N90-26748

# LABORATORY STUDIES, ANALYSIS, AND INTERPRETATION OF THE SPECTRA OF HYDROCARBONS PRESENT IN PLANETARY ATMOSPHERES INCLUDING CYANOACETYLENE, ACETYLENE, PROPANE, AND ETHANE

WILLIAM E. BLASS*, STEPHEN J. DAUNT*,**, ANTONI V. PETERS** and MARK C. WEBER*
*Department of Physics and Astronomy, The University of Tennessee, Knoxville, TN 37996-1200, **Department of Chemistry, Concordia University, Montreal, P.Q. H3G 1M8 Canada

## ABSTRACT

Combining broadband FTS data from the McMath facility at NSO and from NRC in Ottawa and narrow band TDL data from our laboratories with novel computational physics techniques has produced a broad range of results for the study of planetary atmospheres.

Motivation for our effort flows from the Voyager/IRIS observations and the needs of Voyager analysis for laboratory results. In addition, anticipation of the Cassini mission adds incentive to pursue studies of observed and potentially observable constituents planetary atmospheres.

Current studies include cyanoacetylene, acetylene, propane, and ethane. Particular attention is devoted to cyanoacetylene ($H_3$CN) which is observed in the atmosphere of Titan. The results of a high resolution infrared laboratory study of the line positions of the 663, 449, and 222.5 cm$^{-1}$ fundamental bands are presented. Line positions, reproducible to better than 5 MHz for the first two bands, are available for infrared astrophysical searches. Intensity and broadening studies are in progress.

Acetylene is a nearly ubiquitous atmospheric constituent of the outer planets and Titan due to the nature of methane photochemistry. Results of ambient temperature absolute intensity measurements are presented for the fundamental and two two-quantum hotband in the 730 cm$^{-1}$ region. Low temperature hotband intensity and linewidth measurements are planned.

## CYANOACETYLENE

The infrared spectra of two of the bending fundamentals of $HC_3N$ have been observed by Voyager/IRIS in the atmosphere of Titan. The results of a high resolution infrared laboratory study of the $\nu_5$, $\nu_6$, and $\nu_7$ fundamental bands are presented. A complimentary study of $\nu_5$ and $\nu_6$ is in progress at Orsay.[1]

Fourier transform spectra were recorded at the Herzberg Institute for Astrophysics in Ottawa on a Bomem DA.003 interferometer. The $\nu_5$ and $\nu_6$

bending fundamentals were recorded at $0.004\mathrm{cm}^{-1}$ while $\nu_7$ was recorded at somewhat lower resolution. Rotational structure has been assigned for J values up to 78. Ground state constants from a global analysis are in excellent agreement with those derived from microwave data.[2] Upper state constants, including $\ell$ - doubling parameters are obtained. Analysis results, retrieved using the statistically controlled regression system described below, are presented in Tables I-III. Line positions reproducible to better than $0.2 \times 10^{-4}\mathrm{cm}^{-1}$ (~5MHz) for $\nu_5$ and $\nu_6$ should facilitate infrared astrophysical searches. The positions for $\nu_7$ are estimated to be good to $0.7 \times 10^{-4}\mathrm{cm}^{-1}$.

Improved spectra for the long wavelength region have been acquired and are being prepared for analysis. Upon completion of the analysis of the new data, generation of a spectral atlas including line lists is planned.

## ACETYLENE

Understanding of acetylene spectral features observed in the laboratory with high-resolution is a prerequisite for quantitative analyses of acetylene spectra in the planetary atmospheres of Titan, Saturn, and Jupiter. Line-intensity measurements on $^{12}C_2H_2$ near 13.7$\mu$m were made using a swept-frequency tunable diode-laser spectrometer[3,4] with resolution of $0.0005\ \mathrm{cm}^{-1}$. Vibrational band intensities $S_v^o$ at 300K which were determined from the line-intensity measurements are 560(17) $\mathrm{cm}^{-2}\mathrm{atm}^{-1}$ for the $\nu_5$-fundamental band of $^{12}C_2H_2$, 13.5(3) $\mathrm{cm}^{-2}\mathrm{atm}^{-1}$ for the $(\nu_4+\nu_5)^{0-}-\nu_4^{e,f}$ hotband of $^{12}C_2H_2$, and 13.8(1) $\mathrm{cm}^{-2}\mathrm{atm}^{-1}$ for the $(\nu_4+\nu_5)^{0+}-\nu_4^{e}$ hotband of $^{12}C_2H_2$.

Neglecting the rotation-vibration interaction, the intensity of an individual transition $S_J$ can be directly related to the (vibrational) band intensity $S_v^o$ as[5,6]

$$S_J = S_v^o[g_J \exp(-BJ(J+1)hc/kT)/Q_r] \cdot [1-\exp(-\nu_o hc/kT)] \times$$

$$\times \Lambda(J,\Delta J,\ell,\Delta\ell), \qquad (1)$$

where $\nu_o$ is the band-center frequency and $\Lambda(J,\Delta J,\ell,\Delta\ell)$ is the Honl-London factor.[7]

# TABLE I

## RESULTS OF THE ANALYSIS OF THE $\nu_5$ BAND OF CYANOACETYLENE[a]

| | THIS WORK | IR/MW[b] | IR[c] | MW[d] |
|---|---|---|---|---|
| $\nu_0$ | 663.36639(17) | 663.361(12)[e] | 663.37378(98)[e] | -.- |
| $B_0$ | 0.15173928(209) | -.- | -.- | 0.151740238(39) |
| $\alpha^B(10^5)$ | -5.4311(66) | -6.047(37) | -1.143(78)[f]<br>[-1.120(14)[g]] | -5.613(19) |
| $D_0$ | $1.800(26) \times 10^{-8}$ | -.- | -.- | $1.8116(45) \times 10^{-8}$ |
| $\beta^J$ | $0.659(14) \times 10^{-10}$ | $3.56(4.70) \times 10^{-9}$ | -.- | $-2.840(3) \times 10^{-9}$ |
| $H_0$ | 0.0 | -.- | -.- | -.- |
| $\delta^J$ | $-1.37(27) \times 10^{-14}$ | -.- | -.- | -.- |
| $q$ | $8.622(13) \times 10^{-5}$ | $8.573(90) \times 10^{-5}$ | -.- | $8.4638(37) \times 10^{-5}$ |
| $q^J$ | $1.835(73) \times 10^{-10}$ | 0.0[h] | -.- | 0.0[h] |

---

[a] All parameters in units of $cm^{-1}$. Values in parentheses are error estimates of $3\sigma$.

[b] IR: Mallinson and Fayt, Mol. Phys. 32, 473 (1976); MW: Mallinson and de Zafra, Mol. Phys. 36, 827 (1978).

[c] Yamada and Bürger, Z. Naturforsch. 41a, 1021 (1986).

[d] Yamada and Creswell, J. Mol. Spectrosc. 116, 384 (1986).

[e] Corrected from reported values by $-l^2B_v$ term.

[f] $\alpha^B_{eff} = \alpha^B + \frac{1}{2}q$ for the P and R transitions studied in their work.

[g] Calculated from their $\alpha^B_{eff}$ and our q value.

[h] Assumed value by these workers.

## TABLE II

## RESULTS FROM THE ANALYSIS OF THE $\nu_6$ BAND OF CYANOACETYLENE[a]

| | INFRARED | MICROWAVE[b] |
|---|---|---|
| $\nu_0$ | 498.953 37 (90) | [498.953 66 (1 17)]$^{IR,c}$ |
| $B_0$ | 0.151 740 21 (1 45) | 0.151 740 238 (39) |
| $\alpha^B$ | -3.085 84 (59) x $10^{-4}$ | -3.087 55 (65) x $10^{-4}$ |
| $D_0$ | 1.810 2 (29 4) x $10^{-8}$ | 1.811 6 (4 5) x $10^{-8}$ |
| $\beta^J$ | -2.954 (174) x $10^{-10}$ | -3.796 (800) x $10^{-10}$ |
| $q$ | 1.195 6 (10 0) x $10^{-4}$ | 1.194 45 (18) x $10^{-4}$ |
| $q_J$ | 2.69 (87) x $10^{-11}$ | 0.0[d] |

$N/N_0 = 162/166$

$\sigma = 2.35 \times 10^{-4}\ \mathrm{cm}^{-1}$

---

[a] All parameters in units of $\mathrm{cm}^{-1}$. Values in parentheses are error estimates of $3\sigma$.

[b] Yamada and Creswell, J. Mol. Spectrosc. 116, 384 (1986).

[c] Yamada and Bürger, Z. Naturforsch. 41a, 1021 (1986).

## TABLE III

## RESULTS FROM THE ANALYSIS OF THE $\nu_7$ BAND CYANOACETYLENE[a]

| | INFRARED | MICROWAVE[b] |
|---|---|---|
| $\nu_0$ | 222.565 347 (329) | 222.554 (15) $^{IR,c}$ |
| $B_0$ | 0.151 739 74 (52) | 0.151 740 238 (39) |
| $\alpha^B$ | -4.806 53 (1 66) x $10^{-4}$ | -4.821 68 (59) x $10^{-4}$ |
| $D_0$ | 1.869 2 (73 8) x $10^{-8}$ | 1.811 6 (4 5) x $10^{-8}$ |
| $\beta^J$ | UD | -8.148 97 (72) x $10^{-10}$ |
| $q_7$ | 2.170 36 (332) x $10^{-4}$ | 2.180 939 (390) x $10^{-4}$ |

$N/N_0 = 144/144$

$\sigma = 0.81 \times 10^{-4}\ \mathrm{cm}^{-1}$

---

[a] All parameters in units of $\mathrm{cm}^{-1}$. Values in parentheses are error estimates of $3\sigma$.

[b] Yamada and Creswell, J. Mol. Spectrosc. 116, 384 (1986).

[c] Mallinson and Fayt, Mol. Phys. 32, 473 (1976).

Equation (1) can be used as a linear least squares model for band intensity retrieval using observed line strengths as data. Incorporation of a Herman-Wallis term is particularily simple using this technique. The results below were obtained using this model and are thus least squares estimators of the band intensies.

We used direct width measurements and peak transmittance results for intensity retrieval. The results were verified in a number of cases by direct fitting of a Voigt profile to the observed data. In addition,the equivalent width method[8,9] was applied to several transitions to check the peak transmittance results. The two methods were consistent to better than 4%. Table IV presents the equivalent width/peak transmittance comparison. Table V presents present results for acetylene intensities in the 14$\mu$m region.

Table IV. Selected line-intensities from $\nu_5$ determined using the method of equivalent widths. The parameter a is the dimensionless Voigt parameter defined as $a=(b_L/b_D)\sqrt{\ln 2}$. For the Lorentz width $b_L$ the following average self-broadening coefficient $\gamma_L$ retrieved by P. Varanasi, L.P. Giver and F.P.J. Valero, JQSRT 30, 497(1983a) is assumed: $\gamma_L=0.15\text{cm}^{-1}/\text{atm}$. Measurements were carried out at 298K. The averaged line-intensities derived from equivalent width measurements are listed in the sixth column (EQ), and those derived from the peak transmittance determinations (PT) are presented in the last column for comparison.

| Line Identi-fication | p [mtorr] | ℓ [cm] | a [$10^{-2}$] | W equ.wdth [$10^{-3}\text{cm}^{-1}$] | $S_J$ $\text{cm}^{-2}\text{atm}^{-1}$ | $S_J$ avg. (EW) $\text{cm}^{-2}\text{atm}^{-1}$ | $S_J$ avg. (PT) $\text{cm}^{-2}\text{atm}^{-1}$ |
|---|---|---|---|---|---|---|---|
| $Q^{(1)}(3)^{\dagger}$ | 71.3 | 2.54 | 1.325 | 2.120 | 15.805 | | |
| | 58.5 | | 1.087 | 1.900 | 15.876 | **15.62** | **15.74** |
| | 48.7 | | 0.905 | 1.668 | 15.449 | | |
| | 39.3 | | 0.730 | 1.438 | 15.356 | ±0.22 | ±0.117 |
| | 29.2 | | 0.542 | 1.172 | 15.620 | | |
| $Q^{(1)}(6)^{\dagger}$ | 96.0 | 2.54 | 1.784 | 1.768 | 8.516 | | |
| | 82.5 | | 1.533 | 1.588 | 8.408 | **8.343** | **7.896** |
| | 69.5 | | 1.292 | 1.393 | 8.265 | | |
| | 55.5 | | 1.031 | 1.172 | 8.196 | ±0.125 | ±0.082 |
| | 45.8 | | 0.851 | 1.019 | 8.330 | | |

Table V. Comparison of acetylene vibrational band intensities with previous results in$_o$ P. Varanasi, L.P. Giver and F.P.J. Valero, JQSRT 30, 497(1983a). $S_v^o$ for *This Work* is stated for natural abundance samples at 300K.

| Band Identification | Band Freq. $\nu_o$ [$cm^{-1}$] | Varanasi et al $S_v^{(0)}$ [$cm^{-2}atm^{-1}$] | This Work $S_v^{(0)}$ [$cm^{-2}atm^{-1}$] |
|---|---|---|---|
| $\nu_5$-fundamental | 730.33 | 588 | 560. ± 17 |
| $(\nu_4+\nu_5)^{o-}-\nu_4^{e,f}$ | 727.68 | 18.7 | 13.5 ± 0.3 |
| $(\nu_4+\nu_5)^{o-}-\nu_4^{e}$ | 715.20 | 17.7 | 13.8 ± 0.1 |

Figure 1 displays an intensity contour based on the retrieved intensity from our $\nu_5$ observations. Figure 2 indicates the need for inclusion of a Herman-Wallis term in the band intensity model for the hotbands. For both of the $(\nu_4+\nu_5)-\nu_4^1$ hotbands a short-fall of about 50% in observed intensity is indicated. This result agrees with a preliminary analysis by Halsey[10] of KPNO FTS data observed at 0.0025$cm^{-1}$ resolution.[11] In his study a 50% smaller band intensity was observed for all seven two quantum number hotbands involved in the transitions $\nu_4+\nu_5-\nu_4$ and $2\nu_5-\nu_5$ in the 13.7$\mu$m region in addition to observed J dependence due to rotation-vibration interaction. Current investigation of other hotband transitions seem to support these observations. Further measurements are indicated and are in progress.

## COMPUTATIONAL TECHNIQUES

A number of novel computational techniques have been developed to enhance the retrieval of useful information from spectral data. Our approach is to attempt to obtain maximum information from the data at hand. Compared to time on one of a kind facilities, computer machine cycles are very inexpensive.

The multiple regression system in use has evolved over a twenty year period.[12] The most valuable aspects of this least squares system, apart from its stepwise nature, are the use of bi-weights[13] and a Komolgrov-Smirnov[14] statistical test as a termination indicator. The analysis system uses a version of the stepwise regression analysis system used in Lin *et al*.[15] and Daunt *et al*.[16] Modified bi-weights[16] are used beginning with a width of 6 standard deviations, reducing that width by 80% when the variance stabilizes in the iterative regression-weight correction process. At each

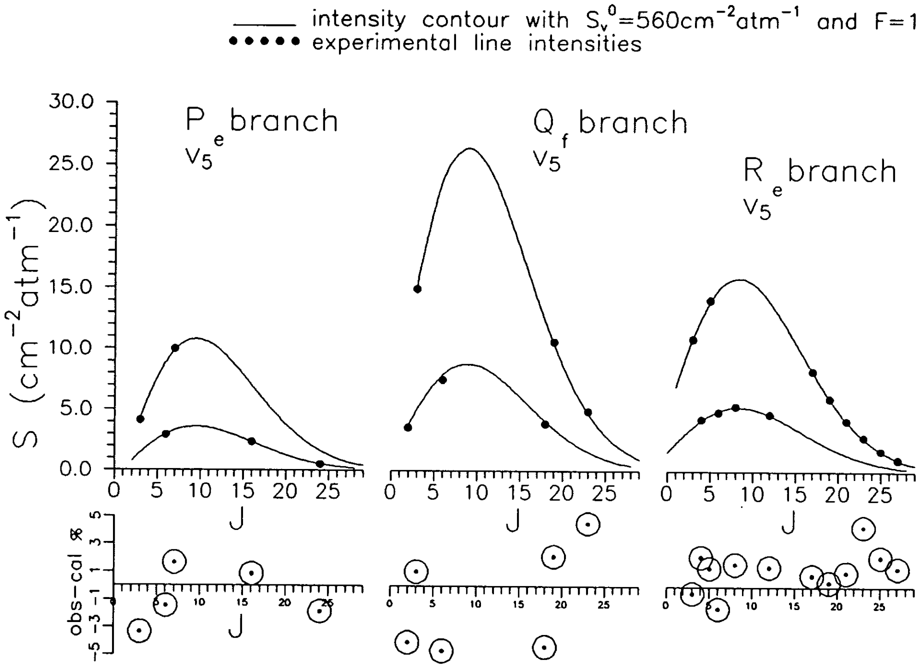

Fig. 1 Intensity contour for $\nu_5$ showing observed strengths.

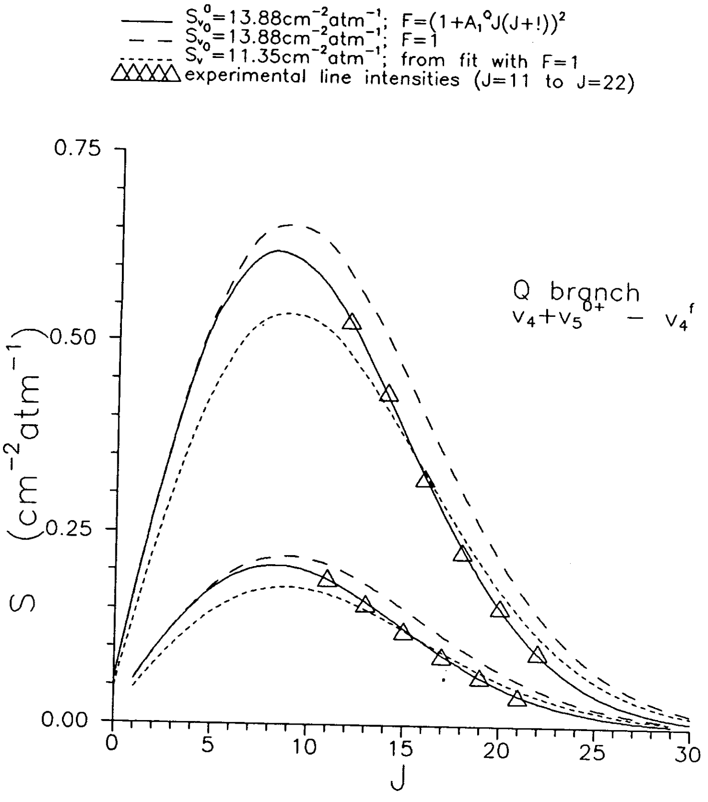

Fig. 2 Intensity contour for the Q-branch of a two quantum hotband showing the sensitivity of the data to the Herman-Wallis model

step, an iterative Komolgrov-Smirnov (K-S) test[14] is performed on the residuals against a model normal distribution with a variance approximating the expected variance in the data. The iterations in the K-S sequence involve varying the expected variance of the model distribution in order to find the maximum probability that the weighted residuals are drawn from a normal distribution. When a maximum probability is achieved in the bi-weighting iterations, the process is terminated and the maximum probability results retrieved. The maximum probability is often above 90%. This system was used to retrieve intensities, analyze the cyanoacetylene data and to recover lower state rotational constants from the KPNO acetylene data in collaboration with J. J. Hillman et al.[17]

Other novel techniques have been developed and include automatic (two dimensional spline interpolation) strength retrieval using equivalent widths. Accidental resonance analysis systems using Hellman-Feynman derivative generation in the iterative non-linear least squares analysis system have also been developed. This system is being used to analyze the $\nu_9+\nu_4-\nu_4$ hotband of ethane and the two and three quantum hotband data for the 14 $\mu$m acetylene data. In both of these cases the data was obtained at KPNO by Donald E. Jennings, et al.

## REFERENCES

1. G. Graner, private communication.
2. R. A. G. Creswell, G. Winnewisser, and M. C. L. Gerry, J. Mol. Spectrosc. <u>65</u>,420(1977).
3. V.W.L. Chin, M.S. Thesis, University of Tennessee, Knoxville, 1985. W.E. Blass and V.W.L. Chin, JQSRT <u>38</u>, 185(1987).
4. D.E. Jennings, Appl.Opt. <u>19</u>, 2695(1980).
5. S.S. Penner, <u>Quantitative Molecular Spectroscopy and Gas Emissivities</u>, Addison-Wesley, Reading, Massachusetts, 1959.
6. M.A.H. Smith, C.P. Rinsland, B. Fridovich, and K.N. Rao, Chapter 3 in <u>Molecular Spectroscopy: Modern Research</u>, Vol.III, ed. K.N. Rao, Academic Press, New York, 1985.
7. D. Papousek and M.R. Aliev, <u>Molecular Vibrational-Rotational Spectra</u>, Elsevier, Amsterdam, 1982.
8. P.A. Jansson, C.L. Korb, JQSRT <u>8</u>, 1399(1968).
9. M. C. Weber, W. E. Blass, and Jean-Luc Salanave, JQSRT in press.

10. G.W. Halsey, private communication (1988).

11. G.W. Halsey, J.J. Hillman, and D.E. Jennings, " The 14 Micron Bands of Acetylene -- the Region of the Bending Modes," Technical Report, Laboratory for Extraterrestrial Physics, Goddard Space Flight Center, Greenbelt MD (June 1985).

12. W. E. Blass, Program FILE5, unpublished.

13. A. E. Beaton and J. W. Tukey, in Critical Evaluation of Physical Structural Information, (D. R. Lide and M. A. Paul, Eds.), pp15-35,National Academy of Sciences, Washington, D. C. 1974.

14. W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, Numerical Recipes, The Art of Scientific Computing, pp. 472-475, 539, Cambridge University Press, Cambridge, 1986.

15. K. F. Lin, W. E. Blass and N. M. Gailar, J. Mol. Spectrosc. **79**, 151-157 (1980).

16. S. J. Daunt, A. K. Atakan, W. E. Blass, G. W. Halsey, D. E. Jennings, D. C. Reuter, J. Susskind, and J. W. Brault, Ap. J. **280**,921-936 (1984).

17. J. J. Hillman, D. E. Jennings, G. W. Halsey, Sacher Nadler, and W. E. Blass, manuscript in revision.