen in the $\sim 5\,\mu$m diameter jet was investigated [26,44,45] by means of rotational and vibrational Raman spectroscopy. In the vibrational spectra, the $Q_1(0)$ peak of liquid hydrogen was found at frequencies higher than 4151.5 cm^{-1}. The solidification is evidenced by a jump of the frequency of the $Q_1(0)$ line to the value in solid hydrogen of ~ 4149.6 cm^{-1} as well as by observation of characteristic "crystal field" splitting of the $S_0(0)$ rotational line also observed [28] in our group. In this work, the observed shift of the main peaks in hydrogen diluted in He clusters (Fig. 2) is different from the shifts observed in the solid and liquid hydrogen, either bulk or clusters. Physically, the shift of the frequency of the $Q_1(0)$ line in the condensed phase correlates with the density [43]. The dependence of frequency of the $Q_1(0)$ transition on density and temperature [43] can be approximated as

$$\nu = \nu_0 - \alpha\rho(T)^2, \tag{2}$$

where ν_0 is the gas phase frequency, $\rho(T)$ is the density of liquid hydrogen, and α is the coefficient obtained from the fitting of the $Q_1(0)$ frequency in the liquid and solid p-H_2. Using Eq. (2) with extrapolated density for supercooled liquid at $T < 3$ K gives the frequency of 4150.4 cm^{-1} [43], which is in very good agreement with the measured frequency in p-H_2 clusters. Therefore, our results are consistent with the supercooled state of p-H_2 clusters as proposed in Ref. [28].

V. CONCLUSIONS

In this work, we have applied CARS spectroscopy to study the state of the mixed o-H_2/p-H_2 clusters obtained in the gas expansion. We have determined that expansion of hydrogen diluted in He yields clusters with density of molecules less than in the bulk solid hydrogen, which is consistent with liquidlike clusters of $N \approx 2.5 \times 10^4$ molecules. The o-H_2 and p-H_2 molecules are mixed inside these clusters. A broad spectral feature at 4157 cm^{-1} is peculiarly immune to changes in the o-H_2: p-H_2 concentration ratio. We tentatively assign this band to the p-H_2 molecules on the surface and consequently suggest a phase separation between an almost exclusively p-H_2 surface and an o-H_2/p-H_2 mixed inner volume of these clusters. The expansion of the neat H_2 was shown to yield the larger clusters with molecule density close to that in bulk solid hydrogen. The gas dynamical cooling of H_2 diluted in He seems to be a promising technique for making mesoscopic low temperature $T \sim 1-2$ K p-H_2 or mixed p-H_2/o-H_2 clusters in the metastable liquid state. The temperature of the embedded hydrogen clusters could be further reduced if similar experiments are performed with the rare isotope ^{3}He [22]. This work opens a possibility for searching for the macroscopic quantum effects in pure p-H_2, o-H_2, and mixed p-H_2/o-H_2 clusters.

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