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Spectroscopic Studies of Quantum Solvation in ^{4}He$_N$-N$_2$O Clusters

Yunjie Xu,[1] Wolfgang Jäger,[1,*] Jian Tang,[2] and A. R.W. McKellar[2,†]
[1]Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2
[2]Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

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High resolution microwave and infrared spectra of He$_N$-N$_2$O clusters were studied in the range $N = 3$ to 12. The apparent cluster moments of inertia increase from $N = 3$ to 6, but then decrease, showing oscillatory behavior for $N = 7$ to 12. This provides direct experimental evidence for the decoupling of helium atoms from the rotation of the dopant molecule in this size regime, signaling the transition from a molecular complex to a quantum solvated system and directly exploring the microscopic evolution of "molecular superfluidity."

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The unique quantum properties of helium nanodroplets are of intense experimental and theoretical interest. Many studies have been carried out using helium nanodroplet isolation (HENDI) spectroscopy to elucidate their superfluid nature [1]. The "microscopic Andronikashvili experiment" of Grebenev *et al.* [2] showed rotationally resolved infrared spectra of carbonyl sulfide (OCS), demonstrating a weakly damped rotation of OCS in ^{4}He droplets, an indicator for the onset of "molecular superfluidity." There has also been progress in developing theoretical models and simulations of molecular superfluidity in nanodroplets. For example, Sindzingre *et al.* performed finite path integral Monte Carlo calculations on medium size pure ^{4}He clusters, finding a superfluid fraction similar to that in the bulk liquid even with as few as 64 atoms [3]. Various models have been advanced to explain the increase in effective moments of inertia of dopant molecules relative to the gas phase and the different linewidths observed in ^{4}He and ^{3}He droplets [4–6]. One interesting prediction is that the rotational constant B (the inverse moment of inertia) saturates already for small clusters ($N = 5$ for He$_N$-OCS [4] and $N = 8$ for He$_N$-SF$_6$ [7]) at the nanodroplet value. This is remarkable since the rigid rotor moment of inertia would normally continue to increase, and thus the rotational constant decrease, upon the addition of further He atoms in small clusters. The implication is that He atoms already decouple from the dopant molecule rotation in relatively small clusters. Experimental observation of rotationally resolved spectra of such clusters ($N \approx 4$–10) could confirm this finding, with interesting implications for the onset of superfluidity.

High resolution spectroscopy of weakly bound clusters in molecular beams provides detailed information on structure and dynamics. However, such studies have mostly been limited to binary or ternary systems. Recently, we reported [8–10] microwave and infrared spectra of He$_N$-OCS clusters with $N = 2$ to 8, providing the first experimental data to test theories of small doped helium clusters. A significant finding was that the B rotational constants of He$_N$-OCS reach the limiting nanodroplet value at $N = 5$ and then undershoot it for $N = 6$, 7, and 8, implying that B must subsequently turn around and increase in order to approach the nanodroplet value. At this critical N value (yet to be determined), additional He atoms will cause some existing He atom density to decouple from the OCS rotation, decreasing their contribution to the moment of inertia. Relevant calculations on He$_N$-OCS clusters were recently reported by Moroni *et al.* [11] and Paesani *et al.* [12], both confirming the observed undershoot. The critical turnaround N value was predicted to be 8–9 [11], or 6 [12]. While the experiment [8] established that the turnaround occurs for $N > 8$, it did not locate the critical N value. Although He$_N$-OCS clusters with $N > 8$ were observed in the infrared region [10], their assignment was hampered by the fact that the corresponding microwave spectra probably occur below the present operating frequency of our spectrometer.

To overcome this technical challenge, we can use a lighter dopant molecule, nitrous oxide (N$_2$O). Previously, a HENDI experiment with N$_2$O has been reported [13], the binary complex He-N$_2$O has been studied by vibrational [14] and rotational [15] spectroscopy, and a potential energy surface [15] has been developed and tested against spectroscopic data. In this Letter, we present a microwave and infrared spectroscopic study of He$_N$-N$_2$O clusters in the range $N = 3$ to 12. These results provide the first direct observation of the sequential evolution of a molecular complex into a molecule solvated in quantum liquid as a function of cluster size N. The experiments were carried out using an infrared diode laser spectrometer [16], a molecular beam Fourier transform microwave spectrometer [17], and a microwave-microwave double resonance spectrometer [18]. The infrared experiments used pulsed supersonic jet expansions of trace amounts (<0.1%) of N$_2$O in He with slit-shaped or pinhole nozzles. Backing pressures up to 35 atm were used, and the nozzle temperature could be varied between −50 and +20 °C. The microwave experiments used a similar pulsed pinhole jet with backing pressures up to 50 atm. Microwave spectra of three minor isotopomers ($^{14}N^{15}NO$, $^{15}N^{14}NO$, $^{15}N^{15}NO$) were measured using enriched sample gas (Cambridge Isotope, 98% ^{15}N).

We studied the infrared spectrum of He_N-N_2O clusters in the region of the strong ν_1 fundamental band of the normal isotope, $^{14}N^{14}N^{16}O$, around 2224 cm^{-1}. As the backing pressure was increased, the known transitions of N_2O [19] and He-N_2O [14] were joined by new "pressure sensitive" lines. Aided by the fact that the N_2O dimer spectrum falls outside the region of interest [20], many new lines could be assigned to He_N-N_2O clusters, based on their pressure dependence and on previous experience with He_N-OCS [8,10]. Figure 1 shows example spectra, obtained using a cooled pinhole jet with backing pressures from 11 to 26 atm. The somewhat complex spectrum of He_2-N_2O is not discussed in detail here. For $N = 3$–5, the infrared line assignments were unambiguously confirmed by microwave measurements, as discussed below. For $N = 6$–9, the situation was less simple, but it was possible to make coherent infrared and microwave assignments. For $N > 9$, clear microwave data are available, but the infrared assignments are not yet definitive.

Pure rotational spectra of four nitrogen isotopomers of ^4He_N-N_2O were measured in the microwave region. The infrared analyses for $N = 3$–5 were confirmed by locating rotational transitions for the normal isotopomers of these clusters within a few MHz of the predictions. To tackle the difficulties associated with larger clusters, we took advantage of the high resolution and double resonance capability of our spectrometer. Wide range searches (4.2 to 13.5 GHz) were carried out at high backing pressure (50 atm). Substitution of the central nitrogen atom causes only small frequency shifts, and the shift from $^{14}N^{14}NO$ to $^{14}N^{15}NO$ is similar to that from $^{15}N^{14}NO$ to $^{15}N^{15}NO$. These isotopic data were crucial for assigning different isotopomers for a given N. Transitions of $^{14}N^{14}NO$ have complex nuclear hyperfine structure due to the two nonequivalent ^{14}N nuclei. Those of $^{14}N^{15}NO$ and $^{15}N^{14}NO$ have simpler patterns which were used to evaluate quadrupole coupling constants for the outer and middle ^{14}N nuclei. The rotational assignments were facilitated by the distinctive hyperfine patterns of a given transition, e.g., $R(0)$ vs $R(1)$. The characteristic ^{14}N hyperfine patterns of the $R(0)$ transitions of He_N-$^{14}N^{15}NO$ clusters assigned to $N = 5$, 7, and 12 are shown in Fig. 2. Microwave double resonance was used to link transitions sharing a common energy level, for example, to locate the

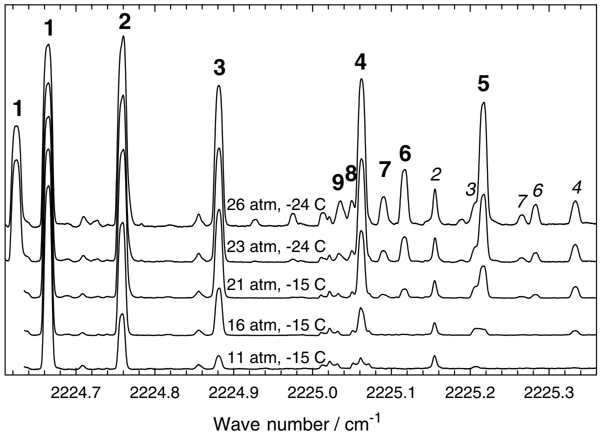

FIG. 1. Part of the observed infrared spectrum of He_N-N_2O clusters, showing increasing clustering with higher backing pressure. Two $R(0)$ ($J = 1 \leftarrow 0$) lines marked "1" for He-N_2O correspond to known a- and b-type transitions of this asymmetric rotor complex [14]. With increasing pressure and decreasing nozzle temperature, they are joined successively by the lines marked "2" to "9" in bold numerals, assigned as $R(0)$ transitions of He_N-N_2O clusters with N equal to the given number. Many additional pressure sensitive lines were assigned to other transitions, for example, the $R(1)$ lines ($J = 2 \leftarrow 1$) marked by italic numerals. Unmarked lines are due to known transitions with $N = 0$ or 1, or to transitions of larger clusters ($N > 7$).

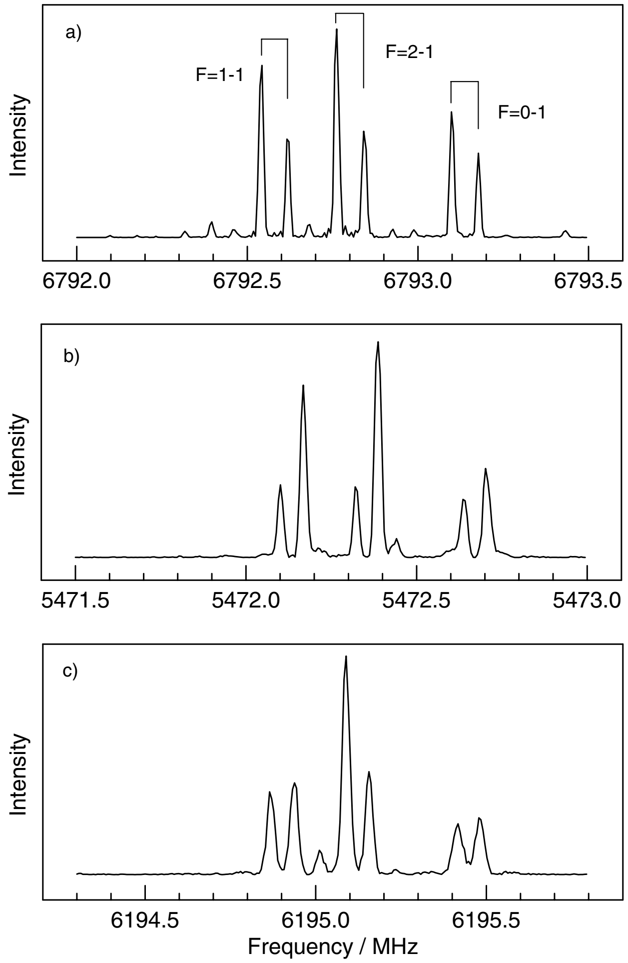

FIG. 2. Spectra of the $J = 1$–0 rotational transitions of He_N-$^{14}N^{15}NO$ clusters showing ^{14}N nuclear quadrupolar hyperfine structure. (a) $N = 5$; (b) $N = 7$; (c) $N = 12$.

$J = 3 \leftarrow 2$ transition corresponding to a given $J = 2 \leftarrow 1$ transition.

Altogether, seven new $R(0)$ transitions were measured for all four N_2O isotopomers with pressure dependence indicating $N > 5$. The size ordering was established on the basis of this dependence and by comparison with infrared data. The N assignments from 6 to 12 are felt to be fairly certain, with perhaps slight uncertainty around $N = 10$. But the conclusions of the paper are not significantly affected by, say, interchanging $N = 9$ and 10. The important points are that the numbering is secure at least up to $N = 7$, and that the hyperfine patterns prove that these are all $R(0)$ transitions. Is it possible that more than one $R(0)$ line might have the same N value (i.e., different types of transitions or isomers)? We believe that such alternate explanations are unlikely. The observed hyperfine splittings are almost equal to that of free N_2O, implying that the cluster c axis is almost coincident with the N_2O axis. Very different hyperfine patterns are expected for a- or b-type transitions. The existence of structural isomers of weakly bound and highly fluxional helium clusters is also unlikely.

The infrared and microwave measurements for the main isotopomer, ^4He_N-$^{14}N^{14}N^{16}O$, were fitted to simple linear molecule (or $K = 0$ symmetric top) energy level expressions, with band origin ν_0, rotational parameter B, and centrifugal distortion parameters D and, if necessary, H. For clusters with $N = 9$–12 the fits were based on the microwave data alone. The key results from these fits are given in Table I. We estimate the uncertainty in the B constants to be of the order of a few MHz. This depends mainly on the deficiencies of the semirigid rotor model and on the number of distortion constants used. The variation of the band origin for $N = 0$ to 9 is shown in Fig. 3(a). This variation shows a virtually linear blueshift of $+0.258\ \mathrm{cm}^{-1}$ per added He atom for $N = 0$ to 4, followed by a smaller blueshift of $+0.204\ \mathrm{cm}^{-1}$ between 4 and 5, and then redshifts varying from -0.052 to $-0.026\ \mathrm{cm}^{-1}$ each from 5 to 9. This result is similar to that observed [8,10] for He_N-OCS clusters, except that the rate of the initial blueshift ($N = 0$ to 5) is almost 2.3 times larger in the present case. Large vibrational shifts for N_2O compared to OCS are typical [14,21]. The turnaround at $N = 5$ can be explained by the "donut model" in which the first five He atoms occupy equivalent

TABLE I. Experimental vibrational frequencies and lower state rotational parameters for ^4He_N-$^{14}N^{14}N^{16}O$ clusters. For $N = 1$ and 2, which are asymmetric rotors, B refers to $(B + C)/2$.

N	Vibrational frequency (cm^{-1})	B (MHz)	D (MHz)
0 [19]	2223.7567	12561.6	0.0053
1 [14,15]	2224.0099	9302.0	9.4
2	2224.266[a]	6080.0[a]	97.0[a]
3	2224.5281	5386.3	33.6
4	2224.7869	4147.5	3.1
5	2224.9905	3396.8	0.56
6	2224.9387	2671.9	13.2
7	2224.9066	2759.8	9.1
8	2224.8809	2556.2	15.9
9	2224.8552	2709.2	32.7
10		3293.6	37.3[c]
11		3357.6	37.3[d]
12		3153.5	21.0
Nanodroplet [13]	[b]	2150.0	21.0

[a] These He_2-N_2O parameters are tentative.
[b] The nanodroplet spectrum was studied in the region of the $\nu_1 + \nu_3$ combination band. The observed origin, $3482.00\ \mathrm{cm}^{-1}$, was shifted $+1.18\ \mathrm{cm}^{-1}$ relative to the free molecule.
[c] Fixed at a value estimated from the He_{10}-$^{15}N^{14}NO$ isotopomer.
[d] Assumed value; only the $R(0)$ line was observed for $N = 11$.

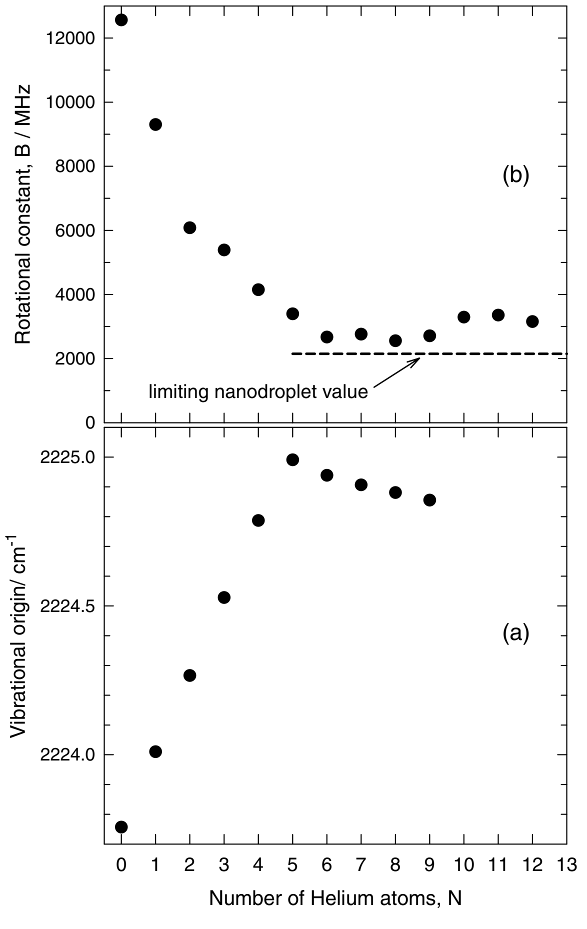

FIG. 3. (a) Observed variation with N of the vibrational band origin for He_N-N_2O clusters. The origin undergoes a large blueshift for $N = 0$ to 5, and then turns around and begins to shift towards the red for $N = 6$ to 9. (b) Experimental B rotational constants of He_N-N_2O clusters with $N = 0$ to 12. The horizontal dashed line indicates the experimental value for N_2O in a helium nanodroplet [13]. Note the oscillation of B for $N > 6$.

positions around the "equator" of N_2O (or OCS) where each exerts a similar blueshifting effect. After the equatorial ring is filled ($N = 5$), subsequent He atoms occupy positions closer to the ends of N_2O, where they exert a redshifting effect on the molecular vibration.

The large magnitudes of many of the centrifugal distortion parameters, D, demonstrate that these clusters are highly nonrigid. The experimental rotational constants, B, are plotted in Fig. 3(b) as a function of cluster size, with the limiting nanodroplet value [13] indicated by a dashed line. Two significant differences from the corresponding plot for OCS (Fig. 3 of Ref. [8]) are apparent. First, for N_2O we find that the lowest B obtained for all these clusters is still significantly above the nanodroplet B value. Even for N up to 12, there is no undershoot such as appears for $N > 5$ with OCS. This could be connected to the fact that the N_2O nanodroplet B value does not follow the trend observed for the related dopants OCS and CO_2 (see Ref. [13] for details). The observed scaling factor ($B_{\mathrm{monomer}}/B_{\mathrm{droplet}}$) is 5.8 for N_2O. A more typical factor of 3 was observed for OCS and CO_2. Second, a particularly intriguing finding is that B oscillates in value for $N > 6$. Even allowing for slight uncertainties in the size numbering, it is clear that B does not uniformly decrease with the addition of helium atoms, contrary to expectation for a rigid or semirigid molecular complex. In other words, the turnaround point discussed in the introduction has been experimentally observed.

The behavior of B indicates that part of the helium density decouples from the rotational motion of the N_2O molecule and does not contribute to the moment of inertia of the cluster. This is the first direct experimental observation of solute-solvent decoupling in this size regime, and it signals the transition from a molecular complex to a quantum solvated system. Theoretical simulations of properties of these clusters would confirm if the unusual behavior of the B constants for these medium sized He_N-N_2O clusters is indeed a result of the onset of the permutation exchanges of helium atoms, the same mechanism invoked to explain superfluidity in infinite systems.

The present He_N-N_2O cluster data provide information on helium density distribution in these intermediate size clusters. The vibrational shifts and moments of inertia confirm that helium atoms 3 to 5 sequentially fill the donut positions around the N_2O molecule. For larger clusters we can anticipate that a fraction of the helium density is decoupled from the rotation of the molecular monomer, based on previous experiments and calculations [8,11,12]. But interestingly, the structural information encoded in our isotopic data is sensitive only to the helium atoms that rotate with N_2O, in other words, the "normal" fluid fraction in analogy with two-fluid models of liquid helium. For clusters with $N > 5$ the moment of inertia differences of the He_N-${}^{15}N{}^{14}NO/He_N$-${}^{14}N{}^{14}NO$ pairs are significantly larger than the corresponding difference for the monomer, indicating preferential solvation (with normal fluid helium) at the oxygen end. Extrapolated to larger clusters, this could explain the corresponding effect found in the N_2O HENDI experiment [13].

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*To whom correspondence should be addressed. Email address: wolfgang.jaeger@ualberta.ca

†Email address: robert.mckellar@nrc-cnrc.gc.ca

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