The Astrophysical Journal, 624:1116–1120, 2005 May 10

FOURIER TRANSFORM EMISSION SPECTRA OF THE (000)–(000) BAND OF THE λ4051.6 BAND OF C_3

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Received 2004 November 30; accepted 2005 January 28

ABSTRACT

The (000)–(000) band of the 4051.6 Å group ($\tilde{A}\ ^1\Pi_u - \tilde{X}\ ^1\Sigma_g^+$) of C_3 was recorded in emission with a Bruker IFS 120HR Fourier transform (FT) spectrometer at the University of Waterloo. The band was excited by a microwave discharge in isopropanol (less than a few mtorr) diluted in helium (2 torr). Our new FT data provide more reliable and accurately calibrated transition wavenumbers than those from the grating spectra given by Gausset and coworkers. Analysis of our new spectrum combined with the data by McCall and coworkers confirmed that the lower J levels in the $\tilde{A}$ state were strongly perturbed, as reported by Gausset and coworkers. The unidentified lines observed by McCall and coworkers could be attributed to extra transitions to an unknown perturbing state.

Subject headings: astrochemistry — ISM: clouds — ISM: molecules — methods: laboratory — molecular data

1. INTRODUCTION

Since its first identification in the emission spectrum from comet Tebbutt by Huggins (1881), a group of spectral bands at 4051.6 Å has been observed repeatedly in various comets (for details of early work, see Bobrovnikoff 1931, 1942). This spectral feature was also found in spectra from the photosphere of the N-type carbon star YCVn (McKellar 1948) and other cool stars (see also a recent review by Jørgensen 1994). The λ4051.6 band is often called the "comet band," or "4050 Å band," so named by Swings et al. (1941) in view of the fact that the band head of the most prominent feature was located at the air wavelength of 4050 Å. The carrier of the spectra, however, had been unknown until Douglas (1951) proved that it was C_3 by carefully analyzing spectra of a flash-photolyzed mixture of $^{12}CH_4$ and $^{13}CH_4$. Gausset et al. (1965) made an extensive investigation into the band system obtained from flash photolysis of CH_2N_2 with a much higher resolving power of $\lambda/\Delta\lambda \sim 300{,}000$ and carried out a comprehensive analysis of many vibronic bands. They concluded that the band system was due to the $\tilde{A}\ ^1\Pi_u - \tilde{X}\ ^1\Sigma_g^+$ transition. A strong Renner-Teller effect complicated the energy level structure of the upper state. They also found systematic line shifts in the low-J transitions in the (000)–(000) band, a most prominent feature of the λ4051.6 band. They concluded, by using combination differences for the ground state, that the line shifts arose from perturbations in the upper $\tilde{A}\ ^1\Pi_u$ state.

Maier et al. (2001) made the first interstellar identification of C_3 by observing this band in absorption in the diffuse clouds toward ζ Oph, 20 Aql, and ζ Per. Carbon chain molecules are of current interest in astronomy, so the λ4051.6 band of C_3 has been monitored in various other sources such as translucent clouds and circumstellar shells (Oka et al. 2003 and references therein). In these astronomical observations, transition wavenumbers determined by Gausset et al. (1965) were usually used as the standard line positions. More recently, Ádámkovics et al. (2003) observed rotationally resolved spectra in 10 translucent sight lines. Because of the high resolution and high signal-to-noise ratio of their spectra, they noticed an apparent discrepancy of the line position of the weak $R(0)$ transition compared with laboratory data by Gausset et al. (1965). McCall et al. (2003) reexamined the (000)–(000) band by using the cavity ring-down technique combined with a supersonic jet expansion source. Their low-temperature spectrum clearly indicated that the $R(0)$ transition was incorrectly assigned in the previous work (Gausset et al. 1965). In addition, they detected a series of unidentified (U) lines in their spectrum. These U lines are very likely to be due to C_3, on the basis of circumstantial evidence.

The vibration-rotation lines of C_3 are also very interesting and useful astronomical probes. Hinkle et al. (1988) detected C_3 in the circumstellar shell of IRC +10216 by identifying the ν_3 band in the absorption spectrum of the star. Although the line assignments were made without laboratory data at the time, the identification was assured by laboratory observations (Matsumura et al. 1988). Kawaguchi et al. (1989) extended the measurements to hot bands (011)–(010), (021)–(020), and a combination band (021)–(000), providing a set of improved molecular constants. A high-resolution spectrum of the bending fundamental band in the far-infrared (FIR) region (~60 cm^{-1}) was recorded by Schmuttenmaer et al. (1990), who used a tunable FIR sideband spectrometer. More recently, Giesen et al. (2001) observed the ν_2 vibration-rotation band with better accuracy. The laboratory measurements led to a definite identification of this molecule in a star-forming region of Sgr B2 by detecting the Q- and R-branch lines of the ν_2 band (Cernicharo et al. 2000; Giesen et al. 2001).

In this study, we recorded Fourier transform (FT) emission spectra of the λ4051.6 band and determined the transition wavenumbers with higher accuracy of typically 0.005 cm^{-1} with reliable relative line intensities. We found from the analysis, combined with the results of McCall et al. (2003), that the U lines are indeed the transitions from the ground state to a perturbing state interacting with the $\tilde{A}\ ^1\Pi_u$ state.

Very recently, Zhang et al. (2005) obtained high-resolution laser excitation spectra from jet-cooled C_3. They performed

lifetime measurements in addition to spectroscopic analysis, and their results are consistent with ours.

2. EXPERIMENTAL PROCEDURE

The λ4051.6 band of C_3 was observed in emission from a microwave discharge of isopropanol [$CH_3CH(OH)CH_3$] diluted in helium. A Bruker IFS 120HR FT spectrometer at the University of Waterloo was used to record the spectra. An Evenson-type microwave cavity was attached to the center of a glass cell (a half-inch [1.3 cm] in diameter and 15 cm in length), and a microwave power of 80 W was applied. Isopropanol was introduced into the cell by flowing helium through a "bubbler," which contained the liquid sample. The partial pressure of the alcohol was less than a few mtorr, and the total pressure was about 2 torr. We also tried to reproduce this band with a DC discharge in helium or argon buffer gases. It was found that only the helium discharge could produce sufficient C_3, and a microwave discharge was more efficient. The isopropanol molecule contains an oxygen atom, and it seemed to prevent soot accumulation during the experiment.

The discharge glow was focused on the entrance aperture of the spectrometer with a CaF_2 lens. The detector was a Si diode, and a visible quartz beam splitter was used to record the spectra. To reduce the influence of strong transitions due to other molecules or atoms, an optical filter (500 nm blue pass) was used. The spectra were recorded in the range from 19000 to 28000 cm^{-1}, and many bands due to various other discharge products (e.g., C_2, CH, CN) also appeared. The emission spectra were accumulated for 180 scans at a spectral resolution of 0.10 cm^{-1}. The observed line width (FWHM) of C_3 was about 0.12 cm^{-1}, and it did not change even when we employed higher spectral resolution. The observed lines were predominantly Doppler broadened, and the widths were rather large because of the high plasma temperature.

Because we did not evacuate the spectrometer during the measurement, we converted the air wavelengths to the vacuum wavelengths with a standard procedure (Hirao et al. 2000). All the transition wavenumbers were calibrated against the standard helium atomic lines (Wiese et al. 1966) that were present in the spectra. The transition wavenumbers of the standard helium lines used for calibration agree with theoretical calculations by Martin (1987) to within 0.01 cm^{-1}, and our He wavenumbers were checked using other He-containing spectra. The precision of the transition wavenumbers in the present measurements was estimated to be 0.005 cm^{-1} for clear unblended lines.

Another electronic transition ($\tilde{b}\,^3\Pi_g$–$\tilde{a}\,^3\Pi_u$) of C_3 in the IR region was also observed in a separate measurement. This band was well studied by FT spectroscopy and by diode laser spectroscopy (Sasada et al. 1991), and therefore no further investigation was carried out.

3. ANALYSIS AND DISCUSSION

Figure 1 shows a portion of the spectra and the assignments. The overall appearance of our emission spectrum is basically similar to that obtained in absorption by Gausset et al. (1965). Among the eight U lines, four higher frequency lines were also visible in our FT spectrum. However, as the rotational temperature was much higher compared with that of the spectra obtained by McCall et al. (2003), the appearance of the low-J transitions is much weaker in the present spectrum, and the remaining four components of the unidentified features of the McCall spectrum were not visible, partly because of overlap with other lines and partly because of broader line widths.

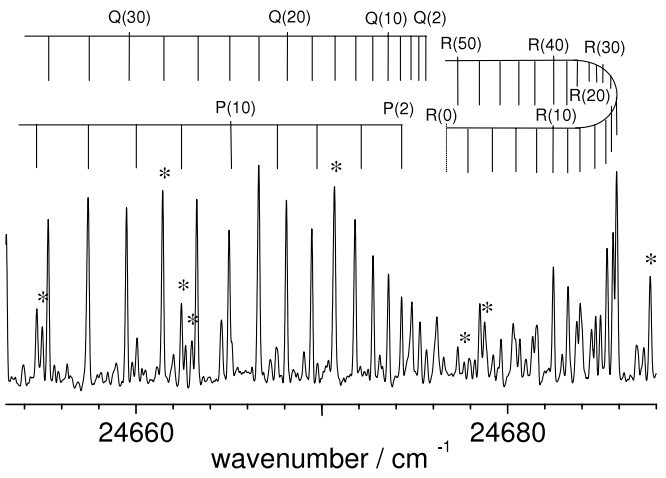

FIG. 1.—Portion of the (000)–(000) band. Lines of the low-J transitions are obscured by stronger high-J lines, and the $R(0)$ line is not clearly resolved in the spectrum. The lines marked by asterisks are the lines of C_2.

Table 1 summarizes the measured transition wavenumbers of the (000)–(000) band together with the residuals of the fit. Although assignments of the transitions agree with those given by Gausset et al. (1965) and McCall et al. (2003), their transition wavenumbers are found to be shifted to lower wavenumbers by about 0.04 cm^{-1}.

The energy level expressions used were, for the (000) state of $\tilde{X}\,^1\Sigma_g^+$,

$$E = BJ(J+1) - D[J(J+1)]^2 + H[J(J+1)]^3, \qquad (1)$$

and for the (000) state of $\tilde{A}\,^1\Pi_u$,

$$E_\pm = \nu_0 + BJ(J+1) - D[J(J+1)]^2 + H[J(J+1)]^3 \pm \frac{1}{2}qJ(J+1). \qquad (2)$$

Here the plus and minus signs refer to states with f and e parity, respectively.

In the analysis, because the low-J lines were weak, the transition wavenumbers from McCall et al. (2003) for the low-J transitions were used after correcting their transition wavenumbers (by adding 0.04 cm^{-1} to their values). As reported by Gausset et al. (1965), the low-J levels ($J \leq 30$) of the (000) state of $\tilde{A}\,^1\Pi_u$ were perturbed. Those perturbed lines were excluded from the fit. In Figure 2, the residuals for each transition are plotted against the upper J. Because of the nuclear spin statistics arising from two equivalent Bosons, only the e parity levels are allowed for odd J' states, while only the f parity levels exist for even J' states. Rotational levels in the ground (000) state are permitted only for even J''. The P- and R-branch transitions are allowed only for the e-parity levels, while the Q-branch transitions are possible for only the f-parity levels. The deviations from the fit ($o - c$) show different patterns for each parity level. The odd J' levels (e parity) are perturbed around $J' = 1$, 13, and 21, while the even J' levels are less affected by the perturbations.

The combination differences for the lower state $\tilde{X}\,^1\Sigma_g^+$ were included in the fit to improve the molecular constants of the ground state. This was important, because the upper state was perturbed. The data of FIR transitions for the (01^10)–(00^00) vibration-rotation band obtained by Schmuttenmaer et al. (1990),

TABLE 1

Transition Wavenumbers of the (000)–(000) Band

J''	P	$o-c$[a]	Q	$o-c$[a]	R	$o-c$[a]
0	...	...	...	...	24676.74[b]	532
2	24674.17[b]	546	24675.52[b]	246	24677.93[b]	177
4	24671.91[b]	184	24675.21[b]	187	24679.17[b]	12
6	24669.689	2	24674.76[b]	131	24680.37[b]	−52
8	24667.481	−28	24674.25[b]	156	24681.44[b]	−106
10	24665.074	−119	24673.52[b]	102	24682.39[b]	−141
12	24662.598	−143	24672.69[b]	87	24683.20[b]	−180
14	24659.982	−174	24671.72[b]	69	24683.93[b]	−163
16	24657.353	−85	24670.604	40	24684.656	−17
18	24654.586	−6	24669.384	38	24685.271	148
20	24651.748	129	24668.024	26	24685.597	152
22	24648.676	154	24666.533	10	24685.786	144
24	24645.454	148	24664.933	7	24685.786	69
26	24642.091	118	24663.203	−6	24685.786	112
28	24638.622	94	24661.364	−11	24685.597	80
30	24635.053	81	24659.415	−14	24685.271	23
32	24631.363	51	24657.353	−22	24684.917	45
34	24627.607	58	24655.201	−14	24684.446	53
36	24623.752	64	24652.940	−14	24683.834	20
38	24619.745	13	24650.587	−8	24683.178	38
40	24615.712	27	24648.138	−5	24682.386	13
42	24611.564	13	24645.599	0	24681.496	−22
44	24607.345	14	24642.973	4	24680.580	2
46	24603.028	−2	24640.259	4	24679.563	7
48	24598.637	−12	24637.453	−5	24678.433	−22
50	24594.177	−13	24634.600	17	24677.243	−35
52	24589.649	−7	24631.633	3	...	...
54	24585.024	−23	24628.602	2	...	...
56	24580.352	−11	24625.503	8	...	...
58	24575.581	−23	24622.320	5	...	...
60	...	...	24619.066	8	...	...
62	24565.857	1	24615.712	−11	...	...
64	24560.866	4	...	...	...	...

[a] Here $o-c$ indicates a value of (observed − calculated) $\times 10^3$ in cm^{-1}.
[b] These values were from McCall et al. (2003). They were corrected by referring to our wavenumber measurements. See text.

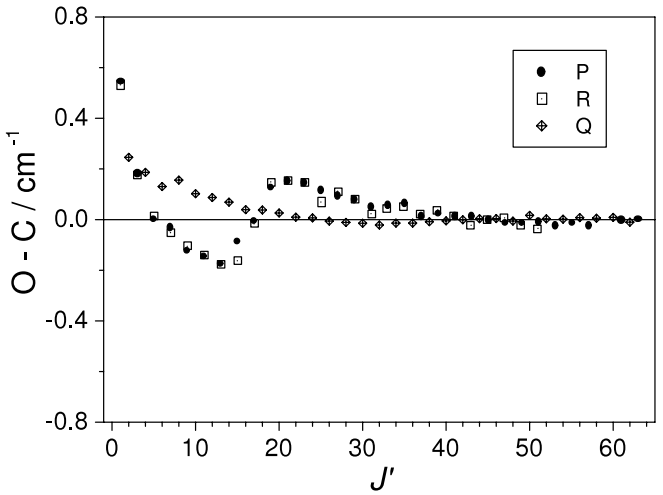

Fig. 2.—Residuals from the least-squares fit of the (000)–(000) band. The values for odd J' levels having e parity are obtained from P- and R-branch transitions, and the values for even J' levels having f parity are obtained from Q-branch transitions.

Giesen et al. (2001), and Gendriesch et al. (2003) were also included in the fit with the ground state constants as the common parameters for both vibration-rotation and electronic transitions. The molecular constants thus determined for the (000) states of the $\tilde{X}\ ^1\Sigma_g^+$ and $\tilde{A}\ ^1\Pi_u$ states are listed in Tables 2 and 3, respectively. The FIR transition wavenumbers are listed together with the residuals of the fit in Table 4. The fit was improved compared with that of the FIR-only analysis owing greatly to the simultaneous analysis with the optical data that extended to the higher J levels. The parameters for the (01^10) state also agree with the values published by Gendriesch et al. (2003) within 2 σ error limits.

TABLE 2

Molecular Constants for the (000) State of $\tilde{X}\ ^1\Sigma_g^+$

Constants	This Work (cm^{-1})	Gendriesch et al. (2003) (cm^{-1})
B	0.4305883 (58)	0.4305726 (47)[a]
$D \times 10^6$	1.437 (13)	1.478 (13)
$H \times 10^{10}$	1.129 (35)	1.357 (61)

Note.—The numbers in parentheses indicate one standard deviation to the last significant digits.
[a] The values originally given in units of MHz were converted to cm^{-1}.

TABLE 3
MOLECULAR CONSTANTS FOR THE (000) STATE OF $\tilde{A}\ ^1\Pi_u$

Constants	This Work (cm^{-1})	Gausset et al. (1965) (cm^{-1})
ν_0	24675.382 (13)	24675.53
B	0.412777 (23)	0.4124
$D \times 10^6$	0.519 (18)	...
$H \times 10^{10}$	0.535 (43)	...
q	−0.0002906 (16)	−0.00042

NOTE.—The numbers in parentheses indicate one standard deviation to the last significant digits.

The molecular constants thus determined can be compared with those obtained from the ν_3 vibrational band in the ground electronic state obtained by IR spectroscopy (Kawaguchi et al. 1989), and these two sets of values agree very well. For the upper $\tilde{A}\ ^1\Pi_u$ state the constants were determined only using the relatively unperturbed high-J levels. In Table 3, those molecular constants are also compared with the values determined by Gausset et al. (1965). The B-constant and the Λ-type doubling parameter q were determined more precisely, and higher order terms such as D and H were determined for the first time.

As mentioned above, the $R(0)$ transition was reassigned in the recent work by McCall et al. (2003). The $J' = 1$ state is affected most strongly by the perturbation, as shown in Figure 2. It naturally follows that the residual for the $P(2)$ transition, which shares the upper level with the $R(0)$ transition, is almost identical with that for the $R(0)$ line. The difference of these two lines was calculated to be 2.57 cm^{-1}, which agreed with the energy difference between $J'' = 0$ and $J'' = 2$ in the $\tilde{X}\ ^1\Sigma_g^+$ state. This confirms that the assignments are correct.

During the analysis, we noticed that some lines listed in Table 2 of McCall et al. (2003) as unassigned lines should be extra lines due to the transitions to the perturbing state involved. The line located at 24675.85 cm^{-1} should be the extra $R(0)$ line, which is the transition to the $J' = 1$ level of the perturbing state, and the line at 24673.27 cm^{-1} is the corresponding $P(2)$ transition that shares the same upper level. The combination difference of these two transitions gives the value of 2.58 cm^{-1}, and the calculated value is 2.583 cm^{-1}. These agree very well. Similarly, the lines at 24671.02 cm^{-1} and at 24677.06 cm^{-1}, which yield the difference of 6.04 cm^{-1}, seem to be the perturber lines of the $P(4)$ and $R(2)$ transitions, respectively. The calculated combination difference is 6.027 cm^{-1}, which agrees well with the observed value. These transition wavenumbers are listed in Table 5. The other four extra lines observed by McCall et al. (2003) are also very likely to be lines induced by perturbations. Unfortunately, we have not succeeded in identifying the other four extra lines. At the present stage of the analysis, the perturbing state is not identified, but the most likely candidate is a vibronic state of $\tilde{b}\ ^3\Pi_g$ or $\tilde{a}\ ^3\Pi_u$, which is likely to be located close to the $\tilde{A}\ ^1\Pi_u$ state.

TABLE 4
FIR TRANSITIONS OF THE (01^10)–(00^00) VIBRATION-ROTATION BAND

Transition	Wavenumber (cm^{-1})	$o - c$[a]
$Q(2)$	63.062229 (8)[b]	1
$Q(4)$	63.267321 (8)[b]	−6
$Q(6)$	63.588588 (8)[b]	0
$Q(8)$	64.024651 (7)[b]	4
$Q(10)$	64.573678 (5)[b]	−1
$Q(12)$	65.233428 (7)[b]	0
$Q(14)$	66.001246 (5)[b]	0
$Q(16)$	66.874128 (100)[b]	−14
$R(0)$	63.853312 (13)[b]	8
$R(2)$	65.665274 (7)[b]	0
$R(4)$	67.54845 (3)[c]	−12
$R(6)$	69.50230 (3)[c]	3
$P(2)$	61.26976 (23)[c]	−66
$P(4)$	59.63761 (23)[c]	50
$P(6)$	58.07760 (23)[c]	127

NOTE.—The values in parentheses are estimated uncertainties quoted in the original references.

[a] The $o - c$ values indicate (observed − calculated) × 10^6 cm^{-1}.

[b] Gendriesch et al. (2003). The transition frequencies given in MHz were converted to cm^{-1}.

[c] Schmuttenmaer et al. (1990). These values were obtained by converting from MHz units.

TABLE 5
TRANSITION WAVENUMBERS OF THE EXTRA TRANSITIONS TO THE PERTURBING STATE

J'–J''	P (cm^{-1})	J'–J''	R (cm^{-1})
1–2	24673.31	1–0	24675.89
3–4	24671.06	3–2	24677.10

NOTE.—From McCall et al. (2003). The transition wavenumbers were corrected to be consistent with our wavenumber calibration.

In extensive laser-induced fluorescence spectra obtained by Zhang et al. (2005), more lines to the perturbing states have been identified, and more comprehensive perturbation analysis has been carried out. From the analysis, they have tentatively assigned one of the perturbing states as the 050^- (Σ^-) vibronic level of the $\tilde{b}\ ^3\Pi_g$ electronic state.

These extra perturbing lines provide a connection to the metastable triplet manifold. Thus, when the C_3 molecule absorbs radiation in a diffuse cloud or a comet, the perturbed $\tilde{A}$ state levels and the new levels can radiate down to the metastable $\tilde{a}$ state. This allows population to accumulate in the $\tilde{a}$ state, which allows the triplet-triplet band to appear and affects the chemistry and dynamics of C_3.

4. SUMMARY

We have observed the (000)–(000) band of the 4051.6 Å group of C_3 in emission with an FT spectrometer. From our analysis combined with the data obtained by McCall et al. (2003), we confirmed that the levels with low J of the upper $\tilde{A}$ state are perturbed, and four of the unassigned lines observed by them in a low-temperature source have been identified as extra transitions to a perturbing state.

The authors thank D. Appadoo for valuable suggestions during the FT measurement and A. Shayesteh for measuring some He calibration lines. T. H. acknowledges a Japan Society for Promotion of Science (JSPS) Fellowship and a Grant-in-Aid for JSPS Fellows. Partial support by the Natural Sciences and Engineering Research Council of Canada and the NASA astrophysics program is also acknowledged. We gratefully acknowledge valuable discussions and correspondence with A. J. Merer and Y.-C. Hsu.

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