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Infrared Spectrum of Crystalline Iron Pentacarbonyl

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The infrared crystal spectrum of iron pentacarbonyl was studied from 4000 to 400 cm^{-1} at the temperature of liquid nitrogen. Crystalline deposits were obtained by vapor condensation at 200°K. Raman-active A_1' and E'' vibrations and the totally inactive A_2' mode (ν_5) were observed in the solid-phase spectrum by "site symmetry" activation. New assignment of the vibrational spectrum is proposed.

Introduction

The vibrational spectrum of iron pentacarbonyl has been widely studied,[1-15] but extensive data on the crystal spectrum are yet not available. Two normal-coordinate analyses were published almost at the same time. The first one[2] was carried out assuming a tetragonal-pyramidal molecular geometry (C_{4v} symmetry); the second one,[10] on the basis of a trigonal-bipyramidal model (D_{3h} symmetry), shows a better agreement of experimental frequencies with those calculated from a Urey–Bradley force field. The Raman spectrum was reported by King and Lippincott[8] and, in greater detail, by Stammreich, *et al.*[7] The latter workers have confirmed that the Raman data can be better interpreted through a D_{3h} molecular symmetry, and recent electronic diffraction studies[16] showed in a definite way that the geometry of the molecule is trigonal bipyramidal.

The crystal structure analysis[17] shows that iron pentacarbonyl occupies in the lattice sites of low symmetry; this means that the infrared crystal spectrum should be very rich in bands, owing to activation of some Raman-active and -inactive vibrations, in solid state. With the aim to observe these vibrations and give by consequence a more complete vibrational description of the molecule, the present study of solid $Fe(CO)_5$ infrared spectrum was undertaken.[18,19]

Experimental Section

Infrared absorption spectra were obtained in the range 4000–400 cm^{-1} using a conventional[20] low-temperature cell with KBr windows and a Perkin-Elmer Model 521 grating spectrometer. Wave number calibration was done using water vapor and indene peaks. The reported frequency values are accurate up to ±1 cm^{-1}. Commercial iron pentacarbonyl was used, after double distillation under vacuum.

It was found that the character of the spectrum was sensitive to the temperature at which vapor was condensed on the cold KBr surface. Spectra of the deposits obtained directly condensing the vapor at 100°K resembled those of liquid samples; this means that such deposits were microcrystalline or glassy in nature. On the other hand, when the deposits were obtained condensing the vapor slowly and at 190–200°K, their spectra were found to have many new bands; in the 700–400-cm^{-1} region, some of these bands appear also split into two components.[21,22] Deposits of the second type showed their spectra unchanged when the temperature was subsequently lowered to 100°K; this fact indicated that no phase transition occurred in the 200–100°K temperature range.

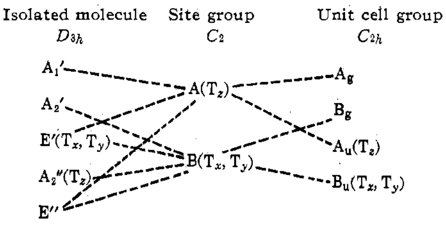
The annealing procedure was attempted but it did not give good results owing to the high vapor pressure of the solid above 200°K.

The crystals of iron pentacarbonyl are monoclinic, with four molecules in the unit cell; its symmetry is $C_{2/c}(C_{2h}^6)$. The site symmetry of the single molecule is C_2.[17]

From Table I, which correlates the symmetry of the free molecule (D_{3h}) with the site symmetry (C_2) and the unit cell symmetry (C_{2h}), one can see that all molecular vibrations become infrared active in the solid state. The A_1', A_2', and A_2'' vibrations remain single; those of E' and E'' species are split into two components (A + B). No other correlation splitting can be observed under the factor group operations, being one of the two components always "gerade" and therefore inactive in the ir crystal spectrum.

TABLE I

CORRELATION TABLE FOR VIBRATIONS OF SOLID $Fe(CO)_5$



Results and Discussion

Figure 1 shows the infrared absorption spectrum of liquid iron pentacarbonyl from 4000 to 400 cm^{-1}. In Figure 2 the crystal spectrum at 100°K of a thick deposit of $Fe(CO)_5$ is reported (solid line). For comparison, in the same figure, the gas-phase spectrum (dotted line) is reported too. Figure 3 gives the C–O stretching and Fe–C–O bending absorption pattern of a thin deposit of crystalline iron pentacarbonyl.

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(1) R. K. Sheline and K. S. Pitzer, *J. Amer. Chem. Soc.*, **72**, 1107 (1950).

(2) M. F. O'Dwyer, *J. Mol. Spectrosc.*, **2**, 144 (1958).

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(4) W. F. Edgell, C. C. Helm, and R. E. Anacreon, *ibid.*, **38**, 2039 (1963).

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(6) C. W. F. T. Pistorius and P. C. Haarhoff, *ibid.*, **31**, 1439 (1959).

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(8) F. T. King and E. R. Lippincott, *J. Amer. Chem. Soc.*, **78**, 4192 (1956); *J. Opt. Soc. Amer.*, **46**, 661 (1956).

(9) W. G. Fateley and E. R. Lippincott, *Spectrochim. Acta*, **10**, 8 (1957).

(10) H. Murata and K. Kawai, *J. Chem. Phys.*, **28**, 516 (1958).

(11) W. F. Edgell, W. E. Wilson, and R. Summitt, *Spectrochim. Acta*, **19**, 863 (1963).

(12) L. H. Jones and R. S. McDowell, *ibid.*, **20**, 248 (1964).

(13) K. R. Loos, *J. Chem. Phys.*, **40**, 3741 (1964).

(14) W. F. Edgell and M. P. Dunkle, *J. Phys. Chem.*, **68**, 452 (1964).

(15) G. Bor, *Inorg. Chim. Acta*, **3**, 191 (1969).

(16) B. Beagley, D. W. J. Cruickshank, P. M. Pinder, A. G. Robbiette, and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, **25**, 737 (1969).

(17) J. Donohue and A. Caron, *ibid.*, **17**, 663 (1964).

(18) After this paper was sent for publication, interesting results appeared in the literature by Bigorgne.[19] Our interpretation of the iron pentacarbonyl crystal spectrum agrees with Bigorgne's Raman laser data, except for the assignment of few frequencies.

(19) M. Bigorgne, *J. Organometal. Chem.*, **24**, 211 (1970).

(20) E. L. Wagner and D. F. Hornig, *J. Chem. Phys.*, **18**, 296 (1950).

(21) It may be mentioned that 200°K is also the temperature at which the crystal structure of iron pentacarbonyl was investigated[22] and that at this temperature the crystalline material is well ordered and reasonably in the state of single crystals.

(22) A. W. Hanson, *Acta Crystallogr.*, **15**, 930 (1962).

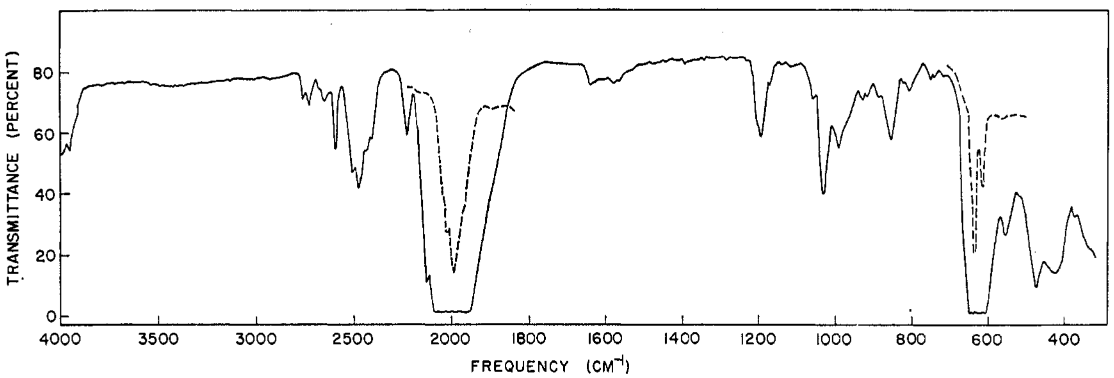

Figure 1.—Ir liquid spectra of $Fe(CO)_5$: solid line, spectrum in 0.5-mm KBr cell; dotted line, spectrum in 0.025-mm KBr cell.

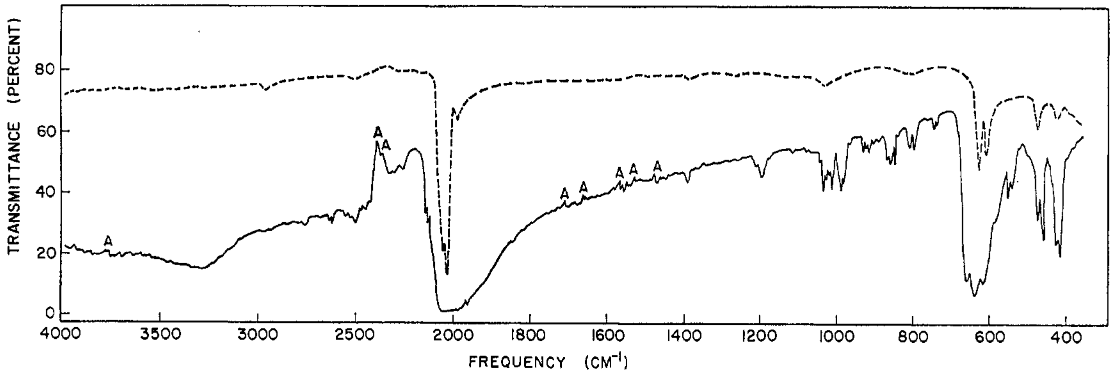

Figure 2.—Ir spectra of $Fe(CO)_5$: solid line, crystal spectrum of a thick deposit; A labels, poorly compensated atmospheric background; dotted line, vapor-phase spectrum at low pressure.

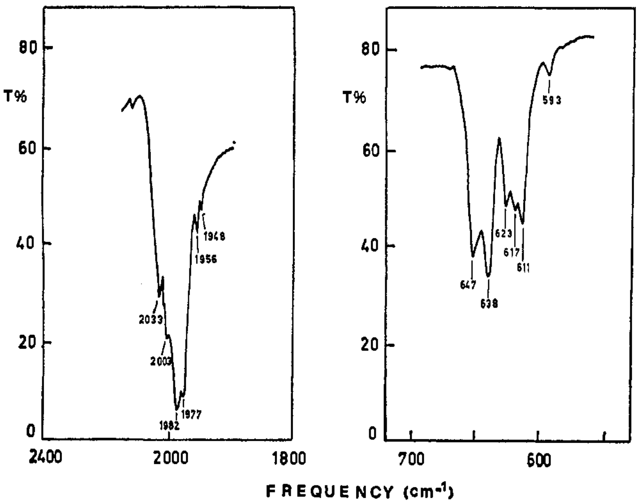

Figure 3.—Details of the $Fe(CO)_5$ crystal spectrum (thin deposit): left, C–O stretching region observed with a Beckman IR 9 spectrometer; right, Fe–C–O bending region observed with double abscissal expansion.

The frequencies observed for the solid samples and the corresponding assignments are given in Table II, together with the values for gas, liquid, and solution spectra.

(a) **Fundamental Vibrations in the C–O Stretching Region.**—All four C–O stretching modes are infrared active in the crystalline state. Frequencies at 2115, 2033, and 2003, cm^{-1} and the doublet at 1982, 1977 cm^{-1} have been assigned to the modes ν_1, ν_2, ν_6, ν_{10}, respectively. This follows from a comparison with the Raman spectrum of liquid $Fe(CO)_5$[7,19] and with Bor's data[15] for the axial and equatorial $Fe(^{12}CO)_4(^{13}CO)$ species. The Raman line at 2114 cm^{-1} is strongly polarized and the same seems to be true for the shift at 2031 cm^{-1};[23] therefore these correspond to the ν_1 and ν_2 modes belonging to A_1' species of the free molecule. The doublet at 1982, 1977 cm^{-1} corresponds to the depolarized Raman line at 1989 cm^{-1} [19] and refers to the ν_{10} mode of the E′ species in the free state; therefore in the crystal spectrum it is split into two parts. The absorption at 2003 cm^{-1}, absent in the Raman effect,[7,19] is assigned to the ν_6 mode of the A_2'' species. Such an assignment which modifies that earlier reported by Edgell, *et al.*,[11] is similar to that proposed by Jones and McDowell[12] for the liquid $Fe(CO)_5$ infrared spectrum.

The isotopic C–O stretching vibration ($\nu(^{13}C\text{–}O)$) is observed as a doublet at 1948, 1956 cm^{-1} in the crystal spectrum. Intermolecular perturbation due to the solid phase may be responsible for the doublet appearance of the mode.

(b) **Fundamental Vibrations in the Range 700–400 Cm^{-1}.**—In this region, assignment of the ν_5 mode (δ(Fe–C–O)$_{eq}$ belonging to the A_2' species) is of particular interest. Such a vibration is inactive in the infrared as well as in the Raman spectrum for the free molecule but becomes active in the infrared crystal spectrum owing to symmetry lowering. We have assigned the weak band arising at 593 cm^{-1} to this Fe–C–O equatorial bending mode, but it is also possible that the Raman shift at 377 cm^{-1} [7] be responsible for the ν_5 mode. The totally inactive vibration may appear in

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[23] This second line was reported as unpolarized in ref 7; later, in a personal communication from Stammreich to Jones and McDowell,[12] it was shown that also this Raman line is probably polarized.

TABLE II

OBSERVED INFRARED ABSORPTION FREQUENCIES FOR $Fe(CO)_5$ IN DIFFERENT PHASES FROM 4000 TO 400 CM^{-1}

			ν(vapor)		ν(liquid)		ν(soln) (CCl$_4$)
ν(solid)	Intens	Assignment	*a*	*b*	*a*	*b*	*a*
2732	vw	$\nu_1 + \nu_7$	2735 $\nu_1 + \nu_7$	2737 $\nu_1 + \nu_7$	2730	2728	2720
2602	vw	$\nu_{10} + \nu_7$					
2596	w	$\nu_1 + \nu_{13}$	2590 $\nu_1 + \nu_{13}$	2593 $\nu_1 + \nu_8$	2592	2590	2582
2498	vw	$\nu_2 + \nu_{13}$	2498 $\nu_2 + \nu_{13}$	2508 $\nu_6 + \nu_{17}$	2492	2492	2498
2468	w	$\nu_2 + \nu_4$	2474 $\nu_2 + \nu_4$	2477 $\nu_{10} + \nu_{13}$	2464	2462	2460
2442	vw	$\nu_6 + \nu_4$	2448 $\nu_{10} + \nu_4$	2448 $\nu_3 + \nu_{16}$			
2418	vw	$\nu_6 + \nu_3$	2425 $\nu_{10} + \nu_3$	2424 $\nu_3 + \nu_6$	2429	2425	2432
2230	vw	$\nu_1 + \nu_{14}$	2218 $\nu_1 + \nu_{14}$	2223 $\nu_1 + \nu_{14}$	2223	2224	2216
2119	vw	$\nu_6 + \nu_{14}$	2125 $\nu_{10} + \nu_{14}$	2124 $\nu_{10} + \nu_{14}$			
2115	w	ν_1					
2105	vw	$\nu_2 + \nu_{15}$	2110 $\nu_2 + \nu_{15}$	2110 $\nu_6 + \nu_{18}$	2108	2110	2100
2081	vw	$\nu_{10} + \nu_{18}$	2086 $\nu_{10} + \nu_{15}$	2087 $\nu_2 + \nu_{14}$	2091	2088	
2033	s	ν_2			2038		
2017	sh	ν_{10} + L[c]			2016		
2003	m	ν_6	2034 ν_6	2034 ν_{10}			2020
1982	vs	ν_{10a}	2012 ν_{10}	2006 ν_6	1984		1995
1977	vs	ν_{10b}			1960		
1956	m	$\nu(^{13}C-O)$	1975 $\nu(^{13}C-O)$	1976 $\nu(^{13}C-O)$		1935	1959
1948	m						
1257	vw	$2\nu_7$					
1203	vw	$\nu_{17} + \nu_5$					
1192	w	$\nu_{11} + \nu_{12}$	1192 $\nu_{11} + \nu_{12}$	1194 $\nu_{13} + \nu_{16}$	1193	1190	1185
1167	vw	$\nu_{17} + \nu_{12}$					
1113	vw	$2\nu_{12}$			1111	1115	
1073	vw	$\nu_5 + \nu_{13}$					
1041	sh	$\nu_{12} + \nu_{16}$			1053	1049	1043
1032	m	$\nu_7 + \nu_3$					
1025	sh	$\nu_{17a} + \nu_3$	1020 $\nu_{17} + \nu_3$	1019 $\nu_4 + \nu_{11}$	1017	1020	1014
1012	m	$\nu_{17b} + \nu_3$					
987	m	$\nu_{12} + \nu_4$	992 $\nu_{12} + \nu_4$	990 $\nu_4 + \nu_7$	992	990	986
981	sh	$2\nu_{16}$					
					933	932	
921	w	$\nu_{16} + \nu_4$			918	918	
903	vw	$\nu_8 + \nu_{13}$	912 $\nu_8 + \nu_{13}$	906 $\nu_{13} + \nu_{17}$			
893	vw	$\nu_8 + \nu_3$			885	884	
853	w	$2\nu_8$			854	853	846
849	w	$\nu_4 + \nu_3$	845 $\nu_4 + \nu_3$	847 $\nu_4 + \nu_8$			
843	sh	$\nu_8 + \nu_3$					
814	sh	$2\nu_3$	796 $2\nu_3$				
811	w	ν_{11a} + L		803 $\nu_4 + \nu_{13}$	805	799	
801	w	ν_{11b} + L					
748	w	$\nu_{11a} + \nu_{18}$	741 $\nu_{11} + \nu_{18}$	743 $\nu_{11} + \nu_{14}$	755	753	
742	w	$\nu_{11b} + \nu_{18}$					
659	vw	$\nu_{12} + \nu_{18}$					
647	m	ν_{11a}	644 ν_{11}	646 ν_{11}	637	638	642
638	s	ν_{11b}					
623	m	ν_7	622 ν_7	620 ν_7	618	615	620
617	m	ν_{17a}					
611	s	ν_{17b}					
593	w	ν_5					
560	m	ν_{12a}	571 $\nu_{13} + \nu_{18}$	569 $\nu_8 + \nu_{18}$	560	552	554
555	w	ν_{12b}	546 ν_{12}	544 ν_{12}			
487	m	ν_{16}					
480	s	ν_{13}	477 ν_{13}	474 ν_8	480	474	476
440	m	ν_4		431 ν_{13}	434	430	430
433	s	ν_8	430 ν_8				
410	w	ν_3					

[a] Present work. [b] W. F. Edgell, W. E. Wilson, and R. Summitt, *Spectrochim. Acta*, **19**, 863 (1963). [c] L stands for lattice modes.

fact weakly in the Raman spectrum of the liquid phase owing to intermolecular interactions, and its first overtone at 755 cm^{-1} [19] may appear strongly polarized in the Raman spectrum, being of A_1' species. Similar vibrations in metal hexacarbonyls[24] and in $Ni(CO)_4$[25] have been assigned in the range 340–370 cm^{-1}.

Among the other Fe–C–O deformations, the ν_{16} and ν_{17} modes also become active in the solid infrared spectrum. Both should have corresponding lines in the Raman spectrum and should be split in the crystalline state. Attribution of the ν_{16} mode to the band at 487 cm^{-1} in the solid phase is straightforward by comparison with Raman[7,19] and infrared spectra of liquid $Fe(CO)_5$, but no assignment can be made for the ν_{17} mode from Raman data. However we have assigned the ν_{17} vibration to the absorption observed around 614 cm^{-1} in the solid spectrum, because the doublet structure just agrees with the E'' character of the mode.

Assignments for the ν_7, ν_{11}, and ν_{12} vibrations are in agreement with those of Edgell[11] and Bigorgne.[19] The two E' modes correspond with the Raman lines at 640

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(24) L. H. Jones, R. S. McDowell, and M. Goldblatt, *Inorg. Chem.*, **8**, 2349 (1969).

(25) L. H. Jones, R. S. McDowell, and M. Goldblatt, *J. Chem. Phys.*, **48**, 2663 (1968).

and 558 cm^{-1} and show a doublet structure in the crystal spectrum. The band at 623 cm^{-1} is assigned as the ν_7 mode (belonging to A_2'' species in D_{3h} symmetry), as it does not have a corresponding Raman shift in the free state.

Fe–C stretching modes are transformed, under the D_{3h} point group symmetry, in the same way as the C–O stretching modes. In the free state two of them (ν_8 (A_2'') and ν_{13}(E')) are infrared active whereas three (ν_{13}(E'), ν_3 and ν_4 (both of A_1' species)) are Raman active. In the crystalline state ν_3 and ν_4 become active in infrared spectra and are assigned to frequencies at 410 and 440 cm^{-1}, respectively, in correspondence with Raman lines at 418 (P) and 448 cm^{-1}.[19] The ν_8 and ν_{13} modes are assigned to frequencies at 433 and 480 cm^{-1}, being the last one relative to the Raman shift at 482 cm^{-1}.[19]

(c) **Fundamental Vibrations in the 100-Cm^{-1} Region.**—The four C–Fe–C deformation modes have been widely investigated;[3–5,8,11,13] however, no definite assignments are available for them. Reasonable interpretation of the far-infrared spectrum of gaseous iron pentacarbonyl is that of McDowell and Jones;[5] this agrees with the present one, performed on the combination mode analysis of the crystal spectrum (see Table II); such an analysis shows that the frequencies at 112, 104, and 75 cm^{-1} should correspond to these fundamentals.

The frequency at 112 cm^{-1}, observed also by Edgell[4] and by Loss[13] in the low-frequency infrared spectrum of liquid and solid $Fe(CO)_5$, is now assigned to the ν_{14} mode (E' in D_{3h} symmetry); this agrees with the occurrence of a Raman line at the same frequency in the spectrum of the liquid complex.[7] For the same reason and according to Edgell,[11] the 75-cm^{-1} frequency has been attributed to the ν_{15} mode; its corresponding Raman shift falls at 68 cm^{-1}.[7] The remaining frequency at 104 cm^{-1} is therefore the ν_{18} mode (E''), having again a corresponding Raman line in the liquid spectrum.

The analysis of the combination bands in the solid spectrum does not indicate any frequency corresponding to the ν_9 mode. This A_2'' vibration cannot have correspondence in the Raman effect; it might be assigned to the band reported by Danti and Cotton[3] in the infrared spectrum of liquid iron pentacarbonyl at 93 ± 3 cm^{-1}. McDowell and Jones[5] observed in the infrared spectrum of vapor an absorption at 104 cm^{-1}; because of the phase change in the two spectra, we think that the frequency observed by McDowell and Jones at 104 cm^{-1} should not correspond to the coincident Raman line reported in ref 7; it might be better assigned to the ν_9 mode, falling around 90 cm^{-1} in the liquid spectrum and shifted to higher frequencies in the vapor spectrum.

Table III gives the proposed reassignment of all the fundamental vibrations of iron pentacarbonyl. Such an assignment, which follows from crystal spectrum study, is compared with that already performed by Edgell, *et al.*,[11] and by Bigorgne.[19]

TABLE III

FUNDAMENTAL FREQUENCIES OF $Fe(CO)_5$

Present work (solid ir spectrum)			Ref 11 (vapor ir spectrum)	Ref 19 (liquid Raman spectrum)
Symmetry	Numbering	Freq, cm^{-1}	Freq, cm^{-1}	Freq, cm^{-1}
A_1'	ν_1	2115	2117	2116
	ν_2	2033	1984	2030
	ν_3	410	414	418
	ν_4	440	377	381
A_2'	ν_5	593	. . .	379
A_2''	ν_6	2003	2014	2022
	ν_7	623	620	615
	ν_8	433	474	430
	ν_0	(93)[a]	. . .	72
E'	ν_{10}	1980[b]	2034	2000
	ν_{11}	643[b]	646	642
	ν_{12}	558[b]	544	553
	ν_{13}	480	431	475
	ν_{14}	(112)	104	114
	ν_{15}	(75)	68	64
E''	ν_{16}	487	752	488
	ν_{17}	614[b]	492	448
	ν_{18}	(104)	95	130

[a] In parentheses are given frequencies not measured, whose values have been taken from the literature. [b] Average between the doublet frequencies.

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