Measurement of the Dynamical Response of a Superfluid via Spectroscopy of the v₄ Band of CH₄ in He Droplets

(Okayama Univ., Toyama Univ., Univ. of Waterloo, Univ. of British Columbia) Susumu Kuma, Katsunari Enomoto, Aakash Ravi, Takamasa Momose

The triply degenerate v_4 asymmetric stretching mode of CH₄ in superfluid He nanodroplets was observed at 7.7 µm by high-resolution infrared depletion spectroscopy for the first time. Five rotational transitions were detected, with a minimum linewidth of only 65 MHz. The observed lines showed slightly asymmetric lineshapes, especially in the case of the P(2) and R(1) rotational lines. Analysis of the lineshape by a chirped rotor model indicates that the superfluid environment has a finite response time of a few nanoseconds to equilibrate upon rotational excitation of CH₄.

Over a decade of experiments have shown that molecules in superfluid He nanodroplets rotate nearly freely, exhibiting quantized rotational states [1]. The embedded molecules typically show a reduction of the rotational constant, B, and an increase of the centrifugal distortion constant, D in the droplet environment. These effects have been discussed in relation to collective excitations or destruction of the superfluid characteristics of the surrounding He, but the nature of the interactions causing these changes in molecular constants is still under considerable debate [1–3]. Heavy molecules, which exist in the so-called adiabatic following regime [1], have been studied extensively, but less work has been devoted to light molecules, in which destruction of the superfluid component around the molecules is expected to be suppressed. Here, we have studied CH₄, which is a prototypical light molecule, in He droplets by high resolution infrared (IR) depletion spectroscopy.

Our experimental setup involves a continuous expansion of He gas though a 5- μ m orifice maintained at a high stagnation pressure (2 MPa) and low temperature ($T_0 = 11$ K–16 K) to produce He droplets at 0.4 K with the mean size of the droplet, $N_{\text{He}} = 20,000-2,000$. The droplet beam enters a pickup cell, where each droplet is doped with a CH₄ molecule on average. Photons from a counter-propagating IR laser beam excite transitions of CH₄ in the droplets at resonant frequencies. Upon subsequent non-radiative relaxation of the excited molecule, roughly 200 atoms per excitation at $\lambda = 7.7$ µm evaporate, and this shrinkage of the droplet size is detected as a depletion of a mass signal. The droplets were ionized by electron impact and collected by a quadrupole mass filter. A tunable external cavity cw quantum cascade laser was used as an IR source at 7.7 µm.

Figure 1 shows an overall depletion spectrum of the v_4 band of CH₄ in He droplets at $T_0 = 16$ K. While the fundamental rotational energy of CH₄ is much higher than the temperature of nanodroplets, the transitions from the J = 1 and J = 2 states are observed due to the nuclear spin modification of CH₄.



Figure 1

IR depletion spectrum of the v_4 band of CH₄ in He droplets. Rotational assignments are given for each peak. The peak marked by an asterisk (*) is a transition of (CH₄)₂.



Figure 2

Lineshapes of the observed P(2), Q(1) and R(1) peaks; the thin traces are the experimental spectra, and the thick traces are fits to the model. The upper and lower traces correspond to the spectra at $T_0 = 16$ K and 11 K, respectively.

The most striking difference between the present v_4 transitions and the v_3 transitions reported previously [4] is the linewidth. Figure 2 shows expansion of the P(2), Q(1) and R(1) peaks. The narrowest linewidth in v_4 is 65 MHz (FWHM) for the Q(1) transition at $T_0 = 11$ K. The corresponding Q(1) transition in v_3 has a linewidth of 11 GHz. The broad linewidths in the v_3 band are accounted for by fast vibration-vibration relaxation [5], as there are some vibrational states whose energy is close but slightly less than that of the v_3 state at 3020 cm⁻¹. Since the v_4 state is the lowest excited vibrational state, no fast intramolecular vibrational relaxation occurs.

Upon closer examination of the observed lines, we noticed that some of the lines exhibited asymmetric lineshapes. The P(2) line has a clear asymmetric tail toward higher frequencies, while the R(1) has a low-frequency tail. Similar line asymmetries have been reported for OCS [6] in He droplets. Recently, van Staveren and Apkarian [7] have interpreted the asymmetry for OCS as arising from the chirping of rotational frequencies due to the response of He environment on rovibrational excitation. The lineshape I(v) of the frequency domain spectrum is represented as the Fourier transform of the time correlation function c(t) of a dipole operator μ , where $c(t) = \langle \mu(0) \cdot \mu(t) \rangle$ is equal to $\exp(2\pi i v' t) \cdot \exp(-2\pi y t)$ with v' and γ being the frequency of the dipole oscillation and its decay rate, respectively. We assume that the change of v' in time is given by $v'(t) = v_c + \Delta[1-\exp(-2\pi\beta t)]$ [7]. The parameter β represents the damping of the frequency chirping.

At $T_0 = 11$ K, the damping rate $2\pi\beta$ of the chirping was determined to be about 250 MHz for both the P(2) and R(1) lines, corresponding to a response time of 4 ns. This slow response time to accommodate the change of rotational states of a central CH₄ is a distinctive characteristic of a superfluid system, as the the motion of nuclei in classical fluids happens on the timescale of picoseconds or faster [8]. As the He around CH₄ is expected to remain nearly completely superfluid, the v_4 band is an ideal probe of the dynamical rotational response of a superfluid.

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