Laser spectroscopy of chemically reactive species

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ABSTRACT

We report the observation of stimulated emission pumping spectra in the NCO radical formed in a supersonic free jet expansion by the reaction between photolytically generated CN radicals and O₂. The spectra give rotationally resolved information on high lying vibrational levels that are difficult or impossible to detect by conventional single photon spectroscopic techniques. These new data provide detailed insight into the Renner-Teller, spin-orbit and Fermi-resonance coupling in the molecule. They also provide a solid basis for future state-selected chemical and dynamical studies involving this important radical species.

2. INTRODUCTION

In this talk, we focus on recent investigations of the vibronic structure of small molecular free radicals at energies far above the zero point level in their ground electronic state. The experiments discussed make use of a technique known as stimulated emission pumping (SEP) spectroscopy which is a laser optical double resonance experiment that allows access to such levels with high sensitivity and specificity. The technique was first described by Kittrell et al.¹ in 1981 and during the following decade was applied to a large number of molecular species and has significantly increased our understanding of intramolecular motion at high internal energies.² The focus of our own work has been on the detection and characterization of vibrationally excited states of chemically reactive species for which little spectroscopic information had previously been available. While modern infrared laser absorption and FTIR absorption and emission experiments have led to a vast increase in our knowledge of the structure of such species in their zero point and vibrational fundamental levels,³ for relatively few such species have vibronic energy levels above the vibrational fundamentals been characterized by high resolution spectroscopy. SEP allows such levels to be routinely accessed and we have reported the application of this technique to investigations of C₃,⁴ NCS⁵ and most recently NCO.^{6,7} In the present paper, we discuss some of the more recent experimental and theoretical results derived from experiments aimed at characterizing the Renner-Teller effect (RTE) in highly excited vibrational levels of NCO. While our interest is primarily spectroscopic, none of the levels relevant to the present work had previously been detected at high resolution. The results also form a sound basis for future state-to-state chemical dynamics studies on this important radical species.

3. EXPERIMENTAL DETAILS

Only a brief outline of the technique will be given here; more details are available in the literature.^{6,7,8} The SEP process involves two photons as shown schematically in fig. 1. A *pump* laser pulse excites the molecule under study from a low energy, single rovibrational level in the ground electronic state to a bound rovibrational level in an excited electronic state. For the species studied in our work, the usual fate of this excited level is fluorescence back to a large number of different rovibrational levels on the ground state surface, schematically indicated by the arrows to the dotted levels in fig. 1. The lifetime of the excited or pumped state is governed by the sum of the rates of the individual transitions to these different levels, which in turn depend on the Franck-Condon and Hönl-London factors for the individual transitions. If, instead of waiting for spontaneous emission to occur, we interrogate the pumped level with light from a second u.v. or visible laser,

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the *dump* laser, tuned to a different wavelength that matches one of the allowed fluorescence transition, we can stimulate transitions from the pumped level to a single one of the ground state levels connected to it by fluorescence transitions. Further, the competition between the spontaneous fluorescence and the laser excited emission can be strongly tilted in favor of the stimulated process by the use of a high power laser pulse. The stimulated process occurs only during the time that the second laser pulse is present and we can detect the occurrence of the process by monitoring the total pump laser induced fluorescence (LIF) which, when viewed at right angles to the direction of propagation of both laser beams, will exhibit a depletion when the dump laser frequency is resonant with an allowed transition.

In practice, in our experiments, the NCO sample was prepared by excimer laser photolysis, at 193 nm, of a mixture of cyanogen, (CN)₂, oxygen, O₂, and nitrogen, N₂ gases in the ratios 1.5:3.0:5.5 respectively. The gas mixture was premixed and expanded in a pulsed supersonic free jet expansion. The photolysis laser beam was focussed to a spot immediately below the nozzle orifice. Absorption of the 193 nm radiation caused dissociation of the cyanogen, and the resulting CN radicals attack the oxygen:

The NCO radical product cooled down to rotational temperatures between 10 and 25 K during the remainder of the expansion in our apparatus. The radicals were probed by beams from two excimer pumped dye lasers in the collision free region of the expansion in the center of a stainless steel vacuum chamber pumped by a 6000 l/min expanded 10" diffusion pump.

Laser induced fluorescence was collected at right angles to both the laser beam direction and the axis of the free jet expansion. The fluorescence was either imaged directly onto a photomultiplier tube or focussed onto the slit of a 0.3 meter monochromator which allowed the LIF to be dispersed. In the former arrangement, the total fluorescence monitored as a function of pump laser wavelength yields a fluorescence excitation spectrum, while dispersing the fluorescence keeping the pump laser fixed on an absorption feature gives a dispersed fluorescence (DF) spectrum. The excitation spectrum primarily gives information on levels in the upper electronic state, while the DF spectrum gives information on levels in the ground state at a resolution sufficient to separate typical vibrational but not rotational energy level spacings. The DF spectra also provide the "low resolution" map of the vibronic level structure necessary before the high resolution and more time consuming SEP experiments can be attempted. Examples of all three techniques are discussed below.

4. RESULTS

4.1. LIF excitation spectra

Figure 2 shows an example of an excitation spectrum of NCO obtained in our apparatus. The electronic band system involved is the well known⁹ $\tilde{A}^2\Sigma^+ - \tilde{X}^2\Pi$ transition and in the figure, we show the $(v_1, v_2, v_3) = (100)-(000)$ $^2\Pi_{3/2}$ band. Note that for NCO, the conventional vibrational numbering system is based on that for a hypothetical molecule of D_{∞h}

Figure 1 Schematic of the SEP process. Two laser pulses sequentially cause excitation and stimulated emission resulting in a single prepared level.

symmetry. ν_1 , nominally the CN stretching vibration, closely approximates to the symmetric stretch of, for example, CO_2 while ν_2 is the bending vibration and ν_3 is the CO stretch which approximates to the antisymmetric stretch in CO_2 . The $\tilde{A}$ - $\tilde{X}$ band system is a perpendicular transition and the rotational structure of the strongest bands is always similar to that shown in fig. 2. Four rotational branches can be recognized in this example: P_1 , Q_1 , R_1 and ${}^3R_{21}$ ¹⁰ in order of increasing frequency. At the low temperature of the source in our experiments, these branches can be clearly resolved for the lowest rotational levels. Although the rotational distribution cannot be accurately characterized by a single temperature, it approximately corresponds to between 10 and 15 K.

Interestingly, we find that the higher (${}^2\Pi_{1/2}$) spin-orbit component is almost completely cooled out; transitions from it are very weak in our source. In contrast, the bending vibration is incompletely cooled and we have recently observed hot bands originating in $\nu_2 = 1$ with good signal to noise. The reaction between CN and O_2 is known¹¹ to result in NCO radicals containing a very high degree of bending excitation so incomplete cooling in the expansion is not entirely unexpected. Although some information on low energy vibrationally excited levels is available from such hot band spectra, the strength of the LIF excitation experiment here lies in establishing vibration-rotation structure in the excited electronic state. This is required before the ground state rovibronic level structure at higher energies can be probed by SEP. Broad, low resolution, information was initially obtained by setting the pump laser to excite a feature in the excitation spectrum and analyzing the LIF using a monochromator.

4.2 Dispersed fluorescence spectra

When the pump laser is held fixed at a wavelength corresponding to a spectral line in the excitation spectrum and the resulting fluorescence dispersed using a small monochromator, a spectrum such as that illustrated in fig. 3 is obtained. Here the laser was tuned to pump a level with one quantum of ν_3 excitation in the $\tilde{A}{}^2\Sigma^+$ state of NCO. The strongest features in the spectrum are transitions to levels involving excitation of the same mode in the ground state of the radical. The x-axis wavenumbers in this figure give the energy in the ground state relative to the lowest (${}^2\Pi_{3/2}$) spin-orbit component of the zero point vibrational level. The first feature above this level represents emission back to the excited spin-orbit component which lies some 96 cm^{-1} above the ${}^2\Pi_{3/2}$ one. The strong pair of lines around 2000 cm^{-1} correspond to the $\nu_3'' = 1$ level, and the $\nu_3'' = 2$ components are located above 3800 cm^{-1} . The only other strong features are

Excitation Fluorescence Spectra of NCO

Figure 2 Excitation spectrum obtained for the $\tilde{A} (100) {}^2\Sigma^+ - \tilde{X} (000) {}^2\Pi_{3/2}$ band of NCO.

NCO DF Pump (001) ${}^2\Sigma^+$

Figure 3 Dispersed fluorescence spectrum of NCO obtained following excitation of the $(100) \tilde{A} {}^2\Sigma^+$ level.

associated with the fine structure states of the (101) level around 3200 cm^{-1} . This spectrum tells us that the electronic band system is nearly Franck-Condon diagonal in the ν_3 vibration and that the ν_3 mode is not strongly mixed with either of the other vibrational modes in either electronic state.

The spectrum can be contrasted with that shown in fig. 4 where the laser pumps the (100) level in the excited electronic state. Here, the simple structure evident in fig. 3 is missing. In fact, the ν_1 vibration is strongly mixed with ν_2 in both electronic states due to Fermi-resonance between (100) and (020). In addition, the simple pattern of pairs of spin-orbit components evident in fig. 3 is completely changed by the RTE in the ground state. The complex pattern of vibronic states that give rise to the spectrum in fig. 4 is due to coupling between the electronic orbital and nuclear vibrational angular momenta which manifests itself in NCO as a strong lifting of the degeneracies associated with the orbitally degenerate electronic state and the doubly degenerate bending vibration. We consider more details of the effect and the interaction between the RTE, Fermi-resonance and spin-orbit coupling below.

Figure 4 Dispersed fluorescence spectrum of NCO obtained following excitation of the (100) $\tilde{A}^2\Sigma^+$ level.

The spectral patterns associated with bending vibrational excitation in the ground state make unambiguous assignments of DF spectra in NCO rather difficult even for the relatively modest vibrational excitation corresponding to the energies in fig. 4. In order to be certain of making the correct assignment, additional higher resolution spectral information, which shows the rotational structure in the vibronic levels, is required. While higher resolution spectra can in principle be obtained by using a larger

grating or Fourier transform instrument, experience tells us that the trade off between sensitivity and resolution limits how far one can travel along this path. In addition, and of central importance to this meeting, it is not possible to employ a spontaneous fluorescence technique to generally prepare specific excited vibronic levels for state-to-state chemistry studies. Both of these shortcomings can be addressed by the use of SEP as we shall now show.

4.3 Stimulated emission pumping spectra

An SEP spectrum is obtained by positioning the pump dye laser wavelength to match a chosen line in the excitation spectrum, as for the DF experiment, and scanning the dump laser wavelength across a vibronic band in the DF spectrum. Experimentally, the SEP spectra were obtained by monitoring the pump laser fluorescence as a function of the dump laser wavelength. A resonance between the dump wavelength and an allowed emission transition is detected as a measured depletion in the pump laser induced fluorescence, viewed at right angles to the direction of propagation of the laser beams, after the dump laser fires. Figure 5 shows some examples of SEP spectra to rotational levels in the (002) $\tilde{X}^2\Pi$ spin-orbit components of NCO. The pump laser was tuned to excite the indicated rotational transitions in the (002) $\tilde{A}^2\Sigma^+$ - (000) $\tilde{X}^2\Pi_{3/2}$ band. In general, we expect, and find, four rotational transitions in each SEP spectrum. These correspond to the four branches in the excitation spectrum discussed above. The weak $^{\circ}R_{21}$ branch lines are sometimes lost in the noise, but may be clearly seen in favorable cases. One strength of the SEP technique is that the spacings between the lines in the spectra give rotational intervals in the prepared level. In addition, the difference between the two laser wavelengths

combined with the known rotational intervals in the pumped level give the absolute energy of the prepared level directly. In more complex spectra, the spectral simplification that SEP shares with all double resonance techniques may be used as an aid to spectral assignment, however this is not necessary in the present excitation spectra.

We have recorded SEP spectra to levels with $v_3 = 1, 2$ and 3 and used the data to determine the absolute positions of these levels to approximately 0.1 cm^{-1} and the low J rotational structure in them to nearly 0.01 cm^{-1} accuracy. Table I summarizes the major results. We see that there is a monotonic increase in the effective spin-orbit coupling constant with increasing v_3 . This reflects a trend towards dissociation to $\text{NC} + \text{O}$ where the spin-orbit splitting correlates with the atomic oxygen value. The rotational constants show the expected decrease for the same reason. The T_0 values can be used to estimate $\omega_3 = 1950.902$ and $x_{33} = 14.78 \text{ cm}^{-1}$. ω_3 here is still an effective number because anharmonicities such as x_{13} and the corresponding $\nu_2 - \nu_3$ cross terms have yet to be determined. Further experiments are planned in order to measure these quantities and so characterize the harmonic and anharmonic force field for the ν_3 mode in NCO more accurately.

Figure 5 SEP spectra to rotational levels in the fine structure states of (002). Pump transitions are in the (002) - (000) $^2\Pi_{3/2}$ band.

Table I Molecular Parameters for $(00v_3)$ levels in $\tilde{X}^2\Pi \text{ NCO}^a$

Level	T_0	A	B
(000)	—	-95.5817(6)	0.389514 ^b
(001)	1921.350(10)	-97.084(10)	0.386178 ^b
(002)	3813.148(11)	-98.9459(66)	0.382875(72)
(003)	5675.082(11)	-102.3154(77)	0.380075(84)

Footnotes

^a In vacuum wavenumbers with one standard deviation in parenthesis.

^b Fixed at values determined previously.⁶

The SEP results for ν_3 also confirm the qualitative result that is illustrated by the DF spectrum in fig. 2. This vibrational mode is only very weakly coupled to the other vibrations in the radical. The (003) $^2\Pi_{3/2}$ level was found to lie between the fine structure components of the (042) $\mu^2\Pi$ level as graphically illustrated in fig. 6. Here the transitions to the (003) level are indicated by the + symbols. They lie within a few wavenumbers of rotational levels of the same J in the (042) level yet are found to be at the position estimated by extrapolation from (000), (001) and (002) within the experimental uncertainty. This remarkable result can be rationalized when it is remembered that, for a $D_{\infty h}$ species, the two levels have different symmetries, another piece of evidence for the "antisymmetric" stretching character of the ν_3 vibration in NCO.

We now move on to the more complicated case of excited vibrational levels in NCO associated with the bending and lower frequency stretching vibrations. As mentioned above, such levels are strongly perturbed in NCO due to a combination of the RTE, spin-orbit coupling and Fermi-resonance. The physical basis of the RTE is an electrostatic interaction between the electrons and the dipole moment of the nuclei in a bent configuration. As the nuclear configuration changes from linear to bent, the two components of the degenerate electronic state separate and we can think of two states described by wavefunctions with maximum amplitudes parallel and perpendicular to the plane of the bent nuclei. These electronic states are degenerate at the linear configuration and diverge in energy as the molecule is bent. Each supports its own set of vibrational levels which, to a zero order approximation, will be given by the solutions to the vibrational wave equation for the individual potentials. Renner's

contribution was to recognize that a term in the Hamiltonian describing the molecule exists that connects vibrational functions associated with the different electronic surfaces. In this case, energy levels cannot be thought of as belonging to one or the other electronic surface independently. Every wavefunction contains contributions from both electronic wavefunctions and their associated vibrational functions. Renner introduced a coupling parameter, ϵ , which is a measure of the gap between the two electronic potential surfaces, and showed how the energies of the vibronic states associated with bending excitation can be expressed in terms of an expansion in powers of ϵ .

Nowadays, the energy levels can be calculated to almost any desired precision by numerical methods and the problem is usually cast in terms of deriving the eigenvalues of an effective Hamiltonian operator, spanning the components of the degenerate electronic state, and whose parameters are related to the shape of the bending potential energy surfaces and electronic properties such as the spin-orbit coupling.

Figure 7 shows some low lying vibronic levels in NCO associated with ν_1 and ν_2 . The levels of $^2\Pi$ vibronic symmetry in the figure may be seen in the DF spectrum shown in fig 4. While approximate vibronic energy level positions may be extracted from DF spectra, some close lying levels are not resolved and ambiguities in assignments cannot be resolved without rotational level information. In addition, accurate level positions are required in order to assess the reliability of model descriptions of the energy levels in molecules such as NCO that suffer strong vibronic interactions. For these reasons, we have measured SEP spectra to many of the levels associated with $\nu_2 \leq 4$ and all the levels involving excitation in ν_1 that are in Fermi-resonance with them. The data provide a good basis for assessing the accuracy of model descriptions and also open up the way for future state selected chemistry studies of discrete levels with different vibronic properties in the radical.

We first consider levels associated with (020) and (100) which as shown in fig. 7 lie within a few hundred wavenumbers of one another. Note that in (020) there are two levels of $^2\Pi$ symmetry, corresponding to $|\Lambda + \ell| = |K| = 1$ where Λ is the electronic orbital and ℓ is the vibrational angular momentum projection on the linear axis. These two are conventionally labeled¹² the μ and κ $^2\Pi$ levels, μ being the lower. In fact levels with $K < \nu_2 + 1$ exist as pairs in general and are termed non-unique levels. Those levels with $K = \nu_2 + 1$, such as the (010) $^2\Delta$, are termed unique levels and to a large extent retain the spin-orbit splitting of the zero point level of the radical. The (020) μ and κ $^2\Pi$ levels together with the (100) level form a Fermi-resonant polyad in NCO comprising of a total of 6 fine structure components. In the non-

Figure 6 SEP spectra to the (003) $^2\Pi_{3/2}$ component which lies very close in energy to the (042) μ $^2\Pi$ levels. The (003) levels are indicated by a +.

unique levels, the spin-orbit splitting is quenched by the RTE and the splitting between the two components is too small to be resolved in the DF spectra in figs. 3 and 4, for example. However, these splittings provide crucial information on the combined RTE, spin-orbit and Fermi-resonance coupling in the molecule and their observation was one of the primary objectives of the SEP experiments.

Figure 8 shows an example of an SEP spectrum to rotational levels in the (020) $\mu^2\Pi$ fine structure components. This spectrum was obtained following excitation of the $P_1(11/2)$ transition in the $(100)\tilde{A} - (000)\tilde{X}$ band around 415 nm.⁹ The usual four rotational branches per fine structure component are clearly evident here. The lines correspond to fluorescence depletion of less than 10% in this case and the transitions are quite difficult to observe despite the fact that in the DF spectrum (fig. 4) the corresponding fluorescence is strong. Part of the reason for this difficulty is due to amplified spontaneous emission (ASE) from the dump laser which excites broad band LIF from weakly populated hot vibrational levels in this region of the NCO spectrum. This additional LIF causes additional noise in the spectrum.

In the region of the (040)/(120)/(200) Fermi-resonant polyad, there are 5 levels of $^2\Pi$ symmetry, hence 10 fine structure components. Previously, we have reported⁷ the observation of SEP transitions to 8 of them. Subsequently,⁸ we have detected the final pair of levels, associated with the (040) $\mu^2\Pi$ vibronic state. These were also detected following excitation of $(100)\tilde{A}^2\Sigma^+$ as the intermediate state. Fluorescence to the (040) $\mu^2\Pi$ levels from this state is very weak; the band in question lies at about 1960 cm^{-1} in fig. 4, between the strong pair of fine structure levels associated with (001) around 2000 cm^{-1} . The detection of SEP spectra for such a weak transition is a remarkable demonstration of the sensitivity of the technique in favorable circumstances. For the dump laser wavelengths required, around 452 nm, there are no hot band absorptions in our jet cooled sample, so ASE induced fluorescence is negligible. Under these circumstances, the dump laser intensity can be increased and appreciable population change for even weakly allowed transitions effected.

The analysis of the data has been carried out using separate perturbation theory-based models for the two sets of Fermi-resonant polyads. Some of the major quantities determined are given in table II. Despite the abundance of the data, it was not possible to determine all of the parameters appearing in the effective Hamiltonian describing these states. The main results so far obtained are the determination of the positions of the various vibrational levels and reliable values for the Fermi-resonance parameters for the first time. The unsatisfactory aspect of the analysis is that although the two sets of

Figure 7 Vibronic levels in NCO with $v_2 = 0, 1$ and 2 and $v_1 = 1$. Levels of $^2\Pi$ symmetry shown here are evident as the strongest features in fig. 4.

Figure 8 SEP spectrum to rotational levels in the (020) $\mu^2\Pi$ level of NCO. The pumped transition is $P_1(11/2)$ in the $(100)-(000)$ band.

levels, (020)/(100) and (040)/(120)/(200), were fit satisfactorily to an approximate model that included perturbation theory corrections to fourth order,^{13, 15} several parameters had to be held fixed. Most notably these included the spin-orbit constants, the RT parameter, ϵ , and the parameter g_K ¹⁴ which represents Coriolis induced mixing between the ground $^2\Pi$ electronic state and excited states of $^2\Sigma$ (presumably mainly the $\tilde{A}$ state in NCO), and $^2\Delta$ symmetry. In the near future, we intend to attempt to fit all the existing high resolution data on bending states in the ground electronic state of the radical to a complete Hamiltonian, including end-over-end rotation and all the smaller anharmonic contributions to the energy

Table II Major parameters determined from SEP data for $^2\Pi$ states with $v_2 \leq 4$, $v_1 \leq 2$.^a

Quantity	Value	Quantity	Value
A_{v00}	-95.5871 ^b	W_1	25.951(37)
A_{v20}	-95.2609 ^c	W_2	0.890(21)
A_{040}	-94.9460 ^c	$\epsilon\omega_2(020)^d$	-75.965(16)
G_{100}	1251.329(53)	$\epsilon\omega_2(040)^d$	-74.6600(63)
G_{200}	2496.038(22)	ϵ	-0.1436 ^e
G_{020}	1070.605(26)		
G_{120}	2319.157(20)		
G_{040}	2151.650(27)		

Footnotes

- In wavenumbers with one standard deviation of the fitting in parenthesis.
- The spin-orbit constant for levels with just v_1 excitation was held fixed at the value for the vibrationless level.
- Spin-orbit constants for (0 v_2 0) levels were extrapolated from the value for the (000) and (010)¹⁰ levels.
- Different effective values for the RT coupling $\epsilon\omega$ were required for the two Fermi-resonant polyads. See text for details.
- The quantity ϵ is dimensionless. It was held fixed at the values determined in ref 10.

identified by Brown and Jørgensen. It seems probable that the absence of states of symmetry other than $^2\Pi$ in the SEP dataset causes some of the indeterminacies identified in our earlier analysis and the inclusion of existing data from earlier work on the high resolution electronic spectrum of the radical¹⁰ should help in this regard. In another attempt to address this shortcoming, we have recorded SEP spectra to $^2\Sigma$ states associated with (030) and (110) another Fermi-resonant pair of levels. Some examples of the spectra are shown in fig. 9. These spectra were also obtained pumping the (100) $\tilde{A}$ intermediate level. Analysis of these data has only just begun and progress will be reported at the meeting.

SUMMARY

Many rovibronic levels in the ground state of NCO have been detected at high resolution for the first time. These results will be of use in future chemical dynamics studies involving the radical and together with the existing data in the literature will provide a large dataset for assessing the reliability and utility of quantum mechanical models of the RTE in linear, 15

Figure 9 SEP spectra to rotational levels in the NCO (030) $\mu^2\Sigma^+$ level. Pump transitions are in the (100) $\tilde{A}^2\Sigma^+$ - (000) $\tilde{X}^2\Pi_{3/2}$ band.

valence electron species, exemplified by NCO. In particular, it is to be hoped that the data will lead to a reliable determination of harmonic and anharmonic parameters describing the potential energy surface of the radical for the first time. Brown and Jørgensen¹⁵ have shown that there are, in principle, 14 anharmonic parameters for a molecule of this type although the effects of some of them are likely to be small for the levels accessed in the SEP experiments to date. Finally, one of the initial aims of these experiments was to investigate regions of the potential surface of NCO where conversion to the higher energy isomer CNO is possible. The exact energy of this isomer is not known but crude estimates place it some 12 000 cm^{-1} above the ground state¹⁶ of NCO. We are likely, therefore, far from reaching this goal but understanding the detailed spectroscopy of the radical at energies of less than half this value has turned out

to be a challenging and fascinating task.

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