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QUANTITATIVE HIGH TEMPERATURE ABSORPTION SPECTROSCOPY OF NCO AT 305 AND 440 nm

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Abstract—A spectral survey of NCO absorption near the $P_2 + {}^{P}Q_{12}$ head of the $[A^2\Sigma^+(00^00) \leftarrow X^2\Pi_i(00^10)]$ band was obtained at 1450°K, 0.6 atm using a remotely located cw ring dye laser source and a shock tube. Mixtures of hydrogen cyanide, oxygen and nitrous oxide diluted in argon were shock heated to provide a reproducible steady-state concentration of NCO, and narrow-line absorption was measured in repeated experiments with the laser set at different wavelengths. The peak absorption was found at 440.479 nm (vac). The experimental spectrum was compared with a theoretical model to yield an average Voigt parameter $a \simeq 0.1$. Additional experiments, in mixtures of cyanogen, oxygen and nitrous oxide diluted in argon, provided a known plateau level of NCO, which was used to infer an absolute absorption coefficient $\beta(1450°\text{K}, 0.60\,\text{atm}) = 110(-50, +130)\ \text{cm}^{-1}\,\text{atm}^{-1}$ at 440.479 nm. This value of β corresponds to an oscillator strength of 0.0026 for the $(00^00 \leftarrow 00^10)$ band.

Similar experiments were conducted to monitor the absorption around the R_1 head of the $[B^2\Pi_i(10^10) \leftarrow X^2\Pi_i(00^10)]$ band of NCO, using a frequency doubled cw ring dye laser. The observed spectrum displayed strong broadening, indicating predissociation of the upper state. At the peak absorption wavelength (304.681 nm, vac), we inferred $\beta(1470°\text{K}, 0.63\,\text{atm}) = 40(-19, +48)\ \text{cm}^{-1}\,\text{atm}^{-1}$ and $a \simeq 9$. This value of β corresponds to an oscillator strength of 0.0031 for the $(10^10 \leftarrow 00^10)$ band.

INTRODUCTION

The species NCO is of interest in combustion; for example, it serves as a critical intermediate in the formation of NO during combustion of nitrogen-containing fuels.[1] The spectral characteristics of NCO have been studied extensively, but few attempts have been made to perform quantitative measurements of NCO in a combustion environment.

Dixon studied the $[A^2\Sigma^+ \leftarrow X^2\Pi_i]$ spectrum of NCO from 360 to 450 nm[2] and the $[B^2\Pi_i \leftarrow X^2\Pi_i]$ system from 265 to 320 nm.[3] Bolman *et al.* also investigated the $[A^2\Sigma^+ \leftarrow X^2\Pi_i]$ spectrum.[4] Measurements of the radiative lifetimes of NCO $[A^2\Sigma^+]$ that lead to total oscillator strengths have been reported by Reisler *et al.*,[5] Charlton *et al.*[6] and Sullivan *et al.*[7] In addition, Sullivan *et al.*[8] examined radiative lifetimes in the $[B^2\Pi_i]$ level using laser-induced fluorescence.

Measurements of NCO concentrations are limited. Anderson *et al.*[9] observed the NCO spectrum in a flame by intracavity laser excitation and reported relative NCO concentration profiles. Bullock and Cooper[10] monitored relative NCO absorptions at 438.48 nm in a kinetic study of the gas-phase reactions of CN at low temperature.

In this study, two novel laser absorption diagnostics of NCO were demonstrated behind incident shock waves in a shock tube. Mixtures of C_2N_2, N_2O and O_2 diluted in argon and mixtures of HCN, N_2O and O_2 diluted in argon were shock heated to generate reproducible levels of NCO under specified conditions of pressure (0.6 atm) and temperature (1450°K). Narrow-linewidth absorption spectra around 440.5 and 304.7 nm were mapped out by conducting a series of nearly identical experiments, each at a different laser wavelength. Using the known levels of NCO from the C_2N_2 mixtures, absolute peak absorption coefficients near 440.5 and 304.7 nm were inferred and compared with theoretical models to extract band oscillator strengths and Franck–Condon factors at both wavelengths.

In this paper, the experimental facility and optical techniques will first be described, then the spectroscopic models and results for the two techniques will be presented.

EXPERIMENTAL STUDIES

The experiments were conducted behind incident shock waves in a 15.24 cm internal diameter pressure-driven shock tube.[11] Shock speeds varied between 1.14 and 1.17 mm/μsec, with attenuation of 0.3%/m or less. Typical leak plus outgassing rates were 3–5×10^{-5} torr/min. Gases were taken directly from commercial cylinders (Matheson) with the following purities: O_2 and N_2O (> 99.9%); C_2N_2 (1.01% diluted in argon; HCN and CNCl < 50 ppmv, $O_2 < 20$ ppmv, $CO_2 < 20$ ppmv); HCN (Airco, 7.4% diluted in argon; H_2O, SO_2, O_2 and $CO_2 < 1$ ppmv).

(a) *Experiments at* 305 nm

The absorption from the R_1 band head of the $[B^2\Pi_i(10^{1}0) \leftarrow X^2\Pi_i(00^{1}0)]$ band of NCO at 304.68 nm (vac) was observed using the optical set-up shown in Fig. 1. The laser system consisted of an Ar^+ laser (Spectra Physics model 164) and a ring dye laser (Spectra Physics 380C), frequency-doubled using an intracavity crystal (AD*A) placed in a temperature-controlled oven.[12] The available power from the Ar^+ laser (4 W all lines) provided a typical u.v. dye laser output of 5 mW. Single-mode operation of the visible dye laser beam was verified using a confocal interferometer (Spectra Physics model 470, free spectral range 2 GHz). A wavemeter (Burleigh model WA-10) was used to set the visible laser wavelength. The u.v. output was single-passed through the shock tube test section as shown in Fig. 1. An iris was used to block extraneous spontaneous emission from the test gas. A small fraction of the beam was split off before and after passing through the shock tube to enable measurement of the fractional transmission. Prior to each experiment, the laser light was chopped and the reference signal (i_0) and transmitted signal (i) were balanced (i.e., equalized) by adjusting the angle of the beam splitters to vary the surface reflectance, hence the reflected intensity. The detectors (EG & G u.v. 100B photo-diodes) were mounted in an amplifier/filter package with a 240 kHz (−3 dB) cut-off frequency and shielded from the room lights by Corning broadband-pass filters (80% transmission from 300 to 400 nm). The difference signal ($i_0 - i$) and the reference signal (i_0) were recorded on two separate channels of a digital storage oscilloscope (Nicolet Explorer III, d.c.-coupled through a 100 kHz upper frequency cut-off filter). The data were subsequently transferred to a computer for analysis.

Fourteen runs were conducted with the following C_2N_2 mixtures and conditions: N_2O:O_2:C_2N_2:Ar $\simeq$ 4:1:8:987, $T_2 = 1470 \pm 15$°K, $p_2 \simeq 0.63$ atm and $\rho_{21} \simeq 3.36$ (ρ_{21} is the density ratio across the shock and also the ratio of particle time to laboratory time.) For these experiments, the laser was set at nine different wavelengths in the range $304.638 \le \lambda \le 304.752$ nm (vac).

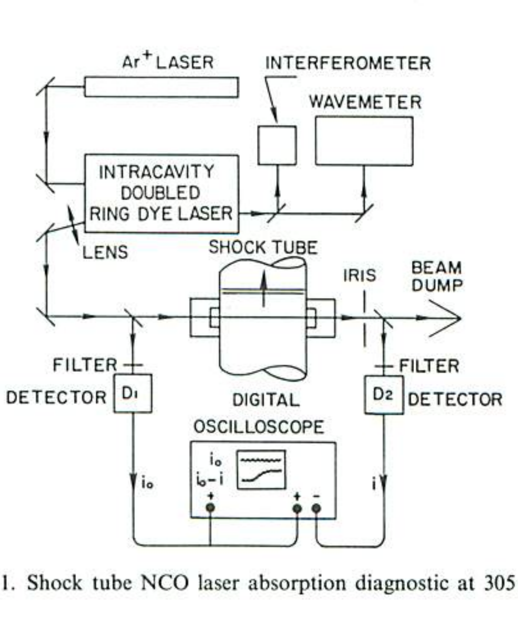

Fig. 1. Shock tube NCO laser absorption diagnostic at 305 nm.

(b) *Experiments at* 440 nm

The absorption from the $P_2 + {}^PQ_{12}$ band head of the $[A^2\Sigma^+(00^00) \leftarrow X^2\Pi_i(00^10)]$ band of NCO at 440.48 nm (vac) was observed using the optical set-up shown in Fig. 2. This system was described in detail elsewhere.[11] It consisted of an Ar^+-pumped ring dye laser with a typical output power of 60 mW (single-mode) at 440.5 nm. After proper amplitude stabilization, the output was transported 65 m via a 200 μm optical fiber to the shock tube facility, where it was double-passed through the shock tube test section. The incident and return beams were filtered (FWHM: 40 nm, center at 450 nm) and monitored on separate detectors, and the signals were electronically balanced prior to each experiment using small dc offset and gain adjustments on one of the differential amplifiers. The difference $(i_0 - i)$ and reference (i_0) signals were recorded on two separate oscilloscope channels.

Nine runs were conducted with the following HCN mixtures and conditions: $N_2O:O_2:HCN:Ar \simeq 8:1:8:983$, $T_2 = 1430 \pm 20°K$, $p_2 \simeq 0.60$ atm, $\rho_{21} \simeq 3.32$, and wavelengths in the range: $440.474 \le \lambda \le 440.482$ nm (vac). Three additional runs were conducted with C_2N_2 mixtures at 440.479 nm, the peak absorption wavelength, and: $N_2O:O_2:C_2N_2:Ar \simeq 4:1:4:991$, $T_2 = 1450 \pm 10°K$, $p_2 \simeq 0.60$ atm, $\rho_{21} \simeq 3.31$.

A few tests were conducted in both systems with the laser blocked to monitor possible spontaneous emission interferences from the test gas, but these emission levels were found to be insignificant.

(c) *Shock tube generation of* NCO

The fractional transmission of both laser systems is related to the level of NCO through the Lambert–Beer law:

$$i/i_0 = \exp[-\beta(\lambda)p_{NCO}L],$$

where i/i_0 is the fractional transmission, $\beta(\lambda)$ is the absorption coefficient at wavelength λ, p_{NCO} is the partial pressure of NCO and L is the optical path length (15.24 cm for the system at 305 nm and 30.5 cm for the system at 440 nm). Under our experimental conditions, both HCN and C_2N_2 mixtures provided reproducible NCO plateau levels. By running nearly identical experiments and recording the plateau absorption levels, we were able to measure relative absorption coefficients of NCO as a function of wavelength. Data for the transmission were obtained by combining (in the computer analysis) the difference and reference intensity data, i.e.: $i/i_0 = 1 - (i_0 - i)/i_0$.

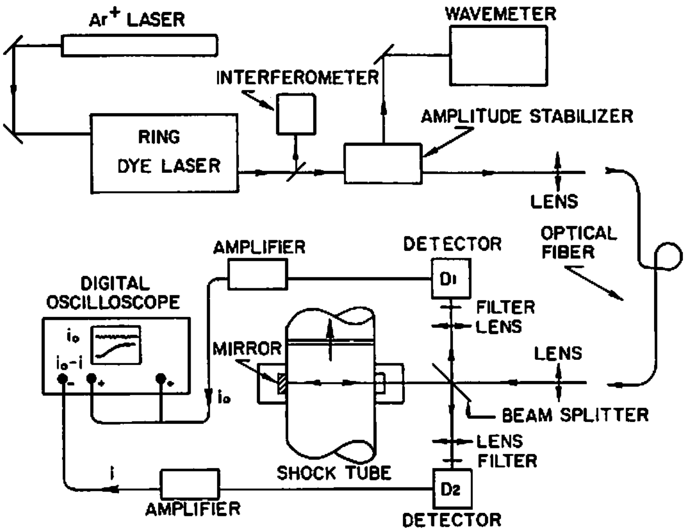

Fig. 2. Shock tube NCO laser absorption diagnostic at 440 nm.

A detailed kinetic mechanism[11,13] for the C_2N_2 mixtures was used to calculate NCO plateau levels, thereby putting the absorption coefficients on an absolute basis. A simplified description of the NCO kinetics can be given using the following reaction sequence:

$$N_2O + M \rightarrow N_2 + O + M, \tag{1}$$

$$C_2N_2 + O \rightarrow CN + NCO, \tag{2}$$

$$CN + O_2 \rightarrow NCO + O, \tag{3}$$

$$NCO + O \rightarrow CO + NO. \tag{4}$$

If C_2N_2 is nearly constant throughout the process, and assuming a steady-state for the CN concentration between reactions (2) and (3), the NCO profile eventually reaches a plateau, where

$$[\mathrm{NCO}]^{\mathrm{plateau}}/[C_2N_2] \simeq 2\,k_2/k_4.$$

Using established values for k_4[11] and k_2,[13] the NCO plateau can be calculated and used to infer the value of the absolute absorption coefficient. Typical NCO absorption traces obtained with the two laser systems are shown in Figs. 3 and 4.

NCO ABSORPTION AT 440 nm—ANALYSIS AND RESULTS

(a) *Spectroscopic model*

Under typical experimental conditions, the $P_2 + {}^PQ_{12}$ band head of the $[A^2\Sigma^+(00^00) \leftarrow X^2\Pi_i(00^10)]$ band of NCO at 440.48 nm is the strongest absorption feature of this electronic system and, apart from a weak ${}^OP_{12}$ branch, it does not overlap with neighboring branches or other vibrational bands.[2] These features are important in establishing a sensitive and quantitative diagnostic for NCO.

A computer program was written to predict the absorption spectrum of the $(00^00) \leftarrow (00^10)$ band under specified conditions. Spectroscopic constants were taken from Dixon.[2] The position, strength and shape of each line were computed to generate a relative

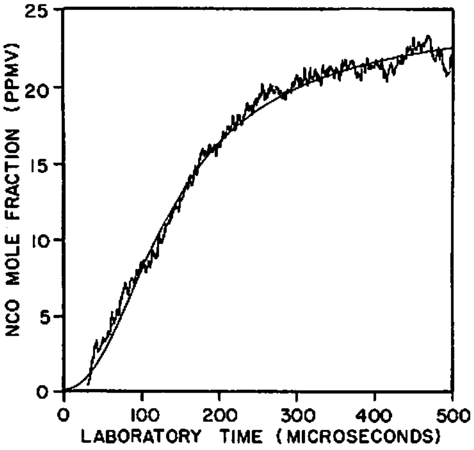

Fig. 3. A typical laser absorption record at 440.479 nm; T_2 = 1440°K, p_2 = 0.60 atm, N_2O:O_2:C_2N_2:Ar $\simeq$ 4:1:4:991. The abscissa gives the laboratory time in microseconds; absorption at 500 μsec = 4.6%; the solid line is the best kinetics computer fit to the data.[11]

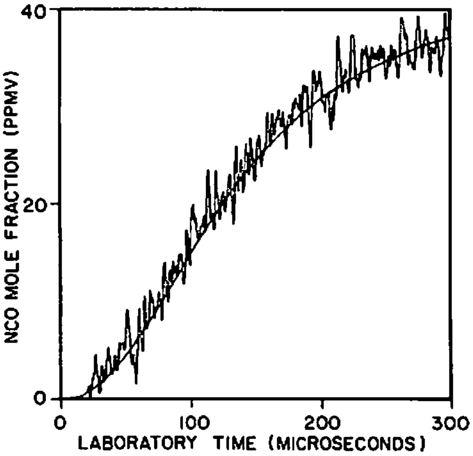

Fig. 4. A typical laser absorption record at 304.681 nm; T_2 = 1460°K, p_2 = 0.61 atm, N_2O:O_2:C_2N_2: Ar ≃ 4:1:4:987. The abscissa gives the laboratory time in microseconds; absorption at 300 μsec = 1.3%; the solid line is the best kinetics computer fit to the data.

absorption coefficient profile $\beta(\lambda)/f_{00}$ as a function of wavelength, viz.,

$$\frac{\beta(\lambda)}{f_{00}} = \left(\frac{\pi e^2}{m_e c^2}\right) \sum_{\text{lines}} \frac{(2J''+1)\exp\left[-\dfrac{hc}{kT}F(J'')\right]}{Q_{\text{total}}} \frac{N}{RT} \frac{S_{J'J''}}{(2J''+1)} \phi(\lambda-\lambda_0) \quad (\text{cm}^{-1}\,\text{atm}^{-1}),$$

where $F(J'')$ is the rotation energy of the lower state (cm^{-1}); R is the universal gas constant (atm · cm^3/mole/°K); N is Avogadro's number; f_{00} is the oscillator strength of the $(00^00) \leftarrow (00^10)$ band; Q_{total} is the total partition function (see below); $S_{J'J''}$ is the rotational line strength; $\phi(\lambda - \lambda_0)$ is the line shape factor (cm) computed using a Voigt profile. (We assume that a uniform value of the Voigt parameter applies for all lines in the band.) The quantity $\pi e^2/m_e c^2$ is equal to $8.826\ 10^{-13}$ cm.

Since the NCO molecule maintains a linear configuration throughout its transition (the bending vibration ν_2 is not excited), the electronic, vibrational and rotational energies can be considered separately, according to the Born–Oppenheimer approximation. Consequently, the rotational line strengths $S_{J'J''}$ are identical to those calculated for diatomic molecules in the appropriate electronic configuration.

By convention, we define the lower energy level of a given rotational transition such that its degeneracy is equal to $(2J''+1)$. For the Π-ground state of NCO, this assumption implies that each term of a K-doubled component is regarded as a separate initial level, despite the small energy difference. As a consequence, the normalization rule for the rotational line strength $S_{J'J''}$ must read for a given J'':

$$\begin{aligned} S(^SR_{21}) + S(Q_1) + S(^QP_{21}) &= S(R_1) + S(^RQ_{21}) + S(P_1) = S(R_2) + S(^PQ_{12}) + S(P_2) \\ &= S(^QR_{12}) + S(Q_2) + S(^OP_{12}) = 2J''+1, \end{aligned}$$

where, for example, $S(^SR_{21})$ is the rotational line strength of the transition:

$$[A^2\Sigma^+(J' = J''+1, \alpha = 2) \leftarrow X^2\Pi_{3/2}(J'', \beta = 1)];$$

our notation follows Mavrodineanu and Boiteaux.[14] The rotational line strengths were taken from Kovacs[15] and multiplied by a factor of two to be consistent with the above normalization rule.

In the calculation of the total partition function, the contribution of excited electronic states of NCO were neglected. For a linear XYZ molecule in a Π-configuration such as NCO in its ground state, Renner,[16] Pople[17] and Hougen[18] have shown that it is generally not a good approximation to consider separately the electronic and vibrational energies, when the ν_2 bending vibration of the molecule is excited. Consequently, the total partition function should not obey the factorization rule, and hence was computed as follows:

$$Q_{\text{total}} = \left(\sum_{v_2'', K'', J'', \pm 1/2} g \exp\left[-\frac{hc}{kT} F_{\pm 1/2}(v_2'', K'', J'') \right] \right) \times Q_{\nu_1} Q_{\nu_3},$$

where v_2'' and J'' are, respectively, the vibration and rotation quantum numbers, and

$$K'' = |\Lambda \pm l| = v_2'' + 1, v_2'' + 1 - 2, \ldots, v_2'' + 1 - 2j, \ldots, 0 \text{ or } 1.$$

$F_{\pm 1/2}(v_2'', K'', J'')$ is the energy of the $X^2\Pi_i(v_2'', K'', J'', \pm 1/2)$ level of NCO with $v_1'' = v_3'' = 0$ (cm^{-1}). The appropriate formulae were derived by Hougen;[18] the zero-point energy follows Dixon's convention.[2] g is the K-doubling degeneracy and is equal to 1 for $K = 0$ and 2 for $K \neq 0$. Q_{ν_1} and Q_{ν_3} are the contributions of the ν_1 and ν_3 stretching modes to the partition function, where

$$Q_{\nu_j} = \left[1 - \exp\left(-\frac{hc}{kT} \omega_j^0 \right) \right]^{-1}$$

for $j = 1, 3$; we used here the values of Milligan and Jacox[19] for ω_1^0 and ω_3^0.

Despite this complicated rovibronic structure of NCO, we have found that the total partition function can be adequately approximated by assuming no interaction between the rotation and electronic energies, and by considering all vibronic states with a given v_2'' as a single level of degeneracy $2 \times 2(v_2'' + 1)$. (There are two levels arising from the possible orientations of the electronic orbital angular momentum, two levels arising from electronic spin, and $(v_2'' + 1)$ levels associated with the degenerate bending.) This simplified approach leads to the approximate expression

$$Q_{\text{total}} \simeq 4 Q_{\text{rot}} Q_{\nu_1} Q_{\nu_2}^2 Q_{\nu_3},$$

where Q_{rot} is the rotational partition function. The agreement between this approximation and the more complete summation presented above is better than 3% in the range $500 \leq T \leq 4000$°K.

(b) *Results*

The reproducible NCO plateau absorption generated by the HCN mixtures (see above) was used for mapping the relative absorption coefficient as a function of wavelength. The measured absorption coefficient (corrected for slight variations in the initial conditions) was plotted along with the computer-predicted profile (Fig. 5). Reasonable agreement was found for Voigt a parameters in the range $0 \leq a \leq 0.4$. This range corresponds to an uncertainty of [× 0.80, × 1.06] in the peak absorption coefficient, which was found near 440.479 nm (in good agreement with Dixon.[2]) This low value of the Voigt a parameter is expected at high temperatures, where u.v. absorption lines are typically dominated by Doppler broadening.[20]

The three additional runs with C_2N_2 mixtures provided an absolute value for the absorption coefficient β at the peak wavelength. From the computer-predicted NCO plateau ($p_{\text{NCO}} \simeq 0.012$ torr) and the corresponding experimental absorption (5%), we inferred:

$$\beta(1450°\text{K}, 0.60 \text{ atm}) \simeq 110(-50, +130)\,\text{cm}^{-1}\,\text{atm}^{-1} \text{ at } 440.479 \text{ nm with } a \simeq 0.1.$$

Uncertainties in β include experimental scatter [× 0.94, × 1.06], uncertainty in the Voigt a parameter [× 0.80, × 1.06], and the uncertain knowledge of some reaction rates [× 0.57, × 2.17] including k_2 and k_4. These three uncorrelated uncertainties combine to

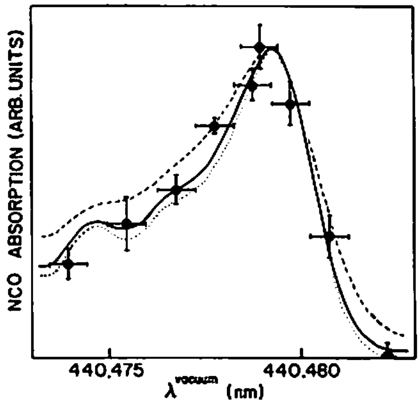

Fig. 5. NCO absorption spectrum around 440.479 nm. The horizontal error bars on the experimental data correspond to the wavemeter resolution; the vertical error bars correspond to uncertainties in the measured absorption. The solid line is a best fit to the spectrum using our spectroscopic model and a Voigt parameter of $a = 0.1$. The dashed lines correspond to computer-generated spectra with $a = 0.4$ (— —) and $a = 0$ (Doppler limit) (· · ·).

give the upper and lower bounds reported above: $60 \leq \beta \leq 240$. A significant reduction in the overall uncertainty could thus be achieved if a better technique for generating known levels of NCO were available.

Using the computer-predicted value of $\beta/f_{00} \simeq 43000\,\text{cm}^{-1}\,\text{atm}^{-1}$, we extract $f_{00} \simeq 0.0026$. This value is in good agreement with Reisler *et al.*[5] and Charlton *et al.*,[6] who respectively reported $f_{el} \simeq 0.0033 \pm 0.0001$ and $f_{el} \simeq 0.0040 \pm 0.0005$. Using the average value of $f_{el} \simeq 0.0037$ and our value for f_{00}, we find for q_{00}, the Franck–Condon factor of the $(00^00) \leftarrow (00^10)$ transition,

$$q_{00} \simeq 0.0026/0.0037 = 0.70,$$

which is consistent (within the uncertainties in f_{el} and β) with the approximate intensity distribution reported by Dixon.[21]

The indicated experimental value of $\beta(1450°\text{K})$ can be extrapolated to other temperatures using our spectroscopic model. Figure 6 is a theoretical plot of β/f_{00} as a function of temperature. Owing mostly to the strong temperature dependence of the total partition function, the peak absorption coefficient decreases substantially as temperature increases. This effect translates into increased NCO detection limits at higher temperatures. At the temperature of our experiments (1450°K), a signal-to-noise ratio (S/N) of 30 was achieved for an absorption of 5%. (The signal-to-noise ratio was limited by laser power fluctuations.) Hence, the detection limit (S/N = 1) was about 0.8 ppmv of NCO at

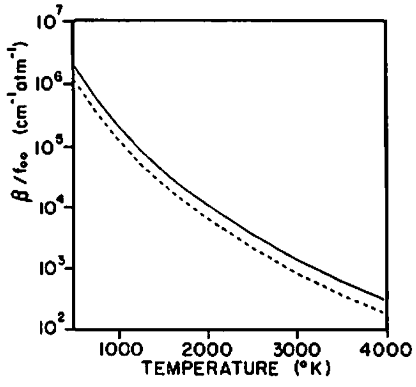

Fig. 6. Theoretical absorption coefficient of NCO $[A^2\Sigma^+ \leftarrow X^2\Pi_i]$ at 440.479 nm as a function of temperature, with a Voigt parameter of $a = 0$ (solid line), and $a = 1.0$ (dashed line).

0.60 atm. The equivalent detection limits calculated at other temperatures and the same pressure are: 11 ppmv at 2500°K and 0.2 ppmv at 1000°K.

NCO ABSORPTION AT 305 nm—ANALYSIS AND RESULTS

The spectrum of the $[B^2\Pi_i \leftarrow X^2\Pi_i]$ transition of NCO is more complicated than the $[A^2\Sigma^+ \leftarrow X^2\Pi_i]$ spectrum that we discussed above. Dixon[3] made tentative assignments of the observed band heads and absorption maxima observed in the range $265 \leq \lambda \leq 320$ nm. Many bands were found to be diffuse, indicating a possible predissociation of the upper state. Only the $(10^10) \leftarrow (00^10)$ vibrational band could be analyzed, but uncertain perturbations made it difficult to determine accurate rotational constants. This band, however, is the least perturbed in rotation, and constitutes our best choice for a quantitative u.v. absorption diagnostic of NCO. Among the four branches available in the band, it is best to use the strong band head of the R_1 branch, which does not overlap with the neighboring R_2, P_1, and P_2 branches. All branches are degraded towards the red.

A computer program was written to calculate the relative absorption coefficient β/f_{10} for the $(10^10) \leftarrow (00^10)$ band. For simplicity, we assumed that the rotational structure obeys the Hill and Van Vleck formula[3] and we used the spectroscopic constants inferred by Dixon.[3] The calculation of β/f_{10} is similar to the one presented above for the $[A^2\Sigma^+ \leftarrow X^2\Pi_i]$ transition. Rotational line strengths were taken directly from Kovacs.[15] No renormalization to Kovacs' published line strengths was required.

The plateau NCO absorption generated by the C_2N_2 mixtures (see Fig. 4) was used to map the relative NCO absorption profile as a function of u.v. wavelength. The time-resolved traces obtained with this diagnostic at 305 nm were similar to the traces recorded using the previous diagnostic at 440 nm; this indicates an absorption free from the interference of other molecular species present in the shock tube. Under the conditions of our experiments ($T \simeq 1470$°K, $p \simeq 0.63$ atm), we observed a very broad spectrum, which was fitted using a Voigt a parameter of 9 by matching the experimental and theoretical full widths at half maximum (see Fig. 7). The peak absorption was found at 304.681 nm, in reasonable agreement with Dixon's measurement at 304.676 nm (vac). We attribute the poor quality of the fit in the wings to the possible interference of unassigned neighboring vibrational hot bands.

Our observation of an exceedingly broad spectrum is consistent with the measurements of Sullivan *et al.*,[8] who reported a short lifetime and a radiationless decay of the $[B^2\Pi_i(10^10)]$ level of NCO. Two of the three criteria for predissociation of the (10^10) level (Auger process[22]) have therefore been checked (observation of radiationless transitions and natural broadening of discrete levels).

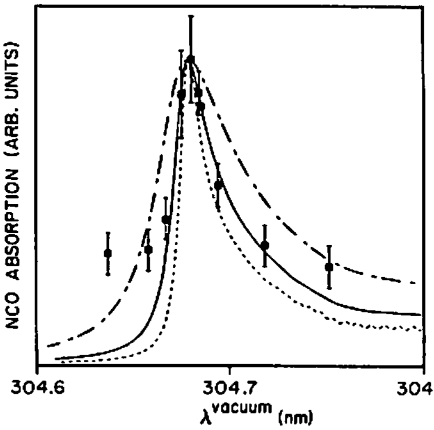

Fig. 7. NCO absorption spectrum around 305.681 nm. The vertical error bars on the individual data correspond to the signal-to-noise ratio of each experiment. The solid line is a best fit to the spectrum using our spectroscopic model and a Voigt parameter of $a = 9$. The dashed lines correspond to computer-generated spectra with $a = 20$ (— · —) and $a = 5$ (· · ·).

Four experiments were conducted at the measured peak absorption (304.681 nm). As before, a kinetics calculation of the NCO plateau enabled determination of the absolute absorption coefficient. We found:

$$\beta(1470°\mathrm{K}, 0.63\,\mathrm{atm}) = 40(-19, +48)\,\mathrm{cm}^{-1}\,\mathrm{atm}^{-1}\ \text{at}\ 304.681\,\mathrm{nm}\ \text{with}\ a \simeq 9.$$

Sullivan,*et al.*[8] measured a decay lifetime of 63 ± 3 nsec for the $[B^2\Pi_i(00^10)]$ level of NCO using laser-induced fluorescence. (This lifetime was considerably longer than that of the $[B^2\Pi_i(10^10)]$ level, indicating a dissociation limit lying between the (00^10) and the (10^10) levels of $[B^2\Pi_i]$.) Since this measurement (63 nsec) was carried out in the near absence of added collision partners (zero-pressure limit), the upper state population decayed through a purely radiative transition to all possible vibrational levels of the lower state with $\Delta J = 0, \pm 1$. Consequently, the total electronic oscillator strength can be estimated from the lifetime of the $[B^2\Pi_i(00^10)]$ state reported by Sullivan *et al.* We infer $f_{el} \simeq 0.022$.

The complexity of this NCO transition at 305 nm may leave some doubts about the validity of the spectroscopic model. Nevertheless, from the computer-predicted value of $\beta/f_{10} \simeq 12700\,\mathrm{cm}^{-1}\,\mathrm{atm}^{-1}$ at 1470°K with $a = 9$, we extract: $f_{10} \simeq 0.0031$ (f_{10} is the oscillator strength of the $(10^10)\leftarrow(00^10)$ band). Using the above estimate for f_{el}, we infer a Franck–Condon factor for the $(10^10)\leftarrow(00^10)$ band in the range:

$$q_{10} = 0.14(-0.06, +0.16).$$

This result is in agreement with a theoretical calculation based on the simplified approach of Sharp and Rosenstock[23] and Smith and Warsop.[24] Using this approach, we calculated: $q_{10} = 0.16$.

CONCLUSION

We have shown that quantitative and sensitive absorption measurements of NCO can be made in high temperature systems, using laser radiation at either 305 or 440 nm. However, the spectrum at 305 nm is highly broadened and cannot entirely be explained in terms of a simple spectroscopic model. By contrast, the spectrum at 440 nm provides a stronger peak absorption coefficient and can be more readily modeled. We recommend therefore the use of the $[A\Sigma^+ \leftarrow X\Pi_i]$ transition for a reliable and sensitive high temperature absorption diagnostic of NCO.

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