Infrared intensity analysis of molecules C_2H_6, C_2D_6, C_2F_6 and CF_4 zero and first order approximations

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Abstract. Infrared intensity formulae for C_2H_6 and C_2D_6 are derived following the first order approximations. Using the experimental intensities in the intensity equations, the first order coefficients are calculated. They are observed to be negligible compared to the accuracy limits within which the intensities can be measured. Correlating the experimental intensities to the intensity expressions of C_2F_6 and following the zero-order approximations, the bond dipole moment μ and its derivative ϵ are calculated for the C—F bond. Substituting these in the intensity equations of CF_4, transferability of the bond moment parameters is discussed.

Keywords. Intensity equations; bond dipole moment; zero order approximation; first order approximation.

1. Introduction

It is well-known that the infrared intensities are due to changes in the dipole moment during the fundamental oscillations. Equations connecting the changes in the dipole moment P with respect to the symmetry coordinates S have been derived by Wilson *et al* (1955), Straley (1955) and Sverdlov (1961). $(\partial P/\partial Q)$ values, where Q is a normal coordinate of the molecule, can directly be calculated from the experimental intensities. Relation between $(\partial P/\partial Q)$ and $(\partial P/\partial S)$ can be written as:

$$(\partial P_\sigma/\partial Q) = (\partial P_\sigma/\partial S)\,(\partial S/\partial Q)$$

$$= (\partial P_\sigma/\partial S)\,L, \tag{1}$$

where $S = LQ$ and σ is the corresponding cartesian coordinate direction X, Y or Z. The term $(\partial P/\partial S)$ is a function of μ_n the bond dipole moment, and ϵ_n its derivative with respect to the bond length r_n ($\epsilon_n = \partial \mu_n/\partial r_n$). Infrared intensity formulae $(\partial P_\sigma/\partial Q)$ for any molecule can be derived as explained by Addepalli and Rajeswara Rao (1976) and Ramachary *et al* (1978). Thus μ and ϵ can be calculated making use of the experimental intensities $(\partial P/\partial Q)$.

In deriving the above intensity formulae, we have followed the zero-order approximation, *i.e.* when one bond is stretched, the dipole moment of that bond alone is changed and that of all the other bonds remains unchanged unless a change in their

length is induced.   Also, the change in the inter-bond angle does not alter the dipole moment of the bond.   This is stated mathematically as:

$$\partial \mu_i / \partial r_j = \epsilon_i \, \delta_{ij},$$

and $$\partial \mu / \partial \, \alpha \; = 0, \tag{2}$$

where δ_{ij} is the Kronecker delta function.

Gribov (1960, 1962) has derived expressions for the J_r part of our equations (explained in our earlier papers) following the first order approximation, *i.e.* assuming that $\partial \mu_i / \partial r_j \neq 0$ and $\partial \mu / \partial \, \alpha \neq 0$.   According to Gribov (1960, 1962), the change in the dipole moment vector in σth direction during a normal vibration is

$$(\partial P_\sigma / \partial \, Q_i) = \Sigma \, [(\partial \mu_{n\sigma} / \partial \, Q_i) \, n\sigma] + \Sigma \, [\mu_{n\sigma} \, (\partial \, n \, \sigma / \partial \, Q_i)]. \tag{3}$$

Then following the method of deriving the intensity equations as explained in our earlier papers

$$(\partial P_\sigma / \partial \, Q_i) = [(\partial P_\sigma / \partial \, d_i) \; \vdots \; (\partial P_\sigma / \partial \, \alpha_i)] \, (\partial r / \partial S) \, (\partial S / \partial \, Q_i)$$

$$+ \, (\partial P_\sigma / \partial n \, \sigma) \, (\partial \, n \, \sigma / \partial \, \rho_i) \, (\partial \rho_i / \partial r) \, (\partial r / \partial S) \, (\partial S / \partial \, Q_i), \tag{4}$$

$$= [J_d \; \vdots \; J_\alpha] \, u'L + J_\phi \, k_i \, \mu \, s' \, u' \, (L^{-1})^1. \tag{5}$$

J_r thus contains two parts *viz.*, J_d represening the change in the dipole moment vector with respect to the change in the bond length $(\partial \mu / \partial d)$, and J_α the change in the dipole moment with the change in the inter-bond angle $(\partial \mu / \partial a)$.

In the present work, intensity equations following the first order approximation are derived for the molecules C_2H_6 and C_2D_6 and the first order coefficients are calculated using the experimental intensities. μ and ϵ are also calculated for the C—F bond in hexafluorethane and carbontetrafluoride, following the zero-order approximation.

The present work on fluorine compounds suffers from one difficulty: unlike hydrogen, fluorine does not have isotopes and hence the validity of the results cannot be judged as in the case of isotopically substituted methanes and ethanes (Addepalli and Rajeswara Rao 1976).   Since the $(\partial P / \partial Q)$ values are published for C_2F_6 and CF_4 (Schatz and Hornig 1953; Mills *et al* 1958), the results obtained can be critically examined to a certain extent giving due tolerence to the structural differences of the two molecules; (C_2F_6 belongs to the point group D_{3d} and CF_4 to T_d).

2. Intensity formulae

2.1 *Ethane and ethane* d_6

The intensity formulae derived for the two infrared active species A_{2u} and E_u of the molecules C_2H_6 and C_2D_6 following the first order approximations are

A_{2u} species :

$$(\partial P/\partial Q_i)^Z = \sqrt{(2/3)} \; [(\partial \mu_1/\partial r_1) + 2(\partial \mu_1/\partial r_2)] \; L_{1i}$$

$$+ \{\sqrt{(1/3)} \; [(\partial \mu_1/\partial a_2) - (\partial \mu_1/\partial a_1)] - 2 \sqrt{(2/3)} \; \mu\} \; L_{2i},$$

$$i = 1 \text{ and } 2. \tag{6}$$

E_u species:

$$(\partial P/\partial Q_i)^{X, Y} = 2 \sqrt{2/3} \; [(\partial \mu_1/\partial r_1) - (\partial \mu_1/\partial r_2)] \; L_{1i}$$

$$+ 2/\sqrt{3} \; \{\mu - \sqrt{2} \; [(\partial \mu_1/\partial a_2) - (\partial \mu_1/\partial a_1)]\} \; (L_{2i} - L_{3i}),$$

$$i = 1, 2 \text{ and } 3. \tag{7}$$

In the above equations, corresponding to μ_1 of C_1H_1 bond, a_2 means $H_1\text{-}C_1\text{-}H_2$, $H_1\text{-}C_1\text{-}H_3$ or $H_1\text{-}C_1\text{-}C_2$, while every other angle is considered to be a_1. The above equations reduce to the zero-order equations if the first order terms $(\partial \mu_1/\partial r_2)$ and $[(\partial \mu_1/\partial a_2) - (\partial \mu_1/\partial a_1)]$ are set equal to zero. Thus the zero order equations are:

A_{2u} species:

$$(\partial P/\partial Q_i)^Z = \sqrt{2/3} \; \epsilon \; L_{1i} - 2 \sqrt{2/3} \; \mu \; L_{2i},$$

$$i = 1 \text{ and } 2. \tag{8}$$

E_u species:

$$(\partial P/\partial Q_i)^{X, Y} = 2 \sqrt{2/3} \; \epsilon \; L_{1i} + 2/\sqrt{3} \; \mu \; (L_{2i} - L_{3i}),$$

$$i = 1, 2 \text{ and } 3 \tag{9}$$

The $(\partial P/\partial Q_i)$ values for C_2H_6 and C_2D_6 as tabulated by Nyquist *et al* (1957) along with the corresponding frequencies ω_i are given in table 1. They state that for C_2D_6 the bands are well separated while for C_2H_6 they are overlapping. For instance, ν_5 and ν_7 are overlapping as also ν_6 and ν_8. It may be stated that ν_6 and ν_8 are also

Table. 1 Experimental intensity data of C_2H_6 and C_2D_6.*

	\multicolumn{3}{c}{C_2H_6}		\multicolumn{2}{c}{C_2D_6}
	ω_i cm^{-1}	$(\partial P/\partial Q_i)$ original	$(\partial P/\partial Q_i)$ altered	ω_i cm^{-1}	$(\partial P/\partial Q_i)$ original
A_{2u} type					
ν_5	3061·0	0·8457	0·8520	2169·4	0·5974
ν_6	1437·5	0·2437	0·2400	1112·2	0·2067
E_u Type					
ν_7	3139·9	0·9592	0·9540	2315·5	0·6892
ν_8	1525·6	0·3145	0·3145	1110·5	0·2582
ν_9	821·8	0·2085	0·2085	593·9	0·1536

*Data from Nyquist *et al* (1957).

overlapping for C_2D_6 as well. But their contribution to $\Sigma\ (\partial P/\partial\ Q_i)^2$ is small. Hence, this overlapping is not taken seriously. The separation of the bands introduces a lot of uncertainty. Hence, we shall first deal with C_2D_6. Substituting for $(\partial P/\partial\ Q_i)$ in (8) and (9) and then squaring and adding individually the intensity equations of each species as explained in our earlier papers, we obtain:

A_{2u} species:

$$\Sigma\ (\partial P/\partial\ Q_i)^2 = 0.3996$$

$$= (2/3)\ (\epsilon^2\ G_{11} + 4\ \epsilon\ \mu\ G_{12} - 4\ \mu^2\ G_{22}). \tag{10}$$

E_u species:

$$\Sigma\ (\partial P/\partial\ Q_i)^2 = 0.5653$$

$$= (4/3)\ [2\ \epsilon^2\ G_{11} + 2\ \sqrt{2}\ \epsilon\ \mu\ (G_{12} - G_{13})$$

$$+ \mu^2\ (G_{22} + G_{33} - 2\ G_{23})]. \tag{11}$$

Substituting the G elements (table 2) in (10) and (11), μ and ϵ can be solved for. We obtain two sets of values for μ and ϵ as the equations are quadratic. Similar equations can be had for C_2H_6 also and using the intensity values given in table 1, μ and ϵ can be calculated. It is also possible to combine the two A_{2u} or the two E_u equations of C_2H_6 and C_2D_6 together and calculate the μ and ϵ values. The results are presented in column 2 of table 3. It can be seen from the table where μ and ϵ values obtained from different combinations of A_{2u} and E_u are presented, that the third set which involves the A_{2u} species of C_2H_6 and C_2D_6 gives rise to sharply different values of μ and ϵ, when compared to the earlier two sets obtained by using the data of C_2H_6 and C_2D_6 separately. The results of C_2H_6 or C_2D_6 are reliable, since, without any modification in their values they lead to mutually consistent results.

Table 2. G—Elements.

G-Expressions	C_2H_6	C_2D_6	C_2F_6
A_{2u} Type			
$G_{11} = \mu_{c/3} + \mu_X$	0.6191	0.3179	0.0484
$G_{12} = (-4/3)\ a\mu_C$	−0.0612	−0.0612	−0.0612
$G_{22} = (16/3)\ a^2\mu_C + 2a^2\mu_X$	1.2326	0.7284	0.1872
E_u Type			
$G_{11} = (4/3)\ \mu_C + \mu_X$	0.6601	0.3681	0.0986
$G_{12} = (4\sqrt{2}/3)\ a\mu_C$	0.0865	0.0865	0.0865
$G_{13} = -(\sqrt{2}/3)\ a\mu_C$	−0.0217	−0.0217	−0.0217
$G_{22} = (8/3)\ a^2\mu_C + (5/2)\ a^2\mu_X$	1.3727	0.8869	0.1205
$G_{23} = -(2/3)\ a^2\mu_C + a^2\mu_X/2$	0.2241	0.0980	−0.0100
$G_{33} = (1/6)\ a^2\mu_C + a^2\mu_X$	0.5113	0.2591	0.0227

Table 3. μ and ϵ values.

Obtained by solving	With original intensities		With altered intensities	
	Set 1	Set 2	Set 1	Set 2
1. A_{2u} and E_u of C_2D_6	$\mu =$ 0·4221	0·3947	0·4221	0·3947
	$\epsilon =$ −0·6823	0·5357	−0·6823	0·5357
2. A_{2u} and E_u of C_2H_6	$\mu =$ 0·4391	0·4237	0·4254	0·4100
	$\epsilon =$ −0·6754	0·5880	−0·6794	0·5948
3. A_{2u} of C_2H_6 and C_2D_6	$\mu =$ 0·4306	0·0220	0·4181	−0·1502
	$\epsilon =$ −0·0297	1·3621	−0·7199	1·2390
4. E_u of C_2H_6 and C_2D_6	$\mu =$ 0·3714	0·1905	0·4324	0·1098
	$\epsilon =$ −0·7134	−0·7679	−0·6752	0·7260

But when A_{2u} or E_u of the two molecules are taken up for calculation, they lead to mutually inconsistent results.

It is often said (Saeki and Tanebe 1969; Tanebe and Saeki 1970 and 1972; Tanebe 1972; Jalovski 1971; Galabov and Orville Thomas 1969; Orville Thomas 1973) that μ and ϵ need not be the same for different species in the same molecule. The results presented in column 2 of table 3 are likely to be interpreted as vindication of this view. Nyquist *et al* (1957) state that they cannot ascribe accurate intensity values to different species of C_2H_6 because of overlapping of the bands. Hence to achieve mutually consistent results for all the four combinations, we altered slightly the intensities of ν_5, ν_6 and ν_7 of C_2H_6 only (column 3, table 1), to calculate the μ and ϵ values, the results of which are presented in column 3 of table 3. The alterations suggested are well within the experimental error limits quoted by Nyquist *et al*. It is highly satisfactory to see that the first set of values of μ and ϵ are almost the same in all the cases and these can be taken for further calculations.

2.2 *First order approximation*

It is now worthwhile to examine whether the first order coefficients $(\partial\mu_i/\partial r_j)$, $(\partial\mu_i/\partial\alpha_i)$ and $(\partial\mu_i/\partial\alpha_j)$ terms can really be ignored in the calculations. In place of ϵ in (8) and (9) we have different coefficients for L_{11} in (6) and (7). Equating the values of ϵ (from 3 and 4 of table 3) to the corresponding coefficients of L_{1i}, the value of $(\partial\mu_1/\partial r_2)$ can be calculated to be − 0·015. Similarly, equating the values of μ to the coefficients of L_{2i} of A_{2u} and $(L_{2i} - L_{3i})$ of E_u, $[(\partial\mu_1/\partial\alpha_2) - (\partial\mu_1/\partial\alpha_1)]$ can be calculated to be − 0·0135. Thus, $(\partial\mu_1/\partial r_2)$ is about 2% of $(\partial\mu_1/\partial r_1)$ and $[(\partial\mu_1/\partial\alpha_2) - (\partial\mu_1/\partial\alpha_1)]$ is 3% of μ. Hence the first order terms need not be taken seriously, when the intensities themselves cannot be determined to this accuracy.

2.3 *Hexafluoroethane*

The zero order intensity equations (8) and (9) derived for C_2H_6 and C_2D_6 can safely be extended to C_2F_6 as well. The intensity values $(\partial P_i/\partial Q_i)$ are taken from Mills *et al* (1958) and presented in table 4. The intensity equations are

Table 4. Experimental intensity data of C_2F_6* and CF_4**.

Symmetry	Frequency and mode	$(\partial P/\partial Q)$
	C_2F_6	
A_{2u}	1116 (C—F Str.)	1·840
	714 (F—C—F Bend.)	0·681
E_u	1260 (C—F Str.)	2·430
	522 (F—C—F—Bend.)	0·237
	219 (C—C—F Bend.)	0·175
	CF_4	
F_2	1283 (C—F Str.)	2·198
	632 (F—C—F Bend.)	0·217

*Data from Mills *et al* (1958)
**Data from Schatz and Hornig (1953)

A_2u *type:*

$$1·840 = \sqrt{(2/3)} \, \epsilon \, L_{11} - 2 \sqrt{(2/3)} \, \mu \, L_{21}, \tag{12a}$$

$$0·681 = \sqrt{(2/3)} \, \epsilon \, L_{12} - 2 \sqrt{(2/3)} \, \mu \, L_{22}. \tag{12b}$$

E_u *type:*

$$2·430 = 2\sqrt{2/3} \, \epsilon \, L_{11} + 2/\sqrt{3} \, \mu \, (L_{21} - L_{31}), \tag{13a}$$

$$0·237 = 2\sqrt{2/3} \, \epsilon \, L_{12} + 2/\sqrt{3} \, \mu \, (L_{22} - L_{32}), \tag{13b}$$

$$0·175 = 2\sqrt{2/3} \, \epsilon \, L_{13} + 2/\sqrt{3} \, \mu \, (L_{23} - L_{33}). \tag{13c}$$

Squaring and adding the $A_{2\mu}$ type equations (12a) and (12b) and using $LL' = G$, we have

$$3·8494 = 0·0323 \, \epsilon^2 + 0·4992 \, \mu^2 + 0·1339 \, \epsilon \, \mu. \tag{14}$$

Similarly from (13a), (13b) and (13c) we get, for E_u type

$$5·9917 = 0·2630 \, \epsilon^2 + 0·2174 \, \mu^2 + 0·3347 \, \epsilon \, \mu. \tag{15}$$

Solving the above two equations we get the following two sets

$$\mu = \pm 3·265, \quad \epsilon = \mp 6·353;$$

or $\quad \mu = \pm 2·282, \quad \epsilon = \pm 3·085.$

In the case of isotopically substituted methanes and ethanes one set of μ and ϵ have been found to be identical for all the molecules and they have been taken to calculate the L and F elements. Since isotopic substitution is not possible in the present case

of hexafluoroethane, it cannot be said as to which set of the above values would give satisfactory results.

2.4 *Carbontetrafluoride*

Infrared intensity formulae for the F_2 species of isotopically substituted methanes (CH_4, etc.) have been derived by us earlier (Addepalli and Rajeswara Rao 1976). The same can safely be extended to CF_4 also. The equations are

$$(\partial P/\partial Q_i) = 2/\sqrt{3} \, (-\,\epsilon \, L_{1i} + L_{2i} \, \mu), \, i = 1, 2. \tag{16}$$

Squaring and adding the above equations and using $LL' = G$, we have

$$\Sigma \, (\partial P/\partial Q_i)^2 = (4/3) \, (\epsilon^2 G_{11} + \mu^2 G_{22} - 2 \, \epsilon \, \mu \, G_{12}). \tag{17}$$

When the two μ and ϵ sets obtained from C_2F_6 are substituted in (17) in succession, the right side comes out to be 2·415 and 4·435 respectively. The $(\partial P/\partial Q_i)$ values for CF_4 are reported by Schatz and Hornig (1953) (table 4) and the experimental $\Sigma (\partial P/\partial Q_i)^2$ comes out to be 4·876, which tallies with one of the above values within the experimental error limits. This indicates that the set to be chosen is $\mu = 2·282$ and $\epsilon = 3·085$.

The deviation between the experimental and computed $\Sigma (\partial P/\partial Q_i)^2$ values of CF_4 may also be attributed to the structural differences between CF_4 and C_2F_6. This deviation is almost the same as the deviation between CH_2D_2, etc., and CH_4, etc., when the μ and ϵ set from the C_{2v} type molecules is substituted in the T_d type molecules.

The choice of $\epsilon = + 3·085$ contradicts the choice made earlier in regard to C_2H_6 and C_2D_6, etc., where we have chosen ϵ to be a negative quantity. The present choice is not a contradiction of the earlier results, but originates out of the vector directions of the dipole moment of the C—F bond. In the case of substituted methanes and ethanes, hydrogen atom is at the positive end and carbon atom at the negative end of the dipole. The bond moment vector is directed from H to C and this by convention is taken as $+ \mu$. In the case of C_2F_6 and CF_4, carbon atom is at the positive end and fluorine atom is at the negative end of the dipole and hence the dipole moment vector is directed from C to F which is in reverse direction to that of C-H in C_2H_6. Hence μ_{C-F} should be represented as a negative quantity: $\mu_{C-F} = -2·282$, to be consistent with the convention. Again, we need not choose μ_{C-F} to be negative arbitrarily, but the negative sign originates out of the solution of the quadratic equations (14) and (15). This automatically leads to the solution $\epsilon = -3·085$, the conventional negative sign, of $(\partial \mu/\partial r)$.

The μ and ϵ set calculated here can be taken to be more reliable than those quoted by Mills *et al* (1958) *viz.*, $\mu = 2·1$ and $\epsilon = 3·3$ in CF_4 and $\mu = 2·2$ and $\epsilon = 3·4$ in A_{2u} and $\mu = 0·7$ and $1·6$ and $\epsilon = 3·8$ in E_u species of C_2F_6. The present set can now be used to calculate the L and F elements.

3. Conclusions

(i) from the analysis of C_2H_6 and C_2D_6 we observe that the first order coefficients need not be taken seriously when the intensities themselves cannot be determined very accurately.

(ii) From the analysis of hexafluoroethane and carbontetrafluoride we observe that μ and ϵ are transferable among the corresponding molecules.

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