Effect of the Symmetry of H_2 Molecules on their Rotations around an OCS Molecule in Superfluid ^{4}He Droplets

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The infrared spectra of OCS-$(H_2)_n$ clusters in cold (0.15 K) superfluid ^{4}He droplets coated with ^{3}He exhibit resolved rotational bands for each n up to $n = 8$ para-H_2 (pH_2) or ortho-D_2 (oD_2) molecules. An analysis of the different Q-branch intensities based on the different spin symmetries of pH_2 and oD_2 indicates the formation of symmetric 5- or 6-membered rings around the linear carbonyl sulfide (OCS) chromophore. The rings of distinguishable oD_2 are found to undergo axial rotations, whereas for 6 pH_2 molecules the symmetry-allowed rotational levels lie too high to be excited at the 0.15 K droplet temperatures.

The unique environment in liquid helium droplets has been shown to open up many new opportunities for molecular spectroscopy and for probing superfluid phenomena on the atomic scale [1]. One of the most surprising observations is the unexpected sharpness of rotational lines ($\delta\nu_{1/2} \cong$ 150–300 MHz) which were first found in infrared depletion spectra of SF_6 [2] and later for carbonyl sulfide (OCS) [3] molecules as well as a number of other molecules [4,5] embedded in cold (0.37 K) ^{4}He [2,6] and even colder (0.15 K) mixed ^{4}He/^{3}He droplets [7]. The excellent agreement of the spectra with simulations based on the Hamiltonian for the free molecules indicates that the molecules rotate nearly freely. By comparing the OCS spectra in ^{4}He droplets with spectra in nonsuperfluid ^{3}He droplets, this phenomenon was attributed to the superfluid nature of the ^{4}He droplets [8]. The major difference with respect to the free molecules is an increase in the moments of inertia (MOI), which are often found to be about a factor of 3 larger than for the free molecules. This deviation is presently under intensive investigation [4,9] since it provides an unusual opportunity to probe superfluidity at a microscopic level.

For the linear OCS molecule, the increase of the MOI for end-over-end rotations was attributed to a symmetric ring of 6 ^{4}He atoms (called a donut) in positions of strongest bonding around the waist of the chromophore [3]. The absence of a Q branch, which is due to $\Delta J = 0$ transitions, indicates that these rings do not rotate around the chromophore axis. This was attributed to the high permutational symmetry of the 6 indistinguishable ^{4}He bosonic atoms for which the selection rules allow only axial rotations with angular momentum quantum numbers $K = 0, 6, 12, \ldots$. The vanishingly small Boltzmann factor for the $K = 6$ rotations at the low droplet temperatures is able to explain the lack of a Q branch [10].

In the present study, evidence for donut rings comes from the Q-branch intensities after adding n para-H_2 (pH_2) molecules one by one to the single OCS molecules

inside the central superfluid ^{4}He core of mixed ^{4}He/^{3}He droplets [11]. Because of their factor 4 greater binding energy [12], the H_2 molecules replace the ^{4}He atoms, forming a ring around the OCS axis [13]. As in the case of the $n = 1$ spectra reported earlier [14], the spectra for $n = 2$–4 [11] now exhibit a Q branch in addition to the well resolved P and R branches ($\Delta J = -1, +1$ transitions, respectively), indicating that rotations with $K \neq 0$ around the OCS symmetry axis are activated. For $n = 5$ and 6 pH_2 molecules, the Q branch disappears [11]. The negligible Q-branch intensity is shown here to be due to the high permutational symmetry of rings of pH_2 molecules. Since all the pH_2 molecules have nuclear spin, $I = 0$ and at the low droplet temperature they are all in the lowest $J = 0$ rotational state and are *indistinguishable* just as the ^{4}He donut atoms. With added ortho-D_2 (oD_2) molecules, which also are bosons, an intense Q branch is found for all $n \geq 1$. Being a mixture of $1/6 \, I = 0$ and $5/6 \, I = 2$ degenerate states, they are essentially *distinguishable,* and $K = 1$ states are allowed and can be excited even at the 0.15 K droplet temperature. By comparing the measured Q-branch intensities with calculations assuming different ring symmetries, it is found that the pH_2 spectra are only consistent with either rings of C_5 or C_6 symmetry. Thus, from the pH_2 Q-branch intensities alone, it has been possible to eliminate other less symmetric structures and confirm the presence of high ring symmetries.

The droplet beam apparatus (see Refs. [2,3]) was equipped with two pickup cells, one for OCS and another for the pH_2 or oD_2 molecules. 99% pure pH_2 and 96% oD_2 were produced in a liquid hydrogen catalytic converter operating at 20 K. Mixed ^{4}He/^{3}He droplets with about $\overline{N}_4 \cong 500$ ^{4}He atoms and $\overline{N}_3 \cong 10^4$ ^{3}He atoms were formed by coexpanding a ^{4}He/^{3}He mixture containing 5% ^{4}He at source conditions of $P_0 = 20$ bars and $T_0 = 9$ K. The absorption of photons from a lead salt diode was detected via the depletion of the mass spectrometer signal [2,3]. The oD_2 and pH_2 pressures in the

pickup cell were chosen to produce OCS-$(pH_2)_n$ clusters with sizes in the range $n = 2$–8.

For oD_2 the vibrational bands [Fig. 1(b)] for each additional D_2 are shifted to the red by about 0.22 cm^{-1} [11]. Although the bands overlap to some extent, the rotational P, Q, R branches for $n = 2$–4 are split into distinct lines, similar to those found previously for $n = 1$ [14]. All the spectra for $n = 1$–8 are dominated by very distinct Q branches.

The pH_2 cluster spectra [Fig. 1(a)] have a slightly larger vibrational shift of 0.27 cm^{-1} per added molecule and, with the exception of the large overlap of the $n = 6$ and 7 spectra, they indicate that the complexes have geometries similar to the oD_2 clusters. As for oD_2 the best fit [11] also reveals that the MOI I_b and I_c for the two end-over-end rotations increase nearly linearly with n (Fig. 2). The best fit temperatures were 0.14 ± 0.02 K and the best fit widths of the individual rotation-vibration lines varied between 0.010 and 0.017 cm^{-1}. The salient difference to the oD_2 spectra is the lack of a Q branch for $n = 5$, which is clearly seen in the spectrum [see inset in Fig. 1(a)]. The ratio of the Q-branch to R-branch intensities is in this case less than $I(Q)/I(R) \leq 3 \times 10^{-3}$. Considerable effort went into extracting reliable upper limits of the Q-branch intensities for $n = 6$ [15]. Simulations for a

wide range of small values of the rotational constants $A(= \frac{\hbar^2}{2I_a})$, where I_a is the axial MOI (see inset in Fig. 2), were compared with the experimental spectra. The upper limit of $I(Q)/I(R) \leq 3 \times 10^{-2}$ for the Q-branch intensity was determined from A values for which the Q branch exceeded the noise level by a factor of 2.

The vanishing of the Q branch (and I_a) for $n = 5$ and 6 attached pH_2 molecules is explained by calculating the Q-branch intensity relative to the R branch. Since $I_b \cong I_c$ within the experimental errors (Fig. 2), the intensities of the Q and R branches can be estimated by assuming a symmetric top [10]

$$I = \sum_{JK} S_{JK} g_{JK} w_{JK} \exp[-E_{rot}(J, K)/kT], \quad (1)$$

where $S_{JK} = K^2[J(J + 1)]^{-1}$ for the Q branch and $S_{JK} = \{(J + 1)^2 - K^2\}[(J + 1)(2J + 1)]^{-1}$ for the R branch. The statistical weight resulting from the M and K degeneracy of the (J, K) levels is given by $g_{JK} = (2J + 1)(2 - \delta_{K,0})$. The rotational energy $E_{rot}(J, K)$ is given by $E_{rot} = BJ(J + 1) + (A - B)K^2$, where $B = C = \hbar^2/2I_b$ and $A = \hbar^2/2I_a$ [10]. The important term in Eq. (1) is the spin weight factor, w_{JK}, which for the indistinguishable pH_2
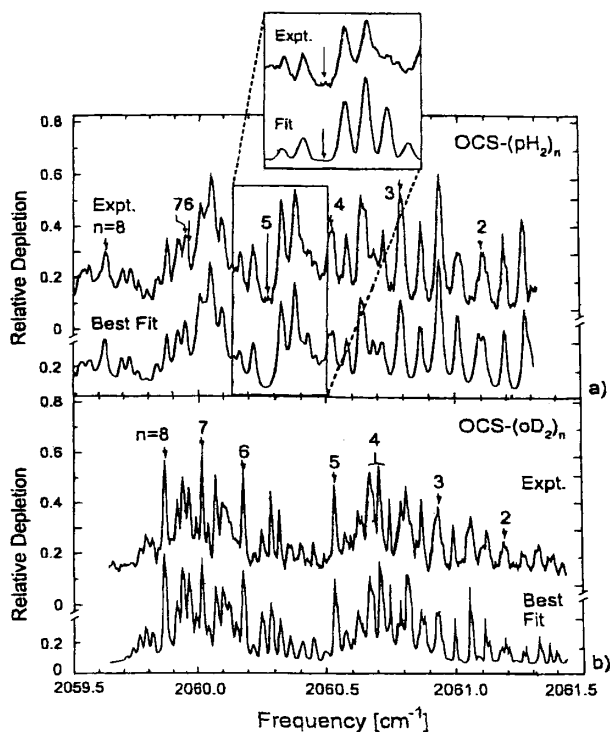

FIG. 1. Comparison of the experimental (a) OCS-$(pH_2)_n$ and (b) OCS-$(oD_2)_n$ spectra measured in ^{4}He/^{3}He mixed droplets with best fit simulations for $n = 2$–8. The arrows indicate the positions of the Q branches. The inset in (a) compares sections of the spectra corresponding to $n = 5$ with a fit from which contributions from the $n = 4$ and $n = 6, 7$ clusters were subtracted.
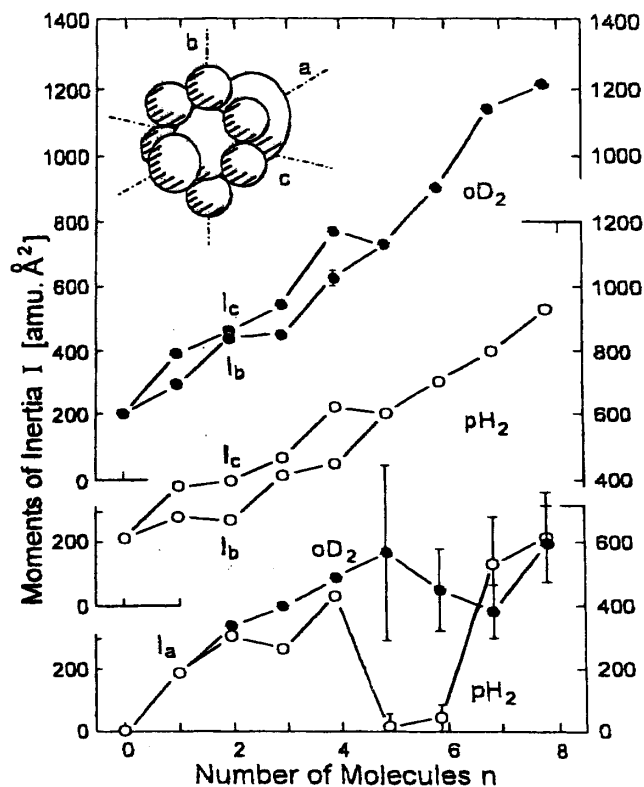

FIG. 2. The experimentally determined effective moments of inertia for the OCS-$(pH_2)_n$ and OCS-$(oD_2)_n$ clusters produced inside ^{4}He/^{3}He mixed droplets are plotted as a function of the number of pH_2 and oD_2 molecules n. For $n = 1$ (Ref. [14]) and $n = 2$, 3, and 4, the distinct differences between I_b and I_c indicate that the embedded clusters have an asymmetric top structure.

molecules is given by $w_{JK} = \delta_{K,ni}$, where n is 0 or a positive integer and i refers to the axial symmetry C_i. For pH$_2$ the lowest allowed state has $J = K = i$ and, with increasing i, $\mathcal{I}(Q)$ is suppressed by the large value of E_{rot}. For oD$_2$, on the other hand, the spin weight factor is a rather complicated function of J and K [16]. It has been calculated to be nearly the same to within 3% for different J and K. Thus, there are no symmetry constraints and all the rotations can be excited. Even at the low droplet temperatures $\mathcal{I}(Q)/\mathcal{I}(R)$ is therefore of the order of unity, in agreement with the observation of the Q branch for all n. The use of these formulas is justified since all the rotational spectra reported here can be very well fitted using the Hamiltonian appropriate for the corresponding free particle, as has also been established for many embedded molecules [2,5,9]. Moreover, assigning well defined asymmetries to floppy rings of particles has been justified by Bunker [17].

To calculate the ratio of the Q- and R-branch intensities for both $n = 5$ and $n = 6$, the MOI I_b and I_c were taken from the best fit values (Fig. 2). For I_a the true values were estimated by interpolating between the experimental data for the pH$_2$ complexes with $n = 4$ and those for $n = 7$ and 8. The data suggest that I_a must definitely lie somewhere between 400 and 600 amu Å^2. The expected values are 500 and 540 amu Å^2 for $n = 5$ and 6, respectively. The values of I_a observed for OCS-(oD$_2$)$_5$ and OCS-(oD$_2$)$_6$ (Fig. 2) also support this expectation. The ratios of the Q-branch to R-branch intensities were then calculated for different structural models of the $n = 5$ and $n = 6$ pH$_2$ complexes with different axial symmetries C_i. The comparison with the experimental data (Table I) strongly suggests that the observed small values of the ratios are compatible with only the highest symmetries C_5 and C_6.

The finding that five H$_2$ molecules can self-organize into a ring of high symmetry is especially surprising since this ring is expected to be very floppy. The estimated distance between the pH$_2$ molecules is about 4.3 Å

and therefore significantly greater than 3.8 Å [18], the average distance in liquid pH$_2$. Since a C_1 symmetry can be ruled out, the penetration of a bath He atom into the ring, which would break the C_5 symmetry, can also be ruled out. This expulsion of He atoms can probably be attributed to the large gain in the zero point vibrational energy of the five-membered pH$_2$ ring, which dominates over the energy which would be gained by incorporating an additional helium atom. The missing Q branch for $n = 6$ pH$_2$ molecules indicates that the $n = 5$ ring can, however, accommodate an additional H$_2$ molecule, which results in a C_6 ring with an average spacing of about 3.4 Å. The equal shift in ν_0 for each added H$_2$ molecule, found up to $n = 6$ [7,11], lends further support for the ring structure since it suggests that each added molecule occupies an equivalent position relative to the chromophore and that the other possible highly symmetric C_5 structure consisting of a five-membered ring and an additional H$_2$ molecule on the OCS axis is unlikely [13]. Further indirect confirmation of the symmetric structures derives from the reappearance of the Q branch for $n = 7$ and 8, indicating new asymmetric top structures once the $n = 6$ donut ring has been saturated. The interaction of the seventh H$_2$ molecule with the underlying $n = 6$ ring may explain the observed overlap of the $n = 6$ and 7 spectra [see Fig. 1(a)].

These observations provide circumstantial evidence for the existence of similar donut rings of ^{4}He atoms surrounding the bare OCS molecule. A corresponding analysis of the spectra of bare OCS in ^{4}He/^{3}He droplets provides an experimental upper limit of Im(Q)/Im(R) = 3×10^{-3}. Calculations based on Eq. (1) also rule out structures with $i < 5$. Since five or six ^{4}He atoms fit around the waist of the OCS molecule, this implies either a C_5- or C_6-symmetric ring, in essential agreement with the donut model [3]. Very recent diffusion Monte Carlo calculations reveal that 6–7 attached ^{4}He atoms are sufficient to explain the decrease in the rotational constant [19]. Density functional [4] and path

TABLE I. The comparison of the experimental ratios of Q-branch to R-branch intensities with those expected for different assumed structural models of OCS-(pH$_2$)$_n$ complexes for $n = 5$ and $n = 6$. "Dimer" and "trimer" indicate that 2 or 3 molecules are closer together, respectively.

n	Overall symmetry	Possible structures	Expected value of ratio $\mathcal{I}(Q)/\mathcal{I}(R)$
5	C_1	1 monomer and 2 dimers	0.51
5	C_5	5 equally spaced monomers	3.3×10^{-4}
5			Experiment: $\leq 3 \times 10^{-3}$
6	C_1	Unequally spaced dimers or trimers	0.51
6	C_2	2 trimers	0.32
6	C_3	3 dimers	0.10
6	C_6	6 equally spaced monomers	2.0×10^{-5}
6			Experiment: $\leq 3 \times 10^{-2}$

integral Monte Carlo (PIMC) calculations [9] also reveal the presence of several rings around the OCS molecule with the largest density in the ring at the waist position.

For both the pH_2 and oD_2 clusters, the measured MOI perpendicular to the axis, $I_b \cong I_c$, are for all n systematically larger by a factor between 3.5 and 4.8 than estimated for the corresponding free clusters. The increase of the MOI with n is surprising in view of the close similarity between the potentials of He bath atoms with donut ring ^{4}He atoms and the bath atom interactions with the $H_2(D_2)$ molecules which replace the ^{4}He atoms at the waist positions. The H_2-He potential well parameters are $R_m = 3.07$ Å (minimum distance) and $\varepsilon = 13.2$ K (well depth), compared to 2.94 Å and 10.8 K for He-He. The larger bond distance in the free OCS-He complex (3.93 Å) [20] compared to OCS-H_2 (≈ 3.2 Å) [12] is largely compensated by the larger zero point energy in the latter. Thus, substituting the ^{4}He atoms in the nonsuperfluid fraction next to the chromophore with $H_2(D_2)$ should not appreciably disturb the particle density distribution of the bath ^{4}He atoms in the immediate vicinity of the molecule. This suggests that in the case of the bare molecule the donut rings of ^{4}He atoms do indeed actively participate in permutation exchanges with their counterparts in the bath as predicted by the PIMC simulations [9] and, moreover, that these exchanges play an active role in minimizing the effective MOI of the bare molecule. Thus, with the exchanges inhibited as in the present experiments, the MOI increase in size.

In summary, the present analysis of the high resolution infrared spectra of OCS-$(pH_2)_n$ ($n = 2$–8) clusters inside an ultracold (0.15 K) superfluid ^{4}He droplet reveals the presence of highly symmetric $n = 5$ and 6 membered donut rings around the axis of the linear OCS chromophore. Whereas the pH_2 rings are not able to rotate, the spectra measured for oD_2 indicate that these rings rotate. As far as we are aware, this is the first time that the structure of a complex has been determined from the differences in spectral *intensities* (as opposed to *frequencies*) of two isotopomers and based solely on their different nuclear spin statistics. Finally, it is interesting to point out the close analogy between these symmetric donut rings and the ubiquitous permutation rings in the bulk which were postulated to be the microscopic basis of superfluidity by Feynman [21]. Both obey the same Bohr-Sommerfeld quantization rules as do also vortices in superfluid ^{4}He [22].

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