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Infrared studies of acetophenone and its deuterated derivatives

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Abstract—The i.r. spectra of acetophenone and their deuterated analogues ($-d_3, -d_5, -d_8$) in the liquid-phase have been recorded and analyzed in the range 4000–130 cm^{-1}. Additional data on band contours in the gas-phase, in conjunction with the deuteration effects, allowed us to assign all the fundamentals for the four isotopic varieties. A valence force field calculation was also used to support the proposed assignment.

INTRODUCTION

In the course of a previous investigation on substituted acetophenones in the far-i.r. region [1], the need for a consistent and reliable assignment of all the fundamentals of the parent molecule ($C_6H_5COCH_3$) clearly emerged.

As shown by a literature survey, a vibrational assignment on acetophenone has been reported in the past [2, 3]. Results of an investigation also comprising the benzene-ring deuterated and the fully deuterated molecules were presented more recently by Mross and Zundel [4]; in 1977 some assignments of the latter authors were discussed and partly changed by Green and Harrison [5] on the basis of a different approach.

The major problem in the analysis arises from a number of normal vibrations which cannot be reasonably assigned to simple motions according to the group frequency viewpoint. Within such a context, we report in this paper the results of a comprehensive study on acetophenone ($-d_0$) and its deuterated analogues ($-d_3, -d_5$ and $-d_8$). As an aid in the assignment, we have also included the gas-phase band contours, and a normal coordinate treatment.

EXPERIMENTAL

Acetophenone $-d_0$ of commercial origin was used without further purification. Its deuterated derivatives were prepared via the Friedel–Crafts method using the appropriate isotopic varieties of benzene and acetyl chloride. The deuterium content of C_6D_6 and CD_3COCl exceeded 99%. The compounds obtained were distilled under reduced pressure and their purity was checked spectroscopically.

The i.r. spectra (4000–130 cm^{-1}) were recorded on a Perkin–Elmer 180 spectrophotometer equipped with a far-i.r. attachment. The calibration was effected using selected gas lines as standards; the wavenumbers of the sharp bands are believed to be accurate within ±0.5 cm^{-1}. Spectra of liquid samples in the range 4000–450 cm^{-1} were obtained by using a KBr cell (pathlength 0.025 mm) while for the far-i.r. measurements a polyethylene cell (pathlength 0.25 mm) was employed. Because of the low vapor pressure of these compounds at room temperature, the gas-phase spectra were recorded using a 20-m variable pathlength cell fitted with KBr lenses as windows.

RESULTS AND DISCUSSION

The liquid-phase spectra of the compounds investigated are shown in Fig. 1, while the wavenumbers and the relative intensities of the observed bands (along with the type of gas-phase band contour, when available) are listed in Table 1.

Acetophenone and its deuterated analogues are planar molecules with a single plane of symmetry (C_s point group); two of the hydrogen atoms of the methyl group are located symmetrically above and below the plane, while the third hydrogen is placed in the plane itself. Theoretical group considerations divide the 45 fundamentals into 30 of species A' (in-plane vibrations) and 15 of species A'' (out-of-plane vibrations), all i.r.-active. In the gas-phase the A' modes give rise to hybrid AB-type bands, while the A'' vibrations produce band contours of C-type.

A complete listing of the observed fundamentals together with the corresponding assignments for the four compounds investigated is given in Table 2. The Mulliken notation [6] with the numbering of the fundamentals in order of decreasing wavenumbers for the A' followed by the A'' modes is used for acetophenone $-d_0$. For simplicity the same numbering is applied to the corresponding vibrations of the deuterated species. In addition, for the benzene-ring modes the Wilson nomenclature with reference to the Varsànyi schemes [7] is also reported.

NORMAL COORDINATE CALCULATION

The normal coordinate tratement was performed by using the Wilson's GF matrix method. The calculations were carried out on a CDC CY 76 Computer System by using a modified version of Schachtschneider's program [8]. The G matrix was formulated on the basis of the geometry of benzene and acetaldehyde; in the evaluation of the **s** vectors of Wilson–Decius, the Hilderbrandt's method to normalize the torsion coordinates [9, 10] was employed. The molecular geometry and the internal coordinates are depicted in Fig. 2. The following structural parameters were used in the calculations: (i) *bond length*: $C_{Ar}—C_{Ar} = 1.39$ Å,

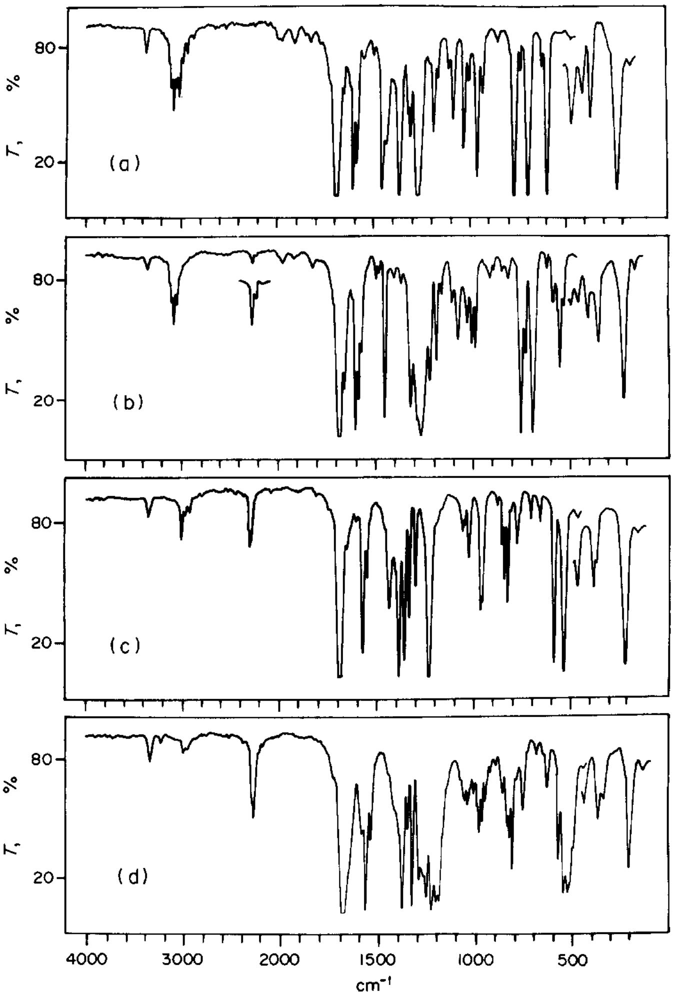

Fig. 1. The i.r. spectra (4000–130 cm^{-1}) of (*a*) acetophenone-d_0, (*b*) acetophenone-d_3, (*c*) acetophenone-d_5 and (*d*) acetophenone-d_8 in the liquid-phase.

C_{Ar}—C_{Al} = C_{Al}—C_{Al} = 1.515 Å; C═O = 1.215 Å, C_{Ar}—H = 1.08 Å, C_{Al}—H = 1.09 Å; (ii) *angles*; all 120°, except those of the —CH_3 group for which a tetrahedral geometry was taken; (iii) *atomic masses*: see Ref. [11].

The force field was assumed to be of the valence type. An initial set of force constants was transferred from benzene [12], toluene [13], and acetaldehyde [14]; some off-diagonal constants were also introduced to account for the interactions between the acethyl-group and the phenyl-ring. Arbitrary values of force constants were taken to give the —CH_3 and the —$COCH_3$ torsional modes at low frequencies. In the refinement procedure (carried out in terms of internal force constants) the calculated frequencies were fitted to the observed ones for all the four isotopic species simultaneously. Firstly, only the diagonal force constants were adjusted and then the other significant off-diagonal terms were processed. The refinement treatment, however, was found to be hampered by the existence of some highly correlated force constants. The average error between observed and calculated frequencies was 12.8 cm^{-1} (1.6%) from a total of 172 experimental frequencies. Further attempts to improve the force field were not successful since the solutions began to diverge from the given set of the observed values.

The final set of the force constants is reported in Table 3, while the calculated frequencies of the fundamentals as well as the most significant elements of potential energy distribution (PED) among the diagonal force constants are given in Table 4.

ASSIGNMENTS OF THE FUNDAMENTALS

The present assignment, mainly based on experimental features (spectral position, isotopic shift, and gas-phase profile of the observed bands), also accounted for the results from the normal coordinate treatment. Since on the basis of the potential energy distribution a number of fundamentals cannot be reasonably assigned to either the acetyl-group or ring localized mode, the only division

Table 1. Wavenumbers (cm^{-1}) of the observed bands for acetophenone $-d_0$, $-d_3$, $-d_5$ and $-d_8$ in liquid phase[a]

$-d_0$		$-d_3$		$-d_5$		$-d_8$	
3352 w	1303 m	3346 w	1181 m	3350 w	1160 vw	3346 w	1046 m
3103 sh	1265 vs (AB)	3100 w,sh	1160 w	3006 m	1100 vw	3235 vw	1040 w,sh
3088 sh	1203 vw	3086 m,sh	1107 w	2969 w	1050 w	3000 w	1033 w,sh
3067 m (AB)	1181 m (AB)	3065 m	1074 m	2924 w	1041 w	2940 w	1017 w
3061 sh	1160 w	3060 sh	1037 w,b	2297 sh	1018 m	2296 m,sh	995 w,sh
3040 mw (AB)	1103 w	3038 m	1026 m	2292 m	959 m	2291 m	987 m
3030 mw (AB)	1078 m	3031 m	1010 sh	2277 m	953 m,b (AB)	2278 m	974 m
3007 mw	1046 vw	2255 w	1002 m	2273 sh	868 w	2268 m,sh	958 mw
2971 mw (C)	1025 s (AB)	2220 vw	997 sh	2267 sh	843 m	2257 w	951 w,sh
2925 w	1021 sh	2176 vw	983 m	1808 vw	832 ms	2221 vw	932 vw
2863 vw	1000 vw	2140 vw	976 w,sh	1742 w	818 ms	2188 vw	905 vw
1992 w	980 vw	2121 vw	924 vw	1684 vs (AB)	796 w,sh	2113 vw	868 mw
1970 w	974 sh	2000 w,b	909 w,b	1645 w	770 mw	1735 w,sh	848 w,sh
1905 w	955 s (AB)	1940 w,b	890 w	1626 w	760 sh	1683 vs (AB)	842 m
1850 w	926 m (C)	1850 w	846 w	1597 vw	697 w	1652 m,sh	831 m
1815 w	848 w,b	1683 vs (AB)	829 sh	1567 s (AB)	662 w	1628 w	818 s
1768 sh	761 vs (C)	1652 m,sh	814 w	1544 m	652 w	1587 m	796 w,sh
1685 vs (AB)	730 w (AB)	1617 w	749 vs (C)	1455 w,sh	580 s (AB)	1566 s	762 m
1647 w	691 vs (C)	1598 s (AB)	728 m	1430 ms	530 vs (C)	1543 m	739 vw
1612 sh	618 w	1587 sh	690 vs (C)	1382 s	495 w (C)	1454 w	696 w
1599 s (AB)	590 vs (AB)	1581 ms	617 w	1353 s	460 m	1427 m	662 w
1582 ms	547 vw	1567 m,sh	584 m (AB)	1328 ms	378 m	1398 m,sh	638 m
1543 w	520 vw	1492 w	558 w	1295 m	364 m,sh	1378 s	591 w,sh
1492 w	467 m	1480 vw	548 s (AB)	1260 w,sh	217 vs	1354 mw	578 s (AB)
1450 s	413 m	1450 s (AB)	530 m (C)	1230 vs (AB)	155 w	1330 s	548 vs
1430 m,b	368 m	1400 w,b	490 w	1187 w		1296 ms	528 vs
1360 s (AB)	226 vs	1360 w	452 w			1278 m,sh	522 sh
1312 w	160 w	1318 s	406 m			1258 ms	516 m,sh
		1313 m,sh	350 m			1230 vs	502 m,sh
		1286 m	220 s			1208 ms	450 m
		1267 vs (AB)	162 w			1192 ms	378 m
		1221 m				1175 m,sh	352 m,sh
						1089 w	213 s
						1068 m	152 w
						1061 m	

[a] Available band contours in the gas-phase are reported between brackets.

effected in the description of the normal modes concerns with the in-plane and out-of-plane vibrations.

(a) *In-plane vibrations*

The adequate resolution achieved here allowed us to establish the spectral position of the five aromatic and the two aliphatic C—H stretches (ν_1–ν_7). Although upon deuteration the frequency range becomes smaller, only in $-d_8$ two modes (ν_3 and ν_4) could not be separated. On the other side the corresponding gas-phase absorptions interfere among themselves and therefore the expected AB hybrid band contours do not exhibit very clear features: a representative spectrum of $-d_0$ is reproduced in Fig. 3 as an example (the characteristic C-type profile of the out-of-plane ν_{31} at about 2971 cm^{-1} will be discussed in the next section).

The location of ν_8 (C═O stretching) at about 1685 cm^{-1} is straightforward. According to the PED, this motion also involves some C—C ring stretching and C_{Ar}—C—C bending. A mixing of the C═O stretch with other coordinates was already found for example in benzaldehyde [15], and aliphatic ketones and aldehydes [14].

The identification of all the five C—C ring stretching (ν_9–ν_{12}, ν_{15}) and of four C—H ring bending modes (ν_{16}, ν_{18},–ν_{20}) is satisfactorily established for all the molecules examined: the AB-type band contour of the more prominent absorptions in the gas-phase and the calculated frequencies add evidence to the assignment. Following the gas-phase AB-type profile of the absorption at 1025 cm^{-1} in $-d_0$ (see Fig. 4), the lowest C—H ring bending (ν_{21}) was placed at about 1025 cm^{-1} in the hydrogenated benzene ring compounds. Upon deuteration of the benzene ring, this absorption shifts towards 765 cm^{-1}. Although a considerable discrepancy between observed and calculated values in $-d_0$ and $-d_3$ exists, no alternative assignment appears reasonable for these two species.

The asymmetric and symmetric methyl deformations are labelled ν_{13} and ν_{14} respectively. The former mode was unambiguously determined in all

Table 2. Observed fundamental wavenumbers (cm^{-1}) for acetophenone $-d_0$, $-d_3$, $-d_5$ and $-d_8$

Assignment[a]		$-d_0$	$-d_3$	$-d_5$	$-d_8$
A' species					
ν_1	νC-H	3088	3086	2297	2296
ν_2	νC-H	3067	3065	2292	2291
ν_3	νC-H	3061	3060	2277	2278[b]
ν_4	νC-H	3040	3038	2273	2278[b]
ν_5	νC-H	3030	3031	2267	2268
ν_6	νCH_3	3007	2255	3006	2257
ν_7	νCH_3	2925	2121	2924	2113
ν_8	νC=O	1685	1683	1684	1683
ν_9	(8a)	1599	1598	1567	1566
ν_{10}	(8b)	1582	1581	1544	1543
ν_{11}	(19a)	1492	1492	1382	1378
ν_{12}	(19b)	1450	1450	1328	1330
ν_{13}	$\delta_{as}CH_3$	1430[b]	1037[b]	1430[b]	1040
ν_{14}	$\delta_{s}CH_3$	1360	983[b]	1353	987
ν_{15}	(14)	1312	1313	1295	1296
ν_{16}	(3)	1303	1318	1041	1046
ν_{17}	(13)X-sens.	1265	1267	1230	1230
ν_{18}	(9a)	1181	1181	868	868
ν_{19}	(15)	1160	1160	843	842
ν_{20}	(18b)	1078	1074[b]	832	831
ν_{21}	(18a)	1025	1026	770	762[b]
ν_{22}	ρCH_3	1021	814	1018	818[b]
ν_{23}	(12)ring	1000	1002	959	958
ν_{24}	(see text)	955	1074[b]	953	1068
ν_{25}	(1)X-sens.	730	728	697[b]	696[b]
ν_{26}	(6b)	618	617	580[b]	591
ν_{27}	δC=O	590	584	580[b]	578
ν_{28}	(6a)X-sens.	547	548	530[b]	548
ν_{29}	δC_{Ar}-C-C	368	350	364	352
ν_{30}	(9b)X-sens.	226	220	217	213
A" species					
ν_{31}	νCH_3	2971	2220	2969	2221
ν_{32}	$\delta_{as}CH_3$	1430[b]	1037[b]	1430[b]	1033
ν_{33}	ρCH_3	1046	829	1050	848
ν_{34}	(5)	980	983[b]	818	818[b]
ν_{35}	(17a)	974	976	796	796
ν_{36}	(17b)	926	924	760	762[b]
ν_{37}	(10a)	848	846	697[b]	696[b]
ν_{38}	(11)	761	749	652	638
ν_{39}	(4)	691	690	530[b]	528
ν_{40}	(16b)X-sens.	520	530	495	516
ν_{41}	γC=O	467	452	460	450
ν_{42}	(16a)	413	406	378	378
ν_{43}	(10b)X-sens.	160	162	155	152
ν_{44}	torsion-CH_3	--	--	--	--
ν_{45}	torsion-$COCH_3$	--	--	--	--

[a] The numbering scheme in the first column is according to MULLIKEN [6], while the notation between brackets of the second column refers to the WILSON's nomenclature for benzene [7].

[b] Frequency taken twice.

the isotopic varieties, while the latter one was clearly identified in $-d_0$ and $-d_5$, but only tentatively assigned in the methyl deuterated derivatives.

The strong absorption at about 1265 cm^{-1} in $-d_0$ and $-d_3(\nu_{17})$, which exhibits a clear AB-type band contour in the gas-phase, shifts of about 35 cm^{-1} towards lower wavenumbers upon ring deuteration. Its assignment to the X-sensitive benzene mode (13) appears straightforward.

The bands at about 1020 ($-d_0$, $-d_5$) and 815 cm^{-1} ($-d_3$, $-d_8$) were connected with the fundamental ν_{22}, well described (PED) as a —CH_3 rocking mode.

The identification of the strong band at 955 cm^{-1}

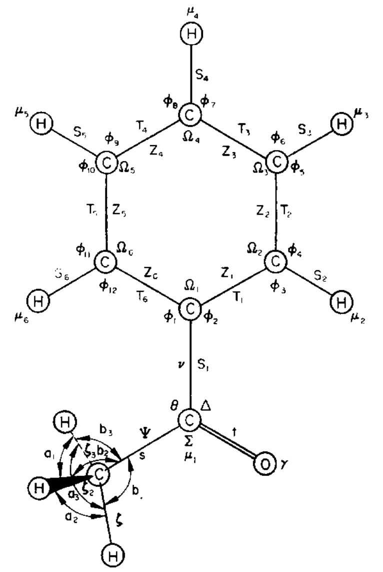

Fig. 2. Molecular geometry and internal coordinates of acetophenone.

in $-d_0$ appears puzzling. It exhibits a clear AB-type band contour in the gas-phase (see Fig. 4) and it is strong enough to warrant consideration as a fundamental. The following sequence 955, 953, 1074, 1068 cm^{-1} ($-d_0$, $-d_5$, $-d_3$, $-d_8$) with increasing in the wavenumbers for the methyl deuterated species could pertain to this vibration labelled ν_{24}. According to the PED elements this is a mixed mode also comprising the aliphatic C—C stretching and the —CH_3 rocking with different relative contribution in the hydrogenated and in the deuterated compounds. Because of the C—C stretching force constant being somewhat involved, besides here only in the X-sensitive ring modes ν_{17} and ν_{25}, quite probably an aliphatic C—C stretching vibration according to the classical picture cannot be well defined in acetophenones.

The fundamental ν_{25}, X-sensitive benzene mode (1), was associated with the sequence 730, 728, 697 and 696 cm^{-1} ($-d_0$, $-d_3$, $-d_5$, $-d_8$). These frequencies, which show a small isotopic shift upon ring

Table 3. Valence force constants of acetophenone

$K(T)$[a]	(1)[b]	7.094[c]	$F(\Phi_{3-12})^{m}$	0.001
$K(S_1)$	(2)	4.800	$F(\Phi_{3-12})^{p}$	0.006
$K(S_{2-6})$	(3)	5.028	$F(\Phi_{3-12}\Omega)^{o}$	-0.066
$K(t)$	(4)	8.700	$F'(\Phi_{3-12}\Omega)^{o}$	0.099
$K(s)$	(5)	4.300	$F(\Omega)^{o}$	-0.097
$K(r)$	(6)	4.790	$f(\mu_{2-6})^{o}$	0.026
$H(\Omega)$	(7)	0.866	$f(\mu_{2-6})^{m}$	-0.026
$H(\Phi_{1,2})$	(8)	1.005	$f(\mu_{2-6})^{p}$	-0.005
$H(\Phi_{3-12})$	(9)	0.511	$f(\mu Z)^{o}$	-0.039
$H(\theta)$	(10)	2.226	$f(\mu Z)^{m}$	-0.001
$H(\Delta,\Sigma)$	(11)	1.086	$f(ZZ)^{o}$	-0.021
$H(a)$	(12)	0.510	$F(s,S_1)$	-0.424
$H(b)$	(13)	0.640	$F(T_{1-6}S_1)$	0.806
$H(Z_{2-5})$	(14)	0.347	$F(T_6 s)$	-0.774
$H(\mu_1)$	(15)	0.610	$F(T_1 t)$	-0.512
$H(\mu_{2-6})$	(16)	0.305	$F(rr)$	0.090
$H(\gamma)$	(17)	0.410	$F(bb)$	-0.044
$H(\nu)$	(18)	0.010[d]	$F(S_1 t)$	0.639
$H(\psi)$	(19)	0.010[d]	$F(st)$	0.692
$H(Z_{1,6})$	(20)	0.410	$F(sb)$	0.167
$F(T)^{o}$		0.878	$F(S_1\Omega)$	0.035
$F(T)^{m}$		-0.718	$F(S_1\theta)$	0.386
$F(T)^{p}$		0.300	$F(S_1\Sigma)$	-0.080
$F(T\Phi_{3-12})^{o}$		0.071	$F(t\theta)$	-0.080
$F'(T\Phi_{3-12})^{o}$		0.034	$F(t\Delta)$	0.213
$F(T\Phi_{3-12})^{m}$		0.180	$F(s\Delta)$	-0.080
$F(T\Phi_{3-12})^{p}$		-0.076	$F(s\theta)$	0.608
$F(T\Omega)$		0.498	$f(Z_1 Z_6)$	0.105
$F(TS_{2-6})$		-0.024	$f(\mu_1 Z_1)$	-0.055
$F(\Omega S_{2-6})$		0.139	$f(\mu_1\gamma)$	0.190
$F(S_{2-6})^{o}$		0.046	$F(\Phi_1\theta)$	0.006
$F(\Phi_{3-12})^{o}$		-0.015	$F(S_1\Phi_{1,2})$	0.500

[a] For the definition of the force constants see Fig. 2 and Ref. [12].

[b] The numbering of the diagonal force constants refers to that used for PED in Table 4.

[c] Stretch constants are in units of mdyn/Å; stretch–bend, mdyn/rad; bend and torsion mdyn Å/$(rad)^2$.

[d] Arbitrary values (see text).

Table 4. Calculated fundamental wavenumbers (cm^{-1}) and potential energy distribution[a] for acetophenone $-d_0, -d_3, -d_5, -d_8$

	$-d_0$		$-d_3$		$-d_5$		$-d_8$	
Designation	ν	PED	ν	PED	ν	PED	ν	PED
A' species								
ν_1	3073	97(3)	3074	97(3)	2290	93(3)	2290	93(3)
ν_2	3065	97(3)	3067	97(3)	2290	92(3)	2290	92(3)
ν_3	3054	98(3)	3057	98(3)	2283	93(3)	2283	93(3)
ν_4	3041	99(3)	3043	99(3)	2273	94(3)	2273	94(3)
ν_5	3039	99(3)	3039	99(3)	2269	94(3)	2269	94(3)
ν_6	2977	101(6)	2229	99(6)	2977	101(6)	2229	98(6)
ν_7	2938	96(6)	2118	95(6)	2938	96(6)	2118	95(6)
ν_8	1721	46(1),26(4),13(10)	1717	48(1),25(4),12(10)	1704	40(1),30(4),14(10)	1700	42(1),29(4),13(10)
ν_9	1601	87(1),25(9)	1601	87(1),25(9)	1570	93(1),13(9)	1569	94(1),13(9)
ν_{10}	1585	69(1),37(9)	1584	69(1),37(9)	1516	66(1),29(4),10(9)	1511	69(1),30(4),10(9)
ν_{11}	1501	44(1),31(4),24(9)	1494	45(1),34(4),27(9)	1416	56(1),37(12)	1417	96(1),16(4),15(9)
ν_{12}	1417	28(1),40(9),25(12)	1418	39(1),54(9)	1322	39(1),14(9),14(12),17(13)	1333	51(1),13(2),20(9)
ν_{13}	1433	13(1),14(9),65(12)	1032	92(12)	1437	36(1),56(12)	1031	89(12)
ν_{14}	1353	13(5),15(9),38(12),48(13)	987	40(1),14(9),14(12),20(13)	1356	26(1),14(5),30(12),37(13)	959	65(1),10(13)
ν_{15}	1369	43(1),71(9)	1369	43(1),72(9)	1284	68(1),27(2),26(9)	1284	68(1),27(2),26(9)
ν_{16}	1317	74(9)	1321	83(9)	1063	14(7),50(9)	1044	65(9),15(12),12(13)
ν_{17}	1261	14(1),44(2),15(5),10(7)	1268	16(1),39(2),26(5)	1225	35(1),17(2),16(5),15(9)	1233	38(1),13(2),25(5),15(9)
ν_{18}	1205	15(1),71(9)	1206	15(1),71(9)	872	74(9)	871	74(9)
ν_{19}	1143	36(1),43(9)	1144	35(1),41(9)	850	11(1),72(9)	850	11(1),72(9)
ν_{20}	1093	40(1),26(9)	1057	34(1),18(9),13(12),16(13)	831	15(1),70(9)	831	15(1),69(9)
ν_{21}	963	108(1),42(9)	966	110(1),42(9)	753	67(1),75(9)	750	70(1),74(9)
ν_{22}	1044	11(1),24(7),15(9),28(13)	812	59(13)	1027	33(9),41(13)	811	54(13)
ν_{23}	1015	77(1)	1018	43(1),29(7)	961	25(1),28(7),19(9)	968	33(7),25(9)
ν_{24}	991	19(1),11(5),14(7),31(13)	1112	27(1),19(5),20(9),14(13)	972	47(1),19(5),13(13)	1083	19(5),12(7),16(9),25(13)
ν_{25}	732	17(2),26(5),32(7),12(9)	716	12(2),18(5),39(7),14(9)	704	15(2),25(5),24(7),20(9)	686	11(2),16(5),35(7),23(9)
ν_{26}	622	42(7),17(9),14(10),16(11)	621	66(7),27(9)	595	62(7),31(9)	593	62(7),30(9)
ν_{27}	625	38(7),15(9),29(11)	566	13(5),35(11),17(13)	618	19(7),43(11)	563	11(5),12(7),33(11),17(13)
ν_{28}	539	18(1),27(10),19(11),14(8)	511	15(8),25(10),16(11),17(1)	522	19(1),11(8),27(10),18(11)	496	18(1),13(8),25(10),16(11)
ν_{29}	363	20(2),20(7),24(11)	351	18(2),17(7),25(11)	357	19(2),20(7),23(11)	345	18(2),18(7),24(11)
ν_{30}	208	69(8),15(10)	199	66(8),17(10)	199	70(8),13(10)	191	67(8),16(10)
A" species								
ν_{31}	2974	101(6)	2218	100(6)	2974	101(6)	2218	100(6)
ν_{32}	1429	90(12)	1026	94(12)	1429	90(12)	1026	94(12)
ν_{33}	1049	80(13)	836	69(13),12(16),15(17)	1049	81(13)	840	74(13),16(17)
ν_{34}	992	31(14),80(16),11(20)	993	31(14),80(16),11(20)	805	10(14),47(15),59(16)	804	10(14),47(15),59(16)
ν_{35}	963	42(14),77(16)	963	42(14),78(16)	798	18(14),95(16)	798	18(14),94(16)
ν_{36}	915	18(14),69(16)	915	19(14),69(16)	756	131(16)	755	130(16)
ν_{37}	861	32(14),105(16)	864	28(14),94(16)	712	14(14),66(16),13(20)	712	14(14),66(16),13(20)
ν_{38}	778	41(15),66(16)	778	40(15),66(16)	648	34(14),16(15),55(16)	646	35(14),14(15),56(16)
ν_{39}	691	17(14),12(15),51(16),28(20)	691	17(14),13(15),51(16),27(20)	530	44(14),44(16),25(20)	529	42(14),48(16),24(20)
ν_{40}	541	26(14),41(15),19(16),29(17)	536	30(14),38(15),22(16),13(17)	453	32(14),11(15),20(16),13(17)	478	17(14),31(15),24(16),50(17)
ν_{41}	485	78(17)	456	10(13),80(17)	498	21(15),19(16),87(17)	442	20(14),11(16),43(17),11(20)
ν_{42}	420	53(14),22(16),13(20)	420	52(14),21(16),13(20)	367	68(14),10(16),16(20)	367	68(14),10(16),16(20)
ν_{43}	168	19(15),97(20)	167	19(15),96(20)	156	11(14),18(15),100(20)	155	11(14),18(15),100(20)
ν_{44}	74	99(19)	53	99(19)	74	99(19)	53	99(19)
ν_{45}	23	100(18)	22	99(18)	23	100(18)	21	99(18)

[a] The numbers between brackets in the PED definitions refer to the diagonal force constants of Table 3.

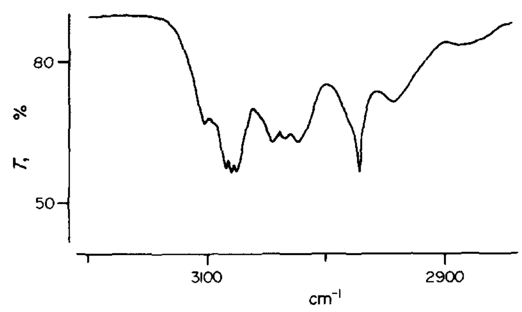

Fig. 3. The gas-phase i.r. spectrum of acetophenone-d_0 in the 3200–2900 cm^{-1} region: path length 1575 cm, equilibrium vapor pressure at 298 K.

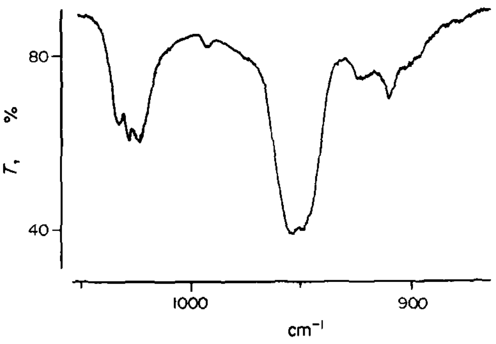

Fig. 4. The gas-phase i.r. spectrum of acetophenone-d_0 in the 1050–850 cm^{-1} region: path length 1575 cm, equilibrium vapor pressure at 298 K.

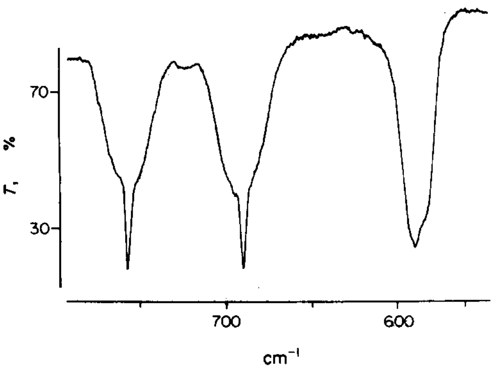

Fig. 5. The gas-phase i.r. spectrum of acetophenone-d_0 in the 800–550 cm^{-1} region: path length 1125 cm, equilibrium vapor pressure at 298 K.

deuteration, satisfyingly agree with the calculated values. The present assignment, in agreement with Ref. [4], differs from the interpretation given by GREEN and HARRISON [5] who related this mode (r in their notation) to the absorptions at 589, 530 and 513 cm^{-1} ($-d_0$, $-d_5$, $-d_8$). Such an assignment, however, seems rather questionable since their proposed values are somewhat below the usual frequency range for this vibration [7], and in addition the strong band in $-d_5$ exhibits a characteristic C-type profile in the gas-phase (Fig. 7).

The strong absorption at 590 cm^{-1} in acetophenone $-d_0(\nu_{27})$ shows a clear AB-type band contour in the gas-phase (Fig. 5) and therefore it cannot be attributed to the γ_{CO} bending as given in Ref. [4]. According to a previous investigation [1] and the present results of Table 4, this band was described as the in-plane C═O bending mode (incidentally, our assignment of ν_{25} and ν_{27} is interchanged in Ref. [5]). In all the deuterated derivatives the δ_{CO} mode was located at about 580 cm^{-1}: representative gas-phase spectra of $-d_3$ and $-d_5$ are depicted in Figs. 6 and 7 respectively. It may be however noted (PED) that this mode also contains a considerable ring participation; on the other side other vibrations receive an appreciable contribution from the δ_{CO} coordinate.

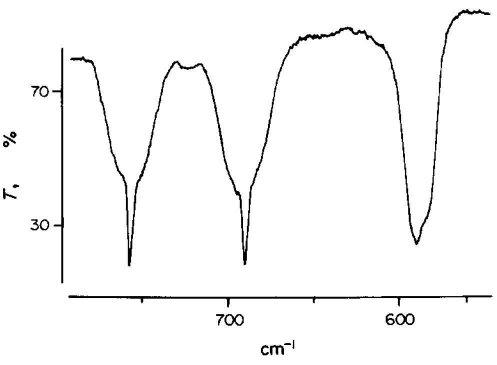

Fig. 6. The gas-phase i.r. spectrum of acetophenone-d_3 in the 800–500 cm^{-1} region: path length 1575 cm, equilibrium vapor pressure at 298 K.

The bands at 547 and 368 cm^{-1} in $-d_0$ (ν_{28} and ν_{29}) as well as the related sequences in the deuterated analogues (Table 2) were ascribed to the X-sensitive benzene ring (6a) and to the C_{Ar}—C—C bending respectively. Although, according to the PED elements, the absorption at higher wavenumbers might have to be assigned to the C_{Ar}—C—C bending (roughly approximate description) an interchange of the assignments seems more preferable. This is suggested by the frequency range of the (6a) mode given by VARSÁNYI [7] and by the results on a group of benzophenones [16]. It should also be mentioned that ν_{28} in $-d_5$ was located at 530 cm^{-1}, where the strong out-of-plane ν_{39} also occurs: the C-type band contour in the gas-phase arising from the A'' mode probably masks the expected AB-type profile of ν_{28}.

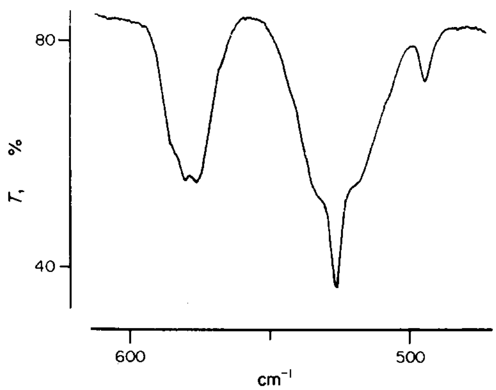

Fig. 7. The gas-phase i.r. spectrum of acetophenone-d_5 in the 600–500 cm^{-1} region: path length 1575 cm, equilibrium vapor pressure at 298 K.

The band at about 220 cm^{-1} designated as ν_{30} was related to the X-sensitive benzene ring (9b). This mode mainly appears in acetophenones as a C—X bending vibration coupled with the internal bending motion of the aliphatic chain.

(b) *Out-of-plane vibrations*

The absorption at about 2970 cm^{-1} in $-d_0$ and $-d_5$ was ascribed to the —CH_3 stretching ν_{31}; the C-type band contour in the gas-phase spectrum of $-d_0$ is clearly recognized by the medium and sharp Q-branch (Fig. 3). Upon deuteration of the methyl group this vibration shifts towards 2220 cm^{-1}. It also seems relevant to note that the calculated frequencies strongly support the experimental assignment in all the isotopic varieties.

ν_{32} and ν_{33} are described as asymmetric deformation and rocking displacement of the —CH_3 group respectively. The former mode, associated with the absorptions at about 1430 ($-d_0$, $-d_5$) and 1035 cm^{-1} ($-d_3$, $-d_8$) remains almost unresolved from the asymmetric —CH_3 in-plane deformation ν_{13}; only a small splitting of 7 cm^{-1} in the liquid-phase spectrum of $-d_8$ was observed. The location of ν_{33} was mainly based on the results of the normal coordinate treatment.

The absorptions arising from the five out-of-plane C—H bending modes (ν_{34}–ν_{38}) show very variable intensity; only for the strong features at 761 and 749 cm^{-1} ($-d_0$, $-d_3$) a distinct C-type band contour in the gas-phase spectra could be observed (Figs. 5 and 6).

The strong bands at 691, 690, 530 and 528 cm^{-1} ($-d_0$, $-d_3$, $-d_5$, and $-d_8$) were related to the vibration (4) designated as ν_{39}. The clear C-type band profiles in the gas-phase spectra of $-d_0$, $-d_3$, and $-d_5$ (Figs. 5–7) also substantiate this assignment. Unfortunately an interference involving several bands did not permit the observation of any definite band contour in $-d_8$. The present assignment agrees with that of MROSS and ZUNDEL [4], while it differs from the interpretation given by GREEN and HARRISON [5], who related this vibration to a shoulder at 690 cm^{-1} in $-d_0$ and to a strong band at 579 cm^{-1} in $-d_5$. The latter absorption, however, exhibits a definite AB hybrid band contour (see Fig. 7) and therefore it cannot be assigned to an out-of-plane vibration.

The absorptions at 520 and 467 cm^{-1} in $-d_0$ (labelled ν_{40} and ν_{41}) and the corresponding sequences in the deuterated derivatives (Table 2) were related to the X-sensitive ring deformation (16b) and to the out-of-plane C═O bending (γ_{CO}) respectively. Although the frequency value of the former mode is a little higher than the usual range [7], such an assignment was preferred by us since the PED elements clearly indicate a predominant contribution of the γ_{CO} force constant to the absorption at 467 cm^{-1}. A more adequate force field could probably make this assignment unquestionable.

The observed and calculated frequency values of ν_{42} and ν_{43} (ring deformation (16a) and X-sensitive vibration (10b) respectively) fall into a satisfying pattern. Within the range investigated no feature related to the torsional frequency of either —CH_3 or —$COCH_3$ groups could be found; therefore the lowest two vibrations ν_{44} and ν_{45} remain unidentified.

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REFERENCES

[1] S. GHERSETTI, S. GIORGIANNI, A. PASSERINI and G. SPUNTA, *Spectr.* Lett. **8,** 391 (1975).

[2] C. GARRIGOU-LAGRANGE, N. CLAVERIE, J. M. LEBAS and M. L. JOSIEN, *J. Chim. Phys.* **58,** 559 (1961).

[3] J. M. LEBAS, *J. Chim. Phys.* **59,** 1072 (1962).

[4] W. D. MROSS and G. ZUNDEL, *Spectrochim. Acta* **26A,** 1097 (1970).

[5] J. H. S. GREEN and D. J. HARRISON, *Spectrochim. Acta* **33A,** 583 (1977).

[6] R. S. MULLIKEN, *J. Chem. Phys.* **23,** 1997 (1955).

[7] G. VARSÀNYI, *Vibrational spectra of Benzene Derivatives.* Academic Press, New York (1969).

[8] J. H. SCHACHTSCHNEIDER and R. G. SNYDER, *Spectrochim. Acta* **19,** 117 (1963).

[9] R. L. HILDERBRANDT, *J. Mol. Spectr.* **44,** 599 (1972).

[10] I. H. WILLIAMS, *J. Mol. Spectr.* **66,** 288 (1977).

[11] *Handbook of Chemistry and Physics,* 56th edition. CRC Press, Cleveland, Ohio (1975).

[12] P. C. PAINTER and J. L. KOENIG, *Spectrochim. Acta* **33A,** 1019 (1977).

[13] C. LA LAU and R. G. SNYDER, *Spectrochim. Acta* **27A,** 2073 (1971).

[14] P. COSSEE and J. H. SCHACHTSCHNEIDER, *J. Chem. Phys.* **44,** 97 (1966).

[15] R. ZWARICH, J. SMOLAREK and L. GOODMAN, *J. Mol. Spectr.* **38,** 336 (1971).

[16] S. GIORGIANNI, A. PASSERINI, A. GAMBI, S. GHERSETTI and G. SPUNTA, *Spectr, Lett.* **13**(1980) (in press).