

Fourier transform emission spectroscopy of the $F^4\Delta-X^4\Phi$ system of TiF

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Abstract

The emission spectra of TiF have been reinvestigated in the 4200–15000 cm^{-1} region using the Fourier transform spectrometer associated with the National Solar Observatory at Kitt Peak. TiF was formed in a microwave discharge lamp operated with 2.5 Torr of He and a trace of TiF_4 vapor, and the spectra were recorded at a resolution of 0.02 cm^{-1} . The TiF bands observed in the 12000–14000 cm^{-1} region have been assigned to a new transition, $F^4\Delta-X^4\Phi$. Each band consists of four sub-bands assigned as, $^4\Delta_{1/2}-^4\Phi_{3/2}$, $^4\Delta_{3/2}-^4\Phi_{5/2}$, $^4\Delta_{5/2}-^4\Phi_{7/2}$, and $^4\Delta_{7/2}-^4\Phi_{9/2}$. A rotational analysis of the 0–1, 0–0, and 1–0 bands has been obtained and spectroscopic constants have been extracted.

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1. Introduction

In recent years, there has been growing interest in experimental and theoretical studies of the transition metal halides. Among the IV B group of the transition metal halide family the electronic spectra of TiF [1], TiCl [2–5], ZrCl [6,7], HfF [8], and HfCl [9] have been investigated recently at high resolution and a number of low-lying electronic states have been characterized. Some ab initio calculations have also been carried out on the spectroscopic properties of these molecules [10–15], providing results in good agreement with the experiments. From these studies, it has been concluded that the TiF and TiCl molecules have $^4\Phi$ ground states while ZrCl, HfF, and HfCl have $^2\Delta$ ground states.

The continued interest in transition metal-containing species arises due to their chemical and astrophysical

importance. Among the titanium containing molecules, TiO has been identified in the spectra of M-type stars [16–18] and sunspots [19,20] and TiH has tentatively been identified in M-type stars [21] and brown dwarfs [22]. There is a possibility that the titanium halides such as TiF and TiCl may also be found, however, only limited spectroscopic data studies are available. For example, the complex TiF bands located in the 380–440 nm region were known for several decades [23,24], but were left uncharacterized due to the complexity of the spectra. Even the identity of the ground state remained in question with some groups suggesting a $^4\Sigma^-$ ground state [24], while others were suggesting a $^2\Delta$ ground state [25]. The first identification of the ground state was made recently when we reported the observation of a $G^4\Phi-X^4\Phi$ transition of TiF near 15033 cm^{-1} [1] using high resolution laser and Fourier transform emission spectroscopy. From this work it was concluded that the ground state of TiF was in fact a $^4\Phi$ state rather than a $^4\Sigma^-$ or a $^2\Delta$ state. This assignment was supported by the theoretical results available for TiF [10–12] and TiH [26]. A high level ab initio study of TiF was initially

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carried out by Harrison [10], who predicted the spectroscopic properties of a number of doublet and quartet states. This work predicted a ${}^4\Phi$ ground state for TiF with a ${}^4\Sigma^-$ state about 0.1 eV above the ground state. The lowest doublet state of TiF was predicted to be a ${}^2\Phi$ state located at about 0.65 eV above the ground state. The more recent ab initio studies of TiF by Boldyrev and Simons [11] and Koukounas et al. [12] also support a ${}^4\Phi$ assignment for the ground state.

Recently the ground state of TiF has been investigated by millimeter/sub-millimeter wave spectroscopy [27] and its assignment as a ${}^4\Phi$ state has been confirmed by observation of pure rotational transitions in the four spin components. These measurements have provided precise rotational, fine structure, and hyperfine parameters for the ground state of TiF.

In the present paper, we report on the observation of a new electronic transition of TiF near $13\,232\text{ cm}^{-1}$. This transition has been labeled as the $F^4\Delta-X^4\Phi$ consistent with available theoretical results for TiF [10–12], TiCl [11,13–15], and TiH [26]. A rotational analysis of the 0–1, 0–0, and 1–0 bands of this transition has been obtained and the results are reported in this paper.

2. Experimental details

The TiF molecules were excited in a microwave discharge through a flowing mixture of 2.5 Torr of helium and a trace of TiF₄ vapor. The spectra were recorded using the 1-m Fourier transform spectrometer associated with the McMath-Pierce Telescope of the National Solar Observatory at Kitt Peak. The spectra in the $3000\text{--}15\,500\text{ cm}^{-1}$ region were recorded in two steps. The $3000\text{--}10\,000\text{ cm}^{-1}$ region was recorded using InSb detectors with silicon and green glass filters. Four scans were coadded at a resolution of 0.02 cm^{-1} in about 40 min of integration. The spectra in the $8000\text{--}15\,500\text{ cm}^{-1}$ region were recorded using midrange silicon diode detectors and a RG715 filter. This time nine scans were co-added in about 60 min of integration at a resolution of 0.02 cm^{-1} . No new bands were observed in the $3000\text{--}10\,000\text{ cm}^{-1}$ region while a number of new bands were observed in the $12\,000\text{--}14\,000\text{ cm}^{-1}$ region in addition to strong TiO bands (although no oxygen was added to the system). The oxygen required to form the TiO bands was probably present in the system as an impurity. The carrier of the new bands was identified as TiF after a rotational analysis.

The spectral line positions were measured using a data reduction program called PC-DECOMP developed by Brault. The peak positions were determined by fitting a Voigt line shape function to each line. The spectra were calibrated using the measurements of TiO lines published in our previous paper [28]. The molecular lines appear with a width of 0.035 cm^{-1} and a maximum

signal-to-noise ratio of about 8:1. The line positions are expected to be accurate to about $\pm 0.003\text{ cm}^{-1}$. However, there is considerable overlapping and blending caused by the presence of different TiF and TiO sub-bands in the same region, so that the error in the measurement of blended and weak lines is expected to be somewhat higher.

3. Observations and analysis

The new TiF bands are located in the $12\,000\text{--}14\,000\text{ cm}^{-1}$ spectral region. The bands with high wavenumber R heads near $12\,584$, $13\,235$, and $13\,783\text{ cm}^{-1}$ have been assigned as the 0–1, 0–0, and 1–0 bands of a new ${}^4\Delta-X^4\Phi$ transition of TiF. The present assignment is supported by the available ab initio calculations on TiF [10–12] and TiCl [11,13–15] as well as the energy level diagram presented in our previous paper on TiF [1]. The TiF bands were easily identified by the expected line spacing based on the rotational constants reported from the analysis of the $G^4\Phi-X^4\Phi$ transition [1]. The structure of each band appears very complex because of overlapping from the four sub-bands. Overlapping from the $A^3\Phi-X^3\Delta$ bands of TiO [28] also contributes to the complex appearance of the TiF bands. For TiF, a ${}^4\Delta-{}^4\Phi$ transition should consist of four sub-bands: ${}^4\Delta_{1/2}-{}^4\Phi_{3/2}$, ${}^4\Delta_{3/2}-{}^4\Phi_{5/2}$, ${}^4\Delta_{5/2}-{}^4\Phi_{7/2}$, and ${}^4\Delta_{7/2}-{}^4\Phi_{9/2}$, which should be separated by substantial spin-orbit interactions in the lower and upper excited electronic states. A careful inspection of each band using a color Loomis-Wood program helped us identify and assign the rotational structure of all four sub-bands. The rotational assignment in the four subbands was obtained by comparing the lower state combination differences to those from the $G^4\Phi-X^4\Phi$ transition of TiF [1]. The Ω -assignment was based on the observed magnitudes of the Ω -doubling constants in the different sub-bands. Ω -doubling constants of unusually large magnitude have been determined for all four spin components of the $F^4\Delta$ state. The observed Ω -doubling splittings follow the trend of ${}^4\Delta_{7/2} < {}^4\Delta_{5/2} < {}^4\Delta_{3/2} < {}^4\Delta_{1/2}$, as expected. The rotational analysis of these bands indicates that the $X^4\Phi$ state is free from Ω -doubling, while the $F^4\Delta$ state has large Ω -doubling.

A compressed portion of the 0–0 band is presented in Fig. 1, in which the high wavenumber R heads of the four sub-bands of TiF have been marked. The R heads of the overlapping TiO bands have also been marked in this figure. The four sub-bands with R heads at $13\,235$, $13\,182$, $13\,125$, and $13\,065\text{ cm}^{-1}$ have been identified as the ${}^4\Delta_{1/2}-{}^4\Phi_{3/2}$, ${}^4\Delta_{3/2}-{}^4\Phi_{5/2}$, ${}^4\Delta_{5/2}-{}^4\Phi_{5/2}$, and ${}^4\Delta_{7/2}-{}^4\Phi_{9/2}$ sub-bands of the 0–0 band. The structure of each band consists of R, Q, and P branches consistent with a $\Delta\Omega = 1$ transition. These branches are doubled due to the Ω -doubling in the excited state. The observation of

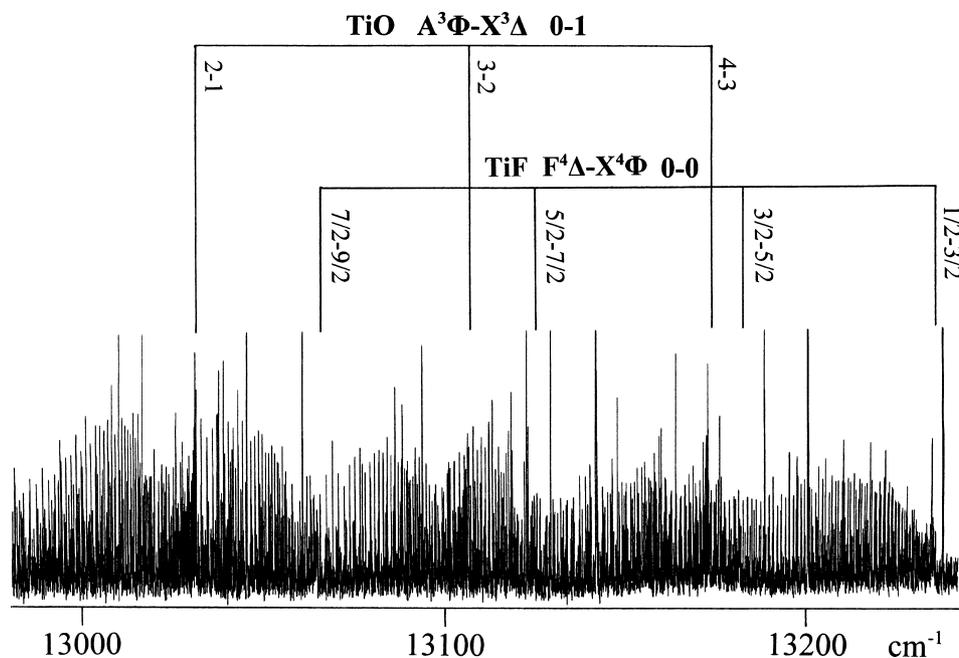


Fig. 1. A compressed portion of the 0–0 band of TiF with the R-heads of the four sub-bands marked. The R-heads of the overlapping TiO bands have also been marked.

large Ω -doubling in the $F^4\Delta$ state is evidence for a strong interaction with a nearby state. Since no bands that cross spin components have been observed in our spectra, the four spin components were treated separately as Hund's case (c) states although they obey Hund's case (a) coupling.

The $^4\Delta_{1/2}-^4\Phi_{3/2}$ sub-band is located on the high wavenumber side of the band as shown in Fig. 1. The 0–1, 0–0, and 1–0 bands of the $^4\Delta_{1/2}-^4\Phi_{3/2}$ sub-band are located near 12584, 13235, and 13783 cm^{-1} , respectively. The rotational assignment in these bands was obtained by comparing the combination differences for the common vibrational levels. Very good agreement was also obtained between the lower state combination differences from the new transition and the corresponding values obtained from the $G^4\Phi-X^4\Phi$ transition [1]. No local rotational perturbations were observed in any of the bands. A portion of the rotational structure of the $^4\Delta_{1/2}-^4\Phi_{3/2}$, 0–0 band between the $^4\Delta_{1/2}-^4\Phi_{3/2}$ and $^4\Delta_{3/2}-^4\Phi_{5/2}$ R-heads is presented in Fig. 2. This portion of the spectrum is free from overlapping by TiO bands.

The band with an R head near 13182 cm^{-1} has been identified as the 0–0 band of the $^4\Delta_{3/2}-^4\Phi_{5/2}$ sub-band. The 0–1 and 1–0 bands of this sub-band are located near 12529 and 13731 cm^{-1} , respectively. Ω -doubling is also present in this sub-band although its magnitude is smaller than that in the $^4\Delta_{1/2}-^4\Phi_{3/2}$ sub-band.

On the lower wavenumber side, the next two R heads at 13125 and 13065 cm^{-1} have been assigned as the 0–0 R heads of the $^4\Delta_{5/2}-^4\Phi_{7/2}$ and $^4\Delta_{7/2}-^4\Phi_{9/2}$ sub-bands. The 0–1 and 1–0 bands of these two sub-bands are located near 12474, 13672, and 12414, 13610 cm^{-1} ,

respectively. It is surprising to note that Ω -doubling is present even in these high Ω sub-bands, although it is only resolved for $J > 49$ in the 0–0 band of the $^4\Delta_{7/2}-^4\Phi_{9/2}$ sub-band.

It is difficult to make a definite e - and f -parity assignment in the bands with resolved Ω -doubling. We have therefore chosen to label the branches in the different sub-bands arbitrarily. The observed $F^4\Delta$ electronic states probably belong to Hund's case (a), however, in the absence of transitions across spin components, it becomes difficult to obtain reliable Hund's case (a) constants. We decided to obtain a fit by using the usual Hund's case (c) empirical term energy expression for each of the spin-components

$$F_v(J) = T_v + B_v J(J+1) - D_v [J(J+1)]^2 + H_v [J(J+1)]^3 \pm 1/2 [p_v (J+1/2) + p_{D_v} (J+1/2)^3 + p_{H_v} (J+1/2)^5]. \quad (1)$$

Initially, band-by-band fits were obtained. Once the lines in each of the observed bands were assigned, the final fits were obtained by combining the lines of all the bands of each sub-band. The hyperfine-free pure rotational line positions in the four spin components of the ground state (extracted using the data published by Sheridan et al. [27]) were also included in the final fits. The fits of the four sub-bands provided a single set of constants for each vibrational level of the four spin components. The observed lines positions in different bands are deposited in the Journal's Electronic Depository, which is available on the World Wide Web. The molecular constants for the upper and lower states are provided in Table 1.

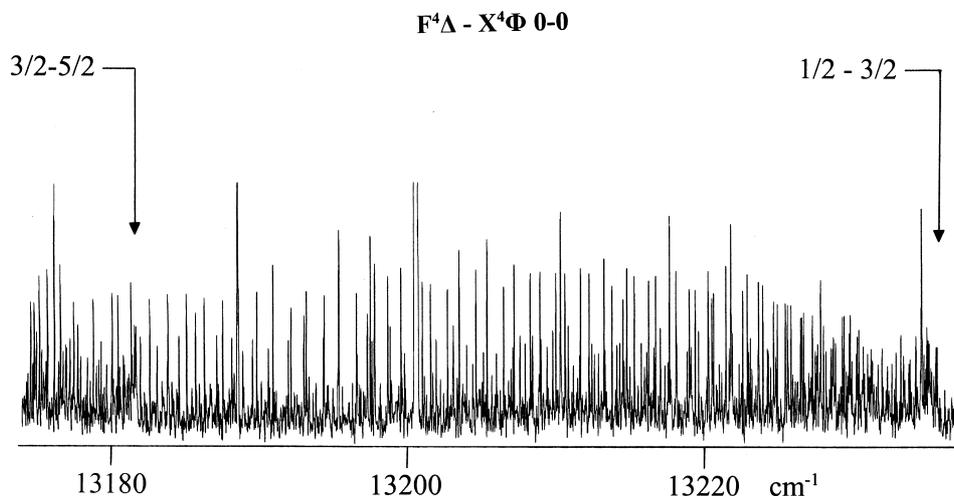


Fig. 2. An expanded portion of the ${}^4\Delta_{1/2}$ - ${}^4\Phi_{3/2}$ sub-band near the R-head.

Table 1
Spectroscopic constants^a (in cm^{-1}) for the $F^4\Delta$ and $X^4\Phi$ states of TiF

Constants	$v = 0$	$v = 1$	$v = 0$	$v = 1$
	$F^4\Delta_{1/2}$		$F^4\Delta_{3/2}$	
T_v	13231.56761(71)	13779.6698(11)	13177.66605(93)	13725.5029(11)
B_v	0.3316835(25)	0.3292612(48)	0.3359967(25)	0.3334928(43)
$10^7 \times D_v$	1.755(24)	1.561(54)	2.745(19)	2.967(42)
$10^{11} \times H_v$	1.751(76)	1.79(17)	-1.694(41)	-1.10(11)
$10^2 \times p_v$	-5.2239(80)	-7.824(11)	0.1360(72)	0.093(12)
$10^5 \times p_{D_v}$	2.009(15)	2.905(21)	1.645(10)	2.284(19)
$10^9 \times p_{H_v}$	-4.614(67)	-6.011(86)	-2.750(31)	-3.897(67)
	$F^4\Delta_{5/2}$		$F^4\Delta_{7/2}$	
T_v	13120.47394(83)	13667.6152(13)	13059.10470(92)	13605.0985(15)
B_v	0.3409074(23)	0.3381944(58)	0.3484275(25)	0.3460614(76)
$10^6 \times D_v$	0.4187(17)	0.3437(64)	1.1909(19)	1.2750(97)
$10^{11} \times H_v$	-1.634(34)	-3.05(19)	2.42(12)	6.95(34)
$10^3 \times p_v$	1.059(62)	1.30(15)	—	—
$10^6 \times p_{D_v}$	-2.652(79)	-3.39(26)	-0.383(33)	—
$10^9 \times p_{H_v}$	-3.70(23)	-3.70(99)	0.242(12)	—
	$X^4\Phi_{3/2}$		$X^4\Phi_{5/2}$	
T_v	0.0	650.60096(97)	0.0	650.6812(12)
B_v	0.364716957(86)	0.3622249(20)	0.367031233(94)	0.3644936(21)
$10^7 \times D_v$	4.1342(11)	4.1532(79)	4.4773(12)	4.4738(73)
	$X^4\Phi_{7/2}$		${}^4\Phi_{9/2}$	
T_v	0.0	650.7310(11)	0.0	650.7815(12)
B_v	0.369404286(96)	0.3668289(20)	0.371865327(88)	0.3692541(20)
$10^7 \times D_v$	4.8468(12)	4.8285(75)	5.2639(11)	5.2434(67)

^a Numbers in parentheses are one standard deviation in the last two digits.

4. Results and discussion

In a previous paper, we have reported the observation of the $G^4\Phi$ - $X^4\Phi$ transition of TiF at 15033 cm^{-1} [1] and have concluded that the ground state of TiF is a ${}^4\Phi$ state. In that paper, we presented an schematic energy level diagram (Fig. 6 of [1]) for the low-lying electronic states of TiF based on the predictions of Harrison [10] for TiF and ab initio results available for TiH from the work of Anglada et al. [26]. From this

figure, we have suggested that the energy levels of TiF, TiH, and Ti^+ follow a remarkably similar pattern. As shown in this figure, there are a number of quartet states below the $G^4\Phi$ state which remain unobserved. The detection of a new ${}^4\Delta$ - ${}^4\Phi$ transition near 13200 cm^{-1} is fully consistent with this energy level diagram for TiF [1] which shows two quartet states, $F^4\Delta$ and $E^4\Pi$, located just below the $G^4\Phi$ state. The new transition can, therefore, be safely assigned as $F^4\Delta$ - $X^4\Phi$. Although no local perturbations have been found, the observation

of large Ω -doubling in the $F^4\Delta$ state is probably due to mixing with the $E^4\Pi$ state, which has not yet been detected.

The spectroscopic constants for the different spin components of the $F^4\Delta$ and $X^4\Phi$ states of TiF are provided in Table 1. The observation of large Ω -doubling constants p_v , p_{D_v} , and p_{H_v} and the higher order centrifugal distortion constant H_v in the different spin components of the $F^4\Delta$ state probably arise because of interaction with the $E^4\Pi$ state. These constants are not needed for the $X^4\Phi$ state, indicating that the ground state is relatively unperturbed.

The spectroscopic constants for the individual spin components of the ground state agree very well with the values reported in our previous paper [1]. The vibrational intervals ($\Delta G_{1/2}$) values for the $X^4\Phi_{3/2}$ [650.60096(97)], $X^4\Phi_{5/2}$ [650.6812(12)], $^4\Phi_{7/2}$ [650.7310(11)], and $X^4\Phi_{9/2}$ [650.7815(12)] spin components are very similar to our previous values [1] within the quoted error limits, and the inclusion of hyperfine-free pure rotational data from Sheridan et al. [27] has greatly improved the rotational constants (Table 1). The present rotational constants provide equilibrium constants of $B_e = 0.3659630(10)$, $\alpha_e = 0.0024921(20)$ cm^{-1} for the $X^4\Phi_{3/2}$ component; $B_e = 0.3683001(11)$, $\alpha_e = 0.0025376(21)$ cm^{-1} for the $X^4\Phi_{5/2}$ component; $B_e = 0.3706920(10)$, $\alpha_e = 0.0025754(20)$ cm^{-1} for the $X^4\Phi_{7/2}$ component; $B_e = 0.3731709(10)$, $\alpha_e = 0.0026112(20)$ cm^{-1} for the $X^4\Phi_{9/2}$ component. The variation of vibrational intervals and equilibrium constants for different Ω states indicates that the ground state is a well behaved case (a) state. The $\Delta G_{1/2}$, B_e , and α_e constants for the excited state are 548.1022(13), 0.3328947 (37), 0.0024223(54) cm^{-1} for the $F^4\Delta_{1/2}$ component; 547.8368(14), 0.3372487(35), 0.0025039(50) cm^{-1} for the $F^4\Delta_{3/2}$ component; 547.1413(15), 0.3422639(39), 0.0027130 (62) cm^{-1} for the $F^4\Delta_{5/2}$ component and 545.9938(18), 0.3496106(48), 0.0023661(82) cm^{-1} for the $F^4\Delta_{7/2}$ spin components. The relatively large variation in the values for the different spin components compared to those for the ground state reflects the presence of interactions in the excited state. The case (a) rotational constants for the $v = 0$ and 1 vibrational levels, determined by averaging the values for the four spin components, provide approximate equilibrium constants of $B'_e = 0.3406$ cm^{-1} , $\alpha'_e = 0.0025$ cm^{-1} , and $r'_e = 2.195$ Å for the $F^4\Delta$ state and $B''_e = 0.3695$ cm^{-1} , $\alpha''_e = 0.0026$ cm^{-1} , and $r''_e = 1.8311$ Å for the $X^4\Phi$ state of TiF.

5. Conclusion

The emission spectrum of TiF has been recorded at high resolution using a Fourier transform spectrometer and a number of new bands have been detected in the 12000–14000 cm^{-1} region. The bands with high wave-

number R-heads near 12584, 13235, and 13783 cm^{-1} have been assigned as the 0–1, 0–0, and 1–0 bands of a new $F^4\Delta$ – $X^4\Phi$ system of TiF. This assignment is supported by the ab initio results available for TiF [10–12] and TiH [26]. A rotational analysis of the 0–1, 0–0, and 1–0 bands has been obtained and spectroscopic constants have been extracted. The observation of large Ω -doubling in the excited state is consistent with the global interaction of the $F^4\Delta$ state with a nearby state, probably the unobserved $E^4\Pi$ state.

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Appendix A. Supplementary data

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://msa.lib.ohio-state.edu/jmsa_hp.htm).

References

- [1] R.S. Ram, J.R.D. Peers, Y. Teng, A.G. Adam, A. Muntianu, P.F. Bernath, S.P. Davis, *J. Mol. Spectrosc.* 184 (1997) 186–201.
- [2] R.S. Ram, P.F. Bernath, *J. Mol. Spectrosc.* 186 (1997) 113–130.
- [3] R.S. Ram, P.F. Bernath, *J. Mol. Spectrosc.* 195 (1999) 299–307.
- [4] T. Imajo, D. Wang, K. Tanaka, T. Tanaka, *J. Mol. Spectrosc.* 203 (2000) 216–227.
- [5] R.S. Ram, P.F. Bernath, *J. Mol. Spectrosc.* 227 (2004) 43–49.
- [6] R.S. Ram, P.F. Bernath, *J. Mol. Spectrosc.* 186 (1997) 335–348.
- [7] R.S. Ram, P.F. Bernath, *J. Mol. Spectrosc.* 196 (1999) 235–247.
- [8] A.G. Adam, W.S. Hopkins, D.W. Tokaryk, *J. Mol. Spectrosc.* 225 (2004) 1–7.
- [9] R.S. Ram, A.G. Adam, A. Tsouli, J. Liévin, P.F. Bernath, *J. Mol. Spectrosc.* 202 (2000) 116–130.
- [10] J.F. Harrison, *Chem. Rev.* 100 (2000) 679–716 (and private communication).
- [11] A.I. Boldyrev, J. Simons, *J. Mol. Spectrosc.* 188 (1998) 138–141.
- [12] C. Koukounas, S. Kardahakis, A. Mavridis, *J. Chem. Phys.* 120 (2004) 11500–11521.
- [13] C. Focsa, M. Bencheikh, L.G.M. Pettersson, *J. Phys. B At. Mol. Opt. Phys.* 31 (1998) 57–69.
- [14] Y. Sakai, K. Mogi, E. Miyoshi, *J. Chem. Phys.* 111 (1999) 3989–3994.
- [15] R.S. Ram, A.G. Adam, W. Sha, A. Tsouli, J. Liévin, P.F. Bernath, *J. Chem. Phys.* 114 (2001) 3977–3987.

- [16] P.W. Merrill, A.J. Deutsch, P.C. Keenan, *Astrophys. J.* 136 (1962) 21–34.
- [17] G.W. Lockwood, *Astrophys. J.* 180 (1973) 845–855.
- [18] R.E.S. Clegg, D.L. Lambert, R.A. Bell, *Astrophys. J.* 234 (1979) 188–199.
- [19] H. Wöhl, *Solar Phys.* 16 (1971) 362–372.
- [20] O. Engvold, *Astron. Astrophys. Suppl.* 10 (1973) 11–45.
- [21] R. Yerle, *Astron. Astrophys.* 73 (1979) 346.
- [22] A.J. Burgasser, *Astrophys. J. Lett.* 616 (2004) L73–L76.
- [23] R.L. Diebner, J.G. Kay, *J. Chem. Phys.* 51 (1969) 3547–3554.
- [24] A. Chatalic, P. Deschamps, G. Pannetier, *C.R. Acad. Sci. Paris* 270 (1970) 146–149.
- [25] E.A. Shenyavskaya, V.M. Dubov, *J. Mol. Spectrosc.* 113 (1985) 85–92.
- [26] J. Anglada, P.J. Bruna, S. Peyerimhoff, *Mol. Phys.* 69 (1990) 281–303.
- [27] P.M. Sheridan, S.K. McLamarrah, L.M. Ziurys, *J. Chem. Phys.* 119 (2003) 9496–9503.
- [28] R.S. Ram, P.F. Bernath, M. Dulick, L. Wallace, *Astrophys. J., Suppl. Ser.* 122 (1999) 331–353.