Vibrational Assignments of Acetyliodide and Deuterated Species, based on Infrared Gas Spectra and Valence Force Field Calculations

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The infrared gas phase spectra (4000−50 cm^{-1}) of acetyliodide (AcI), AcI-d_1, AcI-d_2 and AcI-d_3 are reported. A complete vibrational assignment is given, together with a valence force field calculation. The quality of the frequency refinement is shown to be sensitive to the methyl group structure. Minor corrections to the earlier methyl group structure are suggested.

The occurrence of acetyliodide (AcI) in the spectroscopic literature is rather sparse. A Raman investigation on liquid AcI was reported in 1948,[1] and an infrared investigation on liquid and gaseous AcI was reported in 1968.[2] Recently McKean[3] has reported the CH-stretching frequencies for AcI and AcI-d_2. In the latter work the deviation from C_{3v} symmetry of the methyl group is discussed. The structure of gaseous AcI was determined from microwave spectra[4] and from electron diffraction,[5] the latter reporting a tilt of the methyl group of 1.7±5.4°. In the present work the infrared gas spectra of AcI, AcI-d_1, AcI-d_2 and AcI-d_3 are reported in the region 4000−50 cm^{-1}. A complete vibrational assignment is given, which is in part based on a valence force field calculation. The symmetry co-ordinates used in the calculation allow deviation from C_{3v} symmetry for the methyl group. The frequency fit appeared to be sensitive to the methyl group structure, and a slightly revised methyl group structure is suggested.

EXPERIMENTAL

AcI was synthesized from ketene and HI. Ketene was prepared by pyrolysis of acetic acid

anhydride (600 °C).[6] HI was prepared by adding H_2O to PI_3. Deuterated ketene and DI were made by a similar procedure using deuterated compounds. The isotopic purity (atomic percent) of ketene-d_2 was 99 % and of DI ca. 90 %. AcI-d_3, AcI-d_2 and AcI-d_1 were prepared from ketene-d_2 and DI, ketene-d_2 and HI, and from ketene and DI respectively, the obtained isotopic purity being 90, 99 and 90 %. The syntheses were carried out in a glass system under high vacuum. Excess of ketene or HI was removed by distillation. All contact with water from walls etc. must be avoided due to the rapid hydrolysis of AcI to
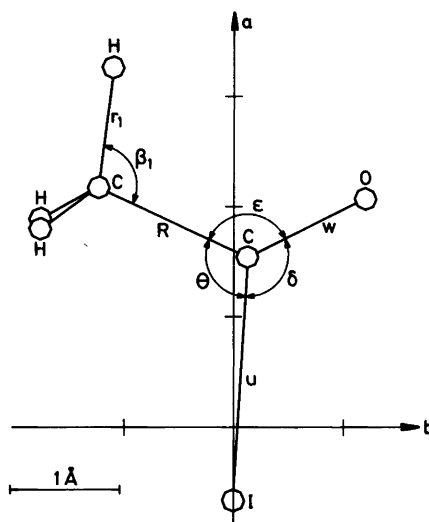

Fig. 1. Acetyliodide in the principal inertial axis system.

acetic acid. Due to their variable relative intensity it was also possible to identify some weak lines in the IR-spectra caused by an unknown impurity (see Fig. 2).

Infrared gas spectra in the region 4000−350 cm^{-1} were recorded, using a 10 cm gas cell with KBr windows, on a Perkin-Elmer Model 580. The spectra were automatically stored in digitalized form in a medium size computer (RC 4000). This allowed computational removal of spectral interference from AcI in AcI-d_1, and from AcI-d_2 in AcI-d_3.

In the FIR-region 500−50 cm^{-1} a Michelson interferometer (RIIC, FS-520), equipped with a 4.6 m gas cell of the light pipe type,[7] was used.

For all the reported spectra a spectral resolution of *ca.* 2 cm^{-1} was used.

RESULTS AND VIBRATIONAL ASSIGNMENT

Acetyliodide is an asymmetric top molecule with a mirror plane as the only symmetry element (point group C_s). In Fig. 1 AcI is shown in the principal axis system for the moments of inertia. The structure used is from Ref. 5. (See also Table 9.)

From symmetry arguments[8] all fundamental frequencies can be expected to appear in the IR spectra, with ten bands of A'-symmetry (A/B-hybrids) and five bands of A''-symmetry (C-type bands). According to Ref. 9 the C-type bands will show a dominant Q-branch, the B-type bands a band minimum and the A-type bands a distinct but weak Q-branch. The P,R-separation is calcu-

lated[10,11] to be 12.6 and 10.5 cm^{-1} for the A- and B-type bands, respectively. The changes in moments of inertia due to isotopic substitution are small and have no significant influence on calculated band contours. The experimental band contours are in good agreement with the calculated values.

For AcI-d_1 and AcI-d_2 two rotamers exist. One of C_s symmetry and two equivalent forms with no symmetry (C_1). The species of C_1 symmetry is expected to be twice as abundant as the species of C_s symmetry. In general all absorption bands of the C_1 species will be $A/B/C$-hybrids.

In Tables 1−4 the observed band center frequencies are given together with relative intensities, band contours and vibrational assignment. In general the vibrational assignment for the parent molecule and the d_3-species is based on group frequencies and band contours.

CH- and CD-stretching frequencies. In Fig. 2 the infrared spectrum of saturated vapours of AcI in a 10 cm cell is shown. The most striking feature is the relatively low intensity of the CH-stretching bands near 3000 cm^{-1}. The relative intensity of the CH-stretching modes for the isotopic compounds are qualitatively as seen in Fig. 2. The CD-stretching bands near 2100−2300 cm^{-1}, which theoretically have half the intensity of the CH-stretching bands, mix with several weak overtone bands in this region, preventing a rigorous assignment of the CD-stretching fundamentals. A tentative assignment is given in Tables 2−4.
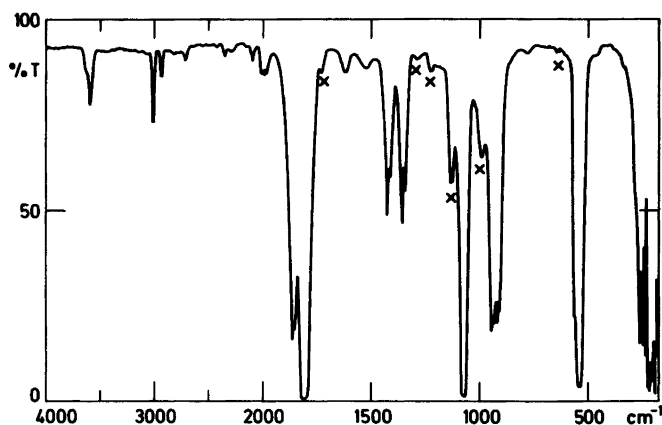

Fig. 2. Survey gas spectrum of acetyliodide (saturated vapours in a 10 cm cell). The bands marked with a cross are due to an unidentified impurity.

Table 1. Tables 1−4 give the observed infrared gas phase data for AcI, AcI-d_3, AcI-d_1 and AcI-d_2. Given for each band is the observed frequency, the band contour, the relative intensity and a vibrational assignment.

For the A- and the C-type bands the frequency corresponds to the value of the Q-branch maximum, and for the B-type bands to the central band minimum. In the spectrum of AcI-d_2 it can be seen that a band frequently has two closely separated Q-branches of nearly equal intensity. Such Q-branches are marked C' and C''. In the calculations the average frequency is used. The relative intensities are given by: s=strong, m=medium, w=weak, vs=very strong etc. F, Fermi resonance; sh, shoulder; *, diffuse band contour; +, overlapping bands.

Infrared gas phase data and vibrational assignment for acetyliodide.

Frequency (cm^{-1})	Band contour	Intensity	Assignment
3595	B	vw	$2v_3$ (3634)
3014	A	w	v_1
2937	A	vw	v_2
2814	*	vw	$2v_4$ (2842)
2717	B	vw	v_3+v_7 (2745)
ca. 2360	*	vw	v_3+v_8 (2368)
ca. 2290	B	vw	v_5+v_7 (2281)
2104	*	vw	v_3+v_9 (2108)
+ {2000	B	vw	v_6+v_7 (2020)
1993	B	vw	v_6+2v_{14} (1993)
1860	B	s	$2v_7$ (1856) } F
1811	B	vs	v_3
+ {1646	*	vw	v_5+v_9 (1644)
1624	A	vw	v_6+v_8 (1630)
+ {1429	C	m	v_{12}
1421	A/B	m	v_4
1408	C	w	v_7+v_{14} (1403)
1353	B	m	v_5
+ {1079	A	vs	v_6
1074	C	w-m	v_{13}
941	A	s	v_7
914^b	A	s	$2v_{14}$ (924) } F
581	*	vw	$2v_9$ (582)
565	A/B	s	v_9+v_{10} (562) } F
545	B	vs	v_8
462^b	C	vw	v_{14}
+ { 291	A	w	v_9
271	A	w	v_{10}

^{a} The band from the C_s-rotamer is supposed to be hidden in the band from the C_1-rotamer. ^{b} The most intense of several Q-branches.

Table 2. Infrared gas phase data and vibrational assignment for acetyliodide-d_3. For symbols used see legend to Table 1. For footnotes see Table 1.

Frequency (cm^{-1})	Band contour	Intensity	Assignment
3604	*	w	$2v_3$ (3634)
2746	A/B	vw	v_3+v_7 (2755)
2616	A/B	vw	v_3+v_6 (2616)
2265	A	vw	v_1
2104	A/B	vw	v_3+v_9 (2105)
2034	A/B	vw	v_5+v_7 (2046)
1903	B	vw	v_5+v_6 (1907)
1873	A/B	m	$2v_7$ (1876)
1817	B	vs	v_3
1300	C	vw	v_9+v_{12} (1325)
1108^b	A	vs	v_5
+ {1052	A/B	w	v_4 }
1037	C	w	v_{12} } F
1020	A/B	w	v_6+v_{10} (1039) }
935	A/B	vs	v_7
799^b	A	w	v_6
529	*	w	v_9+v_{10} (528)
500	A/B	vs	v_8
414^b	C	vw	v_{14}
288	A	w	v_9
240	A/B	w	v_{10}

Fig. 3 shows the CH-stretching region for the AcI, AcI-d_1 and AcI-d_2. All the spectra are of saturated vapours recorded at room temperature in a 10 cm cell, and are presented in transmission. For the parent molecule three bands (two A/B-hybrids and one C-type band) would be expected.[12,13] Only two bands, of pronounced A-type, are observed at 3014 cm^{-1} and at 2937 cm^{-1}, and they are assigned to the asymmetric and symmetric CH-stretching modes, respectively (v_1 and v_2, A').[13] The missing C-type band (v_{11}, asymmetric stretch, A'') might be weak and/or coincident with the Q-branch in v_1. In the C_{3v}-case these two bands (v_1 and v_{11}) are degenerate.

In the d_1-species a total of four bands are expected in the CH-stretching region; an A/B- and a C-type band from the C_s rotamer and two $A/B/C$-hybrid bands from the C_1 rotamer. Only two pronounced A-type bands of nearly equal intensity are observed, as shown in Fig. 3c.

For the d_2-species one A/B-band and one $A/B/C$-band from the C_s and the C_1 rotamer respectively, would be expected. But in fact only

Table 3. Infrared gas phase data and vibrational assignment for acetyliodide-d_1. For symbols used see legend to Table 1. For footnotes see Table 1.

Frequency (cm^{-1})	Band contour	Intensity	Assignment C_s	C_1
3600	B	vw	$2\nu_3$ (3626)	$2\nu_2$ (3626)
3007	A	vw		ν_1
+ {2958	A	vw		ν_2
2953	*	vvw		
+ {2769	B	vvw	$\nu_3+\nu_7$ (2775)	$\nu_4+\nu_9$ (2775)
2754	B	vvw		$\nu_3+\nu_{11}$ (2768)
2640	B	vw	$\nu_4+\nu_5$ (2658)	$\nu_4+\nu_{10}$ (2640)
ca. 2223	*	vvw	ν_2 $\nu_7+\nu_{12}$ (2228)	
2100	*	vw	$\nu_3+\nu_9$ (2103)	$2\nu_8$ (2104) $\nu_4+\nu_{13}$ (2103) $\nu_6+\nu_{10}$ (2101)
{1922	A/B	w	$2\nu_7$ (1924)	$2\nu_9$ (1924)
1891^{sh}	A	m	$\nu_4+\nu_8$ (1913)	
+ {1880	B	m		$\nu_8+\nu_{10}$ (1879) } F
1858	A	m	$\nu_6+\nu_7$ (1873) } F	
1813	B	vs	ν_3^a	ν_4 }
ca. 1655	*	vvw	$\nu_4+\nu_{10}$ (1670)	$2\nu_{10}$ (1654)
ca. 1590	*	vvw		$\nu_8+\nu_{11}$ (1597)
{1429	B	w	$\nu_6+\nu_8$ (1415) } F	
+ {1398	A	w	ν_4	
1412	C	w		ν_5
ca. 1300	*	vw	$\nu_{10}+\nu_{13}$ (1305)	$\nu_8+\nu_{14}$ (1312)
{1274	A	m		ν_6
1266	C	m	ν_{12}	
+ {1260	A	m	ν_5	
1249	B	m		ν_7
1079	C	w		$2\nu_{11}$ (1090)
1071	C	w		$\nu_{10}+\nu_{14}$ (1086)
+ {1052	A/B/C	vs		ν_8
1045	C	vs	ν_{13}	
962	A/B	vs	ν_7	
911	A	w	ν_6	
827	A	w		ν_{10}
552	A/B	s		$\nu_3+\nu_{14}$ (549) } F
540	A	vs		ν_{11}
504^b	A	s	ν_8^a	
290	A	w	ν_9	
+ { 261	A	w	ν_{10}	ν_{13}
259	A	w		ν_{14}

a single pronounced *A*-type band is observed.

The absence of bands might be explained by assuming exact or nearly exact coincidence between bands from the two rotamers. This means that the methyl group has C_{3v} or very near C_{3v} symmetry. However, a very small deviation from C_{3v} symmetry should cause a frequency difference of a few wave numbers, which should be observable. Another explanation of the missing bands, including the absence of the A'' CH-stretching mode in AcI may be as follows.

First the overall weak intensity of the CH-stretching bands must be caused by a small value of the dipole moment derivative $(\delta\bar{\mu}/\delta r)_0$, where r is the CH distance. Secondly, excluding that the low intensity of the A'' CH-stretching mode is

Table 4. Infrared gas phase data and vibrational assignment for acetyliodide-d_2. For symbols used see legend to Table 1. For footnotes see Table 1.

Frequency (cm^{-1})	Band contour	Intensity	Assignment C_s	C_1
3613	B	w	$2v_3$ (3634)	$2v_4$ (3634)
2984	A	vw	v_1	
ca. 2761	*	vw		v_4+v_8 (2770) v_2+v_{11} (2766)
2640	B	vw		v_3+v_{11} (2667)
2264	A/C	vw		v_2
2187	A	vvw		v_3
2165	C	vvw		v_5+v_9 (2196)
2106^b	A	vw	v_3+v_9 (2106)	v_4+v_{13} (2106)
2081	*	vvw	v_6+v_{12} (2074)	
2018	A	vw		v_7+v_8 (2025)
+ {1906	B	w-m		$2v_8$ (1906)
1883	A/B	w	v_4+v_6 (1884)	
1817	A/B	vs	v_3^a	v_4
{1272	C'	m		v_5
+ 1269	C"	m	v_{12}	
1253	A/B	m	v_5^a	v_6
{1079	A	vs	v_4	
+ 1074	C'	vs		v_7
1070	C"	vs		
1002^b	A	m	v_7	
953	A	vs		v_8
929	C'	m		
922	C"	m		v_9
+ { 906	A	m		$v_{11}+v_{12}$
903	A	w-m	v_{13}	
866	A/B/C	vw		$2v_{12}$
{ 823	A/B	w		v_{10}
+ 809	A/B/C'	w		
805	A/B/C"	w	v_6	
+ { 546	A	s	v_8	
532	A/B	m	v_9+v_{10} (539)	
502	A/B	vs		v_{11}
289	A	w	v_9^a	v_{13}
+ { 253	A	w		v_{14}
250	A	w	v_{10}	

accidental, $(\delta\bar{\mu}'/\delta r)_0$ must be significantly larger for the CH-bond in the plane defined by the heavy atoms than for the two other (equivalent) CH-bonds. As a consequence, only vibrations involving the "in plane" CH-bond would be expected to give rise to observable bands, which is in accordance with the number of observed bands. Moreover, because the dipole moment change will be mainly along the "in plane" CH-bond, which is parallel with the a-axis (Fig. 1) all bands will appear as A-type as is in fact observed. Finally the theory qualitatively pre-

dicts the relative intensities of the observed bands. The assignment according to this explanation is given in Tables 1—4.

CH/CD-bendings and skeletal vibrations. AcI and AcI-d_3. The remaining assignment of the parent species requires only a few comments. The assignment is given in Table 1. However, several Fermi resonances occur, and corrections are necessary in order to get the "correct" fundamental frequencies. In Fig. 4a, c and d these Fermi resonances are shown. The corrections are carried out after the method described
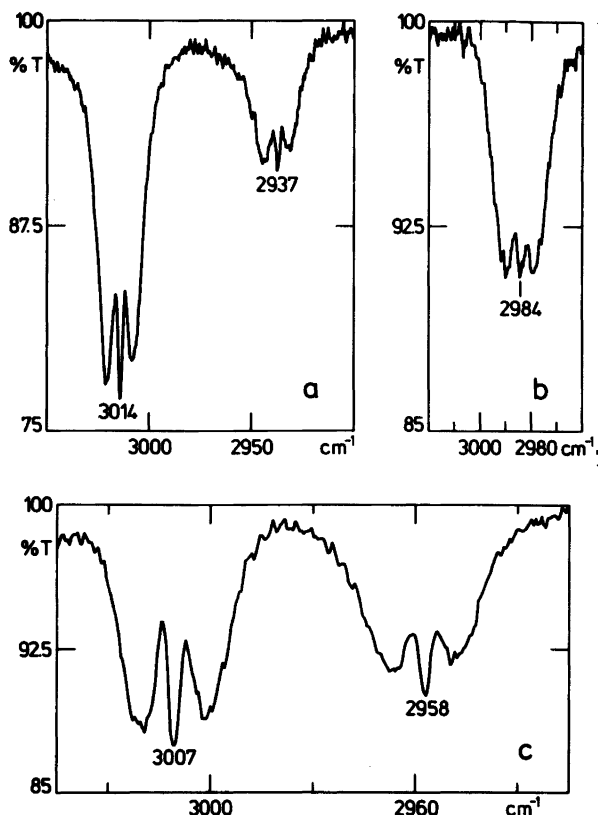
Fig. 3. Infrared gas spectra of the CH stretching region for a. AcI, b. AcI-d_2 and c. AcI-d_1 (saturated vapours in a 10 cm cell).

in Ref. 14 and by using intensity data from spectra recorded in absorbance. The corrected values are given in Table 7. The Fermi resonance near 950 cm^{-1} shown in Fig. 4c is assigned to two fundamentals of A'- and A''-symmetry, respectively in Ref. 2, probably because of spectra of poorer quality. Fig. 4c shows clearly that two A-type bands are present, and only a Fermi resonance can explain this. The A''-fundamental (v_{13}, CH$_3$-rock), assigned to one of the Fermi doublets in Ref. 2, appears as a weak C-type band at 1074 cm^{-1} overlapping the A'-fundamental (v_6, CH$_3$-rock) at 1079 cm^{-1} (Fig. 4b). The two modes (v_6 and v_{13}) are degenerate in the C_{3v}-case and are supposed to be close in frequency. In the far-IR two slightly separated A-type bands are observed, Fig. 5a. They cannot be explained as a Fermi resonance, and must therefore be attributed to two skeletal bending modes.

This assignment is confirmed from the deuterated species. The high frequency band, v_9, is nearly insensitive to deuteration in contrast to the low frequency band, v_{10}, (Fig. 5a and b). This indicates that the CH$_3$-group participates in the v_{10} mode and not in the v_9 mode.

For the d_3-species the remaining assignment is also rather straightforward. The assignment is given in Table 2. It is worth mentioning that the CD$_3$-rock vibration of A''-symmetry (v_{13}) is totally absent. The C-type band at 414 cm^{-1} is assigned to the out of plane skeletal deformation, v_{14}. This band is very weak. In the parent species the corresponding band is observed at 462 cm^{-1}, but it is not as sharp and distinct as in AcI-d_3. The corresponding bands are not observed in the spectra of AcI-d_1 and AcI-d_2 due to insufficient intensity.
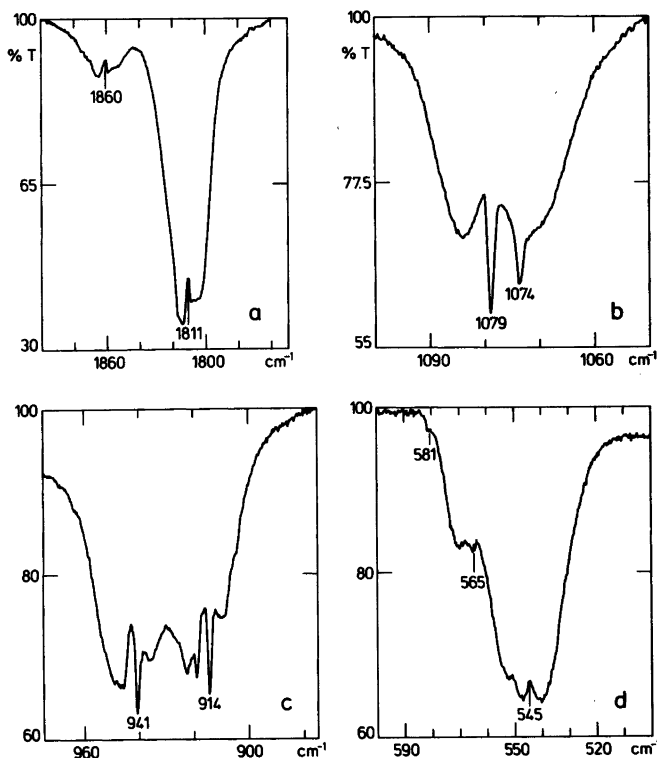
AcI-d_1 and AcI-d_2. In contrast to the parent-

Fig. 4. Details of the infrared gas spectra of acetyliodide. a., c. and d., important Fermi resonance. b. The near degenerate modes ν_6 and ν_{13}.

and the d_3-species the assignment of the d_1- and the d_2-species is quite difficult. The presence of two rotamers doubles the number of bands and gives rise to many overlapping bands. Furthermore, due to the low symmetry of the C_1 rotamer the band contours are of less help in the assignment. A reasonable assignment based on the present experimental material can, in our opinion only be carried out after good estimates of fundamental bands for the involved species have been made. The assignment of the d_0- and the d_3-species and of the CH-stretching frequencies for the d_1- and the d_2-species is used to establish a simple valence force field for acetyliodide (see below), and from this the fundamental frequencies for the d_1- and d_2-species are calculated. The assignment obtained in this way is given in Tables 3 and 4. A detailed discussion will not be given here, but in Figs. 6 and 7 details are shown of the more complicated regions, where the assignment is less certain.

In cases, where bands from the C_1 and the C_s rotamer are calculated as being only slightly separated, and only one band is observed, this band is assigned to the C_1 rotamer. The band from the C_s rotamer, which is believed to have approximately half the intensity of the C_1 rotamer, is in such cases assumed to be hidden in the C_1 band, and the frequency for the C_s band is estimated to be near the C_1 value.

Force field calculations. Coordinates. The force field calculations are carried out after the GF-method.[8] Conventional internal valence coordinates are used with the exception that the H_iCH_j angles are replaced by the corresponding dihedral angles, d_{ij}, between the planes defined by the two carbon atoms and H_i and H_j, respectively. The coordinates are named τ_i after:

$$\tau_1 = d_{23} \qquad \tau_2 = d_{13} \qquad \tau_3 = d_{12}$$

The advantage of these coordinates is discussed in Ref. 15. The torsion of the methyl group is
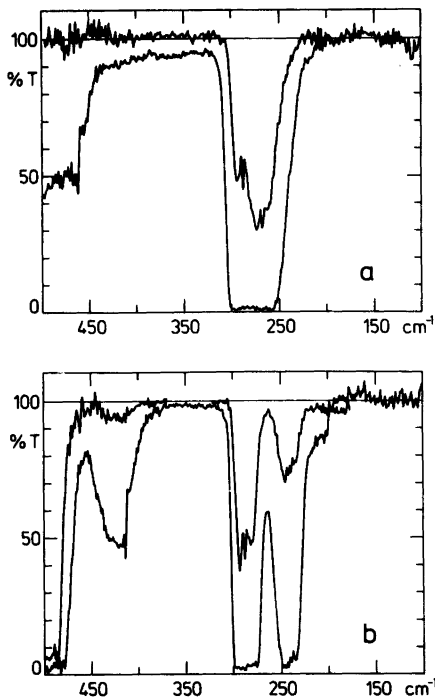
Fig. 5. The far infrared gas spectra of acetyl-iodide and acetyliodide-d_3 at two different pressures (*ca.* 2 and *ca.* 13 mmHg in a 4.6 meter cell).

described by the torsions of the individual H_iCCO-systems:

$$t_i = \text{tors}(H_iCCO) \qquad i = 1,2,3$$

The out of plane skeletal deformation, γ, is defined as the angle between the CO-bond and the plane defined by CCI. The definition of the remaining coordinates is given in Fig. 1 and Table 9. The symmetry coordinates used (C_s) are given in Table 5.

Calculations. A least squares method was applied in adjusting the force constants using a program developed at Chemical Laboratory V, University of Copenhagen. The program is based on well known principles already described in several papers,[16,17,18] and in particular we would draw attention to the papers by Aldous and Mills,[16,17] since they include a fairly comprehensive discussion on the problem of error analysis.

The force constants are adjusted to fit the observed frequencies. The estimated probable error, σ_i, in the i'th observed frequency, ω_i, is taken to be proportional to ω_i and is set to $\sigma_i = 0.01\omega_i$.

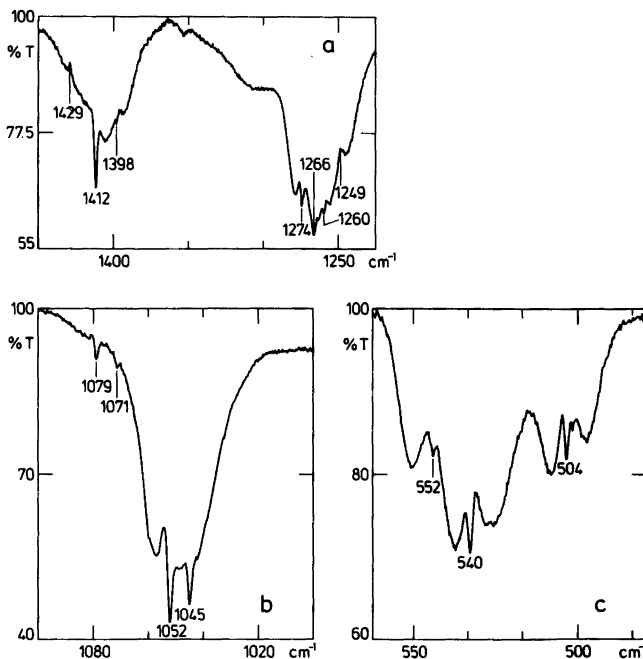A general force field has 55 independent force constants in the A'-class and 15 in the A"-class,

Fig. 6. Details of the infrared gas spectra of acetyliodide-d_1 where the assignment is uncertain.
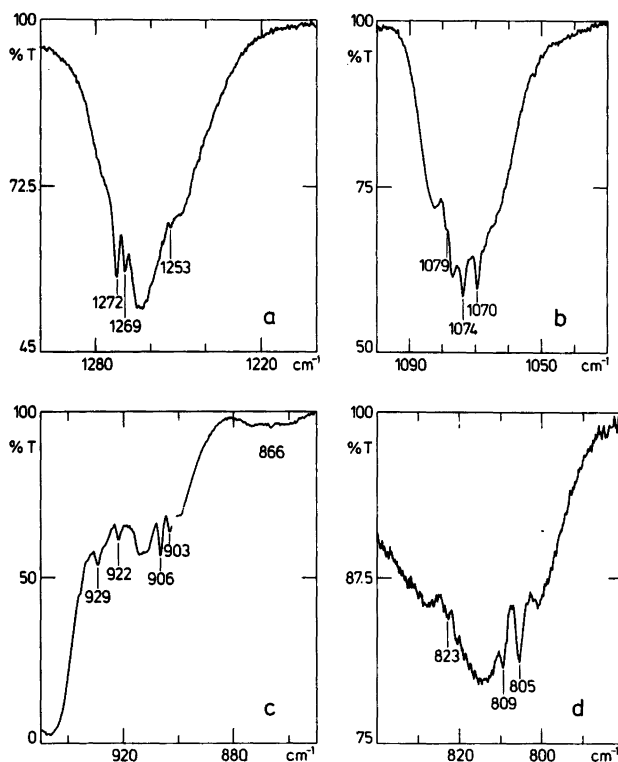
Fig. 7. Details of the infrared gas spectra of acetyliodide-d_2 where the assignment is uncertain.

and it is necessary to fix many of these to zero or literature values. The initial force field values are taken from the standard methyl group of Duncan,[12] HCOCl,[19,20] and CH_3CHO,[21] and are

Table 5. Symmetry coordinates for acetyl iodide.

A' $S_1=6^{-\frac{1}{2}}\ (2\Delta r_1-\Delta r_2-\Delta r_3)$
     $S_2=6^{-\frac{1}{2}}\ (2\Delta\tau_1-\Delta\tau_2-\Delta\tau_3)$
     $S_3=6^{-\frac{1}{2}}\ (2\Delta\beta_1-\Delta\beta_2-\Delta\beta_3)$
     $S_4=3^{-\frac{1}{2}}\ (\Delta r_1+\Delta r_2+\Delta r_3)$
     $S_5=3^{-\frac{1}{2}}\ (\Delta\beta_1+\Delta\beta_2+\Delta\beta_3)$
     $S_6=\Delta R$
     $S_7=\Delta u$
     $S_8=\Delta w$
     $S_9=2^{-\frac{1}{2}}\ (\Delta\varepsilon-\Delta\delta)$
     $S_{10}=6^{-\frac{1}{2}}\ (2\Delta\theta-\Delta\varepsilon-\Delta\delta)$
A'' $S_{11}=2^{-\frac{1}{2}}\ (\Delta r_2-\Delta r_3)$
     $S_{12}=2^{-\frac{1}{2}}\ (\Delta\tau_2-\Delta\tau_3)$
     $S_{13}=2^{-\frac{1}{2}}\ (\Delta\beta_2-\Delta\beta_3)$
     $S_{14}=\Delta\gamma$
     $S_{15}=3^{-1}\ (\Delta t_1+\Delta t_2+\Delta t_3)$

given in Table 6. The methyl group values given by Duncan[12] are converted to the coordinates used here (τ's). The constants not shown in Table 6 are set to zero.

On the asymmetry of the methyl group. The symmetry coordinates used for the methyl group (Table 5) transform according to C_{3v} symmetry, and (S_1,S_{11}), (S_2,S_{12}) and (S_3,S_{13}) transform as degenerate sets of E-species. However, it is well documented that the methyl group in acetyl halides deviate from local C_{3v}-symmetry.[3] McKean has derived the force constants for the individual CH stretching modes (*trans* and *gauche* to the halogen) from observed isolated CH-stretching frequencies in d_2-acetyl halides. The asymmetry is shown to decrease, from being significant in AcF to nearly non-existent in AcI. From the extended material presented in this work, we wished to confirm the methyl group geometry.

The asymmetry of the methyl group force field is most clearly described when using internal

Table 6. Initial and final force constants for AcI. I and II represent a severely restricted force field and a minimum restricted force field, respectively. For details see text.

Force constant [a,b]	Initial	I	II
$F_{1,1}$	4.82[c]	4.862(36)	4.857(21)
$F_{1,2}=F_{11,12}$	-0.10[c]	-0.10	-0.10
$F_{1,3}=F_{11,13}$	0.05[c]	0.05	0.05
$F_{1,4}$	0	0	-0.006(7)
$F_{2,2}$	0.37[c]	0.354(3)	0.352(4)
$F_{2,3}$	0.23[c]	0.221(5)	0.218(7)
$F_{3,3}$	0.81[c]	0.775(16)	0.769(35)
$F_{3,5}$	0	0	-0.010(11)
$F_{3,9}$	0	-0.105(14)	-0.083(21)
$F_{3,10}$	0	0.105(14)	0.128(53)
$F_{4,4}$	4.95[c]	4.988(44)	4.984(19)
$F_{4,5}$	0.04[d]	0.04	0.04
$F_{4,6}$	0.13[d]	0.13	0.13
$F_{5,5}$	1.18[c]	1.111(14)	1.109(33)
$F_{5,6}$	0.52[c]	0.427(25)	0.411(30)
$F_{6,6}$	4.45[c]	4.894(109)	4.821(151)
$F_{6,7}$	0.45[e]	0.450	0.45
$F_{6,8}$	0.68[e]	0.68	0.68
$F_{6,9}$	0.24[e]	0.546(79)	0.506(87)
$F_{6,10}$	0.10[e]	0.318(58)	0.369(43)
$F_{7,7}$	1.86[g]	1.591(78)	1.677(24)
$F_{7,8}$	0.55[e]	0.55	0.55
$F_{7,9}$	-0.29[e]	-0.546(79)	-0.29
$F_{7,10}$	0.19[e]	0.318(58)	0.369(43)
$F_{8,8}$	13.20[e]	13.300(100)	13.334(93)
$F_{8,9}$	0.02[e]	0	0
$F_{8,10}$	-0.27[e]	-0.27	-0.27
$F_{9,9}$	0.79[e]	1.080(66)	0.875(24)
$F_{9,10}$	0.16[e]	0	0
$F_{10,10}$	0.68[e]	0.764(14)	0.786(50)
$F_{11,11}$	4.82[c]	4.862(36)	4.868(12)
$F_{12,12}$	0.37[c]	0.354(3)	0.363(3)
$F_{12,13}$	0.23[c]	0.221(5)	0.209(5)
$F_{13,13}$	0.81[c]	0.775(16)	0.783(19)
$F_{13,14}$	0	-0.146(14)	-0.101(20)
$F_{14,14}$	0.37[f]	0.474(19)	0.442(20)
$F_{15,15}$	0.037[f]	0.037	0.037

[a] *Units.* stretch/stretch: mdyn/Å=aJ Å^{-2}; bend/bend: mdynÅ=aJ; stretch/bend: mdyn=aJ Å^{-1}. [b] When no uncertainty is given the value has been fixed. [c] Ref. 12. [d] Ref. 22. [e] Ref. 19. [f] Ref. 21. [g] Assumed.

coordinates. For AcI the first part of the general harmonic potential function involving the CH-stretching coordinates is:

$$2V = f_r^* \Delta r_1^2 + f_r(\Delta r_2^2 + \Delta r_3^2) +$$

$$2f_{rr}\Delta r_2\Delta r_3 + 2f_{rr}^*\Delta r_1(\Delta r_2 + \Delta r_3) +$$

$$2f_{r\beta}^*\Delta r_1\Delta\beta_1 + 2f_{r\beta}(\Delta r_2\Delta\beta_2 + \Delta r_3\Delta\beta_3) +$$

$$2f_{r\beta}^*\Delta r_1(\Delta\beta_2 + \Delta\beta_3) + 2f'_{r\beta}(\Delta r_2\Delta\beta_3 + \Delta r_3\Delta\beta_2) + \ldots$$

The force constants connected to the internal coordinates involving the "in plane" hydrogen atom are marked with an asterisk.

In the case of local C_{3v}-symmetry $f_r^* = f_r$, $f_{rr}^* = f_{rr}$ etc. It is seen that in the general case, the part of the potential function shown above contains eight different force constants instead of four different force constants in the C_{3v}-case. The potential function must therefore be simplified before it can be used in force field refinement.

A useful approximation is obtained if one *assumes that the asymmetry appears only in the quadratic terms (Δr_1^2 etc.) and not in the mixed terms ($\Delta r_1 \Delta r_2$ etc.).* This means that $f_r^* \neq f_r$, but $f_{rr}^* = f_{rr}$, $f_{r\beta} = f_{r\beta}^*$ and $f'_{r\beta}^* = f'_{r\beta}$. For the total potential function it means that the deviation from local C_{3v}-symmetry is described by adding only three extra force constants (f_r^*, f_β^* and f_τ^*).

The influence of this approximation on the *symmetry force constants* is given below for the coordinates involving the CH-stretchings:

$$F_{1,1}(F_{2,2}, F_{3,3}) = f_r - f_{rr} + 2\Delta f_r/3 \tag{1}$$

$$F_{4,4}(F_{5,5}) = f_r + 2f_{rr} + \Delta f_r/3 \tag{2}$$

$$F_{11,11}(F_{12,12}, F_{13,13}) = f_r - f_{rr} \tag{3}$$

$$F_{1,4}(F_{3,5}) = 2^{\frac{1}{2}}\Delta f_r/3 \tag{4}$$

$$\Delta f_r = f_r^* - f_r \tag{5}$$

Corresponding formulae are obtained for the symmetry coordinates involving the τ's and the β's. The corresponding symmetry force constants are given in parenthesis in the formulae above.

It appears that in this approximation the symmetry force constants are correlated:

$$F_{1,1} - F_{11,11} = 2\Delta f_r/3 = 2^{\frac{1}{2}}F_{1,4} \tag{6}$$

$$F_{3,3} - F_{13,13} = 2\Delta f_\beta/3 = 2^{\frac{1}{2}}F_{3,5} \tag{7}$$

Table 7. Fundamental frequencies for AcI, AcI-d_3, AcI-d_1 and AcI-d_2, and the deviation between observed and calculated values for various refinements (I–IV, see text). If Obs.-Calc. is in parenthesis the frequency has not been used in the refinement.

	Obs. cm⁻¹	I	II	III	IV	Obs. cm⁻¹	I	II	III	IV
	Acetyliodide					Acetyliodide-d_3				
ν_1	3014	3	5	6	3	2265	(27)	(28)	(30)	(25)
ν_2	2937	1	2	1	0	2109ᶜ				
ν_3	1817ᵃ	−2	−2	−2	−2	1817	2	2	2	1
ν_4	1421	−7	−1	−3	−5	1037ᵃ	(7)	(12)	(11)	(10)
ν_5	1353	−2	−2	−4	−4	1108	1	−2	−2	−1
ν_6	1079	−3	−1	−2	−4	799	1	2	2	1
ν_7	928ᵃ	−1	−2	−3	−4	935	−2	1	−1	0
ν_8	551ᵃ	3	3	3	3	500	−1	−1	−1	−1
ν_9	291	0	0	0	0	288	0	0	0	0
ν_{10}	271	1	0	1	1	240	0	−1	−1	−1
ν_{11}	3011ᶜ					2236ᶜ				
ν_{12}	1429	−3	−7	−8	−8	1037	7	2	1	−1
ν_{13}	1074	2	0	−2	−1	882ᵇ	(14)	(2)	(−3)	(−7)
ν_{14}	462	−2	3	2	1	414	1	−2	−1	−1
ν_{15}	134ᶜ					96ᶜ				
	Acetyliodide-d_1, C_s symmetry					Acetyliodide-d_1, C_1 symmetry				
ν_1	2964ᶜ					3007		−3	−4	−2
ν_2	2191ᶜ					2958		−4	−1	0
ν_3	1818ᶜ					2192ᶜ				
ν_4	1409ᵃ	(1)	4	3	3	1818ᶜ				
ν_5	1260	(−4)	−8	−7	−8	1412		−1	6	10
ν_6	911	(−1)	7	5	5	1274		7	7	8
ν_7	962	(13)	10	8	8	1249		−3	−1	−1
ν_8	504	−1	1	0	0	1052		0	5	6
ν_9	290	(2)	0	0	0	987ᶜ				
ν_{10}	261	(0)	−1	0	0	827		−6	−5	−5
ν_{11}	3011ᶜ					545ᵃ		0	0	0
ν_{12}	1266	(−1)	5	4	4	436ᶜ				
ν_{13}	1045	(19)	10	8	7	290		0	0	0
ν_{14}	458ᶜ					259		−1	−2	−2
ν_{15}	116ᶜ					117ᶜ				
	Acetyliodide-d_2, C_s symmetry					Acetyliodide-d_2, C_1 symmetry				
ν_1	2984	−4	−1	−1	−1	2989ᶜ				
ν_2	2151ᶜ					2264		(27)	(27)	(28)
ν_3	1817	(1)	1	1	0	2187		(38)	(40)	(41)
ν_4	1079	(−4)	−6	−6	−7	1817		0	0	1
ν_5	1249ᶜ					1272		8	6	6
ν_6	805	(−4)	3	3	3	1253		(10)	(1)	(2)
ν_7	1002	−1	1	0	2	1072		9	9	10
ν_8	540ᵃ	(0)	−2	−1	−1	953		−10	−6	−5
ν_9	289	(−2)	0	0	0	925		−7	−6	−6
ν_{10}	250	(3)	2	2	3	823		−5	−4	−2
ν_{11}	2236ᶜ					502		0	0	0
ν_{12}	1269	(7)	−5	−6	−6	434ᶜ				
ν_{13}	903	(2)	(21)	(16)	(13)	289		0	0	0
ν_{14}	418ᶜ					253		1	1	0
ν_{15}	106ᶜ					104ᶜ				

ᵃ Corrected for Fermi resonance. ᵇ Calculated from the product rule. ᶜ Calculated in iteration sequence II.

The calculations described below are all carried out in such a way that this correlation is fulfilled.

Iteration procedure. The fundamental frequencies calculated from the initial force field were in near agreement with the assignment of the parent and the d_3-species, and it was suitable as a starting point for further refinements.

Iteration sequence I. In this first iteration sequence severe constraints were used. The methyl group force field was constrained to C_{3v} symmetry. According to eqn. 1–7, with $\Delta f=0$, this yields

$$F_{1,1}=F_{11,11} \quad F_{2,2}=F_{12,12} \quad F_{3,3}=F_{13,13}$$

$$F_{2,3}=F_{12,13} \quad F_{1,4}=F_{3,5}=0$$

The stretch/bend and bend/bend interaction constants of the skeleton were constrained to C_{2v} symmetry with the CO bond as the C_2-axis:

$$F_{6,9}=-F_{7,9} \quad F_{6,10}=F_{7,10} \quad F_{9,10}=0$$

Moreover some force constants were fixed on initial values, or if they turned out to be small and uncertain, to zero. In order to obtain convergence it proved to be necessary to introduce interaction terms between the methyl deformation mode S_3 and the skeleton bendings S_9 and S_{10}. Because they appeared with different sign they were constrained to $F_{3,9}=-F_{3,10}$.

Only frequencies where the assignment is unequivocal were used in this iteration; *i.e.* all assigned frequencies from the d_0- and the d_3-

Table 8. Calculated internal force constants for the methyl group deformations for various refinements. II, III, and IV only differ in the methyl group structure.

Force constants[a]	Iteration sequence (see text)			
	I[b]	II[b]	III[c]	IV[d]
f_r	4.904(51)	4.908(9)	4.902(9)	4.895(8)
f_{rr}	0.042(27)	0.041(3)	0.034(3)	0.035(2)
Δf_r	0	−0.016(14)	−0.006(14)	−0.004(12)
f_β	0.887(21)	0.894(13)	0.892(12)	0.890(10)
$f_{\beta\beta}$	0.112(10)	0.111(6)	0.112(6)	0.114(5)
Δf_β	0	−0.021(24)	−0.013(22)	−0.001(19)
Δf_τ	0	−0.011(7)	−0.011(6)	−0.004(6)

[a] For units see Table 6. [b] $\beta=108.1°$, $\alpha=110.8$. [c] $\beta=\alpha=109.47°$. [d] $\beta=110.1°$, $\alpha_2=\alpha_3=110.34°$.

Table 9. Structure for AcI used in the force field refinements I–IV.

Bond or angle	Symbol	Value[a] I,II[b]	III	IV
CH1 (in plane)	r_1	1.101	–	–
CH2/CH3	r_2/r_3	1.101	–	–
H2CH3	α_1	110.81	109.47	105.84
H1CH2/H1CH3	α_3/α_2			110.34
H1CC	β_1	108.10	109.47	110.10
H2CC/H3CC	β_2/β_3			
CC	R	1.492	–	–
CO	w	1.198	–	–
CI	u	2.217	–	–
CCO	ε	128.8	–	–
CCI	θ	111.7	–	–
OCI	δ	119.5	–	–

[a] Bond lengths in Å and angles in degrees. [b] Ref. 5.

species, v_8 from the d_1-species (C_s), and v_1 and v_7 from the d_2-species (C_s). The result is shown in Tables 6 and 7, column I.

Iteration sequence II. From the force field obtained above the frequencies were calculated for the d_1 and the d_2 species (C_1 and C_s rotamers) and the complete assignment given in the Tables 3 and 4 was carried out.

The new assigned frequencies were then introduced in a new iteration sequence. Some of the constraints could be lifted, and the results are shown in Tables 6 and 7, column II. In this calculation the estimated error, σ_i, on the CH stretching frequencies were lowered from $0.01\omega_i$ to $0.001\omega_i$.

In general all values seem "reasonable" and the deviation from the initial force field is not large. It appears, that the force field of the CH_3 group is very close to C_{3v} symmetry. The values of Δf_r and Δf_β (Table 8) are, if real, opposite in sign relative to the values for other acetyl halides.[3]

In the case of AcI it seems that the CH stretching region is fairly free of Fermi resonance (FR), probably because of the unusually low frequencies of the methyl bending modes. The most favourable case for FR in AcI is between v_2 at 2937 cm^{-1} and a combination band at 2814 cm^{-1}, more than 100 cm^{-1} from the fundamental frequency. FR cannot be excluded. However, if v_2 is significantly affected by FR it should result in a poor refinement for especially that fundamental. From Table 7 is seen that this is not the case. If FR is of minor importance a better refinement might be obtained by changing the methyl group structure.

Iteration sequence III and IV. A series of iterations were carried out with small changes in the methyl group structure. It turned out that f_{rr}, Δf_r and Δf_β were sensitive to the value of the HCC angle (β). In Table 8 column III the results are shown from an iteration similar to that in column II, but with regular tetrahedral structure of the methyl group. It appears that Δf_r and Δf_β goes towards zero, and $f_{rr} = 0.034$, a value McKean[3] suggests as preferable. However, the iteration does not yield a better fit of the CH stretching frequencies. Tilting of the methyl group has no influence either. However, introduction of a difference in the HCH angles (the α's) has a striking effect. This has recently been reported by McKean for a far more constrained

system.[3] The fit of the CH stretching frequencies was improved if $\alpha_{12} = \alpha_{13}$ were increased and α_{23} correspondingly decreased. However, the value of f_{rr} then increased. The frequency data available are not sufficient to give a unique determination of the methyl structure, but the data suggest that corrections to the methyl group structure will have to be made. In Table 8 column IV a calculation is shown which yields both a reasonable value of f_{rr} and an improved fit of the CH stretching frequencies. However, the result is far from unquestionable.

For clearness the different structures used in the refinements are collected in Table 9.

CONCLUSIONS AND DISCUSSION

So far a detailed force field has not been made for other acetyl halides, which precludes any direct comparison with the present study. However, the proximity of the initial and the final force field indicates that acetyliodide behaves roughly as expected. The assignment and calculations presented confirm that the force field of the methyl group in AcI has very nearly C_{3v} symmetry. The calculations also confirm that the fit of the CH stretching and bending modes are very sensitive to the methyl group structure. Our calculations suggest that the (average) CCH angles are larger than the previously published value of 108.1°. The data suggest a value close to the regular tetrahedral angle (109.47°). This is in accordance with the empirical correspondence between the CCH angle and the isolated CH stretching frequency given by McKean.[23] However, the data also suggest that the methyl group structure deviates from C_{3v} symmetry, because the α's (and perhaps also the β's) are different.

The asymmetry in the methyl group *structure* may seem in conflict with the near C_{3v} symmetry of the *force field*. Our explanation is that in the case of AcI the asymmetry of the methyl group is mainly due to different sterical interactions between the individual CH bonds and the COI moiety. The methyl group compensates for this asymmetric interaction by changing the angular symmetry slightly away from C_{3v} symmetry, without perturbing the force field significantly. Significant changes in the symmetry of both the structure (including the bond lengths) and the force field, as observed in AcF,[3,24] must be

caused by a covalent or "through bond" interaction between the unequivalent CH bonds and the skeleton. Because the final methyl group structure is the resultant of two effects, which may be opposite in direction, *there is not necessarily a correlation between the asymmetry in the CH bond lengths (or the CH stretching force constants) and the angular symmetry of the methyl group.* This conclusion is supported by the experimental data of McKean[3] and that obtained from *ab initio* calculations given by Boggs et al.[25] Further work on AcF and AcCN is in progress in our laboratory.

REFERENCES

1. Seewan-Albert, H. and Kahovec, L. *Acta Phys. Aust. 1* (1948) 354.
2. Ramsey, J. A. and Ladd, J. A. *J. Chem. Soc. B* (1968) 118.
3. McKean, D. C. and Torto, I. *J. Mol. Struct. 81* (1982) 51.
4. Moloney, M. J. and Krisher, L. C. *J. Chem. Phys. 45* (1966) 3277.
5. Tsuchiya, S. *J. Mol. Struct. 22* (1974) 77.
6. Szwarc, M. and Murawski, J. *Trans Faraday Soc. 47* (1951) 269.
7. Hansen, E. L. and Nicolaisen, F. M. *Infrared Phys. 19* (1979) 225.
8. Wilson, E. B., Decius, J. C. and Cross, P. C. *Molecular Vibrations,* McGraw Hill, New York 1955.
9. Ueda, T. and Shimanouchi, T. *J. Mol. Spectrosc. 28* (1968) 350.
10. Seth-Paul, W. A. and Dijkstra, G. *Spectrochim. Acta Part A 23* (1967) 2861.
11. Seth-Paul, W. A. *J. Mol. Struct. 3* (1969) 403.
12. Duncan, J. L. *Spectrochim. Acta 20* (1964) 1197.
13. King, W. T. and Crawford, B., Jr. *J. Mol. Spectrosc. 5* (1960) 421.
14. Overend, J. In Davies, M., Ed., *Infrared Spectroscopy and Molecular Structure,* Elsevier, Amsterdam 1963, p. 352.
15. Nicolaisen, F. M. and Hansen, J. S. *Mol. Phys. 47* (1982) 1265.
16. Aldous, J. and Mills, I. M. *Spectrochim. Acta 18* (1962) 1073.
17. Aldous, J. and Mills, I. M. *Spectrochim. Acta 19* (1963) 1567.
18. Bjørklund, S., Augdahl, E., Christensen, D. H. and Sørensen, G. O. *Spectrochim. Acta Part A 32* (1976) 1021.
19. Suzuki, M., Yamada, K. and Takami, M. *J. Mol. Spectrosc. 88* (1981) 207.
20. Davies, D. W. and Gerry, M. C. L. *J. Mol. Spectrosc. 97* (1983) 117.
21. Hollenstein, H. and Günthard, H. H. *Spectrochim. Acta Part A 27* (1971) 2027.
22. Duncan, J. L., McKean, D. C., Mackenzie, M. W. and Peña, J. *J. Mol. Spectrosc. 76* (1979) 55.
23. McKean, D. C. *J. Mol. Spectrosc. 34* (1976) 181.
24. Pierce, L. and Krisher, L. C. *J. Chem. Phys. 31* (1959) 875.
25. Flood, E., Pulay, P. and Boggs, J. E. *J. Am. Chem. Soc. 99* (1977) 5570.