Intramolecular quantum chaos in doped helium nanodroplets

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Abstract

A mass spectrometric depletion spectrum (17 700–18 300 cm\textsuperscript{-1}) is reported for NO\textsubscript{2} in superfluid (0.37 K) helium nanodroplets. Gas phase NO\textsubscript{2} is believed to be vibronically chaotic at these energies. Transitions are broadened and blue-shifted relative to their gas phase counterparts. The spectrum is fitted reasonably well by setting all of the widths and shifts equal to 7 cm\textsuperscript{-1}. Modest dispersions (i.e., 90\% lie within 2 cm\textsuperscript{-1} of the central values) are consistent with quantum chaos in NO\textsubscript{2}. Relaxation is dominated by interactions of NO\textsubscript{2} with its non-superfluid helium nearest neighbors.

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1. Introduction

Superfluid helium nanodroplets (hereafter referred to as He\textsubscript{n}, where \textit{n} is the number of He atoms) provide convenient environments for carrying out detailed studies of embedded molecules and aggregates under well-characterized, ultracold (0.37 K) conditions \cite{1–3}. Research in this area has flourished following the seminal experiments of Vilesov, Toennies, and coworkers, in which molecular-level manifestations of He\textsubscript{n} superfluidity were revealed in a series of elegant spectroscopic studies \cite{4–7}, and several exciting directions have been identified \cite{8–10}.

At this point in time, a significant number of fundamental and overtone vibrations of molecules and weakly bound complexes in their ground potential energy surfaces (PESs) have been examined \cite{11–13}. In addition, molecular electronic spectra have revealed phonon wings, including a ‘roton gap’, radiationless decay, and details of the dopant–He\textsubscript{n} interactions \cite{14–18}. These studies have been carried out mainly in the regime of regular nuclear dynamics, where the goodness of vibrational quantum numbers is high. On the other hand, vibrational congestion, which often goes hand-in-hand with complex dynamics, has been noted in electronic spectra of large molecules, e.g., tetracene and pentacene \cite{15,16}. However, in systems of such high dimensionality (i.e., having 84 and 108 vibrational degrees of freedom, respectively), state-resolved studies in the regime of chaotic dynamics are not feasible.

This article reports the first spectroscopic observations – in a regime where the intramolecular
dynamics are believed to be chaotic — of a small molecule embedded in superfluid helium nanodroplets. Chaotic and regular dynamical regimes differ qualitatively, and quantum-chaotic dynamics of the molecule under consideration (NO₂) has been implicated throughout the energy range of interest [19].

In the study reported here, the chaotic system is coupled weakly to an exceptionally well-characterized bath. The ultracold Heₜ host is used to probe the dopant by introducing two observables that are expected to provide signatures in and near the regime of quantum chaos: spectral shifts and widths.

It is advantageous that a great deal is known about NO₂. Strong mixing of the A²B₂ and X²A₁ states above the conical intersection of these PESs, due to breakdown of the Born–Oppenheimer approximation, yields A₁ and B₂ vibronic species, whose only means of communication in collision-free environments is rotation [20,21]. Each of these vibronic manifolds is believed to be quantum chaotic, e.g., for a given set of good quantum numbers (J and M_J) the nearest neighbor spacings follow a Wigner distribution [22]. Because NO₂ is small, its eigenstates are widely separated, i.e., they are ~10 cm⁻¹ apart on average for each vibronic manifold at E ~ 18 000 cm⁻¹.

Thus, NO₂ is a good candidate for carrying out state-to-state studies of a chaotic molecular system embedded in Heₜ, inviting several questions: Will there be a correspondence between the respective line positions and intensities in the Heₜ and gas phase environments? What will be the shifts of the center frequencies relative to the gas phase values, and what is to be expected for the magnitudes and distributions of the decay widths associated with deactivation by the helium? What are the implications for photochemical studies? And so on.

It will be shown below that absorption lines are readily identified and related to their gas phase counterparts. With the current, admittedly modest, signal-to-noise ratio (S/N), the spectra can be fitted surprisingly well by blue-shifting all of the gas phase R₀ line positions by 7 cm⁻¹, adding 7 cm⁻¹ widths to all of the lines, and adjusting the peak intensities to fit the spectrum. Fits obtained by fine-tuning the individual shifts and widths indicate modest dispersions around the central values. It is suggested that the results can be understood by consideration of the couplings that arise from the Heₜ perturber acting on the states of NO₂.

2. Theoretical considerations

Assume that the helium that surrounds embedded NO₂ acts as a perturbation to the gas phase molecule, and consider matrix elements that account for mixing, shifting, and deactivation of the NO₂ levels. Leaving aside rotation, which plays a secondary role, each of the NO₂ vibronic levels can be expanded in a basis of the vibrational levels of the A²B₂ excited and X²A₁ ground PESs, with the xth wavefunction given by:

\[ \psi^x = \sum_j C_j^x \psi_j^A \phi_j^A + \sum_k C_k^x \psi_k^X \phi_k^X, \]

where the summations, with indices j and k, are over the A²B₂ and X²A₁ vibrational levels, respectively; \( \psi_j^A \) is the A²B₂ electronic wave function; \( \phi_j^A \) is the jth vibrational wavefunction of the A²B₂ PES; and \( C_j^x \) is the expansion coefficient for the jth vibrational level of the A²B₂ PES. Likewise, \( \psi_k^X \) is the X²A₁ electronic wavefunction, etc. The A²B₂ part of \( \psi^x \) is much smaller than the X²A₁ part, as is always the case for internal conversion [23].

Now consider perturbations of the NO₂ states, with explicit helium excitations suppressed; deactivation will be discussed below. The matrix elements of the perturbation brought about by the surrounding helium, \( V \), is expressed as:

\[ V_{\alpha\beta} = \left\langle \sum_j C_j^\alpha \psi_j^A \phi_j^A + \sum_k C_k^\alpha \psi_k^X \phi_k^X | V | \right. \]

\[ \left. \times \sum_j C_j^\beta \psi_j^A \phi_j^A + \sum_k C_k^\beta \psi_k^X \phi_k^X \right\rangle. \]
a separable Hamiltonian basis [24]. For example, in the limit of complete cancellation, the surviving matrix elements are diagonal:

\[ V_{\alpha\alpha} = \sum_j |C_j^\alpha|^2 V_{jj} + \sum_k |C_k^\alpha|^2 V_{kk}, \]

where \( V_{jj} = \langle \varphi_j^A | V | \varphi_j^A \rangle \) and likewise for \( V_{kk} \). It is assumed that \( V \) does not couple zeroth-order \( A^2B_2 \) and \( X^2A_1 \) levels. The \( V_{jj} \) and \( V_{kk} \) are the same for all of the \( \psi^\alpha \); only the expansion coefficients change from one level to the next.

According to Eqs. (1)–(3), for a modest energy interval, such as the one studied here (17700–18300 cm\(^{-1}\)) the energy levels will all be shifted relative to their gas phase values by comparable amounts when the mixing is thorough. This differs from the regime of regular dynamics, where shifts are mode-specific. In other words, the chaotic nature of the \( \psi^\alpha \) levels results in vibrational averaging that leads to modest dispersion about the mean of the distribution of shifts. A similar conclusion is reached with the widths: the randomness of the expansion coefficients results in the different \( \psi^\alpha \) levels having comparable decay widths.

The above considerations are intended to provide qualitative guidance; a detailed treatment will be presented in a full paper.

3. Experimental methods and results

The most relevant experimental parameters are indicated schematically in Fig. 1. There are three separately pumped chambers. In the first, \( \text{He}_n \) droplets are produced by expanding ultrapure helium (99.9999%, Spectra Gases) through a 5 \( \mu \text{m} \) diameter hole (National Aperture) that is cooled by using two closed-cycle helium refrigerators (CTI Cryogenics), one of which pre-cools the helium before it enters the nozzle assembly. For the work reported here, the stagnation temperature was 14.5 K and the pressure was 40 bar. The mean size of the clusters produced under these conditions is \( \langle n \rangle \approx 9000 \) [25]. Temperatures were measured with a Si diode sensor (Lakeshore ±0.1 K). The source chamber operating pressure is \( 2 \times 10^{-4} \) mbar.

After passing through a 400 \( \mu \text{m} \) diameter skimmer, the droplet beam passes through a 3 cm long pickup cell containing \( \text{NO}_2 \) (Matheson, 99.5%, used without purification) that is 10 cm downstream from the nozzle. The background pressure (Granville-Phillips gauge) of the second chamber was \( \sim 10^{-7} \) mbar, and the largest signals were recorded with \( 4 \times 10^{-7} \) mbar.

The detection region is separated from the pickup chamber by a 5 mm diameter aperture that

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Fig. 1. Experimental arrangement (not to scale). The source, pickup, and detection chambers are pumped separately. The nozzle is at 14.5 K, and the He pressure behind the nozzle is 40 bar. The laser beam is brought to a focus in the detection chamber to avoid damaging the nozzle.
is 12 cm from the exit of the pickup cell. The background pressure in the detection chamber is \( \sim 10^{-8} \) mbar. The use of turbomolecular pumps in the second and third chambers minimizes problems that arise from contamination by impurities.

A quadrupole mass spectrometer (Balzers) was used to monitor the depletion of signals arising from droplets containing NO\(_2\). The absorption of laser radiation results in the evaporation of He atoms from the droplets, each atom requiring \( \sim 5 \text{ cm}^{-1} \) for evaporation. Thus, \( \sim 3600 \) He atoms are evaporated following the absorption of an 18000 cm\(^{-1}\) photon. This shrinkage results in less efficient electron impact ionization of those clusters that have absorbed a photon, and consequently have a smaller cross-section. This is the basis of the mass spectrometer depletion spectrum. The largest depletions observed in the present study were \( \sim 7\% \) (Fig. 2). The spectrum shown in Fig. 2 was obtained by monitoring \( m/e = 30 \). No significant differences were observed when monitoring different \( m/e \) peaks, i.e., 46 (NO\(_2^+\)), 30 (NO\(^+\)), and 8 (He\(_2^+\)).

The mass spectrometer was installed with its quadrupole axis perpendicular to the molecular beam axis so the laser beam could be overlapped with the molecular beam. The length of this interaction region is \( \sim 75 \) cm, corresponding to a duration of the depletion signal of \( \sim 2.5 \) ms. The electron multiplier output of the mass spectro-
A dye laser (Continuum ND6000, Fluorescein 548 dye) was pumped by the second harmonic of a Nd–YAG laser (Continuum, Powerlite 7020), yielding radiation in the region 546–565 nm. High energy pulses (40 mJ) were used, because of the small NO\textsubscript{2} absorption cross-sections (i.e., \(\approx 10^{-19} \text{ cm}^2\) for the corresponding gas phase transitions [26]). Note that N\textsubscript{2}O\textsubscript{4} does not absorb in this spectral region, making spectral signatures insensitive to the pickup of a second NO\textsubscript{2} by a cluster already containing one NO\textsubscript{2}. To avoid damaging the nozzle, a 50 cm focal length lens was used. Calibration of the laser frequency was carried out by simultaneously recording opto-galvanic spectra with a commercial hollow cathode Al–Ne discharge lamp, as described elsewhere [27].

Fig. 2a shows the experimental spectrum. The scan used a step size of 0.6 cm\(^{-1}\), with a 0.08 cm\(^{-1}\) laser linewidth; 1000 points were recorded. This large step size was deemed appropriate after many scans over smaller frequency intervals, using smaller step sizes, revealed the large linewidths shown in Fig. 2a. Each point averages the results from 3000 laser pulses; approximately 50 h was required to record the spectrum. Fig. 2b shows the \(R_0\) lines recorded by Georges et al. [22] by using LIF, and in Fig. 2c each of these lines has been assigned a 7 cm\(^{-1}\) width, the entire spectrum has been blue-shifted by 7 cm\(^{-1}\), and the peak heights have been adjusted to fit the experimental spectrum. Fig. 2d shows an overlay of (a) and (c).

Varying all of the widths and center frequencies independently provides, of course, excellent fits. Though not unique, they indicate that the dispersions of the distributions of shifts and widths around their central values are modest. For example, 90% of the shifts and widths thus obtained lie within 2 cm\(^{-1}\) of the central values. More quantitative information about the dispersions will be forthcoming when higher quality spectra are available.

To our surprise, we were unable to find a literature report of a uv/visible spectrum of NO\textsubscript{2} recorded under matrix isolation conditions. Thus, an experiment was carried out in which Ne atoms were added to embedded NO\textsubscript{2}. Even a single Ne atom obliterated the structure shown in Fig. 2, resulting in continuous absorption. This underscores the importance of the weak, homogeneous helium matrix.

4. Discussion

A noteworthy aspect of the spectrum presented here is that the shifts and widths do not differ significantly from line to line. Namely, the region 17700–18300 cm\(^{-1}\) can be fitted reasonably well by using the gas phase line positions and a 7 cm\(^{-1}\) blue-shift and a 7 cm\(^{-1}\) width. Because intramolecular coupling in NO\textsubscript{2} is strong, whereas the coupling of NO\textsubscript{2} to the helium is relatively weak, the shifts and widths can be understood on the basis of the model described by Eqs. (1)–(3). In this section, we: (i) argue against effects other than relaxation as the main origin of the widths; (ii) point out an important earlier paper that is germane to the work discussed here; and (iii) comment on the mechanism and model.

4.1. Origin of the widths

The saturation of allowed electric dipole transitions of gaseous molecular absorbers is encountered frequently in experiments that use pulsed laser radiation [20]. Because of the large laser energies used here (i.e., 40 mJ), effects that might accompany efficient optical excitation must be considered. Specifically, can they account for widths of \(\approx 7 \text{ cm}^{-1}\)?

A useful figure-of-merit is the product \(\sigma_{\text{abs}} \Phi\), where \(\sigma_{\text{abs}}\) is the photon absorption cross section and \(\Phi\) is the fluence [28]. Saturation occurs when \(\sigma_{\text{abs}} \Phi\) is comparable to or exceeds unity. For example, with \(\sigma_{\text{abs}} \sim 10^{-19} \text{ cm}^2\), which is characteristic of gas phase NO\textsubscript{2} transitions [26], \(\Phi \sim 10^{19}\) photons cm\(^{-2}\) will result in saturation. Absorption cross-sections of gaseous species are usually reported as empirical parameters that are valid for a given instrumental resolution, often with a measurement linewidth that exceeds the linewidth of the absorber. The estimate of \(\sigma_{\text{abs}} \sim 10^{-19} \text{ cm}^2\) is conservative in light of the fact that our 0.08 cm\(^{-1}\) laser linewidth is significantly larger than the
widths due to spontaneous emission and Doppler broadening. Because the pulses used in our experiment contain approximately $10^{17}$ photons, saturation should be considered for laser beam diameters comparable to, and smaller than, $\sim 1$ mm, which occurs in the focal region (Fig. 1).

Saturation broadening of NO$_2$ transitions cannot, by itself, be responsible for the linewidths, because this would require $\sigma_{\text{abs}} \Phi$ values of $\sim 10^4$ [29], which is unreasonably large. For example, for a $\sigma_{\text{abs}}$ value of $10^{-19}$ cm$^2$, $\Phi$ would have to be $\sim 10^{23}$ photons cm$^{-2}$, and beam diameters smaller than $\sim 10$ $\mu$m would be required. Even then, saturation would occur only over a small fraction of the region where the laser and molecular beams overlap, i.e., near the focal region indicated in Fig. 1.

Photoexcitation followed by relaxation heats the cluster, resulting in evaporation, with the cluster temperature in excess of 0.37 K for the remainder of the laser pulse, as demonstrated by Vilesov and co-workers [15]. For large clusters, the mass spectrometer ionization cross-section is proportional to the geometric cross-section [25], which varies as $n^{2/3}$. In this regime, the one-photon depletion signal for a given cluster size is given by:

$$I_{\text{depl}} = 1 - \left[1 - 3600/n\right]^{2/3}, \quad n > 3600$$

$$= 1, \quad n \leq 3600, \quad (4a)$$

where it is assumed that the absorption of an 18,000 cm$^{-1}$ photon results in the evaporation of 3600 He atoms. Eqs. (4a) and (4b) must be averaged over the distribution of $n$ values, corrected for the fraction of the molecular beam that is overlapped by the laser beam (including its radial intensity dependence), and multiplied by the fraction of the embedded NO$_2$ molecules that absorb a photon. Note that absorption of the second, third, etc. photons takes place with a higher He$_n$ temperature and the NO$_2$ not necessarily in its ground state, and results in the evaporation of most of the helium. The resulting lineshapes may differ from those of one-photon excitation, i.e., they are expected to be slightly narrower than for the one-photon case.

Two additional observations argue against A$^2$B$_2$ ← X$^2$A$_1$ saturation playing an important role. First, saturated transitions would yield comparable intensities for all lines. This is not what is observed; there is an order of magnitude difference between the strong and weak lines in the spectrum shown in Fig. 2. Second, we have recorded a linear fluence dependence of the depletion signal, as shown in Fig. 3. Thus, it is concluded that the large widths are not the result of A$^2$B$_2$ ← X$^2$A$_1$ saturation. Broadening due to excited state absorption has been reported for gas phase NO$_2$ [30]. Again, we argue that the large observed widths cannot be attributed solely to this effect, because $\sigma_{\text{abs}} \Phi$ values of $\sim 10^4$ would be required.

Transitions originating from the lowest few rotational levels are contained in a narrow band of frequencies for each vibronic transition. For example, the rotational widths for a number of molecules embedded in He$_n$ (SF$_6$, OCS, NCCCH, propyne, trifluoropropyne, tert-butyl-acetylene, etc.) are $<1$ cm$^{-1}$ [4,6,11,31]. Only $\Delta K = \pm 1$ transitions with large $A$ rotational constants display large widths [32]. Thus, we believe that rotations do not account for the large widths reported here. Finally, we note that inhomogeneous broadening [27] is insignificant for the cluster sizes and widths reported here.

4.2. The He–NO$_2$ binary complex

In 1976, Smalley et al. [33] recorded spectra of the He–NO$_2$ binary complex, and noted that the
frequencies were blue-shifted by approximately 1.5 cm\(^{-1}\) relative to those of uncomplexed NO\(_2\) for all of the vibronic bands examined. In addition, widths of approximately 0.8 cm\(^{-1}\) (due to dissociation of the complex) were noted for all of the He–NO\(_2\) bands examined.

The origin of these constancies can now be understood as being due to the quantum chaotic nature of the vibronic eigenstates. The number of helium atoms attached to the NO\(_2\) chromophore does not affect this conclusion. It is reasonable to assume that the first shell of He atoms around the NO\(_2\) increases the shifts and widths, and in this sense our results are in accord with this earlier work, though the two sets of experiments were carried out under quite different conditions.

4.3. Mechanism and model

The vibrational relaxation of polyatomic molecules in the regime of regular intramolecular dynamics is known to be mode-specific. Likewise, the predissociation of weakly bound complexes is also known to be mode-specific. The work presented here deals with vibronic levels that each contain numerous combinations of vibrational modes. The fact that the widths and shifts do not vary significantly from one level to the next is consistent with the levels having little mode specific character. Though the origin of this propensity is conceptually straightforward, we cannot yet predict the magnitudes of the widths and shifts, nor their distributions, i.e., dispersions about their mean values.

In bulk liquid helium at 0.37 K, the superfluid fraction is \(\rho_s/\left[\rho_n + \rho_s\right] = 0.99995\) [34]. Likewise, in 0.37 K He\(_n\) droplets having \(\langle n \rangle = 9000\), there will be little normal fluid. With an embedded dopant, there is a boundary between the helium atoms adjacent to the dopant and the surrounding superfluid. The relaxation of NO\(_2\) vibronic levels on a picosecond timescale involves mainly the helium atoms adjacent to the dopant and the surrounding superfluid. The relaxation of NO\(_2\) vibronic levels on a picosecond timescale involves mainly the helium atoms adjacent to the NO\(_2\). This follows from the fact that picosecond relaxation times are too short for an excitation to appear in the superfluid. Namely, the NO\(_2\)–superfluid distance is \(\sim 5\) Å, which is too large to be accessed in a picosecond, given that the speed of sound in helium is 200 m s\(^{-1}\). Thus, relaxation creates particle-like excita-

The proposed model enables some predictions to be made: (i) Photoinitiated unimolecular reactions will be quenched near their gas phase thresholds, because reaction rates must be at least comparable to deactivation rates if there is to be appreciable reaction. (ii) With NO\(_2\), spectra will show (congested) structure at energies up to 25 000 cm\(^{-1}\) (for gas phase NO\(_2\), \(D_0 = 25128.5\) cm\(^{-1}\) [35]). (iii) Unlike the gas phase, as \(D_0\) is approached from below, the molecular phase space will not increase along the NO\(_2\) reaction coordinate, because a ‘helium blockade’ will deny access to the large-\(r\) region of the molecular phase space.

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