Stark Spectroscopy of Polar Molecules Solvated in Liquid Helium Droplets

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Presented here are the first rotationally resolved Stark spectra of a polar molecule in a liquid. This high-resolution spectroscopy is made possible by the fact that superfluid liquid helium is extremely homogeneous. The results presented here show that the interactions between the molecule and the helium solvent result in a splitting very similar to that induced by the applied electric field, providing new insights into the nature of these interactions. [S0031-9007(99)09227-3]

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The interaction of an external electric field with a polar molecule is of fundamental importance and has been studied extensively in the gas, liquid, and solid phases [1]. The high spectral resolution available in the gas phase allows for the accurate determination of molecular dipole moments for individual quantum states [2,3]. In the condensed phases the spectral resolution is generally much lower. Nevertheless these electric field effects are sufficiently important to have focused considerable attention here [1]. Indeed, polar solvents near charged membranes, macromolecules, and electrode surfaces often experience large electric fields that can fundamentally alter their structural and dynamical properties [4]. Thus, the detailed understanding of such physical, chemical, and biochemical processes requires that these electric field induced modifications be understood.

Stark spectroscopy analogous to that done in the gas phase, namely, where the transitions are resolved into their M components [M being the quantum number representing the projection of the rotational angular momentum (J) on the z axis], has never been done in liquids. In fact, M is usually not a good quantum number in liquids, which is to say that molecules generally do not rotate freely. Much has been written about the problems associated with extracting accurate information from the broad spectra typical of condensed phases [1]. In this paper we report the first M resolved Stark spectra of a polar molecule in a liquid, namely, superfluid helium. In particular, we consider the case of HCN solvated in small droplets of superfluid helium. A newly constructed laser-molecular beam apparatus is used to record the infrared spectrum under conditions where there is a single HCN in each droplet. These Stark spectra provide interesting new insights into the nature of the interactions between the polar molecule and the helium solvent.

High-resolution spectroscopy of molecules solvated in liquid helium droplets is new, the first experiments being done in the infrared on SF_6 [5,6]. Recent studies show that ^{4}He solvated molecules often display rotationally resolved spectra [7–11] characteristic of a temperature of 370 mK [8], in excellent agreement with theoretical calculations based upon evaporative cooling [12]. Both experiment [9,13] and theory [14–16] agree that the majority of the helium in these droplets is superfluid, a requirement for obtaining high resolution. Although the molecules interact weakly with the surrounding helium, a significant increase in its effective moment of inertia is often seen [7–9].

The experimental apparatus is described in detail elsewhere [17]. It incorporates a liquid helium droplet source similar to those reported previously in the literature [6,18]. In brief, droplets consisting of approximately 3700 helium atoms (determined using published scaling laws [19,20]) are formed by the expansion of pure helium (50 bar) from a 20 K, 5-μm-diam nozzle. These droplets pass through a pickup cell, where the pressure is optimized for the capture of a single HCN molecule. A Burleigh F-center laser is used to excite the C-H stretching vibration of the HCN. Subsequent vibrational relaxation results in the evaporation of approximately 600 helium atoms. The corresponding loss in beam flux is monitored using a bolometer detector [21]. The laser-molecular beam interaction region is located between a pair of Stark electrodes used to apply the electric field. The angle between the laser polarization and the dc electric field could be varied from 0° to 90°, changing the selection rule from $\Delta M = 0$ to $\Delta M = \pm 1$, respectively.

The vibrational frequency shifts associated with solvation in helium tend to be small and to the red, so we began the search for the HCN spectrum near the gas phase $R(0)$ transition of the C-H stretching band, revealing the spectrum shown in Fig. 1. Given the proximity of this transition to the gas phase $R(0)$ transition (3314.412 cm^{-1} [22]), the assignment seems clear. Since the rotational constant of HCN in the gas phase (1.47822 cm^{-1} [22]) is quite large compared to the droplet temperature (370 mK [8]), this is the only transition we expect to see; the $J \neq 0$ states have no thermal population. The linewidth observed in this spectrum is extremely narrow (approximately 200 MHz) for a molecule in solution. Nevertheless, it is broad compared to the instrumental resolution (<10 MHz), which we believe is the result of the inhomogeneity of the HCN-helium interactions [23]. Of particular interest is the fact that the line shape is unusual,

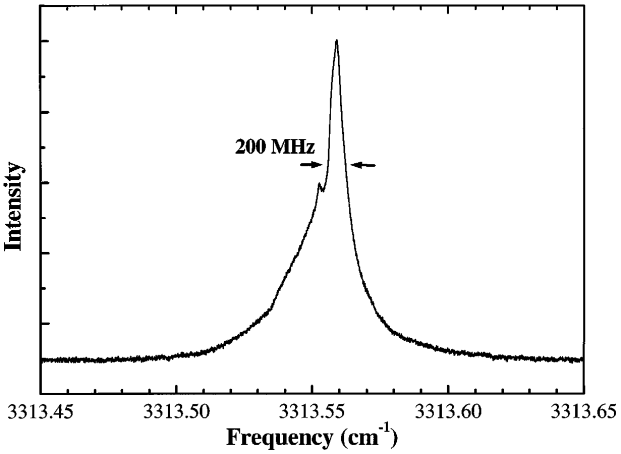

FIG. 1. The $R(0)$ transition of HCN in a liquid helium droplet, showing evidence for splitting into two components.

showing two peaks that are poorly represented by two Lorentzian or Gaussian profiles. The assignment of this splitting and the understanding of its origin constitutes the main focus of the present study.

The dramatic cooling observed here is actually problematic, since a single transition is insufficient to independently determine the vibrational frequency shift and the rotational constant. In previous gas phase studies we have used large electric fields to mix the rotational quantum states of a polar molecule, causing a breakdown in the associated selection rules and the appearance of normally forbidden transitions [24,25]. In particular, for a linear polar molecule this mixing results in the appearance of the "$Q(0)$ transition," as shown in Fig. 2. This spectrum was recorded at an electric field of 10 kV/cm, with the laser electric field polarized parallel to the dc electric field ($\Delta M = 0$).

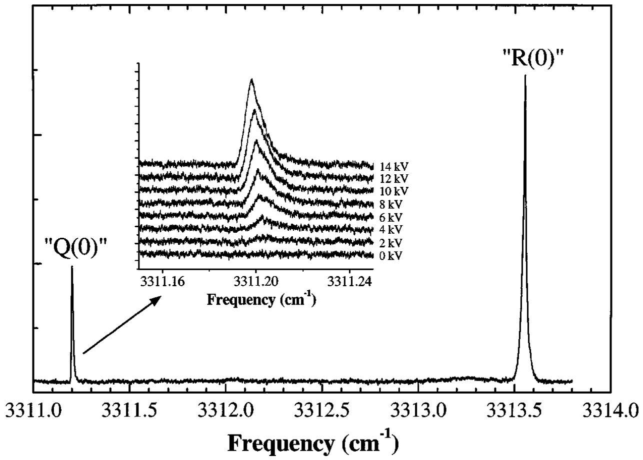

FIG. 2. The spectrum of HCN in helium in the presence of a 10 kV/cm dc electric field. The inset shows the $Q(0)$ transition as a function of electric field strength.

The inset in Fig. 2 shows a series of $Q(0)$ spectra recorded as a function of the electric field. Although its intensity increases with electric field strength, the line shape remains approximately constant and the position shifts slightly, with the latter being due to the fact that the dipole moments and the rotational constants are slightly different in the ground and vibrationally excited states. In the gas phase the dipole moments are $2.985188D$ and $3.017408D$ for the ground [26] and vibrationally excited [26,27] states, respectively, while the corresponding rotational constants are 1.47822 cm^{-1} and 1.46800 cm^{-1} [22]. By fitting the peak position of the $Q(0)$ transition as a function of the electric field, we were able to extrapolate to zero field to determine the vibrational band origin for HCN in helium, namely, 3311.20 cm^{-1} (the absolute accuracy limited by the wave meter used to calibrate the laser frequency).

The combination of the vibrational band origin and the zero field position of the $R(0)$ transition is sufficient to determine the (excited vibrational state) rotational constant of the HCN in helium, yielding 1.175(3) cm^{-1}. Most of the uncertainty in this value comes from the $Q(0)$ measurement, which had to be extrapolated to zero field. The small change in the rotational constant of HCN upon solvation in helium is in contrast with SF_6 and OCS, where the corresponding change is a factor of approximately 3 [8,9]. There is some evidence that the rotational constants of water [10], ammonia [11], and HF [28] are also relatively unaffected by the helium. The general trend seems to be that molecules with large rotational constants (small moment of inertia) rotate more freely in helium than those with small rotation constants. A possible explanation for this is that the lighter molecules rotate so quickly that the helium atoms cannot respond to the motion. The associated rotational averaging of the interactions minimizes the coupling between the two helium and the molecule. On the other hand, for molecules with large moments of inertia, molecular rotation is slow enough for the helium atoms to adiabatically follow the motion. The correlated motion of the helium atoms with the molecule results in an increase in the effective moment of inertia [29]. The present results are particularly important in defining these two regimes, since HCN has the largest moment of inertia of any molecule that has yet been found to fall into the weak coupling regime.

As pointed out above, the $R(0)$ transition shows a splitting, which is clearly not present in the $Q(0)$ transition. A possible explanation for this is that the $R(0)$ transition has two components ($\Delta M = 0$ and $\Delta M = \pm 1$), while the $Q(0)$ transition has only one ($\Delta M = 0$). If this is the source of the structure in $R(0)$, the question is, "What is the cause of the splitting of the M levels?", given that they are degenerate in isotropic (field free) space. We address this question by presenting further evidence linking the splitting in the $R(0)$ transition to the lifting of the

M degeneracy. Indeed, a dc electric field can be used to lift the $M = 0$ and $M = \pm 1$ degeneracy, providing us with a means of assigning the associated transitions. In doing so, the laser polarization can be configured either parallel or perpendicular to the dc electric field, yielding selection rules (in the absence of any other interactions) of $\Delta M = 0$ and $\Delta M = \pm 1$, respectively. Figure 3 shows a series of parallel polarization $R(0)$ spectra, recorded as a function of the electric field strength. Consistent with the above assignment, the separation between the two peaks in the zero field spectrum smoothly increases with applied electric field. In particular, the higher frequency peak shifts to the blue more quickly than the one at lower frequency, consistent with (see the inset of Fig. 3) assigning the higher and lower frequency peaks to $\Delta M = 0$ (the longer arrow) and $\Delta M = \pm 1$ (the shorter arrow), respectively. Further support for this comes from the fact that in parallel polarization the $R(0)$ transition becomes a single peak as the field is increased, which appears at the frequency corresponding to the $\Delta M = 0$ transition in Fig. 3. A comparison between a pair of parallel and perpendicular polarization spectra, recorded at 10 kV/cm, is shown in Fig. 4.

The inset in Fig. 4 shows a plot of the frequency shifts for the two transitions as a function of the electric field. The dashed lines in the figure are Stark calculations of the expected shifts for the $R(0)$ transition, assuming that the dipole moment in the ground and excited vibrational states are unchanged from the gas phase. Within the experimental uncertainty, we see no change upon solvation and the behavior at high fields is consistent with a free rotorlike Stark effect. Future experiments will involve a more accurate calibration of the electric field in an attempt to reveal such changes, which could provide further information on the nature of the HCN-helium interactions. As expected, the calculated splitting goes to zero at zero electric field, while the experimental splitting does not vanish. It is as if there is a residual "field" associated with the interaction between the molecule and the helium. We note here that great care was taken to ensure that no stray applied fields were present.

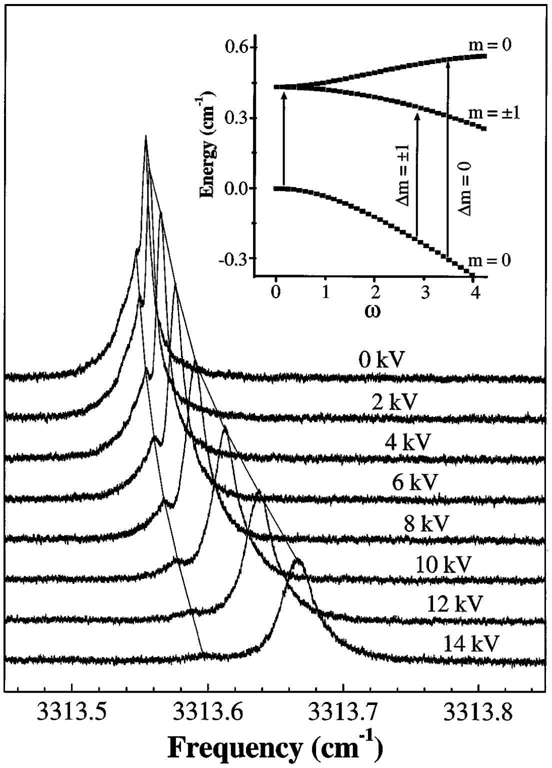

FIG. 3. A series of HCN $R(0)$ spectra as a function of electric field strength (parallel polarization). The field clearly splits the $\Delta M = 0$ and $\Delta M = \pm 1$ transitions in the manner expected from the relevant energy level diagram, shown as the inset ($\omega = 0.0168\mu E/B$, where E is the applied electric field).

We put "field" in quotation marks here since it is not necessary that the interactions that split the M states have the $P_1(\cos(\theta))$ functionality of a dipole-electric field interaction (where θ is the angle between the molecular dipole and the electric field). Indeed, a recent theoretical study by Lehmann [23] shows that, for a polar molecule solvated in a helium droplet, the sum of all the dipole-induced dipole interactions gives rise to an anisotropic interaction that goes as $P_2(\cos(\theta))$. Furthermore, these calculations indicate that the molecule is primarily situated away from the center of the droplet, where this interaction is indeed nonzero. In fact, much of the line broadening in the spectrum is likely the result of the fact that the interaction strength is dependent upon the radial displacement of the molecule from the center of the droplet. In this treatment, the anisotropic interaction is

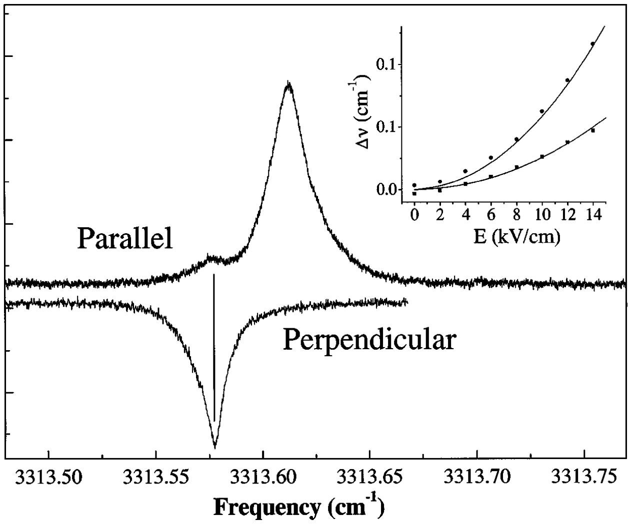

FIG. 4. A comparison between the parallel and perpendicular Stark spectra at 10 kV. The inset shows a plot of the frequency shifts as a function of electric field for the $\Delta M = 0$ and $\Delta M = \pm 1$ transitions. The dashed lines are calculations based on the HCN rotational constant determined here and the gas phase dipole moment.

referenced to an axis that is fixed in the droplet frame of reference (namely, the line joining the molecule's position to the droplet center) and is therefore different for each droplet. In a future paper [30] we will quantify an extension of this model that includes the external field, but for now we note that the size of the observed splitting in the absence of the applied field (6.5×10^{-3} cm^{-1}) is equivalent to the splitting caused by an external electric field of about 4.5 kV/cm. Once again, we do not wish to imply that there is an electric field present in the helium droplets, but rather that the interactions between the molecule and the helium give rise to a splitting of the same magnitude as a field of this strength.

Let us now consider the intensities of the transitions in the above spectra. The fact that we observe both $\Delta M = 0$ and $\Delta M = \pm 1$ transition in the zero field experiment can be understood by noting that the axis that defines the "internal field" is fixed in the droplet fixed coordinate system and is therefore different for each droplet. The experimental spectrum therefore consists of an average over many different polarization directions, allowing both $\Delta M = 0$ and $\Delta M = \pm 1$ transitions. Upon application of an external electric field, the selection rules are determined by the direction of the net field, which becomes increasingly directed along the space fixed electric field direction as the external field increases. Thus, in the spectra shown in Fig. 4, which correspond to parallel polarization in the laboratory frame, the $\Delta M = 0$ transition remains intense at the highest applied fields, while the $\Delta M = \pm 1$ transition loses intensity.

It is interesting to note that the surviving transition in Fig. 3 is substantially broader than the zero field spectrum, as well as more symmetric. This can be understood by noting that, in the presence of the applied electric field, the magnitude of the net field, which determines the absolute frequency of the transition, becomes sensitive to the direction of the internal field relative to the applied field. In essence, the applied field introduces an additional inhomogeneity in the net field, resulting in the additional broadening of the transition. A more detailed discussion of this aspect of the problem will be given elsewhere [30], but it is already clear that the splittings observed in the spectra of polar molecules in helium have the potential of providing important information on the nature of the associated interactions.

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