First overtone helium nanodroplet isolation spectroscopy of molecules bearing the acetylenic CH chromophore

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High-resolution helium nanodroplet isolation spectroscopy of the first overtone (2ν₁) of the acetylenic stretch of several substituted acetylenes (RC≡C–H) at T=0.38 K, have been observed for the first time. A tunable 1.5 μm laser is coupled, using a power buildup cavity, to a beam of He droplets seeded with the molecule to be studied. Absorption spectra are recorded by monitoring the beam depletion as a function of laser frequency with a thermal detector. The spectra of hydrogen cyanide (HCN), monodeuteroacetylene (DCCH), cyanoacetylene (NCCCH), propyne (CH₃CCH), trifluoropropyne (CF₂CCH), 3,3-dimethylbutyne ((CH₃)₂CCCH), and trimethylsilylacetylene ((CH₃)₃SiCCH) have been recorded. Due to the superfluid nature of the droplet, rotational resolution is achieved despite the presence of some solvent-induced broadening. The spectroscopic constants have been extracted by means of spectral simulations. The resulting rotational constants are smaller than for the bare molecule by a factor which depends on the molecule nonsphericity and its gas-phase moment of inertia. The linewidths are found to be at least twice as large as those of the corresponding fundamental (ν₁) transitions observed in a helium droplet by Nauta et al. [Faraday Discuss. Chem. Soc. 113, 261 (1999) and references therein]. The helium-induced spectral shifts are found to be very small, but cannot be easily rationalized. © 2000 American Institute of Physics.

I. INTRODUCTION

In helium nanodroplet isolation (HENDI) spectroscopy, a beam of helium nanodroplets, seeded with one or more guest molecules, is interrogated by laser spectroscopy using beam depletion¹ or fluorescence² detection. This technique combines many of the advantages of conventional cryogenic matrix isolation spectroscopy (i.e., the stabilization of unstable species) with those of molecular beam spectroscopy (i.e., the absolute isolation of the molecule under study). Using this new method it is now possible to study novel chemical species³-⁵ and to elucidate the properties of liquid helium⁶ and its interactions with atomic and molecular impurities.⁷-¹⁰

While the absolute isolation achieved in a molecular beam is desirable because very detailed static and dynamic information can so be obtained via high resolution spectroscopy, molecules in the condensed phase are of course a chemically more interesting system. Disorder, hindered mobility, and strong interactions, all contribute however to degrade the spectral resolution, thus limiting the amount of information that can be obtained spectroscopically from condensed systems. In this respect, the study of intramolecular dynamics, which is an important theme of modern chemical physics research, is no exception. While many important details of the nature of intramolecular dynamical processes in the gas phase are becoming established,¹¹,¹² far less is known about what happens in the condensed phase. In particular there is interest in establishing how the dynamics of the isolated molecule is modified when symmetry, angular momentum, and energy constraints can be lifted by the (perhaps weak) interaction with a solvent. Since superfluid helium is a highly uniform, weakly interacting medium, its potential in this respect is quite clear.

A recent investigation of the ν₁ fundamental vibration of SF₆-doped droplets has shown the possibility of obtaining rotationally resolved spectra, and of measuring the temperature of the system, which turns out to be 0.38 K.¹³,¹⁴ In the same experiment, it was observed that the spectral lines could be adequately described by Lorentzian line shapes, consistent with the initial assumptions that the solvation effects would be dominated by homogeneous broadening mechanisms. On the other hand, the recent observation of pure rotational transitions in the microwave spectrum of cyanoacetylene embedded in helium droplets¹⁵ and a very recent microwave-infrared double-resonance experiment on the same system¹⁶ have shown unambiguously that the line profiles, at least for that molecule, are dominated by inhomogeneous broadening mechanisms, which are likely to arise from the motion of the impurity inside the droplet.¹⁷

For gas phase molecules, two factors are most important in determining the intramolecular dynamics after vibrational excitation: the density of low order resonances through which vibrational energy can be dissipated to the “bath” states, and their coupling to the initially prepared state (the “bright” state). The presence of the liquid helium environment has two consequences: first, it provides a bath with a very high density of states, whose coupling to molecular vibrations is however unknown (one can speculate that the coupling should be weak for high frequency modes, and

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molecules, leaving to Sec. V the conclusions and a summary of the whole paper.

The Wilson notation will be used to label vibrational normal modes. Standard symbols will be used for the molecular constants (see, e.g., Ref. 29); a bar over a symbol will indicate the average of the ground state and vibrationally excited state values.

II. EXPERIMENT

All the compounds used in this experiment were bought at their highest commercially available purity,\textsuperscript{30} with two exceptions. Hydrogen cyanide (HCN) was obtained from the reaction of potassium cyanide with stearic acid, and cyanacetylene was synthesized according to the method of Ref. 31. In both syntheses, the gaseous product of the reaction was collected in a cold trap, and no further purification was performed. The FTIR spectra of both samples were obtained to check that the species of interest was the dominant component.

All the experiments have been carried out using a HENDI spectrometer, which was built by modifying an existing optothermal detection molecular beam spectrometer, previously used to study IVR in isolated molecules.\textsuperscript{21} A schematic of the apparatus is presented in Fig. 1.

A beam of $^4$He nanodroplets is obtained from the free expansion of research grade (99.9999\%) helium gas through a 5 $\mu$m nozzle at a backing pressure of 1500 psi (10.2 MPa). The nozzle is attached to the cold stage of a closed-cycle refrigerator (Cryodyne, Model 1020 CP), and is temperature-stabilized (better than ±0.05 K) by a PID temperature controller (Lake Shore, Model 321). The temperature of the nozzle, $T_n$, is set to a value within the range 35–16 K, which leads to droplets with mean size $\bar{N}$ ranging from 750 to 18,000 atoms, respectively\textsuperscript{32} (see Fig. 2). A smaller refrigerator (Cryodyne, Model 22) is used to precool the He gas, in order to reduce the thermal load on the main refrigerator, and also to condense—before it reaches the nozzle—any impurity that may be present in the gas line. For fixed source
conditions, the droplet-size distribution is believed to follow a log-normal distribution with a spread (standard deviation) of $\sigma \approx 0.6\bar{x}$. Assuming that the average density of the droplets, $\rho_0$, matches the bulk liquid value $1.0218 \ \text{g/cm}^3$, at saturated vapor pressure and 0.38 K temperature, the droplets have a radius of $0.22N^{1/3}$ nm and thus have a cross section of $0.15N^{2/3} \text{nm}^2$.

The droplet beam is collimated by a 500 $\mu$m skimmer, about 1 cm from the nozzle. After collimation, the droplets are seeded with the molecule of interest by passing them through a small (2.5 cm long) gas pick-up cell that contains on the order of 0.05 Pa of the appropriate gas.1,36,37 Pick-up will deflect the small droplets from the beam axis, but the large droplets will continue with little change in direction (e.g., for pick-up of HCN, we estimate an average deflection of $\sim 4/\bar{x}$ rad). It is worth to remark that, once past the seeding region, the droplets are, effectively, isolated systems. Because of the very low temperature of the nanodroplets, the rovibrational spectrum of a typical molecule spans $\sim 1 \text{ cm}^{-1}$; in general then, the spectra of molecular complexes formed in He droplets are shifted enough that they do not overlap with the spectrum of the single molecule. Hence, pick-up of more than one molecule per droplet will only decrease the intensity of the single-molecule spectrum, without affecting its shape. For this reason, high purity of the dopant gas is desirable but not essential. Previous work has demonstrated that the number of solutes in each droplet approximately follows a Poisson distribution, as expected if each pick-up event is statistically independent. Under this assumption, the single-molecule signal is maximum when the mean number of pick-up events is one per droplet, in which case the fraction of droplets containing a single solute molecule is $e^{-1}$ (37%).

The internal initial energy of the molecule and its translational energy (relative to the droplet), as well as the energy of solvation (the latter is $\sim 300 \text{ K}$ for HCN) are believed to be rapidly dissipated into the droplet and result in evaporation of He atoms [each taking off $5.5-7 \text{ K}$ (Ref. 39)] leading to a microcanonical system cooled to 0.38 K. A rough estimate gives about 200–250 evaporated He atoms due to pick-up of one room temperature HCN molecule.

Downstream from the pick-up region, the doped droplets orthogonally cross a resonant Fabry–Pérot cavity where they interact with an infrared laser beam. In the wave number region from 6500 to 6750 cm$^{-1}$ covered in this study, the circulating laser power is enhanced by a factor of about 400 inside the cavity. The laser radiation is provided by a NaOH F-center laser, and is coupled to the buildup cavity via fiber optics. A more detailed description of the cavity setup has been reported previously.27 The laser is scanned under computer control, as previously described.21 For absolute frequency calibration purposes, a reference spectrum is simultaneously recorded in a White-type multipass cell filled with 0.5 Torr (67 Pa) acetylene, and later fitted against a standard.41 A homebuilt wave meter is used to get a coarse reading of the laser wavelength in real time. Relative frequency calibration is obtained with a temperature-stabilized scanning confocal etalon (150 MHz free spectral range).

Beam depletion detection is accomplished by monitoring the total on-axis flux of helium by means of a liquid-helium-cooled semiconducting bolometer with a detectivity of $7.7 \times 10^5 \text{ V/W}$ and a noise equivalent power of $3.5-4.5 \times 10^{-14} \text{ W/Hz}$, as specified by the manufacturer.42 The absolute beam flux can be estimated by mechanically chopping the molecular beam: assuming $T_e = 20 \text{ K}$ and the beam velocity to be $\sqrt{5kT_e}$, we estimate from the measured signal that $\sim 10^3$ He atoms per second are striking the bolometer. A crude estimate based on the gas flux from an ideal supersonic source, neglecting beam attenuation effects and assuming unity accommodation coefficient, gives $\sim 10^{15}$ atoms/s impinging on the bolometer.

When the laser is tuned to a vibrational resonance, the molecule/droplet system absorbs radiation, leading to vibrational relaxation inside the droplet, which is followed by the evaporation of $^4\text{He}$ atoms ($\sim 1300$/photon at 6500 cm$^{-1}$ if the He atoms evaporate at the temperature of the droplet). These evaporating atoms will carry away little net momentum (the rms value is $\sim 0.05\%$ of the droplet momentum, for $N=5000$), and thus all but the smallest droplets are expected to continue on to reach the detector. In the laboratory frame the evaporating atoms trace a forward cone of $\sim 0.1$ rad, and largely miss the detector. The IR spectrum of a solute in He droplets is detected as the depletion of bolometer signal versus laser frequency. To achieve this, the laser is chopped at a frequency of 307 Hz (which corresponds to a minimum of the noise spectral density), and the signal it induces is demodulated with a lock-in amplifier. We observe a significant background signal due to laser radiation that scatters from the buildup cavity and heats the detector. Since this background is by necessity modulated at the chopping frequency, it is not filtered out by the lock-in. While photons instantly reach the detector, it takes $\sim 10$ ms for a He droplet to travel from the interaction region to the detector. This corresponds to a phase lag of almost exactly 90°, which can be exploited, by finely adjusting the phase of the lock-in, to eliminate the background signal with only modest loss in the true beam depletion signal. The operating temperature of the detector ($\sim 1.6 \text{ K}$) is kept below the He superfluid transition ($\sim 2 \text{ K}$)
to eliminate mechanical noise induced by the boiling of helium. Furthermore, a JFET preamplifier has been mounted on the bolometer cold finger to lower output impedance of the bolometer from $12 \, \text{M} \Omega$ (dynamic) to 500 $\Omega$, thus reducing the microphonic noise induced by the refrigerators.

With this apparatus, we obtained a typical signal-to-noise ratio of 70/1 Hz when observing the spectrum of propyne inside helium droplets. For the sake of comparison, roughly the same signal-to-noise ratio can be inferred from visual inspection, assuming comparable acquisition rates for the fundamental of the $n_3$ vibrational band of SF$_6$, measured in Ref. 13 via mass spectrometric detection. However, the CH overtone studied in this work has an integrated power absorption cross section 1300 times smaller than that of the SF$_6$ $n_3$ fundamental, our lines are 5 times wider, and the interaction region (i.e., time spent by the molecule in the laser field) is 2000 times shorter than in the apparatus of Ref. 13. This more than 10$^7$ fold disadvantage is partly compensated by the fact that the laser power circulating in our cavity is about 250 000 times higher than the laser power used in Ref. 13. Thus, we can conclude that bolometric detection is 50 times more sensitive than mass spectrometric detection.

### III. RESULTS

#### A. HCN

Hydrogen cyanide is the simplest molecule containing the $\equiv$C–H stretching mode chromophore that is common to all the molecules considered in this study. It has a very sparse set of vibrational energy levels in the region of the first overtone, $2n_1$, and thus does not display any IVR in the isolated molecule. For the same reason, solvation in liquid He is not expected to greatly change this picture. Since the maximum energy for elementary excitations [~20 K (Ref. 47)] is much smaller than the vibrational level separation in HCN (the closest known vibrational levels below $2n_1$ are $[0,3^{1},2]$, $[0,3^{1},2]$, and $[0,0,3]$, at distances of 223, 252, and 291 cm$^{-1}$, respectively), vibrational energy dissipation into the He bath is a high-order process, and as such, strongly suppressed in comparison to the heavier molecules discussed later. For this reason we decided a priori that HCN would be a good yardstick to measure vibrational relaxation in $^4$He for our series of molecules.

We scanned the HCN spectrum in the region of the gas phase $2n_1$ transition. Only one transition was observed, with a width much less than the expected separation of rotational lines. Figure 3 shows this transition as a function of nozzle temperature, which, as discussed above, determines the mean size of the droplets. The integrated intensity of the spectrum as a function of mean droplet size is shown in Fig. 4. The observed dependence can be only qualitatively justified, since many factors contribute to it:

(i) as the pressure in the pick-up cell is kept constant, the probability of one pick-up per droplet decreases rapidly, away from the optimal droplet size.

(ii) small droplets have a smaller chance of surviving the pick-up event.

(iii) the average droplet size, $\bar{N}$, grows approximately as $1/T_n^2$ (see Fig. 2), while the total He flux only grows as $1/\sqrt{T_n}$, hence the number of available He droplets decreases with increasing size.

(iv) the droplet beam kinetic energy, which is ultimately the quantity measured by the bolometer, is linear with $T_n$, hence detection efficiency decreases with increasing size.

We have assigned this transition to the R(0) line of the

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**FIG. 3.** R(0) line of HCN at different droplet sizes. The spectra shown have been recorded at nozzle temperatures from 19 K (top trace) to 33 K (bottom trace) at 1 K intervals. The shift is measured from the asymptotic limit: 6521.434 cm$^{-1}$ (see Fig. 5).

**FIG. 4.** Normalized integrated intensity of the R(0) line of HCN as a function of average droplet size, $\bar{N}$.
2ν₁ vibrational band. Because of the low temperature of He nanodroplets (0.38 K) it is expected that only the J = 0 rotational level will have significant population, unless the effective rotational constant in the droplet is considerably smaller than in the gas phase. The UNC group has observed the ν₁ fundamental of HCN using an apparatus of similar design, which uses a 3 μm F-center laser to excite the droplets. An important additional feature of the UNC machine is the ability to apply a large static electric field in the region where the molecules interact with the laser. This method was used to induce transition intensity in the zero-field-forbidden Q line, thus allowing the rotational constant of HCN (in the ν₁ state) to be measured as 1.175 cm⁻¹ (35.225 GHz). From this rotational constant, neglecting the small change with vibrational excitation, the estimated population of the J = 1 level at 0.38 K is 0.04%, consistent with our failure to detect any ro-vibrational transitions from any but the ground rotational state.

The R(0) transition in Fig. 3 is seen to narrow and shift to lower wave number as the average droplet size, ̅N, is increased. Similar behavior has also been reported for the ν₅ transition of SF₆. Both experiments and theory indicate that rotational constants should not change with droplet size, at least for fully solvated molecules. Thus we can exclude a variation of the rotational constant as the cause of the observed shift.

If ν is the position of the R(0) line, as measured by its center of mass, a simple model based on the energetics of solvation (see Sec. IV A) predicts ν(̅N) − ν(∞) ∝ ̅N⁻¹. Figure 5 shows a set of experimental values of ν(̅N), and the best fit to the formula ν(̅N) = ν(∞) + a/(̅N − ̅N₀); the quantity ̅N₀ has been added to the original model of Sec. IV A as an extra parameter to compensate for our imperfect knowledge of the droplet size as a function of T₀. The best fit parameters are: ν(∞) = 6521.434 ± 0.001 cm⁻¹, a = 42 ± 2 cm⁻¹, ̅N₀ = 350 ± 30. ̅N₀ is just a “first order correction” to the estimated value of ̅N, but it can also be interpreted as the number of He atoms evaporated from a droplet upon pick-up of an HCN molecule. It is interesting to observe that our estimate of the latter quantity (Sec. II) is very close to the best fit value of ̅N₀.

Because the transition frequency varies with droplet size, we can anticipate that the spread of droplets sizes produced at any given source condition would lead to an inhomogeneous broadening in the spectrum. Using the log-normal droplet size distribution inferred from previous work, we can predict what the line shape would be if there were no other sources of line broadening. In Fig. 6, the observed and predicted line shapes, at T₀ = 23 K (̅N = 4500) are compared. One can see that the droplet-size-induced linewidth is only a fraction of the total linewidth, hence other sources of broadening must be present. Also, the linewidth induced by the droplet-size distribution grows larger at smaller droplet sizes, but so does the total width; as a consequence, the ratio between the two remains approximately constant.

Figure 7 shows the R(0) line behavior as a function of the laser power incident on the molecular beam (P). If the line was homogeneously broadened, the available power would be insufficient to saturate the transition, and the signal would be expected to increase linearly with P. Instead a sub-linear power dependence is observed, clearly demonstrating the presence of saturation and of inhomogeneous broadening. Quantitative information can be extracted from the integrated intensity of the R(0) line (I_R0) as a function of P (Fig. 8, bottom curve). For this purpose we used a simple model for the saturation of an inhomogeneous line, which predicts the following functional form:

\[ I_{R_0}(P) \propto \frac{P}{\sqrt{1 + P/P_{sat}}} \]  

The best fit to this functional form gives a saturation power \( P_{sat} = 2 \pm 0.7 \) W, from which a homogeneous linewidth of 17 ± 6 MHz can be estimated (the details of this derivation are reported in Appendix A). The intracavity power was estimated from the power incident onto the buildup cavity, assuming a gain factor of 400. Obvious sources of error...
which have not been included in this estimate (approximate knowledge of the gain factor, and of the coupling to the cavity) will result in a correspondingly inaccurate estimate of the saturation power and of the homogeneous linewidth. What is important to observe is that the estimated homogeneous linewidth is narrower than the observed linewidth by more than an order of magnitude.

A moderate increase of the linewidth, as measured by its second central moment (Fig. 8, top curve), is observed at high $P$. If this width increase was due to power broadening of the inhomogeneous line shape, it should become observable, given our estimate of the homogeneous linewidth, at much higher $P$. One alternative explanation is that the saturation power is not the same for the whole line, but rather increases at the wings. As a consequence, the intensity of the line would grow faster at the wings than at the center.

B. DCCH

We also attempted to observe the $\nu_1 + \nu_3$ band of HCCH, which in the local-mode picture corresponds to two quanta of vibration in one CH bond; despite repeated attempts, no such spectrum could be detected. In order to establish that this was not due to some artifact related to the reactivity of the molecule, we also investigated DCCH, which has a CH stretching overtone in the same spectral region, with an estimated band strength approximately one-half that of the $\nu_1 + \nu_3$ band of HCCH. Figure 9 shows the spectrum obtained. As in the case of HCN, we observe only a single line, which we interpret to be the R(0) line of the 2$\nu_1$ vibrational band. Also using HENDI spectroscopy, the UNC group successfully observed, in the 3 $\mu$m region, the R(0) line both for HCCH ($\nu_3$, asymmetric CH stretch), and DCCH ($\nu_1$, CH stretch); the former turns out to be ~4 times broader than the latter. Our current hypothesis is that the presence of the 2$\nu_1$ state just 54 $\text{cm}^{-1}$ below the $\nu_1 + \nu_3$ state, greatly facilitates energy exchange with the droplet, thereby decreasing the lifetime of the transition, and making it too broad to be detected.

It is interesting to observe that HCN and DCCH are quite similar molecules, in size and structure, yet their spectra in He droplets are remarkably different: the R(0) line of HCN is visibly asymmetric and is split into two components. The same line in DCCH can be nicely fit with a Lorentzian shape—centered at 6571.076 $\text{cm}^{-1}$ and with a full width at half maximum (FWHM) of 920 MHz. We believe the difference is due to the polar versus nonpolar nature of the two molecules, as suggested by experimental investigation of HCN in He droplets.

C. NCCCH

NCCCH is a linear molecule whose gas phase spectrum in the region of the second overtone ($3\nu_1$) was previously
studied in this laboratory. The density of vibrational states ($\approx 31/cm^{-1}$) placed this spectrum in the intermediate regime of IVR; in the first overtone the density of states is low enough that no IVR is expected. It was therefore possible that in the liquid He environment, where strict intramolecular energy conservation is no longer required, solvent-mediated vibrational energy transfer could lead, already in the first overtone, to an accelerated relaxation of the optically excited state, thus causing additional line broadening.

Figure 10 shows the $2\nu_1$ spectrum observed at $T_n=26$ K, for which $\bar{N}=2700$ is estimated. As in the case of the $\nu_3$ band of OCS, the spectrum clearly displays the rotational structure of a linear molecule, but with considerably reduced rotational constants. Except for overall broader lines, the spectrum has remarkable similarities with that measured for the fundamental ($\nu_1$) transition, in particular the pronounced asymmetry of the R(0) and P(1) lines. For this reason, just as in Ref. 16, we fit these two lines with the convolution of a Lorentzian and a half exponential, and use a simple Lorentzian to fit all other features.

The entire spectrum is fit as a whole, with the intensity (integrated area) and position (center of gravity) of each line dictated by a linear rotor Hamiltonian. The free parameters of the fit are the Lorentzian linewidths, the decay constant of the exponential [for the R(0) and P(1) lines only], the rotational temperature, and the parameters of the Hamiltonian up to third order. Table I gives the spectroscopic constants determined by the least squares fit, along with the statistical uncertainties ($1\sigma$) of the parameters. For all the fits performed in this work, long-term fluctuations of dopant pressure are not accounted for, when estimating the accuracy of the measured signal. As a result, the uncertainties on the fitting parameters, particularly the droplet temperature, are most likely underestimated. The FWHM of each line is plotted as a function of the transition number $m$ in the inset of Fig. 10. The estimated temperature (0.39 K) is in agreement with prior observations. One interesting feature of the spectrum is that the linewidth of the rotational lines decreases with increasing rotational quanta, is minimum at $|m|=3$, and then increases again. The same has been observed for the $\nu_1$ band.

### Table I. Molecular constants from the fit of the NCCCH spectrum displayed in Fig. 10. Units are MHz, unless otherwise indicated.

<table>
<thead>
<tr>
<th>$\nu_0$ (cm$^{-1}$)</th>
<th>$B$</th>
<th>$\Delta B$</th>
<th>$D_J$</th>
<th>$T$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free 6551.980(2)a</td>
<td>4549b</td>
<td>-14.14(5)a</td>
<td>5.4x10^{-4} b</td>
<td>0.391(2)</td>
</tr>
<tr>
<td>In $^4$He 6551.804(1)</td>
<td>1552(2)</td>
<td>-44(1)</td>
<td>4.7(1)</td>
<td>0.391(2)</td>
</tr>
</tbody>
</table>

From Ref. 67.

Ground state values, truncated, from Ref. 68.

D. CH$_3$CCH

Propyne is the first molecule we studied for which evidence of (limited) IVR was observed in the gas phase spectrum of the first overtone, $2\nu_1$. In that spectrum, the $K=0$ sub-band showed no evidence of IVR, but sub-bands with higher $K$ did. The IVR dynamics of this molecule has been extensively studied, over a wide range of overtone and combination states. Because in the gas phase $2\nu_1$ state, the density of states is high enough that the onset of IVR is observed, one could in principle expect that solvent-induced effects will be evident in this case.

Figure 11 shows the measured spectrum, acquired at $T_n=24.5$ K. The spectrum clearly displays a Q branch in addition to the P and R branches. While the A rotational constant of propyne is sufficiently large that one would expect no thermal population in the $K\neq 0$ levels (and thus no Q branch), quantum symmetry effects have to be taken into account. The $C_{3v}$ symmetry of the molecule, in connection with the symmetry of the nuclear wave function, insures that...
two symmetry modifications (A and E) of the rotational
wave function are present, associated to \( K = 0, 3, 6, \ldots, \) and
\( K = 1, 2, 4, 5, \ldots, \) respectively. For an isolated molecule, only
very weak spin–rotation coupling of different rotational lev-
els can induce relaxation between the two modifications, and
this can be expected to take far longer than the few hundred
microseconds elapsing between the pick-up and optical inter-
rogation in our experiments.\(^5^5\) For example, a timescale of
several hours has been measured for nuclear spin relaxation
of methane in an argon matrix.\(^5^6\) Hence at 0.38 K both the
\( K = 0 \) and \( K = 1 \) states, and only these two, will be popu-
lated. Similar “conservation of nuclear spin species” has
been observed in the spectrum of \( SF_6 \) in He droplets.\(^5^3\)

Due to the rather large rotational constants and slightly
narrower lines, this molecule gives the best resolved rota-
tional spectrum. The rotational lines are in this case quite
symmetric, and are best fitted by Lorentzian shapes. As we
did for NCCCH, we fit the entire spectrum as a whole, this
time using a symmetric top Hamiltonian. Although there is
no \textit{a priori} reason to assume that the same symmetry should
be used as that of the gas phase molecule, this, has, so far,
proven to be correct for almost all the molecules studied (for
an exception, see Ref. 57). This is another consequence of
the weakness of the perturbation induced by the liquid He
environment.

In order to perform the fit, it is necessary to assume a
partition of populations between the A and E modifications.
In the limit of long nuclear spin relaxation time, the room
temperature equilibrium partition should apply. By including
the proper degeneracy over nuclear spin and rotational states,
one obtains equal populations for the two modifications.
Table II shows the spectroscopic parameters determined
from the fit. Note that, even though the \( K \) structure in the
higher transitions is not resolved, the position of the Q
branch (to which only \( K = 1 \) contributes) relative to the R(0)
and P(1) lines (to which only \( K = 0 \) contributes) dictates the
value of \( \Delta(A - B) \). The Q branch shows an unresolved set of
lines which, in the fit, we constrain to have the same width,
independent of \( J \). Given the small value of \( \Delta B \) and the low
number of populated rotational levels, the whole Q branch is
only \( \approx 150 \) MHz broader than each of the lines contributing
to it. Likewise, \( \Delta(A - B) \neq 0 \) leads to a splitting, too small to
be observed, between the \( K = 0 \) and \( K = 1 \) lines in the R and
P branch. The global fit is shown in Fig. 11 as a thick solid
line. A droplet temperature of 0.394 K is estimated from it.
Note that with these fit parameters the R branch has a band-
head, and as a consequence the R(3) and R(4) lines overlap
and cannot be resolved [also, the R(5) line overlaps with the
R(2)]. For this reason the R(3), R(4), R(5) lines have been
constrained to share the same linewidth parameter in the fit.
The FWHM of the lines are plotted versus the transition
number in the inset of Fig. 11. Note the behavior, somewhat
similar to that of NCCCH, and the peculiar narrowness of the
Q branch.

Since it is narrower, more intense, and only slightly
overlapping with the neighboring lines, the Q branch was
chosen to test the saturation behavior of propyne. In contrast
to the case of HCN, a linear dependence of the IR signal as
a function of laser power was found up to an intracavity
power of 27 W, indicating negligible saturation over the
available range of laser intensity. By comparison with the
HCN R(0) line, the homogeneous linewidth of propyne must
be at least 10 times broader than that of HCN (for the sake of
simplicity the same band strength as HCN is assumed, see
Appendix A).

\section*{E. \textit{CF}_3CCH}

Trifluoropropyne is the first molecule in the present
study for which extensive IVR was previously observed in
the gas phase \( 2 \nu_1 \) spectrum.\(^2^2\) The lowest \( J \) transitions were
found to consist of very dense “clumps” of lines, and the
measured density of states in the R(0) transition was found to
be consistent with the total density of vibrational energy lev-
els of \( A_1 \) symmetry. Finally, the spacing statistics of the
states was of the type expected for a spectrum with chaotic
dynamics.

Figure 12 shows the spectrum measured in He droplets.
Because \( A - B \), the Q branch is much more intense (relative
to the P and R branches) than in the case of propyne. Be-
cause of the much smaller rotational constants and increased
linewidth, the P and R branches are only partially resolved.
Nevertheless, a global fit of the whole spectrum is still pos-
sible, as long as the populations of rotational levels are reli-
ably constrained by the molecular parameters. As in the case
of propyne, the spectrum has been simulated as that of a
symmetric top, using Lorentzian line shapes. Since both \( ^1H \)
and \( ^19F \) atoms have nuclear spin 1/2, the same considera-
tions made for propyne also hold for trifluoropropyne. In this case
too, equal populations in the A and E modification have been
assumed; unlike the case of propyne, now the value of the
rotational constant \( A \) is low enough that levels with \( K > 1 \) are
thermally populated. The relative intensity of the Q branch
then allows an estimate of \( A \) to be made, despite the fact that
the position of the transitions does not depend upon this
spectroscopic constant.

The spectroscopic parameters of the fit are given in
Table III, and the fit is plotted in Fig. 12. The widths of

\begin{table}[h]
\centering
\caption{Molecular constants from the fit of the propyne spectrum displayed in Fig. 11. Units are MHz, unless otherwise indicated.}
\begin{tabular}{cccccc}
\hline
\( n \) & \( v_0 \) (cm\(^{-1}\)) & \( B \) & \( \Delta B \) & \( D_J \) & \( D_{JK} \) & \( \Delta(A - B) \) & \( T \) (K) \\
\hline
Free & 6568.1716(2)\(^a\) & 8546\(^b\) & -45.59(8)\(^a\) & 0.0029\(^b\) & 0.16\(^b\) & 569(9)\(^a\) & \\
In \( ^4\)He & 6567.965(1) & 2151(2) & -78(1) & 14.6(1) & -59(4) & -104(6) & 0.394(2) \\
\hline
\end{tabular}
\end{table}

\(^a\)From Ref. 26.
\(^b\)Ground state values, truncated, from Ref. 69.
individual lines are plotted versus the transition number, \( m \), in the inset of the figure. In order to obtain an accurate partition of populations, all the levels with \( J \) up to 11 and \( K \) up to 8 have been included, but unresolved high-\( J \) transitions (\( |m| \geq 5 \)) within the same branch are constrained to share the same linewidth parameter. As in the case of propyne, the Q branch is narrower than its immediate neighbors.

Interestingly, the value of the \( A \) rotational constant is about 50% of the gas phase value. So far it was observed that heavy molecules with high nonsphericity undergo a much larger reduction of rotational constants (typically to 1/3 of the gas phase value), while light, quasispherical molecules undergo little or no change at all. This intermediate case is discussed in Sec. IV C.

**F. (CH\(_3\))\(_2\)SiCCH and (CH\(_3\))\(_3\)CCCH**

(CH\(_3\))\(_2\)SiCCH (TMSA) and (CH\(_3\))\(_3\)CCCH (TBA) have been shown to display “large molecule limit” (i.e., statistical) IVR in the gas phase spectra of both \( \nu_1 \) and \( 2\nu_1 \). For both molecules, the lines of the \( 2\nu_1 \) band were found to have a Lorentzian shape with homogeneous widths of 50 and 1400 MHz, respectively\(^{21} \) (some additional, inhomogeneous, broadening was also present, due to the \( K \) structure). It is commonly believed that the total density of states, as opposed to the density of low-order resonances, is the relevant quantity in determining IVR rates. The much narrower line-

width for TMSA, despite a 50-fold larger density of states,\(^{20} \) and despite the fact that the two molecules are otherwise extremely similar, convincingly demonstrated the limitation of this assumption.

The \( 2\nu_1 \) spectrum of TMSA is shown in Fig. 13, along with the best fit simulation as a symmetric top. Another, less intense spectrum, clearly identifiable as that of a symmetric top (most likely a dimer of TMSA), appears to the red of it. Since the two spectra partly overlap, we chose to fit them simultaneously, but we will describe their fit separately, starting with that of TMSA. As before, nuclear spin symmetry has to be taken into account. Due to the presence of the three equivalent methyl groups, the symmetry group is no longer \( C_{3v} \), but the much more complicated \( G_{162} \). The nuclear spin weights for this class of molecules have been calculated by Lehmann and Pate,\(^{58} \) and will be used here.

Even for this extremely heavy, highly anisotropic molecule, the spectrum clearly shows the remnants of a resolved rotational structure. It was in fact possible to use the widths of the Q and R branch lines as free parameters in the fit. Due to lack of resolution in the P branch, the corresponding linewidths had to be constrained to a fixed value. The latter has been arbitrarily set at 700 MHz (FWHM), which best reproduces the barely resolved structure of the P branch. In order to properly evaluate the partition function, all states with \( J \)

\[ \text{TABLE III. Molecular constants from the fit of the trifluoropropyne spectrum displayed in Fig. 12. Units are MHz, unless otherwise indicated.} \]

<table>
<thead>
<tr>
<th>( \nu_0 ) (cm(^{-1}))</th>
<th>( B )</th>
<th>( \Delta B )</th>
<th>( D_J )</th>
<th>( D_{KK} )</th>
<th>( A - B )</th>
<th>( \Delta(A - B) )</th>
<th>( T ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free</td>
<td>6557.872(5)(^a)</td>
<td>2878(^b)</td>
<td>(-7.75(10))(^c)</td>
<td>(2.7 \times 10^{-4}) (^d)</td>
<td>(6.3 \times 10^{-3}) (^b)</td>
<td>284(^i)</td>
<td>8.01(^f)</td>
</tr>
<tr>
<td>In (^3)He</td>
<td>6557.496(1)</td>
<td>1065(2)</td>
<td>(-26(1))</td>
<td>2.38(5)</td>
<td>(-7(2))</td>
<td>1945(45)</td>
<td>17(3)</td>
</tr>
</tbody>
</table>

\(^a\)Extrapolated from Ref. 22. 
\(^b\)Ground state values, truncated, from Ref. 70. 
\(^c\)Twice the \( \nu_1 \) value, from Ref. 22. 

FIG. 12. Trifluoropropyne overtone spectrum, recorded at \( T_n = 23 \) K. The thick line is a fit to a symmetric top, with the parameters of Table III. The inset shows the FWHM linewidths.
TABLE IV. Molecular constants from the fit of the trimethylsilylacetylene spectrum displayed in Fig. 13. Units are MHz, unless otherwise indicated.

<table>
<thead>
<tr>
<th>$\nu_0$ (cm$^{-1}$)</th>
<th>$B$</th>
<th>$\Delta B$</th>
<th>$D_{J}$</th>
<th>$D_{JK}$</th>
<th>$\Delta(A-B)$</th>
<th>$T$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free 6520.305$^a$</td>
<td>196$^b$</td>
<td>$\approx$6.8$^a$</td>
<td>2.5 $\times$ 10$^{-4}$</td>
<td>1204$^c$</td>
<td>$\approx -\Delta B$</td>
<td></td>
</tr>
<tr>
<td>In $^4$He 6521.170(1)</td>
<td>431(1)</td>
<td>1.0(2)</td>
<td>0.469(7)</td>
<td>1.1(1)</td>
<td>392(12)</td>
<td>0.469(3)</td>
</tr>
</tbody>
</table>

$^a$From Ref. 21.
$^b$Ground state values, truncated, from Ref. 71.
$^c$Calculated from $A$ of (CH$_3$)$_2$SiH (Ref. 72).

up to 13 and $K$ up to 11 have been included. In order to limit the number of free parameters in the fit, all the high-$J$ transitions of the R branch ($m \approx 8$) share the same linewidth parameter. Quite to our surprise, Lorentzian lineshapes gave us a poor fit. Therefore we chose a Voigt profile parameter. From this observation we deduce that for this molecule line broadening is predominantly inhomogeneous. As in the case of propyne, the linewidths are approximately constant with $J$, with the difference that in that case the broadening mechanism was predominantly homogeneous.

Table IV gives the constants determined from the fit. The rotational temperature (0.47 K) is slightly higher than usually observed. Even conceding that we may be somewhat underestimating the uncertainty on the rotational temperature, our data are not consistent with the usual value of 0.38 K.

It is also remarkable that the lines are substantially narrower than even those of HCN and DCCH. Power-dependent measurements of the Q branch of this spectrum, analogous to those shown in Figs. 7 and 8, demonstrated that we could saturate this transition. The saturation power is estimated to be 10±5 W.

The less intense spectrum to the red of the TMSA spectrum clearly belongs to a highly symmetric, heavy rotor, which is likely a van der Waals complex containing TMSA. In order to fit it, we assume that the complex has the same symmetry and rotational temperature as TMSA itself. While these assumptions are not totally justified, they are reasonable for the amount of information that we want to extract from this spectrum. The parameters of the fit are reported in Table V.

From the measured average $B$ constant we can roughly estimate the size of this complex: if we assume the same effective mass as TMSA, its gyration radius is 2.25 larger than that of TMSA, while if we assume a mass twice as large the gyration radius is 1.6 times larger than that of TMSA. If this spectrum was due to a complex between an impurity present in the experimental chamber and TMSA, the most likely candidates would be N$_2$, O$_2$ or water, which are very light partners and therefore not consistent with the above estimates. For this reason we tentatively assign the spectrum to a dimer of TMSA.

The 2$\nu_1$ spectrum of TBA is shown in Fig. 14. In this case, no fit is possible, due to lack of rotational resolution and to a rather intense background (evidenced by the sloping baseline and by the unphysical fact that the intensity of the P branch appears to be greater than that of the R branch). The band center, and an estimate of the linewidth can still be extracted; we obtain: $\nu_0=6558.196(3)$ cm$^{-1}$; Q-branch width (FWHM) = 2800 MHz. We note that unlike TMSA which has the narrowest lines, TBA has the largest linewidth of all the molecules considered in this study.

IV. DISCUSSION

A. Solvation shifts

Table VI lists the solvent-induced shifts of the vibrational band origins. For both HCN and DCCH, we only observe one transition; the vibrational origins can only be calculated if we have estimates of the rotational constant of the molecules in liquid He droplets. The rotational constant of HCN in the $\nu_1$ level (35.225 GHz) has been recently determined by the UNC group, as already mentioned. More recently, we have observed the millimeter wave $J=0\rightarrow1$ transition of HCN in He droplets at 72.14 GHz.$^{30}$ From these data, we can produce a first-order formula for the rotational

![bolometer signal](image)

FIG. 14. Tert-butyl-acetylene overtone spectrum, recorded at $T_\text{ex}=22$ K.
constant as a function of the vibrational quanta, \( \nu \), in the \( \nu_1 \) mode: 
\[
B = \frac{36.07 - 0.845 \nu}{34.38 \text{ GHz}}.
\]
For DCCH, we can also estimate the value of \( B \) (more crudely) from the spectrum of the \( \nu_1 \) fundamental of HCCH, measured in \(^4\)He droplets by the UNC group.\(^{53}\) Because of the symmetry of HCCH, both \( J' = 0 \) and \( J' = 1 \) remain populated, and so the position of the \( J' = 0,1,2 \) levels has been determined in the excited state. From the \( J' = 0,1 \) spacing, the effective rotational constant in the \(^4\)He droplet can be estimated (30.08 GHz). From this quantity, the increase in moment of inertia \( \Delta I \) (relative to the bare molecule) can be estimated. By assuming the same \( \Delta I \) for DCCH, we can then estimate the rotational constant of DCCH in \(^4\)He droplets. As a result of these approximations, the solvent shift for DCCH is estimated with less accuracy than for the other molecules.

For most of the molecules, we see a small shift to a lower wave number. This is consistent with the shifts observed for other stretching modes of molecules in He droplets. In contrast, the two molecules with tert-butyl groups have positive shifts, which previously had only been observed for bending modes. The solvent-induced shift of vibrational transitions are known to include contributions of opposite sign. The presence of a solvent hinders the vibrational motion, via short-range repulsive forces, and causes a blueshift of the transition. On the other side, vibrational excitation normally increases the long-range, attractive interactions (induction and dispersion) between the molecule and the solvent, and causes a redshift of the transition.

More specifically, the blueshift is caused by the following effect: As the CH stretch is excited, the bond length increases, much faster than the solvent can respond, and the H atom pushes against the repulsive wall of the H–He potential. This increases the effective force constant of the mode, relative to the free molecule, and thus raises the vibrational frequency. This effect is the largest for low frequency bending vibrations, both because they have small force constants and because they involve large displacements against the solvent. One would like to assume that the “blue-shift” for the acetylenic CH stretch be approximately constant across the series of molecules studied. Indeed, this mode is very localized, and as such, not greatly affected by the series of very different substituents we span: It is then plausible that the motion of the H atom “into” the He, caused by vibrational excitation, stays the same regardless of the substituent. However the assumption of constant blue-shift is only reasonable if also the density of He in the direction of the CH motion is approximately the same for all the substituents; in reality it is known that the van der Waals interaction between the molecule and the helium is strong enough to induce the formation, around the solute, of a highly inhomogeneous solvent shell, whose structure and density change from molecule to molecule. Therefore we neither have a quantitative model for the blueshift, nor can we assume that it is approximately constant for the series of molecules studied here.

The redshift is easier to model because it depends on long-range interactions, whose functional form is known. Also, information can be extracted from the droplet-size dependence of the shift, for which, short-range effects cancel out. Normally, the interaction between the molecule and the solvent atoms is treated as pairwise additive, and only the leading term of the long-range molecule–atom interaction (of the form \( -C_6 r^6 \)) is retained. Further, it is assumed that the molecule is confined near the center of the droplet, which has been predicted to be the case, based on the energetics of solvation.\(^{17}\) It is then easy to demonstrate that the absolute redshift \( \Delta \nu_1 \) is given by

\[
\Delta \nu_1 = -\Delta C_6 \int \frac{\rho(r)}{r^6} dr,
\]

where \( \rho(r) \) is the density of the droplet and \( \Delta C_6 \) the change in \( C_6 \) upon vibrational excitation. With the asymptotic value of \( \Delta \nu_1 \) taken as 0, the dependence on droplet size is given by the “excluded volume” model

\[
\Delta \nu_1(N) = \left( \frac{4}{3} \pi \rho_0 \right)^2 \frac{\Delta C_6}{N}
\]

which is minimum (redmost) for \( N \to \infty \); this formula is the equivalent of the one introduced in Sec. III A. We have made the tacit assumption that the first solvation layers around the molecule do not change with droplet size, so that the deviation from the asymptotic value is due solely to the “missing long range interaction” as the amount of He interacting with the molecule is decreased; note that this allows to replace \( \rho(r) \) with its average value for the pure droplet, \( \rho_0 \).

We will now analyze the three mechanisms that contribute to \( \Delta C_6 \). Note that usually the permanent dipole moment \( \mu \) and polarizability \( \alpha \) of a molecule increase upon vibrational excitation, hence all the contributions to \( \Delta C_6 \) listed below are usually positive. We will also give the numerical results for HCN, and demonstrate that the observed shift must result from partial cancellation of larger redshift and blueshift. We take the He–HCN interaction parameters mostly from Atkins and Hutson,\(^{61}\) experimental dipole moments from Smith et al.,\(^{62}\) and polarizability derivatives from Dion et al.;\(^{63}\) we calculate \( \rho(r) \) for a HCN–He\(_{1000}\) droplet by use of a density functional method.\(^{6} \)

The three separate contributions are as follows:

1. The dynamic dipole-induced dipole effect discussed by LeRoy.\(^{59}\) It gives \( \Delta C_6 = \Delta \nu \alpha_{\text{He}} \mu_{\text{HCN}}^2 \), where \( \Delta \nu \) is the
change in vibrational quantum number, $\alpha_{1He}$ the static polarizability of He, and $\mu_{01}$ the transition dipole moment for the fundamental ($\nu_1$) transition. For HCN we obtain an absolute redshift $\Delta \nu_r = 0.14$ cm$^{-1}$, and a droplet-size dependence $\Delta \nu_r(N) = (0.25/N)$ cm$^{-1}$.

(2) The change of permanent dipole moment upon vibrational excitation, which gives $\Delta C_6 = \alpha_{1He}^2 \mu_{v=2}^2 - \mu_{v=0}^2$.

For HCN we obtain $\Delta \nu_r = 1.67$ cm$^{-1}$, $\Delta \nu_r(N) = (3.04/N)$ cm$^{-1}$.

(3) The change in polarizability upon vibrational excitation, which gives $\Delta C_6 = C_6 \Delta \alpha/\alpha$. For HCN, keeping into account the angular dependence of $\Delta C_6$, we obtain $\nu_r = 4.98$ cm$^{-1}$, $\Delta \nu_r(N) = (10.4/N)$ cm$^{-1}$.

In total, we have an absolute redshift of $\approx 6.8$ cm$^{-1}$, which is more than 10 times larger than the experimental value ($\approx 0.5$ cm$^{-1}$). Since the above estimate is unlikely to be off by an order of magnitude, we have to conclude that redshift and blueshift are, at least for HCN, of comparable magnitude and nearly cancel out. The shifts observed by the UNC group for the HCN dimer do, in our opinion corroborate this picture: the outer CH stretch—the analogous of the mode probed here—is found to be shifted by $-0.25$ cm$^{-1}$, which is comparable to the $-0.47$ cm$^{-1}$ we observe. The inner CH stretch is instead found to be shifted by $-3.99$ cm$^{-1}$ relative to the inner CH stretch of the gas phase dimer; the UNC group proposes that the presence of the He might strengthen the HCN–HCN hydrogen bond, thus increasing the large redshift induced by dimerization ($\approx 70$ cm$^{-1}$ in the gas phase). We propose an alternative explanation: upon solvation in He, the inner CH stretch—being shielded by the other HCN molecule—suffers no further blueshift, hence the observed redshift ($-3.99$ cm$^{-1}$) directly measures the long-range effects discussed above. It is encouraging to see that for $\nu = 1$ our above estimates would predict a redshift of $-3.4$ cm$^{-1}$.

The droplet-size dependence of the shift sums out to $\approx (14/N)$ cm$^{-1}$, which is a factor of 3 smaller than our experimental value (Sec. III A). The discrepancy may come from an incorrect estimate of either the droplet size (which is based on scaling laws) or the value of $\Delta C_6$. In conclusion, one can see that the various contributions to the redshift would be straightforward to calculate, from quantities that can in principle be obtained via accurate ab initio calculations. Such calculations are necessary if the cause of the surprising blueshift observed for TMSA and TBA is to be determined; at present too many factors (polarizability, dipole moment, molecular volume, and He density in the nearest solvation shells) are not known with sufficient precision.

B. Spectral broadening and solvent mediated vibrational relaxation

We chose the molecules studied in this experiment with the goal of studying the effect of the He superfluidity on the intramolecular vibrational relaxation. A few reasonable assumptions can be made: (1) That the observed mode has a strongly local character, virtually independent of the substituent. (2) That direct interaction between the CH stretch and the He does not significantly accelerate the relaxation.

(3) That a molecule with well separated modes, such as HCN, would exhibit the narrowest lines, whose width would be an accurate measure of solvent-induced effects. Condition (1) is certainly true for the acetylenic CH stretch, whose spectral parameters (harmonic frequency, anharmonicity) in the gas phase are largely independent of the molecule it belongs to. The intramolecular relaxation rate of the mode, which is the quantity we want to study, does of course depend on the molecule. Condition (2) is expected to hold because of the large mismatch between the high frequency of the CH stretch and the low frequency of the He modes. Further, the superfluid properties of the droplet preserve rotational coherence, which suggests that dephasing effects should be minimal for vibrations too. Condition (3) is based on the assumption that for a molecule with well separated modes, which does not exhibit intramolecular relaxation in the gas phase, very slow, if any, intramolecular relaxation would be induced by the helium, for the same reasons given at point (2).

With the R(0) line of HCN as a yardstick, one would interpret any extra width in the larger molecules as evidence of intramolecular vibrational relaxation. The latter would occur because the presence of the helium increases either the coupling to, or the density of, molecular states into which vibrational energy is relaxed. This analysis is, however, complicated by the fact that the R(0) line of HCN is clearly broadened by inhomogeneous mechanisms, whose effects need to be factored out. Inhomogeneous broadening was originally not expected, because of the superfluid state of the solvent, but several facts demonstrate that it is indeed present if not dominant: (1) We can saturate the HCN R(0) transition. If the line were homogeneously broadened, the saturation power would be at least 30 times larger than what we measured in Sec. III A. The model presented in Appendix A lets us estimate an homogeneous width of 17 MHz, compared with a total linewidth of almost 1 GHz. (2) In the large droplet limit, the line is clearly asymmetric and split into at least two transitions. In the fundamental transition, measured by the UNC group, the line is narrower by more than a factor of 2 and the two components of the transition are more clearly separated. (3) Inhomogeneous broadening of comparable magnitude has been observed for the purely rotational transitions of NCCCH in He droplets.

One of us has devised a quantitative model in which the confined motion of HCN inside a finite-size He droplet combines with the thermal spread of translational velocities to produce inhomogeneous broadening of rotational lines. The hydrodynamic part of this model appears to correctly predict the R(0) line shape, and shows that the two peaks arise from the splitting of the triply degenerate $J = 1$ state, as experimentally verified, but the linewidth is a factor of 6.5 narrower than the experimental measurement in the fundamental. Given our estimate of the homogeneous linewidth of the R(0) line in the overtone, most of the linewidth difference between the $\nu_1$ and the $2\nu_1$ transition must be due to increased inhomogeneous broadening. We note that the model of Ref. 17 does not deal with vibrationally excited molecules, but contains quantities (such as the $C_6$ HCN–He interaction coefficients) which do change upon vibrational
excitation. These changes would probably increase the amount of inhomogeneous broadening without modifying its functional form, thus giving a better agreement between theory and experiment.

We will proceed with the hypothesis that inhomogeneous broadening is roughly the same for all the molecules considered here. Also, we assume that the homogeneous linewidth of those molecules which in the gas phase exhibit either no IVR or statistical IVR, is not measurably affected by solvation in He. The first case (no IVR) has been justified above; the second (statistical IVR) is a restatement of the idea that direct interaction between the CH stretch and the solvent, and similarly for the acetylenic CH stretch in the same molecule.65

The line shape of molecules in an intermediate condition will instead be affected by solvation in He. For example, in the gas phase, the $2\nu_1$ transition of propyne is split into a few components, which are well separated because the couplings are of intermediate strength. Solation in He will increase the density of states and, as a consequence, the line profiles will fill in and the homogeneous part of the linewidth will increase.

Note that we are implicitly assuming that the couplings between the states are not greatly affected by the helium, particularly in the case of the (high energy) states participating in low-order resonances. Indeed, if the couplings did increase significantly upon solvation, we would expect homogeneous lines that are one or more orders of magnitude broader than what we observe here. For sake of comparison, the strongly coupled OH stretch of propynol has, already in the fundamental, an IVR lifetime in the gas phase of $\approx 62$ ps, i.e., an order of magnitude faster than that of the acetylenic CH stretch in the same molecule.65

We have taken saturation measurements for one molecule in each class, which allows us to estimate the corresponding homogeneous linewidth: for HCN we get 17 MHz which is close both to our experimental resolution and to the limit one obtains from the rotational lifetime of NCCCH in He.15 For TMSA we obtain $\approx 30$ MHz, consistent with the 50 MHz measured for the gas phase molecule. Finally, for propyne we get a lower limit of 100–200 MHz, which is to be compared with the value (26 MHz) obtained for the gas phase molecule from Fermi’s golden rule. The latter estimate uses the average coupling matrix element for $K = 1$ states ($1.8 \times 10^{-3}$ cm$^{-1}$) and the density of coupled states (42 cm$^{-1}$) experimentally determined in Ref. 26. Even if the above data are scarce and of limited accuracy, they are consistent with our initial hypothesis that solvation in He will not change the IVR rate, but will fill in the line profiles for molecules in the intermediate IVR regime.

Table VI shows the observed widths of the transitions. For HCN we list two widths, the observed FWHM of the line and the width of the “narrower” feature, assuming that the line is in fact the sum of two transitions. For NCCCH, we list the narrowest of the observed widths. By extrapolation from the molecules whose homogeneous linewidths we know, it can be seen that in all cases it is reasonable to assume a more or less constant inhomogeneous contribution in the 500–1000 MHz range. Given our present inability to quantitatively account for the inhomogeneous linewidth, even in the simplest case of HCN, we cannot make definitive statements about the changes in solvent-induced vibrational relaxation for this series of molecules. Still, the data are consistent with very modest solvent-induced vibrational relaxation and/or changes in the intramolecular IVR rates. We expect that the concepts used to treat IVR in the gas phase will prove to be transferable to vibrational dynamics inside liquid He, without strong modifications.

### C. Rotational constants

In this section we will not follow the practice, standard in rovibrational spectroscopy, of directly reporting the values of the molecular constants extracted from the measured spectra. Instead, in Table VII, we list the measured moments of inertia. We choose this approach because moments of inertia are additive quantities, hence it is physically meaningful to speak of the contribution of the solvent to the moment of inertia. Centrifugal distortion constants, where available, were reported in the preceding sections and will be qualitatively discussed here.

Some definitions: $I$ is the moment of inertia of the bare molecule, $\Delta I$ its change upon vibrational excitation; $I_{\text{eff}}$ and $\Delta I_{\text{eff}}$ are the corresponding quantities for the molecule solvated in He; $I_i = I_{\text{eff}} - I$ is the moment of inertia associated with the solvent, and $\Delta I_i = \Delta I_{\text{eff}} - \Delta I$ its change upon vibrational excitation. Unless otherwise indicated, the value of $I$ (and similarly $I_{\text{eff}}$) is the average of the ground and vibrationally excited states values, and has been obtained via the formula: $I \cdot B = 505.379.05$ MHz u Å$^2$. Entries have been arbitrarily truncated. Units are in u Å$^2$.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$I$</th>
<th>$\Delta I$</th>
<th>$I_{\text{eff}}$</th>
<th>$\Delta I_{\text{eff}}$</th>
<th>$I_i$</th>
<th>$\Delta I_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCN</td>
<td>11.49</td>
<td>0.166</td>
<td>14.35</td>
<td>0.688</td>
<td>2.86</td>
<td>0.522</td>
</tr>
<tr>
<td>DCCH</td>
<td>17.11</td>
<td>0.227</td>
<td>19.56$^a$</td>
<td>2.45$^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NCCCH</td>
<td>111.10</td>
<td>0.345</td>
<td>325.63</td>
<td>9.232</td>
<td>214.54</td>
<td>8.886</td>
</tr>
<tr>
<td>CH$_2$CCH</td>
<td>59.14</td>
<td>0.315</td>
<td>234.95</td>
<td>8.520</td>
<td>175.81</td>
<td>8.204</td>
</tr>
<tr>
<td>CF$_3$CCH</td>
<td>175.60</td>
<td>0.481</td>
<td>474.53</td>
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<td>298.93</td>
<td>11.104</td>
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<tr>
<td>CF$_3$CCH$^c$</td>
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<td>167.90</td>
<td>79.53</td>
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<td></td>
</tr>
<tr>
<td>TBA</td>
<td>188.35</td>
<td>0.404</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>TMSA</td>
<td>257.56</td>
<td>0.445</td>
<td>1172.57</td>
<td>$-2.721$</td>
<td>915.01</td>
<td>$-3.166$</td>
</tr>
</tbody>
</table>

$^a$Calculated as $I + I_i$.
$^b$Assumed to be the same as for HCCH (Ref. 53).
$^c$Rotation around B axis.
$^d$Rotation around A axis.
having (depending on the point of view) either as a liquid hindering the motion of the solute molecule, or as a solid rotating with it. In both cases it causes an increase of the moment of inertia. It has been established that the very lightest rotors have only a small increase (up to 25%) in moment of inertia upon solvation in $^4$He, both because they tend to have weakly anisotropic interactions, and because their rotation is fast (i.e., because the helium cannot adiabatically follow the rotational motion$^{51}$). For heavier (i.e., slower) and more anisotropic molecules, the helium density is believed to adiabatically follow the rotation of the solute molecules, and the increase is substantial (200–300%). We have recently solved the hydrodynamic equations for superfluid $^4$He surrounding a rotating solute molecule, from which we obtained a hydrodynamic contribution to the moments of inertia.$^9$ The agreement with experiment is excellent for all the heavy molecules that could be analyzed (likely within the accuracy limits of density functional theory in estimating the true He density profiles). HCN and DCCH are intermediate between fully decoupled and fully coupled molecule-superfluid motion, and for them the hydrodynamic model predicts values of $I_s$ larger than those measured experimentally.

Rotation of trifluoropropyne around its symmetry axis is an interesting case of mixed behavior, because the relatively low value of the gas phase $A$ constant (which makes trifluoropropyne a slow rotor) is associated to a low anisotropy. The balance of these two facts is reflected in an increase of the corresponding moment of inertia (90%), which is intermediate between the two classes into which all other molecules fall.

With the exception of TMSA, the value of $\Delta I_s$ is, when available, always positive, and larger than the corresponding gas-phase quantity, $\Delta I$. Vibrational excitation causes a slight distortion of the solute molecule (which increases the volume of liquid displaced) and a slight increase of the He-solute interaction (which results in a higher density of the first solvation layer). Both of these effects cause $\Delta I_s$ to increase, the second effect being in all likelihood larger than the first. The small negative $\Delta I_s$ observed for TMSA is difficult to rationalize. Notice however that TMSA, and TBA (for which $\Delta I_s$ could not be measured), are the only molecules exhibiting blueshifts upon solvation in He; a blueshift and a negative $\Delta I_s$ are both consistent with a decreased molecule–He interaction in the vibrationally excited state. Also notice that this decrease in interaction only needs to occur locally, in a region where the density of the solvation shell is high, such as (likely) the “bay” between the methyl groups and the CC triple bond. As for many quantities measured in this work, very accurate (but feasible) calculations would be needed to confirm this picture. Finally, the particularly large value of $\Delta I_s$ for HCN has to be interpreted as an amplification effect due to the fact that coupling between the He and fast rotor improves as the rotor slows down.$^9,50$

The last molecular constant to consider is the centrifugal distortion constant $D_J$ whose value in He is a few MHz for all our molecules. Such a dramatic increase (a factor of $\sim 10^4$) relative to the gas phase value was already observed for OCS and SF$_6$. In a recent paper on the OCS spectrum, Grebenev et al. attempted to estimate this constant, considering the weak binding of He to the OCS molecule, and obtained a result $\sim 30$ times smaller than the observed value. Notice that even the sign of the $D_J$ value is surprising. As discussed above, it is expected that as a molecule rotates faster, the He will have greater difficulty to “follow” the rotational motion; as a result the hydrodynamic inertia will decrease, which expressed in terms of a rotational Hamiltonian corresponds to a negative $D_J$ value. Further, it should be noted that faster rotational motion reduces the solvation energy, as the helium effectively interacts with a “rotationally averaged molecule.” Based upon these considerations, it appears inevitable that the large positive $D_J$ values obtained from the fit will only describe the low rotational quantum number levels of the spectrum; we can anticipate that at some $J$ value, the energy level spacing will begin to increase faster than what predicted by a rigid rotor formula. In particular, this must happen before we get to a $J$ value such that $BJ(J+1)-D_J2(J+1)^2<0$, otherwise levels with higher $J$ would be energetically favored. Unfortunately, it appears that the low temperature of liquid He droplets results in negligible rotational population for levels where this “uncoupling” of molecular rotation and hydrodynamic motion will occur.

V. SUMMARY

Rotationally resolved spectra of the acetylenic CH stretch in the first overtone have been measured for the following molecules embedded in a superfluid He droplet: HCN, DCCH, NCCCH, CH$_3$CCH, CF$_2$CCH, (CH$_3$)$_2$CCCH, and (CH$_3$)$_3$SiCCCH. Several spectroscopic parameters have been extracted from the spectra, including the band shifts upon solvation, the effective rotational constants, and the homogeneous and inhomogeneous linewidths. The latter two quantities have been discussed in the attempt to determine the influence of the superfluid He environment on intramolecular vibrational relaxation (IVR). Although more data are needed to draw a definite conclusion, our results indicate that a strong, inhomogeneous broadening is always present, and is in fact almost constant across our series of molecules. If the homogeneous linewidth is taken as a measure of the IVR rate, our data indicate that the latter undergoes, upon solvation, at most a modest increase. Finally, we have tried to quantitatively account for most of the observables we measured, and we have shown that in most cases accurate models are available for this purpose. These models are in general computationally demanding (more so for those quantities which result from small variations, or near cancellation, of larger quantities), but likely within the current capabilities of molecular modeling; it is our hope that the results presented here stimulate further activity in this direction.

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APPENDIX: SATURATION MODEL

We describe here the model used to predict the saturation behavior of an inhomogeneously broadened line given our experimental geometry. The model was used to fit the saturation data of the R(0) line of HCN (Sec. III A) and the Q branch of propyne (Sec. III D) and TMSA (Sec. III F). Since we want to know the absolute magnitude of the saturation power, we need estimates of the laser power circulating inside the buildup cavity, and of the strength of the transition been observed.

The first estimate is made by measuring the laser power immediately before the interface with the vacuum chamber; this value is then rescaled by our typical coupling losses ($\times 0.65$) and gain inside the cavity ($\times 400$).

For the second estimate we assume the following.

1. That the $2\nu_1$ band strength of HCN in the droplet is the same as that measured in the gas phase ($S = 1.4 \times 10^{-19}$ cm). This same value has been used for propyne and TMSA; to account for the fact that the Q branch actually consists of multiple lines, an average transition strength has been used, where single lines are weighed by the appropriate population and Hönzl–London factors. For both molecules the average Q branch transition strength turns out to be $\approx 1/3$ of the HCN R(0) line strength.

2. That doped droplets can absorb at most one IR photon during the transit time through the spot of the laser beam ($T_I = 0.7$ μs).

3. That the inhomogeneous broadening in the spectrum is static on that timescale of transit through the laser spot so that the same subset of molecules is pumped the entire time.

Numerical simulation of inhomogeneous saturation behavior under these assumptions leads to the following relationship between homogeneous width ($\Delta \nu$) and saturation power ($P_s$):

$$\Delta \nu = \frac{1.7SP_s}{\sqrt{2\hbar\nu\pi v}\alpha_0} c,$$

where $\hbar\nu$ is the energy of the transition, $S$ is the band strength, $v$ the droplet velocity, $\alpha_0$ is the waist (radius) of the laser beam inside the buildup cavity, and $c$ is the speed of light. The saturation power is obtained from a fit of the line intensity $I(P)$ versus circulating power $P$, according to the equation

$$I(P) = \frac{aP}{\sqrt{1 + P/P_s}}.$$

where $a$ and $P_s$ are the fit parameters. The parameters for the HCN R(0) line are $\hbar\nu = 6521$ cm$^{-1}$, $P_s = 2$ W (from fit), $v = 500$ m/s (beam velocity at 23 K), and $\alpha_0 = 172$ μm.$^{36}$ The weakest assumption in this model is likely that the inhomogeneous shifts are static. Our microwave double resonance measurements in NCCCH have indicated that the $T_I$ time for microwave absorption is $\approx 10$ ns.$^{15}$ In our model, if we reduce $T_I$, we will have to decrease the homogeneous width by the same factor, so the above estimate is likely to be only an upper bound.


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64 Assuming that the redshift and blueshift scale approximately at the same rate (specifically, linearly) with vibrational quantum number, this almost exact cancellation should occur independent of vibrational quantum number. Linear scaling of the redshift is justified by the fact that former is proportional to quantities that in the lowest order approximation scale linearly with v (Sec. IV A). Linear scaling of the blueshift can be tested by adding a suitable repulsive term to the CH stretch potential and solving the appropriate Schrödinger equation by brute force. We did it by placing an infinitely massive He atom at the equilibrium position of the HeHCN complex, and found a blueshift of 1.5 cm⁻¹ (v = 1) and 3.7 cm⁻¹ (v = 2). Empirical evidence that the redshift and blueshift must scale at the same rate also comes from experiments on analogous systems. Extensive data H.-C. Chang and W. Klemperer, J. Chem. Phys. 98, 2497 (1993); C.-C. Chuang et al., J. Chem. Phys. 109, 484 (1998) exists on the van der Waals complexes ArₜHF (n = 1–3, v = 1–3), which show that, at a given n, the total shift of the HF stretch frequency scales linearly with v.


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