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J-dependent linewidths for the (110)–(000) band of the $\tilde{A}\,^1A''$–$\tilde{X}\,^1A'$ transition of HNO studied by cavity ring-down spectroscopy

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Cavity ring-down spectroscopy of HNO in the range 17 540–17 590 cm^{-1} reveals that lifetime broadening contributes to the linewidths of the $\tilde{A}\,^1A''$–$\tilde{X}\,^1A'$ (110)–(000) $K' = 4$–$K'' = 3$ subband rotational transitions. The deconvoluted predissociation-induced widths for the rotational levels of the upper state depend on the value of J', with the deduced lifetimes decreasing from 310 ± 160 to 40 ± 6 ps for $J' = 4$–16.

Cavity ring-down spectroscopy (CRDS), first developed by O'Keefe and Deacon,[1] has been shown by a number of recent studies to be a highly sensitive absorption spectroscopy technique. The CRDS method has to date been applied to high-overtone[2,3] and cluster[4–8] spectroscopy, the determination of absolute transition strengths,[9] and studies of the kinetics of phenyl radical reactions,[10,11] and has been used as a diagnostic for diamond-growth reactors[12,13] and combustion.[14] These studies employed a variety of wavelengths from the infrared[15] to the ultraviolet.[12] In this work, we report first results from a CRDS study of the predissociated $\tilde{A}\,^1A''$–$\tilde{X}\,^1A'$ (110)–(000) band of HNO, from which we have obtained accurate linewidths for the various rotational features. We follow Bancroft *et al.*[16] and label the vibrational states of HNO using the notation $(v_1 v_2 v_3)$, where v_1, v_2 and v_3 refer, respectively, to the number of quanta of the N—H stretch, the N═O stretch, and the HNO bending vibration, rather than using the notation of Freedman[17] who reversed the assignment of v_2 and v_3. The CRDS method, being a direct absorption spectroscopy technique, does not suffer from the loss of signal at the onset of predissociation [$(D_0(H—NO) = 16\,450 \pm 10\ cm^{-1}$] that restricts laser induced fluorescence (LIF) studies of HNO in this spectral region.[18–20]

Line broadening has been reported previously for transitions to the $\tilde{A}\,^1A''$ state of HNO. Bancroft *et al.*[16] observed diffuseness of some rotational lines in the (101)–(000) band. The linewidths in this band increase with increasing K' from *ca.* 0.3 cm^{-1} for lines involving $K' = 1$ to *ca.* 0.7 cm^{-1} for $K' = 4$, with no apparent broadening in the $K' = 0$–$K'' = 1$ subband. Freedman[17] studied the rotational dependence of the observed predissociation of the (101) state, and found J'-dependent linewidths only in the Q branch of the $K' = 1$–$K'' = 0$ subband of the (101)–(000) transition. He reported no line broadening in the (110)–(000) and (030)–(000) bands, both of which lie to shorter wavelength than the (101)–(000) band. For the $K' = 1$–$K'' = 0$ subband of the (101)–(000) transition, Freedman[17] observed linewidths that were greatest for $J' = 5$–9, and invoked a predissociation mechanism involving coupling to one or more accidently near-resonant levels of the $\tilde{X}\,^1A'$ state, which are themselves coupled to the continuum: arguments were presented in favour of this latter coupling being J dependent. In this preliminary communication, we report J'-dependent linewidths in the $K' = 4$–$K'' = 3$ subband of the $\tilde{A}$–$\tilde{X}$ (110)–(000) transition which previous studies of this subband have failed to observe.[16,17] A more complete study of the line broadening in a number of bands of the HNO $\tilde{A}\,^1A''$–$\tilde{X}\,^1A'$ transition using CRDS is in progress and we will report a full survey of the (101)–(000), (030)–(000), (110)–(000) and (111)–(000) bands in a forthcoming publication.[21]

The experimental apparatus is shown schematically in Fig. 1. HNO is formed in a continuous flow by reaction of NO with H atoms, generated in a microwave discharge in H_2, at a total pressure in the range 4–8 Torr. The gas mixture flows through a glass cell, 2.5 cm in diameter, evacuated by a partially throttled turbomolecular pump. The ring-down cavity (RDC) end mirrors are mounted on stainless-steel bellows located at the two ends of the glass cell, and micrometers are used to tilt the mirrors to align the cavity. The mirrors are concave, with a radius of curvature of 1 m, and are mounted at a separation of 1.58 m. Laser light from a dye laser (Spectra Physics PDL-3) pumped by the 532 nm output of an Nd : YAG laser (Spectron), is injected into the RDC through one of the end mirrors. For a specified mirror reflectivity of >99.98% in the wavelength range 550–600 nm, and an incident laser energy of *ca.* 20 mJ per pulse, the initial laser energy entering the cavity is, at most, 4 μJ per pulse. Light escaping from the cavity is detected by a photomultiplier and decay traces are recorded using a digital oscilloscope (LeCroy 9400) and computer. A typical ring-down time (1/*e*) observed for this experimental set-up at a wavelength of 568 nm is 100 μs, corresponding to a laser path length of 30 km. As the spectrum is scanned, the laser wavelength is calibrated using an I_2 LIF cell and an etalon (free spectral range = 0.492 cm^{-1}). We follow the analysis of Romanini and Lehmann[2] and take the logarithm of the ratio of signals measured in two gates set on the exponential ring-down decay to determine absorbances.

In Fig. 2 we present a portion of the $K' = 4$–$K'' = 3$ subband of the (110)–(000) vibrational band of the $\tilde{A}\,^1A''$–$\tilde{X}\,^1A'$ transition of HNO. The accuracy of measured line positions improves on previous grating-spectrometer studies; a full report including more accurate spectroscopic constants and details of positional perturbations for the HNO $\tilde{A}\,^1A''$ state will be published elsewhere.[21] Under the conditions of our experiment, the light pulses propagating in the cavity are not subject to interference effects[22] and thus we are able to scan the spectrum continuously without cavity-mode hopping resulting in missed spectral features. The line shapes and absorption intensities are also expected to be accurately determined. We deduce the contribution to spectral linewidths and line shapes from Doppler broadening and the laser bandwidth by analysis of sharp spectral lines in, for example, the $K' = 0$–$K'' = 1$ subband, that do not exhibit any obvious predissociative broadening. From such features we determine an effective experimental lineshape that is well approximated by a Gaussian function with FWHM of 0.065 cm^{-1}. This linewidth will also include contributions from pressure and power broadening, but at the low pressures of the experiment and the very low laser-pulse energies present in the RDC, these effects are expected to be negligible. Asymmetry doubling contributions to the linewidths are also negligible for $K > 2$: for example, for the $K' = 4$–$K'' = 3$ subband we calculate the splitting of the two components underlying the $^RQ_3(10)$ rotational line to be 0.004 cm^{-1}. Using the experimentally determined Gaussian lineshape function, we fit each of the unoverlapped, predissociation-broadened features to a Voigt

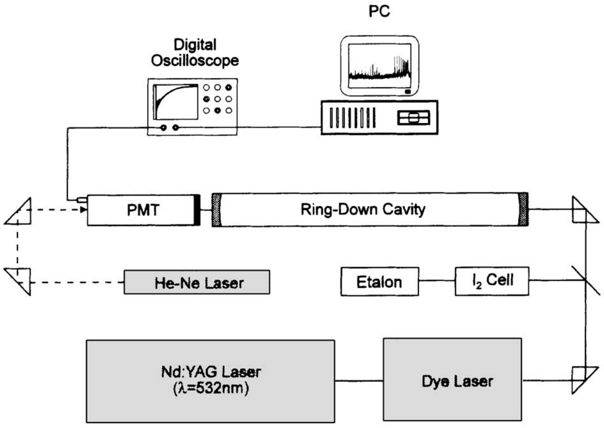

Fig. 1 Schematic diagram of the experimental apparatus used to record absorption spectra of HNO. HNO is generated in a continuous flow upstream of the ring-down cavity. Laser light is injected into the cavity through one end mirror, and the light escaping from the cavity through the other mirror is detected by a photomultiplier tube (PMT). The He–Ne laser is used to aid cavity alignment.

profile and deconvolute the known Gaussian contribution from the Lorentzian component arising from homogeneous (lifetime) broadening. A typical line profile and fit are shown in Fig. 3. The lineshapes show no obvious asymmetry.

We present the measured Lorentzian linewidths (FWHM) obtained from our fits to rotational transitions involving the $J' = 4$–16 levels in the $K' = 4$–$K'' = 3$ subband in Table 1. The corresponding lifetimes[23] of these predissociative J' states are also listed in the table. The measured lifetimes of these levels are clearly dependent on J', as Freedman also found for some members of the (101) state, and we observe a predissociation rate that increases with J'. Freedman[17] argued that the line broadening that he observed in the (101)–(000) band was a consequence of coupling, with an operator of the appropriate (A″) symmetry, inducing predissociation *via* more heavily predissociated but nonetheless still discrete levels of the $\tilde{X}\,{}^1A'$ state. He attributed the J'-dependence of his measured linewidths to a type-c (A′ symmetry) Coriolis coupling of these 'quasi-bound' levels of the $\tilde{X}\,{}^1A'$ state with the continuum associated with this electronic manifold.

Density of state considerations[24] similarly lead us to attribute the present predissociation of the $\tilde{A}\,{}^1A''$ (110) $K' = 4$ rotational levels to coupling with high-lying, discrete rovibrational levels of the $\tilde{X}\,{}^1A'$ electronic state (rather than with accidentally near-resonant levels of the $\tilde{A}\,{}^1A''$ or $\tilde{a}\,{}^3A''$ states). The present observations can be understood by assuming that type-a Coriolis (*i.e.* A″ symmetry, $\Delta K = 0$) interaction provides the dominant coupling between the initially populated $\tilde{A}\,{}^1A''$ state $K' = 4$ levels and an accidentally near-resonant stack of rotational levels associated with a high-lying level of the $\tilde{X}\,{}^1A'$ state. These latter rotational levels are themselves coupled (perhaps by a type-c Coriolis interaction or Fermi resonance) to a continuum of ground-state levels which are dissociative in the N—H stretching coordinate. Rather than attributing the observed J' dependence of the $K' = 4$ predissociation rate to this coupling to the continuum,[17] we explain it by assuming that the two stacks of rotational levels move into closer resonance as J' increases. We observe, but have not yet fully analysed, still broader lines for the $K' = 5$–$K'' = 4$ subband of the (110)–(000) transition, consistent with a model in which the initial $\tilde{A}$–$\tilde{X}$ coupling is brought about by type-a Coriolis coupling. Additional analysis of data for the (110)–(000) band, including the variation of the linewidths with K' as well as J' and the shifts in rotational line positions caused by perturbing states, will help to clarify the predissociation mechanism further.

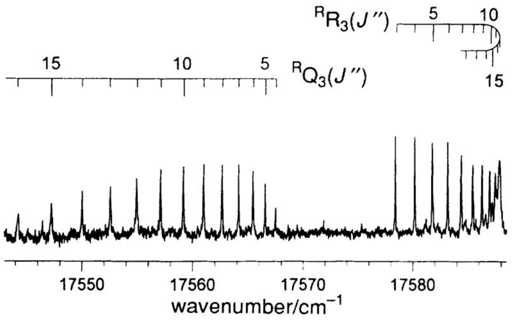

Fig. 2 Absorption spectrum of HNO showing the Q- and R-branches of the $K' = 4$–$K'' = 3$ subband of the $\tilde{A}\,{}^1A''$–$\tilde{X}\,{}^1A'$ (110)–(000) transition

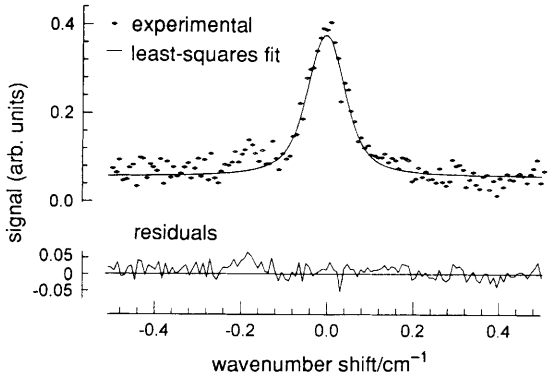

Fig. 3 The ${}^RQ_3(11)$ line together with a Voigt-profile fit to the lineshape. Shown on an expanded vertical scale beneath the data and fitted lineshape are the residuals of the fit. Note that there is no apparent asymmetry to the lineshape.

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Table 1 Lorentzian linewidths (FWHM) and corresponding lifetimes of the J' levels obtained from Voigt-profile fits to the rotational features observed in the HNO $\tilde{A}\,{}^1A''$–$\tilde{X}\,{}^1A'$ (110)–(000) band

J'	Lorentzian linewidth/cm^{-1}	lifetime/ps
4	0.017 ± 0.009	310 ± 160
5	0.020 ± 0.009	260 ± 120
6	0.030 ± 0.009	180 ± 60
7	0.035 ± 0.009	150 ± 40
8	0.046 ± 0.009	120 ± 20
9	0.057 ± 0.009	93 ± 18
10	0.056 ± 0.009	95 ± 15
11	0.081 ± 0.009	65 ± 7
12	0.094 ± 0.009	56 ± 6
13	0.097 ± 0.009	55 ± 6
14	0.100 ± 0.015	53 ± 8
15	0.119 ± 0.015	45 ± 6
16	0.133 ± 0.018	40 ± 6

The quoted errors are $\pm 3\sigma$ from the fit. These errors are consistent with the reproducibility of the linewidths from independent spectra.

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