Determination of Vibrational Resonance Parameters in the Spectra of Polyatomic Molecules *

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An approximation method for determination of vibrational resonance parameters, based upon the invariance of anharmonicity constants against phase changes, is described. Several examples, including resonances in the spectra of CO_2, OCN^-, CH_3I, and some 1,1-disubstituted ethylenes, are given.

A very large number of vibrational levels may be indentified in the spectra of molecules with more than three or four atoms. For experimental reasons most of these levels are obtained from the infrared spectra. If such molecules are of low symmetry, vibrational resonances of Fermi or of higher order type become very probable. Generally, this means that it is no longer possible to fit the observed levels to an expression of the form[1]

$$E(v_1, v_2, \ldots, v_n) = \sum_{i=1}^{n} \omega_i (v_i + 1/2)$$
$$+ \sum_{i=1}^{n} \sum_{j \geqq i}^{n} x_{ij} (v_i + d_i/2)(v_j + d_j/2) + \sum_{i=1}^{n} \sum_{j \geqq i}^{n} g_{ij} l_i l_j \, .$$

The unfortunate result of this failure is that the harmonic frequencies (ω_i) of most polyatomic molecules will be inaccessible from the vibrational spectra alone.

Several methods have been used in the literature for correcting the frequencies affected by local resonances by including information obtained from microwave spectra[2,3], rotation-vibration bands[4,5], and band intensities[6,7]. However, the first two methods are not generally applicable, and the intensity methods are uncertain[8] or elaborate to use.

Theory

As it has been stated by Durocher and Sandorfy[9] the Buckingham theory[10] of solvent effects implies a solvent independent anharmonicity constant. This constant will be equal to the one from the vapour phase spectrum. The theory is mainly considering diatomic molecules, but it should also apply to isolated bond stretching vibrations of polyatomic molecules. In the paper by Durocher and Sandorfy on OH, NH and CH stretching vibrations and in a recent paper by Perrot et al.[11] on HCl the phase and solvent independency of anharmonicity constant holds within 10% in inert solvents.

A similar observation has been made by Schettino and Hisatsune[12], who found the anharmonicity constants of the cyanate ion independent of the matrix material. From an infrared investigation of some 1,1-disubstituted ethylenes[13] it has been found that the anharmonicity constants determined from non-resonant bands in the gas and liquid phase generally agree within the accuracy of measurement ($5-0.5$ cm^{-1}, depending on the band concerned). Most of the assigned bands were binary or ternary combinations, and deviations from this rule might arise for combination bands of higher order.

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The consequence of phase-(or solvent-) invariant anharmonicity constants is that the higher order force constants and thus the vibrational resonance parameters (W) are phase-independent. FERNÁNDEZ BERTRAN et al.[7] have made implicit use of the solvent-independence of W in their method of calculating Fermi resonances.

For simplicity, the term anharmonicity (x) shall be used in the following, and the subscripts g and l shall denote the gas and liquid phase, respectively.

$$x_\mathrm{g} \approx x_\mathrm{l} \approx \sum_{i=1}^{n} \sum_{j \geqq i}^{n} x_{ij} (v_i + d_i/2) \cdot (v_j + d_j/2) + \sum_{i=1}^{n} \sum_{j \geqq i}^{n} g_{ij} l_i l_j .$$

It should be recalled that in the case of non-degenerate vibrations $d_i = d_j = 1$ and $g_{ij} = 0$.

Assuming x and W phase invariant and further perturbations such as Coriolis interactions absent, the usual perturbation treatment may be applied to a resonance of the Fermi type with ν representing observed and E unperturbed levels:

$$\begin{vmatrix} E_{1\mathrm{g}} - \nu_\mathrm{g} & W \\ W & E_{2\mathrm{g}} - \nu_\mathrm{g} \end{vmatrix} = \begin{vmatrix} E_{1\mathrm{l}} - \nu_\mathrm{l} & W \\ W & E_{2\mathrm{l}} - \nu_\mathrm{a} \end{vmatrix} = 0 .$$

Because there are two perturbated levels, ν' and ν'', the two determinants yield four equations, which together with two equations from the anharmonicity condition allow the calculation of all six unknowns: $E_{1\mathrm{g}}$, $E_{2\mathrm{g}}$, $E_{1\mathrm{l}}$, $E_{2\mathrm{l}}$, x, and W.

$$\begin{aligned} (E_{1\mathrm{g}} - \nu_\mathrm{g}')(E_{2\mathrm{g}} - \nu_\mathrm{g}') - W^2 &= 0 , \\ (E_{1\mathrm{g}} - \nu_\mathrm{g}'')(E_{2\mathrm{g}} - \nu_\mathrm{g}'') - W^2 &= 0 , \\ (E_{1\mathrm{l}} - \nu_\mathrm{l}')(E_{2\mathrm{l}} - \nu_\mathrm{l}') - W^2 &= 0 , \\ (E_{1\mathrm{l}} - \nu_\mathrm{l}'')(E_{2\mathrm{l}} - \nu_\mathrm{l}'') - W^2 &= 0 , \\ E_{2\mathrm{g}} &= \sum \nu_{i\mathrm{g}} + x , \\ E_{2\mathrm{l}} &= \sum \nu_{i\mathrm{l}} + x . \end{aligned}$$

In this case E_2 has been assumed to be the combination level and E_1 to be the fundamental. ν_i are the observed frequencies of the fundamentals involved in E_2. These levels must be unperturbed or corrected for the effect of vibrational resonance.

If both E_1 and E_2 are combination levels (Darling-Dennison type), the equation system may be expanded by two expressions containing only one more unknown anharmonicity (x_1)

$$\begin{aligned} E_{1\mathrm{g}} &= \sum \nu_{j\mathrm{g}} + x_1 , \\ E_{1\mathrm{l}} &= \sum \nu_{j\mathrm{l}} + x_1 . \end{aligned}$$

This means that an internal consistency check may be obtained.

A vibrational resonance is normally repeated through a whole series of higher levels involving the resonating pair and some other vibration. In principle, the calculation of such resonances is analogous to the Darling-Dennison case. It is advisable to use this extra information to obtain two independent anharmonicity values, since these are generally more sensitive to errors than the resonance parameter.

If three vibrational levels are interacting, one of which is a fundamental, the perturbation treatment yields:

$$\begin{vmatrix} E_{1\mathrm{g}} - \nu_\mathrm{g} & W_1 & W_2 \\ W_1 & E_{2\mathrm{g}} - \nu_\mathrm{g} & W_3 \\ W_2 & W_3 & E_{3\mathrm{g}} - \nu_\mathrm{g} \end{vmatrix} = \begin{vmatrix} E_{1\mathrm{l}} - \nu_\mathrm{l} & W_1 & W_2 \\ W_1 & E_{2\mathrm{l}} - \nu_\mathrm{l} & W_3 \\ W_2 & W_3 & E_{3\mathrm{l}} - \nu_\mathrm{l} \end{vmatrix} = 0 .$$

The anharmonicity condition is:

$$\begin{aligned} E_{2\mathrm{g}} &= \sum \nu_{i\mathrm{g}} + x_1 , & E_{3\mathrm{g}} &= \sum \nu_{j\mathrm{g}} + x_2 , \\ E_{2\mathrm{l}} &= \sum \nu_{i\mathrm{l}} + x_1 , & E_{3\mathrm{l}} &= \sum \nu_{j\mathrm{l}} + x_2 . \end{aligned}$$

Upon expanding, the two determinants give six equations of the type:

$$(E_1 - \nu)(E_2 - \nu)(E_3 - \nu) + 2 W_1 W_2 W_3 - W_1^2 (E_3 - \nu) - W_2^2 (E_2 - \nu) - W_3^2 (E_1 - \nu) = 0 .$$

Three equations contain the observed gas phase levels ν_g', ν_g'', and ν_g''' and three the corresponding liquid phase measurements. A total of 10 equations with 11 unknowns has thus been obtained, and this system can only be solved if one parameter may be determined independently. For instance, W_3 may be set equal to zero.

If all three vibrational levels are combinations, two more equations with just one additional anharmonicity are obtained. This system of 12 equations with 12 parameters may have one or more exact solutions.

Like the resonance diads, triads are often repeated as higher combinations with other vibrations. This also brings additional information, but in the Fermi resonance case the system of equations does not become solvable because one fundamental is involved in the basic resonance triad.

For ease of calculation it is advisable to determine the resonance parameters and the unperturbed levels as functions of one of the anharmonicities, e.g. x_1. Fig. 4 shows the type of functions generally obtained. Because W_i must be real, all possible values of x_1 are found below the parabola $\sum W_i^2 \geqq 0$. The sign of one single W_i is not known, but only certain combinations giving the correct sign of the product $W_1 W_2 W_3$ are allowed. One such sign combination is given in the Figs. 4 and 5.

Applications

As an example, the classical Fermi resonance between ν_1 and $2\nu_2^0$ of CO_2 has been considered. In Fig. 1 $|W|$ $(= |W|_{122})$ and x $(= 2x_{22} - 2g_{22})$ have been plotted against $2 \cdot \nu_{21}^1$. The frequencies, except ν_{21}^1, were taken from HERZBERG[1], p. 535. For experimental reasons the missing frequency was approximated by measuring the infrared spectrum of a saturated solution of CO_2 in CS_2, and a value of 656.8 ± 1 cm^{-1} was obtained. From Fig. 1 is seen that $|W|$ is rather insensitive to small variations in ν_{21}^1 and the resonance parameter, 50 cm^{-1}, virtually agrees with the value given by SUZUKI[14], $|W_e| = 52.8$ cm^{-1}. However x is found equal to 13 cm^{-1}, whereas SUZUKI finds $x = 4.6$ cm^{-1}.

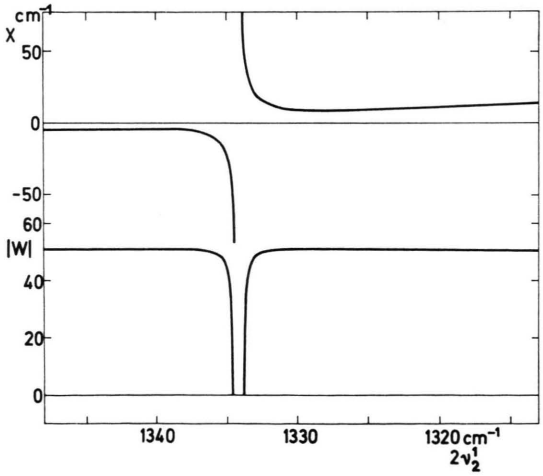

Fig. 1. CO_2. Fermi resonance $\nu_1 \rightarrow 2\nu_2^0$. W is imaginary for $666.9 \leqq \nu_{21}^1 \leqq 667.3$ cm^{-1} and $x \rightarrow \pm\infty$ for $\nu_{21}^1 \rightarrow 667.1$ cm^{-1}.

Another example is the Fermi resonance $\nu_1 \rightarrow 2\nu_2^0$ of the cyanate ion, whose infrared spectra in potassium halide matrices have been investigated by SCHETTINO and HISATSUNE[12]. They found the anharmonicity constants to be independent of the matrix material, and accordingly the frequencies from two different matrices may be used to calculate $|W|$ by substituting them for the gas and liquid phase frequencies used so far. In the case of $^{16}O\,^{14}C\,^{11}N^-$ $|W| = 43$ cm^{-1} and $x = -4.7$ cm^{-1} are obtained for the three possible matrix combinations. S. and H. obtain mean values of $|W| = 41$ cm^{-1} and $x = -2.6$ cm^{-1}.

The Fermi resonance $\nu_5 \rightarrow \nu_3 + \nu_6$ in the spectrum of methyl iodide has been studied by several authors[4, 5, 15, 16]. The resonance parameter calculated from the intensity ratio of the bands in the crystal phase (12 cm^{-1}) and in an argon matrix (13 cm^{-1})[16] agrees fairly well with $|W|_{536} = 9.9$ cm^{-1} obtained from the gas phase rotational analysis[4]. Using the gas phase frequencies from[4] and [17] and CCl_4 solution measurements by GLASS and PULLIN[18], the results of Fig. 2 were calculated. As in the case of CO_2, $|W|$ is rather insensitive to small frequency errors in ν_{6s} (or ν_{3s})* apart from a narrow frequency interval near 881.6 cm^{-1}. However, unlike the CO_2 resonance, ν_{6s} falls within this critical frequency interval, and the value of 882 ± 2 cm^{-1} given in [18] is not accurate enough for a determination of W.

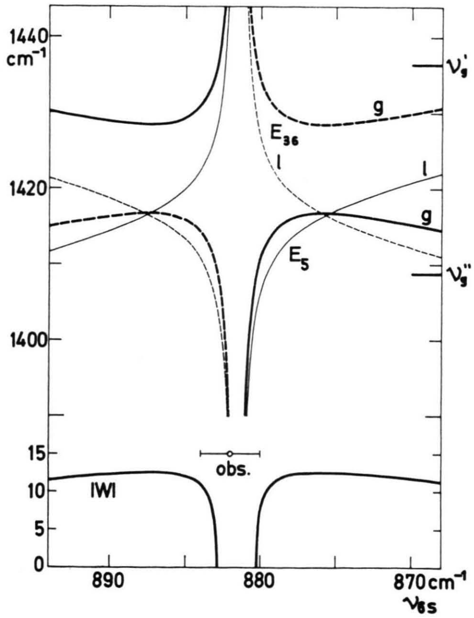

Fig. 2. CH_3I. Fermi resonance $\nu_5 \rightarrow \nu_3 + \nu_6$. The E_5 levels are shown as full, E_{36} as dotted curves. The two observed gas phase frequencies shown, ν_g' and ν_g'', are from[4].

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* subscript s = solution.

	Observed levels			Unperturbed levels			
cm^{-1}	Gas	Liquid	Solution	Gas	Liquid	Gas	Solution
$\nu_9+\nu_{11}$	689.1	706.9	699.0	681.0	703.1	682.1	663.1
ν_8	660.0	658.2	658.8	668.1	662.0	667.0	694.7
ν_9	516.1	525.6	522.4	$\|W\|_{8.9.11}=13.0$		$\|W\|_{8.9.11}=12.5$	
ν_{11}	173.2	185.8	179.5	$x=-8.3$		$x=-7.2$	

Table 1. H_2C_2ClCN.

Considering the error limits, $0 \leqq |W| \leqq 11\ cm^{-1}$ is obtained.

This example emphasises the necessity of highly accurate frequency measurements for the liquid phase to make the present method of calculation useful. Such measurements of known vibrational resonances are rare, and the rest of this paper shall, therefore, be confined to examples from the infrared spectra of 1,1- disubstituted ethylenes for which precise gas and liquid phase frequencies were available[13].

In the spectrum of 1-chloro-1-cyanoethylene (2-chloroacrylonitrile) a Fermi resonance is found between ν_8 and $\nu_9+\nu_{11}$ [13,19]. The frequencies of the resonating bands ν_9 and ν_{11} have been measured for gas, liquid, and dilute hydrocarbon (n-heptane and cyclohexane) solution. The observed and calculated levels are given in Table 1. The agreement between the two calculated sets of constants is satisfactory and $|W|_{8.9.11}=13\ cm^{-1}$ and $x_{9.11}=-4\ cm^{-1}$ are of reasonable magnitudes.

The resonances $\nu_8 \to \nu_6 \to \nu_{12}$ and $\nu_k+\nu_8 \to \nu_k+\nu_6+\nu_{12}$ are very pronounced in the spectra of 1,1-dibromo-, 1-bromo-1-chloro- and 1,1-dichloroethylene. As an example, Fig. 3 shows ν_8 and $\nu_6+\nu_{12}$ in the infrared spectrum of gaseous and liquid $H_2C_2Br_2$. Tables 2, 3 and 4 give some observed and calculated levels of this compound and H_2C_2BrCl.

For $H_2C_2Br_2$ the consistency of both $|W|$ and x values is pleasing whereas the values for H_2C_2BrCl scatter somewhat. This is partly due to a rather uncertain ν_{61} frequency ($\pm 1.5\ cm^{-1}$), and it is possible to obtain better agreement between the $|W|$ values by chosing $\nu_{61}=677.0\ cm^{-1}$. However, $|W|$ from the $\nu_1+\nu_8$ resonance remains at 18 cm^{-1} after this correction. It seems most probable that this is due to a slight resonance perturbation of ν_1 by $\nu_2+\nu_3$ and $\nu_2+\nu_8+\nu_{10}$, which has not been corrected for. It is interesting to note that the resonance component associated with the fundamental (or binary combination band in the higher levels) is always the component of highest intensity. A comparison of Fig. 3 and Table 3 also shows that the intensity reversal of ν_8 and $\nu_6+\nu_{12}$ between gas and liquid reflects a reversal of the frequency order of the unperturbed levels.

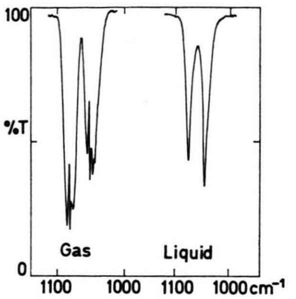

Fig. 3. $H_2C{=}CBr_2$. Fermi resonance $\nu_8 \to \nu_6+\nu_{12}$. Intensity reversal between gas and liquid phase.

In the spectrum of $H_2C_2Cl_2$ the resonance $\nu_8 \to \nu_6+\nu_{12}$ is augmented by $\nu_5+\nu_9$. If all three

cm^{-1}	ν_{12}	ν_6	ν_2	ν_1	ν_7	ν_5	ν_9
$H_2C_2Br_2$, gas	401.6	665.5	1600.4	3037.2	3121.7		
liquid	400.6	671.7	1593.5	3021.6	3109.1		
H_2C_2BrCl, gas	427.6	674.0	1609.9	3039.6	3130.3		
liquid	426.1	677.6	1602.9	3027.8	3120.0		
$H_2C_2^{35}Cl_2$, gas	456.3	680.2		3046.0	3138.2	298.0	795.8
liquid	454.5	685.0		3035.3	3129.3	298.6	786.2

Table 2. Fundamentals.

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cm^{-1}	Observed levels Gas	Observed levels Liquid	Unperturbed levels Gas	Unperturbed levels Liquid	$\|W\|_{8.6.12}$	x
ν_8	1052.1	1046.3	$\underline{1070.4}$	$\underline{1055.5}$*	14.3	
$\nu_6+\nu_{12}$	1081.5	1077.6	1063.2	1068.4		-3.9
$\nu_2+\nu_8$	2643.0	2629.8	2661.4	2638.9	14.4	-9.4 -10.1
$\nu_2+\nu_6+\nu_{12}$	2672.6	2661.6	2654.2	2652.5		-9.4
$\nu_1+\nu_8$	4081.1	4059.6	4097.6	4068.2	14.1	-10.0 -8.9
$\nu_1+\nu_6+\nu_{12}$	4109.6	4091.3	4093.1	4082.7		-7.3
$\nu_7+\nu_8$	4167.1	4147.1	4185.4	4155.5	13.9	-6.7 -9.1
$\nu_6+\nu_7+\nu_{12}$	4196.0	4178.7	4177.7	4170.3		-7.2

* The underlined ν_8 levels were used in the calculation of $\nu_k+\nu_8$.

Table 3. Resonances, $H_2C_2Br_2$.

cm^{-1}	Observed levels Gas	Observed levels Liquid	Unperturbed levels Gas	Unperturbed levels Liquid	$\|W\|_{8.6.12}$	x
ν_8	1074.7	1066.6	$\underline{1085.7}$	$\underline{1074.1}$*	15.5	
$\nu_6+\nu_{12}$	1107.5	1106.1	1096.5	1098.6		-5.1
$\nu_2+\nu_8$	2674.2	2658.0	2683.1	2664.1	14.9	-12.4 -12.8
$\nu_2+\nu_6+\nu_{12}$	2707.9	2700.2	2699.0	2694.1		-7.5
$\nu_1+\nu_8$	4108.6	4085.8	4129.3	4097.1	18.0	4.0 -4.8
$\nu_1+\nu_6+\nu_{12}$	4145.0	4125.9	4124.3	4114.6		-11.8
$\nu_7+\nu_8$	4198.8	4176.9	4211.5	4184.5	16.1	-4.5 -9.6
$\nu_6+\nu_7+\nu_{12}$	4231.9	4218.6	4219.2	4211.0		-7.6

* The underlined ν_8 levels were used in the calculation of $\nu_k+\nu_8$.

Table 4. Resonances, H_2C_2BrCl.

levels are used in the calculation, the picture shown as Fig. 4 emerges. All parameters are given as function of x_1, the anharmonicity of $\nu_6+\nu_{12}$. Two sets of $|W|$ solutions are found, plotted in Figs. 4 and 5 as full and dotted lines. From the analogous dibromo and bromchloro compounds it may be expected that $|W| \approx 15\ cm^{-1}$ and $x_1 = -3$ to $-6\ cm^{-1}$. This means that the most probable solution falls in the extreme right part of the $|W|$ curves, yielding the values of Table 5. According to expectation, $|W|_{5.9.6.12} \approx 0$, since this resonance is of higher order.

cm^{-1}	Observed levels Gas	Observed levels Liquid	Unperturbed levels Gas	Unperturbed levels Liquid	$\|W\|$	x
ν_8	1086.1	1076.5	1106	1091	18*	
$\nu_5+\nu_9$	1097.1	1087.0	1088	1079	5**	-6
$\nu_6+\nu_{12}$	1139.0	1138.9	1129	1132	0–3†	-8
$\nu_1+\nu_8$	4125.0	4105.5	4142	4117	16.5*	-10 -9
$\nu_1+\nu_5+\nu_9$	4137.9	4118	4129	4112	6**	-8
$\nu_1+\nu_6+\nu_{12}$	4180.0	4170	4172	4164	0–5†	-10.5
$\nu_7+\nu_8$	4216.7	4199.0	4241	4211	18*	-3 -9
$\nu_5+\nu_7+\nu_9$	4231.9	4209	4218	4203	5.5**	-10.5
$\nu_6+\nu_7+\nu_{12}$	4270.8	4260.5	4260	4254	0–2†	-15

* $|W|_{8.6.12}$ ** $|W|_{8.5.9}$ † $|W|_{5.9.6.12}$.

Table 5. Resonances, $H_2C_2^{35}Cl_2$.

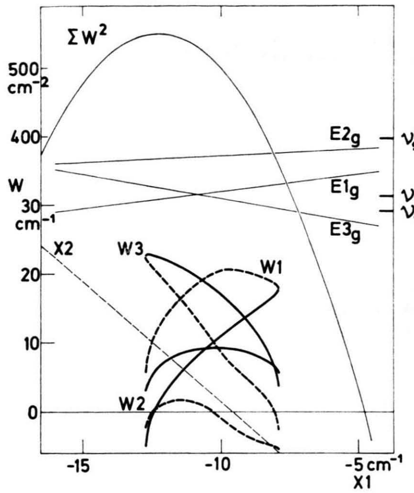

Fig. 4. $H_2C = CCl_2$. Resonance triad $\nu_8 \rightarrow \nu_5 + \nu_9 \rightarrow \nu_6 + \nu_{12}$. $W1 = |W|_{8.6.12}$, $W2 = |W|_{8.5.9}$, $W3 = |W|_{5.9.6.12}$, $X1 = 2x_{6.12}$, $X2 = 2x_{5.9}$, $E1 = E_8$, $E2 = E_{6.12}$, $E3 = E_{5.9}$. The two possible sets of W values are given as full and dotted curves. E_1 functions have not been drawn, since they are linear and parallel to E_g.

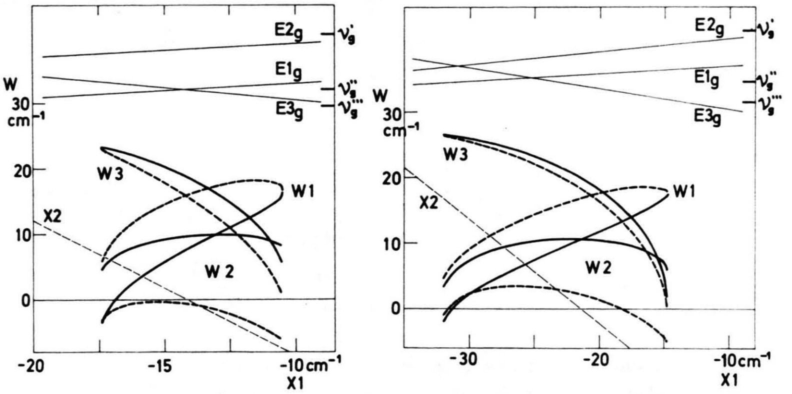

Fig. 5. $H_2C{=}CCl_2$. Resonance triads $\nu_1 + \nu_8 \rightarrow \nu_1 + \nu_5 + \nu_9 \rightarrow \nu_1 + \nu_6 + \nu_{12}$ (left) and $\nu_7 + \nu_8 \rightarrow \nu_5 + \nu_7 + \nu_9 \rightarrow \nu_6 + \nu_7 + \nu_{12}$ (right).

$$W1 = |W|_{8.6.12}, \quad W2 = |W|_{8.5.9}, \quad W3 = |W|_{5.9.6.12},$$
$$X1 = 2x_{k.6} + 2x_{k.12} + 2x_{6.12}, \quad X2 = 2x_{k.5} + 2x_{k.9} + 2x_{5.9},$$
$$E1 = E_{k.8}, \quad E2 = E_{k.6.12}, \quad E3 = E_{k.5.9}$$

(k = 1 and 7, respectively). — See also caption of Fig. 4.

By applying the condition $|W|_{5.9.6.12} \approx 0$ to two resonances involving $\nu_1 + \nu_8$ and $\nu_7 + \nu_8$ the other values of Table 5 were determined from Fig. 5.

The resonance $\nu_2 + \nu_8$, etc. was not used because its bands are badly overlapped in the infrared spectrum of $H_2C_2Cl_2$. The conditions $x_{1.8\,g} = x_{1.8\,l}$ and $x_{7.8\,g} = x_{7.8\,l}$ were not applied to the calculation, but the values in braces in the last column of Table 5 show the degree of agreement obtained between x_g and x_l.

Conclusion

The approximation method presented here relies only on frequency measurements and implies no knowledge of band intensities. However, it seems advisable to collect more experimental evidence of the condition $x_g \approx x_s \approx x_l$, since its assumed validity is based on a limited material at present. Care should be taken to avoid association effects and to obtain very accurate frequencies for the liquid phase. The method may be used with confidence in the case of strong vibrational resonances with significant gas-liquid (solvent) frequency shifts. Resonance parameter and unperturbed levels of resonance diads may always be calculated and triads may be treated in favorable cases, where one or several variables are known from other sources.

Appendix

For Fermi resonance diads the following expressions are obtained where the subscripts g and l refer to frequencies from gas and liquid phase measurements:

$$K = \sum \nu_i, \quad S = \nu' + \nu'',$$
$$N = S_g - S_l - 2(K_g - K_l),$$
$$x = 1/N\,[K_g(K_g - S_g) - K_l(K_l - S_l) + \nu'_g \nu''_g - \nu'_l \nu''_l],$$
$$E_1 = S - K - x, \quad E_2 = K + x,$$
$$|W| = ((E_1 - \nu')(E_2 - \nu'))^{1/2}.$$

For resonance triads between a fundamental and two combination bands, $\sum W_k{}^2$ and x_2 may be determined rather easily for a fixed value of x_1. Afterwards the single $W_k{}^2$ are found by iteration and a possible sign combination determined. All calculations have been carried out on a DIGITAL PDP-8/I computer, and corresponding FOCAL programmes are available from the author.

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