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Investigations on the Spin-Crossover Complex $[Fe(bzimpy)_2](ClO_4)_2$ and its Mn^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+} Analogues**

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Summary. A series of transition metal complexes $[M(bzimpy)_2](ClO_4)_2$ ($M = Mn^{2+}$, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}; *bzimpy* = 2,6-bis(benzimidazol-2′-yl)pyridine) was synthesized and characterized by elemental analysis, UV–Vis and far-IR spectroscopy. The electronic spectra of $[Ni(bzimpy)_2](ClO_4)_2$ in solution and solid state reveal a ligand field splitting parameter Δ_0 in the range of 11470 cm^{-1} to 11840 cm^{-1}. The simultaneous existence of two species with distinct spin state is found for $[Fe(bzimpy)_2](ClO_4)_2$ by means of variable temperature far–IR measurements. Assignments of the observed far–IR bands are given on the basis of the investigations of the variation of the metal ion in $[M(bzimpy)_2](ClO_4)_2$.

Keywords. 2,6-bis(benzimidazol-2′-yl)pyridine; Spin-crossover; Transition metal complexes.

Untersuchung des Spin-Crossover-Komplexes $[Fe(bzimpy)_2](ClO_4)_2$ und seiner Mn^{2+}, Co^{2+}, Ni^{2+} und Zn^{2+} – Analoga

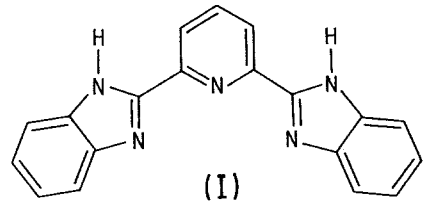
Zusammenfassung. Es wurde eine Reihe von Übergangsmetallkomplexen $[M(bzimpy)_2(ClO_4)_2$ ($M = Mn^{2+}$, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}; *bzimpy* = 2,6-bis(benzimidazol-2′-yl)pyridin) hergestellt und durch Elementaranalyse, UV–Vis–Spektroskopie und ferne IR–Spektroskopie charakterisiert. Die Elektronenspektren von $[Ni(bzimpy)_2](ClO_4)_2$ in Lösung und im Festkörper zeigen eine Ligandenfeldaufspaltung Δ_0 zwischen 11470 cm^{-1} und 11840 cm^{-1}. Die gleichzeitige Existenz zweier Spezies mit unterschiedlichem Spin-Zustand wird durch temperaturabhängige ferne IR-Messungen an $[Fe(bzimpy)_2](ClO_4)_2$ nachgewiesen. Eine Zuordnung der IR-Banden wird aufgrund der Untersuchungen der Variation des Metallions in $[M(bzimpy)_2](ClO_4)_2$ gegeben.

Introduction

Iron(II) complexes of ligands with imine-structure exist in both the low-spin (LS) and high-spin (HS) electronic ground states. Thermally populated equilibria of both states (spin-crossover behaviour) have been reported for several compounds in the solid state and in solution [1–6].

** This paper is dedicated to Professor Ulrich Wannagat on the occasion of his 70th birthday with warmest personal wishes.

Recently, the nitrogen donor ligand 2,6-bis(benzimidazol-2′-yl)pyridine (bzimpy) (**I**) has been reported to form tris-diimine and bis-triimine Fe(II) complexes in solution, both showing spin-crossover behaviour [7].



(I)

For the solid state complex $[Fe(bzimpy)_2](ClO_4)_2$, the onset of a spin-crossover has been suggested on the basis of variable temperature magnetic measurements [8]. This method yields only statistical informations, which cannot disclose the simultaneous existence of two different spin states. This led us to investigate the electronic states of $[Fe(bzimpy)_2](ClO_4)_2$ by means of UV–Vis and variable temperature far–IR measurements in comparison with its firstly obtained transition metal analoga $[M(bzimpy)_2](ClO_4)_2$ ($M = Mn^{2+}$, Co^{2+}, Ni^{2+}, Zn^{2+}).

Experimental Part

2,6-Bis(benzimidazol-2′-yl)pyridine was prepared by the method of Addison and Burke [9] and recrystallized three times from pure *Me*OH. $[Fe(bzimpy)_2](ClO_4)_2$ was prepared according to literature [8]. $[M(bzimpy)_2](ClO_4)_2$ with $M = Mn^{2+}$, Co^{2+}, Ni^{2+}, Zn^{2+} were prepared by mixing hot methanolic solutions of *bzimpy* (~ 1g/100 ml) with stoichtometric amounts of $M(ClO_4)_2 \cdot 6H_2O$ (Fluka, p.a.) dissolved in a minimum volume of methanol. The precipitated metal(II)perchlorate complexes were filtered off and washed twice with a few ml of methanol. Drying in vacuo over $CaCl_2$ yielded in all cases more than 90% (about 1.3 g).

UV–Vis absorption spectra (190–1100 nm) were obtained on a Hitachi U-2000 spectrophotometer. For solution spectra 1 cm quartz cells were used, solids were applied as a Nujol mull using a modification of the method of Rowley [10]. A filter paper covered with a viscid complex-Nujol suspension on both sides was placed in the beam and a filter paper saturated with Nujol served as a reference. Discontinuities of the solid state spectra at 380, 600, 740, and 1020 nm were identified as instrumental in source, using clean filter paper and glass plates as reference. The experimental electron-transition spectra were converted to a linear energy scale (cm^{-1}) and deconvoluted subsequently to a baseline correction. This procedure was done by the software-package "Spectracalc", assuming Gaussian line shapes.

Table 1. Analytical data for the $[M(bzimpy)_2](ClO_4)_2$ complexes calculated as $C_{38}H_{26}N_{10}O_8Cl_2M$

Metal	MW	% Found				% Calcd.				
		C	H	N	Cl	C	H	N	Cl	Color
Mn	877.44	50.96	2.94	15.54	7.90	52.07	2.99	15.98	8.09	yellow
Fe	880.52	51.94	2.96	15.96	8.13	52.02	2.93	15.96	8.08	magenta
Co	880.29	50.84	2.92	15.61	7.88	51.84	2.98	15.91	8.05	yellow-brown
Ni	876.53	50.74	2.91	15.59	8.01	51.85	2.98	15.91	8.05	white-green
Zn	886.97	52.22	3.06	15.89	7.14	51.46	2.95	15.79	7.99	white

Infrared spectra (650–50 cm^{-1}) were recorded on a Nicolet 20F far-IR Fourier transform spectrometer with an optical bench held under reduced pressure (< 0.3 Torr). A resolution of 4 cm^{-1} using 5376 data points (8192 Fourier transformation points) and a mirror velocity of 1.4 mm s^{-1} was selected; band positions could be reproduced within $\pm 0.3\,cm^{-1}$. All samples were recorded as polyethylen pellets. For low temperature measurements a variable temperature cell P/N 21.500 (Specac, Inc.) was used. The temperature of the sample holder was monitored with an CC-thermocouple. To ensure a thorough temperature balance between sample and holder, spectra were recorded 15 minutes after reaching temperature constancy of the cell holder.

Results and Discussion

Electron Transition Spectra

The spectrum of $[Mn(bzimpy)_2](ClO_4)_2$ consists of an intense peak at 22900 cm^{-1} and a broad band between 26400 cm^{-1} and 49000 cm^{-1} (Fig. 1). Since d–d-transitions of Mn(II) are all spin-forbidden and therefore weakly absorbing, we attribute the observed bands to charge transfer (CT) transitions. The spectrum of the iron(II) complex (Fig. 1) coincides with the UV-Vis reflectance spectrum of this complex reported in [8]. The Co(II) compound shows a broad d–d-band with a maximum around 9100 cm^{-1}, which is attributed to a $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$-transition. Further d–d-absorptions appear as shoulders at 18200 cm^{-1} and about 21000 cm^{-1} (likely a $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition with a spin orbit splitting of the $^4T_{1g}(P)$-state) in a CT-band raising up from 17400 cm^{-1}. For $[Zn(bzimpy)_2](ClO_4)_2$ only one intense band at wavenumbers greater than 23000 cm^{-1} is observed.

The electronic spectra of $[Ni(bzimpy)_2](ClO_4)_2$ in solution and in the solid state are given in Fig. 2. Molar extinction coefficients have been found to be $\varepsilon_{v1}(850\,nm) = 23.1 \pm 0.71\,mol^{-1}\,cm^{-1}$ and $\varepsilon_{v2}(560\,nm) = 12.6 \pm 1.01\,mol^{-1}\,cm^{-1}$ in acetone at

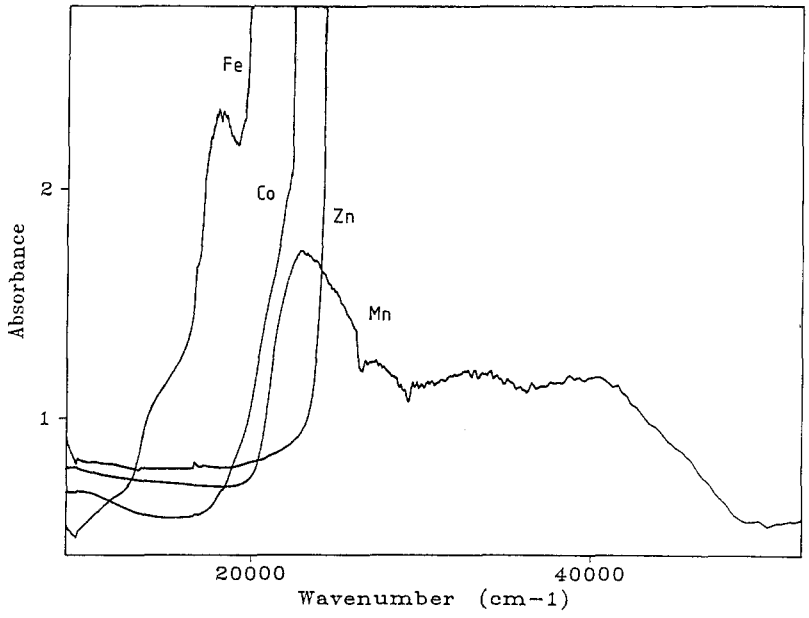


Fig. 1. Nujol-mull electron spectra of $[M(bzimpy)_2](ClO_4)_2$ at room temperature

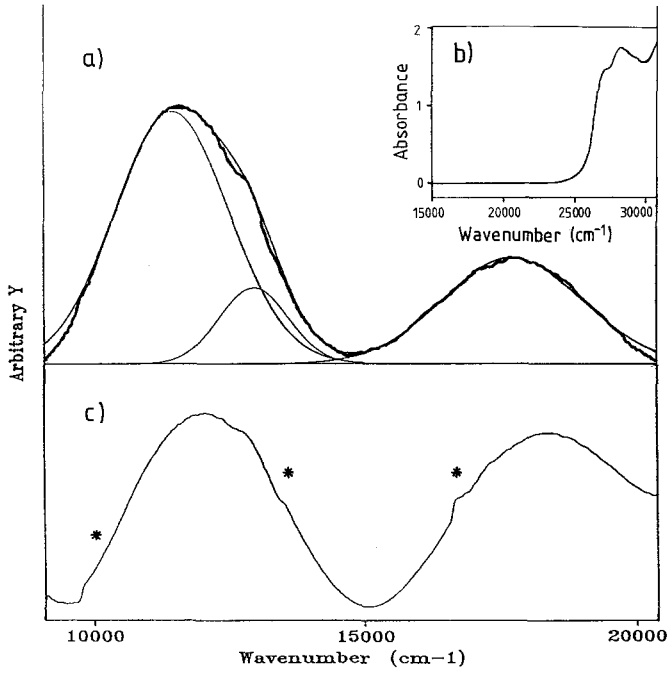


Fig. 2. Electronic spectra of [Ni(*bzimpy*)$_2$](ClO$_4$)$_2$ at 20 °C. a) Saturated solution in acetone deconvoluted into its Gaussian components; b) $4.2 \cdot 10^{-5}$ *M* solution in *Me*OH; c) Solid state spectrum (Nujol mull); instrumental discontinuities are marked by "*"

20 °C. Deconvolution of the solution spectrum revealed the band positions given in Table 2. The same procedure applied to the solid state spectrum provided unreliable results due to the "discontinuities" (*, Fig. 2c) of the spectrum.

The spectra of [Ni(*bzimpy*)$_2$](ClO$_4$)$_2$ are typical for octahedral Ni^{2+}-complexes. According to the assignments in Table 2, the transition $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_3) has been calculated from the deconvoluted solution spectrum, using the d^8-Tanabe-Sugano-Diagramm with C = 4.709 B [11]. In the region of the expected value $\nu_3 = 27220\,cm^{-1}$ (367 nm), an intense band is found with an absorbance maximum at 353 nm ($\varepsilon \sim 42000\,l\,mol^{-1}\,cm^{-1}$) and a shoulder in the region of 363–369 nm (Fig. 2b). Deconvolution of the shoulder yielded a charge-transfer peak at 373 nm

Table 2. Ligand field band positions (cm^{-1}) of [Ni(*bzimpy*)$_2$](ClO$_4$)$_2$

	Observed	Calculated[a]	Deconvoluted[b]	Assignment
Solution	11620	11616	11471	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1)
	12820	12308	12968	$^3A_{2g}(F) \rightarrow {}^1E_g(D)$ (ν')
	17800	–	17727	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2)
Solid	12060	11836	–	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1)
	12820	12132	–	$^3A_{2g}(F) \rightarrow {}^1E_g(D)$ (ν')
	18410	–	–	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2)

[a] According to [14]

[b] Gaussian components

($\varepsilon \sim 11000\,l\,mol^{-1}\,cm^{-1}$). Due to the intense absorbance in the range <400 nm, the d–d band within this region is obscured.

As a common rule, spin-crossover-behaviour of Fe(II)complexes is expected, when Δ_o of the corresponding Ni(II) compound is found between 11300 and $1900\,cm^{-1}$ [2]. In detailed studies on appropriate Ni(II) complexes it appeared that the interesting range of Δ_o-values is always close to the energetic crossover point of the Ni(II) $^3T_{2g}(F)$ and $^1E_g(D)$ energy levels [14]. In order to find Δ_o (which is equivalent to the $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ transition for d^8-configuration), deconvolution methods [12, 13] as well as a method based on empirical corrections have been used [14].

A more close analysis of the d–d-transitions of $[Ni(bzimpy)_2](ClO_4)_2$ in the range of 400–1100 nm revealed the following details:

i) Applying the Tanabe-Sugano diagram to the deconvoluted spectrum, a Racah B parameter of $656\,cm^{-1}$ was obtained. Compared to the value of the free Ni^{2+}-ion ($1130\,cm^{-1}$), a strong nephelauxetic effect is found ($\beta = 0.58$). The calculated value of the spin- forbidden transition v' is $11992\,cm^{-1}$ which is $976\,cm^{-1}$ below the position of the deconvoluted peak.

11) The method of empirical correction for the mixing of the excited states is based upon a plot of the ratios of intensities at the experimental peak positions v_1 and v' versus the corresponding v_1-position [14]. While our data fit excellent this correlation, there are significant deviations in a plot of v_2 versus v_1 and versus v'. Furthermore, the distance between v_1 and v' in the solid state $[Ni(bzimpy)_2](ClO_4)_2$ spectrum is only $760\,cm^{-1}$ while the empirical correction term is based upon a value of $1200\,cm^{-}$ for this distance.

Both models used to calculate Δ_o result in some differences between experimental and calculated band positions. This is probably due to a deviation from a strictly octahedral symmetry as found for the structurally similar $[Ni(terpy)_2]^{2+}$ [15]. For this compound, distortion has been dedected by means of EPR spectroscopy while UV-Vis spectroscopy was too insensitve to indicate any splitting due to the large bandwidth of the d–d transitions. This observation may account for the deviations between experimental and calculated values for out system since both calculation methods are based on a strictly octahedral model.

Regardless of these inconsistencies both methods lead to values of Δ_0 where spin-crossover behaviour of $[Fe(bzimpy)_2](ClO_4)_2$ has to be expected for the solid state as well as for solution.

Vibrational Spectroscopy

The metal-ligand bond lengths of the HS-forms of Fe(II) spin-crossover compounds have been found to exceed the bond lengths of the LS-forms by 0.14–0.23 Å [6]. Both species are clearly distinct in vibrational frequencies and iron-ligand bond strengths. As the spin transition is slow ($k = 4 \cdot 10^5 - 3 \cdot 10^8\,s^{-1}$) compared to the excitation of the vibrational modes, LS- and HS- form can be detected simultaneously by IR spectroscopy [16, 17].

The far IR spectra of $[Fe(bzimpy)_2](ClO_4)_2$ at different temperatures are given in Fig. 3. Two bands at 436 and $281\,cm^{-1}$ show a significant change with temperature.

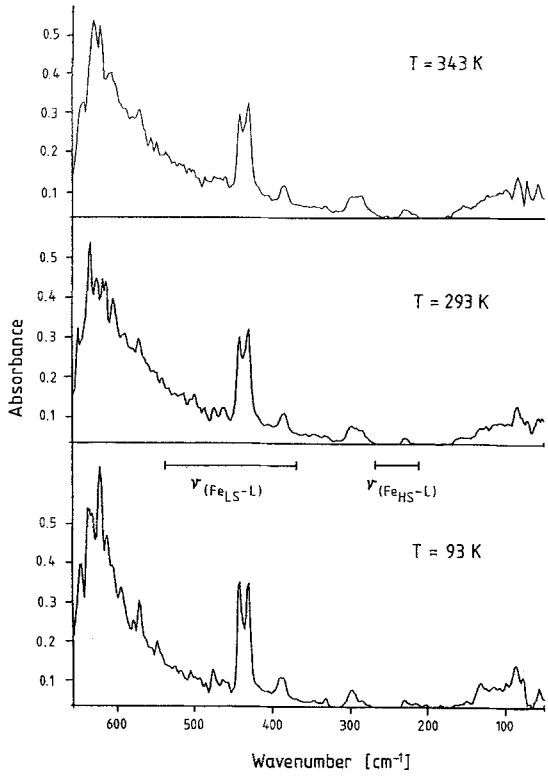


Fig. 3. Temperature dependence of the infrared spectrum of $[Fe(bzimpy)_2](ClO_4)_2$ in the 650–50 cm^{-1} region. –: Ranges of metal-ligand stretching frequencies of Fe(II) spin-crossover compounds [5]

While the first one decreases with increasing temperature, the latter increases in intensity. Since LS-HS equilibria are generally shifted to the HS-side by raise in temperature, we attribute the band at 436 cm^{-1} to a LS- and the lower energetic one to a HS-species. The range of all metal-ligand stretching frequencies known for Fe(II) spin-crossover compounds is marked in Fig. 3. According to this, both temperature dependent bands are supposed to reflect Fe-N stretching vibrations. In order to support these findings and to achieve an assignment of further bands, a series of transition metal complexes $[M(bzimpy)_2](ClO_4)_2$ with $M = Mn^{2+}$, Co^{2+}, Ni^{2+} and Zn^{2+} has been prepared. The far- IR spectra of these compounds are given in Fig. 4.

Assignments (Table 3) have been made in comparison with the extensively studied $[M(AMP)_3](ClO_4)_2$-system (AMP = 2-Aminomethylpyridine) [18]. The 281 cm^{-1} band of the Fe(II) complex is confirmed as HS since the frequencies in this range follow the crystal field stabilization energy (CFSE)-sequence for HS-complexes (Mn < Fe < Co < Ni > Zn). Due to the additional existence of a band in the uncomplexed ligand and to the moderate dependence of the band positions on the metal ion, a combination mode is indicated. The band around 220 cm^{-1} is more indicative for a metal-ligand stretching mode due to the absence of any ligand band in this range and to the strong dependence on M^{2+} in the CFSE-sequence. While this band also falls within the range of other $\nu(Fe_{HS}\text{-}L)$-modes (Fig. 3), its intensity in $[Fe(bzimpy)_2](ClO_4)_2$ is too weak to follow the temperature dependent behaviour. For the 436 cm^{-1}-band of the Fe(II) complex, the absence of

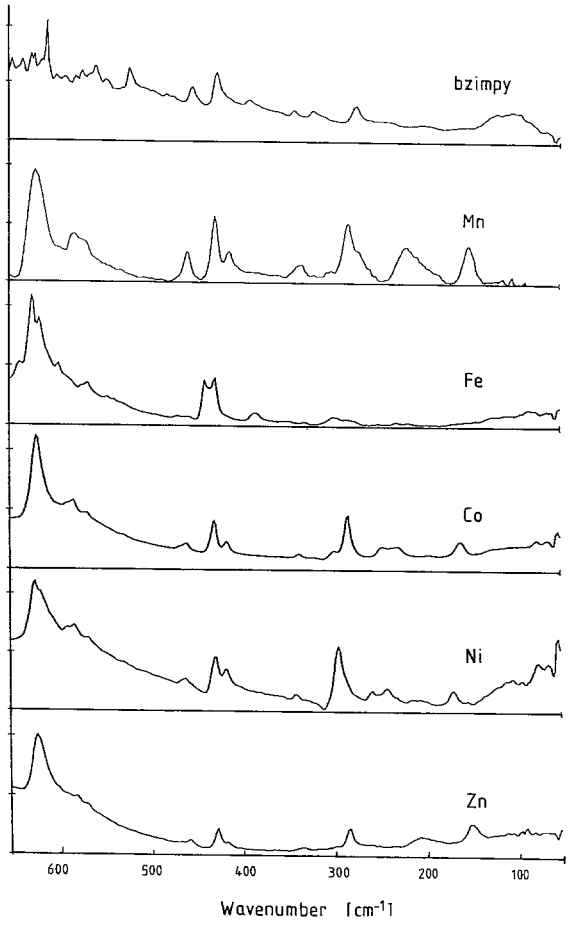


Fig. 4. Far infrared spectra of several $[M(bzimpy)_2](ClO_4)_2$ species at room temperature

related bands in the ligand as well as in the $[M(bzimpy)_2](ClO_4)_2$-series is consistent with the assignment $\nu(Fe_{LS}\text{-}L)$, reflecting the strong CFS of low-spin Fe(II).

To conclude, we have shown the existence of a LS and HS-species for $[Fe(bzimpy)_2](ClO_4)_2$ in the solid state by means of variable temperature far-IR measurements. The ratio of both spin isomers is altered towards the HS-side with increasing temperature. This is an evidence of a spin-crossover as it has been expected on the basis of variable temperature magnetic measurements on the same compound as well as electron spectroscopical studies on its Ni(II) analogue.

Table 3. Frequencies (cm^{-1}) and assignments in the far IR spectra of $[M(bzimpy)_2](ClO_4)_2$ at room temperature

bzimpy	Metal ion					Assignment
	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Zn^{2+}	
646.4 m						
634.7 m		638.5 w				
624.3 m		624.6 s				
620.9 m	621.0[a] s	617.5 s	620.7 s	623.2 s	621.2 s	δ(Py) i.p.
607.4 s						
597.9 w		596.3 w				
588.4 w				587.9 w		
576.5 w	579.0 m		580.6[b] m	580.5 m	578.5 w	ligand
569.1 w	~569 m	564.6[b] m	566.9 w	565.3 w	568.1 w	ligand
555.0 m						
543.8 w						
518.7 m						
		~467 w				
449.4 m	454.7 m	~454 w	457.0 m	459.1 w	455.2 w	M–L combination mode
		436.0 s				ν_{LS} (Fe–L)
422.6 s	424.2 s	424.7 s	426.1 s	425.4 m	424.4 m	δ(Py) o.o.p.
	408.9 m		412.8 m	414.1 s	414.4 w	
386.7 w		380.5 m				
339.0 w	329.8 m		~334 w	338.3 w		
318.1 w						
		~296 w	~295 w			
270.9 m	279.1[a] s	~281 w	280.3 s	291.2 s	280.4 m	M–L combination mode
		~227 w	243.1 m	254.7 m		
	214.9[a] s	~214 w	226.9 m	238.8 m	202.6 m	ν M–L (ev. Py)
	147.6 s		157.5 m	165.8 m	147.3 m	M–L mode

[a] Shoulder at lower wavenumbers
[b] Shoulder at higher wavenumbers

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