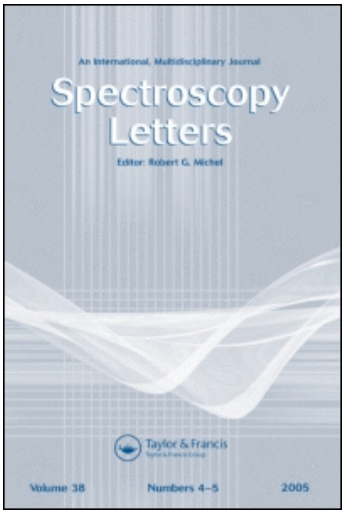

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Infrared Spectra and Vibrational Features of Acetophenones in the Range 700-50 cm^{-1}

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INFRARED SPECTRA AND VIBRATIONAL FEATURES OF ACETOPHENONES IN THE RANGE 700-50 cm^{-1}

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Although various structural properties can be determined by investigating the far-infrared, the lack of systematic results for most classes of organic molecules seems to hinder a number of workers from undertaking studies in this region. As a part of an extensive investigation in this field (1), we report here the data and our interpretation for a group of acetophenones.

The spectra, from 700 to 400 cm^{-1}, were recorded on Perkin-Elmer 225 and 180 Spectrophotometers, and from 400 to 50 cm^{-1} on a vacuum operating Hitachi-Perkin Elmer F.I.S. 3 spectrophotometer (for further details see (2,3)). Most of the compounds were commercially available; a few were synthesized by conventional methods. All were purified by vacuum distillation and/or vacuum sublimation. Sample purity was checked spectroscopically.

The first studies by Garrigou-Lagrange et al. (4), and Lebas (5) were limited to the molecule of acetophenone. Later, Mross and Zundel (6) presented results also for its d_5- and d_8- derivatives.

The far-infrared data of the acetophenones investigated are presented in tables 1 and 2: the wavenumbers are for 0.4M solutions in CCl_4. For a better understanding, the vibrational absorptions were divided into two categories: a) those somewhat related to the motions of the benzene ring and b) those internal of the substituent groups. It should be noted that the interpretation made here shows a rather consistent pattern throughout the series of compounds.

a) Ring vibrations: These vibrations comprise in-plane and out-of-plane skeletal and X-sensitive modes. Their assignment was mostly made with reference to the spectra of simpler disubstituted benzene derivatives, for some of which quantitative results are now available (7-10). The assigned frequencies are given in table 1 where the Wilson's numbering convention was used (10).

Three out-of-plane skeletal modes (4, 16a and 16b) which are not sensitive to the mass of the substituents and two X-sensitive modes (γ_{C-X} and γ_{C-Y}; X = -Cl,-Br,$-CH_3$,$-OCH_3$,$-SCH_3$; Y = $-COCH_3$) were observed and identified in the spectral range investigated.

The assignment of the in-plane vibrations (radial skeletal modes 1, 12, 6a, 6b, and X-sensitive modes ν_{C-X}, β_{C-X}, β_{C-Y}) however does not appear so straightforward, since as result of strong coupling effects no simple pattern can be predicted. For several compounds the actual values of the motions labelled 1, 12, and ν_{C-X} were not reported since they are located above 700 cm^{-1}. For the same reason the column related to the ν_{C-Y} stretching mode was omitted. The two X-sensitive bending vibrations, i.e. β_{C-X} and β_{C-Y}, were observed in the range 320-140 cm^{-1}. It may be noticed that only one of these (i.e. β_{C-Y}) shifts when the carbonyl group is H-bonded (see below). Therefore it seems that in acetophenones the β_{C-Y} vibration predominantly involves the in-plane bending mode of the $-COCH_3$ group while

TABLE 1

Ring and X-sensitive Vibrations for Substituted Acetophenones in the Range 700-50 cm^{-1}

	in-plane vibrations								out-of-plane vibrations				
X=	1	12	6a	6b	ν_{C-X}	β_{C-X}	β_{C-Y}		4	16a	16b	γ_{C-Y}	γ_{C-Y}
H	§	§	§	617m			221s,b	(228)	688s	415w	458w,b		150w,b
4·Cl-	§	524s	621m	628sh	316m	305m	181s	(192)		442w	465m	254m	100m
4·Br-	§	496m†	607s	627m	248m	287s	162s	(170)		421m	453m	230w	98m
4·CH_3S-	§	525m	618s	631w	296m	234m,b†	154m	(164)		440w	468m	234m,b†	98m,b†
4·CH_3-	671s	568s	353s†	638m	§	320w	197s	(210)	691m		460m,b	266m	128sh
4·CH_3O-	674w	563s	336m†	632m	§	290m	177s	(190)		437w	458w	278m,b†	138m,b
3·Cl-	673s	§	416m†	§		315s	166s	(176)	683s	416m†	467m,b		150sh
3·Br-	660s	§	384m	§	306m	286s	142s	(152)	682s	415w	457m,b	190w	155sh
3·CH_3S-	672s	§		§	314m	245m,b	144m	(153)	686s	418w	462sh	162sh	154sh
3·CH_3-	§	§	380w,b	522m	§	310w,b	193m	(200)	690s	412w	463m,b	220m	150w
3·CH_3O-	698s	§	398w	514m	§	270w,b	165s	(174)	689s		461w	220w,b	150sh
2·Cl-	§	§	669m	437m		293m	201m	(208)		395w	465m	220w	128m
2·Br-	§	§	653s	394s	297m	264w,b	184m	(192)	690w		452m	222w	125w
2·CH_3S-	§	§	667m		318m	258m,b	188s	(198)	680w		460w	210w	114sh
2·CH_3-	§	§	560w	386m	§	265w,b	226s,b†			405w	457m	226s,b†	132w
2·CH_3O-	§	§	532m	388w	§	260sh	204w				458w	225w	142m,b

§ values out of the range investigated † frequency used again

TABLE 2

Internal Vibrations of the $-COCH_3$, $-SCH_3$, $-OCH_3$ Groups and few other Spectral Features Related to Substituted Acetophenones in the Range 700-50 cm^{-1}

X=	β_{CO}		β_{CCC}	β_{COC} β_{CSC}	γ_{CO}	τ_{OCH_3} τ_{SCH_3}		ν_σ	
H-	587s		368m		505w		75m,b	125w	
4·Cl-	586s						85m,b	120m,b	
4·Br-	586s				496m[§]		80m,b	121m,b	
4·CH_3S-	588s		364m	260w,b	517m	98m,b[§]	80m,b	124m	
4·CH_3-	588s		353s[§]		520w		75m,b	126m,b	
4·CH_3O-	589s	577s[ϕ]	336m[§]	278m,b[§]	500m	100w	80w,b	125w,b	148m[†]
3·Cl-	596s	587s	366m		490sh		75m,b	116m,b	
3·Br-	594s	586s	374sh		485w		75m,b	119w,b	
3·CH_3S-	596s	587s	342w	264w,b	475w,b	100sh	75m,b	119w	
3·CH_3-	599s	587s	350m		485sh		75m,b	123m,b	
3·CH_3O-	588s	564s	363m	285m,b	505sh	114m,b	85m,b	120m,b	146w[†]
2·Cl-	593s	533w	361m		490w		70m,b	116w,b	
2·Br-	592s	531w	368m,b				70m,b		
2·CH_3S-	597s	545w,b	352m	278m,b	480m	100m,b	70m,b	124m	
2·CH_3-	602s				485w,b		65m,b	124m,b	
2·CH_3O-	595s		349m	283m,b	512sh	120m,b	80m,b	127m,b	150m[†]

[§] frequency used again [†] see ref. (2) [ϕ] see text

the expected coupling with the β_{C-X} mode (10) is probably only feeble.

b) Internal vibrations of polyatomic substituent groups: The wavenumbers of the vibrations arising from the $-COCH_3$ group as well as from other polyatomic groups ($-OCH_3$, $-SCH_3$) and lying below 700 cm^{-1} are listed in table 2. Since no vibrational mode of the benzene nucleus was left unidentified (see above) there is no doubt in assigning to the $-COCH_3$ group three bands at about 580, 490, and 360 cm^{-1} which were observed throughout the compounds investigated. By taking as reference the spectrum of acetone (bands near 530, 490 and 390 cm^{-1}), such absorptions should be related to two in-plane (β_{CO}, β_{CCC}) and one out-of-plane (γ_{CO}) bending modes. However although the molecule of acetone has been investigated in some details, only the assignment of the band at 530 cm^{-1} (β_{CO}) seems out of doubt, while for the bands at 490 and 390 cm^{-1} no conclusive interpretation was reached yet (uncertainty in the countours of the i.r. vapor phase bands, and conflicting results on the depolarization degree of the Raman line at 490 cm^{-1} (11-14). It may be recalled that in acetone only the β_{CCC} mode is expected to be polarized. On the other hand, Raman results (6) for the unsubstituted acetophenone assume the line at 580 cm^{-1} to be depolarized and the line at 360 cm^{-1} polarized (no Raman line was reported around 490 cm^{-1}). On the basis of such features the band at 580 cm^{-1}, which should correspond to the absorption at 530 cm^{-1} in acetone, can be described as the β_{CO} mode and the band at 360 cm^{-1} as the β_{CCC} mode. It follows that the absorption observed in infrared at 490 cm^{-1} would be associated to the γ_{CO} vibration.

Some complexity in the spectra of 3-substituted acetophenones was also noticed. First, it was observed a medium weak absorption near 600 cm^{-1} which could not be identified. Second, the band at about 580 cm^{-1} (β_{CO}) consistently appeared in these compounds as a doublet (see table 2). Doubt remains concerning the interpretation of this fact since no further absor-

ption is expected in this range and besides, attempts to relate it to a Fermi resonance were not successful. Also the presence of two conformers having slightly different spectral features could not be proved at this stage of work: in fact the carbonyl stretching band at about 1700 cm^{-1} was found to be a singlet, and on the other side the 2-substituted acetophenones, for some of which the existence of a conformational equilibrium was established (15),do not show a similar trend unless to consider a weak band near 530 cm^{-1}.

To assign the bands related to the methoxy- and thiomethoxy- groups, the vibrational results for anisoles (16) and thioanisoles (17) were used as reference. Vibrations which can be approximately described as in--plane bending modes (β_{COC}, β_{CSC}) and torsions around the O-Ø and S-Ø bond were observed respectively in the range 260-285 cm^{-1} and 98-120 cm^{-1}. The strong band at 577 cm^{-1} in the spectrum of 4·CH_3O- acetophenone does not appear to have any counterpart in the other derivatives and remains unassigned.

Finally the medium broad band at about 75 cm^{-1} seems not to be characteristic of acetophenones since it has been already found in the solution spectra of several series of organic compounds (2).

Following previous investigations performed in this laboratory (1-3), the spectra of ternary systems (i.e. phenol (0.5M), X-Ø$COCH_3$(0.4M), CCl_4) were also examined in order to test the spectral behaviour of the H-bonded complexes as well as to establish the relative sensitivity of the hydrogen bonding stretching vibration (ν_σ) to the effects of the ring substituents. No major modifications in the spectra of the complexes were observed; only the band related to the β_{COCH_3} bending mode (see above) moved toward higher frequencies (the observed wavenumbers, which refer to 1:1 complexes with phenol, are reported between brackets in table 1). The ν_σ

values of the complexes with phenol (see table 2) although scarcely sensitive to the substituent parameter, linearly correlate with those. Relations of this type were already observed by us in other series of compounds (2, 18).

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