

Fermi resonance studies in condensed phases

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ABSTRACT

And overview of Fermi Resonance studies in condensed phases is given including theory and applications as well as an ample bibliography.

RESUMEN

Se ofrece una panorámica de los estudios de Resonancia de Fermi en fase condensada incluyendo la teoría y aplicaciones de la misma, junto con una amplia bibliografía.

1. INTRODUCTION

1.1. FERMI RESONANCE, AN UNWELCOME ANOMALY

When two vibrational levels of the same symmetry are accidentally quasi-degenerate, the anharmonic terms in the potential function produce strong perturbation, leading to a repulsion of the energy levels and a mixing of

the vibrational wave functions [1]. If one of the interacting levels is an allowed fundamental in IR or Raman spectra, and the other is an overtone or combination level, the resonance produces an intensity transfer from the allowed to the forbidden transition, giving rise to a spectral doublet. The phenomenon was first observed in the Raman spectra of gaseous CO_2 , where the first harmonic of the symmetric bending $2\nu_2$ falls near the fundamental symmetric stretch ν_1 . The phenomena was interpreted by Enrico Fermi as a perturbation of the two levels by the anharmonic force constant K_{122} [1]. For this reason the perturbation received the name of Fermi resonance (FR) and the spectral doublet, a Fermi doublet (FD).

Accidental degeneracy of vibrational levels leading to FR are present in many triatomic molecules as can be observed in table 1. In polyatomic molecules the possibility of accidental degeneracy of vibrational levels is rapidly enhanced with the increasing number of vibrational modes ($3N-6$). For this reason it can be safely stated that in medium and large molecules, FR is an omnipresent anomaly [2 - 21], see tables 1 - 6.

The presence of FR is usually regarded as a nuisance. Spectroscopists working in high resolution gas-phase studies of simple molecules with the purpose of performing complete vibrational analysis have to cope with the perturbation a priori [22-26]. The physical-organic chemists interested in correlating frequencies and intensities with molecular structural parameters, have to evaluate their unperturbed values [27-32]. The analytical chemist using characteristic bands for quantitative analysis has to cope with the frequency and intensity changes introduced by solvents and temperature [33-39]. The structural chemist involved in the determination of molecular structures of new synthetic or natural products can mistake this anomaly for the presence of more than one functional group, rotational conformers, etc. For all these researchers, life would be simpler without FR.

1.2. THE IMPORTANCE OF FR STUDIES

FR studies provide a unique method to probe molecular vibrational potential functions and to determine with accuracy anharmonic terms in polyatomic molecules [40-42]. FR is sensitive to solute-solvent interactions and is a good sensor of molecular associations. FR is responsible for spectral characteristics of many biologically important macromolecules [43-50], as well as synthetic polymers [51-54]. All these topics illustrate the importance of FR and will be discussed in this article.

2. METHODS OF DETECTION OF FR AND CALCULATION OF ITS PARAMETERS

2.1. FR THEORY

Perturbation theory allows us to calculate the equations relating the observed frequencies ν_+ and ν_- of the FD to the unperturbed frequencies

ν_+^0 and ν_-^0 and to the anharmonic term in the potential function causing the interaction of the allowed ν_a and forbidden ν_f vibrational levels. The integral $\langle \psi_+^0 / H / \psi_-^0 \rangle$ is designated by W and called the Fermi coupling constant [1,2]. Calling Δ and Δ^0 the frequency separation of the perturbed and unperturbed levels we can write for ν_+ and ν_- :

$$\nu_{\pm} = \frac{1}{2} \left[(\nu_+^0 + \nu_-^0) \pm (\Delta^2 + 4W^2)^{\frac{1}{2}} \right] \quad (1)$$

$$\nu_{\pm}^0 = \frac{1}{2} \left[(\nu_+ + \nu_-) \pm (\Delta^2 + 4W^2)^{\frac{1}{2}} \right] \quad (2)$$

$$W = H' = \langle \psi_+^0 / H' / \psi_-^0 \rangle = \frac{1}{2} (\Delta^2 - \Delta_0^2)^{\frac{1}{2}} \quad (3)$$

The perturbed wave functions are linear combinations of the harmonic wave functions:

$$\psi_+ = a\psi_+^0 \pm b\psi_-^0 ; \quad \psi_- = a\psi_-^0 \mp b\psi_+^0 \quad (4)$$

The sign is determined by the value of W . The degree of mixing is given by the squares of the coefficients:

$$a^2 = \frac{\Delta + (\Delta^2 - 4W^2)^{\frac{1}{2}}}{2\Delta} ; \quad b^2 = \frac{\Delta - (\Delta^2 - 4W^2)^{\frac{1}{2}}}{2\Delta} \quad (5)$$

Maximum mixing corresponds to $\Delta = 2W$ and the values of a^2 and b^2 are 0,5. See figures 1 and 2.

The intensities of the perturbed transitions can also be related to the unperturbed intensities. Normally, the ratio of intensities of the FD, components, R , rather than the absolute value of the intensities I_+ and I_- are required [55]:

$$R = \left\{ \frac{\left[\Delta + (\Delta^2 - 4W^2)^{\frac{1}{2}} \right]^{\frac{1}{2}} R_0^{\frac{1}{2}} \pm \left[\Delta - (\Delta^2 - 4W^2)^{\frac{1}{2}} \right]^{\frac{1}{2}}}{\left[\Delta - (\Delta^2 - 4W^2)^{\frac{1}{2}} \right]^{\frac{1}{2}} R_0^{\frac{1}{2}} \mp \left[\Delta + (\Delta^2 - 4W^2)^{\frac{1}{2}} \right]^{\frac{1}{2}}} \right\}^2 \quad (6)$$

If the intensity of the unperturbed forbidden transition is negligible with respect to the allowed fundamental, equation (6) can be simplified to:

$$W = \Delta R \frac{1}{2} (R + 1)^{-1} \quad (7)$$

These equation are necessary in the calculation of the FR parameters, that is, the unperturbed frequencies and intensities and the Fermi coupling constant W .

2.2. METHODS OF DETECTION OF FD

The most convincing evidence that a spectral doublet is a FD is provided by isotopic substitution. If the doublet disappears in the isotopically

labelled molecule, it can be concluded that FR was the origin of the phenomena. However, if the doublet remains, one can not conclude that it is not a FR since the isotopic substitution might not alter the vibrational levels involved in the resonance. Common substitutions are ^2D for ^1H , ^{18}O for ^{16}O , ^{15}N for ^{14}N and ^{13}C for ^{12}C [56-67].

Another test is the effect of solvents on the intensity ratio R and frequency separations Δ of the FD components. The solvents alter the position of the interacting levels and the values of the observables R , Δ fall in a nose shaped curve corresponding to equation 6, see figure 2.

2.3. METHODS OF CALCULATION OF RESONANCE PARAMETERS

The effects of solvents provide not only a detection method of FD but permit the calculation of resonance parameters. The most simple procedure is to measure R and Δ in a single solvent and calculate W by equation 7 [55]. A more reliable approach is to measure R and Δ in a series of solvents and fit the experimental data to equation 6 by computer, using W and R_0 as adjustable parameters [55], see figure 2. This approach has received the denomination of the Solvent Variation Method (SVM) and has been applied to a large number of molecules [20, 29, 31, 32, 40, 48, 68 - 82], see table 2.

Another procedure for calculation of W was devised by Winther [83] employing only frequency data. If the FD frequencies ν_a and ν_f and the fundamentals involved in the forbidden level (for example ν_i and ν_j) are measured in two phases, one can calculate the resonance parameters from the secular equation and anharmonicity of the forbidden level. The assumption is made that W and the anharmonicity A are constant in the two phases. If more phases are available, the calculation are performed pairwise and the results compared for consistency. This method has been adapted by Fernández Bertrán, Ortiz and Ballester [69] to the framework of a solvent variation technique.

The values of ν_a , ν_f , ν_i and ν_j are measured in a series of solvents and the following frequency function are constructed:

$$x = 2(\nu_i + \nu_j) - (\nu_a + \nu_f)$$

$$y = \frac{1}{4} \left[(\nu_a - \nu_f)^2 + x^2 \right] \quad (8)$$

These functions have the property of being linearly related [69]:

$$Y = A X + B \quad (9)$$

The slope A measures the anharmonicity of the forbidden level and the value of W can be obtained from the intercept B :

$$B = A^2 + W^2$$

(10)

This approach has been labeled the Modified Winther Method [69] (MWM) and has permitted the reliable evaluation of W in many molecules, see table 3 and figure 3. There is excellent agreement of results by the SVM and the MWM as can be observed in figure 4 [38, 42, 55, 69, 70, 81, 82].

3. STUDIES OF ANHARMONIC FORCE CONSTANTS

3.1. DETERMINATION OF ANHARMONIC FORCE CONSTANTS

In small, symmetric molecules it is possible to determine the vibrational potential function up to quartic level by adjusting the force constants to fit the experimental frequencies in several isotopic species [22-24]. The physical significance of these anharmonic force constants beyond that of carefully determined adjustable parameters is questionable [84]. Anharmonic resonances provide a unique way to obtain accurate values of the anharmonic force constants causing the perturbation.

The method gives results in small as well as complex molecules and has provided very valuable data, enabling studies of the behaviour of anharmonic force constants with substitution, solvents, temperature and pressure. In table 4 we present the denomination of the most common anharmonic resonances and the order of the force constants involved. The highest order reported corresponds to a third order resonance in CH_2Br_2 [105, 106].

3.2. SUBSTITUENT EFFECTS ON ANHARMONIC FORCE CONSTANTS

In the last decade several characteristic resonances with vibrational motions localized in small atomic groups have been studied in families of compounds, allowing the determination of the effect of substituents on harmonic force constants. They include the effect of electronegativity [84] and of resonance effects [82] on W . Linear relations have been obtained between W and the pertinent substituent parameters. The magnitude of the effect seems to depend on the length of the transmission path. The main results are collected in table 5.

3.3. SOLVENTS EFFECTS ON ANHARMONIC FORCE CONSTANTS

The effect of solvents on quadratic force constants is a well explored field since the data can be obtained from the solvent shifts of the vibrational transitions in a straight forward manner. Solvent effects on anharmonic force constants are scarce and most work has been limited to anharmonicity constants of small vibrators [85, 86]. Fernández Bertrán has studied resonances in systems with strong solute - solvent interactions and found appreciable changes in W with solvents basicity [38, 40, 74, 78]. An interesting case is the linear dependence found for the anharmonic force constant K_{122} (stretch-bend-bend) of the NH_2 -group in trifluoroethylamine

with the logarithm of the solvent basicity constant K_b [40, 78], see figure 6. Another example is afforded by K_{122} in CO_2 , which changes appreciably on passing from pure CO_2 (in gas, liquid and solid) to solutions in H_2O and D_2O [27, 48, 93]. In figure 7 we can observe the different RA curves for this system, see table 6.

3.4. TEMPERATURE EFFECTS ON ANHARMONIC FORCE CONSTANTS

Strictly speaking, the potential function should be temperature independent and therefore W should not be altered by temperature [39]. However two effects give rise to changes in W with temperature, one due to different occupation of rotational levels and the other to the shift in equilibria between different types of associated species.

A good example of the latter phenomena is the observed dependence of K_{144} of NH_3 with temperature [25, 71], see figure 8.

3.5. PRESSURE EFFECTS ON ANHARMONIC FORCE CONSTANTS

Pressure has been used as a scanning variable to study FD. Sherman has published several papers applying this technique to FR in SO_4^{2-} [88], NH_4^+ [87], BH_4^+ and BD_4^+ ions in matrices or as crystals. Wu and Nichols have studied pressure effects on FD in polyethylene [28] and Buback and Schultz in super dense gaseous NH_3 [102]. However, studies of changes in W with pressure are very limited. Several authors have studied CO_2 under pressure in gas, liquid and solid [21, 27, 91, 92]. In figure 8 we present the RA curve for solid CO_2 under pressure which indicates changes in K_{122} at pressure above 50 Kilobars [20] of the order of 20 %.

4. DETERMINATION OF UNPERTURBED FREQUENCIES AND ASSIGNMENT OF INTERACTING LEVELS

4.1. DETERMINATION OF UNPERTURBED FREQUENCIES

The determination of unperturbed frequencies ν_+^0 and ν_-^0 of the FD components is important not only in spectroscopic research but also in many physical - chemical studies where the characteristic frequencies of certain group vibrations are correlated with physical and chemical properties of the molecules. The calculation on ν_+^0 and ν_-^0 is easily accomplished once W has been determined, as for example by vibration - rotation analysis in the gas phase or by SVM and MWM in condensed phases, by means of equation 2. A harder problem is to assign ν_+^0 and ν_-^0 to the unperturbed transitions, that is the allowed fundamental ν_a^0 and the forbidden transition ν_f^0 , which will be dealt with in the next paragraph.

4.2. ASSIGNMENT OF THE UNPERTURBED FREQUENCIES ν_+^0 and ν_-^0 to ν_a^0 and ν_f^0

The assignment of the unperturbed levels to the allowed fundamentals ν_a^0 and the forbidden transition ν_f^0 is important in correlational studies since

a mistaken assignment will lead to errors in the dependence of ν_a^0 on substituent constants or solvent effects, for example. When the resonance is weak, one can generally assume that the intense transition corresponds to ν_a and the weak transition to ν_f . When the resonance is strong, the assignment of the most intense component to ν_a could lead to serious errors as in the case of CO_2 [93, 94] and OCN^- [95, 96] resonance. This is due to the fact that the intensity of ν_f^0 is not negligible with respect to ν_a^0 . The SVM affords a firm criterion for maximum resonance and level assignment [55]. Degeneracy of ν_a^0 and ν_f^0 occurs at the apex of RA curve at minimum Δ . The upper and lower branches of the curve correspond to different locations of ν_a^0 with respect to ν_f^0 . The assignment can be made by taking into consideration that along one of the branches the allowed fundamental gains in intensity as Δ increases while the forbidden transition decreases. The MWM also provides excellent determination for maximum resonance which occurs at $X = -2A$ [38]. To the left, for $X < -2A$, ν_+ corresponds to ν_a while to the right, for $X > -2A$, ν_- corresponds to ν_a . This method is illustrated with the XY plots of isotopic species of OCN^- [38, 69], whose levels have been previously misassigned [95, 96], see figure 9.

4.3. ASSIGNMENT OF THE NATURE OF THE FORBIDDEN LEVEL ν_f

In small molecules, the assignment of the fundamental level ν_a to a vibrational mode is normally known and the assignment of the forbidden transition ν_f to a harmonic or combination band is usually an easy matter. In larger molecules, the number of possible forbidden bands near an allowed fundamental grow very fast with an increasing number of atoms in the molecule. For this reason, assignments of forbidden levels of FD in complex molecules are most of the time well educated guesses. Fernández Bertrán [97] has shown how the MWM can be used to determine the nature of ν_f , illustrated in the FR of the carbonyl fundamental of cyclopentanone. Several assignments of ν_f were published in the literature [98 - 100] and these combinations were used in the calculations of the XY functions of the MWM. If an erroneous assignment is made, several things can happen:

- a) There is no linearity between X and Y
- b) If there is linearity, the slope A can result in very abnormal values of the anharmonicity of the forbidden level. Also the values of W obtained from the XY correlation can differ considerably from the experimental value obtained from intensity data if the chosen assignment is incorrect.

Using these criteria, the correct assignment for ν_f in cyclopentanone was made from a set of nine different harmonic or combination bands [97].

5. ANALYTICAL APPLICATION OF FR

Although FR is normally a nuisance for analytical chemists, it can be an useful sensor of structural features. Doerffel has proposed the use

of solvent effects on FD to avoid interference of bands by shifting the intensity of a selected component of the FD. This also has the advantage of improving sensitivity by increasing the intensity of the analytical band. This approach has been applied in the IR analysis of sulfones [80].

FR can aid in structural determinations. For example the CH-aldehyde stretch is normally split by FR and this doublet serves as a characteristic band of the aldehyde group [100].

Davies has observed that the stretching vibration of the CC-triple bond in methyl undecyneate is affected by FR in the triple bond is not conjugated to the ester group or in the position [101]. All intermediate positions of the triple bond give rise to a FD. Snyder [50, 52] and Zerbi [53, 54] have made use of the FD in the CH_2 symmetric stretch at 2940 and 2850 cm^{-1} in the Raman spectra of long chain hydrocarbons, to monitor the ordering of the chains. They found that the intensity ratio R of the FD is a sensor of the abundance of trans and gauche conformations. Schneider [51] has used the FD of the NH stretch at 3300 - 3100 cm^{-1} of polyamides to measure the stereochemical characteristics of these important synthetic materials. Zundel [48] has also used this resonance to monitor the helical order and the denaturation of polynucleotides. Krim has also studied a triple FR in the ND region of poly-L-alanine for a similar purpose [49]. An important line of research in the study of the structure of proteins using Raman enhanced spectroscopy is the use of the FD at 810 - 850 cm^{-1} of the tyrosyl residues [43 - 47]. The relative intensity of this FD indicates whether the tyrosyl residues are buried in the protein, bound to CO_2^- groups or metal ions or whether they are external and exposed to solvent interactions.

A word of caution is in order to chemists using FD as sensor of molecular interactions. They must bear in mind that the frequencies and intensities of the FD components are related and can not be used independently. An important example is the study of the intensity - pressure relation of ν_s of superdense gaseous NH_3 by Raman spectroscopy [102]. In this conditions the FR of ν_s with 2δ is weak but the interaction is pressure dependent.

The use of the intensity of ν_s only led to erroneous conclusions of the deformations of the NH_3 pyramid with pressure on molecular packing. Use of the combined intensities of ν_s and 2δ indicate increasing deformation towards planarity of the NH_3 molecule with pressure [71].

TABLE 1. Fermi resonance in triatomic molecules

| Molecule | References |
|------------------|------------------|
| CO ₂ | 3- 5, 20, 21, 68 |
| COS | 7 |
| COSe | 8 |
| CS ₂ | 9, 10 |
| H ₂ O | 11, 18 |
| N ₂ O | 12, 13 |
| F ₂ O | 14, 19 |
| XCN | 15- 17 |
| HCN | 7 |

TABLE 2. Fermi resonance studies by the SVM

| Molecules | References | Molecules | References |
|------------------------|------------|---------------------------------|------------|
| Carbon dioxide | 20, 48, 68 | Sulphites | 79 |
| Cyanate anion | 38, 69 | Sulphoxides | 38 |
| Ammonia | 38, 71 | Sulphones | 80 |
| Acetylene | 38 | 5-X-Furan acrolein | 81 |
| Acetonitrile | 38, 72 | N,N-Diphenyl formamide | 29 |
| Acetone | 38 | N,N-Diphenyl carbamoyl chloride | 29 |
| Cyclopentanone | 55, 73 | Diphenyl carbonate | 29 |
| p-Benzoquinone | 55 | Benzoyl cyanide | 29 |
| Ethylene carbonate | 55 | Methyl naphthylketone | 29 |
| Furfural | 74, 75 | -Naphthaldehyde | 29 |
| Aniline | 38, 76 | p-X-Phenyl acetates | 29 |
| p-X-Phenyl azalactones | 77 | p-X-Benzaldehydes | 31 |
| Trifluoro ethylamine | 40, 78 | CH ₂ Br ₂ | 106 |
| p-X-Benzoyl chlorides | 32, 82 | | |

TABLE 3. Fermi resonance studied by the MWM

| Molecule | References |
|------------------------|------------|
| Carbondioxide | 38, 42 |
| Cyanate anion | 38, 42 |
| Cyclopentanone | 42, 45 |
| p-X-Benzoyl chlorides | 42, 55, 82 |
| p-X-Benzaldehydes | 38, 42 |
| Furan acrolein | 42, 81 |
| Cinnamaldehyde | 38, 42 |
| Bourgeonal | 38, 42 |
| Lilial | 38, 42 |
| Ammonia | 38, 42 |
| Ammonia-d ₃ | 38, 42 |
| Methyliodide | 42, 69 |
| α-Cl Acrylonitrile | 42, 69 |

TABLE 4. Important Types of Anharmonic Resonances

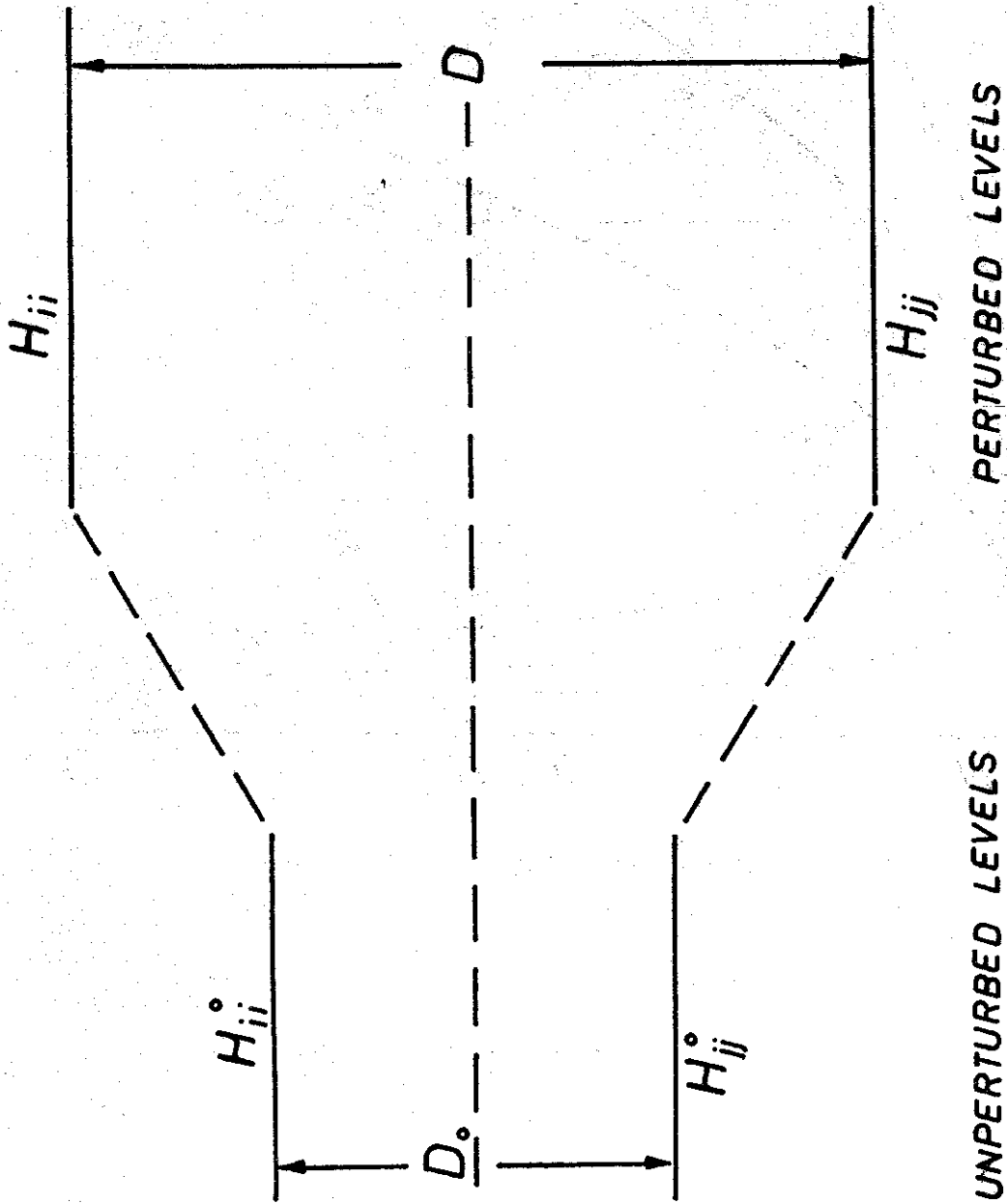
| Order | Interacting Levels | Force Constant | Examples |
|-----------------|---|-----------------------|--|
| 1 st | $\langle v, v', v'' v \pm 1, v' \pm 1, v'' \pm 1 \rangle$ | $K_{vv'v''}$ | Cyclopentanone Acetonitrile |
| | $\langle v, v' v \pm 1, v' \pm 2 \rangle$ | $K_{vv'v'}$ | CO ₂ , OCN- |
| 2 nd | $\langle v, v', v'', v''' v \pm 1, v' \pm 1, v'' \pm 1, v''' \pm 1 \rangle$ | $K_{vv'v''v'''}$ | Acetylene |
| | $\langle v, v' v \pm 2, v' \pm 2 \rangle$ | $K_{vv'v'v'}$ | 2ν ₂ , 2ν ₃ in H ₂ O |
| 3 rd | $\langle v, v' v \pm 3, v' \pm 2 \rangle$ | $K_{vvvv'v'}$ | 2ν ₃ , 3ν ₁ in HCN |
| | $\langle v, v', v'', v''' v \pm 1, v' \pm 2, v'' \pm 1, v''' \pm 1 \rangle$ | $K_{vv'v''v''v''v''}$ | ν ₁ -2ν ₃ , ν ₈ , ν ₉ in CH ₂ Br ₂ |

TABLE 5. Substituents Effects on Anharmonic Force Constants

| Family of Compounds | ν_a | dW/ds^2 (cm^{-1}) | Correlation Coefficient | References |
|--------------------------------|---------------------|--------------------------------|-------------------------|------------|
| p-X-Anilines | ν_{NH_2} | 7,5 | 0,935 | 38, 70 |
| p-X-Benzaldehydes | ν_{CH} | 8,1 | 0,980 | 31, 38 |
| p-X-Benzoylchlorides | ν_{CO} | 5,2 | 0,969 | 38, 82 |
| p-X-Benzenesulphonyl-chlorides | ν_{SO_2} | 6,8 | 0,992 | 103 |
| 5-X-Furanacroleins | ν_{CH} | 2,5 | 0,985 | 81 |
| p-X-Phenylazalactones | ν_{CO} | 1,9 | 0,990 | 38, 77 |

TABLE 6. Solvent Effects on Anharmonic Force Constants

| Compound | Resonance | Phase | $\omega(\text{cm}^{-1})$ | % Change | References |
|---|-------------------|------------------------------------|--------------------------|----------|------------|
| CO ₂ | $\nu_1 - 2\nu_2$ | gas, liquid | 51 | 18 | 93 |
| | | solid | | | |
| NH ₃ | $\nu_1 - 2\nu_4$ | H ₂ O, D ₂ O | 42 | 20 | 81 |
| | | gas and dil. CCl ₄ | 34, 7 | | |
| | | conc. CCl ₄ and liquid | 42, 6 | | |
| CF ₃ CH ₂ NH ₂ | $\nu_S - 2\delta$ | Pyridine | 41, 7 | 22 | 74 |
| | | Triethylamine | 53, 7 | | |
| Thioacetamide | $\nu_S - 2\delta$ | Acetonitrile | 61 | 27 | 104 |
| | | Pyridine | 84 | | |



$$D_0 = H_{ij}^0 - H_{jj}^0$$

$$D = H_{ij} - H_{jj}$$

$$W = H_{ij}$$

$$D = (D_0^2 + 4W^2)^{1/2}$$

Figure 1. Fermi resonance of perturbation of energy levels.

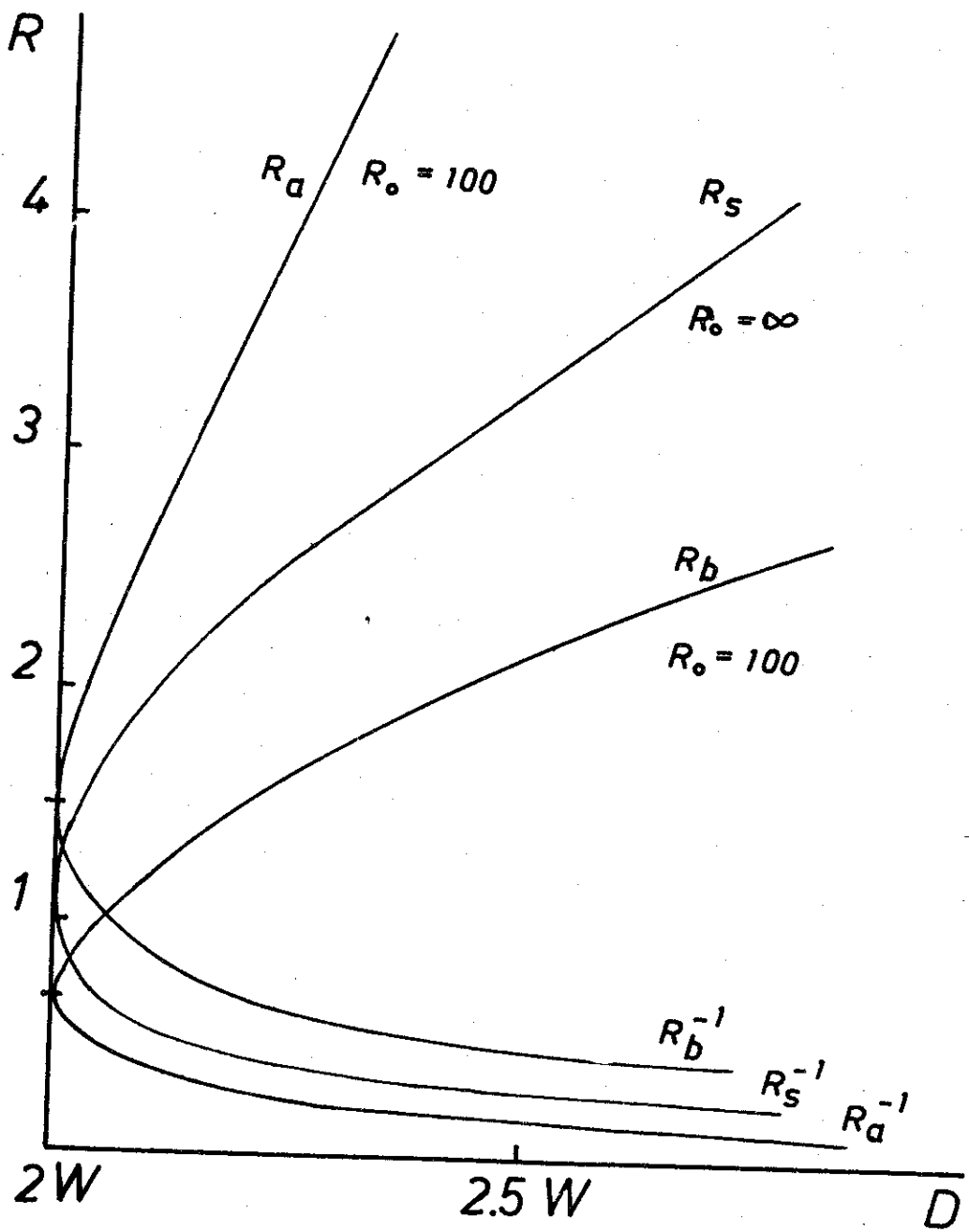


Figure 2: Different types of R-D curves.

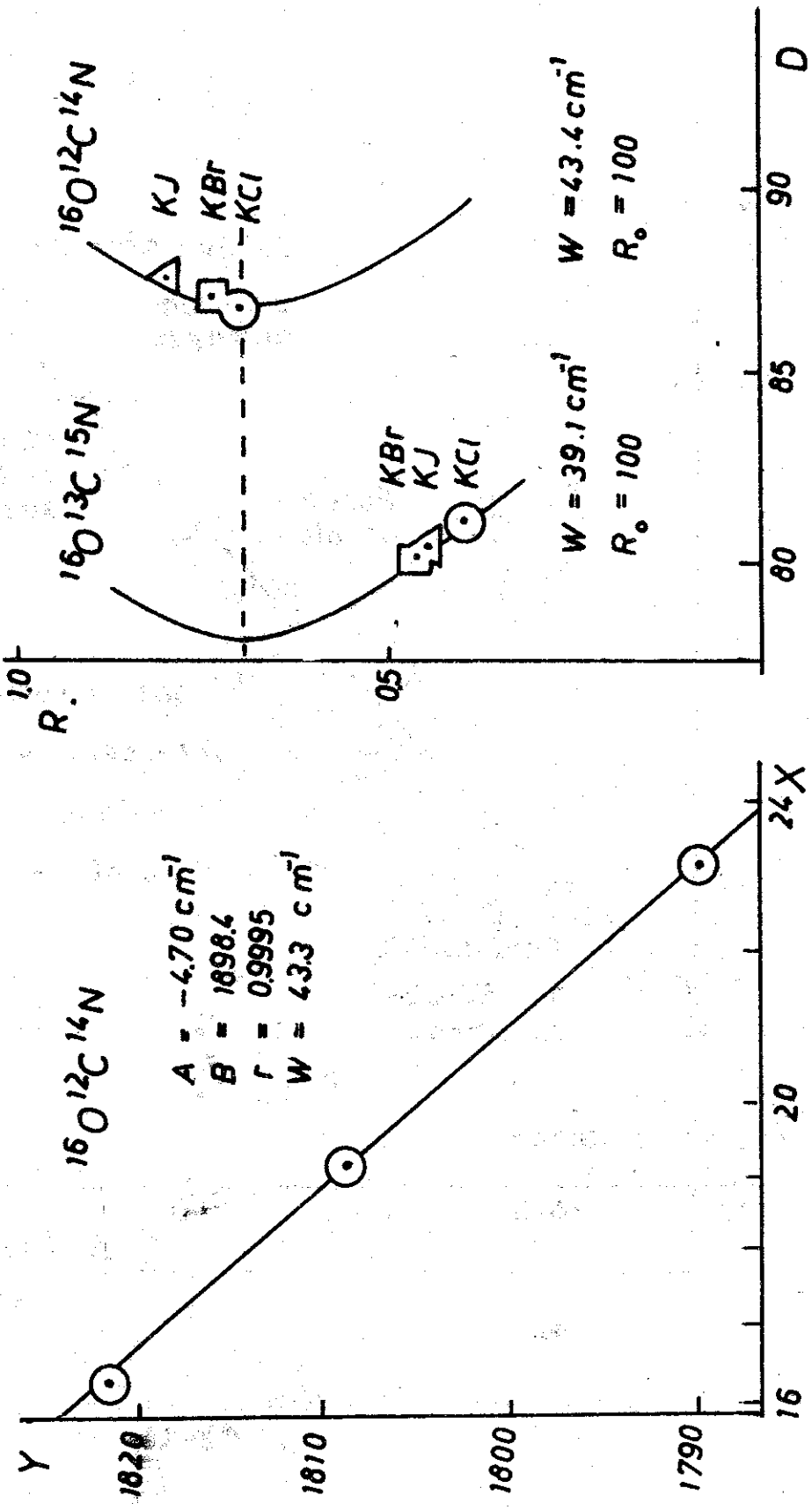


Figure 3. OCN^- resonance in crystalline matrices.

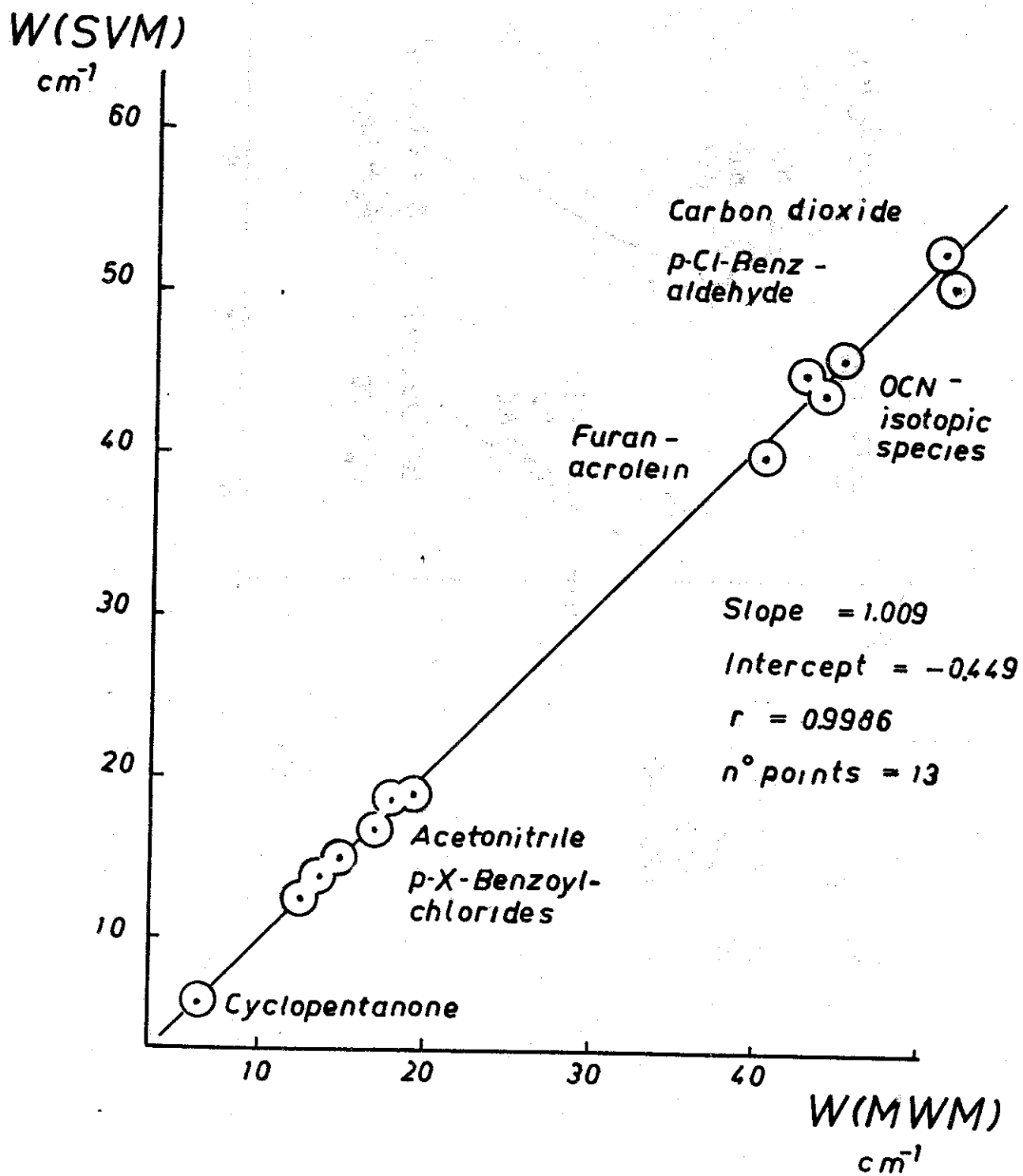


Figure 4. Comparison of results from MWM and SVM

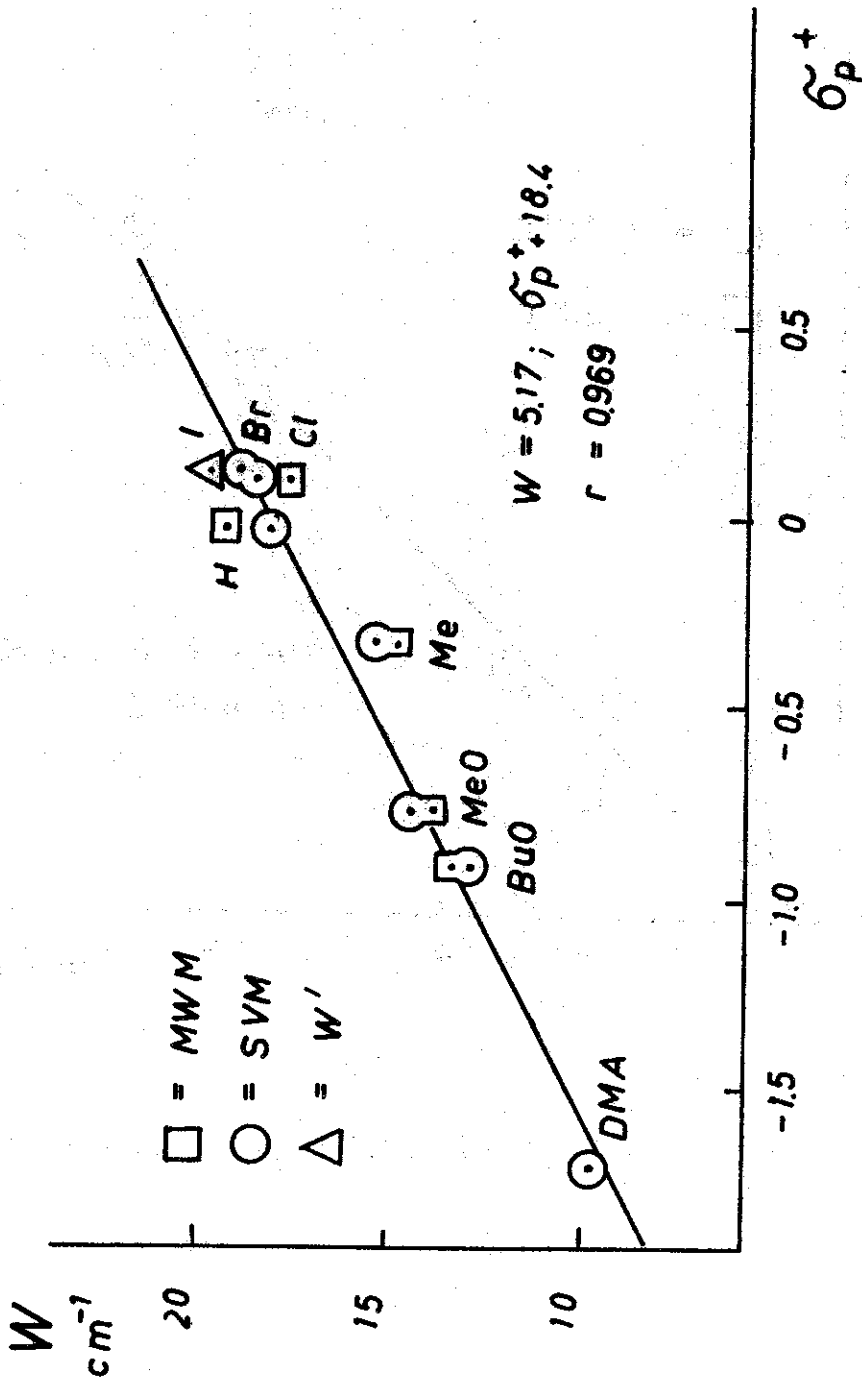


Figure 5. Dependence of W on σ_p^+ in p -substituted Benzoylchlorides.

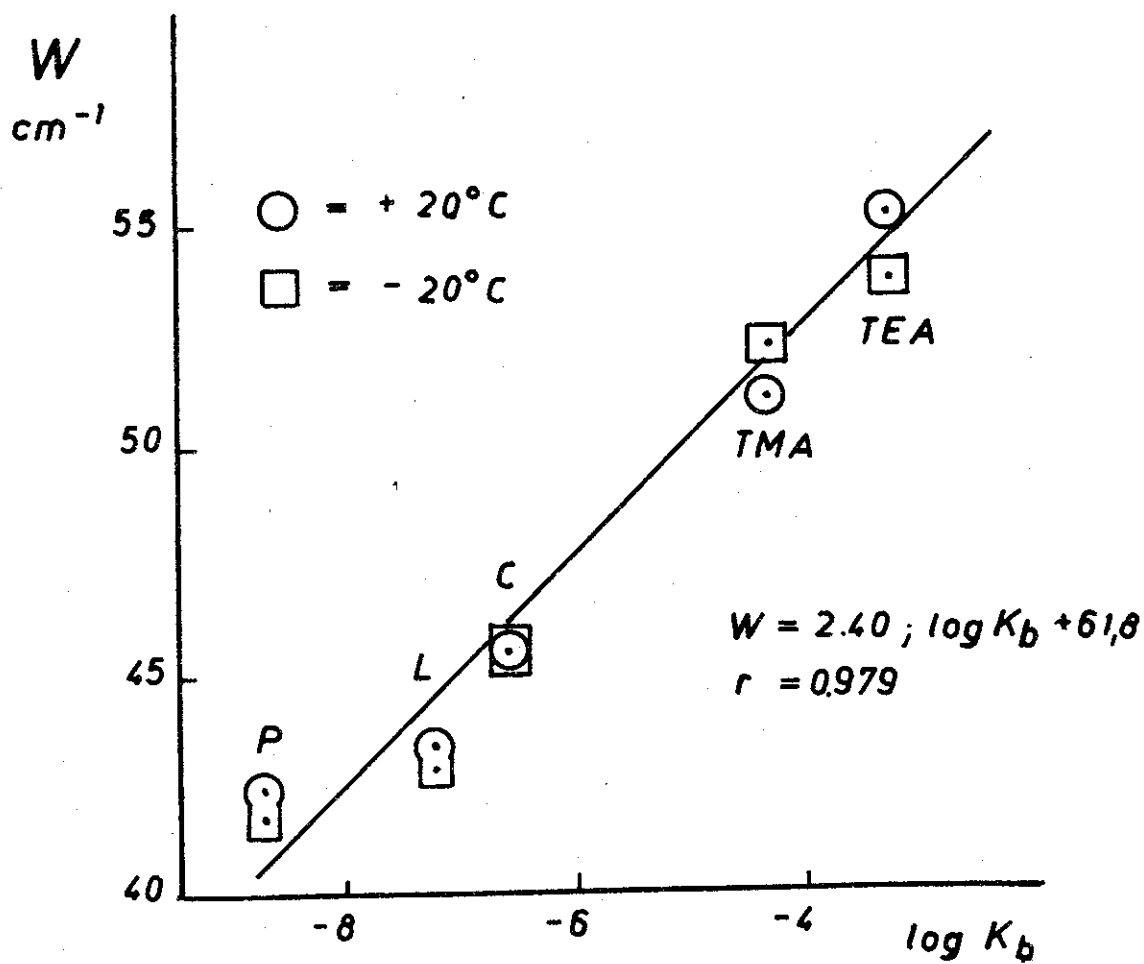


Figure 6. W versus $\log K$ in $\text{CF}_3\text{CH}_2\text{NH}_2$ - base in CCl_4 .

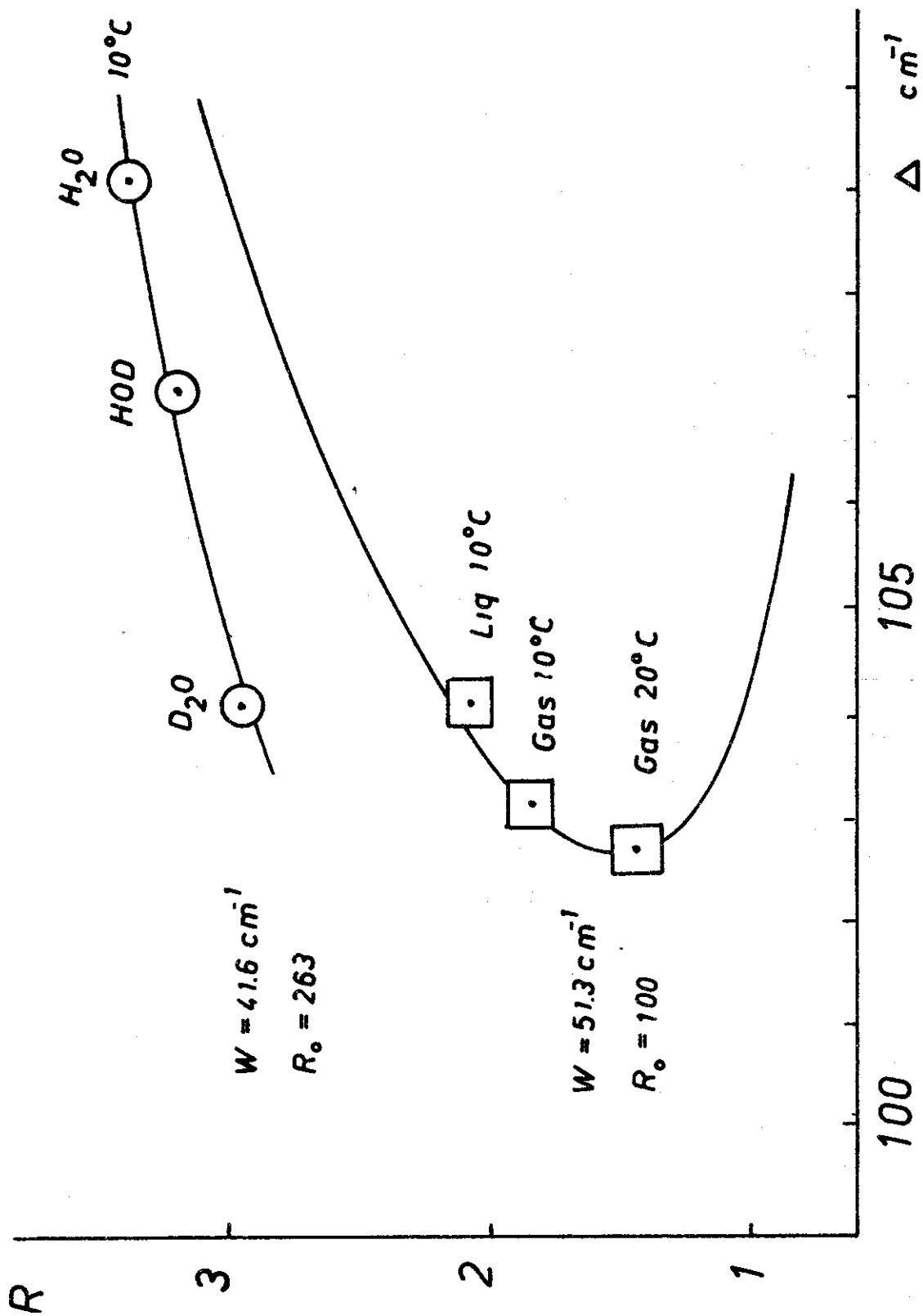


Figure 7. R-D plots for CO₂ in gas, liquid and solution.

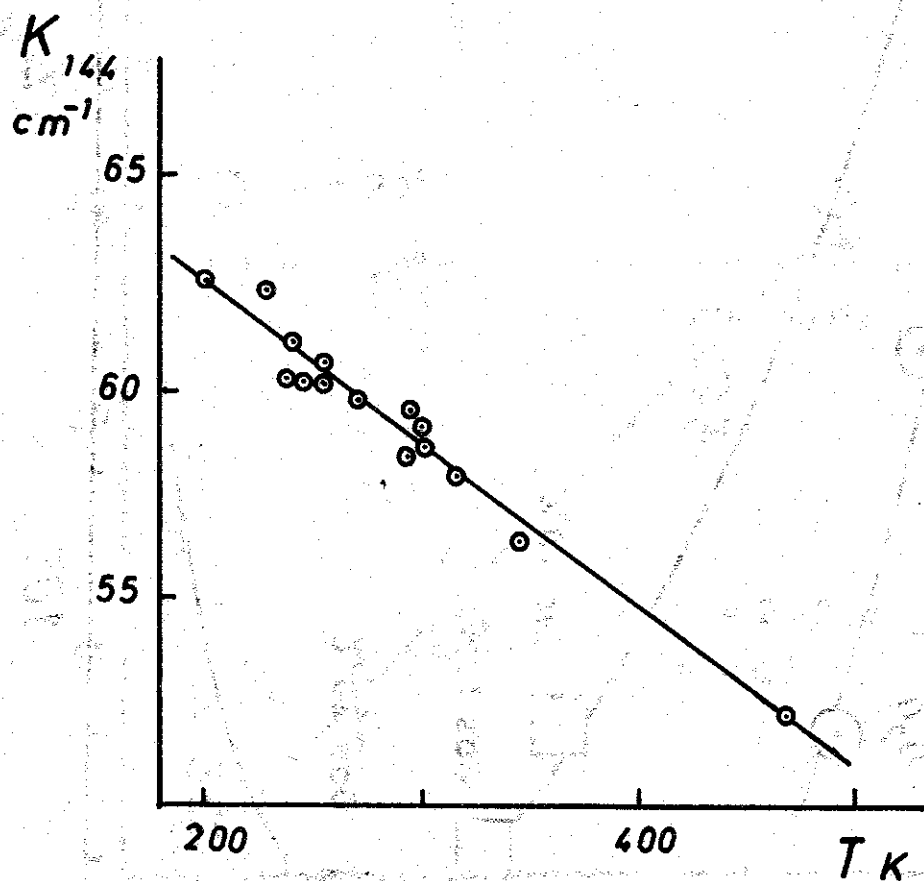


Figure 8. Temperature dependence of K_{144} in NH_3 .

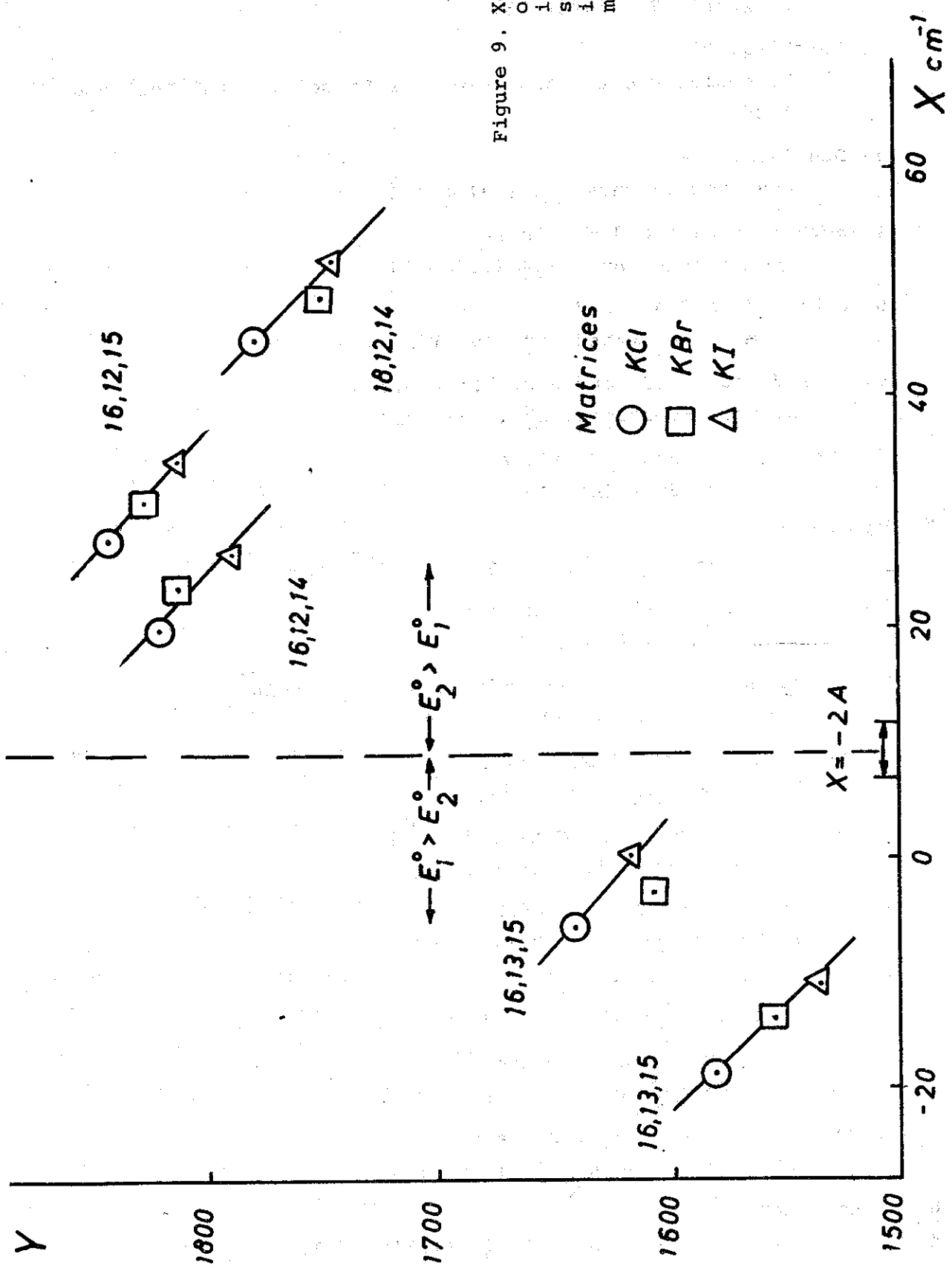


Figure 9. X-Y plots of OCN^- isotopic species in KX matrices.

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