



Rotationally-resolved spectroscopy of the ν_{16} band of 1,3,5-trioxane



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ABSTRACT

Rotationally-resolved spectra of the ν_{16} band of 1,3,5-trioxane, centered near 1177 cm^{-1} , have been obtained via cavity ringdown spectroscopy using a continuous-wave external-cavity quantum cascade laser and a slit expansion nozzle. 219 transitions were identified and fitted to determine the excited state rotational constants for this band. In addition to fundamental interest, these data could facilitate spectroscopic detection of trioxane in cometary comae as a tracer for polyoxymethylene.

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1. Introduction

1,3,5-trioxane is a three-unit cyclic polymer of formaldehyde, making it one of the smallest members of the polyoxymethylene (POM) class of molecules. For many years various forms of POM have been proposed as extended sources of formaldehyde in cometary comae, which would make them highly relevant to studies of prebiotic chemistry [1,2]. Although various forms of POM, including trioxane, have been observed in laboratory simulations of cometary conditions [1], to date there have been no conclusive astronomical detections. Since trioxane is both a relatively volatile example of POM and a photodegradation product of larger polymers, it could serve as a useful tracer for POM in general in future work.

Trioxane is a symmetric top of the C_{3v} point group. Its ground state microwave spectrum was observed in 1963 by Oka et al. [3], and the rotational spectra of a number of excited states have been observed since [4–8]. The ν_{17} ro-vibrational band was observed by Henninot et al. in 1992 [9]; prior to the present work, this was the only portion of trioxane's vibrational spectrum observed with rotational resolution.

In this work, we present a rotationally-resolved absorption spectrum of the ν_{16} band of trioxane, centered near 1177 cm^{-1} , observed through cavity ringdown spectroscopy with a continuous-wave external-cavity quantum cascade laser (EC-QCL). The availability of an atmospheric window in this region makes this band well suited for astronomical observations, as it would allow the use of ground- or stratosphere-based telescopes. A successful detection

of cometary trioxane could provide a greater understanding of the formation of formaldehyde and other important organic compounds.

2. Experimental

The spectrometer used in this work (Fig. 1) is a modified version of the QCL-based cavity ringdown spectrometer we have described previously [10,11]. Briefly, continuous-wave laser light is coupled into a high-finesse optical cavity around a continuous supersonic expansion containing the molecule of interest. A germanium acousto-optic modulator (AOM) (ISOMET) is used as a fast shutter, triggered when the light transmitted by the cavity passes a user-defined threshold to initiate a ringdown event. Using the non-diffracted beam, relative frequency calibration is obtained using a Bristol 621B wavemeter; absolute frequency calibration is obtained from the diffracted beam using a triple-pass direct absorption SO_2 reference cell. Rather than locking the laser to the ringdown cavity, the cavity length is dithered by >1 free spectral range at a rate of approximately 250 Hz using a piezo-electric modulator, ensuring that the laser will be on-resonance with the cavity twice per cycle. Back reflection isolation is achieved using a linear polarizer and a Fresnel rhomb.

The primary difference between the current spectrometer and its past incarnations is the incorporation of an EC-QCL in place of the Fabry-Pérot QCL (FP-QCL) used previously. Our EC-QCL uses a Littrow configuration based on designs by Wysocki et al. [12] and utilizes a gain chip provided by the Wysocki lab. In comparison to the FP-QCL, our new EC-QCL features significantly improved tuning range (Fig. 2) and thermo-electric rather than cryogenic cooling at similar output power. The tuning range could also be

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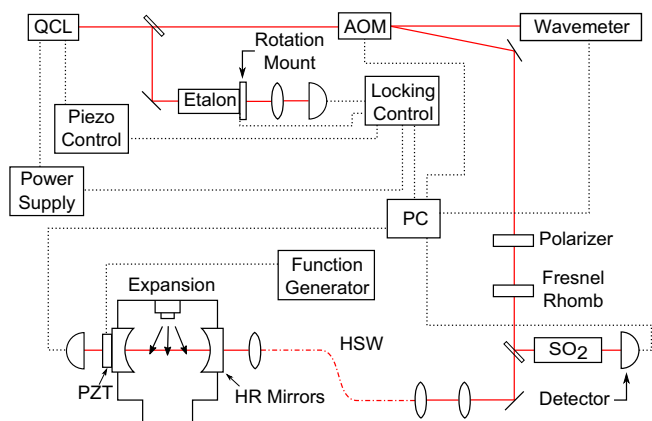


Fig. 1. Experimental layout. Solid red traces indicate the path of the laser in free space; the red dot-dash trace shows the path through the hollow silica waveguide (HSW). Black dotted traces indicate electronic connections. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

easily shifted by swapping gain chips without otherwise altering the laser. These features significantly increase the breadth of spectroscopic targets available to our instrument.

However, the addition of wavelength-selective elements that are highly sensitive to mechanical vibrations and acoustic noise caused significant issues with the stability of the lasing frequency. Immediately after completion, the EC-QCL frequency had a peak-to-peak frequency jitter of over 450 MHz at short (~ 1 s) timescales. Floating the optical table on vibrational isolation legs and detaching the table from our vacuum chamber decreased this jitter to 150 MHz, but made it difficult to maintain consistent alignment of the ringdown cavity, which is attached to the vacuum chamber. To keep alignment consistent, the gap between the optical table and the ringdown cavity was bridged with a hollow silica waveguide (Opto-Knowledge). This solved the alignment issues while maintaining vibrational isolation.

To further improve the frequency stability of the EC-QCL, a tilt-tuned germanium etalon locking system was implemented. This system, which is described in detail elsewhere [13], improved the frequency stability to ~ 1 MHz over a one-second integration time. The laser is adjusted by applying corrections to the injection current, the external cavity length, and the grating angle at fixed ratios that were determined experimentally. The lock point, and thus the laser frequency, is tuned by tilting the germanium etalon

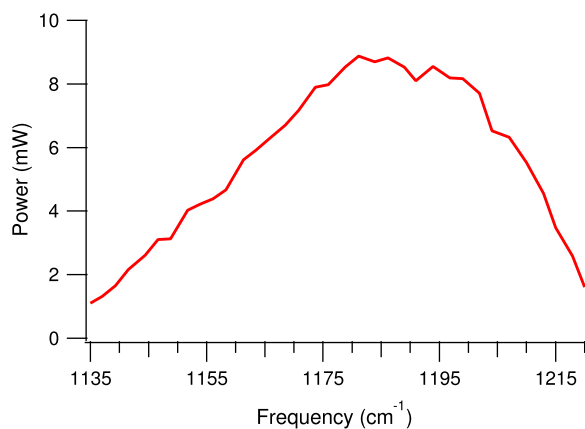


Fig. 2. EC-QCL output power versus frequency. The inclusion of an EC-QCL in our spectrometer has expanded our useful tuning range from 1180–1200 cm^{-1} to 1135–1220 cm^{-1} in comparison to the FP-QCL used previously [10,11].

relative to the incident laser. In the current configuration, this allows a single-scan, mode-hop-free tuning range of $\sim 0.4 \text{ cm}^{-1}$ and an average step size of $\sim 12 \text{ MHz}$; either could be easily adjusted by changing the parameters of the locking system. At present, the locking system is the limiting factor for the mode-hop-free tuning range; for the free-running laser, the range was limited by the cavity length travel to approximately 0.7 cm^{-1} .

To obtain relative calibration, ringdown data collection is paused once per 100 data points to collect a wavemeter reading. Because the germanium etalon used for locking is temperature sensitive, it is possible for significant thermal drift to occur between wavemeter readings; the spacing between these readings therefore entails a tradeoff between accurate calibration and scanning speed. Laser power limitations prevent us from using an experimental layout that would allow for constant wavemeter readings. The readings we do obtain are fit to a fifth-degree polynomial to produce a frequency scale, which is in turn offset by matching the SO_2 reference cell data to HITRAN08 [14]. This corrects for the Bragg shift of the AOM and any systematic offset in the wavemeter readings.

A supersonic expansion of argon produced by a $12.7 \text{ mm} \times 150 \mu\text{m}$ slit at 2 atm backing pressure was used for this work. The argon flow was split between two paths before being recombined prior to the slit; the first path consisted of unobstructed tubing, while the second passed through a bed of solid trioxane before encountering a needle valve. The ratio of argon flow through each arm could be controlled by adjusting the needle valve, allowing an adjustable amount of trioxane in the expansion. Furthermore, in order to limit the effect of high temperature gas outside of the expansion, tubes were extended between the ringdown mirrors and the expansion nozzle. A flow of nitrogen through these tubes limited the amount of high-temperature trioxane in the beam path.

3. Results and discussion

Ro-vibrational spectra were obtained for trioxane between 1175.93 and 1179.28 cm^{-1} (Figs. 3 and 4), with an average step size of 12 MHz. This range included several Q-branches and portions of both the P and R branches. Fitting was performed using PGOPHER [15]; 219 transitions were assigned with an average fitting residual of 26.02 MHz. The rotational parameters obtained are presented in Table 1. Ground state parameters were fixed at the values obtained by Gadhi et al. [8] where available, and excited-state values for D_J and the sextic centrifugal distortion constants have been fixed at the ground-state values. C'' has not yet been determined experimentally, but was fixed at an estimated value of 2950 MHz for this work [8,16]. We note that ν_0 , ζ , and C' are dependent upon the value of C'' ; expressions independent of the value of C'' have been provided instead.

The relatively large uncertainty in the fit can be attributed to the uncertainty of our relative frequency calibration. Approximately two minutes pass between wavemeter readings; during this time, the laser's frequency can drift from the expected tuning curve. We estimate that, between fitting errors and uncertainty in the wavemeter readings, our frequency calibration is accurate to approximately $\pm 32.7 \text{ MHz}$. This could be remedied by obtaining continuous wavelength measurements, though present laser power limitations prevent us from doing so via wavemeter.

Additionally, we note that relative intensities are inconsistent between experimental and simulated spectra. This appears to be due to undersampling of the absorption peaks in the experimental spectrum. Scans with smaller step sizes matched simulated intensities well, but the slower scan rate exaggerated the effects of etalon drift on the frequency calibration. As we are more

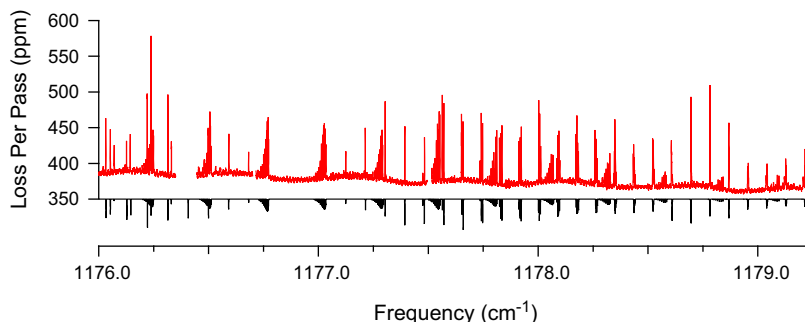


Fig. 3. Experimental and simulated spectra of the ν_{16} band of 1,3,5-trioxane. The red top trace shows the experimental spectrum; the blank regions were not scanned or included in fitting. The slow baseline drift results from changes in mirror reflectivity. The lower black trace shows a simulated spectrum produced using PGOPHER [15]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

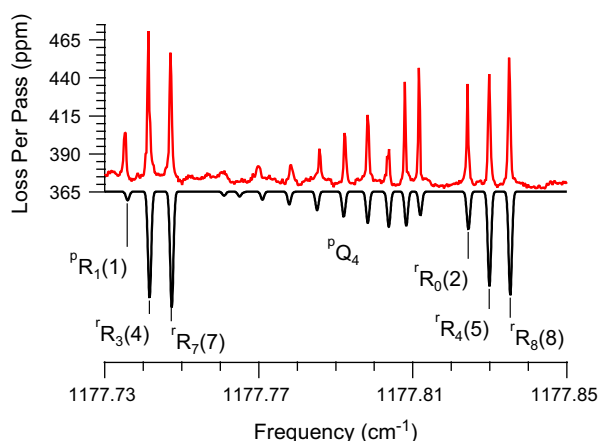


Fig. 4. Expanded view of experimental and simulated spectra. The red top trace shows the experimental spectrum; the lower black trace shows the simulated spectrum. Differences in relative intensities are due to undersampling of peaks in the experimental spectrum. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

Listing of spectroscopic constants for 1,3,5-trioxane. The band origin is given in cm^{-1} . Quartic centrifugal distortion constants and the $J(J+1)$ dependence of the Coriolis constant (η_j) are given in kHz; sextic centrifugal distortion constants are given in Hz. All other constants are given in MHz. Note that C'' is fixed at an estimated value of 2950 MHz. D_j' and the excited-state sextic centrifugal distortion constants were fixed to their ground state values.

	$\nu_{16} = 1$	$\nu = 0$ [8,16]
$\nu_0 + (C' - B' - 2C'\zeta)$ (cm^{-1})	1176.77314(11)	–
B (MHz)	5262.624(51)	5273.25767(20)
$C'' - C'$ (MHz)	5.93(12)	–
D_j (kHz)	1.34622	1.34622(34)
D_{JK} (kHz)	–1.97(80)	–2.0243(15)
H_j (Hz)	0.00118	0.00118(10)
H_{JK} (Hz)	–0.00430	–0.00430(40)
H_{KJ} (Hz)	0.0031	0.0031(10)
$C' - B' - C'\zeta$	–3905.81(53)	–
η_j (kHz)	66(11)	–
q^+ (MHz)	2.40(20)	–

concerned with frequency accuracy than intensities in this work, the faster scans were used.

4. Conclusion

The increased tuning range afforded by our new EC-QCL light source has allowed us to record the ν_{16} band of 1,3,5-trioxane,

which has not previously been observed at rotational resolution. We have been able to assign 219 transitions in this band and obtain excited-state rotational constants. In addition to demonstrating the capabilities of our improved spectrometer, these data could be suitable for astronomical observations of trioxane, which is a potential tracer for the prebiotically-important polyoxymethylene class of molecules.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jms.2015.09.003>.

References

- [1] H. Cottin, M.-C. Gazeau, J.-F. Doussin, F. Raulin, J. Photochem. Photobiol. A 135 (2000) 53.
- [2] H. Cottin, Y. Bénilan, M.-C. Gazeau, F. Raulin, Icarus 167 (2004) 397.
- [3] T. Oka, K. Tsuchiya, S. Iwata, Y. Morino, Bull. Chem. Soc. Jpn. 37 (1964) 4.
- [4] J. Bellet, J.-M. Colmont, J. Lemaire, J. Mol. Spec. 34 (1970) 190.
- [5] J.-M. Colmont, J. Mol. Spec. 58 (1975) 220.
- [6] J.-M. Colmont, J. Mol. Struct. 62 (1980) 85.
- [7] J.-M. Colmont, J. Mol. Spec. 80 (1980) 166.
- [8] J. Gadh, G. Włodarczak, D. Boucher, J. Demaison, J. Mol. Spec. 133 (1989) 406.
- [9] J.-F. Henninot, H. Bolvin, J. Demaison, B. Lemoine, J. Mol. Spec. 152 (1992) 62.
- [10] B.E. Brumfield, J.T. Stewart, S.L. Widicus Weaver, M.D. Escarra, S.S. Howard, C.F. Gmachl, B.J. McCall, Rev. Sci. Instrum. 81 (2010) 063102.
- [11] B.E. Brumfield, J.T. Stewart, B.J. McCall, J. Mol. Spec. 266 (2011) 57.
- [12] G. Wysocki, R. Lewicki, R.F. Curl, F.K. Tittel, L. Diehl, F. Capasso, M. Troccoli, G. Hoffer, D. Bour, S. Corzine, R. Maulini, M. Giovannini, J. Faist, Appl. Phys. B 92 (2008) 305.
- [13] B.M. Gibson, B.J. McCall, Opt. Lett. 40 (2015) 2696.
- [14] L.S. Rothman, I.E. Gordon, A. Barbe, D. Chris Benner, P.F. Bernath, M. Birk, V. Boudon, L.R. Brown, A. Campargue, J.-P. Champion, K. Chance, L.H. Coudert, V. Dana, V.M. Devi, S. Fally, J.-M. Flaud, R.R. Gamache, A. Goldman, D. Jacquemart, I. Kleiner, N. Lacome, W.J. Lafferty, J.-Y. Mandin, S.T. Massie, S.N. Mikhailenko, C.E. Miller, N. Moazzen-Ahmadi, O.V. Naumenko, A.V. Nikitin, J. Orphal, V.I. Perevalov, A. Perrin, A. Predoi-Cross, C.P. Rinsland, M. Rotger, M. Šimečková, M. A.H. Smith, K. Sung, S.A. Tashkun, J. Tennyson, R.A. Toth, A.C. Vandaele, J. Vander Auwera, J. Quant. Spectrosc. Radiat. Transfer 110 (2009) 533.
- [15] C.M. Western, PGOPHER, A Program for Simulating Rotational Structure, <<http://pgopher.chm.bris.ac.uk>> (accessed 04.01.15).
- [16] M. Motamedi, N. Khademi, E.J. Chem. 6 (S1) (2009) S259.