

High-Resolution Spectroscopy of NO in Helium Droplets: A Prototype for Open Shell Molecular Interactions in a Quantum Solvent

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We have measured the high-resolution infrared spectrum of the radical NO in the ${}^2\Pi_{1/2}$ state in superfluid helium nanodroplets. The features are attributed to the Λ -doubling splitting and the hyperfine structure. The hyperfine interaction is found to be unaffected by the He solvation. For the Λ -doubling splitting, we find a considerable increase by 55% compared to the gas phase. This is explained by a confinement of the electronically excited NO states by the surrounding He. The rotational level spacing is decreased to 76% of the gas phase value. The IR transition to the $J = 1.5$ state is found to be homogeneously broadened. We attribute both observations to the coupling between the molecular rotation and phonon/roton excitations in superfluid ${}^4\text{He}$ droplets.

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Spectroscopy of molecules in He nanodroplets is a very promising technique for investigating chemical reactions at ultralow temperatures. In such reactions, radicals play an important role [1]. It is, therefore, of interest to probe the influence of the He environment on a radical. While at present quite a number of closed shell molecules have been studied in He droplets [2], only little is known about the influence of the helium droplets on the spectra [3] and the electronic structure of radicals. The infrared spectra of many radicals exhibit hyperfine splitting and Λ -type doubling. These effects are well known in the gas phase but have never been studied in solvents.

In this Letter, we report the measurement of the IR spectrum of NO in He droplets. NO is an open shell molecule and has a ${}^2\Pi_{1/2}$ electronic ground state. The rotational levels of NO show hyperfine structure and Λ -type doubling. While the hyperfine splitting reflects the magnetic interaction, Λ -type doubling arises from rotational interaction of the Π ground state with higher electronic states. The coupling to the higher electronic Σ^+ or Σ^- states splits the degenerate energy levels of the ${}^2\Pi_{1/2}$ ground state. We will show that the droplets increase the magnitude of the Λ -type doubling and discuss the implications for the electronically excited states of NO within the He solvent.

The lower rotational energy levels of NO lie in the interesting region of the collective excitations of superfluid He. In particular, they are close to the roton excitations. NO is therefore a good candidate to investigate the role of these excitations in the rotational energy relaxation or in the shift of the rotational levels, as recently pointed out by theory [4,5]. For this purpose, NO as a diatomic molecule is ideal because it has only a single vibrational mode. The vibrational energy is much larger than the collective excitations of liquid He ($\sim 1875 \text{ cm}^{-1} \gg \sim 10 \text{ cm}^{-1}$). Therefore, vibrational relaxation is extremely slow.

The experiments have been carried out using a new apparatus at Bochum. The setup is similar to that used by Hartmann *et al.* and explained in detail elsewhere [5,6]. Here we give only a brief description. Helium is expanded at 40 bar and 20 K through a nozzle of $5 \mu\text{m}$ in diameter into the vacuum, which leads to the formation of large droplets of a mean size of $\bar{N} = 3000$ atoms. These are doped with NO while passing through a chamber, which is filled with NO gas at a pressure of $\sim 1 \times 10^{-5}$ mbar. On average, the droplets collide with one molecule, which is subsequently embedded in the liquid drop. The doped droplets then interact with laser light, which is collinearly coupled into the vacuum chamber. After 1240 mm distance, they enter the ionization region of a quadrupole mass spectrometer. Infrared radiation is generated by means of a lead salt laser diode. Frequency calibration is achieved by simultaneously measuring the absorption lines of 20 mbar carbonyl sulfide in a cell whose frequencies are well known [7]. The laser beam also passes through a confocal etalon in order to linearize the spectrum. The accuracy in absolute frequencies is 0.004 cm^{-1} .

Absorption of IR photons is detected by means of beam depletion. We assume that after IR excitation the NO molecule remains in a vibrationally metastable state. An energy transfer to the He can occur by pickup of a second molecule. This will cause coagulation into a van der Waals complex, which possesses many low lying combination modes. These can couple efficiently to the He modes and, thus, release the vibrational excess energy, similarly as for HF [8].

An energy transfer to the He droplet leads to the evaporation of 300–400 He atoms due to the vibrational excess energy. Droplets of smaller diameter have a lower electron impact ionization cross section. The depletion signal is measured at low mass resolution on a broad range of He_n^+ fragment masses peaked at 10 amu, which revealed the best signal to noise ratio.

He droplets of $\bar{N} = 3000$ were produced and doped with NO molecules. While scanning the diode laser from 1875 to 1876 cm^{-1} , sharp absorption lines were detected (Fig. 1). We assigned these lines to the ${}^2\Pi_{1/2}; \nu = 1, J = 0.5 \leftarrow \nu = 0, J = 0.5$ transition according to their proximity and similarity to the gas phase $Q(0.5)$ transition frequencies [9]. Another line was detected at 1879.386 cm^{-1} (Fig. 3), which we assigned to the ${}^2\Pi_{1/2}; \nu = 1, J = 1.5 \leftarrow \nu = 0, J = 0.5$ $R(0.5)$ transition. The knowledge of both the $Q(0.5)$ and $R(0.5)$ transition frequencies enables us to deduce the rotational constant B_{eff} in He droplets using $B_{\text{eff}} = [R(0.5) - Q(0.5)]/3 = 1.253 \text{ cm}^{-1}$. We can, therefore, state that the effective rotational constant B_{eff} in He droplets amounts to 76% of that of the gas phase (Table I).

In the gas phase, eight $Q(0.5)$, ${}^2\Pi_{1/2}$ transitions are observed which originate from Λ -type and hyperfine splitting of the upper and lower rovibrational levels. An appropriate energy diagram for the gas phase transitions is shown in Fig. 2.

The hyperfine interaction, which is due to the coupling of the nuclear spin I with the angular momentum J , splits each of the Λ -type doublets into two levels: $F = 1.5$ and 0.5 , respectively, where F is the total angular momentum of the molecules.

According to symmetry selection rule, eight transitions between the e and f or f and e vibrational ground and excited levels which are listed in Table I are observed (Fig. 2) for the free molecule. Thus, the four lines in He droplets correspond to two Λ -type doublets, which are further split into hyperfine transitions, some being too close to be resolved. The width of these lines is equal to our laser band width.

The center of mass of the four lines is redshifted by 0.43 cm^{-1} with respect to the gas phase frequencies. The magnitude of the Λ -type doubling Δ_{Λ} was deduced from

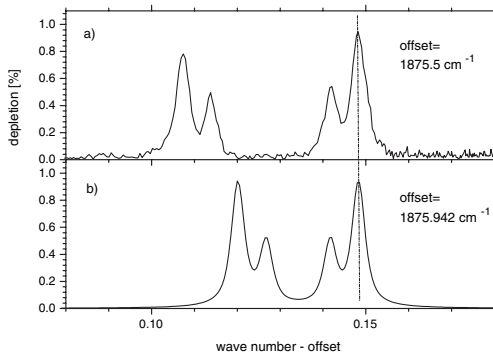


FIG. 1. (a) The $Q(0.5){}^2\Pi_{1/2}$ transitions of NO in He droplets of the size $N = 3000$. (b) A simulation of the respective spectrum of NO in the gas phase. These lines have been convoluted with a Gaussian function in order to account for the line width of the laser. Both spectra have been offset by 1875.5 and 1875.942 cm^{-1} , respectively.

the combination differences of the eight lines, assuming that the splitting is identical for the ground and the excited vibrational state as in the gas phase.

We find that in He droplets Δ_{Λ} is 0.017 cm^{-1} , which is 55% increased compared to the gas phase.

The hyperfine structure is unchanged with respect to the gas phase. This shows that the averaged electron distribution is unaffected by the He solvent. However, the Λ -doubling energy of NO is influenced by the He solvent.

According to the theory of Λ -type doubling as was developed first by Van Vleck [11] and later by Mulliken and Christy [12] for ${}^2\Pi$ states, the magnitude of the splitting Δ_{Λ} is expressed by two parameters p and q :

$$\Delta_{\Lambda} = -\left(\frac{1}{2}p + q\right)\left[1 \mp \frac{2 - Y}{X}\right]\left(J + \frac{1}{2}\right) \mp \frac{2q}{X}\left(J - \frac{1}{2}\right)\left(J + \frac{1}{2}\right)\left(J + \frac{3}{2}\right), \quad (1)$$

with $Y = \frac{A}{B}$ and $X^2 = Y(Y - 4) + 4\left(J + \frac{1}{2}\right)^2$. The parameters A and B are the fine structure and rotational constant of the ${}^2\Pi$ ground state of NO, respectively. The upper sign in Eq. (1) refers to the ${}^2\Pi_{3/2}$ state, the lower to the ${}^2\Pi_{1/2}$. While the parameter q is small and may be neglected here, p can be calculated by means of perturbation theory. Dousmanis *et al.* proposed approximate expressions for p and q in which the vibrations were neglected and the

TABLE I. Line frequencies of the $Q(0.5){}^2\Pi_{1/2}$ and $R(0.5){}^2\Pi_{1/2}$ transitions of NO, the Λ -type splitting, and ground state B constants in He droplets and in the gas phase, respectively. It has to be noted that two lines of the hyperfine multiplet overlap in He droplets. The gas phase values are obtained from the Hitran database [10]. All units are cm^{-1} . See also Fig. 2.

Transition	He droplets	Gas phase
$F = 1.5e \leftarrow F = 1.5f$		1876.061 845
$F = 0.5e \leftarrow F = 1.5f$	1875.607	1876.062 519
$F = 1.5e \leftarrow F = 0.5f$		1876.068 692
$F = 0.5e \leftarrow F = 0.5f$	1875.614	1876.069 366
$F = 0.5f \leftarrow F = 0.5e$		1876.083 091
$F = 0.5f \leftarrow F = 1.5e$	1875.642	1876.083 757
$F = 1.5f \leftarrow F = 0.5e$		1876.089 927
$F = 1.5f \leftarrow F = 1.5e$	1875.648	1876.090 594
$F = 2.5e \leftarrow F = 1.5e$		1881.034 24
$F = 1.5e \leftarrow F = 0.5e$		1881.034 99
$F = 1.5e \leftarrow F = 1.5e$		1881.035 66
$F = 0.5e \leftarrow F = 0.5e$		1881.035 89
$F = 0.5e \leftarrow F = 1.5e$		1881.036 55
$F = 0.5f \leftarrow F = 1.5f$	1879.386	1881.047 86
$F = 1.5f \leftarrow F = 1.5f$		1881.049 99
$F = 2.5f \leftarrow F = 1.5f$		1881.053 56
$F = 0.5f \leftarrow F = 0.5f$		1881.054 71
$F = 1.5f \leftarrow F = 0.5f$		1881.056 83
Λ doubling	0.017	0.011
B	1.253	1.655

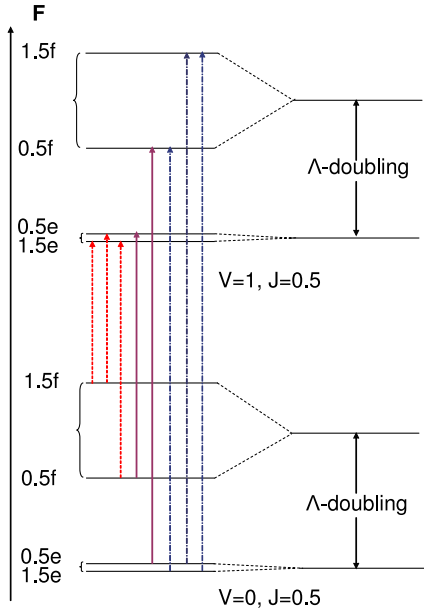


FIG. 2 (color online). Energy level scheme of the hyperfine Q transitions of NO in the gas phase.

internuclear distance was considered to be fixed [13].

$$p = 4 \sum_{\Sigma} (-1)^S \frac{(\Pi | H_{SO} | \Sigma)(\Sigma | B L_y | \Pi)}{E_{\Sigma} - E_{\Pi}}. \quad (2)$$

Here only ${}^2\Sigma$ states have to be taken into account. S is the parity, H_{SO} is the operator for spin-orbit interaction, and L_y is the operator for the y component of the electronic angular momentum. The relevant perturbing electronic ${}^2\Sigma$ states are listed in Table II.

According to Eq. (2), the Λ -doubling parameter p is influenced by three effects: First, p is proportional to the rotational constant B . Since B_{eff} is reduced to 76% of the gas phase value, we expect a decrease of Δ_{Λ} for NO in He droplets in contradiction to our experimental result. Second, the energy denominators in Eq. (2) depend on the energies of the excited Σ states. While the valence states of NO are expected to shift only slightly in an inert matrix, the Rydberg levels are shifted quite strongly to higher energies, because the interaction between the

TABLE II. Overview over the perturbing ${}^2\Sigma$ states [14,15]. Some of the states have valence, others have Rydberg character.

State	Type	Configuration	T_e (cm $^{-1}$)
$X^2\Pi$	Valence	$\dots 5\sigma^2 1\pi^4 2\pi^1$	0
$A^2\Sigma^+$	Rydberg	$\dots 5\sigma^2 1\pi^4 3s\sigma$	43 966
$D^2\Sigma^+$	Rydberg	$\dots 5\sigma^2 1\pi^4 3p\sigma$	53 085
$E^2\Sigma^+$	Rydberg	$\dots 5\sigma^2 1\pi^4 4s\sigma$	60 629
$G^2\Sigma^-$	Valence	$\dots 5\sigma^1 1\pi^4 2\pi^2$	62 913
$H^2\Sigma^+$	Rydberg	$\dots 5\sigma^2 2\pi^4 3d\sigma$	62 473
$I^2\Sigma^+$	Valence	$\dots 5\sigma^1 1\pi^4 2\pi^2$	(63 500)

Rydberg electron of NO and the ground state He atoms is repulsive. Indeed, Vigliotti *et al.* found a blueshift of $0.58 \text{ eV} = 4700 \text{ cm}^{-1}$ for the $A^2\Sigma^+$ state of NO in a H_2 matrix [16]. We assume that the situation is similar for NO in He droplets [17]. In numerical calculations by de Vivie and Peyerimhoff [18], it was shown that the dominant contributions to the Λ doubling in NO are due to the valence excited $G^2\Sigma^-$ and $I^2\Sigma^+$ states, and only about 10% of p is attributed to the Rydberg states. Thus, a blueshift of the Rydberg states would cause only a small decrease of Δ_{Λ} .

Third, the off-diagonal matrix elements in the numerator of Eq. (2) will also be modified as soon as the wave functions involved are exposed to a confinement. The changes in the H_{SO} matrix elements are expected to be small, since the $1/r^3$ weighting in the microscopic spin-orbit Hamiltonian implies that only the inner parts of the wave functions are probed, which are less sensitive to the confinement. Our experimental observation of an unchanged hyperfine coupling which also scales with $1/r^3$ supports this expectation. The L_y matrix elements are expected to increase more strongly, because they are more sensitive to the confinement, since they probe the outer part of the orbitals.

Another possible explanation for the increased Λ -doubling constant could be that, by density fluctuations in the He droplet, the rotational symmetry around the NO axis is slightly perturbed. This effect would lead to a first-order splitting of the twofold degeneracy of the ${}^2\Pi_{1/2}$ ground state of NO. However, it needs large scale dynamics simulations to check this hypothesis.

Next, we discuss the implications of the observation of the $R(0.5)^2\Pi_{1/2}$ transition (Fig. 3) at 1879.386 cm^{-1} . This

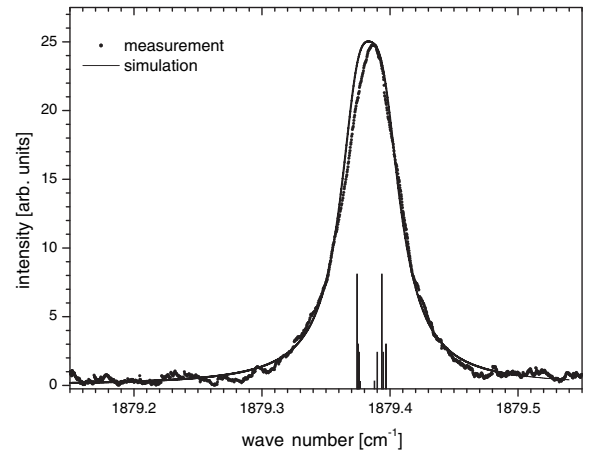


FIG. 3. The $R(0.5)^2\Pi_{1/2}$ transitions of NO in He droplets of the size $N = 2600$. A simulation yields a width of 0.035 cm^{-1} (FWHM) of each of the 10 hyperfine transitions. The simulation accounts for an increased Λ -doubling energy. A stick spectrum shows the line centers according to the redshift and increased Λ -type doubling in He droplets.

line consists of a multiplet of 10 hyperfine transitions [10]. The feature can be fitted to Lorentzian profiles of these transitions while we take into account the increased Λ -type doubling. The fit yields a line width of 0.035 cm^{-1} (FWHM) for each of the hyperfine transitions, which is by more than a factor of 10 increased compared to the Q lines. The analysis of the $Q(0.5)$ and $R(0.5)$ features allows the following conclusions on the coupling to elementary excitations and their role in the relaxation mechanism: (i) The different line widths of the Q and R lines and the Lorentzian line shape of the latter indicate that rotational relaxation from the $J = 1.5$ to $J = 0.5$ level within the vibrationally excited state is the dominating relaxation channel. The widths of the R transitions correspond to a rotational lifetime of 1.52×10^{-10} s for the upper state. (ii) The reduction of the B constant is attributed to a coupling to elementary excitations, most likely the rotons. In bulk liquid He, the roton energy amounts to ca. 6.0 cm^{-1} [19], which is close to the rotational energy of the ($J = 1.5$) level of free NO. The excess energy when relaxing from the $J' = 1.5$ to the $J'' = 0.5$ in the gas phase amounts to $\Delta E(J) = 2BJ'' = 4.965 \text{ cm}^{-1}$. When this is in resonance with the rotons, which provide a very high density of states, we expect increased rotational relaxation rates and a considerable reduction of the $J = 1.5$ rotational energy. An analysis by correlated basis function–diffusion Monte Carlo theory has revealed a very sensitive dependence on the rotational energy for the case of HCCH when its $J = 2$ rotational energy was tuned artificially across the roton energy [4]. However, by experiment it is difficult to study vibrational and rotational relaxation of HCCH separately due to the presence of low lying vibrational modes [20]. We propose that a similar process occurs in our experiments; however, vibrational relaxation can be excluded for NO.

In conclusion, we have measured the infrared absorption of NO embedded in He droplets and resolved for the first time the hyperfine and Λ -type splittings of a radical in superfluid He droplets. We find an increased Λ -type doubling and have discussed the underlying mechanism. The hyperfine structure was found to be unchanged with respect to the free molecule.

The possibility to obtain high-resolution spectra of open shell radicals in helium droplets opens the possibility to study important reactions involving the atmospherically important radical OH and CH in the future.

While the $Q(0.5)$ lines are sharp, the $R(0.5)$ line was found to be broad and Lorentz shaped. This was attributed to rotational relaxation within the vibrationally excited state. The rotational lifetime was deduced to be 1.52×10^{-10} s; the B amounts to only 76% of the gas phase value. Both the rotational lifetime and the reduction of B were

attributed to coupling to elementary excitation of He, in particular, the roton.

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