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The Use of Absolute Vibrational Band Intensities in Structural Analysis. I. n-Alkanes and Derived Ketones

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A systematic investigation of group absorption band intensities in tetrachloromethane of n-alkanes and methyl n-alkyl ketones is described. Contributions to the total intensity in given regions from each structural group are established and the results used to predict the spectral intensities of methyl cyclohexane, di-n-hexyl ketone and cycloheptanone. The variations in CH_2 and CH_3 group contributions arising from proximity to the carbonyl are discussed in relation to the constancy of King's effective atomic charge.

Raman group frequencies and intensities of the CH_3S and CH_3CH_2S are established. It appears likely that Raman band intensities, though less easily measured, could also be useful in structural analysis.

INTRODUCTION

The prime role of vibrational spectroscopy in chemistry is in structural analysis. Since the vibrational spectrum is so complex (constituted out of $3N - 6$ fundamentals, where N is the number of atoms) the methods employed are almost invariably based on empirical correlations. In such procedures the chemist is using the long established observation that a particular group of atoms in a given local environment in different molecules has unchanged physical and chemical properties. Provided that the energies of certain fundamental modes arise primarily from distortions within that group of atoms then it follows that absorption or scattering resulting from excitation of those vibrations will result in bands at closely similar positions in the spectra of all the molecules containing that grouping. A vast compilation of such structure-band correlations exist in texts such as those of Bellamy[1,2], though the spectral data is restricted to frequency information and usually very qualitative intensity data. The latter is generally of the form "weak" or "strong", but these very imprecise terms are never defined, and what appears to be a strong band in perhaps a hydrocarbon spectrum may appear very weak compared with bands of a silicone.

Commencing in the 1930's detailed intensity studies were made of a number of molecules of high symmetry and attempts made to interpret the band intensities in terms of bond oriented parameters. The popularity of

such studies rapidly waned when it became clear that, even when experimental problems had been overcome, simple bond dipole models did not work. Different symmetry species led to different estimates for the bond dipole moment[3]. There are three theories explaining this. The first used the concept that as angles changed, then rehybridisation at the central nucleus caused electron flow in the opposite direction to the bond which was particularly marked when the bond moved in a plane perpendicular to that of π bonds[4,5]. Thus as the CH bond of ethene moves out of the equilibrium nuclear plane the hybridisation at carbon moves towards sp[3] and a lone electron pair builds up on the opposite side of the plane to CH. While some indirect experimental evidence for this exists, ab initio calculations suggested that incomplete bond following was responsible for the variable effective bond moment[6]. Not incompatible with this explanation are recent results[7] which show that in a variety of molecules, including CH_2F_2 and ethene the *ab initio* experiment of deforming one C—X bond produces a dipole change off the bond line for stretching and off the perpendicular for bending. Deforming two bonds (or angles) leads to a dipole change which is the vectorial sum of the individual components.

Even without these model problems serious difficulties have occurred because of force field uncertainties. Fortunately scaled *ab initio* computed fields are rapidly becoming far more reliable than experimentally derived fields and great progress is being made by combining the two.

Where does all of this leave the use of intensities in analysis? There are various hopeful signs in the morasse of data. King[8] defined an effective atomic charge ε_α related to infrared absorption intensities by

$$\sum_\alpha \frac{\varepsilon_\alpha^2}{M_\alpha} = \sum_i A_i + \Omega$$

where M_α is the mass of the α atom, A_i is the integrated absorbance and Ω is a rotational angular momentum correction necessary for polar molecules. ε_α is also related to the atomic polar tensor P_x^α by

$$\varepsilon_\alpha^2 = Tr\,[\,P_x^\alpha \, \tilde{P}_x^\alpha\,] = \left|\frac{\partial p}{\partial x_\alpha}\right|^2 + \left|\frac{\partial p}{\partial y_\alpha}\right|^2 + \left|\frac{\partial p}{\partial z_\alpha}\right|^2 + \qquad (1)$$

where P_x^α is the cartesian polar tensor for the atom, α and P is the dipole moment. Remarkably the effective atomic charge for the hydrogen atom is found to remain roughly constant in a diverse range of compounds and in all hydrocarbons except ethyne. Thus for saturated hydrocarbons, olefins and benzene $\varepsilon_H = 0.100 \pm 0.005$ e. These clearly indicate that wild variations in intensity parameters do not occur between similar bonds. Person and his coworkers have exploited the transferability of atomic polar tensors in metal fluorides and fluorocarbons by using transfered parameters to predict the spectra of unknown or related species[9,10].

In Raman scattering intensities were interpreted on the basis of the Wolkenstein assumptions, and polarisability bond derivatives for CC bonds were found to be approximately proportional to bond order[11]. CH derivatives were also found to be reasonably constant in aliphatic systems. It has often been

remarked that polarisabilities are less susceptible to intermolecular interactions and that higher derivatives than the first of the polarisability are generally very small as witnessed by general absence of combination bands. These points would indicate that characteristic vibration bands should show more intensity consistency in the Raman than in the infrared. It is remarkable then that little systematic work has been reported on Raman band intensities for characteristic bands in related series of molecules.

For infrared spectroscopy there is a considerable literature on band intensities, mostly dating from the 1960's. The data prior to 1967 is well reviewed by Wexler[12]. Many cases are well established where group intensities exist though in other situations complicated electron lone pair and inductive effects occur. Nevertheless with the vastly improved data handling facilities of modern spectrometers it is very surprising that group intensity studies have gone out of fashion and that few analysts ever seriously think of using infrared intensities in structural analysis. We shall present some initial results of a systematic study of some homologous series and demonstrate that the power of infrared and Raman analysis is greatly enhanced by the use of intensities.

EXPERIMENTAL

In measuring absorption intensities care needs to be taken to avoid the following sources of error.

1. Inadequate resolution. Instrumental slit widths need to be significantly less than half of the experimental half height width (HHW). For the compounds studied the narrowest bands had HHW of about 10 cm^{-1}.

2. Incorrect zero transmission measurements.

3. Non linearity of the detection system.

4. Interference effects due to internal reflection in the cell.

5. Incorrect allowance for background absorption.

Spectra were measured on a PE983 with spectral resolutions varying from 3.6 cm^{-1} at 3000 cm^{-1} to 2.1 at 1200 cm^{-1} (mode 5 filter 4). Data was collected and processed using a PE3600 data station. Before correction using the instrument's microprocessor routine (shift zero, page 4) the zero error was 0.1—0.2%. After correction the error was within the noise level. To ensure that all spectra were measured under the same conditions solutions in carbon tetrachloride were used at suitable concentrations between 3% and 20% and in a cell of path length of 0.103 mm. To correct for the cell background and for the CCl$_4$ absorption the following procedure was adopted.

i) Spectra of CCl$_4$ were measured at path lengths of 0.103 and 0.025 mm. By ratioing, the spectrum of CCl$_4$ was established in absorbance units.

ii) The spectrum of say a 10% (volume) solution (known weight ratios) was now recorded and ratioed against the spectrum of CCl$_4$ in the same cell. This overcompensates for the CCl$_4$ absorptions — in this case by 10% or 0.0103 mm. Addition to the spectrum of the absorbance spectrum of CCl$_4$ (as measured in (i)) of the appropriate path length serves to remove all traces of CCl$_4$ bands, except in the intensely absorbing 800 cm^{-1} region, while at the same time avoiding general cell background distortions.

During the procedure checks are made to ensure the correct positioning of the background (error source 5). In acquiring the initial difference spectrum (using SDIFF function) the VDU image is magnified by at least 30 using the EXPAND facility. At this level the noise is readily apparent and the backround is adjusted up or down so that at the point of minimum absorption, (usually 2200—2000 cm^{-1} in the scan range 3600—2000 cm^{-1}, and 2000—1800 cm^{-1} in the range 2000—400 cm^{-1}) the noise is fluctuating about the origin (located by bars on screen). Of course

regions of CCl$_4$ absorption, especially near 1550 cm^{-1} and 800 cm^{-1} are excluded in this procedure. Examination of the absorbance data in the memory using the TYPE facility can be used as a final verification that the origin is correctly located. The general noise level is found to be about 0.0010 absorbance units except where water vapour absorbs strongly when it may be 2—3 times as large. Occasionally there are some evidence of channel spectra but with the solutions or with pure CCl$_4$ in the cell these were weak. In such cases the background was adjusted to pass through the zero phase points (error source 2).

Linearity of the detection system was verified using calibrated sectors and by Beer's law plot tests. Linearity was better than 1%, thus error source 3 is negligible.

To maintain consistency with the majority of the literature on solution intensities the integrated intensities are defined by

$$\frac{1}{cl} \int_{\nu_e}^{\nu_u} \log_{10} (I_1/I) \, d\nu$$

By contrast most vapour studies use the more fundamental $\int \log_e (I_o/I) \, d\nu$ and preferably $\int \log_e (I_o/I) \, d\log_e \nu$.

Raman spectra were recorded using a modified Coderg PHO spectrometer with NPL holographic gratings, a low noise EMI 9863B photomultiplier and interfaced through a Brookdeal photoncounting system to a Tektronix 4052 computer with a 4907 disc system. Polarisations were recorded using a Pockel cell to rotate the plane of polarisation of the incident laser beam between acts of stepping the grating motor[13]. This has the merit of reducing the time separation between readings of intensities for parallel and perpendicular polarisations (actually $I_{VV} + I_{VH}$ and $2I_{HH}$) to time for a single reading, thereby significantly increasing measurement accuracy.

RESULTS

Separation into component bands is a process which is subject to considerable error due to uncertainties in the number of components and in the band contours. For this reason and because the intention is to develop a simple to apply analytical procedure no such band deconvolutions have been attempted. For the initial survey work reported here the CH stretching and deformation regions have been sub-divided at frequencies at which absorption minima occur in the higher n-alkanes. These are shown on a typical spectrum in Figure 1. For the stretching region the four regions so produced are, as is well established[1] and clear from the plots to follow, due primarily to CH$_3$ anti-symmetric, CH$_2$ anti-symmetric, CH$_3$ symmetric and CH$_2$ symmetric modes respectively from high to low frequencies. For the deformation region some extra subdivision was made to allow for the CH$_2$ bands which are significantly perturbed in frequency by the carbonyl. Plots of the integrated intensities of these regions against the number of CH$_2$ units in the alkane chain are shown in Figures 2 and 3. Good linear plots are obtained except for points for propanone (acetone) and butanone (methyl ethyl ketone). It is also to be noted that the gradients for the alkanes and the alk-2-ones are equal within experimental error (see Figures 2 and 3). The data was fitted by least squares analysis to

$$\text{Intensity} = YINT + GRAND \cdot N \qquad (2)$$

where N is the number of CH$_2$ units and $YINT$ and $GRAD$ are constants.
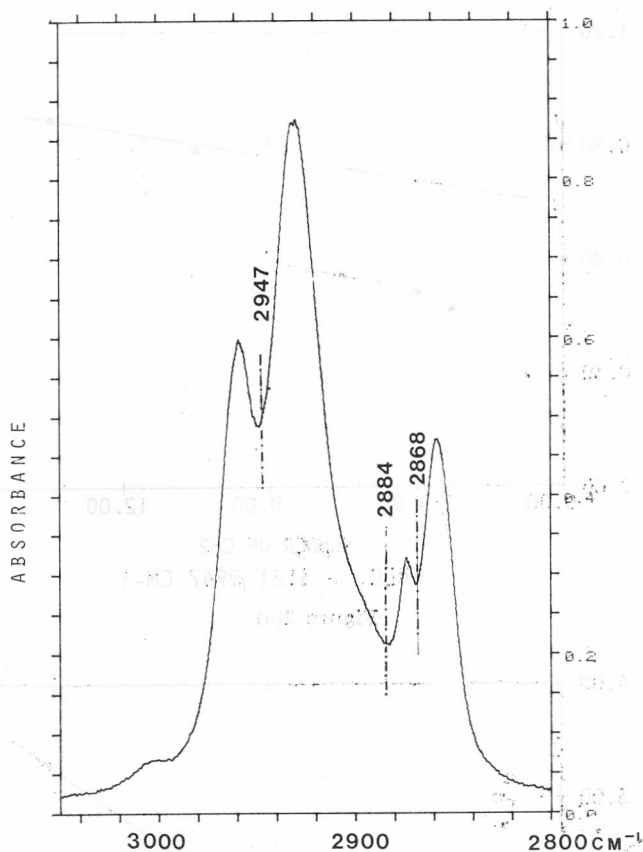
Figure 1. Spectrum of 2 nonanone in range 3050—2800 cm⁻¹; showing the break points used in integrating the intensities (concentration 0.2892 mol·dm⁻³ in 0.0103 cm cell).

For the alkanes the intensity axis intercepts are all positive, though varying in *YINT* from magnitudes ranging from zero within two standard deviation to 7427 ± 275 dm³ mol cm⁻². By contrast the methyl *n*-alkyl ketones generally show negative *YINT*. For the alkanes the gradient clearly represents the contribution to the integrated intensity in the spectral region per alkane CH₂ unit. *YINT* is the contribution to the intensity due to the two methyl units. Application of these results to alkyl cyclohexanes serves to check the wider applicability of the results. The measured and predicted intensities of methylcyclohexane, with the tertiary hydrogen atom ignored in the predictions, are shown in Table I. Some movement of intensity to lower frequencies in the CH stretching region is apparent though overall the result is very pleasing. Scaling of the intensity by 14/13 to allow for the tertiary H improves the total intensity. Clearly further studies of branched chain systems will allow more satisfactory allowance for this CH bond which does not give rise to any clearly identified band.
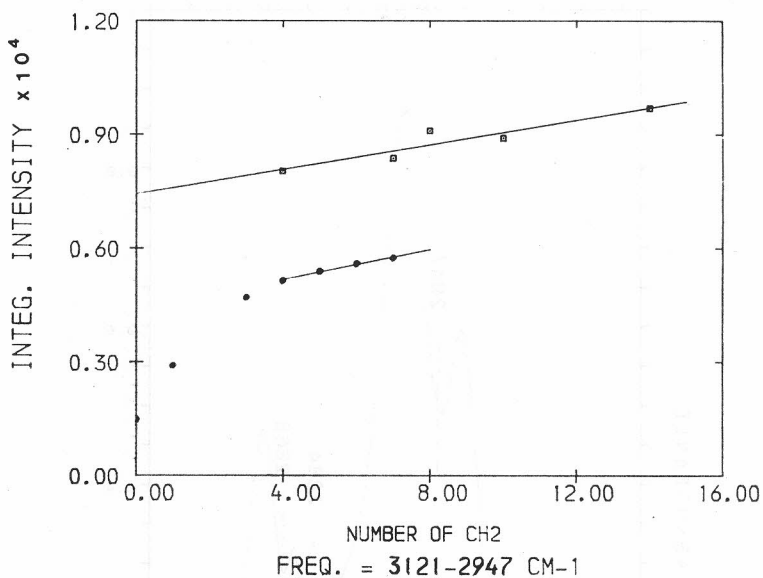
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Figure 2(a)
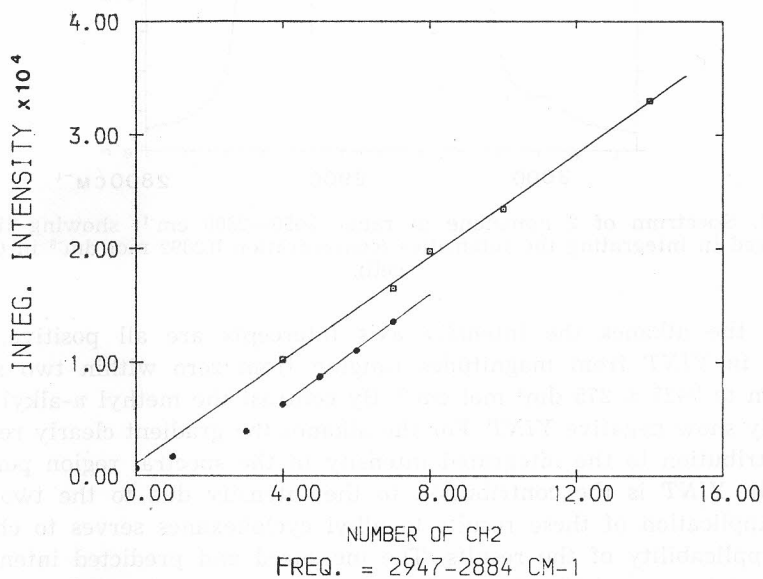

Figure 2(b)

In the alk-2-ones the parallel displaccment of the lines for CH stretching to higher n is understandable as due to the general weakening of the CH bands in the CH_3COCH_2 unit. This weakening has long been recognised. What has not been ascertained is whether the effect is restricted to the CH bonds alpha to the carbonyl and whether the intensity effects are transferable bet-
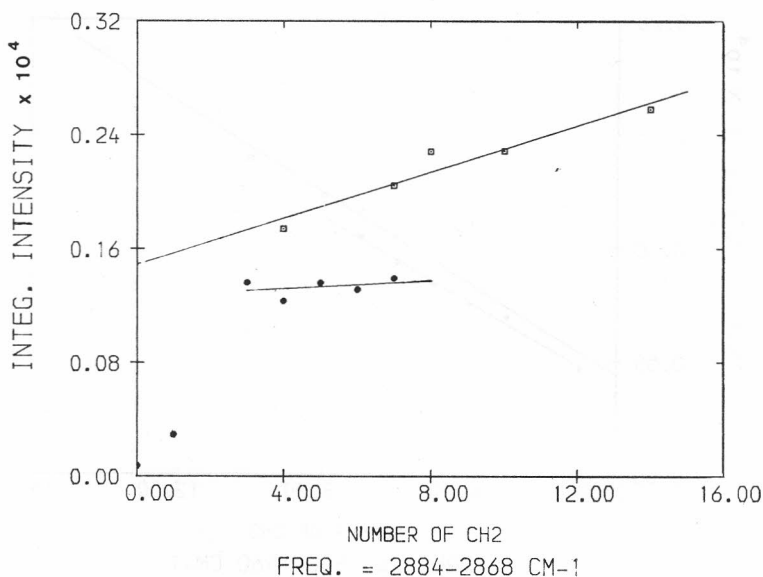
NUMBER OF CH2

FREQ. = 2884–2868 CM–1

Figure 2(c)

NUMBER OF CH2

FREQ. = 2868–2761 CM–1

Figure 2(d)

Figure 2. Integrated absorption intensities (mol^{-1} dm^3 cm^{-2}) in defined spectral ranges (stretching region) for alkanes □ and methyl *n* alkyl ketones ⊞ *versus* the number of CH$_2$ units in the alkyl chain.

ween similar molecules. Examination of the data shows that the answer to the former question is that the effect carries at least to the beta CH bonds.

Examination of Figures 2(a) and 2(b) in particular demonstrate that even for $n = 3$ there appears to be a slight deviation from the linear section of the

NUMBER OF CH2

FREQ. = 1500-1460 CM-1

Figure 3(a)

NUMBER OF CH2

FREQ. = 1460-1445 CM-1
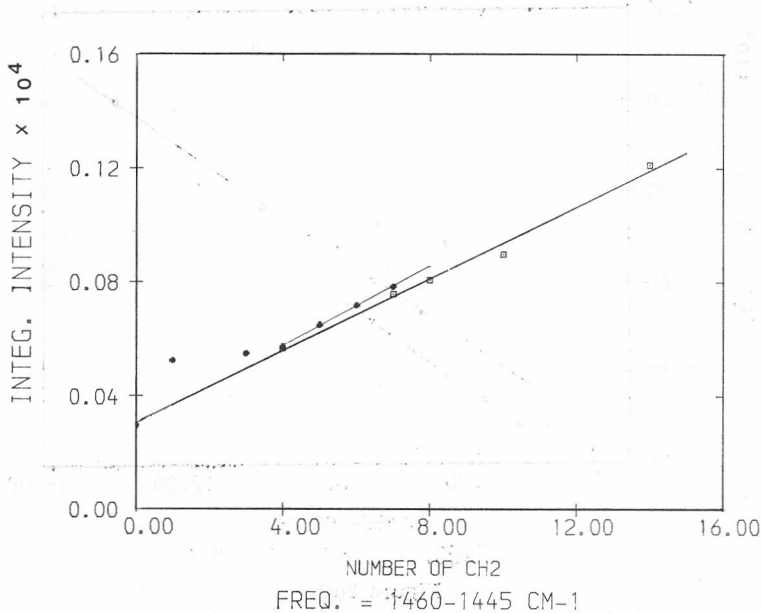
Figure 3(b)

graph. Possibly a very small intensity movement from the 3121—2947 cm^{-1} region to lower frequencies could explain the $n = 3$ points, but it seems highly probable by extrapolation that for $n = 2$ (no data currently available) the points lie off the lines. As we will see, data on such as cycloheptanone and methyl ethyl ketone reinforce the occurrence of an effect out to the β carbon.

FREQ. = 1445–1400 CM–1

Figure 3(c)

FREQ. = 1375–1350 CM–1
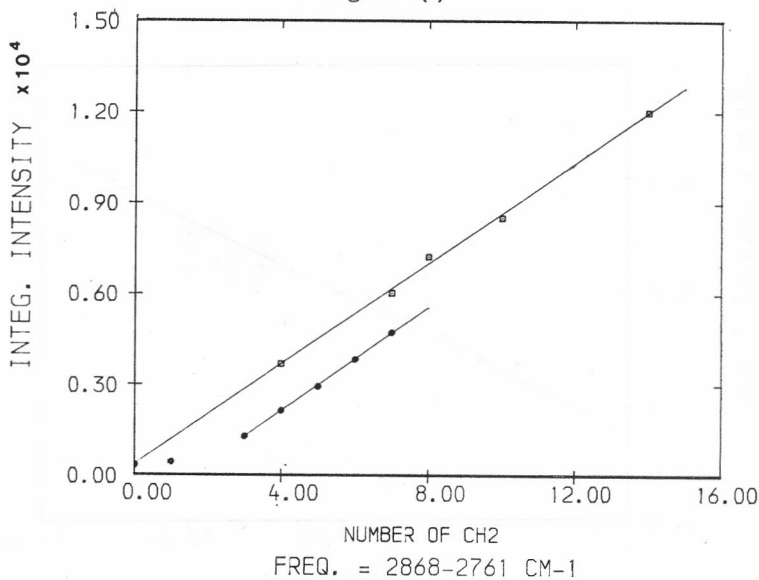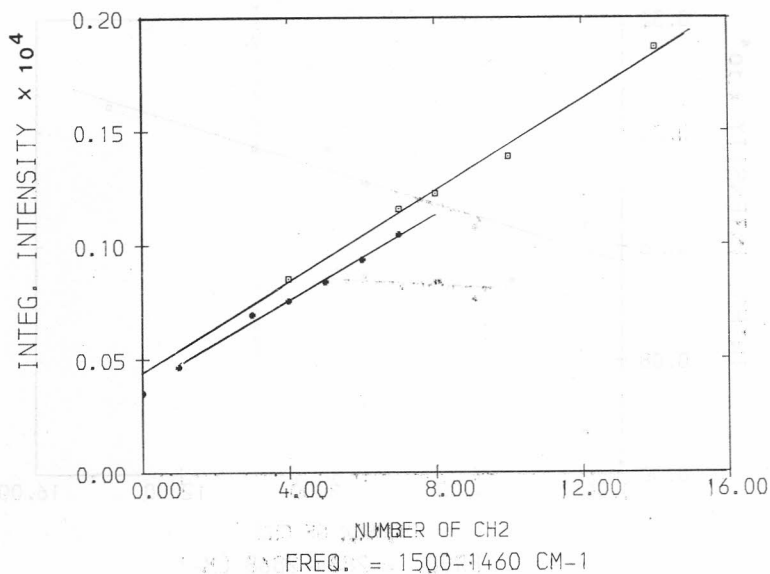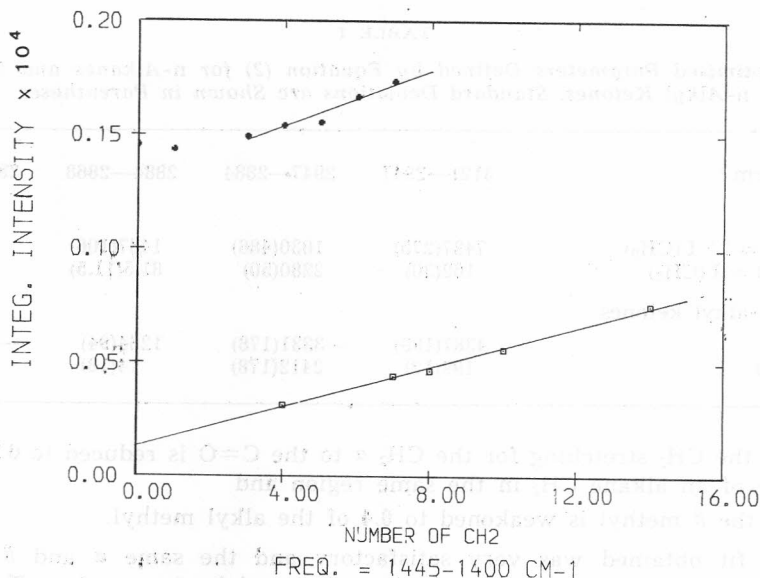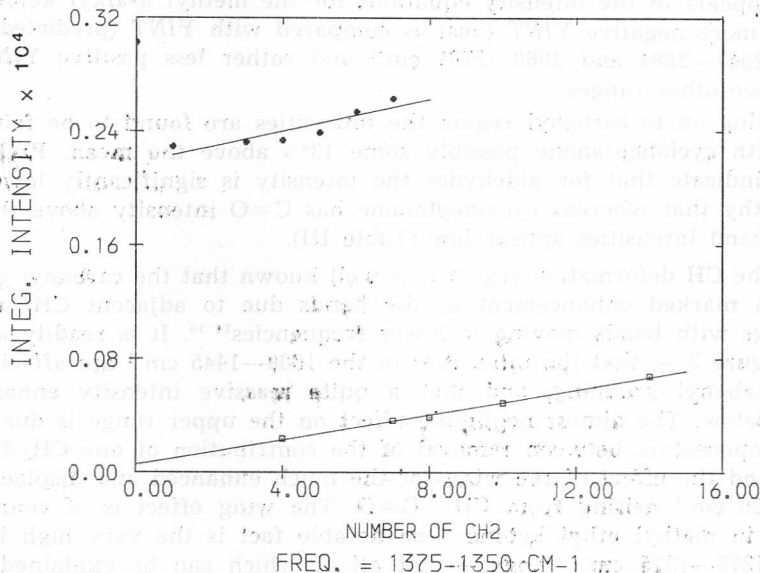
Figure 3(d)

Figure 3. Integrated absorption intensities (mol^{-1} dm^3 cm^{-2}) in defined spectral ranges (scissoring region) for alkanes ☐ and methyl *n*-alkyl ketones ⊞ *versus* the number of CH$_2$ units in the alkyl chain.

For methyl ethyl ketone the following assumptions were tried:

(i) that the contribution of CH$_3$(CO) to each region is equal to 1/2 of the intensity of acetone (propanone) in the same range;

TABLE I

The Optimised Parameters Defined by Equation (2) for n-*Alkanes and Methyl*
n-*Alkyl Ketones. Standard Deviations are Shown in Parentheses*

ν Range/cm^{-1}	3121—2947	2947—2884	2884—2868	2868—2761
alkanes				
YINT $= 2 \cdot$ I (CH$_3$)	7427(275)	1030(486)	1487(106)	368(195)
GRAD $=$ I (CH$_2$)	162(30)	2280(50)	81.5(11.5)	830(21)
methyl n-alkyl ketones				
YINT	4387(199)	—3331(178)	1264(94)	—1273(41)
GRAD	199(12)	2412(178)	14(18)	854(8)

(ii) the CH$_2$ stretching for the CH$_2$ α to the C$=$O is reduced to 0.2 of the intensity of an alkane CH$_2$ in the same region and

(iii) the β methyl is weakened to 0.4 of the alkyl methyl.

The fit obtained was very satisfactory and the same α and β factors serve to produce reasonable predictions for cycloheptanone (see Table II). There is some slight shift of intensity indicated towards lower frequencies, which appears in the intensity equations for the methyl n-alkyl ketones as a slightly more negative YINT (obs) as compared with YINT (predicted) in the ranges 2947—2884 and 2868—2761 cm^{-1} and rather less positive YINT (obs) in the two other ranges.

Moving on to carbonyl region the intensities are found to be fairly constant with cycloheptanone possibly some 13⁰/₀ above the mean. Preliminary studies indicate that for aldehydes the intensity is significantly lower. It is noteworthy that whereas cycloheptanone has C$=$O intensity above the mean its CH band intensities appear low (Table III).

In the CH deformation region it is well known that the carbonyl grouping causes a marked enhancement of the bands due to adjacent CH$_2$ and CH$_3$ groupings with bands moving to lower frequencies[14-16]. It is readily apparent from Figure 3 — that the intensities in the 1500—1445 cm^{-1} are affected little by a carbonyl grouping, and that a quite massive intensity enhancement occurs below. The almost negligible effect on the upper range is due in part to a compensation between removal of the contribution of one CH$_2$ from the region and the effect of the wings of the much enhanced and displaced band near 1420 cm^{-1} arising from CH$_2$—C$=$O. The wing effect is of course most marked in methyl ethyl ketone. One notable fact is the very high intensity in the 1375—1325 cm^{-1} range — not all of which can be explained by the CH$_3$ C$=$O umbrella vibration. Di-n-hexyl ketone shows about an extra 1000 cm^{-2} mol^{-1} dm^3 compared with expectations for an alkyl. There is clearly an enhancement of the CH$_2$ wagging vibration (alkanes near 1305 cm^{-1}) just as there is for the CH$_3$ umbrella vibration.

The results of fitting the observed intensities of the methyl deformation region to equation (2) for both n-alkanes and n-alk-2-ones are given in Table IV. The methyl umbrella region is enhanced by a factor of 10 and the CH$_2$ wagging region by a factor of 40. Taking half of the intensity of acetone

TABLE II

Observed and Predicted CH Stretching Intensities (mol⁻¹ dm³ cm⁻²) for a Variety of Ketones

v̄ Range/cm⁻¹	3121—2947		2947—2884		2884—2868		2868—2761	
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
compound								
methyl cyclohexane	4213	4524	16170	11915	1366	1151	5532	4334
methyl ethyl ketone	2907	2258	1711	985	295	351	456	411
cycloheptanone	2403	842	8494	11856	644	424	2345	4316
di n-hexyl ketone	10518	8593	17230	17446	2586	2074	6114	6344
acetone	1481		650		74		342	
methyl n-alkyl ketones								
YINT	4387(66)	4259	−3331(178)	−2353	1264(94)	555	−1273(41)	−807

TABLE III

Intensities of C = O Stretch (mol⁻¹ dm³ cm⁻²) in Range 1750—1675 cm⁻¹

acetone	6640	non-2-one	6680
but-2-one	6490	dec-2-one	7170
hept-2-one	6700	cycloheptanone	7610
oct-2-one	6580	di-n-hexyl ketone	6570

as representative of the contribution of CH_3CO and half of *YINT* for alkanes as the intensity due to the alkane CH_3 then an estimate of the CH_2CO may be made from the intensities of methyl ethyl ketone (but-2-one). These figures are also given in Table IV. Using these the *YINT* for methyl n-alkyl ketones can be estimated by

$$YINT \text{ (pred)} = I\,(CH_3CO) + I\,(CH_3 \text{alk}) + I\,(CH_2CO) - GRAD(\text{alk}) \qquad (3)$$

The results agree very favourably with the observed, though a slight shift to higher frequencies is discernible. The group contributions can now be used to predict the intensities of cycloheptanone and of di-n-hexyl ketone, for both of which we have data. Agreement is very good for di n-hexyl ketone, though the experimental values for cycloheptanone do seem low. As mentioned earlier it may be significant that the carbonyl intensity is high.

In the Raman studies, for which we are only able to report preliminary results, measurements have been made on a series of dialkyl sulphides. From Table V. it is clear that CH_3S- and CH_3CH_2S- both lead to bands, not only at characteristic frequencies, but with characteristic intensities.

The intensities are defined by

$$I = \frac{I_{\text{obs}}\,(1 - \exp\,(-hc\bar{\nu}/kT))}{(\bar{\nu} - \bar{\nu}_e)^4\,\bar{\nu}} \qquad (4)$$

where I_{obs} is the measured intensity corrected for instrumental effects, $\bar{\nu}$ is the Raman shift and $\bar{\nu}_e$ is the exciting wave number. The intensities are scaled so that the 459 cm⁻¹ band complex of CCl_4 has an intensity of 100 units.

DISCUSSION

The earliest integrated intensity studies of the characteristic bands of alkanes were carried out by Francis[17]. The integrated intensities of stretching and bending bands were shown to be approximately proportional to the number of hydrogen atoms, though strong substituent effects were later identified in a number of investigations exemplified by that of Higuchi, Kuno, Tanaka and Kamada[18]. For alkanes themselves the current results show values for CH_3 stretching (= (sum of *YINT*)/2) and for CH_2 stretching (= sum of *GRAD*) of 5150 (± 530) and 3353 (± 112) mol⁻¹ dm³ cm⁻² respectively.* These are in the ratio 3 : 2 well within experimental error. Wexler[19] and Francis[17] quote

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* 1 mol⁻¹ dm³ cm⁻² ≡ 1 dark ≡ 0.01 km mol⁻¹, respectively.

TABLE IV

Observed and Predicted Intensities $(mol^{-1} \cdot dm^3 \cdot cm^{-2})$ for Methyl Deformation Regions of Alkanes and Alkones

ν Range/cm⁻¹	1500—1460		1460—1445		1445—1400		1400—1375		1375—1325	
	AINT	GRAD	AINT	GRAD	AINT	GRAD	AINT	GRAD	AINT	GRAD
Alkanes	439(40)	100(4)	303(28)	63(3)	129(13)	44(1.4)	264(7)	12(1)	55(14)	44(1.5)
Alk-2-ones	385(16)	93(4)	294(8)	70.5(1.5)	1294(40)	61(18)	620(18)	6(4)	2176(57)	56(12)
Int/CH₃(alk)	220		152		65		132		28	
Int/CH₃C : O	175		149		728		258		1512	
Int⁺/CH₂C : O	70		224		640		90		720	
AINT predicted from above	365		461		1389		4689		2216	
di n-hexyl ketone										
pred.	1379		1255		1761		540		1847	
obs.	1434		969		1694		790		1904	
cycloheptanone										
pred.	940		700		1456		228		1616	
obs.	325		947		1251		164		1210	

* As derived by fitting methyl ethyl ketone taking contribution from CH₃ (CH₂) as in alkanes.

TABLE V

A Listing of Frequencies and Raman Scattering Cross Sections, as Defined by Equation (4), of Bands Which are Characteristic of CH_3S—, CH_3CH_2S— and of —CH_2S—. The Intensity Scale is such that the 459 cm^{-1} Band of CCl_4 has an Intensity of 100

CH₃SCH₃ v	I''	CH₃SC₂H₅ v	I''	C₂H₅SC₂H₅ v	I''	CH₃S(nC₃H₇) v	I''	CD₃SCD₃ v	I''	Mode
693	48.0	658	26.9	641	15.4	647	9.6	642	37.1	
				658	19.4	669	4.3			
744	14.8	682	10.8	694	14.7	699	10.1	707	11.5	CS
						724	10.8			
		729	16.9	766	0.8	749	5.3			
						785	3.1			
600—800	62.8	1050	53.6	1048	50.3		43.2		48.6	Total $v_{c—s}$
		2728	2.4		4.6					v (S—C₂H₅)
			0.8	2733	2.5	2735	1.2			
2834	4.6	2836	3.2			2829	2.1	2037	1.8	v_{CH} (S — CH₂)
		2931	17.9	2932	18.6	2936	13.3			v_{CH} (S — CH₃)
2987	13.3	2967*	21.3			2986	10.5	2240	15.3	v_{CH} (S — CH₂)
										v_{CH} (S — CH₃)

4500 and 3700 and 3900 and 3300 mol^{-1} dm^3 cm^{-2} Francis's CH$_3$ values appear rather low and Wexler's CH$_3$ and CH$_2$ values seem to have some of CH$_3$ intensity transferred to the CH$_2$. In the deformation region it is necessary to define frequency limits and to be consistent in background definition. In the present work we consistently include all absorption in the spectral region of interest without seeking to decompose absorptions into contributions from different bands. Such latter procedures offer great scope for error and ambiguity. The presence of unidentified bands, of Fermi resonance components, of intrinsic band asymmetries (due for example to Coriolis coupling), and of uncertainties in wing shapes — all of these, and no doubt many others, render band deconvolution procedures undesirable. Jones[20] measured the molecular extinction coefficients of the component bands of *n*-alkanes — in the process identifying a third component at 1460 cm^{-1}. As quoted by Wexler[12] the data of references 19 and 17 both support values for the CH$_3$ antisymmetrical scissoring intensity (1460 cm^{-1}) of 480 mol^{-1} dm^3 cm^{-2} and for the umbrella mode of 200 mol^{-1} dm^3 cm^{-2}. Taking 1400 cm^{-1} as the separation point and extending the range of integration from 1500 to 1325 cm^{-1} leads to values of 435 and 160 mol^{-1} dm^3 cm^{-2} with uncertainties of about 10%.

Francis quoted an intensity reduction of CH stretching bands of 7 to 10 if a carbonyl groups is present (adjacent). In our interpretation of the intensity data the intensity ratio is given as

YINT (alkanes)/Intensity (acetone).

As the CH$_3$ symmetric stretch is moved to lower frequencies by the carbonyl it is necessary to combine the range 2884—2868 and 2868—2761 cm^{-1}. The ratios in the two upper ranges are little affected by the C=O but for consistency these too are combined. With these combinations the intensity reductions are 4.0 and 4.5 respectively, significantly less than proposed earlier.

Having established on a more quantitative basis than has previously been done the group intensities in CH stretching and deformation regions the question of the constancy of the effective atomic charge of the hydrogen atom can be re-examined. There does indeed appear to be a complimentarity in the effects of perturbing groups in that the carbonyl group greatly reduces the stretching intensity but enhances the bending intensities. We shall simply note at this stage that $\sum_i A_i/\nu_i^2$, where the sum is over the group vibrations, is much more constant that $\sum_i A_i$. Indeed for cycloheptanone where we note a general reduction in the CH$_2$ group intensities compared with that expected for an open chain ketone there is a compensatory increase in the C=O intensity, which may be a geometrical effect. This problem needs much more experimental and theoretical investigation.

So far we have not mentioned a recent important paper by Castiglioni, Gussoni and Zerbi[21]. The total integrated intensities in the CH stretching region and in the HCH scissoring region are reported for gaseous alkanes as well as a variety of ethenes, aldehydes, methanol, acetone and dimethylether. In Table VI. we compare the intensity predicted by the parameters in Table I. with the intensities as measured by Gussoni and colleagues. To conform with normal practice for gaseous intensity measurements our predictions are scaled by log$_e$ (10). The intensity ratio of the solution and gaseous intensities is seen

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TABLE VI

A Comparison of Solution Intensities of n-Alkanes Based on This Work With Gaseous Phase Results from Reference 12. All Intensities are in mol⁻¹ dm³ cm². »A'« Refer to Intensities Defined Using log_e (I_o/I) and »A« to the Base 10 Counterparts

Molecule	A_{calc}^{CH} (soln)	$A_{calc}'^{CH} \cdot 2.303$ $= A^{CH}$ (soln)	A'^{CH} (gas) Ref. 21	A' (gas)/A' (soln)
C_2H_6	10302	23725	17088	1.388
C_3H_8	13656	31444	22496	1.398
C_4H_{10}	17020	39190	28720	1.365
C_5H_{12}	20374	46913	34752	1.350
C_6H_{14}	23718	54613	40376	1.353

to range only from 1.350 to 1.398. This is close to the predictions of the Polo Wilson equation

$$\frac{A_L}{A_S} = \frac{(n^2 + 2)^2}{9n}$$

where n is the refractive index. Using n_D for CCl_4 the ratio predicted is 1.299. An analysis of the intensities was made in terms of the electrooptical parameters, the charge fluxes, $\partial q/\partial r_{CH}$, and the atomic equilibrium charges, q_H°. It was shown that for all alkanes, alkenes and alkynes the ratio of the total intensity in the deformation region (1500—400 cm⁻¹) to the total CH stretching intensity (3000—2500 cm⁻¹) varies in a smooth fashion with the derived atomic charge q_H° as one might expect. However for the alkynes both the stretching and deformation intensities are considerably higher than for alkanes in accord with their higher King's effective charges.

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SAŽETAK

Uporaba apsolutnih intenziteta vibracijskih vrpci u strukturnoj analizi.
I. n-Alkani i derivirani ketoni

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Opisano je sustavno istraživanje intenziteta skupinskih apsorpcijskih vrpci n-alkana i metil-n-alkilketona u tetraklorugljiku. Utvrđeni su doprinosi svake strukturne skupine ukupnom intenzitetu u određenom području, a rezultati su upotrijebljeni za procjenu spektralnih intenziteta metilcikloheksana, di-n-heksilketona i cikloheptanona. Varijacije u doprinosima skupina CH_2 i CH_3 uzrokovane blizinom karbonila, razmatraju se s obzirom na konstantnost Kingova efektivnog atomskog naboja.

Utvrđene su Ramanove skupinske frekvencije i intenziteti za CH_3S i CH_3CH_2S. Čini se da su intenziteti Ramanovih vrpci, iako teže mjerljivi, također uporabivi u strukturnoj analizi.