



# High resolution analysis of the $\nu_{26}$ and $2\nu_9 - \nu_9$ bands of propane: Modeling of Titan's infrared spectrum at $13.4\ \mu\text{m}$

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J. M. Flaud, K Kwabia Tchana, W.J. Lafferty, C. Nixon. High resolution analysis of the  $\nu_{26}$  and  $2\nu_9 - \nu_9$  bands of propane: Modeling of Titan's infrared spectrum at  $13.4\ \mu\text{m}$ . Molecular Physics, 2010, 108 (06), pp.699-704. 10.1080/00268970903501709 . hal-00588658

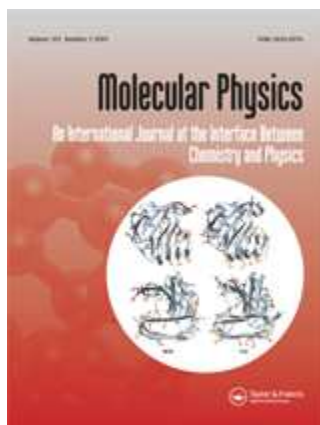
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Journal:	<i>Molecular Physics</i>
Manuscript ID:	TMPh-2009-0301.R1
Manuscript Type:	Special Issue Paper -HRMS Stabia 09/ High Resolution Molecular Spectroscopy
Date Submitted by the Author:	03-Nov-2009
Complete List of Authors:	Flaud, J. M.; LISA, Uni. Paris Est Kwabia Tchana, K; LISA, Uni. Paris EST Lafferty, W.J.; NIST Nixon, C.; University of Maryland, Department of Astronomy
Keywords:	High resolution IR, Propane, Molecular parameters
Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.	
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**High resolution analysis of the  $\nu_{26}$  and  $2\nu_9 - \nu_9$  bands of propane: Modeling of Titan’s infrared spectrum at 13.4  $\mu\text{m}$**

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**Abstract**

Using high-resolution Fourier transform spectra of propane recorded in the 13.4  $\mu\text{m}$  (resolution of 0.002  $\text{cm}^{-1}$ ) and in the 27.4  $\mu\text{m}$  (resolution 0.0011  $\text{cm}^{-1}$ ) spectral regions, it was possible to perform a thorough assignment of both the  $\nu_{26}$  band at 745  $\text{cm}^{-1}$  and the  $2\nu_9 - \nu_9$  band at about 370  $\text{cm}^{-1}$ . This simultaneous assignment was necessary since the  $26^1$  and  $9^2$  rotational levels interact strongly through an A-type Coriolis interaction. The experimental upper-state rotational levels were fit using a Hamiltonian matrix which takes into account explicitly this strong A-type Coriolis interaction. With this model the experimental energy levels were fit to within their experimental uncertainties and accurate band centers, rotational, centrifugal distortion and coupling constants were determined. The following band centers were derived:  $\nu_0(\nu_{26}) = 748.530882(80) \text{ cm}^{-1}$  and  $\nu_0(2\nu_9) = 740.29213(10) \text{ cm}^{-1}$ . Finally, we show how the use of these new spectral parameters greatly improves the accuracy of modeling of Titan's infrared spectrum at 13.4  $\mu\text{m}$ , relative to the currently available GEISA atlas for the same band.

I. Introduction

The 13.4  $\mu\text{m}$  absorption region of propane is of very high interest since this is the spectral region that led to the first detection of this molecule in the atmosphere of the giant planets [1,2] and Titan [3]. Note as well that the  $748\text{ cm}^{-1}$  band has been exclusively and extensively used to derive the abundance and/or concentration profiles of propane in the Titan atmosphere (see for example refs. [4-6]). In fact, it is only recently that other spectral regions have been used for this purpose [7]. The propane absorption at  $13.4\text{ }\mu\text{m}$  is mostly due to the  $\nu_{26}$  band [8]. It has been studied at high resolution using a tunable diode laser spectrometer and analyzed assuming that the  $26^1$  vibrational state was isolated [9]. In this case such an assumption was valid given the J and  $K_a$  range of the observed transitions.

In this paper, we present an extensive analysis of the  $13.4\text{ }\mu\text{m}$  absorption region of propane combined with an analysis of the  $27.4\text{ }\mu\text{m}$  region. It was necessary to work simultaneously in these two spectral regions since the  $26^1$  ro-vibrational levels interact strongly with the  $9^2$  ro-vibrational level through an intense A-type Coriolis resonance. While the  $26^1$  rotational levels were observed in the  $13.4\text{ }\mu\text{m}$  spectral domain, the  $9^2$  rotational levels were derived from assigning the  $2\nu_9 - \nu_9$  hot band in the  $27.4\text{ }\mu\text{m}$  spectral region. The  $2\nu_9$  band is quite weak and cannot be observed at  $13.4\text{ }\mu\text{m}$  except where the  $9^2$  levels resonate with  $26^1$  levels.

Propane is an asymmetric top with  $C_{2v}$  symmetry. Its structure and symmetry properties are given in Fig. 1 of ref. [10].

II. Experimental details

The high-resolution absorption spectrum of propane was recorded using the Bruker IFS 125HR Fourier transform spectrometer<sup>1</sup> (an upgraded version of the IFS 120HR) at LISA in Créteil. The spectrometer was equipped with a Globar source, a Ge/KBr beamsplitter and a MCT photovoltaic detector cooled by liquid nitrogen. The Fourier transform spectrometer (FTS) was

<sup>1</sup> Certain commercial equipment instruments or materials are identified in this paper to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

evacuated down to 6.7 Pa (0.05 Torr) pressure (to minimize residual H<sub>2</sub>O and CO<sub>2</sub> absorption in the spectra), and a 1.3 mm entrance aperture diameter was used. The spectrum was the result of the co-addition of 600 interferograms collected with a Maximum Optical Path Difference (MOPD) of 450 cm (which corresponds to a resolution of 0.002 cm<sup>-1</sup>, as defined by Bruker) and was not numerically apodized.

The White-type multipass absorption cell, made of pyrex glass and equipped with CsBr windows, was connected to the FTS with a dedicated optical interface (six mirrors) inside the sample chamber of the FTS. Its base length is 0.80 m, and, for the experiment described here, an optical path of 19.2 m was used. The sample of propane was obtained from Sigma Aldrich. The chemical purity of propane was specified to 99.97% and was used without further purification. The absorption cell was evacuated and filled with 273.6 (7) Pa (2.052 (5) Torr) of pure propane. Sample pressure in the cell was measured using calibrated MKS Baratron gauge (accuracy of 0.25%) with a full scale reading of 10 Torr. The White-type long path cell was at a room temperature of 22 °C.

The spectrum was calibrated with residual CO<sub>2</sub> and H<sub>2</sub>O lines observed in the spectrum between 600 and 1400 cm<sup>-1</sup>, with their wavenumbers taken respectively from HITRAN04 [11] and Toth [12]. The spectral calibration is accurate to within 0.0003 cm<sup>-1</sup> (RMS).

Fig. 1 gives an overview of the propane spectrum showing the high signal-to-noise ratio which was obtained. The distinctive shape of the C-type  $\nu_{26}$  band with its narrow Q-branch is easily recognizable.

### III. Analysis and results

The assignment process was started using the upper state constants of [9] and considering 26<sup>1</sup> as an isolated vibrational state. It was possible to assign transitions with low and medium J and K<sub>a</sub> quantum numbers rather easily. However, as soon as K<sub>a</sub> values around 15 and 16 were reached, it appeared that the predicted positions obtained using a single Watson-type Hamiltonian were incorrect; the predictions clearly became worse with increasing K<sub>a</sub> values. Looking for possible interacting states, one option was to consider an A-type Coriolis interaction between the rotational levels of the 26<sup>1</sup> and 9<sup>2</sup> vibrational states. The corresponding Hamiltonian matrix is given in Table 1. As preliminary band centers and rotational and centrifugal distortion constants for the 9<sup>2</sup> state, we extrapolated the values previously obtained for the 9<sup>1</sup> state [13]. In this way, high K<sub>a</sub> transitions of  $\nu_{26}$  could better predicted and confidently assigned. As a result, good predictions could be made for the

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2  $2\nu_9$  transitions with  $K_a$  values ranging from 18 to 23. These transitions could be observed and  
3 together with the  $\nu_{26}$  transitions were fitted using the two state model (Table 1). Note that these  $2\nu_9$   
4 transitions could be observed only because they borrow their intensity from the strong resonating  $\nu_{26}$   
5 lines. In fact,  $2\nu_9$  is very weak and no other transitions belonging to this band could be observed at  
6  $13.4\ \mu\text{m}$ . We then decided to look for the  $2\nu_9 - \nu_9$  hot band located at about  $370\ \text{cm}^{-1}$ . At room  
7 temperature this band has an intensity of about 33% of the corresponding cold band,  $\nu_9$ . Assigning  
8 this hot band proved to be not too difficult given the previous assignments at  $13.4\ \mu\text{m}$  and the quality  
9 of the model. We worked simultaneously in both regions until it was not possible to assign any  
10 additional new lines.  
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14 Table 2 gives the number of levels and the range of quantum numbers,  $J$  and  $K_a$  which were  
15 observed for both states. These levels were fit using the two state Hamiltonian model given in Table  
16 1. The fit is quite nice as can be seen from the statistical analysis of Table 2 and the standard  
17 deviation of  $0.41 \times 10^{-3}\ \text{cm}^{-1}$ . The corresponding spectroscopic constants are given in Table 3. Using  
18 these spectroscopic constants, we have generated a line list of positions and intensities for the  $\nu_{26}$   
19 and  $2\nu_9$  bands at  $13.4\ \mu\text{m}$  and for the  $2\nu_9 - \nu_9$  hot band at  $27.4\ \mu\text{m}$ . Fig. 1 presents a simulation of the  
20 entire  $13.4\ \mu\text{m}$  region showing the good agreement between the observed and calculated spectra.  
21 Note the appearance of hot bands around  $749.5$  and  $750.9\ \text{cm}^{-1}$  which are not included in the  
22 simulation. Fig. 2 shows a portion of the  $\nu_{26}$  spectrum where high  $K_a$  'R' transitions are clearly visible.  
23 One high  $K_a$  'R' transition of  $2\nu_9$  is seen in the spectrum. We note that these  $2\nu_9$  transitions can be  
24 seen only because high  $K_a$  levels of  $9^2$  resonate with high  $K_a$  levels of  $26^1$  through a strong A-type  
25 Coriolis resonance. Finally, in Fig. 3 the  $^{\text{P}}\text{Q}_9$ -branch of the hot band  $2\nu_9 - \nu_9$  is clearly visible. In all  
26 cases the agreement between simulation and observation is quite good showing the quality of the  
27 simulations.  
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36 **IV. Application to Titan**

37 Recently, Titan's mid-infrared spectrum was searched for the presence of multiple propane  
38 bands [7], using data recorded by the Cassini Composite Infrared Spectrometer [15]. This research  
39 demonstrated that at least five further bands are now clearly detected, in addition to the  $\nu_{26}$  band  
40 traditionally used to measure propane in outer planet atmospheres, and providing the opportunity to  
41 make multiple independent estimates of the abundance of the gas. Using a newly-available line list  
42 for several bands near  $7\ \mu\text{m}$  [10], Nixon et al. made the first measurement of propane's abundance  
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via the  $\nu_{18}$  band at  $7.3 \mu\text{m}$ , applied to Titan low-latitude limb data, comparing it to a simultaneous measurement using the  $\nu_{26}$  band. The resulting abundances (Volume mixing ratio (VMR)):  $(5.7 \pm 0.8) \times 10^{-7}$  and  $(4.2 \pm 0.5) \times 10^{-7}$  respectively did not quite overlap at  $1-\sigma$  level of error, and in addition it was clear that the GEISA 2003 spectral data [16] used to model the  $\nu_{26}$  was not fitting all the propane emission, especially a suspected hot band on the short wavelength side of the main band.

We have therefore sought to check whether the new parameters for the  $\nu_{26}$  and other bands at  $13.4 \mu\text{m}$  improve the fitting of the Titan spectrum in this region, using the same dataset and model as [7]. Fig. 4 shows the comparison between the Titan spectrum ( $0.5 \text{ cm}^{-1}$  apodized resolution) and three models (see [7] for details), including a no-propane model for reference. It is immediately apparent that the new propane list<sup>2</sup> provides a significantly improved fit to the spectrum ( $\chi^2/n$  reduces from 6.9 to 2.4) especially in the hot band emission centered near  $749.75 \text{ cm}^{-1}$ . Moreover, the inferred abundance in VMR of propane at 2 mbar increases by a factor of  $\sim 1.6$  to  $(6.6 \pm 0.7) \times 10^{-7}$ , reducing the discrepancy with the  $\nu_{18}$  band from  $-1.5 \times 10^{-7}$ , to  $+0.9 \times 10^{-7}$  – an agreement finally to within the predicted measurement error.

## V. Conclusion

A complete and simultaneous analysis of high-resolution Fourier transform spectra recorded in the  $748$  and  $370 \text{ cm}^{-1}$  regions has permitted the assignment of a large number of transitions of the  $\nu_{26}$  and  $2\nu_9$  bands of propane at  $13 \mu\text{m}$  and of the accompanying hot band  $2\nu_9 - \nu_9$  at  $27.4 \mu\text{m}$ . A set of accurate spectroscopic constants was obtained for both upper states using a two state Hamiltonian model taking explicitly into account the strong A-type Coriolis interaction linking the rotational levels of the  $26^1$  and  $9^2$  vibrational states. Application of the new line list to the modeling of a low-latitude Titan spectrum significantly improves the fitting between model and data relative to the publicly available GEISA data, and should provide a substantial increase in accuracy for researchers using the  $\nu_{26}$  band to measure propane's abundance in planetary atmospheres.

## Acknowledgments

<sup>2</sup>The linelist can be obtained from the authors..

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The part of this study carried out at NIST was supported by the Upper Atmospheric Program of NASA. JMF thanks the Optical Technology Division for support during his stay at NIST. CAN acknowledges the support of the NASA Cassini Data Analysis Program Grant NNX09AK55G.

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## Captions to figures

**Fig. 1.** Overview of the  $\nu_{26}$  band of propane. The distinctive shape of this typical C-type band is clearly visible.

**Fig. 2.** High  $K_a$  lines of the  $\nu_{26}$  band of propane. The  $2\nu_9$  line is visible only because it borrows its intensity from  $\nu_{26}$  through a strong A-type Coriolis resonance.

**Fig. 3.** The  $^PQ_9$ -branch of the  $2\nu_9 - \nu_9$  hot band of propane. The lines marked with a \* belong to the  $\nu_9$  cold band [11]. All the  $2\nu_9 - \nu_9$  lines are well modeled.

**Fig. 4.** Upper panel: Titan spectral average, 30°S-30°N latitude, 100-150 km detector centers (black line) compared to three models: (i) no propane,  $C_2H_2$ ,  $C_2H_6$  and HCN only (blue); (ii) GEISA 2003 propane atlas (green); (iii) propane atlas from this work (red). Lower panel: the data-model residual. Note that the GEISA 2003 atlas lacks the hot band emission at  $749.75\text{ cm}^{-1}$  that is fitted in the new model.

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**List of Tables**

**Table 1:** Hamiltonian matrix used to calculate the  $\{26^1, 9^2\}$  interacting states of propane.

**Table 2:** Range of quantum numbers observed for experimental energy levels of the vibrational states  $26^1$  and  $9^2$  of propane.

**Table 3:** Vibrational band centers, rotational and Coriolis interaction constants (in  $\text{cm}^{-1}$ ) for the  $\{26^1, 9^2\}$  interacting states of propane.

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Table 1

	$26^1$	$9^2$
$26^1$	$H_W$	Herm conj
$9^2$	$C^A$	$H_W$

v-diagonal operators:

$$H_W = E_v + [A^v - \frac{1}{2}(B^v + C^v)]J_z^2 + \frac{1}{2}(B^v + C^v)J^2 + \frac{1}{2}(B^v - C^v)J_{xy}^2$$

$$-\Delta_K^v J_z^4 - \Delta_{JK}^v J_z^2 J^2 - \Delta_J^v (J^2)^2 - \delta_K^v \{J_z^2, J_{xy}^2\} - 2\delta_J^v J_{xy}^2 J^2$$

$$+ H_K^v J_z^6 + H_{KJ}^v J_z^4 J^2 + H_{JK}^v J_z^2 (J^2)^2 + H_J^v (J^2)^3$$

$$+ h_K^v \{J_z^4, J_{xy}^2\} + h_{KJ}^v \{J_z^2, J_{xy}^2\} J^2 + 2h_J^v J_{xy}^2 (J^2)^2$$

$$+ L_K^v J_z^8 + L_{KKJ}^v J_z^6 J^2 + L_{KJ}^v J_z^4 (J^2)^2 + L_{JK}^v J_z^2 (J^2)^3 + L_J^v (J^2)^4$$

$$+ l_K^v \{J_z^6, J_{xy}^2\} + l_{KJ}^v \{J_z^4, J_{xy}^2\} J^2 + l_{JK}^v \{J_z^2, J_{xy}^2\} (J^2)^2 + 2l_J^v J_{xy}^2 (J^2)^3$$

$$+ P_K^v J_z^{10} + P_{KKKJ}^v J_z^8 J^2 + P_{KKJ}^v J_z^6 J^4 + \dots$$

v-off-diagonal operators:

$$C^A = h_1^A J_z + h_2^A \{i J_y, J_x\} + h_3^A J_z J^2 + h_4^A \{\{i J_y, J_x\}, J_z^2\}$$

$$\text{with } \{A, B\} = AB + BA, J_{\pm} = J_x \mp i J_y \text{ and } J_{xy}^2 = J_x^2 - J_y^2$$

Table 2

Vibrational State	26 <sup>1</sup>	9 <sup>2</sup>
Number of levels	1062	741
J <sub>max</sub>	58	46
K <sub>max</sub>	31	26
0.0000≤δ<0.0003	78.5%	70.6%
0.0003≤δ<0.0006	13.3%	18.1%
0.0006≤δ<0.0012	6.4%	7.3%
0.0004≤δ<0.0035	1.8%	4.0%
Std, Deviation (10 <sup>-3</sup> cm <sup>-1</sup> )	0.41	

$\delta = |E_{\text{Obs.}} - E_{\text{Calc}}| \text{ in cm}^{-1}$

Table 3

	$0^0$	$26^1$	$g^2$
$E_v$		748.530882(80)	740.29213(10)
A	0.9742562313 <sup>a</sup>	0.97455697 (170)	0.99582808(210)
B	0.2817271865	0.280898922(500)	0.281336087(650)
C	0.2488055608	0.248098043(410)	0.247503322(560)
$\Delta_K \times 10^6$	5.324721011	5.356984 (5000)	6.799600(8900)
$\Delta_{JK} \times 10^7$	-8.998168326	-8.85088(2500)	-8.49929(2100)
$\Delta_J \times 10^7$	2.402258565	2.389984(2300)	2.346993(3200)
$\delta_K \times 10^7$	1.035202827	1.1900(1500)	6.6482(3000)
$\delta_J \times 10^8$	4.659136555	4.69748(1300)	4.67524(2000)
$H_K \times 10^{10}$	1.147493844	1.20062(4600)	2.20292(9100)
$H_{KJ} \times 10^{11}$	-4.071816910	-4.6480(3700)	b
$H_{JK} \times 10^{13}$	5.193592962	b	b
$H_J \times 10^{13}$	2.755239426	b	b
$h_K \times 10^{12}$	-2.568443533	b	b
$h_{KJ} \times 10^{12}$	1.377953277	b	b
$h_J \times 10^{13}$	1.197995448	b	b
$L_K \times 10^{15}$	-2.625149429	b	b
$L_{KKJ} \times 10^{16}$	4.703253742	b	b
$L_J \times 10^{19}$	-7.104915228	b	b

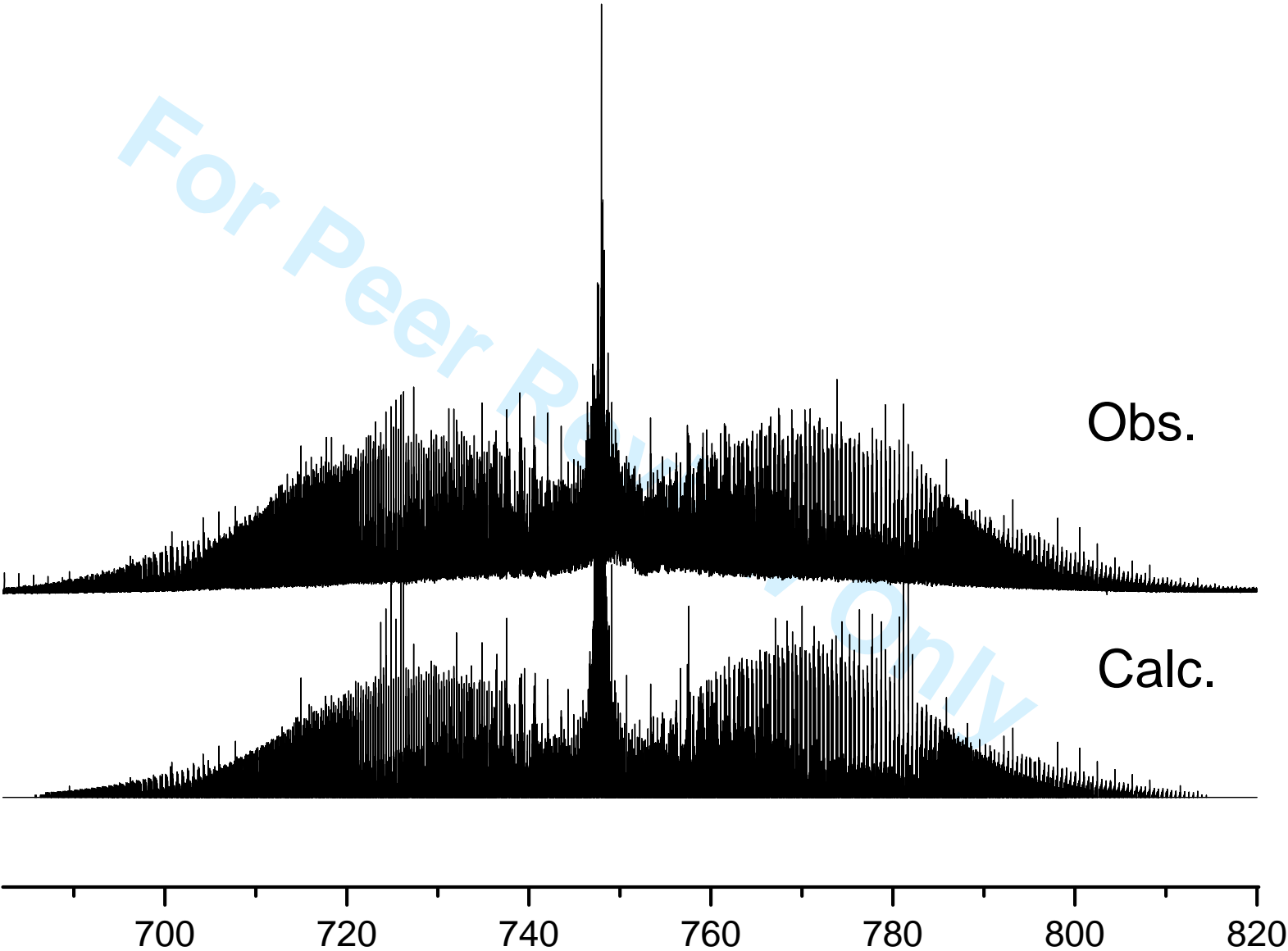
  

$\langle g^2   26^1 \rangle$	
$h_1^A$	$0.4458926(1400) \times 10^{-1}$
$h_2^A$	$0.4739(1700) \times 10^{-5}$
$h_3^A$	$0.98996(2000) \times 10^{-6}$
$h_4^A$	$-0.20140(9000) \times 10^{-6}$

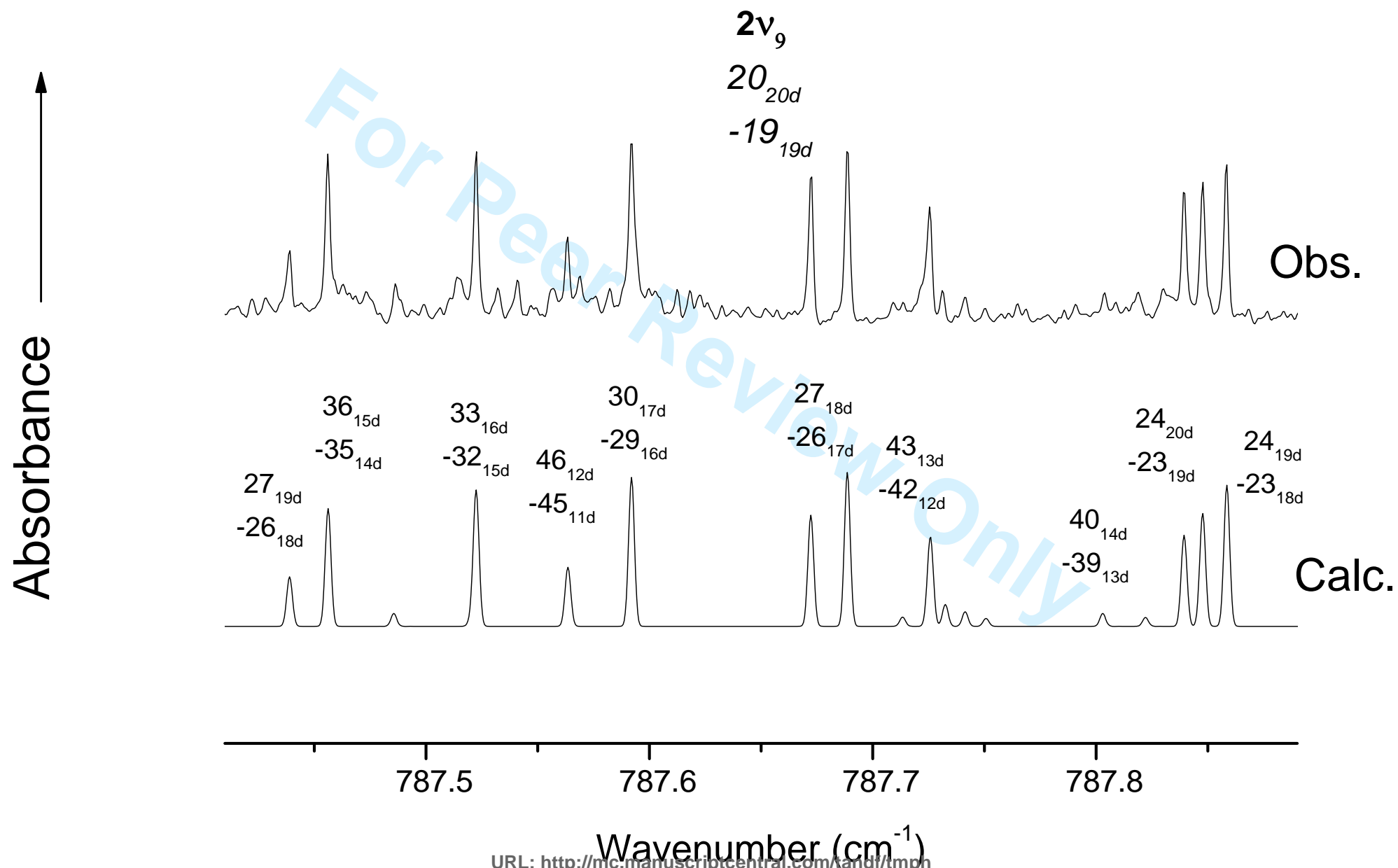
<sup>a</sup> Ground state values from ref. [14].<sup>b</sup> Fixed at ground state values.<sup>c</sup> Uncertainties are  $1\sigma$ .

Overview of the  $\nu_{26}$  band of propane

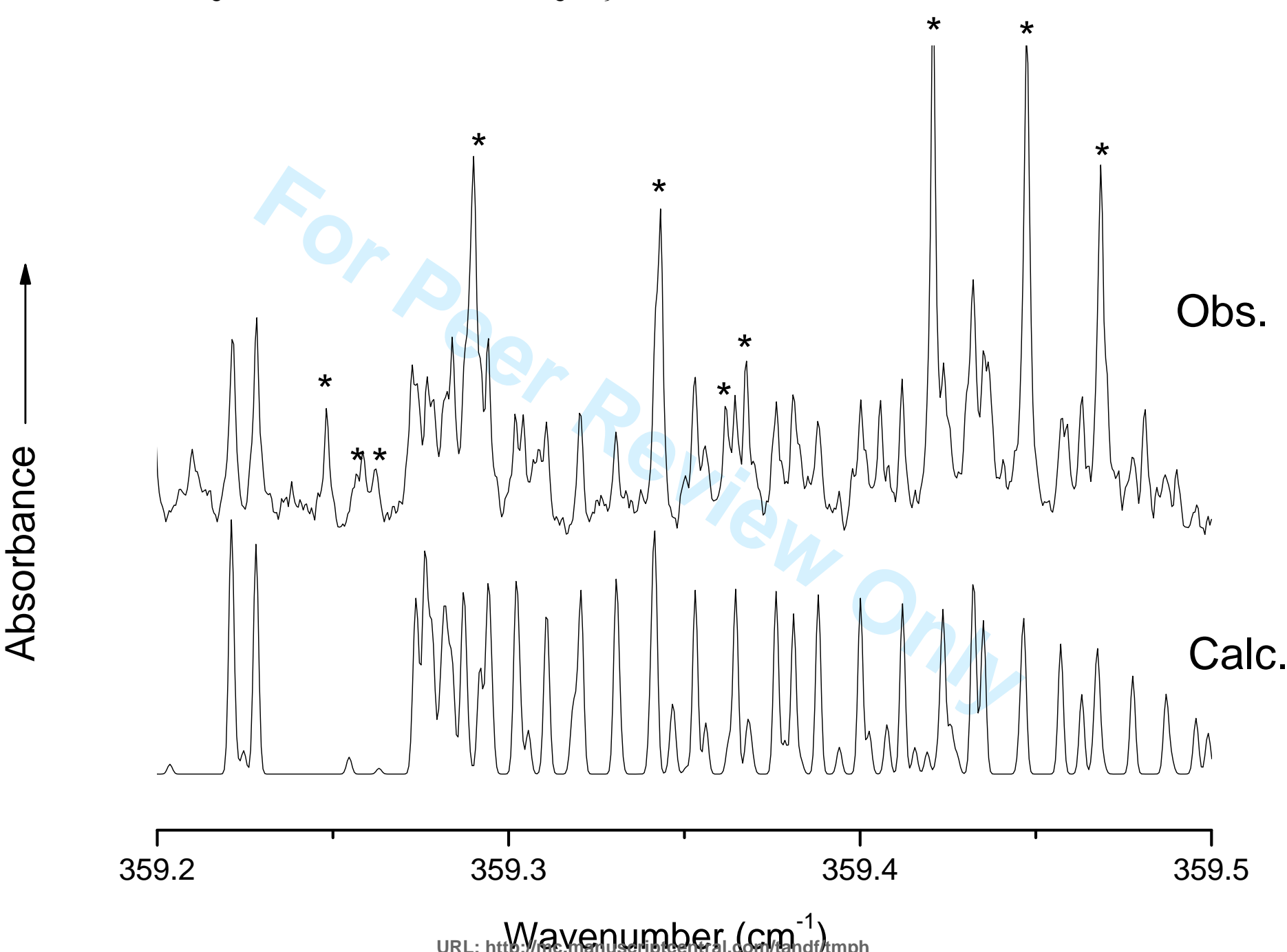
Absorbance

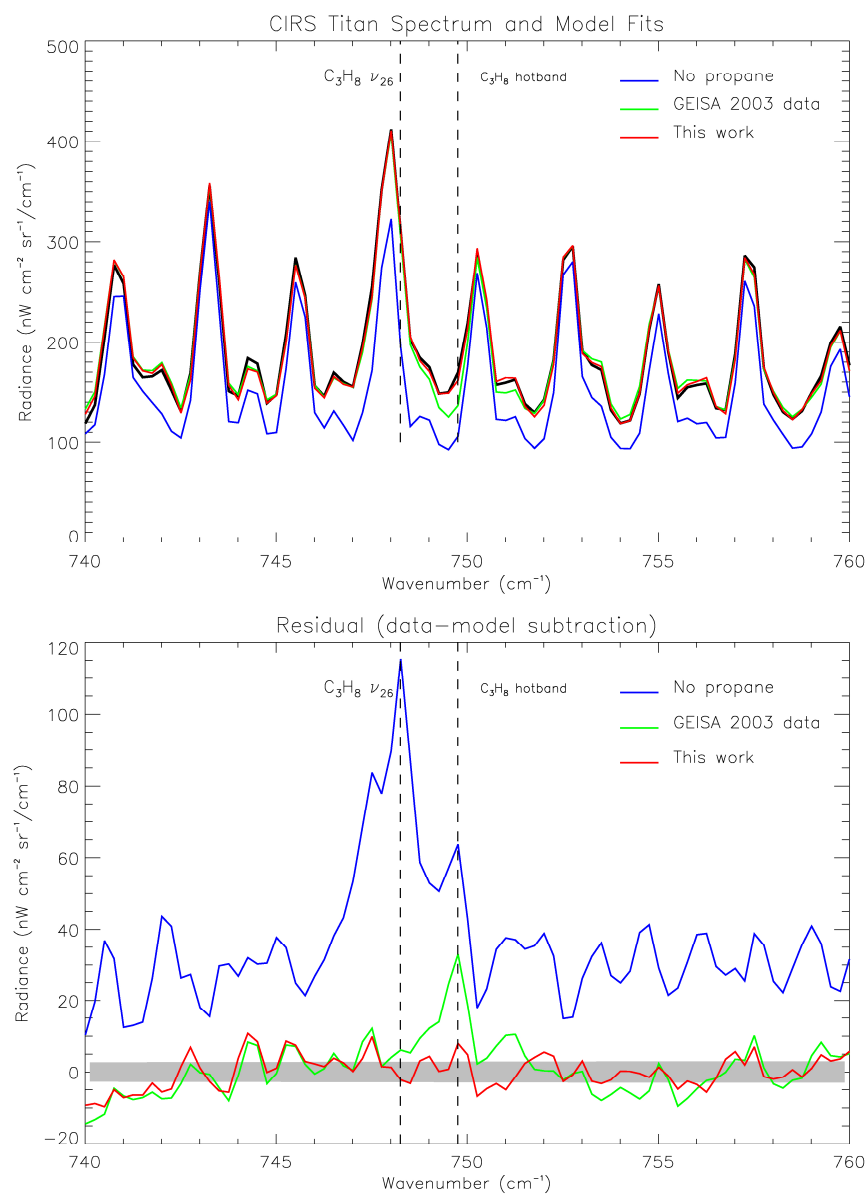


Wavenumber ( $\text{cm}^{-1}$ )

High  $K_a$  lines of the  $\nu_{26}$  band of propane

# The $^pQ_9$ -branch of the $2\nu_9$ - $\nu_9$ hot band of propane





1322x1763mm (72 x 72 DPI)