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Infrared and Near Infrared Transient Absorption Spectroscopy of Molecular Free Radicals

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1. ABSTRACT

Recent results obtained using absorption techniques with continuous wave lasers to measure vibrational and electronic spectra of small free radicals are reported.

2. INTRODUCTION

The advantages of absorption spectroscopy at low absorbances include a linear relationship between signal size and number of absorbing molecules, line of sight measurement and easily interpretable lineshape functions. The main disadvantage is due to the necessity for measuring a small change in light intensity, usually in the presence of a strong background, which limits the sensitivity. In this paper, we report the results of experiments designed to measure spectra of small free-radical species by direct absorption techniques in the mid- and near- infrared (IR). The radical of interest was generated by excimer laser photolysis of a chemically stable precursor molecule and detected by measuring the transient decrease in power of a continuous wave probe laser that traversed the photolyzed volume before being imaged on to a detector.

In the mid-IR, we have used diode lasers to record the vibrational spectrum of the HOCO radical in the region of its ν_2 (C=O stretch) fundamental. Some results of this study have already been published¹ and this first high resolution spectroscopic work has led to a number of other investigations at wavelengths from the millimeter wave², far infrared^{3,4} and two recent investigations of the ν_1 (H-O stretch) fundamental.^{5,6} With convenient spectroscopic probes of this important species now available, measurements of the kinetics of chemical reactions involving the radical are possible and two groups^{7,8} have reported measurements of the rate of the reaction:

This is important in atmospheric chemistry and combustion systems. The rate, $k_1(296 \text{ K})$, was found to be $1 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ within experimental errors, by both groups.

In the present paper, we describe additional measurements of the infrared spectrum of HOCO in the ν_2 fundamental region. These were originally designed to detect the *cis*- isomer of the radical. Previous experimental^{1,9} and theoretical¹⁰ work confirmed that this is the higher energy isomer, but that it probably lies only 500-1000 cm^{-1} above the *trans*- configuration. Infrared spectra of the radical trapped in a low temperature matrix⁹ determined that the ν_2 fundamental of *cis*-HOCO lies some 60 cm^{-1} below that of *trans*-HOCO and this region was not searched in our earlier experiments. We were not successful in detecting absorptions which could be attributed to the higher energy isomer, however a large number of new spectral lines have been measured and these considerably improve the precision with which the $\nu_2=1$ level of *trans*-HOCO is known.

For the measurement of spectra in the near-IR we have recently built a new spectrometer based on a Ti:sapphire ring laser which oscillates in the 700-1000 nm wavelength region. Many free radicals of practical importance have low lying excited electronic states at energies corresponding to these wavelengths. Conventional photographic techniques become more difficult and dye lasers have low efficiencies at these wavelengths hence few high resolution studies have been carried out. We have obtained new spectra of the CH_2 radical in its $\tilde{b}^1\text{B}_1 - \tilde{a}^1\text{A}_1$ band system around 850 nm and results of a preliminary analysis of some of these data are presented here.

Finally, we describe the results of some very recent experiments that combine the transient absorption technique with frequency modulation spectroscopy (FMS). The results are very encouraging and hold the promise of increasing the sensitivity of the absorption experiment by several orders of magnitude.

3. EXPERIMENTAL DETAILS

The measurements were made using the transient absorption spectrometers at Brookhaven National Laboratory. In the mid-IR, the diode laser based system was described by Sears et al.¹ and is essentially unchanged. In the near-IR, the spectrometer was described by Hall and Wu.¹¹ In both cases, photolysis laser light was provided by a Questek series 2000 excimer laser. For experiments on HOCO, the 193 nm ArF transition was used to dissociate acrylic acid ($\text{C}_2\text{H}_3\text{COOH}$) while CH_2 was generated

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by 308 nm dissociation of ketene (CH_2CO), formed as required by dehydration of acetic anhydride on a hot filament in a flow system.

4. RESULTS

4.1 New Infrared Spectra of HOCO near $5.44\mu\text{m}$.

Figure 1 HOCO P-branch lines near 1836 cm^{-1} .

New absorption spectra were recorded between 1820 and 1850 cm^{-1} with the aim of identifying absorptions due to the perturbing levels and characterizing the interactions more completely. Searches at still longer wavelengths were hampered by strong precursor molecule absorption lines and the fact that the sensitivity of the InSb detector used falls off rapidly in this region. An example of a spectrum obtained near 1836 cm^{-1} is shown in figure 1. The strong lines in this region can all be assigned to high- J P-branch lines in the ν_2 fundamental of *trans*-HOCO. A large number of new vibration-rotation transitions in this band have now been assigned. In view of these new data and the fact that the rotational spacings in the vibrational ground state are now better known from a far-IR laser magnetic resonance study³ we have refitted the entire IR dataset to an effective rotational Hamiltonian describing the $\nu_2=1$ level. For completeness, the current best fit ground state rotational constants are given in table I.

In view of the perturbations in the $\nu_2=1$ state noted above, we fitted the data for each K_a separately in the manner described previously¹ to determine the energies of each K_a level in the excited vibrational state together with an effective rotational constant for the end-over-end rotational motion, $(B+C)/2$. For levels with $K_a=1$, we also included the combination $(B-C)/2$ to take account of the K_a -doubling. The results are summarized in table II and these parameters, together with those in table I can be used to calculate the positions of the observed lines to close to the experimental measurement accuracy. The presence of perturbations in the $\nu_2=1$ level is graphically illustrated in fig 2 where we plot $[E_{K_a}(\nu_2=1) - E_{K_a=0}(\nu_2=1)] - E_{K_a}(\nu=0)$ against K_a^2 . In the absence of perturbations, this plot will be a straight line with a slope depending

The infrared spectrum of HOCO in the ν_2 fundamental region was reported by Sears et al.¹ and was the first gas phase spectrum detected for this radical. Many vibration-rotation transitions were measured and assigned to a parallel, a -dipole, vibrational transition. The vibration involved is the ν_2 ($\text{C}=\text{O}$ stretch) fundamental previously identified at 1844 cm^{-1} in an argon matrix.⁹ The gas phase spectrum showed that the excited vibrational state was perturbed because the K_a subband spacings in the spectrum were highly irregular. A similar situation has been identified in many tetra-atomic monohydrides including HNCO ^{12,13} which, although a closed shell species, bears many resemblances to the HOCO radical in its vibrational structure. In HNCO , the major perturbation mechanisms were identified as being anharmonic (Fermi- type) resonances and a -type Coriolis couplings with combinations of lower frequency vibrations. The speculation was that similar interactions were present in the radical.

Table I. Ground state rotational constants for *t*-HOCO^a

Parameter	Value / cm^{-1}
A	5.5960782
B	0.3813800
C	0.3564640
$10^4 \Delta_K$	7.8689
$10^6 \Delta_{NK}$	-9.882
$10^7 \Delta_N$	3.033
$10^6 \delta_K$	3.67
$10^8 \delta_N$	4.10
$10^9 \Phi_{KN}$	-4.69
$10^2 \epsilon_{aa}$	5.1662
$10^4 \epsilon_{bb}$	3.19
$10^4 \epsilon_{cc}$	-9.15
$10^5 \Delta_K^{(s)}$	-1.802

^a Taken from reference 3, uncertainties are in the last two significant digits. Any parameters not specified are set to zero.

Figure 2 HOCO $v_2=1$ K_a subband energies / cm^{-1} .

anharmonic resonance mechanism that is diagonal in the rotational quantum numbers. Table III summarizes the vibrational levels in HOCO expected to lie in the region of 1850 cm^{-1} . We make the assumption that the observed additional Q-branch is due to $K_a=3$

Figure 3 Weak additional Q-branch in the v_2 fundamental region of HOCO.

of $3\nu_5$ and from the spectrum we can estimate its energy to be 1898.73 cm^{-1} which compares with the same K_a in $v_2=1$ of $1899.0163 \text{ cm}^{-1}$ (table II).

We have set up a simple perturbation calculation which includes three interacting states: the v_2 level, one level interacting with it via an anharmonic resonance ($3\nu_5$) and a third state interacting with the first two via an α -type Coriolis mechanism, ie with a K_a dependent interaction matrix element. For HOCO, this third level would correspond to $2\nu_5 + \nu_6$ or $\nu_3 + \nu_6$ which are the closest combinations containing an odd number of quanta in the out of plane torsional mode, ν_6 . The diagonal elements of the problem are the K_a dependent energies so that, schematically, the interaction matrix is as given in (2), where $E_K(l) = (A_l - (B_l + C_l)/2)K^2$, $l = a, b, c$ and ν_l is the vibrational origin of the vibration l . X_F is a Fermi (anharmonic) resonance interaction constant and X_C is a Coriolis interaction constant. The eigenvalues of this interaction matrix are to be fitted to the observed

on the difference in the combination $A-(B+C)/2$ of rotational constants between the two levels. From this plot, we can see that $K_a'=2$ and $K_a'=3$ in particular appear to be shifted from their expected positions while the very highest K_a levels also deviate from a hypothetical straight line but in a smoother fashion. Interestingly, we searched quite hard for the $K_a=8$ subband Q-branch but were unable to identify it, although the $K_a=7$ one is reasonably strong. In the region immediately below the $K_a=7$ Q-branch, there are many weak lines and the low-J P-branch lines belonging to lower K_a sub-bands, but no obvious Q-branch structure.

Figure 2 suggests that there is a fairly strong local perturbation in the region of the $K_a'=3$ level and some evidence for the perturbing level might be expected in the spectrum. After some searching, the spectrum shown in figure 3 was obtained. Here a weak additional Q-branch may be seen beginning at around 1851.75 cm^{-1} . From the fundamental frequencies measured in an argon matrix, we can identify this band as most likely belonging to the $3\nu_5$ (ν_5 is the in-plane OCO bend) overtone which will perturb v_2 via an

Table II. Effective rotational constants for different K_a levels in the $v_2=1$ level

K_a	ν_K (cm^{-1})	$(B+C)/2$ (cm^{-1})	$10^6 \Delta_N$ (cm^{-1})
0	1852.5678(3)	0.3672707(17)	0.2965(20)
1	1857.7632(3)	0.3672728(13)	0.2879(16) ^a
2	1873.3624(3)	0.3672962(12)	0.2685(15)
3	1899.0163(3)	0.3673780(16)	0.3475(19)
4	1935.3213(3)	0.3672923(16)	0.3107(19)
5	1981.7322(3)	0.3672715(15)	0.3188(17)
6	2038.4694(4)	0.3673137(60)	^b
7	2105.2182(4)	0.3674021(65)	^b

^a For $K_a=1$, $(B-C)/2=0.012403(2)$ and $\delta_N=0.360(12) \times 10^{-7}$.

^b Fixed at the ground state value of 0.3033.

$$\begin{array}{ccc}
\nu_a + E_K^{(a)} & X_F & X_C^{(a,c)} \times K \\
h.c. & \nu_b + E_K^{(b)} & X_C^{(b,c)} \times K \\
h.c. & h.c. & \nu_c + E_K^{(c)}
\end{array} \quad (2)$$

vibrational intervals.

Unfortunately, there are insufficient experimental data to solve uniquely for all the unknowns in the matrix (2). We fix the rotational constants for $3\nu_5$ (b) to 5.507 cm^{-1} and for ν_c ($\nu_3 + \nu_6$ or $2\nu_5 + \nu_6$) to 5.227 cm^{-1} . The former is obtained by assuming a 5% increase in A on excitation to the bending overtone while the latter is the ground state value. We also fixed $X_F^{(a,b)}$ at 0.15 cm^{-1} and both Coriolis interaction constants at 0.05 cm^{-1} arbitrarily, and fit the data to values for E_2 , ($A_2 - \bar{B}_2$) and E_b (for $3\nu_5$). Table IV summarizes the results.

Table III. Vibrational levels in *t*-HOCO near 1850 cm^{-1}

Vibrational Level ^a	Estimated Energy / cm^{-1}	Interaction Mechanism ^d
ν_2	1852.568 ^c	-
$\nu_4 + \nu_5 + \nu_6$	2195	C
$\nu_4 + 2\nu_6$	2095	A
$3\nu_5$	1845	A
$\nu_3 + \nu_5$	1826	A
$2\nu_5 + \nu_6$	1745	C
$\nu_3 + \nu_6$	1730	C
$\nu_4 + \nu_5$	1680	A

^a ν_2 is the C=O stretch, ν_3 is the HOC bend, ν_4 is the C-O stretch, ν_5 is the OCO bend and ν_6 is the torsion.

^b From reference 9 except where indicated.

^c This work.

^d With ν_2 ; A = anharmonic resonance, C = α -type Coriolis coupling.

If the observed additional Q-branch is gaining intensity purely from the mixing with ν_2 then we estimate from the eigenvector coefficients of the perturbation matrix that it will have an intensity of approximately 12% of the ν_2 , $K_a=3$ Q branch, which is slightly less than seen in figure 3. Other, equally good (or bad), fits of the vibrational intervals with slightly different X_F and rotational constants in the perturbing level yielded estimates of up to 25% for this quantity. We find that the relative intensities of all the other Q-branches are predicted to be below the experimental sensitivity limit, hence explaining their non-observation.

Clearly, the residuals in table IV are much larger than the experimental uncertainties, especially for the higher K_a values. Adjusting the parameters for mode (c) within physically reasonable bounds did not affect this result to any significant degree, hence the model does not fully explain the vibrational structure of HOCO in this region. In order to vary both the interaction parameter (X_F , or X_C), and the vibrational energies, we need experimental information on other rotational levels in the perturbing vibrational states. Gas phase information on the lower frequency vibrations would also be very useful. In particular, direct observation of the lowest frequency fundamental, ν_6 , would be most interesting. Experiments around

$16\mu\text{m}$ are planned in the near future, and the extension of the transient FM technique, demonstrated in the near-IR (see below), to mid-IR wavelengths using the diode laser spectrometer is also under development.

4.2 The $\tilde{b}^1B_1 - \tilde{a}^1A_1$ spectrum of CH_2 near 830 nm

The electronic spectrum of singlet methylene was originally obtained and analyzed by Herzberg and Johns¹⁴ in a classic study. Since that time, a large amount of experimental and theoretical work on the spectrum has been published. On the experimental side, the shorter wavelength region of the spectrum has been extensively studied using dye laser absorption and laser induced fluorescence spectroscopy. Most relevant to the current work is the transient absorption spectrum obtained by Petek et al.^{15,16} using a c.w. single mode dye laser. Very recently, stimulated emission pumping (SEP) spectroscopy¹⁷ has been used to provide the first information on highly excited vibrational levels in the lower, $\tilde{a}$, state involved in the transition. In combination with infrared spectra of the stretching vibrations in this state,¹⁸ these data provide a wealth of information on the rovibronic structure of the $\tilde{a}^1A_1$ state.

Table IV. Results of a deperturbation analysis of vibrational resonances in HOCO

Assignment (K_a)	Observed ^a Wavenumbers cm^{-1}	Observed - Calculated Wavenumbers cm^{-1}
0	1852.5678	-0.0988
1	1857.7632	-0.0622
2	1873.3624	-0.0595
3 ($3\nu_5$)	1898.725	0.1000
3 (ν_2)	1899.0163	-0.1157
4	1935.3213	0.1423
5	1981.7322	0.1252
6	2038.4694	0.1221
7	2105.2182	-0.1846

^a This Work

^b Fitted Parameters are $E(\nu_2) = 1852.6605$, $(A_2 - \bar{B}_2) = 5.15802$ and $E(3\nu_5) = 1849.1075 \text{ cm}^{-1}$.

were as follows. A 25 sccm flow of argon was passed over a room temperature sample of acetic anhydride ($(\text{CH}_3\text{CO})_2\text{O}$) and the mixture flowed over a heated filament, forming ketene, through a dry ice trap to remove water and residual acetic anhydride and thence to the absorption cell. The pumping rate was adjusted to give a total pressure of 1.6 torr in the experimental chamber, measured using a capacitance manometer. The spectrum in figure 4 is the average of 20, 308 nm, excimer laser shots per 400 MHz step in a time gate of 1 μs , beginning 6 μs following the photolysis event to allow for the relaxation of the initial CH_2 internal energy distribution. Under these survey scan conditions, absorptions of as little as 0.04% can easily be identified. The Doppler linewidth for CH_2 at 300 K and 12200 cm^{-1} is 1.2 GHz FWHM so that accurate lineshape measurements would require a smaller step size.

Many new rovibronic transitions have been identified; a result that might have been predicted following the work of Petek et al.^{15,16} at shorter wavelengths. Many of these new lines are due to $\Delta K_a = \pm 3$ and higher transitions,^{17,20,21} however others are certainly due to transitions to previously unobserved vibronic states calculated by Green et al.¹⁹ Table V lists assignments for the 080-000 vibronic band whose $K = 0$ component is calculated to be the

The $\bar{b}$ and $\bar{a}$ states of CH_2 form a Renner-Teller pair that correlate with a $^1\Delta$ state at the linear configuration. At energies approaching that of the linear configuration, the effects of electronic orbital angular momentum become pronounced, leading to severe complications in some parts of the observed spectrum, particularly at the longer wavelengths included in the original study.¹⁴ A recent high level *ab initio* calculation¹⁹ provided sufficiently accurate results that it was used to assign some observed vibronic bands whose identity had remained unclear since the original spectroscopic work.¹⁴ Many of the band assignments made by Herzberg and Johns were also modified in the light of the computational results. Interestingly, the calculation indicated that many of the upper state levels with $K_a > 0$ are mainly $\bar{a}^1A_1$ in character. From an experimental standpoint, perhaps the most interesting aspect of the calculation was the prediction that many new vibronic states should be observable in the spectrum given only a modest increase in sensitivity over the original work.

All these results put the ball firmly back in the experimentalist's court and we have recorded survey spectra at wavelengths between 813 and 893 nm ($12300 - 11400 \text{ cm}^{-1}$ respectively). Figure 4 shows a typical example of the new data in the region of the $K_a = 0-1$ Q-branch of the $\nu_1, \nu_2, \nu_3 = 0, 8, 0 - 0, 0, 0$ band. In the earlier work, all the closely spaced lines in this spectrum were unresolved. Experimental conditions

Figure 4 CH_2 spectrum around 12205 cm^{-1} .

strongest in the entire band system. Ground state combination differences can be used to make many new assignments for the other bands observed by Herzberg and Johns and in a similar way, we have been able to tentatively assign several new $K=1$ vibronic levels based on the *ab initio* results. Much additional work remains to be done on this spectrum, however the measurements will vastly increase the precision with which the region of the CH_2 singlet potential near where the $\tilde{a}$ and $\tilde{b}$ state surfaces become degenerate is known.

Table V. Observed rotational lines in the (0,8,0)-(0,0,0) transition of CH_2 .^a

J'	K_a'	K_c'	J''	K_a''	K_c''	ν/cm^{-1}	J'	K_c'	K_c'	J''	K_a''	K_c''	ν/cm^{-1}
2	0	2	1	1	0	12234.824	2	2	0	1	1	0	11740.288
3	0	3	2	1	1	12240.471	2	2	1	1	1	1	11744.343
4	0	4	3	1	2	12242.545	3	2	1	2	1	1	11749.780
5	0	5	4	1	3	12242.009	3	2	2	2	1	2	11761.672
1	0	1	1	1	1	12207.863	4	2	2	3	1	2	11756.770
2	0	2	2	1	2	12206.550	4	2	3	3	1	3	11779.640
3	0	3	3	1	3	12205.073	5	2	3	4	1	3	11763.861
4	0	4	4	1	4	12204.085	5	2	4	4	1	4	11799.637
5	0	5	5	1	5	12204.193	6	2	4	5	1	4	11769.827
6	0	6	6	1	6	12206.708	2	2	0	2	1	2	11712.030
0	0	0	1	1	0	12188.326	2	2	1	2	1	1	11699.563
1	0	1	2	1	1	12163.276	3	2	1	3	1	3	11714.202
2	0	2	3	1	2	12134.133	3	2	2	3	1	2	11689.263
3	0	3	4	1	3	12102.454	4	2	2	4	1	3	11677.302
4	0	4	5	1	4	12070.101	5	2	3	5	1	5	11686.434
5	0	5	6	1	6	12039.194	5	2	4	5	1	4	11655.566
							6	2	4	6	1	6	11734.520
							2	2	0	3	1	2	11638.446

^a Experimental error limit 0.007 cm^{-1} . $K_a = 2-3, 4-3$, and $4-1$ transitions were also observed. The analysis is still in progress.

4.3 Transient frequency modulation spectroscopy

The dominant noise source in the transient absorption experiments described above is due to amplitude fluctuations in the probe laser. In the case of the Ti:sapphire laser, amplitude fluctuations are of the order of 1-5%. In order to measure absorptions down to the 0.01 % level, a dual beam method was used. It partially, but not fully, corrects for the problem. In the mid-IR, diode laser source noise is less severe, however it still limits the sensitivity of the technique.

During the past decade, the technique of frequency modulation spectroscopy (FMS) has received considerable attention.²² In this technique, the required signal is detected at radio (rf) or microwave frequencies, far above the high frequency cut off of the source noise spectrum. At visible and near-IR wavelengths, the basic technique is simple. The output from the single frequency laser is passed through a phase modulator driven at an rf frequency, ω_{rf} , to produce a frequency modulated beam consisting of a strong carrier at frequency ω_c and two relatively weak sidebands at $\omega_c \pm \omega_{\text{rf}}$. The modulated beam is passed through the sample and then imaged onto a fast photodiode. The amplified detector electrical output is then passed to the signal input of a double balanced mixer referenced to the rf oscillator. The mixer output, which is the Fourier component of the input signal at the oscillator frequency is then passed to the usual data acquisition system, in the present case a LeCroy digitizing oscilloscope. In almost all FMS experiments reported to date, the sample has been a chemically stable species or some other static or only slowly varying sample. One notable exception was the work of Whittaker et al.²³ who demonstrated very high sensitivity absorption measurements on HCO and NH_2 radicals formed by photochemically modulated mercury sensitized decomposition of suitable precursor molecules. In these experiments, the time resolution was modest, limited by the rate at which the mercury discharge lamps that initiate the process could be modulated. However the modulation of the molecular absorption signals was very successfully used to discriminate against spurious FM signals caused by accidental étalons in the laser beam path.

In the current experiments, we replace the mercury lamps with a beam from a pulsed excimer laser. CN radicals formed in the 193 nm photolysis of cyanogen (NCCN) were chosen for the initial experiments. The $\tilde{A} - \tilde{X}$ band system of CN²⁴ lies

in the Ti:sapphire laser operating range and we have exploited this in several studies of photodissociation dynamics.^{11,25} Figure 5 shows a scan through a region of the CN $\tilde{A}^2\Sigma - \tilde{X}^2\Pi$ $v = 2 - 0$ band around $12\,800\text{ cm}^{-1}$. Here, the sideband frequency was 260 MHz, the Ti:sapphire laser was scanned in 130 MHz steps with 5 photolysis laser shots averaged per point. 2 sccm of NCCN was slowly flowed through the absorption cell at a total pressure of 60 mtorr and approximately 5 mJ of 193 nm photolysis laser light entered the cell per shot. The output from a silicon photodiode was amplified and passed to a mixer referenced to the rf oscillator. The mixer output was digitized using a LeCroy 9450 oscilloscope and the spectrum obtained by sampling 200 ns slices of the transient waveform before and immediately following the photolysis laser pulse and subtracting the two signals. Changes in the baseline noise occur as the probe laser scan segment is changed, we are not sure why this is so.

The strongest FM signals in figure 5 correspond to absorptions of the order of 0.5% and we have retained sufficient bandwidth in the detection system to characterize the time dependence of the lineshape due to collisional realignment and velocity relaxation.²⁵ For purely spectroscopic investigations, a low pass filter can be used after the mixer in order to significantly increase the signal to noise ratio. Even with the wide bandwidth, integration of the FM derivative lineshape spectrum of figure 5 yields the spectrum shown in the lower panel of figure 6. For comparison, a transient absorption spectrum obtained using the standard dual beam configuration under exactly the same experimental conditions is shown in the upper panel. Normally, many hundreds of laser shots would be averaged at each probe laser frequency to yield acceptable signal to noise ratios for Doppler resolved lineshape measurements.

These preliminary results are extremely encouraging. We are planning to attempt similar FM transient absorption studies in the mid-IR using the diode laser system. Here the FM sidebands can be directly obtained by applying a sinusoidal rf frequency to the diode injection current. Several studies have been published^{26,27,28} however we are not aware of any time resolved measurements. Successful application of FM techniques to infrared kinetic spectroscopy would enable a huge leap in sensitivity that would open up possibilities for spectroscopic studies of many challenging and chemically important systems.

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Figure 5 CN FM transient absorption.

Figure 6 Comparison of transient absorption (top) and integrated FM signals.

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