Infrared and Raman Spectra of Chloral, and Normal Coordinate Analyses of Acetaldehyde, Fluoral, Chloral, and Bromal

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Force fields for acetaldehyde, fluoral, chloral, and bromal have been calculated from observed vibrational frequencies. The force fields have been used to calculate mean amplitudes of vibration. Thermodynamic functions have also been calculated from the observed frequencies. The Raman spectrum of chloral has been recorded, as well as infrared spectra in the region $4000-25$ cm^{-1}. The normal coordinate calculations and the interpretations of the spectra have been carried out by assuming C_s symmetry for all the studied molecules.

The infrared and Raman spectra of acetaldehyde and some of its deuterated isotopes have been studied by several researchers, among which are Evans and Bernstein,[1] Capwell,[2] and Cosse and Schachtschneider.[3] Many earlier works are cited by these authors. Cosse and Schachtschneider [3] have also carried out a normal coordinate calculation for some isotopic acetaldehydes. The present calculated force field for acetaldehyde shows generally good agreement with Cosse and Schachtschneider's results.

The structure of acetaldehyde has been investigated by microwave spectroscopy (Kilb *et al.*[4]) and by electron diffraction (Kato *et al.*[5]). The latter workers [5] also report the observed mean amplitudes of vibration for acetaldehyde.

The infrared and Raman spectra of fluoral and its deuterated analogue have been recorded by Berney,[6] and a complete vibrational assignment has been proposed, but no normal coordinate analysis has been performed.

Lucazeau and Novak [7] have reported a careful investigation of the vibrational spectra of chloral-d_0, chloral-d_1, and bromal-d_0 in the infrared and Raman. The present polarization ratios in Raman seem to be more accurate than those of Lucazeau and Novak,[7] but the observed vibrational frequencies are in excellent agreement, and together with the normal coordinate analysis they strongly support the assignments made by Lucazeau and Novak.[7]

The vibrational spectra of chloral-d_0 with assignments are reported in the present paper. Force constant calculations for acetaldehyde, fluoral, chloral, and bromal with some of their deuterated isotopes have been carried out, and the calculated thermodynamic functions and the mean amplitudes of vibration are given.

EXPERIMENTAL

The sample of chloral from Fluka was purified by fractionated distillation in a Vigreux column and finally distilled in vacuum.

The infrared spectrum of chloral was recorded in the region $5000-200$ cm^{-1} with a Perkin-Elmer model 225 spectrometer. The vapour spectrum was investigated in a 10 cm cell fitted with KRS5-windows. Liquid cells with KBr-windows were used in the high frequency region and polyethylene cells in the low frequency region.

The far-infrared spectrum in the region $150-25$ cm^{-1} was obtained using a Michelson interferometer (RIIC, model FS 520) in connection with Fourier transformations of the digitalized interferograms carried out on a GIER electronic computer. The vapour spectrum of chloral was obtained, using a 1 m multiple reflection cell with the pressure at about 5 mm Hg.

A Cary model 81 spectrometer equipped with a Spectra Physics No. 125 helium-neon laser was used for recording the Raman spectrum. The chloral liquid was filled into a capillary silica cell containing approximately 20 μl. The polarization ratios for chloral were calculated from the spectra obtained in the perpendicular excitation with the 2.5 ml multiple reflection cell from Perkin-Elmer. The polarization ratios were calibrated against the 220 and 461 cm^{-1} bands of CCl_4.

The numerical calculations connected with the normal coordinate analysis were performed on a UNIVAC 1108 digital computer.

STRUCTURE

All the molecules of the present study are supposed to possess C_s symmetry in their equilibrium configuration (cf. Fig. 1). Hence the normal vibrations are
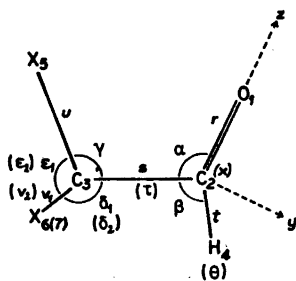
Fig. 1. Numbering of atoms and orientation of cartesian axes in the CX_3CHO molecular model. The valence coordinates used are also shown in the figure. r, s, t, u, v indicate valence stretches; α, β, γ, δ, ε, are angle deformations; θ represents the out-of-plane bending of the $O_1C_3C_2-H_4$ group; and, finally, the $C-C$ torsion coordinate is denoted by τ.

Fig. 2. Orientation of the principal axes in chloral.

divided into the species as $10a' + 5a''$. This structure has also been adopted by several other authors who have studied these molecules, although the orientation of th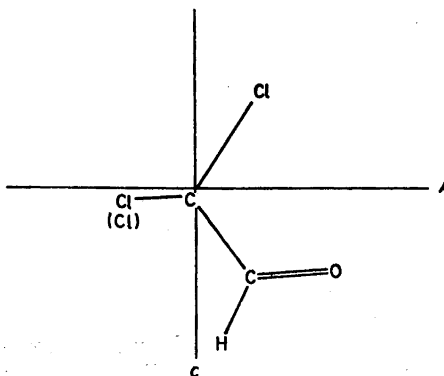e CX_3-group with respect to the CHO-group is not quite clear. The acetaldehyde molecule has been investigated by microwave spectroscopy [4] and electron diffraction,[5] and evidence has been found for the oxygen atom to be in the *cis* position to one of the H atoms in the methyl group.

For fluoral, chloral, and bromal a complete structural analysis has not been found in the literature. Chloral has been studied by means of electron diffraction by Degard,[8] but this work is rather old (1938) and does not seem to give

Table 1. Structural parameters for acetaldehyde, fluoral, chloral, and bromal (CX_3CHO).

	CH₃CHO[4]	CF₃CHO[6]	CCl₃CHO[8]	CBr₃CHO[a]
C−H (Å)	1.114	1.09	1.1[a]	1.1
C=O (Å)	1.216	1.204	1.15	1.15
C−C (Å)	1.501	1.54	1.52	1.52
C−X (Å)	1.086	1.332	1.76	1.94
CCO	123.92°	121.8°	124°[a]	124°
CCH	117.48°	118.2°	117°[a]	117°
CCX	109.5°[a]	109.5°[a]	109.5°[a]	109.5°
X₆CX₇	108.27°	108.7°	109.5°[a]	109.5°

[a] Assumed.

reliable information about the orientation of the CCl_3 group. Although Lucazeau and Novak [7] with reference to Degard's [8] work have adopted a configuration where the CCl_3 group is rotated 180° around the C−C bond, compared with the orientation shown on Fig. 1, it is in the present work preferred to use the same orientation as in acetaldehyde for all the molecules studied.

In Table 1 the structural parameters used in the present normal coordinate analysis are collected. From these data (Table 1) the following principal moments of inertia are calculated (all in amu·Å²). CH₃CHO: 8.96, 49.62, 55.46, CF₃CHO: 91.78, 168.42, 171.17; CCl₃CHO: 265.33, 303.43, 331.06; CBr₃CHO: 567.31, 586.73, 821.69. The asymmetry parameter, $\varkappa = (2B - A - C)/(A - C)$, is -0.96, -0.97, -0.27, and 0.79 for acetaldehyde, fluoral, chloral, and bromal, respectively. This shows that only acetaldehyde and fluoral are close to a prolate, symmetric top.

Fig. 2 shows the orientation of the principal axes in chloral. From this figure one can see that the totally symmetric a' vibrations should give rise to various mixtures of A and C type bands in the infrared. Vibrations antisymmetric to the molecular symmetry plane belong to the a'' species and give rise to pure B type bands. The same should be the case for bromal. In acetaldehyde and fluoral, the A and B axes lie in the molecular symmetry plane and therefore the a' vibrations will show band contours that are mixtures of A and B types, and the a'' vibrations will be pure C type bands. In the Raman spectra, the lines due to a' vibrations will be polarized, and those of the a'' vibrations depolarized.

Table 2. Infrared and Raman spectra of chloral.

Vapour Infrared cm⁻¹	I	Liquid Infrared cm⁻¹	I	Raman Δcm⁻¹	I	ϱ^b	Interpretation			
4630	w^a	4630	m				$\nu_1 + \nu_2$	= 4633	A'	
3535	m	3510	s				$2\nu_2$	= 3526	A'	
2920	vw	2920	vw				$\nu_1 + \nu_{15}$	= 2933	A''	
2860⎫ 2856⎬ 2845⎭	vs	2858	s	2860	m	0.32 P	ν_1		a'	
2800	w	2785	m				$\nu_2 + \nu_4$	= 2805	A'	
2685	w	2682	w	2690	w	0.43 P	$2\nu_3$	= 2710	A'	
2095	vw	2080	vw				$\nu_2 + \nu_8$	= 2092	A'	
2045	vw	2035	vw				$2\nu_4$	= 2056	A'	
1975	w	1965	w				$2\nu_{11}$	= 1970	A'	
1833	w	1850	w				$\nu_5 + \nu_{11}$	= 1842	A''	
1818	w	1805	w				$\nu_1 - \nu_4$	= 1828	A'	
1783⎫ 1777⎬ 1770⎭	vs	1765	vs	1763	vs	0.36 P	ν_2		a'	
1738	m	1725	m				$2\nu_5$	= 1714	A'	
1635	vw	1635	w				$\nu_3 + \nu_9$	= 1621	A'	
1520	w	1520	vw				$\nu_2 - \nu_9$	= 1511	A'	
1361⎫ 1355⎬ 1346⎭	s	1355	vs	1357	s	0.39 P	ν_3		a'	
		1265	w				$2\nu_6$	= 1252	A'	
1205	vw	1210	w				$\nu_{11} + \nu_{14}$	= 1190	A'	
1035⎫ 1028⎬ 1020⎭	vs	1025	vs	1025	s	0.79 P?	ν_4		a'	
991⎫ 985⎬ 979⎭	vs	987	vs	989	s	0.79 D?	ν_{11}		a''	
857	vs	853	vs	854	vs	0.65 P	ν_5		a'	
812	m	810	m				$\nu_{12} + \nu_{15}$	= 817	A'	
788	m						$\nu_{11} - \nu_{10}/\nu_{14}$	= 780	A'' or A'	
780	m	760	m				$\nu_5 - \nu_{15}$	= 780	A''	
740	vs	732	vs	734	vs	0.80 D	ν_{12}		a''	
668	w						$\nu_{12} - \nu_{15}$	= 663	A'	
661	w						$\nu_5 - \nu_{10}/\nu_{14}$	= 652	A' or A''	
625	vs	617	vs	619	vs	0.26 P	ν_6		a'	
444	m	442	s	446	vs	0.03 P	ν_7		a'	
315	s	315	s	319	vs	0.67 P	ν_8		a'	
266	s	268	s	270	vs	0.73 P	ν_9		a'	
		241	m	246	vs	0.80 D	ν_{13}		a''	
		200	s	205	s	0.76 P?	ν_{10} and ν_{14}		a' and a''	
83⎫ 77⎬ 71⎭	s			90	s	0.80 D	ν_{15}		a''	

^{a} s=strong, m=medium, w=weak, v=very.
^{b} ϱ=polarization ratio, $\varrho < 0.80$: polarized.
P=polarized band. D=depolarized band.

VIBRATIONAL ASSIGNMENT

The infrared spectrum of chloral in the vapour phase is shown in Fig. 3 for the region $4000-200$ cm^{-1}, and in Fig. 4 for the region $150-25$ cm^{-1}. Figs. 5 and 6 show the infrared spectrum of chloral as a liquid. The Raman spectrum of chloral is reproduced in Fig. 7, whereas the observed infrared and Raman frequencies are listed in Table 2.

The Raman spectrum of chloral has been recorded earlier by Seewan-Albert [9] in the region $2863-90$ cm^{-1} and recently by Lucazeau and Novak [7] in the same region. The locations of the various bands observed in the present study of chloral are in excellent agreement with the above cited works. The polarization ratios given in Table 2 are in good agreement with the results of
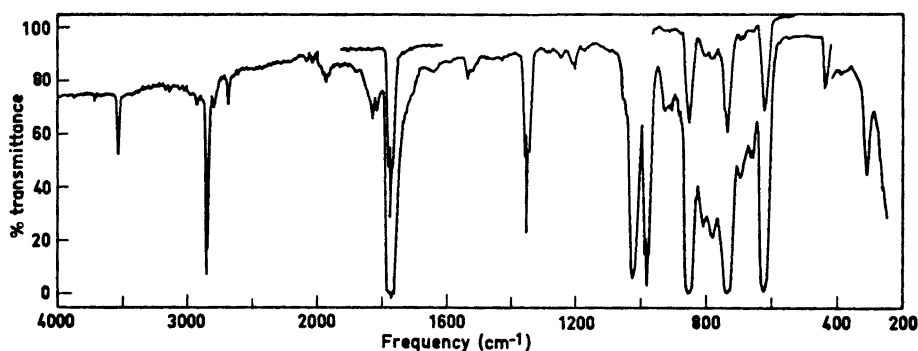
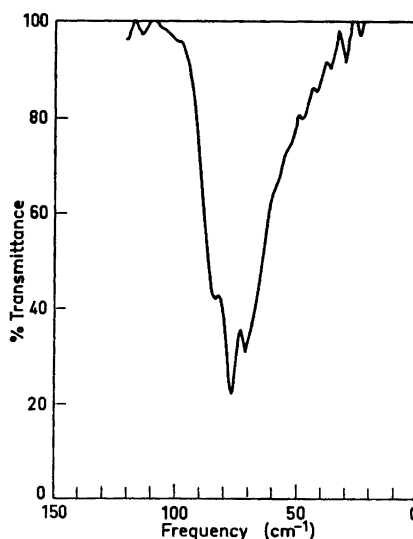*Fig. 3.* Infrared absorption spectrum of gaseous chloral; 10 cm path, 35 and 5 torr.

Fig. 4. Far-infrared absorption spectrum of gaseous chloral: 1 m path, 5 torr.

Lucazeau and Novak,[7] but are in disagreement with the work of Seewan-Albert [9] for the bands at 90, 989, and 1025 cm^{-1}. The 90 cm^{-1} band is certainly depolarized and therefore must belong to species a'' (CC-torsion). The two bands at 1025 and 989 cm^{-1} cannot be distinguished by the polarization ratios (cf. Table 2). But the vibrational spectrum of CCl$_3$CDO given by Lucazeau and Novak [7] indicates that the band at 989 cm^{-1} (870 cm^{-1} in CCl$_3$CDO) must involve mainly the CH out-of-plane bending vibration, and that the 1025 cm^{-1} (981 cm^{-1} in CCl$_3$CDO) band must be connected with the CC-stretching vibration. This assignment is also suggested by the band type contours in the infrared.
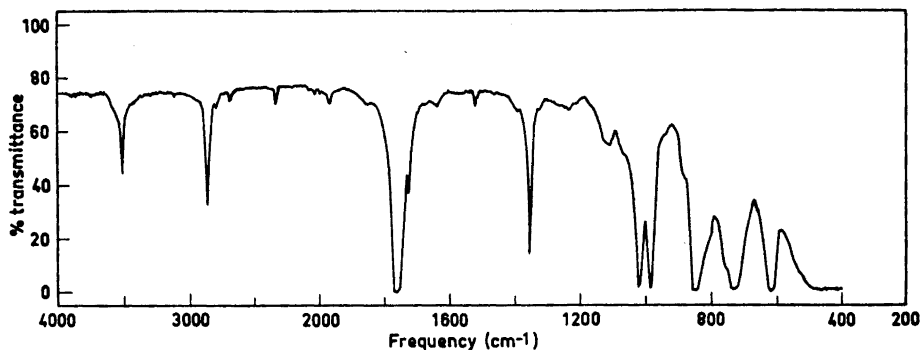
Fig. 5. Infrared absorption spectrum of liquid chloral: 0.025 mm NaCl cell.
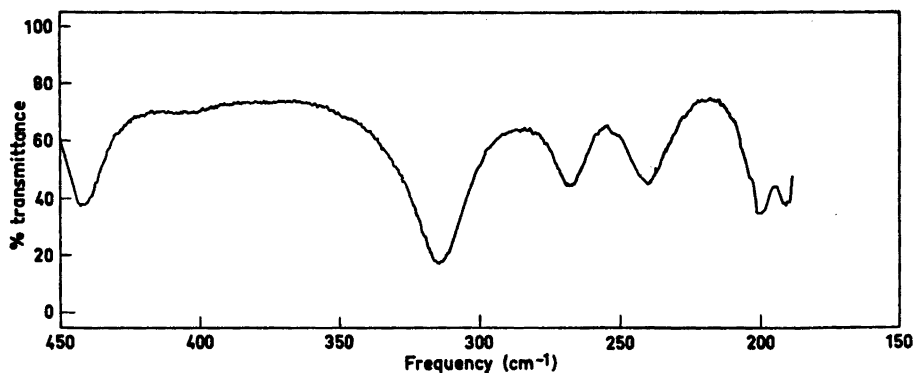
Fig. 6. Infrared absorption spectrum of liquid chloral: 0.5 mm polyethylene cell.

The infrared spectrum (cf. Table 2) of chloral is in good agreement with the investigations made by Silver and Wood [10] and by Lucazeau and Novak,[7] except that the band at 104 cm^{-1}, which Silver and Wood [10] describe as the CC-torsion, is not observed. The CC-torsion is instead supposed to be the 77 cm^{-1} band, which is also observed by Lucazeau and Novak.[7]
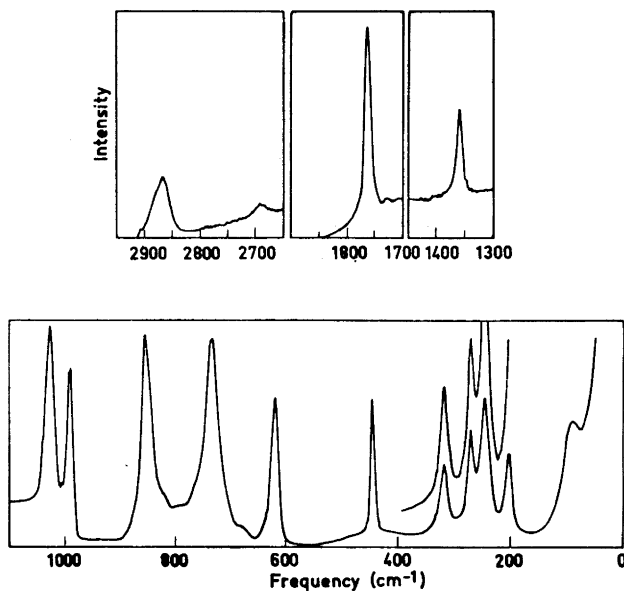
Fig. 7. The Raman spectrum of liquid chloral.

Table 3. Fundamental frequencies (in cm^{-1}) for acetaldehyde and some of its deuterated isotopes.

Species	Descrip-tion	CH$_3$CHO			CH$_3$CDO		CD$_3$CHO		CD$_3$CDO	
		Obs.[a]	Obs.[b]	Calc.	Obs.[b]	Calc.	Obs.[c]	Calc.	Obs.[d]	Calc.
a'	1 CH$_3$ str.	2964	2967	2997	2970	2997	2257	2247	2265	2250
	2 HCH$_2$ str.	2863	2917	2846	2946	2846	2115	2059	2060	2059
	3 C−H str.	2826	2840	2822	2071	2130	2812	2822	2130	2121
	4 C=O str.	1734	1743	1800	1743	1712	1753	1781	1737	1700
	5 CH$_3$ def.	1405	1441	1469	1420	1461	960	898	938	879
	6 C−H bend	1395	1390	1312	1080	1003	1393	1321	1028	963
	7 HCH$_2$ def.	1352	1352	1344	1353	1342	1038	1038	1045	1096
	8 C−C str.	1105	1122	1080	1109	1076	1131	1262	1151	1243
	9 CH$_3$ rock	912	919	854	849	840	774	656	747	648
	10 CCO bend	509	509	556	500	545	443	496	436	491
a''	11 HCH$_2$ str.	2997	3024	2992	3028	2992	2223	2228	2225	2228
	12 HCH$_2$ def.	1436	1441	1423	1420	1423	1028	1031	1028	1030
	13 C−H bend (o.p.)		882	867	896	668	676	761	867	677	763
	14 CH$_3$ rock	764	763	764	802	851	626	598	573	566
	15 Torsion	−	150	152	−	145	−	120	116	113

[a] This work. [b] Evans and Bernstein.[1] [c] Capwell.[2] [d] Cosse and Schachtschneider.[3] [e] The numbering of the frequencies refers to the CH$_3$CHO molecule.

A detailed discussion of the IR and Raman spectra of chloral will not be given here, since the present results are in excellent agreement with the observations of Lucazeau and Novak.[7] The assignments for chloral are also supported by the normal coordinate analysis (see text below). The observed fundamental frequencies for CCl_3CHO and CCl_3CDO are shown in Table 5.

Table 4. Fundamental frequencies (in cm^{-1}) for CF_3CHO and CF_3CDO.

Species		Description[a]	CF$_3$CHO		CF$_3$CDO	
			Obs.[6]	Calc.	Obs.[6]	Calc.
a'	1	C−H str.	2864	2847	2150	2154
	2	C=O str.	1788	1854	1770	1752
	3	C−H bend	1384	1406	1033	962
	4	CF$_3$ str.	1310	1303	1302	1352
	5	FCF$_2$ str.	1202	1213	1244	1292
	6	C−C str.	840	837	811	817
	7	CF$_2$ def.	706	697	693	692
	8	FCF$_2$ def.	580	591	580	577
	9	C−C=O bend	431	427	428	427
	10	CF$_3$ rock	256	250	253	249
a''	11	FCF$_2$ str.	1183	1174	1174	1160
	12	C−H bend (o.p.)	958	977	842	844
	13	FCF$_2$ def.	531	525	521	523
	14	CF$_3$ rock	322	330	318	305
	15	C−C torsion	55	55	52	51

[a] This approximate description is adopted from Ref. 6; besides, *cf.* the potential energy distribution in Table 12.

Table 5. Fundamental frequencies (in cm^{-1}) for CCl_3CHO and CCl_3CDO.

Species		Description[a]	CCl$_3$CHO			CCl$_3$CDO	
			Obs.[b]	Obs.[c]	Calc.	Obs.[b]	Calc.
a'	1	C−H str.	2856	2856	2859	2155	2143
	2	C=O str.	1778	1777	1810	1759	1739
	3	C−H bend	1355	1355	1307	1064	1095
	4	C−C str.	1030	1028	1038	987	988
	5	CCl$_3$ str.	857	857	887	849	825
	6	C−C=O bend	626	625	618	603	603
	7	ClCCl$_2$ str.	443	444	443	442	437
	8	CCl$_3$ def.	314	315	317	313	315
	9	ClCCl$_2$ def.	271	266	268	268	268
	10	CCl$_3$ rock	197	200	197	196	197
a''	11	C−H bend (o.p.)	986	985	936	870	904
	12	ClCCl$_2$ str.	740	740	767	718	685
	13	ClCCl$_2$ def.	236	241	257	230	227
	14	CCl$_3$ rock	197	200	200	196	200
	15	C−C torsion	77	77	75	70	71

[a] This approximate description is adopted from Ref. 7; besides, *cf.* the potential energy distribution in Table 13.
[b] From Ref. 7.
[c] This work.

The infrared spectrum of acetaldehyde-d_0 was also recorded but will not be reproduced here. It supports the assignments made by Evans and Bernstein [1] with some minor changes. The fundamental frequencies for CH_3CHO are given in Table 3 together with Evans and Bernstein's [1] results for CH_3CHO and CH_3CDO. Table 3 also includes the vibrational frequencies for CD_3CHO and CD_3CDO observed by Capwell [2] and by Cosse and Schachtschneider.[3]

Table 6. Fundamental frequencies (in cm⁻¹) for CBr_3CHO and CBr_3CDO.

Species	No.	Description[a]	CBr₃CHO Obs.[7]	CBr₃CHO Calc.	CBr₃CDO Calc.
a'	1	C−H str.	2839	2839	2121
	2	C=O str.	1748	1748	1703
	3	C−H bend	1351	1351	1075
	4	C−C str.	999	999	972
	5	CBr₃ str.	784	784	739
	6	C−C = O bend	547	547	534
	7	BrCBr₂ str.	322	322	318
	8	CBr₃ def.	276	276	274
	9	BrCBr₂ def.	209	209	208
	10	CBr₃ rock	151	151	151
a''	11	C−H bend (o.p.)	975	975	930
	12	BrCBr₂ str.	636	636	569
	13	BrCBr₂ def.	187	187	164
	14	CBr₃ rock	137	137	137
	15	C−C torsion	79	79	76

[a] This approximate description is adopted from Ref. 7; besides, cf. the potential energy distribution in Table 14.

The vibrational assignments for fluoral-d_0 and fluoral-d_1 are taken from Berney [6] and are reproduced in Table 4.

The infrared and Raman spectra of bromal were also recorded. These spectra strongly support the assignments made by Lucazeau and Novak,[7] but unfortunately they also show some bands which can only be explained by presence of impurities in the bromal probe, and for that reason these spectra are not reproduced here. The vibrational assignment for bromal is shown in Table 6.

NORMAL COORDINATE ANALYSIS

The valence coordinates used for construction of the following set of symmetry coordinates are indicated on Fig. 1.

Species a' $S_1 = r$ CO str.
$S_2 = s$ CC str.
$S_3 = t$ CH str.
$S_4 = u$ CX str.
$S_5 = 2^{-1/2} (v_1 + v_2)$ CX₂ str.
$S_6 = (RS)^{1/2} \alpha$ CCO bend

$$S_7 = (ST)^{1/2}\,\beta \qquad\qquad\qquad \text{CCH bend}$$
$$S_8 = (SU)^{1/2}\gamma \qquad\qquad\qquad \text{CCX bend}$$
$$S_9 = (SV/2)^{1/2}(\delta_1 + \delta_2) \qquad\quad \text{CCX}_2 \text{ bend}$$
$$S_{10} = (UV/2)^{1/2}(\varepsilon_1 + \varepsilon_2) \qquad\quad \text{XCX}_2 \text{ bend}$$

Species a''
$$S_{11} = 2^{-1/2}\,(v_1 - v_2) \qquad\qquad \text{CX}_2 \text{ str.}$$
$$S_{12} = (SV/2)^{1/2}\,(\delta_1 - \delta_2) \qquad\quad \text{CCX}_2 \text{ bend}$$
$$S_{13} = (UV/2)^{1/2}\,(\varepsilon_1 - \varepsilon_2) \qquad\quad \text{XCX}_2 \text{ bend}$$
$$S_{14} = (T(RS)^{1/2})^{1/2}\theta \qquad\qquad \text{CH out-of-plane bend}$$
$$S_{15} = (RU)^{1/2}\tau \qquad\qquad\qquad \text{OCCX torsion}$$

Here R, S, T, U, V indicate the equilibrium CO, CC, CH, CX, and CX$_2$ distances, respectively, and X symbolizes one of the atoms H, F, Cl, or Br depending on the molecule considered.

For each of the molecules acetaldehyde, fluoral, chloral, and bromal a simple diagonal force field was used as a first approximation. This force field reproduced fairly well some of the observed frequencies, but in all the molecules those frequencies expected to involve CO and CC stretching, CX$_2$ stretching, and CCX$_2$ and XCX$_2$ bending were not well reproduced.

A new set of force constants (F) was calculated, using the matrix relation [11]

$$F = \widetilde{L}^{-1}\lambda\,L^{-1}$$

for each molecule by inserting the observed frequencies in the diagonal matrix λ, and using the normal coordinate transformation matrix (L) from the first calculation. These new sets of force constants all showed appreciable coupling of the CO and CC stretching vibrations. For acetaldehyde and its isotopes

Table 7. Symmetrized force constants (in mdyne/Å) for acetaldehyde.

Species a'

	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
S_1	10.74	0.7	0	0	0	0	−0.1	−0.1	0.1	0
S_2		5.3	0	0	0	0	0	0	0.1	−0.1
S_3			4.3	0	0	0	0	0	0	0
S_4				4.8	0	0	0	0	0	0
S_5					4.61	0	0	0	0	0
S_6						0.84	0	0	0	0
S_7							0.8	0	0	0
S_8								0.73	0	0.2
S_9									0.79	0.2
S_{10}										0.51

Species a''

	S_{11}	S_{12}	S_{13}	S_{14}	S_{15}
S_{11}	4.77	0	0	0	0
S_{12}		0.25	0	−0.02	0
S_{13}			0.43	0	0
S_{14}				0.21	0
S_{15}					0.02

this turned out to be the largest coupling constant in the F matrix (corresponding to the symmetry coordinates). For the rest of the molecules, several other significant coupling constants also emerged from this calculation. Large differences were also observed between force constants for the symmetric modes in species a' and the corresponding antisymmetric modes in species a''; cf. the final force constants given in Tables 7 – 10.

Table 8. Symmetrized force constants (in mdyne/Å) for fluoral.

Species a'

	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
S_1	10.0	0.4	−0.2	0	0.2	0.3	0	0	0.3	0.1
S_2		5.7	−0.1	0.5	0.5	0.6	0	0	0.4	0
S_3			4.4	0	0	0	0	0	0	0
S_4				5.5	0.5	0.1	0	0.2	−0.5	0.1
S_5					5.6	0.2	0	0	0	0
S_6						1.2	0	0.2	0	0
S_7							0.8	0	0	0
S_8								1.3	0	0
S_9									1.3	0
S_{10}										0.97

Species a''

	S_{11}	S_{12}	S_{13}	S_{14}	S_{15}
S_{11}	5.24	0.25	0.6	0	0
S_{12}		0.37	0	0	0
S_{13}			0.79	0	0
S_{14}				0.28	0
S_{15}					0.01

Table 9. Symmetrized force constants (in mdyne/Å) for chloral.

Species a'

	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
S_1	10.1	−0.3	0	0	0.6	0	−0.1	0.2	0.2	0
S_2		4.0	0	0.3	0.7	0.2	0	0	0.3	0
S_3			4.4	0	0	0	0	0	0	0
S_4				2.7	0.3	0	0	0.2	0.1	0.1
S_5					3.6	0	0	−0.1	0	−0.1
S_6						0.6	0	0.1	0	0
S_7							0.73	0	0	0
S_8								0.88	0.12	0.13
S_9									0.99	0.35
S_{10}										0.9

Species a''

	S_{11}	S_{12}	S_{13}	S_{14}	S_{15}
S_{11}	1.76	0	−0.15	0.04	0
S_{12}		0.31	0	0.01	0
S_{13}			0.31	−0.01	0
S_{14}				0.19	0
S_{15}					0.02

Table 10. Symmetrized force constants (in mdyne/Å) for bromal.

Species a'

	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
S_1	9.9	−0.6	0	0	0.4	0	−0.4	0.2	0.2	0
S_2		4.3	0	0.4	0.5	0.3	0	0.2	0.2	0
S_3			4.4	0	0	0	0	0	0	0
S_4				2.9	0.2	0.2	0	0.5	0	0.2
S_5					2.7	0	0	−0.2	−0.2	−0.2
S_6						0.63	0	0.25	−0.05	0.02
S_7							0.73	0	0	0
S_8								0.99	0.11	0.23
S_9									1.08	0.56
S_{10}										1.06

Species a''

	S_{11}	S_{12}	S_{13}	S_{14}	S_{15}
S_{11}	2.14	−0.06	0.04	−0.08	−0.02
S_{12}		0.22	0	0.02	−0.02
S_{13}			0.24	0.02	0
S_{14}				0.17	0
S_{15}					0.02

The final force field for acetaldehyde (Table 7) was calculated by a least squares adjustment to the observed frequencies (Table 3) for acetaldehyde and three of its deuterated analogues. During this procedure most of the off-diagonal elements in the F matrix were put equal to zero. The calculated frequencies obtained from the final force field for acetaldehyde and its isotopes are given in Table 3 together with the observed frequencies. The final force field for acetaldehyde (Table 7) shows generally good agreement with the force constants for acetaldehyde calculated by Cosse and Schachtschneider.[3] For instance, the valence stretching force constants are calculated to be f_r (CO) $= 10.74$ (10.77), f_s (CC) $= 5.3$ (4.82), f_t (CH) $= 4.3$ (4.24), f_u (CH-methyl) $= 4.80$ (4.88), f_v (CH$_2$ − methyl) $= 4.69$ (4.88), where the figures in parentheses are calculated by Cosse and Schachtschneider [3] with (VF.1); all values are in mdyne/Å.

For fluoral, chloral, and bromal new sets of force constants were constructed by trying to maintain some force constants from acetaldehyde invariant (f_r, f_s, f_t, f_{rs}, f_β, etc.) and varying the others as to fit the observed frequencies for each molecule. This was not achieved without introducing some abnormally large off-diagonal elements in the F matrices. A certain relaxation of the constraint on the fixed force constants was therefore necessary in order to obtain a reasonable force field for each molecule.

The final force field for fluoral (Table 8) was obtained by using relation (1) with the observed frequencies for each isotope and the L matrices from the last iterative calculation described above, and taking the average of the two resulting force fields.

In the same way the final force field for chloral was produced (Table 9). The final force field for bromal (Table 10) has been fitted to the observed frequencies for CBr$_3$CHO alone, since no data are available for CBr$_3$CDO.

Table 11. Distribution of potential energy (PED)[a] among symmetry coordinates for CH_3CHO, CH_3CDO, CD_3CHO, and CD_3CDO.

	CH_3CHO		CH_3CDO		CD_3CHO		CD_3CDO	
Species	Freq.	PED	Freq.	PED	Freq.	PED	Freq.	PED
a'								
1	2997	$0.8S_4, 0.2S_5$	2997	$0.8S_4, 0.2S_5$	2822	$0.9S_3$	2250	$0.7S_4, 0.2S_5$
2	2846	$0.8S_5, 0.2S_4$	2846	$0.8S_5, 0.2S_4$	2247	$0.8S_4, 0.2S_5$	2121	$0.8S_3$
3	2822	$0.9S_3$	2130	$0.9S_3$	2059	$0.7S_5, 0.2S_4$	2059	$0.7S_5, 0.3S_4$
4	1800	$0.6S_1, 0.4S_7$	1712	$0.6S_1, 0.1S_7, 0.1S_2$	1781	$0.6S_1, 0.3S_7$	1700	$0.7S_1, 0.1S_7, 0.1S_2$
5	1469	$0.8S_9, 0.2S_2$	1461	$0.9S_9, 0.1S_2$	1321	$0.6S_7, 0.3S_1$	1243	$0.5S_9, 0.5S_2, 0.1S_{10}$
6	1344	$0.7S_8, 0.3S_{10}, 0.1S_1$	1342	$0.8S_8, 0.4S_{10}$	1262	$0.5S_2, 0.5S_9, 0.1S_{10}$	1096	$0.4S_8, 0.3S_7, 0.2S_1$
7	1312	$0.6S_7, 0.2S_1, 0.1S_8$	1076	$0.4S_2, 0.1S_7, 0.1S_{10}$	1038	$0.8S_8, 0.1S_{10}$	963	$0.4S_8, 0.4S_7, 0.2S_{10}$
8	1080	$0.6S_2, 0.1S_6$	1003	$0.6S_7, 0.1S_2$	898	$0.6S_9, 0.3S_{10}, 0.1S_2$	879	$0.5S_9, 0.2S_{10}, 0.2S_2$
9	854	$0.7S_{10}$	840	$0.6S_{10}$	656	$0.6S_{10}, 0.1S_6$	648	$0.6S_{10}, 0.1S_6$
10	556	$0.8S_6, 0.1S_2$	545	$0.8S_6, 0.1S_2$	496	$0.5S_6, 0.5S_{10}, 0.1S_8$	491	$0.7S_6, 0.1S_8, 0.1S_{10}$
a''								
11	2992	$1.0S_{11}$	2992	$1.0S_{11}$	2228	$1.0S_{11}$	2828	$1.0S_{11}$
12	1423	$0.9S_{13}$	1423	$0.9S_{13}$	1031	$0.9S_{13}$	1030	$0.9S_{13}$
13	896	$0.7S_{14}, 0.3S_{12}$	851	$0.7S_{12}, 0.3S_{14}$	876	$0.9S_{14}, 0.1S_{12}$	763	$0.8S_{14}, 0.3S_{12}$
14	764	$0.6S_{12}, 0.3S_{14}$	676	$0.7S_{14}, 0.2S_{12}$	598	$0.9S_{12}$	566	$0.7S_{12}, 0.2S_{14}$
15	150	$0.9S_{15}$	144	$0.9S_{15}$	120	$0.9S_{15}$	113	$0.9S_{15}$

[a] The potential energy distribution is defined as $X_{ik} = F_{ii}L_{ik}^2/\lambda_k$, cf. Ref. 12.

The reliability of the force fields for fluoral, chloral, and bromal are certainly questionable, since the number of unknown force constants far exceed the number of observed frequencies. For acetaldehyde the number of observed frequencies almost equals the number of force constants; hence for this molecule the calculated force field should be fairly reliable. Still it is believed that some of the changes in force constants, when going through the series acetaldehyde, fluoral, chloral, and bromal, are significant and physically reliable. For example, the decrease in the CO stretching constant from acetaldehyde to bromal seems to be real. This is also true for the change in sign of the interaction constant between the CO and CC stretching vibrations. The decrease in the CC stretching constant from acetaldehyde to bromal also seems to be inevitable. A force constant for the torsional vibration about $0.01 - 0.02$ seems to be acceptable for all these molecules. On the contrary, the differences between the three force constants concerning the CCl stretches in chloral (F_{44}, F_{55}, and $F_{11\ 11}$) seem to be unreasonably large compared with the corresponding values in the rest of the molecules considered.

In any case the calculated force fields seem to be realistic enough to be useful in the calculation of mean amplitudes of vibration, since these quantities are known to be relative insensitive to minor changes in the force constants.

Potential energy distribution. In Tables $3 - 6$ the fundamental frequencies have been described in the usual way as characteristic CH, CO, CC stretches, and CCH, CCO bendings, etc. This is an oversimplified picture of the normal modes of vibration. As pointed out by Morino and Kuchitsu [12] a more accurate description of the normal modes of vibration can be obtained in terms of the potential energy distribution (PED). The elements of λ (eqn. 1) are given by $\lambda_k = \sum_i \sum_j L_{ik} L_{jk} F_{ij}$. The largest contributions to λ_k (normal frequency

Table 12. Distribution of potential energy (PED)^a among symmetry coordinates for CF$_3$CHO and CF$_3$CDO.

Species	CF$_3$CHO Freq.	PED	CF$_3$CDO Freq.	PED
a' 1	2847	$1.0S_3$	2154	$0.8S_3$
2	1854	$0.5S_1,0,4S_7,0.1S_2$	1752	$0.5S_1,0.2S_2,0.2S_7,0.1S_3$
3	1406	$0.3S_2,0.2S_4,0.2S_7,0.2S_9,0.1S_{10}$	1352	$0.4S_4,0.3S_2,0.3S_9,0.1S_{10},0.1S_6$
4	1303	$0.4S_1,0.3S_5,0.1S_2,0.1S_8$	1292	$0.4S_5,0.3S_1,0.1S_8,0.1S_2$
5	1213	$0.4S_7,0.3S_4,0.1S_5,0.1S_6$	962	$0.7S_7,0.1S_1$
6	837	$0.5S_6,0.3S_4,0.2S_2$	817	$0.4S_6,0.3S_4,0.2S_2$
7	697	$0.4S_5,0.2S_6,0.1S_8$	692	$0.4S_5,0.2S_6,0.1S_8$
8	591	$0.3S_9,0.2S_2,0.1S_{10},0.1S_4$	577	$0.3S_9,0.2S_2,0.1S_{10}$
9	427	$0.4S_8,0.2S_6$	427	$0.4S_8,0.2S_6$
10	250	$0.5S_{10},0.3S_9,0.1S_8$	249	$0.5S_{10},0.3S_9,0.1S_8$
a'' 11	1174	$0.8S_{11},0.1S_{14},0.1S_{13}$	1159	$1.0S_{11},0.1S_{13}$
12	977	$0.8S_{14},0.2S_{11}$	844	$0.8S_{14},0.1S_{11}$
13	525	$0.9S_{13}$	523	$0.9S_{13}$
14	330	$0.9S_{12}$	305	$0.9S_{12}$
15	55	$1.0S_{15}$	51	$1.0S_{15}$

^{a} See footnote in Table 11.

Table 13. Distribution of potential energy (PED)[a] among symmetry coordinates for CCl₃CHO and CCl₃CDO.

Species		CCl₃CHO Freq.	PED	CCl₃CDO Freq.	PED
a'	1	2859	$1.0S_3$	2143	$0.9S_3$
	2	1810	$0.6S_1,0.3S_7$	1739	$0.6S_1,0.1S_7,0.1S_2$
	3	1307	$0.6S_7,0.2S_1$	1095	$0.3S_7,0.2S_4,0.2S_9,0.2S_2,0.2S_{10}$
	4	1038	$0.6S_2,0.3S_9,0.2S_{10},0.1S_4,0.1S_6,0.1S_1$	988	$0.5S_2,0.3S_1,0.2S_7,0.1S_5$
	5	887	$0.5S_5,0.4S_8,0.2S_4,0.1S_2,0.1S_1$	825	$0.4S_5,0.3S_7,0.2S_8,0.2S_6$
	6	618	$0.4S_6,0.2S_4,0.2S_{10},0.1S_2$	603	$0.4S_6,0.3S_4,0.2S_{10},0.1S_2$
	7	443	$0.5S_5,0.2S_6,0.1S_8$	437	$0.5S_5,0.2S_6,0.1S_8$
	8	317	$0.4S_{10},0.4S_9,0.4S_4$	315	$0.4S_{10},0.4S_9,0.4S_4$
	9	268	$0.4S_8,0.3S_6,0.1S_9$	268	$0.4S_8,0.3S_6,0.1S_9$
	10	197	$0.3S_{10},0.3S_9,0.1S_8$	197	$0.3S_9,0.3S_{10},0.1S_8$
a''	11	936	$0.4S_{14},0.2S_{11},0.2S_{12}$	904	$0.4S_{11},0.3S_{14},0.2S_{12},0.1S_{13}$
	12	767	$0.5S_{14},0.3S_{11},0.1S_{13}$	685	$0.6S_{16},0.2S_{11}$
	13	257	$0.8S_{12},0.2S_{11}$	227	$0.7S_{12},0.2S_{14},0.1S_{11}$
	14	200	$0.8S_{13},0.3S_{11}$	200	$0.9S_{13},0.3S_{11}$
	15	75	$0.9S_{15}$	71	$0.9S_{15}$

[a] See footnote in Table 11.

Table 14. Distribution of potential energy (PED)[a] among symmetry coordinates for CBr₃CHO and CBr₃CDO.

Species		CBr₃CHO Freq.	PED	CBr₃CDO Freq.	PED
a'	1	2839	$1.0S_3$	2121	$0.9S_3$
	2	1748	$0.6S_1,0.2S_7,0.1S_2$	1703	$0.6S_1,0.1S_2,0.1S_7$
	3	1351	$0.7S_7,0.1S_1$	1075	$0.6S_7,0.1S_4,0.1S_9,0.1S_{10}$
	4	999	$0.7S_2,0.3S_9,0.2S_{10},0.1S_1,0.1S_6,0.1S_4$	972	$0.7S_2,0.3S_1,0.2S_9,0.1S_{10}$
	5	784	$0.5S_8,0.4S_5,0.3S_4,0.1S_6,0.1S_1,0.1S_2$	739	$0.5S_8,0.3S_5,0.3S_4,0.2S_7,0.1S_6$
	6	547	$0.5S_6,0.4S_{10},0.3S_4,0.1S_8$	534	$0.5S_6,0.4S_{10},0.3S_4,0.1S_8$
	7	322	$0.5S_5,0.2S_9,0.2S_6$	318	$0.5S_5,0.3S_6,0.2S_9$
	8	276	$0.3S_9,0.3S_8,0.2S_6$	274	$0.3S_9,0.3S_8,0.1S_6$
	9	209	$0.6S_{10},0.3S_4,0.2S_8,0.2S_5,0.2S_9$	208	$0.6S_{10},0.3S_4,0.2S_8,0.2S_5,0.2S_9$
	10	151	$0.3S_9,0.2S_{10},0.1S_8$	151	$0.3S_9,0.2S_{10},0.1S_8$
a''	11	975	$0.4S_{16},0.2S_{11},0.1S_{12}$	930	$0.3S_{11},0.3S_{14}.0.2S_{12}$
	12	636	$0.6S_{14},0.5S_{11}$	569	$0.7S_{14},0.4S_{11}$
	13	187	$0.9S_{12},0.2S_{15},0.2S_{11}$	164	$0.9S_{12},0.2S_{11},0.1S_{15}$
	14	137	$0.9S_{13},0.1S_{11}$	137	$0.9S_{13}$
	15	79	$0.8S_{15}$	76	$0.9S_{15}$

[a] See footnote in Table 11.

parameter) are supposed to come from the diagonal terms of F. The potential energy distribution may therefore be defined as[12] $X_{ik} = L_{ik}^2 F_{ii}/\lambda_k$. Since only diagonal terms in F are considered, the $\sum_i X_{ik}$ may exceed the value 1.

In Tables 11 − 14 the PED for acetaldehyde, fluoral, chloral, and bromal are given. As can be observed from these tables only a few of the calculated frequencies can be described as characteristic modes of vibration. The descriptions made in Tables 3 − 6 are therefore highly approximate and do not give a real picture of the normal modes according to the Tables 11 − 14. For example, a frequency in the region around 1700 − 1800 cm^{-1} is normally supposed to represent a characteristic $C=O$ stretching vibration. But inspection of the PED in CH_3CHO (Table 11) shows that this frequency consists of 60 % $C=O$ stretching and 40 % CCH bending. This is also the case in fluoral, chloral, and bromal. On the other hand, the CH stretching vibration (CHO − group) seems to be characteristic in all of the here studied molecules. The lowest

Table 15. Mean amplitudes of vibration (in Å units) for CH_3CHO, CH_3CDO, CD_3CHO and CD_3CDO.

Distance^a	Equil. dist.	CH_3CHO $u(0°K)$	$u(298°K)$	CH_3CDO $u(0°K)$	$u(298°K)$	CD_3CHO $u(0°K)$	$u(298°K)$	CD_3CDO $u(0°K)$	$u(298°K)$
$C=O$	1.216	0.0389	0.0390	0.0383	0.0383	0.0386	0.0387	0.0384	0.0384
$C-C$	1.501	0.0473	0.0477	0.0468	0.0472	0.0484	0.0489	0.0478	0.0483
C_2-H_4	1.114	0.0803	0.0803			0.0805	0.0805		
C_2-D_2				0.0695	0.0695			0.0686	0.0686
C_3-H_5	1.086	0.0785	0.0785	0.0783	0.0783				
C_3-D_5						0.0666	0.0666	0.0668	0.0668
C_3-H_6	1.086	0.0786	0.0786	0.0779	0.0779				
C_3-D_6						0.0671	0.0671	0.0673	0.0673
$O..H_4$	2.004	0.0991	0.1002			0.0992	0.1003		
$O..D_4$				0.0862	0.0880			0.0858	0.0876
$O..H_5$	2.542	0.1291	0.1342	0.1294	0.1345				
$O..D_5$						0.1129	0.1210	0.1128	0.1211
$O..H_6$	3.096	0.1325	0.1644	0.1324	0.1640				
$O..D_6$						0.1117	0.1403	0.1147	0.1530
$O..C$	2.402	0.0574	0.0610	0.0573	0.0610	0.0568	0.0607	0.0571	0.0612
$C_2..H_5$	2.126	0.1026	0.1031	0.1027	0.1032				
$C_2..D_5$						0.0890	0.0904	0.0887	0.0901
$C_2..H_6$	2.126	0.1114	0.1127	0.1118	0.1133				
$C_2..D_6$						0.0949	0.0974	0.0961	0.0992
$C_3..H_4$	2.244	0.0991	0.0993			0.0986	0.0989		
$C_3..D_4$				0.0846	0.0851			0.0857	0.0863
$H_4..H_5$	3.115	0.1250	0.1253						
$H_4..D_5$						0.1149	0.1157		
$D_4..H_5$				0.1156	0.1161				
$D_4..D_5$								0.1062	0.1072
$H_4..H_6$	2.578	0.1744	0.2037						
$H_4..D_6$						0.1559	0.1798		
$D_4..H_6$				0.1631	0.1949				
$D_4..D_6$								0.1453	0.1821
$H_5..H_6$	1.779	0.1299	0.1303	0.1301	0.1306				
$D_5..D_6$						0.1092	0.1102	0.1095	0.1106
$H_6..H_7$	1.760	0.1447	0.1461	0.1460	0.1477				
$D_6..D_7$						0.1204	0.1244	0.1211	0.1251

^{a}Numbering of atoms according to Fig. 1.

Table 16. Mean amplitudes of vibration (in Å units) for CF_3CHO and CF_3CDO.

Dist.[a]	Equil. dist.	CF₃CHO		CF₃CDO	
		$u(0°K)$	$u(298°K)$	$u(0°K)$	$u(298°K)$
C = O	1.204	0.0395	0.0396	0.0391	0.0391
C − C	1.540	0.0468	0.0474	0.0468	0.0474
C − H	1.090	0.0799	0.0799		
C − D				0.0685	0.0685
$C_3 − F_5$	1.332	0.0450	0.0456	0.0453	0.0459
$C_3 − F_6$	1.332	0.0454	0.0459	0.0455	0.0459
O..H	1.987	0.0987	0.0993		
O..D				0.0842	0.0851
$O..F_5$	2.629	0.0654	0.0746	0.0656	0.0750
$O..F_6$	3.284	0.0842	0.1867	0.0820	0.1823
O..C	2.403	0.0507	0.0527	0.0513	0.0533
$C_2..F_5$	2.348	0.0553	0.0588	0.0554	0.0590
$C_2..F_6$	2.348	0.0600	0.0678	0.0587	0.0658
$C_3..H$	2.269	0.0993	0.0997		
$C_3..D$				0.0852	0.0859
$F_5..H$	3.341	0.0952	0.0967		
$F_5..D$				0.0832	0.0851
$F_6..H$	2.743	0.1437	0.2308		
$F_6..D$				0.1244	0.2172
$F_5..F_6$	2.180	0.0543	0.0591	0.0546	0.0594
$F_6..F_7$	2.165	0.0688	0.0881	0.0692	0.0889

[a] Numbering of atoms according to Fig. 1.

frequency in a'' is also fairly characteristic, and may be described as the OCCX torsional mode.

Mean amplitudes of vibration. With the force constants in Tables 7 − 10 the mean amplitudes of vibration [13] have been calculated for acetaldehyde, fluoral, chloral, bromal, and their deuterated isotopes (Tables 15 − 18).

Kato *et al.*[5] have given the mean amplitudes of vibration (electron diffraction at 21.5°C) for the following distances in acetaldehyde: $u_{CO} = 0.038_1 \pm 0.004_0$, $u_{CC} = 0.049_7 \pm 0.006_5$, $u_{CH} = 0.085_1 \pm 0.015_8$, and $u_{C..O} = 0.060_5 \pm 0.009_0$. The same quantities are calculated here (Table 15, at 25°C) as $u_{CO} = 0.0390$, $u_{CC} = 0.0477$, $u_{CH(CHO)} = 0.0803$, $u_{CH(CH_3)} = 0.0785$ and $u_{C..O} = 0.0610$, all in Å units. As one can see, all these calculated values are well within the experimental limits.

No experimental data from electron diffraction have been found in the literature for the rest of the molecules, but the calculated mean amplitudes of vibration (Tables 16 − 18) seem to be quite realistic.

Thermodynamic quantities. Finally, some thermodynamic quantities have been calculated for CH_3CHO, CF_3CHO, CCl_3CHO, and CBr_3CHO by the usual rigid rotator-harmonic oscillator approximation method as outlined by Herzberg.[14] The results from these calculations are shown in Table 19.

Table 17. Mean amplitudes of vibration (in Å units) for CCl₃CHO and CCl₃CDO.

Dist.[a]	Equil. dist.	CCl₃CHO		CCl₃CDO	
		$u(0°K)$	$u(298°K)$	$u(0°K)$	$u(298°K)$
C = O	1.150	0.0392	0.0393	0.0388	0.0389
C − C	1.520	0.0509	0.0520	0.0507	0.0518
C − H	1.100	0.0798	0.0798		
C − D				0.0680	0.0680
C₃ − Cl₅	1.760	0.0494	0.0528	0.0493	0.0527
C₃ − Cl₆	1.760	0.0507	0.0554	0.0506	0.0553
O..H	1.939	0.0999	0.1017		
O..D				0.0870	0.0894
O..Cl₅	2.840	0.0734	0.0972	0.0732	0.0969
O..Cl₆	3.579	0.0798	0.1535	0.0800	0.1579
O..C	3.364	0.0591	0.0646	0.0584	0.0639
C₂..Cl₅	2.682	0.0575	0.0655	0.0574	0.0656
C₂..Cl₆	2.682	0.0621	0.0779	0.0606	0.0758
C₃..H	2.245	0.1009	0.1016		
C₃..D				0.0882	0.0894
Cl₅..H	3.710	0.0953	0.0994		
Cl₅..D				0.0836	0.0885
Cl₆..H	2.981	0.1544	0.2158		
Cl₆..D				0.1340	0.2067
Cl₅..Cl₆	2.873	0.0589	0.0802	0.0595	0.0822
Cl₆..Cl₇	2.875	0.0600	0.0843	0.0610	0.0872

[a] Numbering of atoms according to Fig. 1.

Table 18. Mean amplitudes of vibration (in Å units) for CBr₃CHO and CBr₃CDO.

Dist.[a]	Equil. dist.	CBr₃CHO		CBr₃CDO	
		$u(0°K)$	$u(298°K)$	$u(0°K)$	$u(298°K)$
C = O	0.150	0.0394	0.0395	0.0394	0.0395
C − C	1.520	0.0503	0.0511	0.0502	0.0511
C − H	1.100	0.0800	0.0800		
C − D				0.0685	0.0685
C₃ − Br₅	1.940	0.0474	0.0518	0.0474	0.0518
C₃ − Br₆	1.940	0.0486	0.0538	0.0485	0.0538
O..H	1.939	0.1003	0.1022		
O..D				0.0873	0.0899
O..Br₅	2.944	0.0659	0.0866	0.0659	0.0866
O..Br₆	3.728	0.0747	0.1431	0.0743	0.1431
O..C	2.364	0.0594	0.0646	0.0593	0.0645
C₂..Br₅	2.836	0.0534	0.0608	0.0531	0.0606
C₂..Br₆	2.836	0.0622	0.0850	0.0614	0.0850
C₃..H	2.245	0.1016	0.1021		
C₃..D					0.0880	0.0892
Br₅..H	3.873	0.0930	0.0967		
Br₅..D				0.0808	0.0854
Br₆..H	3.103	0.1622	0.2337		
Br₆..D				0.1412	0.2252
Br₅. Br₆	3.167	0.0483	0.0778	0.0483	0.0778
Br₆..Br₇	3.169	0.0493	0.0806	0.0493	0.0806

[a] Numbering of atoms according to Fig. 1.

Table 19. Thermodynamic quantities (cal/mol/deg) for CH_3CHO, CF_3CHO, CCl_3CHO and CBr_3CHO.
Heat capacity $c_p°$, enthalpy $H°$, free energy $G°$ and entropy $S°$.

	$T(°K)$	$c_p°$	$(H°-H_0°)/T$	$-(G°-H_0°)/T$	$S°$
CH_3CHO	100	9.44	8.55	42.89	51.44
	200	11.39	9.43	49.08	58.52
	300	14.21	10.54	53.11	63.65
	400	17.16	11.83	56.32	68.15
	500	19.83	13.17	59.10	72.27
CF_3CHO	100	11.23	9.57	50.59	60.16
	200	15.54	11.47	57.79	69.25
	300	19.57	13.51	62.82	76.33
	400	22.96	15.47	66.98	82.44
	500	25.68	17.25	70.63	87.87
CCl_3CHO	100	13.80	10.18	53.97	64.15
	200	19.51	13.55	62.10	75.65
	300	23.35	16.21	68.11	84.32
	400	26.22	18.37	73.08	91.45
	500	28.37	20.17	77.38	97.55
CBr_3CHO	100	15.76	11.16	58.67	69.82
	200	21.09	14.93	67.65	82.58
	300	24.54	17.59	74.23	91.82
	400	27.11	19.66	79.59	99.25
	500	29.04	21.35	84.16	105.51

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