Single and Double Resonance Microwave Spectroscopy in Superfluid ^{4}He Clusters

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Purely rotational transitions of a molecule embedded in large ^{4}He clusters have been detected for the first time. The saturation behavior shows that, in contrast to previous expectations, the microwave line profiles are dominated by inhomogeneous broadening mechanisms. Spectral holes and peaks produced by microwave-microwave double resonance have widths comparable to those of single resonance lines, indicating that relaxation occurs among quantum states of the inhomogeneous distribution of each rotational level, at a rate $\approx$10 times faster than rotationally inelastic relaxation. [S0031-9007(99)09422-3]

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The spectroscopy of molecules embedded in large ^{4}He clusters has recently received considerable experimental and theoretical attention [1,2]. Nanometer scale helium clusters (nanodroplets), containing from several hundreds to more than 10^4 He atoms, provide a unique environment for high resolution matrix spectroscopy where the advantages of both conventional matrix spectroscopy and molecular beam spectroscopy are combined [3]. Since these clusters will pick up molecules or atoms that they encounter on their path without being appreciably deflected [4], they allow for a high degree of synthetic flexibility, and, in particular, for the formation and stabilization of weakly bound and unstable species [5–9]. Evaporative cooling has been found to maintain ^{4}He nanodroplets at a temperature of 0.4 K [10,11], well below the predicted superfluid transition temperature which ranges from 2.14 K in bulk liquid helium to 1.5 K for clusters of only 10^2 He atoms [12]. As the perturbations imposed on the guest molecules by the helium host are minimal, the shift and width of spectroscopic lines in ^{4}He clusters are considerably less than for traditional matrix environments [1]. Furthermore, rotationally resolved spectra have been observed for a large variety of molecules [11,13–18] which show the structure predicted by the gas phase symmetry of the molecules with, however, reduced rotational constants. By showing that rovibrational spectra in ^{3}He clusters collapse into a single line, the weakly damped molecular free rotation present in liquid ^{4}He has recently been demonstrated to be a direct consequence of the boson nature of ^{4}He and is considered a microscopic manifestation of superfluidity [16].

An important unresolved question posed by the ir spectra relates to the physical process responsible for the line broadening observed in rovibrational transitions, which ranges from 150 MHz in the case of the R(0) line in the ν_3 fundamental in OCS [17] to 5.7 cm^{-1} for the case of the P(1) line in the ν_3 asymmetric stretch in H_2O [18]. For the carefully studied case of the ν_3 fundamental of SF_6 [11], the lines were found to have a Lorentzian shape of width $\approx$300 MHz independent of the rotational transition, which led to the suggestion that the linewidth reflected vibrational relaxation and/or dephasing [17].

Since He clusters remain fluid down to zero temperature and because of the very large zero point motion of the ^{4}He atoms, it appears natural to assume that the spectra of molecules seeded in this medium should not display inhomogeneous effects other than contributions from the cluster size distribution via size-dependent frequency shifts which, however, have been shown to be small [19]. In solids, variations of local binding sites lead to a distribution of vibrational frequencies, which results in inhomogeneous broadening that dominates the linewidths at low temperature. In contrast, in liquids local solvation fluctuations lead to dynamic dephasing. Treating the clusters as a classical liquid, one may expect the time scale of the solvation fluctuation (due to the large zero point kinetic energy of the He atoms) to be much faster than the dephasing times observed in most rovibrational spectra, and hence the effect of fluctuating solvation would likely be strongly motionally averaged [20], leading to homogeneous, Lorentzian line shapes. The spectra of SF_6 [11] and CH_3CCH [13], which are well described with a free rotor Hamiltonian and Lorentzian line shapes, seem to confirm the assumption that the major source of line broadening is of homogeneous nature.

However, at temperatures as low as 0.4 K in a superfluid medium solvation fluctuations are probably more appropriately described in terms of the interaction with the thermally populated fundamental modes of the cluster. For typical cluster sizes (well below $N = 10^5$) only surface excitations (ripplons) have to be considered [10]. The coupling of the molecular vibration to these modes has been estimated and found to be too weak to explain the observed linewidths [21].

The observation of rotational structure in vibrational transitions suggests that pure rotational spectroscopy, by excitation with microwave (MW) radiation, should provide a useful probe of the rotational dynamics of the dopant molecules in the superfluid helium environment. It should be noted that it was not clear *a priori* whether such

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spectra could be observed at all. Because of the short absorption path and low densities characteristic of molecular beams, direct MW absorption measurements are not viable. Whereas transitions in the uv and visible spectral range can be efficiently detected by laser induced fluorescence [7,8,22], beam depletion spectroscopy is employed to detect transitions in the near and mid ir [5,11]. In this method, photon absorption and subsequent relaxation of the molecular excitation energy leads to He atom evaporation from the cluster and a decrease in the flux of He atoms in the droplet beam is observed. While absorption of a single ir photon leads to the evaporation of hundreds or more He atoms from a droplet, at least 10 microwave photons per droplet need to be absorbed to provide sufficient energy to evaporate a single He atom ($\sim$5 cm^{-1} [23]). In order to produce a signal of sufficient size to be detected, many He atoms per cluster must be evaporated. This requires the rotational relaxation to occur on a time scale significantly shorter than 10 μs. Although a lower limit of the rotational relaxation time of the order of hundreds of ps is established by the linewidth of typically 1 GHz observed in the ir spectra [13], the upper limit could be as high as tens of μs, in which case no signal would be observed. The upper limit is imposed only by the fact that for all observed ir spectra the rotational populations are fully thermalized at the temperature of the He droplets by the time the clusters reach the laser interaction region.

Here we report measurements of the microwave spectrum of HCCCN in He nanoclusters detected by the method of beam depletion spectroscopy. HCCCN was used because of its large dipole moment (3.7 D) and its linear structure (rotational constant $B = 1.5$ GHz in the helium nanodroplets [13,14]), which leads to strong and well resolved rotational transitions.

The molecular beam setup will be described in detail elsewhere [13]. Here we will give only a short summary highlighting the aspects unique to the present study. Clusters are formed in a supersonic free-jet helium expansion from a cold 5 μm diameter nozzle which, in the measurements presented here, is operated at 26 K and a stagnation pressure of 100 atm yielding an average cluster size of $\approx 3 \times 10^3$ atoms/cluster (estimated from Ref. [24]). After collimation by a conical skimmer, the clusters pass through a pickup cell containing typically 3×10^{-4} torr of the gas of interest and collect (on average) one foreign molecule each. Subsequently the clusters pass through a 10 cm long P-band microwave guide (nominal 12–18 GHz) which is aligned parallel to the cluster beam. The MW amplitude is modulated at 310 Hz. The molecular beam enters and exits the waveguide through two 3 mm holes in E bends located at each end of the device. If multiple resonant photon absorption and subsequent relaxation of the molecule-helium cluster system occurs, the beam depletion signal is recorded by a liquid helium cooled silicon bolometer using a lock-in technique.

The microwave radiation is produced by a sweep generator (HP 8350B) with a 0.01–26.5 GHz plug-in (HP 8359A) and is amplified by a traveling wave tube amplifier (Logi Metrics A310/IJ) to a power level between 0.05 and 3.4 W (corresponding to a field strength of 0.78 to 6.5 kV/m in the center of the P-band waveguide). The power transmitted through the waveguide is attenuated by 30 dB and measured by a crystal detector (HP 8473B), the output of which is used to level the power of the sweep generator during frequency scans.

Spectra of the $J = 3 \rightarrow 4$ and the $J = 4 \rightarrow 5$ transitions in the ground vibrational state of HCCCN obtained for various MW field strengths between 0.78 and 6.5 kV/m are shown in Fig. 1. The line centers agree well with the line positions predicted from the molecular constants obtained from the rovibrational ir spectrum of HCCCN in the helium clusters [13]. The linewidths (FWHM) are observed to increase from $\sim$0.6 to $\sim$1 GHz for the $J = 3 \rightarrow 4$ transition and from $\sim$0.8 to $\sim$1.2 GHz for the $J = 4 \rightarrow 5$ transition when the microwave field is increased from 0.78 to 6.5 kV/m. At low MW fields these linewidths are comparable to the width of the corresponding rovibrational transitions in the spectra of the fundamental CH stretching mode [14], indicating that vibrational relaxation and dephasing which frequently are the dominant line broadening mechanisms in the spectra of impurities in classical liquids [20] are not the main source of broadening for a molecule such as HCCCN in a superfluid helium cluster. Similar linewidths have been observed by

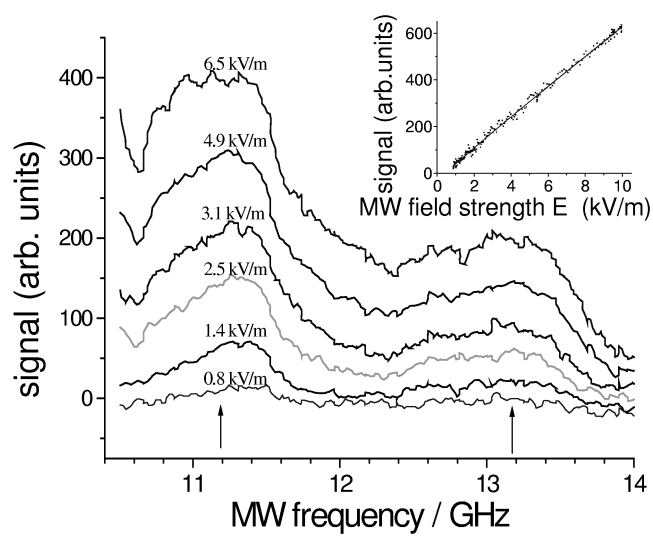

FIG. 1. Microwave spectra of the $J = 3 \rightarrow 4$ and $J = 4 \rightarrow 5$ transition in HCCCN in ^{4}He droplets measured at various MW field strengths. The arrows indicate the line positions predicted from the molecular constants obtained from the rovibrational spectrum of HCCCN in He clusters. Inset: Signal amplitude of the $J = 4 \rightarrow 5$ transition at 13.1 GHz as a function of microwave field strength. The linearity of this plot demonstrates the inhomogeneous nature of the dominant line broadening mechanism.

us for the corresponding microwave transitions in CH_3CN and CH_3CCH.

The dependence of the signal amplitude S on the microwave field strength E has been measured for HCCCN with the MW frequency fixed at the top of either the $J = 3 \rightarrow 4$ or the $J = 4 \rightarrow 5$ transition and is well described by $S \propto E^2/(1 + E^2/E_{\mathrm{sat}}^2)^{1/2}$ with the saturation field $E_{\mathrm{sat}} = 1.1(2)$ kV/m (see the inset of Fig. 1). This saturation behavior, resulting in a linear dependence of the absorption as a function of the MW field intensity for $E \gg E_{\mathrm{sat}}$, demonstrates that, in contrast to the previous expectations, the linewidth is dominated by inhomogeneous broadening [25]. With the saturation parameter $(E/E_{\mathrm{sat}})^2$, the homogeneous unsaturated linewidth is calculated to be at least a factor of 6 narrower than the inhomogeneous linewidth observed at a MW field intensity of 6.5 kV/m. This sets the lower limit of the rotational relaxation time to about 2 ns.

An upper limit for the rotational relaxation time has been set by a MW amplitude modulation experiment: With the MW frequency fixed on top of the $3 \rightarrow 4$ transition at a MW field of 7.8 kV/m, the signal height is monitored while the MW field is 100% square wave modulated at a frequency f. By modeling the $3 \rightarrow 4$ transition as a driven two-level system, the absorbed microwave power is calculated to increase by a factor of 2 when f changes from $f \ll 1/T_1$ to $f \gg 1/T_1$, where $1/T_1$ is the population relaxation rate for the transition. This is basically independent of the dephasing rate $(1/T_2)$, as long as the microwave power is sufficiently large to allow for saturation. From the fact that no increase in signal is observed for modulation frequencies up to 10 MHz we estimate an upper limit for the rotational relaxation time of about 20 ns. This limit is in agreement with the independent but less stringent estimate inferred from the comparison of the strengths of the MW spectra and the ir spectra [13], which implies that the rotational relaxation takes place at a rate not slower than in tens of ns.

In order to determine the homogeneous linewidth of the rotational transition, microwave-microwave double resonance experiments have been carried out. A second microwave source (HP 8690B, plug-in HP 8694B: 8–12.4 GHz) is employed to generate microwave radiation at a fixed frequency. While the first microwave field (the probe) is frequency scanned across the $3 \rightarrow 4$ and the $4 \rightarrow 5$ transitions, the second microwave field pumps the $J = 3 \rightarrow 4$ transition at about 11.1 GHz.

As the probe frequency approaches the pump frequency a strong decrease in signal is observed due to the depletion of the $J = 3$ state by the pump, whereas the $4 \rightarrow 5$ transition signal is increased according to the enhanced population of the $J = 4$ state (Fig. 2). Remarkably, the hole burnt into the $3 \rightarrow 4$ transition has a width of ≈50%–70% of the single resonance linewidth, implying that the rotational population inversion relaxation time is larger than 4 ns. The increase in the $4 \rightarrow 5$ signal even occurs over

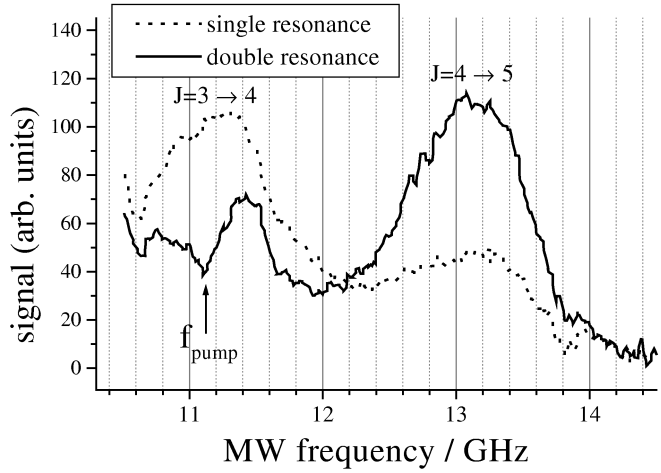

FIG. 2. MW-MW double resonance spectrum of HCCCN in ^{4}He clusters compared to a single resonance spectrum. The depletion in the $J = 3 \rightarrow 4$ and the enhancement in the $J = 4 \rightarrow 5$ transition occur over a significant part of the linewidths indicating rapid relaxation among the substates of the inhomogeneous broadening of the individual rotational levels with a rate much faster than the rotational population inversion rate. The $J = 3 \rightarrow 4$ transition is pumped with a fixed frequency at 11.1 GHz and a field of 3.75 kV/m while the probing field is 5.3 kV/m.

the total width of the signal, indicating that there is a fast relaxation within the inhomogeneous distribution of each individual J level. This observation is important as it implies that a substantial part of the inhomogeneous line broadening is due to a dynamic effect rather than to a static effect such as the cluster size distribution.

The phenomenon of "dynamic" inhomogeneous broadening can be understood assuming that there are additional degree(s) of freedom associated with a splitting of the rotational state into several substates and that the molecule may transit among these substates. Such transitions, which may well change the kinetic and potential energy of the molecule, but produce only a small change in its rotational energy, will be denoted as "elastic." If the elastic relaxation rate is much less than the spectral linewidth, the line shape reflects the distribution of resonance frequencies of the molecules in these additional quantum states. Each substate has a homogeneous width much narrower than the width of the inhomogeneous line. A double resonance experiment would be expected to show a correspondingly narrow hole in the pumped transition and a peak on top of the transition starting from the population enhanced rotor level. However, if the relaxation rate for the rotor quantum number is slower still than the relaxation between the substates, then the population disequilibrium produced by the MW pumping will be spread over many or all of the substates. This produces, in our case, a broad depletion in the lower rotor level and an enhancement over the complete width of the higher rotor level.

The relative areas of the depletion and enhancement signals compared to the single resonance MW signal can be

used to extract the relative rates of the two relaxation processes. By kinetic modeling of the transition rates between the $J = 3$ and $J = 4$ rotational levels and among the substates of each individual rotational state we estimate that the elastic relaxation within one rotational state is about 1 order of magnitude faster than the inelastic population inversion relaxation.

In order to determine possible mechanisms underlying the observed inhomogeneous broadening one of the authors has analyzed the dynamics of a neutral impurity in a nanometer scale ^{4}He cluster [21] showing that for an anisotropic impurity significant sources of line broadening arise from the coupling of the molecular rotation with the center of mass motion of the dopant. These couplings arise both from an anisotropic effective potential for the dopant when shifted from the exact center of the clusters, and from an orientationally dependent hydrodynamic contribution to the effective inertial mass of the dopant. It should be noted, however, that it is not clear how the molecular energy is transferred to the cluster since the energy released or absorbed by the molecular rotationally inelastic or elastic transition in general is not likely to match the quantized energy of the lowest cluster excitations.

The measurements presented here are the first observation of a purely rotational spectrum of any molecule in a liquid He environment, and have provided a unique window on the sources of line broadening and, in particular, onto the rotational dynamics of the dopant in the superfluid helium environment. It has been unambiguously demonstrated that the rotational lines are dominated by inhomogeneous broadening which is attributed to the coupling of the center of mass motion of the molecule within the finite size cluster to the molecular rotation. The second major observation is that the molecule transits among the quantum states of the inhomogeneous distribution on a time scale much faster than the rotational relaxation. These MW-MW double resonance measurements have been followed by a separate study using microwave-infrared double resonance which provides new information on the relaxation dynamics of the dopant in the cluster and its dependence on the finite cluster size [26].

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