Double Resonance Modulation as a Standard Technique in Microwave Spectroscopy

II. Line Shape and Integrated Intensity [1]

Otto L. Stiefvater

School of Physical and Molecular Sciences, University College of North Wales
Bangor, Gwynedd, U.K.

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It is shown that there occur two easily distinguishable line shapes in DRM spectroscopy. These reflect the change of the integrated intensity of the signal transition when pump radiation is applied. They readily permit deductions concerning the position of the shared energy level. This result is useful for the analysis of complicated spectra, as is illustrated with examples.

An expression is derived which permits the determination of the integrated intensity of absorption lines by DRM techniques alone. It does not require knowledge of the absolute value of the pump power and provides, therefore, a convenient basis for relative intensity measurements without recurrence to Stark effect modulation.

I. Introduction

The routine use of the double resonance effect (see Part I, Ref. 1) [2] in place of the Stark effect for the observation and analysis of rotation spectra entails, at first sight, a considerable loss of spectroscopic information because of the absence of easily observable effects which relate to the degenerate M-states of rotational levels. Thus, the value of the principal quantum number J, or at least its change ΔJ, can often by inferred by inspection of the 'Stark-lobes' (transitions between M-states in the presence of an electric field) in the Stark effect modulated spectrometer (I[21]), but no information of comparable specificity can be derived from the observation of the same transition in the double resonance modulation (DRM) spectrometer. In principle, of course, the double resonance doublet [see Part I, Fig. 2 b and Eq. (4)] of a DRM signal should show an analogous fine-structure (I[14]) as arises from the M-components in Stark spectroscopy, since the differing values of the transition moments for individual M-components of the pump transition should produce different splittings of corresponding M-components of the signal transition. However, in most DRM spectrometers the resolution of this fine-structure is prevented by the inhomogeneous distribution of the electric field of the pump radiation inside the absorption cell. The only information that appears extractable from a successful DRM experiment is, therefore, the existence of a shared energy level between a pump and a signal transition of known frequency. Since this is hardly sufficient for the analysis of a complex spectrum without recurrence to Stark spectroscopy, there arises a need for procedures that furnish additional information.

One such procedure which can be applied with great ease is the main topic of the present paper. It is based on the examination of DRM line-shapes and allows, as will be shown, the division of DRM signals into two categories which clearly reflect the position of the common energy level with respect to the other two. While this result greatly facilitates the analysis of spectra, there also emerge other features of the DRM-technique from the study of the integrated intensity of DRM signals. Thus, a method will be described (Sect. V b) which permits the efficiency of the pump process to be determined without knowledge of the power output of the pump oscillator. In addition, an expression is derived which enables the integrated intensity of a normal absorption line to be extracted from DRM experiments alone. This, in turn, provides the basis for relative intensity measurements which can then be used either for the determination of relative population numbers, or the ratio of dipole moment components, or for

Reprint requests to Otto L. Stiefvater, School of Physical and Molecular Sciences, University College of North Wales, *Bangor*, Gwynedd, U.K.

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[2] References quoted in Part I (O. L. Stiefvater, Z. Naturforsch. **30 a**, 1742 [1975]) will be marked in this way. Similarly, Eq. (4) of Part I, for example, will be referred to as: Equation (I, 4).

the purpose of referencing ([I20b]) collision-induced signals ([I19,20]) without recurrence to Stark spectroscopy.

II. Instrumental

The DR-experiments which form the basis of the present paper were begun (Harvard, 1966/67) on the hybrid spectrometer described in Part I. They were continued (at Bangor) after the construction of a DRM spectrometer proper with an 'empty' K-band absorption cell of 21.8 meters length. Details of the construction and operation of the second instrument may be found in reference [I6g].

III. The two DRM Line-shapes and Preliminary Studies

In examining the DRM spectra of a variety of molecules ([I7,8]) we have long noticed that, although the majority of signals conforms with the generally accepted DRM line-shape (Fig. 1 a), there occur

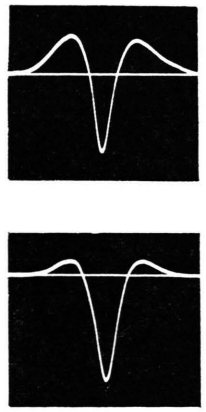

Fig. 1. The two distinguishable DRM line-shapes with strong and weak double resonance 'lobes'.

signals which differ from this 'normal' shape through a striking weakness of their DR 'lobes' (Figure 1 b). As is seen from Fig. 1, the two types are easily distinguishable and we shall refer to them as type I and type II, respectively.

Since it appeared tempting to ascribe this difference simply to undermodulation (Part I, Sect. VI, 5) caused by too little pump power or a weak transition moment of the pump transition, we first compared the shapes of different signal transitions that were modulated via the same pump transition. In this way, variations of the pump power or the transition moment could be positively eliminated. However, the accepted as well as the 'anomalous' line-shape were still observed for different signal transitions (compare Fig. 2, columns 1 or 2, with 3, and Fig. 3, column 2 with 4). This proved conclusively that under-modulation can not be true cause of the observed effect.

As another possible source for weak DR-lobes, differing intensity distributions of the unresolved M-components ([I14]) within the DR-lobes appeared worth consideration. In this case, the occurrence of weak lobes would be expected to be linked with particular combinations of ΔJ values of the pump and signal transition. For example, if a Q-branch transition ($\Delta J = 0$) is DR-modulated via another Q-branch transition, the highest M-component of the signal line will be split furthest so that a similar intensity distribution should result as for an unresolved, Stark-modulated Q-branch transition. If however, a $\Delta J = 1$ transition was modulated via a pump transition with $\Delta J = 0$, the strongest M-component ($M = 1$) of the signal would be split by the smallest amount. In this case, one would expect the intensity of the DR-lobes to drop off steeply with $|\nu_s - \nu_s^0|$. In addition, one might expect to observe zero-pump lines (central component of DRM signal) with a narrower width than for a DRM signal between two Q-branch transitions. This would be the result of the cancellation of the flanks of the zero-pump line by the strong M-components of the DR-doublet. Our experiments to test this hypothesis revealed only a partial correlation (see Sect. V a below) between the line-shape and the ΔJ-values, and variations in the width of the zero-pump line escaped quantitative experimental verification.

From these experiments it had to be concluded that the prime cause for the occurrence of two distinguishable line-shapes must lie in the disposition of the energy levels.

IV. Disposition of Energy Levels and DRM Line Shapes

a) Observations. – In our preferred mode of operation with $\nu_p < \nu_s$ any particular DRM signal must originate from one of the four three-level schemes that are shown in the lower halves of Figs. 2 and 3. These level schemes can be divided into two pairs, type I and type II; in the level schemes of 'type I' the common level is intermediate in energy whereas in the 'type II' schemes it is the highest or

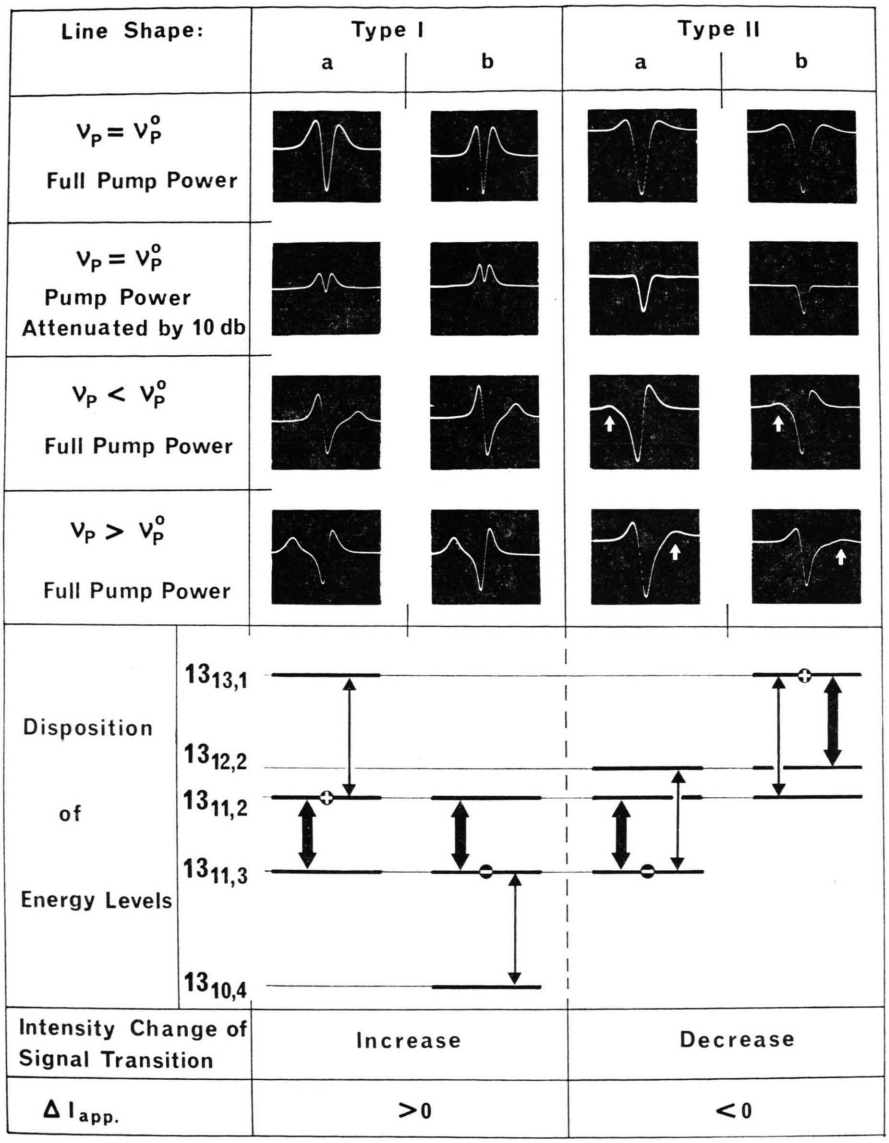

Fig. 2. Disposition of energy levels and associated DRM line shapes in a molecule (isoxazole (I^{7p}) with two non-zero dipole components.

lowest of the three[3]. It is apparent from the oscilloscope traces in the upper halves of Figs. 2 and 3 that this distinction leads not only to a different intensity distribution in the total DRM signal (row 1), but also results in a different behaviour of the two signal types under reduction of the pump power (row 2). It also leads, as has in fact been known for some time (I^4) to opposite asymmetry of the DR signal if the frequency of the pump radiation is de-tuned from exact resonance by a small amount (here: 2 – 3 MHz). This is shown in rows 3 and 4 of Fig. 2 and row 3 of Figure 3. It can also be verified by the study of the eight examples of Fig. 2 (molecule: isoxazole, intense absorptions, two dipole components) and Fig. 3 (molecule: propionic acid, comparatively weak absorptions, one dipole component) that the correlation between the position of the common level and the two lineshape categories defined above is not affected by the intensity of transitions, nor by the number of non-zero dipole components, nor by the ΔJ-values of the signal and pump transitions.

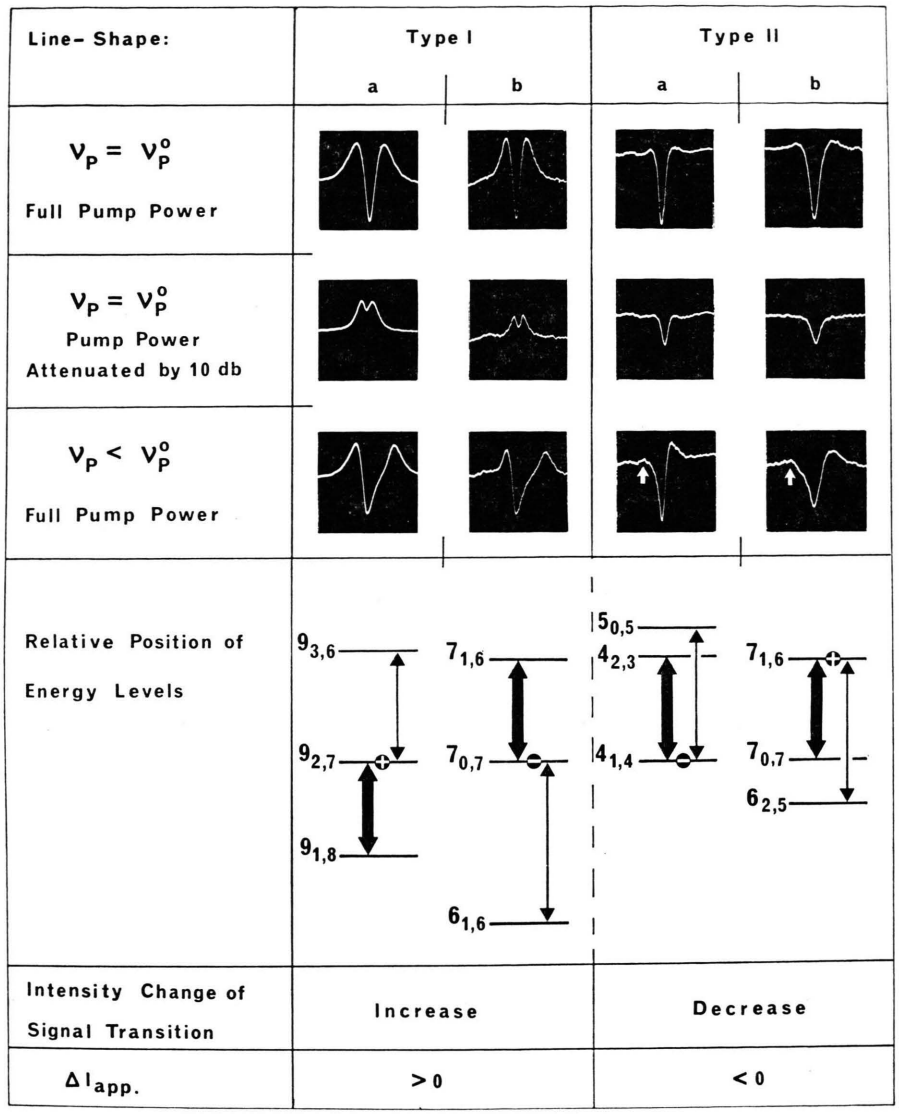

Fig. 3. Disposition of energy levels and associated DRM line shapes for transitions of *cis*-propionic acid (I^{7b}) with only one dipole moment component.

b) Theory. – To account for the described observations we consider the integrated intensity J of a signal transition in the absence ($E_p = 0$) and presence ($E_p \neq 0$) of exactly resonant pump radiation ($\nu_p = \nu_p^0$):

$$J(E_p = 0) = \int L^{E_p = 0}(\nu_s)\, d\nu_s\,, \qquad (1\,a)$$

$$J(E_p \neq 0) = \int L^{E_p \neq 0}(\nu_s)\, d\nu_s\,. \qquad (1\,b)$$

Here, $L^{E_p = 0}(\nu_s)$ and $L^{E_p \neq 0}(\nu_s)$ describe the absorption of power from the signal radiation as given by Eq. (I,1) and Eq. (I,4). For a level scheme of type I a (see Figs. 2 or 3) where $W_1 < W_2 < W_3$ and $\nu_p^0 = (W_2 - W_1)/h$, the integrals of Eq. (1) become

$$J(E_p = 0) = C(n_c^0 - n_3^0)\,|\mu_s|^2\,, \qquad (2\,a)$$

$$J(E_p \neq 0) = C(n_c^+ - n_3^0)\,|\mu_s|^2\,. \qquad (2\,b)$$

In Eq. (2), μ_s is the dipole matrix element for the signal transition at frequency $\nu_s^0 = (W_3 - W_2)/h$, and

$$C = (E_s^2/4\hbar\pi\tau) \int f^{E_p = 0}(\nu_s)\, d\nu_s \qquad (3)$$

$$= (E_s^2/4\hbar\pi\tau) \int f^{E_p \neq 0}(\nu_s)\, d\nu_s = E_s^2 \pi^2 \nu_s^0/h$$

where $f^{E_p = 0}(\nu_s)$ and $f^{E_p \neq 0}(\nu_s)$ are the frequency dependent parts of Eq. (I,1) and Eq. (I,4), re-

spectively. E_s is the electric field of the signal radiation, and τ is the relaxation time. The Boltzmann population of the shared level $W_2 = W_c$ is given as n_c^0, while

$$n_c^+ = n_c^0 + \delta n_c \qquad (4)$$

is the population of this level in the presence of pump radiation. We now recall (Part I, Sect. II) that the signal amplitude $S^{DRM}(\nu_s)$ displayed by the DRM spectrometer is proportional to the difference between the signal power absorbed in the presence and absence of pump radiation,

$$S^{DRM}(\nu_s) = L^{E_p \neq 0}(\nu_s) - L^{E_p = 0}(\nu_s) \; . \qquad (I, 6)$$

Since the DR-doublet [described by $L^{E_p \neq 0}(\nu_s)$] and the zero-pump line [given by $L^{E_p = 0}(\nu_s)$] will normally overlap to some extent, only a portion, $J_{app.}$, of the integrated intensity of each of these component signals is instrumentally apparent. This is taken into consideration by writing

$$J_{app.}(E_p = 0) = J(E_p = 0) - J_{overlap}(E_p = 0) \quad (5\,a)$$

and

$$J_{app.}(E_p \neq 0) = J(E_p \neq 0) - J_{overlap}(E_p \neq 0) \; . \quad (5\,b)$$

However, since

$$J_{overlap}(E_p \neq 0) = J_{overlap}(E_p = 0) \qquad (6)$$

we obtain with the definition

$$\Delta J_{app.} \equiv J_{app.}(E_p \neq 0) - J_{app.}(E_p = 0) \qquad (7)$$

from Eq. (5):

$$\Delta J_{app.} = J(E_p \neq 0) - J(E_p = 0) \; . \qquad (8\,a)$$

On account of Eqs. (1), (6), (2) and (4) this may also be written as

$$\Delta J_{app.} = \Delta J = \int S^{DRM}(\nu_s)\, d\nu_s \qquad (8\,b)$$

$$= C(n_c^+ - n_c^0)\,|\mu_s|^2 = C\,\delta n_c\,|\mu_s|^2 \; . \quad (8\,c)$$

Equations (8 a) and (8 c) state that, despite the overlap, the instrumentally apparent difference between the integrated intensity of the DR-lobes and the zero-pump line (which is the signal area above and below the base-line in the traces of Figs. 1 – 3) is equal to the true increase of the integrated intensity of the signal transition when pump radiation is applied. Equation (8 c) summarises Eq. (2) and merely re-states that the change $\Delta J_{app.}$ of the integrated intensity of a signal is proportional to the population increase of the common energy level due to the pump radiation.

While Eq. (2) and Eq. (8 c) contain the explicit assumption of a level scheme of type I a, it is easily shown that

$$\Delta J_{app.} = \begin{cases} +C\,|\delta n_c|\,|\mu_s|^2 > 0 & \text{for type I}, \\ -C\,|\delta n_c|\,|\mu_s|^2 < 0 & \text{for type II}. \end{cases} \qquad (9)$$

This implies that the apparent intensity of the DR-lobes will always exceed the apparent intensity of the zero-pump line ($\Delta J_{app.} > 0$) when the common energy level lies in between the other two levels (type I or 'progressive'[3] DR), and that the reverse holds true ($\Delta J_{app.} < 0$) when the shared level is either the highest or lowest in energy (type II or 'regressive' DR). Conversely, type I or type II level schemes must be inferred from the observation of $\Delta J_{app.} > 0$ or $\Delta J_{app.} < 0$, respectively.

c) Practical Aspects. – The positive or negative value of $\Delta J_{app.}$ for a particular DRM signal can normally be assessed by inspection. This is obvious from the predominance and nearly complete absence of DR-lobes in the examples of Figs. 2 and 3. In dubious cases, on the other hand, a simple experimental test on the sign of ΔJ is afforded by the attenuation of pump power. Due to the increased overlap between the DR-lobes and the zero-pump line under reduced pump power, the former extinguish the latter for DRs of type I, which clearly indicates that ΔJ approaches zero from positive values. For DRM signals corresponding to a type II scheme, ΔJ approaches zero from negative values and the zero-pump line extinguishes the weaker DR-lobes when the pump power is reduced. This simple effect is illustrated in the second row of traces in Figs. 2 and 3 which show the signals with the pump power attenuated by a factor ten.

It will have been noticed that the arguments of the previous Sect. b are based on the tacit assumption of complete power modulation of the pump radiation, so that the zero-pump condition (Part I, section IV a) is met exactly during one half of the modulation cycle. For frequency modulation of the pump radiation this condition is only approximated, and the validity of Eq. (9) depends on the modulation scheme and the modulation depth. While we have not encountered any ambiguities in the sign of ΔJ when using the 'on-off' scheme with modulation depths above 20 MHz, uncertainties can arise for modulation depths much below that value because too large a portion of the integrated intensity of the zero-pump line is then diverted into the nearby double-quantum signal ('creeper'). For symmetrical

modulation with a small modulation depth (I^5), type I and type II level schemes can not be distinguished at all on account of the line shape, because the integrated intensity of the two asymmetrical doublets that are characteristic of this mode of modulation (Part I, Fig. 5) become equal and ΔJ is zero for all four level schemes.

Fortunately, if the unequivocal determination of the sign of ΔJ from the two criteria described so far should be prevented by instrumental limitations (as, for example, a narrow mode of the pump klystron and hence unacceptably large power modulation for large frequency modulation) a third criterion may be used for the distinction of the two level schemes. As has been realised before (I^4), DRs from type I and type II level schemes differ also in the direction of the displacement of the double-quantum transition from ν_s^0 when the pump frequency ν_p is detuned from exact resonance. According to the approximate relation ($I^{1,4}$)

$$\nu_p - \nu_p^0 = \pm (\nu_s^d - \nu_s^0) \qquad (10)$$

the double-quantum transition (frequency ν_s^d) is displaced to the high-frequency side of the signal (frequency ν_s^0) when ν_p is detuned to the low-frequency side of the pump transition (frequency ν_p^0) for DRs that originate from a type I scheme, whereas the lower sign of Eq. (10) applies for a type II scheme and the creeper moves in the same direction as the pump frequency. This is shown in the traces of row 3 and 4 in Fig. 2 and row 3 in Figure 3. However, as is also apparent from these traces, it is normally quite difficult to detect the creeper (marked by the white arrows in Figs. 2 and 3) for a type II level scheme. This results from the combined effects of the population change and the intensity reduction which accompanies the displacement of the pump frequency from exact resonance (Part I, Figs. 2 c, 3 a and 3 c). It may finally be mentioned that although we have assumed that the pump frequency is always lower than the signal frequency, our conclusions are not affected if the rôle of the signal and pump transition is interchanged (I^4), as long as the absorption at ν_s^0 does not turn into emission. The conclusions are also independent from the relative orientation of the electric field vectors of the signal and pump radiation. This would be expected from Sect. b above which does not involve ΔM selection rules, and can be verified by examination of the DRM traces obtained by Rudolph (I^{22}) and collaborators in their experiments with perpendicularly polarised signal and pump radiation. The level scheme which these investigators studied belongs to type II and shows all three characteristic features which we have described, including the near undetectability of the 'creeper' for slightly off-resonant pump radiation (Fig. 7 of reference I^{22a} and Fig. 3 of reference I^{22b}).

V. Applications

While we have made frequent use of the line-shape of DRs in the analysis of spectra, a method for the determination of the true integrated intensity of the zero-pump line can be developed from Eq. (8) above. We describe these two applications separately.

1. Analysis of Spectra

a) Initial Assignments. – The possibility to distinguish between two categories of level schemes merely by inspection of the DRM line-shape restricts the number of otherwise reasonable interpretations of an observed DRM signal in terms of rotational quantum numbers. It provides, therefore, helpful clues in the initial investigation of an unassigned spectrum. This is particularly useful in cases where characteristic features of the overall spectrum (Q-branch sequences (I^{6g}) or R-branch families) can not be predicted with confidence or when the rigidity of the molecule under investigation prevents the exploitation of vibrational satellites (Part III) for the purpose of assignment. In general, it is advantageous to incorporate (compare Fig. 4) the line-shape criterion in the compilation of the

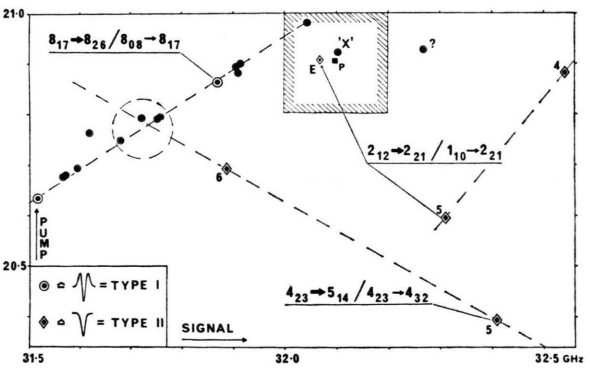

Fig. 4. Section of the double resonance map of *cis*-propionic acid (I^{7b}) with DRM signals from different rotational transitions.

DR-map (Part I, Sect. V) for the assumed model structure. This, in turn, facilitates the correlation of a set of observed DRs with their model counterparts by a factor two, at least in principle. In practice, we have found that the type II line-shape occurs less frequently than the type I, and the observation of a type II signal contains a correspondingly larger amount of information. This can be rationalised from the examination of the selection rules which govern the most intense transitions

$$(\Delta\tau \equiv \Delta K_{-1} - \Delta K_{+1} < 4).$$

In spectra which arise from a single dipole component all DRs involving two Q-branch or two R-branch transitions produce the type I signal shape. The observation of a type II signal implies in such a case that different values of ΔJ must be involved in the signal and pump transition. This condition for the type II signal is relaxed in the presence of a second dipole component since type II signals can then also occur between two Q-branch lines and two R-branch lines provided these component transitions arise from different components of the dipole moment. For molecules with all three dipole components different from zero, the restriction on the ΔJ values becomes still more diluted and we find it then advisable to combine the line-shape considerations with the fact that most pump transitions produce more than just one signal. We have used this latter approach for the assignment of iso-butyric acid (I^{7e}) ($\mu_a \neq \mu_b \neq \mu_c \neq 0$, $\varkappa = -.383$) without reference to Stark spectroscopy.

b) Isotopic Species and Vibrational Satellites. – Clearly, DRs that are associated with isotopic forms (Part IV) and vibrational satellites (Part III) of a given combination of rotational transitions must produce the same DRM line-shape as the ground state transition of the parent species. Hence, in frequency areas which contain satellites from two different rotational combinations, the DRM line-shape provides a convenient criterion for the separation of the two groups of satellites provided these arise from distinguishable level schemes.

An application of this idea may be followed with the help of figure 4 which shows an area of the DR-map of *cis*-propionic acid (I^{7b}). It contains satellites from at least three different rotational combinations. These are: $8_{17} - 8_{26}/8_{08} - 8_{17}$ which is a level scheme of type I, and $2_{12} - 2_{21}/1_{10} - 2_{21}$ and $4_{23} - 5_{14}/4_{23} - 4_{32}$ which both belong to the type II category. DRs associated with identical rotational quantum numbers are connected by dashed lines for clarity. From the line-shape criterion it follows in this example that, while the DRs numbered 4, 5, and 6 can not be distinguished from each other on account of the line-shape, DR 6 can clearly not belong to the group of $J = 8$ signals because of its type II line-shape. Conversely, the encircled (Fig. 4) group of signals can not be assigned to the type II sequence $4_{23} - 5_{14}/4_{23} - 4_{32}$, since they exhibit the characteristic of type I. This also applies to the signals marked 'X' and '?', which can not belong to the combination $2_{12} - 2_{21}/1_{10} - 2_{21}$.

c) Non-rigid Rotor Spectra. – The relation between level schemes and DRM line-shape is also valuable for the identification of transitions which do not conform to a pseudo-rigid rotor spectrum, and hence prevent an easy check on their rotational assignment by frequency consistency with other DRs. In such cases we have successfully employed the line-shape considerations for the analysis of spectra which involve internal motions in double-minima potentials ($I^{7c,d}$), internal rotation of CH_3-groups, and in spectra perturbed by other (I^{7b}) rotation-vibration interactions.

It is convenient to illustrate this point with the second excited state of the internal rotor mode of *cis*-propionic acid. Here, knowledge of the barrier parameters derived from the first excited state and the DRM analysis of the A-spectrum [4] permitted the approximate prediction of the non-rigid rotor transitions that constitute the E-spectrum. The transitions $2_{12} - 2_{21}$ and $1_{10} - 2_{21}$, in particular, which are separated from their A-components by ~ 0.9 GHz and ~ 1.2 GHz, respectively, were estimated to deviate by no more than ± 100 MHz (shaded area in Fig. 4) from the originally predicted position (point P in Figure 4). However, two DRs of the expected low intensity were found in the double search experiment reasonably close to prediction. For one of these (marked 'X') the signal frequency agreed well with expectation but the pump frequency deviated by ~ 20 MHz. For the other one, the pump frequency was in good agreement with prediction but the signal deviated by 45 MHz. A tentative selection of the correct DR was, therefore, impossible on the basis of frequency considerations alone. However, since the level system $2_{12} - 2_{21}/1_{10} - 2_{21}$ belongs to type II, the signal 'X' could be safely ruled out since it showed the characteristics of a type I level scheme.

2. Integrated Intensity of the Zero-Pump Line

As far as we are aware, DRM spectrometers with 'empty' absorption cells have never been used for measuring the intensity of the ordinary absorption signal which occurs in the absence of pump radiation (zero-pump line). Because the total DRM signal involves considerable overlap between the zero-pump line and the DR-doublet, the peak height as well as the integrated intensity of the normal signal appear much reduced under DRM. All investigators have therefore returned to Stark modulation for determining the intensity of the normal absorption signal. This inconvenience can be eliminated on the basis of the following consideration which relates the readily measurable quantity ΔJ, introduced in section IV above, to the integrated intensity $J(E_p=0)$ of the ordinary signal line.

The Boltzmann population differences for a pump and a signal transition of frequency ν_p^0 and ν_s^0 in the microwave range ($h\nu \ll kT$) are related by

$$(n_c^0 - n_3^0)_s = (\nu_s^0/\nu_p^0)\,(n_1^0 - n_c^0)_p \qquad (11)$$

where, for simplicity, we have again assumed a level scheme of type I a. Subscripts are added to the population differences in order to emphasise the pump and signal transition. It is clear from Eq. (11) that any measurable quantity which depends on the Boltzmann difference for the pump transition will also provide a measure for $(n_c^0 - n_3^0)_s$ which is the population difference for the connected signal transition in the absence of pump radiation.

Introducing a pump parameter [compare Eq. (I,3)]

$$\Pi = 4\,|Y|^2\,\tau^2 = |\mu_p|^2\,\tau^2\,E_p^2/\hbar^2 = |\mu_p|^2\,\tau^2\,P/G\,\hbar^2 \qquad (12)$$

which incorporates the line strength μ_p of the pump transition, the relaxation time τ and the cross-section G of the absorption cell along with the pump power $P \propto G\,E_p^2$, we have from Sect. IV, Eq. (8 c):

$$\Delta J(\Pi) = C\,\delta n_c(\Pi)\,|\mu_s|^2 = C\,(n_1^0 - n_c^0)_p\,|\mu_s|^2\,\{\Pi/2\,(\Pi+1)\} \qquad (13)$$

where use has been made of the Karplus-Schwinger (I^{18}) formula [Eq.. (I,3 b)] to relate δn_c, and hence ΔJ, to the Boltzmann population difference for the pump transition and to the pump parameter Π. After elimination of $(n_1^0 - n_c^0)_p$ with Eq. (11) we obtain next:

$$\Delta J(\Pi) = [C\,(n_c^0 - n_3^0)_s\,|\mu_s|^2]\,(\nu_p^0/2\,\nu_s^0) \cdot \{\Pi/(\Pi+1)\}. \qquad (14\,a)$$

The first bracket in this equation is just the integrated intensity of the zero-pump line as given in Sect. IV, Eq. (2 a), and we have, therefore,

$$\Delta J(\Pi) = J(E_p=0)\,(\nu_p^0/2\,\nu_s^0)\,\{\Pi/(\Pi+1)\}. \qquad (14\,b)$$

Before one can utilise Eq. (14 b) to measure $J(E_p=0)$ in terms of ΔJ one needs the pump parameter Π. That, however, is readily accomplished from the variation of ΔJ with pump power. Denoting, for example, by R(10) the ratio between the largest value of ΔJ (which results from the maximum available pump power) and that value which is measured when the pump power is reduced by a factor of ten, i.e.

$$R(10) = \Delta J(\Pi_{max})/\Delta J(\Pi_{max}/10) \qquad (15\,a)$$

we obtain from Eq. (13) or (14)

$$\Pi_{max} = [10 - R(10)]/[R(10) - 1] \qquad (15\,b)$$

with corresponding expressions for Π_{max} when the pump power is attenuated by other factors. With Π thus determined spectroscopically from several values of $\Delta J(\Pi)$, rather than from the more usual estimates of the pump power, the relaxation time, and the effective cross-section of the absorption cell, we have finally:

$$J(E_p=0) \equiv C\,(n_c^0 - n_3^0)\,|\mu_s|^2 = (2\,\nu_s^0/\nu_p^0)\,\{(\Pi_{max}+1)/\Pi_{max}\}\,\Delta J_{max}. \qquad (16)$$

From this equation, ΔJ_{max} is seen to provide an experimental measure for the integrated intensity of the zero-pump line, and it can therefore be used for the determination of the relative population numbers, or the relative size of dipole moment components.

It is a particularly important feature of Eq. (16) that it does not impose conditions on the power level of the pump radiation or its constancy when the pump frequency is moved from one transition to another. When a variation of pump power with pump frequency is obvious or suspected, Π_{max} is simply redetermined for each value of ν_p^0.

It must not be overlooked, however, that the derivation of Eq. (16) presupposes that the modulation frequency, ν_{mod}, of the spectrometer is low enough to enable the pumped population n_c^+ to return to the equilibrium value within a small fraction of the modulation period T, i.e. $\tau \ll T/2 = 1/2\,\nu_{mod}$. Although this condition is not critical for the determination of vibrational frequencies, isotopic abundances, or the ratio of dipole moment components, too high a modulation frequency will

cause systematic deviations of the unpumped population from the true Boltzmann value. Before Eq. (16) is used to determine equilibrium populations, as for example, for referencing collision-induced signals (I[20]), it is advisable to estimate the relaxation time τ and, if necessary, to reduce the modulation frequency to a suitably low value ($\nu_{\mathrm{mod}}/2 > 10/\tau$). A convenient way for estimating τ is to measure the splitting $\Delta\nu_{\mathrm{s,max}}$ of the DR-doublet for maximum pump power since, according to Eq. (I,5) and Eq. (12) above,

$$\tau = \sqrt{\Pi}_{\mathrm{max}}/2\pi\Delta\nu_{\mathrm{s,max}}\,. \qquad (17)$$

Of course, only qualitative significance can be attached to relaxation times determined with Equation (17). For small pump power the splitting $\Delta\nu_{\mathrm{s}}$ appears exaggerated due to the overlap of the zero-pump line with the DR-doublet. For large pump powers, on the other hand, a very accurate measurement of $\Delta\nu_{\mathrm{s}}$ is prevented because the peaks of the doublet are then smeared out as a result of the different splitting of individual M-components which remain unresolved due to the inhomogeneity of the pump field.

[3] It is pleasure to acknowledge a comment from Professor D. H. Whiffen, FRS, who pointed out that the terms 'progressive' and 'regressive' are used for analogous situations in NMR spectroscopy.

[4] For an introduction to Internal Rotation see, for example; C. C. Lin and J. D. Swalen, Rev. Mod. Phys. **31**, 841 [1959].