Microwave spectra of HCN and DCN in $^4$He nanodroplets: A test of adiabatic following

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The purely rotational microwave spectrum of HCN and DCN embedded in $^4$He nanodroplets has been measured. The $J=0\rightarrow1$ transitions for both molecules have been recorded at 72.21 and 59.90 GHz, respectively. The increase in moment of inertia due to the presence of liquid helium, which the assumption of adiabatic following of the helium density predicts should be almost identical for both molecules, is found to be 9% smaller for the faster of the two rotors, HCN. This result is interpreted as a breakdown of the adiabatic following approximation, which is valid for the slower rotors. Power-saturation measurements have also been performed, and show that the rotational relaxation time for these molecules is on the order of $10^{-8}$ s.

Helium nanodroplet isolation spectroscopy (HENDI) provides a way to study the finite-size properties of this unique quantum liquid, as well as a way to form and study novel metastable chemical species. An unusual feature of rovibrational spectra in this condensed medium is the extremely slow rate of rotational dephasing, which allows heavy and/or highly anisotropic molecules, such as OCS, SF$_6$, HCCCN, and (HCN)$_2$, to display resolved rovibrational transitions with the same spectral structure as dictated by the symmetry of the isolated molecule. Such rotationally resolved spectra have allowed the determination of the rotational temperature of the solute [0.38 K (Ref. 5)], which is found to be largely independent of cluster size and is in agreement with previous predictions of the droplet temperature based on evaporative cooling. The moments of inertia of a molecule that rotates in liquid $^4$He have been found, however, to be larger, up to a factor of 5, than those of the isolated molecule.

The ability to reliably calculate the rotational constants of molecules solvated in liquid helium would provide insight into the interactions between the molecule and the quantum liquid that surrounds it, and into the dynamics of atomic motion in the latter. Furthermore, such a theory would improve our ability to use rotationally resolved HENDI data to obtain structural information. At present, two models have been put forward to explain the observed increase in the moment of inertia. The first is based on the idea that a fraction of the atoms in the first He solvation shell is subtracted from the superfluid and rotates rigidly with the molecule, leading to an increased moment of inertia. With judicious choice of the “normal fluid” fraction, this model has been able to explain the observed increase in the moment of inertia of SF$_6$ and OCS. The rather ad hoc nature of this definition of “normal fluid” density has recently been addressed by Kwon and Whaley who have proposed a computational definition of a spatially dependent “normal fluid” density which is evaluated by finite temperature Path Integral Monte Carlo (PIMC) calculations. These authors have reported that they can predict the rotational constant of SF$_6$ to within the experimentally determined accuracy of $\approx 1\%$.

The second model is based on the notion that rotation of a rigid body in superfluid helium produces fluid displacement, which leads to an increased inertia. Such a hydrodynamic contribution to the effective moment of inertia of a molecule solvated in an ideal liquid of uniform density (equal to that of bulk liquid He) had been considered earlier but had been found to be a minor fraction of the experimental value. Recently, however, we have performed hydrodynamic calculations that properly account for the anisotropy of the He density around the solute molecule. Accordingly, the increase in the rotational inertia has been found to be sufficient for the quantitative prediction of the observed effective moments of inertia for several molecules. An important assumption of the hydrodynamic model is that while the helium flow remains irrotational, the fluid’s density adiabatically follows, much like a wave, the rotation of the molecule. Thus both existing models include adiabatic following of the molecular rotation by the surrounding helium, although under two quite distinct forms.

Recent fixed-frame, fixed-node, diffusion Monte Carlo calculations for SF$_6$ in small He clusters have reproduced the experimental rotational spectrum of this molecule in He droplets. Further, it was found that when the static rotational constant of the free SF$_6$ molecule was artificially increased by a factor of 10, greatly increasing the rotational speed, the modulation of the helium density in the rotating molecular frame as well as the corresponding solvation-induced increase in the moment of inertia were substantially reduced. This indicates that the helium density does not perfectly follow the molecular rotation, at least for lighter rotors. Experimentally, it has been found that rotors with large rotational constants (i.e., fast rotational speeds), such as H$_2$O and NH$_3$, experience, at most, a modest increase of their moments of inertia upon solvation in He. However, the

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interaction potential of such molecules with He is also more isotropic than for molecules such as SF₅ and OCS, which, independently, leads to smaller solvation-induced changes in the moment of inertia. Therefore, from these observations alone, it is not possible to assess quantitatively any deviation from the adiabatic following hypothesis.

To address this problem, we present, in this communication, the measurement of the $J=0\rightarrow1$ pure rotational transition in both HCN and DCN by use of microwave (MW) spectroscopy. The magnitude of the solvent-induced increase in moment of inertia for the two molecules (which, to a very good approximation, experience the same interaction with He) is, under perfect adiabatic following conditions, expected to be almost identical. Any difference, yielding a smaller increase for the faster of the two rotors, could be attributed to a breakdown of the adiabatic following approximation. As the isotope substitution has also the effect of shifting the center of rotation for the two molecules, a hydrodynamic correction is also present, which is however much smaller than, and opposite in sign to, the changes measured here (see below).

The experiment was carried out with the same beam spectrometer used in the previous study of HCCCN in He nanodroplets. The principal difference was the microwave frequency band in which this experiment was carried out, hence the use of a different microwave source and hardware.

A beam of helium droplets is produced by supersonic expansion, into a vacuum chamber, of high pressure (800 psi = 5 MPa) He gas (99.9999% purity) from a cooled nozzle (10 μm diam). The average droplet size is controlled by setting the nozzle temperature (in the range 19–32 K, actively stabilized within 0.1 K) and is calculated via known scaling laws. The center portion of the beam is admitted into a second vacuum chamber through a 500 μm diam skimmer, and passed through a 2.5 cm long pick-up cell containing the gas of interest. The pressure in the cell (typically $7 \times 10^{-5}$ Torr $\approx 10^{-2}$ Pa) is adjusted to maximize the amount of singly-doped droplets, as monitored by their spectroscopic signal. Further downstream, the droplets pass through a 10 cm long Q-band waveguide (nominal range 33–50 GHz) which is aligned parallel to the cluster beam. Although a V-band (nominal range 50–75 GHz) would have been more appropriate for optimum propagation of the microwave radiation, this lower frequency waveguide was chosen because of its larger dimensions ($5.7 \times 2.8$ mm²) to minimize alignment problems. Microwave radiation is coupled in and out of the waveguide through two E-bends located at each end of the latter; a microwave dump (VSWR $= 1.03:1$) at the exit end minimizes reflections back into the waveguide, thus preventing occurrence of an unwanted standing wave pattern. The droplet beam enters and exits the waveguide through two 2.8 mm diam holes in the E-bends.

Multiple successive resonant photon absorption and energy relaxation by the rotor in the droplet “bath,” leads to evaporation of He from the droplet. This is detected as a beam depletion signal by a liquid-helium-cooled silicon bolometer. The microwave radiation is produced by a synthesized sweeper (HP 83752B, 0.01–20 GHz) and a frequency quadrupler (mm-wave source module HP 83557A, 50–75 GHz). The MW synthesizer is amplitude modulated at ~310 Hz for lock-in detection. All critical parameters (MW frequency, power, modulation frequency and amplitude) are internally controlled by the MW synthesizer to specifications exceeding the requirements of the present experiment.

Figure 1 shows the MW spectra measured for HCN and DCN. These molecules have sufficiently large rotational constants that only the $J=0$ rotational state is significantly populated at the temperature of the droplets (0.38 K), thus the observed line is assigned to the R(0) transition. For both spectra, +9.3 dBm ($\approx 8.5$ mW) of microwave radiation have been used. This value corresponds to the highest available power that remained leveled through the entire spectrum, and has been chosen in order to maximize the signal amplitude; the corresponding intensity at the center of the waveguide is $107$ mW/cm². Saturation measurements (see Fig. 2) were performed to ensure that the spectra were not power broadened. The data show that at this power level both transitions are fully saturated. No position- or line-shape-dependence has however been observed when using lower MW power, down to $+3.0$ dBm ($\approx 2$ mW), thus confirming that the observed line broadening is mostly inhomogeneous, and that power broadening is not significant, even at the highest power used.

From the saturation data of Fig. 2, under some simplify-
We then fit the data in Fig. 2 to the intensity at zero detuning depending on the functional form chosen, as long as the latter above assumptions, the value of $T_2$ is supposed to be the convolution of a that at the center of the waveguide. The observed line is are irradiated with the same intensity, which we take to be $~$. cyanoacetylene.\textsuperscript{16} comparable to those previously measured for DCN. More likely, $T_2$ is 12 ns for HCN and $~$ ns for DCN. These values are of comparable magnitude, $T_1$ and $T_2$ are of comparable magnitude, i.e., $\approx 12$ ns for HCN and $\approx 17$ ns for DCN. These values are comparable to those previously measured for cyanoacetylene.\textsuperscript{16} The solid lines are the fitting curves associated with the parameters of Table I.

\begin{table}[h]
\centering
\caption{Best fit parameters for the line shapes of Fig. 1 and the saturation data of Fig. 2.}
\begin{tabular}{lllll}
\hline
 & $v_0$ (GHz) & $w_-$ (GHz) & $w_+$ (GHz) & $I_s$ (mW/cm$^2$) & $T_1T_2$ (ns) \\
\hline
HCN & 72.17 & 0.45 & 0.25 & 30 & 150 \\
DCN & 59.90 & 0.098 & 0.075 & 14 & 300 \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{Moments of inertia of HCN and DCN as free molecules ($I_m$) or solvated in $^4$He ($I_{eff}$). Their difference is to be compared to the increase ($I_s$) in moment of inertia predicted by the superfluid hydrodynamic model (Ref. 9) in the assumption of perfect adiabatic following. The small variation in $I_m$ for the two isotopomers is due to the different position of their centers-of-mass (see text). Units are $\mu\text{A}^2$.}
\begin{tabular}{lllll}
\hline
 & $I_m$ & $I_{eff}$ & $I_{eff} - I_m$ & $I_s$ \\
\hline
HCN & 11.39 & 14.00 & 2.61 & 5.7 \\
DCN & 14.00 & 16.87 & 2.87 & 5.6 \\
\hline
\end{tabular}
\end{table}

If higher order terms (the leading one being centrifugal distortion) are ignored, the rotational constants are simply one half of the R(0) transition frequency. The value of the resonance frequency constants cannot be exactly defined from the experimental spectra, since one could arbitrarily use the position of the maximum or that of the center of mass. We decided to use the former quantity (see Fig. 1), and to use the difference between the two as an estimate of the uncertainty. For HCN the maximum at 72.21 GHz is used; the center of mass is calculated to be at 72.02 GHz. For DCN the maximum is located at 59.90 GHz and the center of mass (with the calculation restricted to the 58.6–60.7 GHz range) is found to be at 59.86 GHz. With these values, rotational constants of 36.11(10) and 29.95(2) GHz are determined for HCN and DCN, respectively.

The rotational constant for the $\nu(CH)=1$ vibrational state of HCN in He nanodroplets was previously determined, using Stark spectroscopy, to be 1.175 cm$^{-1}$ (35.23 GHz) by Nauta and Miller.\textsuperscript{19} Ours is the first determination of the rotational constant of HCN in its ground state. One can see that vibrational effects are small but not negligible ($\Delta B = 0.88$ GHz). In Table II we report the observed moments of inertia for both HCN and DCN, in gas phase and in $^4$He droplets and their difference. Also given in Table II is the increase in moment of inertia predicted by the superfluid hydrodynamic model\textsuperscript{9} if perfect adiabatic following is assumed. The predicted increase is negligibly smaller for DCN than for HCN because in the latter molecule, the center of mass and the geometric center are closer together, hence in a sense DCN is, dynamically, slightly more spherical. This effect is, however, small and more importantly, its contribution is opposite in sign to the experimentally observed trend in which the increase in moment of inertia induced by the liquid is 9% smaller for HCN than DCN.

We interpret the present results as unequivocal experimental evidence for the breakdown of the adiabatic following models (regardless of whether the “normal fluid fraction” or “pure superfluid” picture applies) in fast rotors. A 23% increase of the rotational speed (comparing gas phase HCN to gas phase DCN) results in a 9% decrease in the solvent-induced component of the moment of inertia. In order to evaluate the qualitative significance of the present results, we need a theory able to quantify the degree of adiabatic following as a function of the rotational period of the rotor. Diffusion Monte Carlo calculations could likely provide this information in the near future, considering the promising results already obtained for SF$_6$ (Ref. 13) and the...
availability in the literature of an excellent He–HCN inter-
action potential.20

In closing, we would like to point out that qualitatively dif-
ferent lineshapes have been observed for the HCN and
DCN transitions. The HCN R(0) line is similar to that previ-
ously observed for the R(0) transition of the 2ν(CH) over-
tone in the same molecule,10 while the DCN transition looks
more similar to that reported for the R(0) transition of the
ν(CH) fundamental in HCN.19 A thorough analysis of two
sources of line broadening in He nanodroplet spectroscopy
was recently published,12 in which the J = 0 → 1 transition
was simulated. The predicted HCN R(0) line shape was too
narrow, unless the effect of one source of broadening (a hy-
drodynamic coupling of translation and rotation) was made
≈ 6 times larger than the a priori estimate.10 The shape of
the DCN R(0) line measured here is instead in good agree-
ment with the predictions of Ref. 12, with no need to scale
the interaction parameters. However, the model of Ref. 12
does not contain any physical mechanism by which the re-
markable difference between the two isotopomers can be jus-
tified. The qualitative difference between the line shapes ob-
served here was unexpected and is as yet unexplained.

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18 The formula used (in MKS units) is: T1/T2 = (1/2)εℏ/kε[(1/3)μ2I1],
where μ is the electrical dipole moment of the molecule, and I1 is the
saturation intensity [see, e.g., A. Yariv, Quantum Electronics
(Wiley, New York, 1975), Chap. 8].