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### Group Additivity for the Band Strength of the CF-Chromophore for IR-Photochemistry

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### Absorptionsspektren, Infrarot / Dipolmoment / IR-Photochemie / Isotope / Photochemie / Quantenmechanik

Integrated band strengths for rovibrational absorption in the frequency range of the CF-chromophore (800 to 1300 cm<sup>-1</sup>) have been obtained from vapour phase IR-spectra of twelve fluoroalkanes containing one or more CF groups. It is found that the chromophore band strength is about 1.7 (pm)<sup>2</sup> for each CF group with some minor variations due to neighbouring substituents at the CF carbon atom. These variations can be accounted for by a simple, empirical equation. The results are discussed in relation to the chromophore principle in IR-photochemistry. The frequency distribution of the chromophore absorption for primary, secondary, and tertiary alkyl fluorides is considered. The primary CFchromophore (R – CH<sub>2</sub> – F) is suggested to be a particularly useful general chromophore for CO<sub>2</sub>-laser pumping. The foundations of the group additivity for chromophore band strengths and some further applications are discussed as well.

#### 1. Introduction

Integrated band strengths for the fundamental absorption of strongly IR-active vibrations are of crucial importance for IRphotochemistry [1, 2]. In a simple, approximate limiting case, the optimum steady state rate coefficient for IR-photochemistry is proportional to the integrated band strength G of a vibrational fundamental pumped by a laser with appropriate frequency [3]. Furthermore, there is good evidence, that a chemical reaction occurring under ordinary conditions in IRphotochemistry is largely independent of the type and "location" of the pumped vibration within a molecule. Ideally, one should thus be able to obtain a fast IR-photochemical reaction by attaching to a desired reactive molecule a nonreactive *chromophore*, which absorbs strongly the radiation from easily available laser light sources, such as the  $CO_2$ -laser (we shall call

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this the "chromophore principle for IR-photochemistry"). This expectation was the main impetus for our starting systematic investigations of the properties of IR-chromophores.

Although the difficulties of the pioneer period [4] of the determination of band strengths have long been overcome and an appreciable number of band strengths are now available [5-8], there are still surprisingly few systematic investigations and band strengths are not routinely determined in a spectroscopic context. In fact, there is a severe lack of adequate band strength data. In our search for simple rules connecting chromophore band strengths with molecular structure, we therefore had to rely largely on new measurements in our laboratory. In a previous investigation it could be shown that the band strength of the isolated CH-chromophore depends in a simple, predictable way upon the local environment at the C-atom [9, 10]. The CH-chromophore is ideally suited for model investigations, because it is so well separated in frequency from other absorptions. However, it is not directly important for IR-photochemistry. We shall therefore discuss in the present contribution the properties of the "isolated" CFchromophore, which leads to strong absorptions in the range of the emission of the CO<sub>2</sub>-laser, which is the most widely used light source for IR-photochemistry.

Beyond the scope of IR-photochemistry, a systematic understanding of band strengths of IR-chromophores is valuable for analytical purposes and for understanding the radiative transport in gases, for instance in polluted atmospheres. In an even more general context, the band strengths are related to molecular electronic properties (the electric dipole moment derivatives to zero order) and thus they help our understanding of molecular electronic structure [11-14]. We should mention here also the recent work of Toennies and coworkers on energy transfer in collisions of ions (Li<sup>+</sup>, H<sup>+</sup>) with fluorocarbons and other molecules containing highly polar bonds [15, 16]. Here, too, the dipole moment derivatives play an important role and correlations with band strength data may be possible.

#### 2. Experimental

1-F-butane was prepared by fluorination of 1-Br-butane with KF [17]. 2-F-butane was prepared by addition of HF to butene-1 [18]. 1,4-difluorobutane was prepared by fluorination of 1,4-dichlorobutane with KF [19]. 2-F, 2-methylpropane (t-butylfluoride) was prepared by Dr. H. Henle through fluorination of t-butanol with HF. 1-F, 1-D-butane was prepared here for the first time in a three step synthesis. First, we prepared 1-D-butanol by reduction of butanal-1 with LiAlD<sub>4</sub> [20]. In the second step the butanol was brominated with PBr<sub>3</sub>, giving the bromobutane [21]. The fluorination was then performed in the third step as for 1-F-butane above. CFDCl<sub>2</sub> was prepared by Hans-Rolf Dübal through partial fluorination of CDCl<sub>3</sub>. The other compounds were obtained from Fluorochem (CFHCl<sub>2</sub>, 1-F-ethane), from Ventron (1-F-hexane, 1-F-octane, m-F-toluene, and 2,3,5,6-tetrafluorotoluene), and from Merck, Darmstadt (CDCl<sub>3</sub>, butane). The identity of the compounds was checked by their IR and NMR spectra [22] and the purity was checked by gaschromatography using various columns. Four of the substances were found to be practically pure, all others were further purified gaschromatographically before taking the spectra. T-butylfluoride and 2-F-butane were found to be somewhat unstable and were therefore stored at liquid nitrogen temperature. The substances were outgassed by several freeze-pumpthaw cycles in order to remove dissolved air. They were handled in a standard vacuum line equipped with Setra and Baratron capacitance manometers which were recalibrated absolutely, using dibutylphtalate and mercury manometers. The sample cells were made of glass,

stainless steel and teflon and had various lengths (49 to 201 mm) in order to check for adsorption effects. For the substances with high boiling points, adsorption presented some problem. This was taken care of by first saturating the walls and O-rings with increased pressure and by then controlling the IR-adsorption at one frequency during the time of the measurement.

Most spectra were measured with a grating spectrometer (Zeiss IMR 25) using spectral bandwidths (FWHM) between  $0.5 \text{ cm}^{-1}$  and  $1.4 \text{ cm}^{-1}$ . The bandwidth- and frequency-calibration was performed using NH<sub>3</sub> and CH<sub>3</sub>F [24]. With 10<sup>5</sup> Pa of N<sub>2</sub> (Messer Griesheim 4.6) added for pressure broadening the resolution is adequate for obtaining accurate band strengths for all but the lightest molecules, where corrections of at most a few percent would have to be applied because of the limited resolution [23]. The spectra were plotted in an appropriate manner and evaluated using a Hewlett Packard 9821 A desk calculator and digitizerplotter (9864 A and 9862 A). In addition, some spectra were taken on our new BOMEM DA.002 interferometric spectrometer at a higher resolution, up to 0.01 cm<sup>-1</sup> apodized resolution in the cases where rotational structure could be resolved. However, the high resolution results and their evaluation are only of indirect relevance for the present work and will be reported in detail elsewhere [25].

#### 3. Results and Discussion

# 3.1. The Chromophore Principle and the Dynamics of the CF-Chromophore in Halogenated Hydrocarbons

In a standard discussion of vibrational band intensities one might derive a separable harmonic Hamiltonian using normal coordinates Q and relate the integrated band strengths G for the fundamentals approximately to the derivatives of the components of the electric dipole moment  $\mu$  with respect to the normal coordinates:

$$G_{\text{band}} = \int_{\text{band}} \sigma(v) \, \mathrm{d} \ln v \propto \left| \left( \frac{\partial \mu}{\partial Q} \right)_{\mathrm{e}} \right|^2 \tag{1}$$

 $\sigma(v)$  is the frequency dependent molecular absorption cross section. As normal vibrations are in general delocalized, this procedure does not provide a simple understanding of the intensity contributions of localized groups or chromophores within a molecule. Particularly for very strongly absorbing chromophores such as CF we know in advance, that the absolute value of the derivative with respect to one local coordinate, the CF bond length, will be particularly large. It is thus natural to write the Hamiltonian in a basis of local states  $\varphi_k$ , which carry most of the oscillator strength:

$$\hat{\mathbf{H}} = \hat{\mathbf{H}}_0 + \hat{\mathbf{H}}_1 \tag{2}$$

$$\hat{\mathbf{H}}_0 \varphi_k(\mathbf{r}) = E_k^0 \varphi_k(\mathbf{r}) \,. \tag{3}$$

In an ideal situation with one strong chromophore (coordinate  $r_n$ ), one will have

$$\left| \left( \frac{\partial \mu}{\partial r_n} \right)_{\mathbf{e}} \right|^2 > \left| \left( \frac{\partial \mu}{\partial r_j} \right)_{\mathbf{e}} \right|^2.$$
(4)

In a zero order picture, the strong vibrational transitions will involve changes of one quantum in the chromophore vibration. The Hamiltonian  $\hat{\mathbf{H}}_1$  couples the zero oder states. This leads to the appearance of further absorption bands. If  $\hat{\mathbf{H}}_1$  is small, such that

$$|\mathbf{H}_{kj}| = |\langle \varphi_k | \hat{\mathbf{H}} | \varphi_j \rangle| \ll E_k^0$$
(5)

$$|\mathbf{H}_{kj}| \ge |E_k^0 - E_j^0| \tag{6}$$

for a typical absorbing  $(E_k^0)$  and nonabsorbing  $(E_j^0)$  state, then the band strength will remain concentrated in a relatively small frequency range. The transition moment for an absorbing chromophore state  $\varphi_k$  in the zero order picture would be (for each component of the dipole operator  $\hat{\mu}$  in a Cartesian system):

$$M_{k0}^{0} = \langle \varphi_{k} | \hat{\mu} | \varphi_{0} \rangle . \tag{7}$$

One has a conservation of band strength under the perturbation  $\hat{\mathbf{H}}_1$  (basis  $\chi_k$  of eigenstates of  $\hat{\mathbf{H}}$ ):

$$\chi_k = \sum_j c_{kj} \varphi_j \tag{8}$$

$$M_{kj} = \langle \chi_k | \hat{\mu} | \chi_j \rangle \tag{9}$$

$$|\mathcal{M}_{k0}^{0}|^{2} = \sum_{l} |\mathcal{M}_{l0}|^{2} .$$
 (10a)

More generally, if several ground states m contribute to absorption, one has the conservation law

$$\sum_{n} \sum_{m} |M_{nm}^{0}|^{2} = \sum_{n} \sum_{m} |M_{nm}|^{2}$$
(10b)

$$G^0 = G_{\rm chr.} \tag{11a}$$

$$G_{\rm chr.} = \int_{\rm chromophore\ range} \sigma(\nu) \, d \ln \nu \,. \tag{11b}$$

In practice this implies that a chromophore band strength can be obtained by integrating all the band strengths in a sufficiently large frequency range, provided that there are no appreciable contributions from other chromophores to the absorption in this range. This reasoning holds independently of the zero order picture used or the nature of the perturbing Hamiltonian  $\hat{\mathbf{H}}_1$ . For instance in the case of the isolated CH-chromophore, the zero order Hamiltonian can be taken to be a separable normal or local coordinate Hamiltonian, since the isolated local high-frequency CH-stretching coordinate coincides practically with a normal coordinate.  $\hat{\mathbf{H}}_1$  arises then mainly through anharmonic and rovibrational interactions. We have found in this case Fermi-resonances spreading the intensity over a few hundred cm<sup>-1</sup> at most. For the CF-chromophore the situation is quite different. The local basis states  $\varphi_k$  are no good approximations even for harmonic potentials. There will be strong couplings to close lying C - C (local) states and, perhaps to a lesser extent, to CH<sub>2</sub>-wagging, CH<sub>3</sub>-rocking and CH<sub>2</sub>-twist- and rocking states. All of these are close in frequency to the C-Fstretching local vibration [26] and will couple. Particularly in larger molecules these fundamental vibrational states are then further coupled to a dense set of overtone and combination states from lower frequency vibrations. This situation is shown schematically in Fig. 1. Of course the order, in which the various couplings are introduced, is arbitrary. There are two main questions which have to be answered empirically: (i) Can one derive a simple group additivity rule for band strengths that can be associated with the CF-chromophore? This would apply to the frequency range of about 800 to 1300 cm<sup>-1</sup>, where unsubstituted alkanes absorb weakly compared to the fluorinated ones. (ii) How is the chromophore intensity distributed within this frequency range?

We shall see that one CF group contributes roughly a constant amount of band strength to the frequency range of the CF



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chromophore, but that in this frequency range a considerable redistribution of intensity occurs, depending upon details of the vibrational dynamics. These results allow us to use the chromophore principle for the CF-chromophore in IR-photochemistry. Efficient absorption of radiation is guaranteed by the conservation of chromophore intensity. However, the states prepared by IR-absorption in large polyatomic molecules are nonlocal under ordinary conditions, because it can be concluded from the relatively large frequency spreads that extremely short time scales would be needed to create a local CF excitation by irradiation with infrared light.

#### 3.2. Band Strengths

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Table 1 summarizes our results for the band strengths of the CF-chromophore in 14 molecules, including a few results from the literature. For most molecules there were no previous data available. The second column shows several (at most three) frequencies for different bands in the CF-chromophore range with intensities decreasing in the order shown (i. e. the strongest band first etc.). Because most bands are very broad (see Fig. 2 below) their frequency has only been given to within 10 cm<sup>-1</sup>. Some accurate band centers can be determined for the small

Table 1 Summary of the experimental results

Molecule	$\tilde{v}_j/\mathrm{cm}^{-1}$	$G_{\rm Chr.}/(\rm pm)^2$	Reference
CH <sub>4</sub> F	1050 (1180)°)	1.7	a)
C,H,F	1050, 880, 1120	1.77	this work
n-C₄H₀F	1040, 1080, 960	1.73	this work
s-C₄H₀F	1130, 910, 990	1.85	this work
t-C₄H₀F	890, 1200, 1260	1.91	this work
F(CH <sub>2</sub> )₄F	1060, 1040, 960	3.28	this work
n-C <sub>4</sub> H <sub>8</sub> DF	1070, 950, 1130	1.85	this work
n-C <sub>4</sub> H <sub>10</sub>	800 to 1200	0.12	b)
n-C <sub>6</sub> H <sub>13</sub> F	1060, 1030, 920	1.72	this work
n-C <sub>8</sub> H <sub>17</sub> F	1030, 1070, 960	1.97	this work
CFHCi,	1080	2.43	this work
CFDCl,	1090, 950°)	2.41, 2.00°)	this work
CDCl,	910°)	2.17 (1.3)	this work <sup>d</sup> )
CFCl	1090	2.53	a)
C,H,F	1270, 1150, 930	1.9	this work
$C_7H_4F_4$	1070, 1170, 1020	7.0	this work

<sup>a)</sup> See ref. 23 and the literature quoted there, see also ref. 8 and the literature quoted there; <sup>b)</sup> see ref. 27. We have remeasured a slightly lower value; <sup>c)</sup> C-D bending vibration; <sup>d)</sup> see ref. 28, quoted in ref. 29, Tanabe and Saeki, ref. 30 quoted also by Pugh and Rao [8], report 1.6 (pm)<sup>2</sup>, somewhat closer to our value; <sup>e)</sup>  $\nu_6$  (1180 cm<sup>-1</sup>) is coupled to  $\nu_3$  (1050 cm<sup>-1</sup>) by Coriolis interaction [31]. However, the intensity transfer is small and the band intensity of 1.7 (pm)<sup>2</sup> includes only the band at 1050 cm<sup>-1</sup>.

molecules and for t-C<sub>4</sub>H<sub>9</sub>F [25], but these are not of interest in the present context. The third column contains  $G_{chr}$ , the sum of integrated band strengths for all vibrational bands in the CFchromophore range, the limits of which are 800 and 1300 cm<sup>-1</sup>. For most molecules the strong absorptions are concentrated in a much narrower range. It is seen immediately that  $G_{chr}$  is about the same for all molecules containing one CF-bond, with minor systematic variations. The absolute error, including systematic errors is estimated to be substantially less than 30% in all cases but the toluenes, where the adsorption problems were most serious. This precision is sufficient for our considerations.

Some trends in table 1 deserve specific discussion. When we consider the series of fluorobutanes (CH<sub>3</sub>)(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>F, CH<sub>3</sub>CHFCH<sub>2</sub>CH<sub>3</sub>, and (CH<sub>3</sub>)<sub>3</sub>CF we find a slight, systematic increase of  $G_{chr}$ . Also, m-fluorotoluene has a somewhat stronger absorption. These changes can be interpreted by the slightly different molecular environment. The value of  $G_{chr}$  for  $n-C_8H_{17}F$  is somewhat larger. This can be partly related to the absorption from other vibrations, which contribute some intensity in such a large molecule. We have given in table 1 for comparison also the integrated band strength of butane in the CF-chromophore range. This is small, which justifies our basic assumption of the previous section. The value of  $G_{chr}$  for  $\alpha, \omega$ difluorobutane is about twice the value for n-fluorobutane. This supports simple group additivity for the band strengths of the two practically noninteracting CF groups. The minor effects discussed so far are all hardly significant within experimental error. A more significant increase in the CF band intensity can be observed for the chlorinated methanes CFHCl<sub>2</sub>, CFDCl<sub>2</sub>, and CFCl<sub>3</sub>, where one has about  $G_{chr}$  2.5 (pm)<sup>2</sup>. For CFDCl<sub>2</sub> this refers only to the band strength of the CF-stretching band at 1090 cm<sup>-1</sup>. The CD-bending vibration at 950 cm<sup>-1</sup> has appreciable intensity ( $G = 2.0 \text{ (pm)}^2$ ) and can be used for isotope selective IR-photochemistry [32]. Although this band falls into the CF chromophore range and some interaction with the CF stretching vibration must be anticipated, the separation of band strengths in table 1 makes sense, as demonstrated by the intensity of the isolated CD-bending vibration in CDCl<sub>3</sub>. This point is also supported by the consideration of band strengths in CHCl<sub>2</sub>F and CFCl<sub>3</sub>. The case of n-C<sub>4</sub>H<sub>8</sub>DF, also shown in table 1, is different, because the CD absorption in non-chlorinated alkanes seems to be generally much smaller. For instance, in the case of  $CH_3D$  it is less than 0.4 (pm)<sup>2</sup> (see Ref. [8]).  $n-C_4H_8DF$  nevertheless allows for interesting applications of the CF chromophore in selective IR-photochemistry [33].

The influence of alkyl groups and chlorine atoms can be taken into account using the empirical eq. [10]:

$$\ln \left[ G/(\mathrm{pm})^2 \right] = A + B \sum_j n_j c_j \tag{12a}$$

A and B are constants and the  $n_j$  are the number of atoms or groups of kind j in the immediate neighbourhood of the CF-chromophore. The coefficients  $c_j$  indicate the relative influence of the group j. Setting  $c_{Cl} = 1$  by definition, neglecting hydrogen and treating the aromatic compounds separately one obtains for the present series of molecules an equivalent form:

$$\ln \left[ G/(\mathrm{pm})^2 \right] = \alpha + \beta (n_{\mathrm{Cl}} + \gamma n_{\mathrm{alkyl}})$$
(12b)

A good fit (correlation coefficient = 0.99) is obtained with  $\alpha = 0.52$ ,  $\beta = 0.17$ , and  $\gamma = 0.25$ . In contrast to the weaker and much more sensitive CH-chromophore, the influence of neighbouring groups is hardly significant for the CF-chromophore: The chromophore intensity is essentially a constant.

Much more significant is the influence of the structural environment of the CF-chromophore upon the distribution of absorption strength within the rather wide chromophore frequency range. This point is of obvious importance for the practical application of the group additivity for band strengths in IR-photochemistry. The low resolution traces of spectra in Fig. 2 demonstrate the coarse redistribution of chromophore intensity for the series of alkylfluorides. For the primary alkylfluorides the band strength remains concentrated in a small range of frequencies around  $1050 \pm 40 \text{ cm}^{-1}$ . For the secondary and tertiary alkylfluorides the intensity spreads more



The absorption of fluoroalkanes in the frequency range of the CF-chromophore. For  $t-C_4H_9F$  the band at 1030 cm<sup>-1</sup> has been shown for a higher pressure and one weaker low frequency band has not been included in the figure. One may note the "spreading of intensity" when going from the primary to the tertiary fluoroalkanes

to the outer boundaries of the chromophore frequency range. This effect is so pronounced, that for instance in the case of (CH<sub>3</sub>)<sub>3</sub>CF an efficient resonant pumping with a CO<sub>2</sub>-laser would not be possible (note that for the purpose of visualization the central band has been presented for a factor of 15 higher pressure compared to the outer bands). Very similar spectral structures are seen in other secondary and tertiary alkylfluorides. They can be interpreted by the more important coupling to the close lying C-C vibrations. Because this coupling is largely harmonic, the redistribution of intensity might be partly predicted by an appropriate normal coordinate analysis. However, the couplings and frequency spreads are of the same order of magnitude as the anharmonic resonances found in the series of 1-H-perfluoroalkanes, for instance, and we prefer the "naive" view in terms of coupled local vibrational states for the reasons already discussed in section 3.1. Some interesting additional considerations arise in the case of symmetric molecules such as (CH<sub>1</sub>)<sub>3</sub>CF, but these questions are best dealt with separately [25].

## 3.3. Conclusions for the use of the CF-chromophore in IR-photochemistry

The present investigation of the CF-chromophore constitutes the first systematic approach to the quantitative use of the chromophore principle in IR-photochemistry. From the properties of the CF-chromophore summarized in table 1 and Fig. 2 we can draw the following main conclusions:

(i) For primary alkylfluorides (R-CH<sub>2</sub>F) the chromophore band strength is about constant, independent of R, and equal to  $G = 1.7 \, (\text{pm})^2$ . Minor variations due to the substitution of H by other atoms or alkyl groups can be accounted for using a simple, empirical equation.

(ii) The chromophore intensities from several primary, separate  $-CH_2F$  groups within the same molecule are additive.

(iii) For primary alkylfluorides the chromophore intensity remains concentrated in the frequency range accessible to the  $CO_2$ -laser (900 to 1100 cm<sup>-1</sup>). This fact and the high activation energy for HF elimination (270 to 300 kJ mol<sup>-1</sup>) render the primary CF-chromophore a rather convenient, nonreactive chromophore for IR-photochemistry.

(iv) The secondary or tertiary CF-chromophores ( $R_2$ CHF and  $R_3$ CF) are less suitable for practical use in IR-photochemistry. Although the total chromophore intensity  $G_{Chr.}$  seems to be large and fairly constant, it is spread over a very wide range of frequencies. Of course, some of the resulting absorption bands may still be useful for CO<sub>2</sub>-laser pumping. However, there is in general no guarantee for this, particularly in the case of tertiary fluorides. In addition, the secondary and tertiary fluorides tend to be less stable chemically.

Beyond the applications in IR-photochemistry the group additivity established here for the CF-chromophore is of interest in various ways, of which we mention as a practical example the determination of the concentration of fluoroalkanes, for which the band strength has not been measured and may not be easily measurable. For instance, we have found this method useful for estimating low vapour pressures of nonvolatile compounds at high temperatures [25]. On a more fundamental level, the rather constant, additive chromophore band strengths correspond to a "local" electronic property of a group within a molecule. There is thus a direct relationship to the chemist's concept of local group properties, of which molecules are built. This should be seen in contrast to vibrational or rovibrational molecular states, which are in general highly delocalized, particularly so for the states associated with the CF-chromophore in large fluoroalkanes.

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