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Reinvestigation of the $2v_1$ Band in Trifluoropropyne using a Frequency Stabilized 1.5 μm Color Center Laser in Conjunction with a Laser Field Build-up Cavity

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The highly perturbed spectrum of the first overtone of the acetylenic CH stretch in trifluoropropyne has been reinvestigated with an improved multi-laser, optothermal detection, molecular beam spectrometer. The modifications include installing a build-up cavity to enhance the coupling between a 1.5 μm color center laser and the molecular beam, and stabilizing the laser frequency to improve the spectrometer's resolution. Upon injecting 25 mW into the cavity, a power enhancement of about 600 is measured. The laser frequency is stabilized by locking it to an external, temperature stabilized, etalon and applying the feedback to an intracavity electro-optic crystal. The frequency stability reached is estimated to be less than 4 parts in 10^{10} or 75 kHz (in a 30 Hz bandwidth centered at 300 Hz).

Utilizing infrared/infrared double resonance, the K components of this highly perturbed spetrum were assigned. The results indicate that the lifetime of the acetylenic CH stretch is approximately 1.4 ns and does not change as a function of J' for $0 \le J' \le 4$. In agreement with a previous lower resolution study [J. Chem. Phys. 95, 3891 (1991)], the P(1) clump shows an experimental density of states almost equal to the calculated one and the level spacing distribution is similar to that of a Gaussian Orthogonal Ensemble indicating chaotic classical dynamics.

I. Introduction

During the last two decades, high resolution molecular beam spectroscopy has made important contributions to our knowledge of molecular structure and dynamics. Particularly active is, at present, the study of intramolecular vibrational energy distribution (IVR), which is relevant to the goal of bond-selective chemistry. The understanding of vibrational energy flow in medium size polyatomic molecules (5 – 15 atoms) has made tremendous progess due to the combination of molecular beam techniques and continuous wave, tunable lasers [2]. The prerequisites for a quantitative analysis of the resulting spectra are high resolution (the eigenstates of the system need to be resolved), a large dynamic range (weak transitions need to be detected) and the ability to make accurate quantum number assignments to the observed features.

Color center lasers have proven to be extremely useful for many IVR studies near 3 μm, because they can excite and often saturate the fundamental CH [3], OH [4] or NH stretches [5]. The effect of IVR is to distribute the oscillator strength of the "bright" state (an acetylenic CH stretch for example) into various "dark" combination and overtone states of almost the same energy. The result is that more power is needed to saturate the individual features that now contain only a fraction of the total oscillator strength. Using multipass devices the effective power impinging on the molecules can easily be increased by a factor of ten. In a typical bolometer detected infrared experiment the dynamic

range for transitions such as those of HCN is 10^4, meaning that signals with only a tiny fraction of the total oscillator strength will still be observed above the noise.

Exciting first overtone transitions by similar means is more difficult, since the vibrational band strength of a typical CH stretch is two orders of magnitude below that of the fundamental [6]. In addition, the Doppler broadening is about a factor of two larger in the overtone compared to the fundamental. Our Burleigh 1.5 μm color center laser gives about eight times higher power than the 3 μm laser, partially offsetting the above factors. Thus while our overtone signal to noise ratio is reduced by more than a factor of ten compared to the fundamental region, we have successfully recorded and analyzed eigenstate resolved overtone spectra of propyne [7], diacetylene [8], diacetylene-d_1 [8] and allene [9], where the calculated density of states with the proper vibrational symmetry is 8, 15, 42, and 7 state per cm^{-1} respectively.

The first overtone of the acetylenic CH stretch ($2v_1$) in trifluoropropyne ($CF_3C\equiv CH$) was studied by Dubal and Quack using FTIR spectroscopy with a 0.02 cm^{-1} resolution [10]. The spectrum was recorded at several temperatures and it was found that all of its structure could be attributed to inhomogeneous effects, though the possible existence of homogeneous structure below their resolution was discussed. The high resolution spectrum of the $2v_1$ band was later recorded in our laboratory, using bolometric detection of a skimmed molecular beam [1]. However due to the extreme degree of fractionation (the density of states is $1260/cm^{-1}$) the spectrum was not resolved and, except for R(0) and P(1) which contain only one K component, was virtually unassignable.

In order to meet the goals of higher resolution and increased signal to noise ratio, we have recently improved the frequency stability of our overtone 1.5 μm color center laser

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(Burleigh FCL-220), and have constructed a resonant, power build-up, cavity to increase the fractional excitation of the molecular beam. To test its performance, the improved spectrometer has been used to record portions of the trifluoropropyne $2\nu_1$ spectrum. In addition, infrared/infrared double resonance, using the 1.5 μm color center laser and a 3.0 μm laser, has allowed us to selectively observe the spectra of an individual rotational level of the ground vibrational state. This is achieved by scanning the overtone region with the 1.5 μm laser while the 3 μm laser is used to modulate the ground state population of a previously assigned ν_1 ro-vibrational transition.

II. Experimental Procedures

A. General Description

Trifluoropropyne [Farchan] was subjected to one freeze/thaw cycle and then used without further purification. Our experiments are carried out using a molecular beam machine which has been described in detail in Ref. 3. In short, the molecules of interest are premixed at about 1% concentration level in helium and are expanded through a 50 μm nozzle held at room temperature, with a typical backing pressure of 60 psi (410 kPa), resulting in an average beam velocity of 1600 m/s. The beam, skimmed by a 0.5 mm diameter conical skimmer, passes through the laser interaction region, and impinges on a detector 44 cm downstream from the nozzle. The detector used is a liquid helium cooled bolometer which senses any changes in the energy content of the molecular beam.

The two laser used in this experiment are both single mode, color center lasers [Burleigh] which are continuously scannable under computer control. The first laser, a FCL-20, lases near 3.0 μm and has about 20 mW of power in the region of acetylenic CH stretches. The second laser, which emits around 1.5 μm, has been modified from a FCL-120 to FCL-220 by replacing the color center crystal and has about 180 mW of single mode power in the region of the first overtone of acetylenic CH stretches. In previous experiments, either or both lasers were introduced into the machine about 10 cm upstream of the bolometer and propagated through a multipass cell constructed with two gold coated, plane parallel, mirrors. Due to the slightly nonorthogonal crossings between the laser and the molecular beam in the multipass cell, the detected spectral features had a residual Doppler broadening of about 8 MHz at 3 μm and 16 MHz at 1.5 μm. The gain in signal produced by the multipass cell, with respect to a single crossing, was about a factor of 10. This, however, is obtained at the expense of the linewidth which increases by about a factor of 2 (16 MHz versus 8 MHz at 1.5 μm).

The double resonance experiments were done by locking the amplitude modulated 3 μm laser onto a known $\nu_{CH} = 1 \leftarrow 0$ transition in the multipass, scanning the unmodulated 1.5 μm laser in the build-up cavity, and detecting the bolometer signal at the modulation frequency of the 3.0 μm laser. The 3 μm laser frequency is locked to an external,

temperature insulated, confocal etalon [Burleigh CFT-500] by applying the feedback directly to the laser cavity-folding mirror, as described in detail in Ref. 11. In spite of the frequency stabilization, the noise in these double resonance experiments increases by a factor of 5 in comparison to a single resonance experiment, mainly due to fluctuations in the number of molecules pumped by the 3.0 μm laser. Since the molecular beam interacted with the 1.5 μm laser prior to entering the multipass cell, the double resonance signal consisted of a dip in the signal induced by the 3 μm laser.

B. External Power Build-up Cavity for the 1.5 μm Color Center Laser

To improve both effective power and resolution, a fiber-coupled, build-up cavity system has been developed for use with the 1.5 μm Burleigh FCL-220 color center laser. This single mode laser is continuously scannable by means of an AT compatible computer which controls the intracavity etalon, the cavity end mirror and the grating.

A 1.5 μm single mode fiber is used to bring the light from the laser into the build-up cavity, which is mounted inside the molecular beam machine. The laser beam is coupled into the fiber with a commercial fiber coupler [Newport]. A Faraday isolator prevents back reflections from destabilizing the laser. Light is coupled out of the fiber and mode matched into the build-up cavity via a gradient refraction index lens with a focal length of 25 mm. The overall loss is about 5 to 6 dB. An important advantage of the fiber coupling system is that the output end of the fiber can be fixed in position with respect to the cavity so that mechanical vibrations of the laser table and the molecular beam machine do not cause changes in the coupling of the light into the cavity. Further, the cavity position and orientation with respect to the molecular beam can be adjusted without changing the optical alignment of the fiber output with the cavity.

The build-up cavity is constructed using the core element of a Newport SR-170-C SuperCavity optical spectrum analyzer. The cavity mirrors coatings are centered at 1.55 μm and fall off at about 1.52 and 1.58 μm. The free spectral range is 6 GHz and the finesse greater than 5000, resulting in a fringe width of 1.2 MHz. From the reported finesse of the cavity, the reflectivity of the mirrors (R) can be calculated to be 0.9994. Assuming a mirror absorbance (A) in the range of 0 to 0.0003 the theoretical build-up achievable with this cavity is:

$$I/I_0 = T/(1-R)^2 = 800 \text{ to } 1600 \ , \tag{1}$$

where T is the transmittance of the mirrors and is equal to $(1-A-R)$. The cavity consists of two mirrors, antireflection coated on the backside, attached as the two end faces of a cylinder to a single 25 mm long tube made of piezoelectric material. Two 2 mm holes drilled perpendicularly to the axis of the tube provide a flight path for the molecular beam through the cavity. Eighty volts must be applied to change the cavity length by one free spectral range. The

maximum allowable input power (as specified by Newport) is 25 mW which is easily achievable with the current laser power and fiber coupling system.

The build-up cavity is placed immediately after the skimmer because it is desirable to produce as large as possible a "shadow" of the beam waist (which has a 0.3 mm diameter) on the bolometer. In our current machine, the skimmer has a diameter of 0.5 mm and is located 42.8 cm from the bolometer which measures 1.5 mm in width and 3.0 mm in height. This corresponds to an average beam divergence of 3.5×7 mrad. At a distance of 5 cm from the skimmer, the size of the spot imaged onto the bolometer is 0.67×0.85 mm or 0.57 mm^2. The laser diameter ($2 * \omega_0$) is about 0.6 mm and so only about 70% of the molecules that hit the bolometer pass through the laser focus.

The expected transition linewidth, in the absence of laser frequency instabilities, can be predicted given the size of the optical beam waist and the molecular beam velocity and divergence. Transit time broadening is a result of the finite time that the molecules spend in the radiation field. For a Gaussian laser beam this is given by [12]:

$$\Delta\nu_t = 2 * \sqrt{(2\ln 2)} * v/(2\pi * \omega_0) \ . \tag{2}$$

For a beam velocity $v = 1600$ m/s and spot size $\omega_0 = 0.3$ mm, this results in a linewidth of 2.0 MHz. Residual Doppler broadening is due to the spread of the molecular beam in the horizontal direction. With an average beam divergence in the horizontal direction of 3.45 mrad this corresponds to:

$$\Delta\nu_D = (v/c) * \text{laser frequency} * \text{divergence (rad)} \tag{3}$$

or 3.6 MHz at 6560 cm^{-1}. Convolution of these two sources of broadening gives a total linewidth of 4.1 MHz.

The build-up cavity is locked to the frequency of the laser through a proportional-integral-derivative (PID) control loop. A 14 kHz sine wave is applied to the cavity and the transmission through it is monitored with a PbSe detector. The signal from this detector is fed into a lockin amplifier operating with a 30 ms time constant. The output of the lockin is sent to the PID circuit and this is fed back to the cavity. When the laser jitter (approximately 6 MHz) is greater than the linewidth of the cavity (1.2 MHz), the lock loop is somewhat unstable and the cavity must be modulated by several times the width of the resonances in order to maintain lock.

C. Frequency Stabilizing the 1.5 μm Color Center Laser

The frequency jitter of the free-running laser, in addition to posing a problem for the operation of the build-up cavity, is one of the major sources of linewidth in the spectrometer. The two sources of frequency noise in the laser are mechanical vibrations and thermally induced changes in the index of refraction of the color center crystal. These thermal variations, which are the predominant source of laser linewidth, are caused by fluctuations in the pump laser

power. A change of one milliwatt in power from the Nd:YAG pump laser results in a frequency shift of about 100 kHz in the color center laser [13].

In order to reduce the linewidth of the laser, a frequency stabilization system has been implemented, using an electronic feedback loop to lock the frequency of the laser to the resonant frequency of an external, temperature controlled, confocal etalon [Burleigh CFT-500]. Attempts to apply the feedback to the intra-laser cavity PZT mounted end mirror proved unsuccessful due to numerous, high Q, mechanical resonances within the noise bandwidth of the laser (up to a few kHz). Attempts to solve this problem with narrow band notch filters also failed. Instead, a feedback signal, provided by the demodulation of the light intensity transmitted through the etalon, was applied to an electro-optic crystal mounted within the laser cavity, as was done previously, for a 3 μm color center laser, by Hall and collaborators [14].

The crystal used here is a $4 \times 4 \times 40$ mm^3 LiNbO$_3$ crystal [Inrad, Inc.] with the long dimension corresponding to the z-axis. Gold electrodes are plated onto the two x-faces while the z faces are anti-reflection coated for 1.5 μm light. The crystal is placed in the laser cavity in such a way that the light propagates along the z axis. This "x-cut" crystal is about ten times less electro-optically effective as a "z-cut" crystal, but was chosen because an AR coated crystal was available from stock. The crystal x and y-axes are rotated by 45° with respect to the horizontally polarized laser radiation, so that the polarization vector of the light is parallel to the electrically induced y'-axis, providing maximum phase modulation. A voltage across the x-face electrodes tunes the laser at a rate of approximately 100 kHz per volt. The power loss due to the crystal is 5 to 10% at 1.55 μm.

A fraction of the output beam of the laser is directed into a temperature stabilized Fabry-Perot etalon which is used as the frequency reference. The etalon has a free spectral range of 150 MHz and a finesse of approximately 75, resulting in a minimum resolvable frequency bandwidth of 2 MHz (FWHM). The transmitted light from the interferometer is monitored by a germanium photodiode. The laser frequency is modulated at 75 kHz and lock-in detection is used. The lock-in output is sent through a high voltage amplifier to the crystal electrodes, thereby providing feedback to correct for jitter in the laser optical frequency. In order to scan the 1.5 μm laser frequency stabilized, a voltage is applied via the computer to the external reference etalon, and the laser then follows this frequency.

A rough estimate of the residual frequency instability of the laser can be made from the observed variation of the transmitted intensity through the etalon. This is roughly 10% of the total height of the peak, with a full width at half maximum of 1.2 MHz, yielding a laser linewidth around 500 kHz. However within the bandwidth used in connection with the bolometer based detection system (around 300 Hz with a 300 ms time constant) the laser linewidth is less than 75 kHz. This figure is obtained from the increased bolometer noise level when the laser is locked onto a molecular transition in the beam.

III. Results and Discussion

The first overtone of the CH stretch in trifluoropropyne was reinvestigated using the improved 1.5 μm laser. A portion of the R(0) clump recorded in the multipass cell is shown in Fig. 1a. The additional power available in the b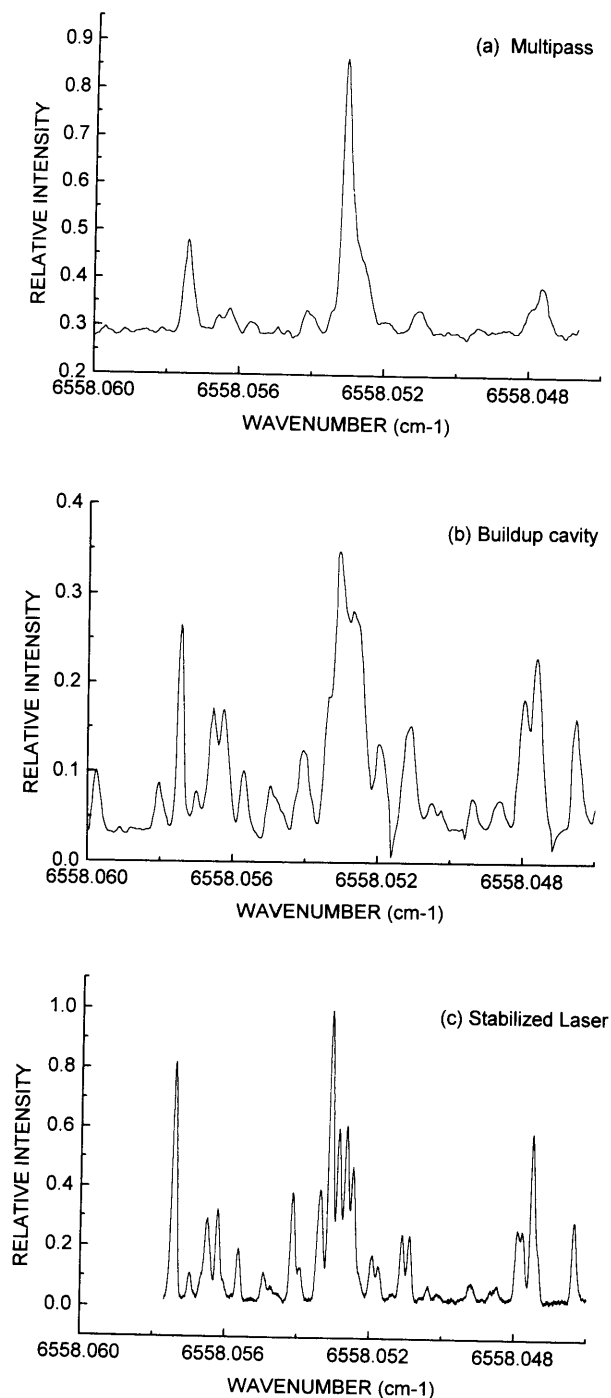uild-up cavity dramatically alters the appearance of the spectrum with many new features rising up from the baseline while the strong central transition is clearly saturated (Fig. 1b). The improvement in resolution obtained by the use of a frequency stabilized laser (Fig. 1c) also dramatically alters the spectrum, in that many features are now actually resolved into their doublet or multiplet components. Both of these experimental parameters, signal to noise ratio and resolution, alter the quantitative interpretation of the spectrum with regard to the dynamics of intramolecular vibrational redistribution.

Currently, with 25 mW of laser power measured out of the fiber end (just prior to injection into the build-up cavity), we measure a 3 to 4-fold gain in signal for an unsaturated transition, over injecting 180 mW in the multipass. Taking into account the reduced number of molecules excited and the gain of the multipass over a single crossing, this corresponds to a gain in intensity (cavity/single pass) of about 600. As shown in Sect. IIB, the expected linewidth from transit time broadening and the residual Doppler broadening of the molecular beam is 4 MHz. The linewidth of the features in Fig. 1c are all in the range 4 to 6 MHz, indicating little, if any, additional broadening from laser instabilities.

The spectrum of the P(1) and R(0) clumps were recorded in single resonance since these features only contain one K component and the spacing between J components (0.19 cm^{-1}) is larger than the spread of a single J clump (0.03 cm^{-1}). Double resonance is therefore not necessary to obtain a pure spectrum for these two clumps. Table 1 summarizes the information obtained from the P(1) and R(0) clumps. The increased power that the molecules experience in the buildup cavity results in saturation of some of the strong features. Saturation occurs first in the transitions which contain the largest amount of oscillator strength. These strong lines no longer grow in intensity but the added power manifests itself as a broadening in the linewidth. In our case, this broadening is beneath the residual Doppler linewidth and so is not observed. In this near-saturation regime, the relative intensities of a saturated spectrum are no longer useful in calculating lifetimes. The P(1) spectrum recorded in the build-up cavity was therefore corrected for the effects of saturation by scaling five of the largest transitions using the intensities published in Ref. 1. In the R(0) clump only one transition was corrected for the

Fig. 1
A portion of the R(0) clump in CF$_3$CCH recorded in: (a) the multipass cell with an 16 MHz linewidth, (b) the build-up cavity, where the linewidth is reduced to about 10 MHz and (c) the build-up cavity with the laser frequency stabilized, resulting in an average linewidth of 5 MHz

Table 1
Summary of information obtained from the P(1) and R(0) clumps of the $2v_1$ band in trifluoropropyne

	P(1)	R(0)
Number of eigenstates	22	36
Density of states (/cm^{-1})	1154	2330
Lifetime (ns)	1.49	1.40
Normalized moments from nearest neighbor distributions:		
$\langle s^2 \rangle / \langle s \rangle^2$	1.32	1.38
$\langle s^3 \rangle / \langle s \rangle^3$	2.00	5.35
$\langle s^4 \rangle / \langle s \rangle^4$	3.34	5.35
% GOE	95.0	80.0

effects of saturation. The R(1), R(2) and R(3) clumps did not show any signs of saturation in the build-up cavity spectra. It is expected that P(1) and R(0) will be the easiest to saturate since they contain only one M_J component and show the lowest fractionation.

The result of the increased resolution and effective power is the identification of many more eigenstates than originally reported [1]. An average experimental density of states can be obtained by counting the number of eigenstates minus one (the bright state) appearing in the energy window of the clump. For R(0) this estimate gives 2330/cm⁻¹ in comparison to the value of 600/cm⁻¹ obtained previously. A theoretical direct count of the harmonic density of states gives 5900/cm⁻¹. The effect of anharmonicity can be estimated by scaling against the ratio of anharmonic to harmonic density for propyne because the diagonal anharmonicities of the latter molecule are known [15]. The anharmonic density of states so calculated for trifluoropropyne is about 7540/cm⁻¹. Trifluoropropyne is of C_{3v} symmetry and the acetylenic CH stretch of A_1 symmetry. The number of states that can couple to this band exclusively through anharmonic interactions is 1/6 of the total or about 1260/cm⁻¹ [16]. For P(1), where only anharmonic interactions are allowed, the experimentally observed density of states, 1154/cm⁻¹, is about 90% of the calculated anharmonic density. This indicates that the dynamics within the molecule are highly mixed, with many or all of the modes eventually receiving the excitation. The R(0) clump, as mentioned before, has an experimental density of states of 2330/cm⁻¹. This is greater than the calculated density of A_1 vibrational states, indicating that ro-vibrational interactions are mixing states of other vibrational symmetry.

A lifetime for the energy redistribution of the CH stretch can be calculated by taking the Fourier transformation of the autocorrelation function of the spectrum [17]. This lifetime is exact if all oscillator strength arises from the 2ν₁ state and if we have observed all of the eigenstates with a significant fraction of 2ν₁ character. Using this method a lifetime of 1490 ps was calculated for the P(1) clump. This is slightly shorter than the 1800 ps lifetime reported in the original paper [1], the difference being due to the addition of several small lines particularly in the wings of the spectrum. It is interesting to compare with this value the lifetime calculated from the original (uncorrected for saturation) data. In this case, the lifetime is calculated to be 600 ps, a factor of 2.5 too short!

Level spacing statistics can also be calculated from a pure sequence of energy levels obtained from a frequency resolved spectrum. Information about the underlying classical dynamics within the molecules is manifested in the manner in which the quantum eigenstates are spaced, at least in the semiclassical limit [18]. For example, regular, non-chaotic dynamics results in a random spacing of energy levels or a Poisson distribution [19]. Chaotic dynamics results in the levels strongly repelling each other and so the distribution of levels becomes almost evenly spaced. This distribution has been described by Wigner and is often modeled with the Gaussian Orthogonal Ensemble (GOE) of levels [20]. For the case of a GOE distribution, the effect on the moments of the distribution of levels that are not observed (due to insufficient signal-to-noise ratio) has been calculated [21].

The moments of the level spacing distribution for P(1) (see Table 1) correspond to a GOE distribution with 90 to 95% of the levels observed which is in excellent agreement with the ratio between the observed and the calculated density of states. The level spacing statistics for R(0) corresponds to a GOE model with about 80% of the levels observed. In this clump, weak Coriolis interactions may be skewing the statistics and the results are not as clear cut.

IR/IR double resonance was used to assign the K structure of the R(1), R(2) and R(3) clumps. An example of this is shown in Fig. 2. By modulating a particular J'', K'' population, using a $v_{CH} = 1 \leftarrow 0$ transition, only those transitions sharing this ground state level will appear in the $v_{CH} = 2 \leftarrow 0$ spectrum. Since for these experiments, the 1.5 μm laser was not yet stabilized, the average linewidth of the $v_{CH} = 2 \leftarrow 0$ spectrum was 10 MHz. Overlaying the $K = 0$ spectrum with the full R(1) spectrum shows that almost all features in the R(1) clump can be assigned to $K = 0$. The intensity ratios for the $K = 0$ spectrum are not identical with that of the full R(1) spectrum and the differences can be attributed to the presence of $K = 1$ lines in the full R(1) spectrum. The $K = 1$ spectrum has lower signal to noise than the $K = 0$ spectrum, although nuclear spin statistical weights dictate that it should have equal integrated intensity (the finite temperature of the beam will not change this significantly) [1]. In addition, the features of the $K = 1$ spectrum are not well resolved, leading to the natural conclusion that the $K = 1$ transition is substantially more fractionated than the $K = 0$. Even the $K = 0$ spectrum is not fully resolved into individual lines as was the case for P(1) and R(0). For this reason, from these clumps only the lifetimes were calculated. For R(2) and R(3), an attempt to use double resonance to extract the $K = 2$ clumps resulted in very low signal to noise spectra which were not analyzed further. In this case, the intensity of the $K = 2$ lines are expected to be somewhat reduced because of the 5 K beam temperature; however, most of the intensity loss was probably due to a further increase in fractionation.

The lifetimes calculated for each measured J', K' clump are listed in Table 2. For the $K = 0$ clumps the lifetime is ap-

Table 2

Lifetimes calculated from the rotationally assigned spectrum of the 2ν₁ band in trifluoropropyne

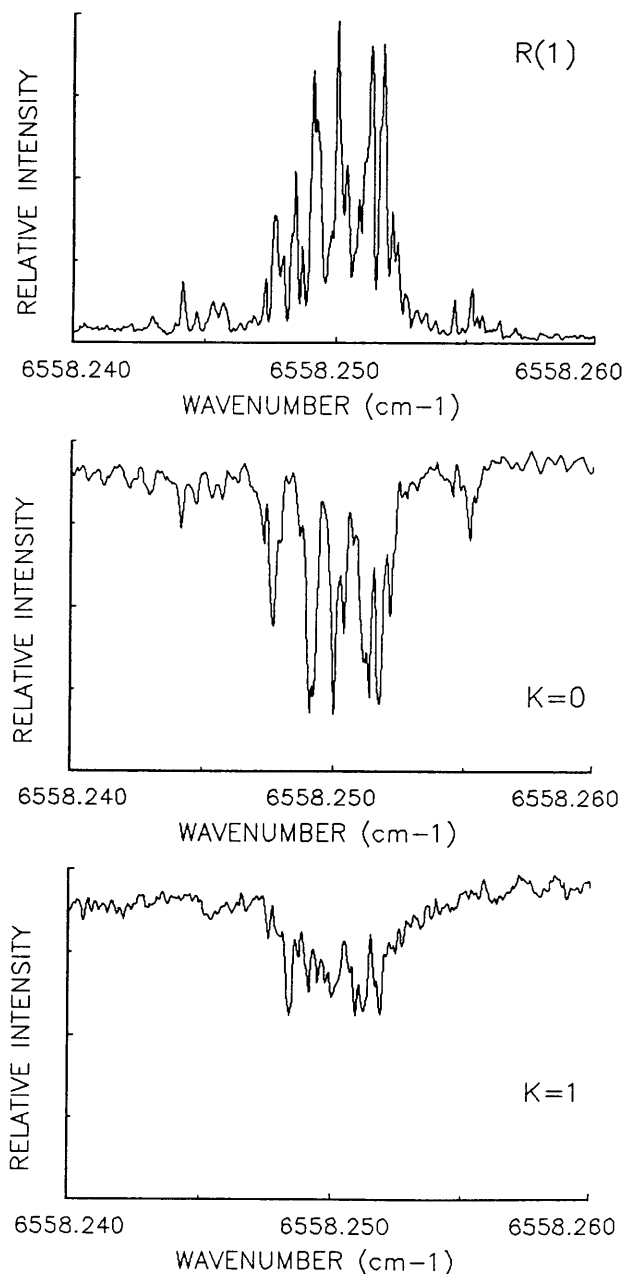| $J'_{K'}$	Lifetime (ns)
0_0	1.49
1_0	1.40
2_0	1.36
3_0	1.42
4_0	1.33
1_1	1.18
2_1	1.72*)
3_1	1.27

*) Very poor signal to noise ratio.

Fig. 2

Assignment of the R(1) clump. The 3 μm laser is used to modulate a $1 \leftarrow 0$ transition; for the $K = 0$ spectrum the line at 3330.2527 cm^{-1}[(1)] and for the $K = 1$ spectrum the line at 3330.2486 cm^{-1}[(1)]

proximately constant at 1.4 ns for $0 \leq J' \leq 4$. The $K = 1$ spectra also indicate similar lifetimes, however the lower signal to noise ratio of these clumps may sometimes result in artificially long lifetimes. The dynamical picture obtained from the above analysis, i.e. of a nearly constant lifetime but an increasing density of states as the rotational quantum number increases, has been observed before in the $3\nu_1$ spectrum of propyne [11]. It was interpreted there, as it can be done here too, as evidence for the existence of a lifetime controlled by anharmonic mixing of the overtone state with the dense background of vibrational states. The increasing level density with J indicates that the background states are

themselves strongly mixed by Coriolis and/or centrifugal interactions, leading to a breakdown of K as even an approximate quantum number, indicating that the intramolecular dynamics scrambles the molecular alignment.

IV. Conclusions

The conclusions drawn from the earlier work on the title molecule [1], that the underlying dynamics in this system are chaotic and nearly all energy levels in the neighborhood of the bright state are coupled, are confirmed. The long lifetime measured in this spectrum (1.4 ns) cannot just be attributed to the isolated nature of the acetylenic CH stretch (leading to little mixing at the normal mode level), since much faster lifetimes have been measured at ν_1 and $2\nu_1$ in $(CH_3)_3CCCH^3$ and $(CF_3)_3CCCH^{21}$ and at $3\nu_1$ in CH_3CCH^{11}. Instead, the long lifetime must be due to the "accidental" absence of low order resonance as it was observed previously in $(CH_3)_3SiCCH^3$ and SF_5CCH^{23}.

The new information gained from the present reinvestigation of the $2\nu_1$ band of trifluoropropyne, is due to the increased strength of the laser field in the build-up cavity, the increased resolution due to the frequency stabilization and the selectivity provided by the double resonance, which allows for the full rotational assignment of this congested spectrum. As usual, however, we would still benefit from even more power and resolution, since that would allow extension to higher J, K levels, which are more highly fractionated and thus more difficult to pump.

References

[1] B.H. Pate, K.K. Lehmann, and G. Scoles, J. Chem. Phys. *95*, 3891 (1991).

[2] K.K. Lehmann, B.H. Pate, and G. Scoles, Ann. Rev. Phys. Chem. (1994) *45*, 241 (1994).

[3] E.R.Th. Kerstel, K.K. Lehmann, T.F. Mentel, B.H. Pate, and G. Scoles, J. Phys. Chem. *95*, 8282 (1991).

[4] G.T. Fraser, B.H. Pate, G.A. Bethardy, and D.S. Perry, Chem. Phys. *175*, 223 (1993).

[5] A.M. Andrews, G.T. Fraser, and B.H. Pate, J Phys Chem, submitted.

[6] The power to saturate vibrational transitions in HCN were calculated using transition dipole moments obtained from the potential functions derived in reference: K.K. Lehmann and A.M. Smith, J. Chem. Phys. *93* 6140 (1990) assuming the resolution was limited by tramnsit time broadening, in which case the saturation power is independent of laser spot size.

[7] A. McIlroy, D.J. Nesbitt, E.R.Th. Kerstel, K.K. Lehmann, B.H. Pate, K.K. Lehmann, and G. Scoles, J. Chem. Phys. *100*, 2596 (1994).

[8] J.E. Gambogi, R.Z. Pearson, X. Yang, K.K. Lehmann, and G. Scoles, Chem. Phys. *190*, 191 (1995).

[9] J.H. Timmermans, K.K. Lehmann, and G. Scoles, Chem. Phys. *190*, 393 (1995).

[10] (a) H.-R. Dübal and M. Quack, Chem. Phys. Lett. *90*, 370 (1982).
(b) K. von Puttkamer, H.-R. Dübal, M. Quack, Faraday Discuss. Chem. Soc. *75*, 197 (1983).
(c) M. Quack, Ann. Rev. Phys. Chem. *41*, 839 (1990).

[11] J.E. Gambogi, E.R.Th. Kerstel, K.K. Lehmann, and G. Scoles, J. Chem. Phys. *100*, 2612 (1994).
[12] W. Demtröder, in: Atomic and Molecular Beam Methods, Vol 2, p 218, ed. G. Scoles, Oxford, University Press, New York 1992.
[13] C.R. Pollock, J.F. Pinto, and E. Georgiou, Appl. Phys. *48*, 287 (1989).
[14] Ch. Breant, T. Baer, D. Nesbitt, and J.L. Hall, Laser Spectroscopy VI: Proceedings of the Sixth International Conference: Interlaken, Switzerland; June 27 – July 1, 1983; eds. H.P. Weber and W. Luthy, Springer Verlag, New York 1983.
[15] A. McIlroy and D.J. Nesbitt, J. Chem. Phys. *91*, 104 (1989).
[16] M. Quack, J. Chem. Phys. *82*, 3277 (1985).
[17] K.F. Freed and A. Nitzan, J. Chem. Phys. *73*, 4765 (1980).
[18] M.V. Berry, Proc. R. Soc. London Ser. A *400*, 229 (1985).
[19] M.V. Berry and M. Tabor, Proc. R. Soc. London Ser. A *356*, 375 (1977).

[20] E.P. Wigner, Phys. Rev. *40*, 749 (1932).
[21] K.K. Lehmann and S.L. Coy, J. Chem. Phys. *87*, 5415 (1987).
[22] J.E. Gambogi, K.K. Lehmann, B.H. Pate, G. Scoles, and X. Yang, J. Chem. Phys. *98*, 1748 (1993).
[23] M. Becucci, J.E. Gambogi, J.H. Timmermans, K.K. Lehmann, G. Scoles, G.L. Gard, and R. Winter, Chem. Phys. *187*, 11 (1994).