

From Intermolecular Forces to Condensed Phase Spectroscopy: Ro-vibrational Spectroscopy Inside Superfluid Nanodroplets.

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I. INTRODUCTION

Nanometer scale helium droplets [1–3] provide a unique solvent in which to perform molecular spectroscopy and are likely to become widely used by the molecular spectroscopic community in the coming years. Currently, this new technique is in its early stage of development and is being practiced in only a few laboratories, but the early results firmly support our view that this type of spectroscopy combines many of the most attractive features of more traditional molecular beam and matrix isolation spectroscopies. In particular, unstable and sometime exotic molecules can be synthesized in the condensed fluid nano-matrices without giving up the possibility of obtaining rotational resolution and therefore, of obtaining direct structural information [4]. A review describing the early results has been published [5].

Large He clusters, $N \approx 10^2 - 10^6$ are formed upon the expansion of low temperature gas ($\approx 15 - 25$ K) or liquid He through a $5 - 20 \mu\text{m}$ nozzle into a vacuum. Such clusters cool by evaporation, reaching temperatures of 0.4 K for ^4He and 0.15 K for ^3He [6]. Uniquely, they remain liquid as He will not freeze even at zero K, except above 25 atm. In order to emphasize the liquid nature of these clusters, and also their characteristic size, they are referred to as nanodroplets. The ^4He nanodroplets are believed to be superfluid [7], while the colder and less dense ^3He clusters are believed to be well above their superfluid transition temperature.

As for their heavier noble gas counterparts, helium nanodroplets can be doped with one or more atoms or molecules using the pick-up technique [8] in which a beam of droplets passes undeflected through a scattering chamber containing a small pressure (≈ 0.1 mtorr) of the dopant species. Spectroscopic study of doped He nanodroplets began with the work of Goyal *et al.* [9], where line tunable CO_2 lasers were used to probe the spectra of SF_6 and its dimer. This work demonstrated that the SF_6 spectrum in He clusters was qualitatively different from that observed in other inert gas nanoclusters [10] in that the lines were much narrower and the matrix-induced shift smaller. However, the line tunable lasers did not provide enough spectral coverage to rotationally resolve the spec-

trum. This was achieved at the Max Planck Institute in Göttingen using a tunable diode laser counter propagating with the droplet beam, which allowed for a continuous scan of the spectrum at high resolution [11]. In that investigation it was discovered that the spectrum had the characteristic ro-vibrational structure of a gas phase spherical top molecule, including the first order Coriolis splitting [12]. This work provided the first measurement of the cluster temperature, which was found in excellent agreement with that predicted by both classical [6] and quantum [13] evaporation models. Ro-vibrational spectra of a range of other molecules that have now been studied has confirmed that ^4He nanodroplets have a temperature of 0.38 K essentially independent of the dopant, but somewhat dependent upon cluster size. The SF_6 spectrum of ref. [11] also showed that the effective rotational constant measured in ^4He droplets is $1/3$ of the gas phase value, while the centrifugal distortion constant is four orders of magnitude larger than that of the isolated dopant. These trends have been confirmed by the recent experiments in Göttingen, Chapel Hill, and our own laboratory were the rotationally resolved spectra for several other molecules have been obtained [14–16]

Many of the spectroscopic experiments performed to date on doped He nanodroplets have focused on electronic spectroscopy. This is largely due to the fact that the highly sensitive method of laser induced fluorescence could be used to detect absorption and possible subsequent dynamics. We mention in particular only the work of our laboratory on alkali doped droplets, where spectra of Li, Na, and K atoms, dimers and trimers have been extensively studied, including the Jahn-Teller coupling and time resolved photochemistry of the quartet state of Na_3 , which had never previously been observed [17–19]. One problem with electronic excitation, however, is that the transition-induced changes in He solvation can result in most of the intensity being found in the ‘phonon side band’, though ‘zero phonon lines’ have been observed in several systems. This makes it difficult to extract unambiguous rotational information in such experiments, particularly since the low energy excitation region of the spectra, in the neighborhood of the zero phonon line, is not yet understood [17,18]. For transitions that substantially change the size of the electronic cloud of the atom or molecule, very broad structures are observed and have been explained by the ‘bubble’ model originally developed to treat electrons solvated in bulk liquid He [5]. In contrast, vibrational transitions induce only small changes in the solvation of He around the dopant, and as a result, infrared spectra have almost all their intensity in the ‘zero phonon’ line, where no direct optical excitation of the internal degrees of the He droplet occurs. In fact, to date no ‘phonon side band’ has been observed in the IR.

IR spectra are normally observed by the method of beam depletion.

In the time between IR absorption and detection of the droplet beam (typically $\approx 100\mu\text{s}$), vibrational relaxation of the dopant leads to He evaporation. Each departing He reduces the internal energy of the droplet by $\approx 5\text{ cm}^{-1}$, so near-IR excitation reduces the size of the droplets by about one thousand atoms. This photoinduced beam depletion has been detected either optothermally with a bolometer [20] or by reduction in the electron impact ionization yield combined with detection of all ions above a certain mass threshold [11].

II. ROTATIONAL AND RO-VIBRATIONAL SPECTRA IN HE NANODROPLETS: RECENT PRINCETON CONTRIBUTIONS

We have recently constructed an optothermal spectrometer, which is described elsewhere [16], to study the rotational and ro-vibrational spectra of molecules seeded in helium nanodroplets. While our goal is to use this technique to synthesize and characterize new free radicals and other unstable species, we began by studying the first acetylenic C-H overtone spectra of a series of terminal acetylene compounds. This affords us the possibility of addressing the problems of understanding the changes in moment of inertia induced by solvation as well as reliably predicting spectral shifts and lineshapes in this unusual and highly quantum environment. We hope to be able to use the helium-solute and helium-helium pair potentials to predict ‘condensed phase’ behavior of molecules dissolved in liquid helium. Furthermore we had previously used eigenstate resolved molecular beam spectroscopy to determine the rates of IVR of these and similar molecules [21] and we wanted to determine if solvation in liquid He would substantially change this rate.

The first molecule we studied was HCN, since at this energy it is not expected to have IVR and likely has slow vibrational relaxation even in He (due to its low density of vibrational states). Thus, this molecule provides a ‘baseline’ for the spectral width induced by interaction with the He. Due the low temperature and large rotational constants of HCN, only an R(0) line could be detected. The line proved to be asymmetric with a width of $\approx 850\text{ MHz}$, suggesting the presence of two lines. Power dependent studies showed that the line could be saturated and allowed an estimate of the homogeneous width of $\sim 10\text{ MHz}$ to be made, showing that most of the linewidth is due to inhomogeneous effects. Nauta and Miller have studied the fundamental CH stretching spectrum of this molecule and found a much narrow but also asymmetric line shape [22]. This implies that the inclusion of the vibrational dependence of the interaction between HCN and He will be required to explain these results.

FIG. 1. $2\nu_1$ band (C-H stretch first overtone) of CH_3CCH embedded in a ^4He droplet. Due to the large distortion constant, the R(3), R(4), and R(5) lines form a band head.

Other molecules studied in our laboratory include HCCD , HCCCN , CH_3CCH , CF_3CCH , $(\text{CH}_3)_3\text{CCCH}$, and $(\text{CH}_3)_3\text{SiCCH}$. Figure 1 shows the spectrum of CH_3CCH with its resolved P, Q, and R branches. Table I contains the list of shifts in the vibrational origins and the observed full width of the spectroscopic lines. For some of the molecules, the line widths are J dependent and we give a range of widths. When the gas phase transition has an IVR limited linewidth, Table I also shows these FWHM values. While it is not possible from such data to unambiguously separate the effects of the He on the IVR rate from other sources of solvent induced dephasing, if we take the HCN linewidth as representative of other effects, we can conclude that the IVR rate is not qualitatively changed upon solvation in liquid He. One exception may be propyne, which in the gas phase is known to have at $\nu(\text{CH}) = 2$ a density of vibrational states almost sufficient to show isolated molecule IVR on the ~ 200 ps time scale [23]. The presence of the He solvent seems to push this molecule over this threshold, likely due to relaxed energy and angular momentum constraints in the condensed environment.

Work in other laboratories on very light rotors (HF [24], H_2O [25], and NH_3 [26]) indicate that the linewidths of these molecule are much broader than what we have found in the series of CH bearing molecules reported here. This may reflect the very rapid rotation of these molecules. We note that while Nauta and Miller have been able to detect the fundamental vibrational spectrum of HCCH , and we have detected the C-H overtone spectrum of HCCD , we have been unable to observe the overtone spectrum of HCCH . This is likely due to very rapid solvent induced vibrational relaxation, with $\nu_1 + \nu_3 \rightarrow 2\nu_1$ a reasonable candidate.

By irradiating the doped droplets with a tunable microwave field in a microwave waveguide, we have also observed pure rotational transitions of HCCCN [27]. To evaporate even a single He atom requires an individual cluster to absorb ~ 12 microwave photons. Based upon the relative strengths of the microwave and overtone signals, we estimate that many thousands of microwave photons are absorbed during the $\approx 100\mu\text{s}$ time of interaction with the microwave field. Based upon microwave double resonance experiments and experiments with a variable frequency of amplitude modulation, we have estimated a rotational relaxation time of $\sim 5 - 100$ ns. The microwave work also demonstrates that the lines are largely inhomogeneously broadened, but in a dynamic sense. We estimate that molecules change the quantum numbers responsible for the inhom-

geneous broadening at a rate one order of magnitude faster than the rate of rotational relaxation. Microwave-IR double resonance measurements, performed in collaboration with Roger Miller [28] have confirmed the dynamic nature of the broadening and have demonstrated an interesting size dependence to the nature of the state-to-state rotational relaxation.

The nature of the inhomogeneities that cause the broadening in the spectra is not clear at present. They are certainly not dominated by the droplet size distribution in our source. We presently believe that the most likely explanation is a coupling between the center of mass motion of the solute with its rotation. A thorough analysis of the motion of the impurity, assuming that the superfluid droplets provide no friction, has been recently given [29]. The long range interactions between the solute and the ‘missing He’ outside the cluster produces a potential that confines the solute to near the center of the droplet. Anisotropic long range forces and a hydrodynamic coupling of center of mass motion with orientation lead to an inhomogeneous line broadening which is too small (in the case of HCN) to reproduce the experimental results. It is hoped that by including the vibrational dependence of the He-HCN interaction and by providing a more realistic calculation to estimate the strength of the hydrodynamic coupling, the lineshape of HCN could be explained.

III. THE PROBLEM OF THE CHANGES IN ROTATIONAL CONSTANTS INDUCED BY THE HELIUM NANODROPLET

It appears to be generally true that molecules in liquid He have effective rotational constants, B , smaller than their gas phase values. Table II summarizes the situation for a range of molecules. Molecules with large rotational constants have only modest reduction in B , while heavier molecules have much larger fractional reductions. A theory based upon a ‘normal fluid’ density that rotates rigidly with the molecule has been proposed [7]. A microscopic definition of this ‘normal fluid’, based upon path integral Monte-Carlo calculations, has recently been proposed and found to reproduce the observed rotational constant for SF_6 [30]. We have recently [31] made calculations based upon a hydrodynamic model that, given the low temperature of the droplets, treats the He as 100% superfluid. This implies that the molecules do not ‘drag’ any He atoms around with them as they rotate since the He flow field must be ‘irrotational’. We further assume that the He density (which we calculate using Density Functional Theory [32]) adiabatically follows the rotation of the molecule. To date, we have only been able to treat cases where the He-solute interaction is (or can be approximated as) cylindrically symmetric, as this reduces the numerical solution required to two dimensions. From

the above stated assumptions, we are able to derive a partial second order differential equation for the ‘velocity potential’ that determines the He flow field from which we extract the hydrodynamic moment of inertia I_H . Table III contains a comparison of the calculated hydrodynamic moment of inertia with the incremental moment ($\Delta I = I_{\text{cluster}} - I_{\text{gas phase}}$) calculated from the comparison of the observed rotational constants in the gas phase with those in the He droplets. Except for the lightest rotors, the agreement is excellent, especially considering the uncertainties in the density of the He solvation structure around the molecules. For the very lightest rotors, it may well be that the assumption of ‘adiabatic following’ is breaking down [33].

In summary, the field of helium droplet isolation spectroscopy has evolved very rapidly from esoteric experimentation to a useful technique in chemical dynamics. Novel unstable species are being prepared and the behavior of the guest molecules in this cold but frictionless medium is starting to be understood. We can confidently look forward to several years full of exciting further developments.

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	band shift (cm^{-1})	line width (MHz)	
		cluster	gas phase
HCN	-0.60	850	
HCCD	-0.01	820	
HCCCN	-0.213	1000–1800	
CH ₃ CCH	-0.26	1300	
CF ₃ CCH	-0.41	1500	80
(CH ₃) ₃ CCCH	1.135	2500	1300–1500
(CH ₃) ₃ SiCCH	0.845	370	75–100

TABLE I. $2\nu_1$ band shifts and (range of) rotational line widths for the molecules studied in this work.

	B_{cluster} (cm^{-1})	$\frac{B_{\text{gas phase}}}{B_{\text{cluster}}}$	ref.
SF ₆	0.0326	2.8	[11]
(SF ₆) ₂	0.0044	1.9	[34]
OCS	0.0744	2.7	[7]
NH ₃	7.4	1.3	[26]
H ₂ O	27.9,14.5,9.3	1	[25]
HF	20.56	1	[24]
HCN	1.203	1.23	this work and [35]
HCCH	1.05	1.13	[35]
HCCCN	0.051	3.0	this work and [35]
CH ₃ CCH	0.072	3.9	this work and [35]
CF ₃ CCH	0.035	2.75	this work
(CH ₃) ₃ CCCH	0.03	3.0	this work
(CH ₃) ₃ SiCCH	0.0145	4.5	this work
(HCN) ₂	0.019	3.0	[36]

TABLE II. Measured rotational constants of molecules in ⁴He droplets.

	$I_{\text{gas phase}}$	I_{cluster}	ref.	ΔI	I_{H} (calc.)
HCN	11.39	14.0	this work and [35]	2.6	5.4
HCCH	14.26	16.1	[35]	1.8	6.6
OCS	83.10	230	[7]	147	184
HCCCN	111.1	331	this work and [35]	220	261
HCCCH ₃	59.14	224	this work and [35]	165	169
(HCN) ₂	289.5	872.5	[36]	583	550

TABLE III. Moments of inertia for the molecules studied in this work. Units are $\text{u}\cdot\text{\AA}^2$; experimental values are computed from the spectroscopically measured rotational constants, via the conversion factor $505.38 \text{ GHz}\cdot\text{u}\cdot\text{\AA}^2$.

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