MOLECULAR SPECTRA
and
MOLECULAR STRUCTURE

II. Infrared and Raman Spectra of Polyatomic Molecules

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have been observed. Thus one is led to $\nu_2 \approx 1520$ cm^{-1} for CH_4 and it is necessary to consider the Raman line 3071.5 cm^{-1} as the first overtone of this frequency. The analogous interpretation for CD_4 gives $\nu_2 \approx 1054$ cm^{-1}. The fact that for both CH_4 and CD_4 the first overtone $2\nu_2$ occurs in the Raman spectrum whereas the fundamental (which is Raman active) has not been observed can be easily explained as due to Fermi resonance. It is seen that $2\nu_2$ is close to ν_1. Of the two sublevels

TABLE 80. FUNDAMENTAL FREQUENCIES (1–0 TRANSITIONS) OF GASEOUS CH_4 AND CD_4.

Assignment	CH_4		CD_4	
	ν_{vacuum} (cm^{-1})	References	ν_{vacuum} (cm^{-1})	References
$\nu_1(a_1)$	2914.2 (R.)	(287) (146) (594) (610)	2084.7 (R.)	(594)
$\nu_2(e)$	(1526)[107]	(276)	(1054)[108]	(594)
$\nu_3(f_2)$	3020.3 (I. R.)[109]	(656) (287) (594)	2258.2 (I. R.)[110]	(594) (658)
$\nu_4(f_2)$	1306.2 (I.)	(656)	995.6 (I.)[111]	(658)

of the upper state of $2\nu_2$ (having species A_1 and E; see Table 32) the one of species A_1 can resonate with the upper state of ν_1, and since ν_1 gives the strongest Raman line even a slight interaction will cause $2\nu_2$ to appear much more strongly than it otherwise would.

The correctness of the assignment of the fundamentals can be further checked by the *isotope relations*. Taking the observed values for ν_1 in Table 80 one obtains $\nu_1{}^D/\nu_1{}^H = 0.7154$ (where the superscripts D and H refer to CD_4 and CH_4 respectively), while according to (II, 327) $\omega_1{}^D/\omega_1{}^H = \sqrt{m_H/m_D} = 0.7074$. Similarly $\nu_3{}^D\nu_4{}^D/\nu_3{}^H\nu_4{}^H = 0.5699$, while according to (II, 328) $\omega_2{}^D\omega_4{}^D/\omega_3{}^H\omega_4{}^H = 0.5597$. Considering the neglect of anharmonicity, the agreement is quite satisfactory (compare Table 52). Conversely, by assuming exact agreement for the zero-order frequencies and further assuming that if $\omega_i{}^H = (1 + \alpha_i)\nu_i{}^H$ for CH_4, $\omega_i{}^D = [1 + (\omega_i{}^D/\omega_i{}^H)\alpha_i]\nu_i{}^D$ for CD_4, Dennison (280) calculated the *zero-order frequencies* ω_i from the observed fundamentals ν_i. He obtained for CH_4 (in cm^{-1})

$$\omega_1 = 3029.8, \quad \omega_2 = 1390.2,[112] \quad \omega_3 = 3156.9, \quad \omega_4 = 1357.6,$$

and for CD_4 (in cm^{-1})

$$\omega_1 = 2143.2, \quad \omega_2 = 983.4,[112] \quad \omega_3 = 2336.9, \quad \omega_4 = 1026.4.$$

It must be realized, however, that the second of the above assumptions is only roughly fulfilled [compare equation (II, 286)], so that the values obtained cannot claim a high degree of accuracy.

A large number of *overtone and combination bands* of CH_4 have been observed in the ordinary and photographic infrared. They are given in Table 81. As mentioned in Molecular Spectra I (p. 525), some bands occurring in the long-wave-length part of the spectra of the planets Jupiter, Saturn, Uranus, and Neptune have been definitely identified with bands of CH_4 observed with thick absorb-

[107] This value is not very accurate since it is determined indirectly. The value given here is taken from the band $\nu_2 + \nu_3 = 4546$ cm^{-1}. It is approximately the average of the value 1520 frequently quoted in the literature and obtained from $\nu_2 + \nu_4 = 2823$ cm^{-1} and the value obtained from the Raman band $2\nu_2 = 3071.5$ (neglecting anharmonic terms). Dennison (280) has included the effect of anharmonicity and obtained a value of 1499.4 cm^{-1}.

[108] This is half the frequency of the Raman shift 2108.1 cm^{-1} observed by MacWood and Urey (594), assuming that it corresponds to $2\nu_2$ and neglecting anharmonicity. Dennison gives 1036.4 cm^{-1} including anharmonicity.

[109] Average of infrared and Raman values.

[110] Average of Raman and infrared determination. Dennison (280) gives 2259.4 for the infrared value but the vacuum corrected value of Nielsen and Nielsen (658) is 2258.4 cm^{-1}.

[111] Dennison (280) gives 996.5. But this seems to be a mistake since Nielsen and Nielsen (658) give 995.86 and the vacuum correction is −0.27.

[112] From the Raman line $2\nu_2$ (see Table 81).

Such forbidden transitions have been observed by Straley, Tindal, and Nielsen (817) (866) (818) for SiH_4 and GeH_4, for which the active fundamental $\nu_4(f_2)$ and the inactive fundamental $\nu_2(e)$ are fairly close together, and therefore the Coriolis perturbation is relatively large. They found in both cases, in addition to the fundamental band ν_4, another much weaker band in the infrared which must be interpreted as the "inactive" fundamental ν_2. Confirmation of this interpretation is supplied (1) by the agreement with the value for ν_2 obtained from combination bands, (2) by the fact that the Q branches of the two bands are shaded in opposite directions, away from each other, as would be expected on the assumption of a perturbation (repulsion) that increases with J.

It appears likely that as more detailed investigations are carried out more such forbidden vibrational transitions will be found, not only for tetrahedral but also for other molecules. Their actual occurrence for SiH_4, GeH_4, emphasizes that in the interpretation of weak Raman or infrared bands the possibility of a violation of the vibrational selection rules even in the gaseous state must be considered (see the case of C_2H_4, p. 328). Thus the (weak) occurrence in the Raman or infrared spectrum of a certain vibration that is forbidden by the selection rules for a certain structure (point group) of a molecule does not necessarily rule out that structure, unless it can be shown that no Coriolis coupling could produce these bands. Fortunately, as can be seen from Jahn's rule (p. 376) by no means all forbidden transitions can be made weakly active by Coriolis interaction. For example, the rule of mutual exclusion for molecules with a center of symmetry (p. 256) holds rigorously even when Coriolis interaction is taken into account.

(c) *Raman spectrum*

Selection rules. Again for the Raman spectrum as for the infrared spectrum, if the interaction of vibration and rotation is not too strong the vibrational selection rules remain the same as for the pure vibration spectrum. The selection rule for J is the same as for the symmetric top:

$$\Delta J = 0, \pm 1, \pm 2; \qquad J' + J'' \geq 2. \tag{IV, 88}$$

However, for the totally symmetric Raman lines of tetrahedral molecules, only $\Delta J = 0$ can occur [see Placzek and Teller (701)], since during the whole vibrational motion the polarizability ellipsoid remains a sphere.

Unlike the case of symmetric top molecules there is here no selection rule for the three Coriolis sublevels $F^{(+)}$, $F^{(0)}$, $F^{(-)}$ of a triply degenerate state. The rule (IV, 81) that only rotational levels of the same species can combine with one another holds of course here, as well as for the infrared spectrum.

A_1—A_1 transitions. Since for totally symmetric Raman lines (A_1—A_1) only $\Delta J = 0$ occurs, and since for Raman transitions always $B' \approx B''$, only *one strong sharp "line"* (the superposition of all Q lines) is to be expected, without any accompanying branches even for heavy overexposure. This is in conformity with observation, for example for CH_4, although in most other cases, even when they should occur, other branches have not been observed.

E—A_1 transitions. If the upper state of a Raman band of a tetrahedral molecule is doubly degenerate, all five branches given by (IV, 88) may occur. The structure would therefore be expected to be very similar to that of a totally symmetric Raman band of a symmetric top molecule, except that the intensity distribution would not be as regular. No such band has as yet been observed. The separation of successive lines in the P, R and O, S branches would be $2B$ and $4B$ respectively, since there is no vibrational angular momentum for $\nu_2(e)$. In CH_4, SiH_4, and GeH_4 the higher rotational lines would be split on account of the Coriolis interaction with $\nu_4(f_2)$ which has a similar frequency.

F_2—A_1 transitions. Since there is no selection rule for the $F^{(+)}$, $F^{(0)}$, $F^{(-)}$ levels of an F_2 vibrational level, we obtain from (IV, 88) *fifteen branches* for an F_2—A_1 transi-

tion, five for each sub-band F_2^+—A_1, F_2^0—A_1, and F_2^-—A_1. These fifteen branches are shown schematically in Fig. 142. The superscripts +, 0, − indicate the upper vibrational sublevel concerned. According to (IV, 77) and (IV, 78) the spacings in the three pairs of branches S^+O^-, S^0O^0, S^-O^+ would be (neglecting the difference between B' and B'') $2B(2 + \zeta_i)$, $4B$, and $2B(2 - \zeta_i)$ respectively; in the three pairs R^+P^-, R^0P^0, R^-P^+ the spacing would be $2B(1 + \zeta_i)$, $2B$, and $2B(1 - \zeta_i)$ respectively; in the three branches Q^+, Q^0, Q^- it would be $2B\zeta_i$, 0, and $-2B\zeta_i$ respectively.

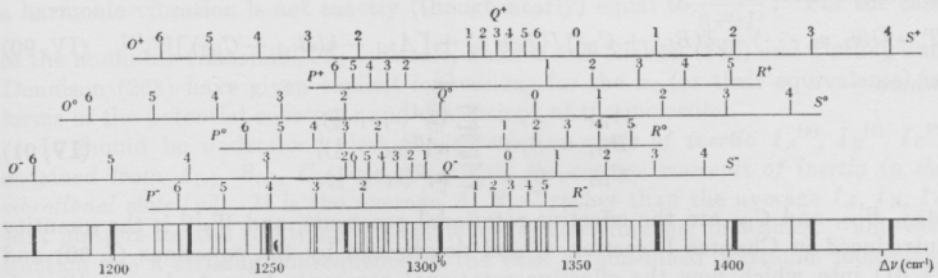

FIG. 142. **Branches of an F_2—A_1 Raman band of a tetrahedral molecule.**—The figure is drawn approximately to scale for ν_4 of CH_4 with $B = 5.2$ cm^{-1} and $\zeta = 0.45$. The difference of the B values in the upper and lower state is neglected. The three predominating branches are indicated by heavy lines. For small ζ values, as in the only observed case (ν_3 of CH_4), many of the branches here separated will almost coincide.

Fortunately, as has been shown theoretically by Teller (836), the S^+ series with spacing $2B(2 + \zeta_i)$ and the Q^0 branch with spacing 0 and the O^- series with spacing $2B(2 + \zeta_i)$ (that is, the transitions F_2^+—A_1 for $\Delta J = +2$, F_2^0—A_1 for $\Delta J = 0$, and F_2^-—A_1 for $\Delta J = -2$) have predominant intensity.

The Raman band ν_3 of CH_4 observed by Dickinson, Dillon, and Rasetti (287) in the gaseous state does indeed show these three branches. The observed spacing of the lines, 21.5 cm^{-1}, is therefore $2B(2 + \zeta_3)$, whereas the line spacing 9.93 cm^{-1} of the infrared band ν_3 is $2B(1 - \zeta_3)$. The sum of the two spacings yields $6B = 31.43$ or $B = 5.24$ cm^{-1}. This result is independent of the sum rule for ζ_i and the somewhat doubtful spacing in the infrared band ν_4, but is in very satisfactory agreement with the B value for CH_4 obtained above. If this Raman band could be measured more accurately with larger dispersion, and particularly if also the other branches could be observed, it would appear to supply the best method of obtaining a really precise value for the moment of inertia of CH_4 (and similar molecules).

Since the upper states of the S^+ and O^- branches of an F_2—A_1 Raman band are the same as those of the P^+ and R^- branches of the corresponding F_2—A_1 infrared band, *combination differences* may be used for the evaluation of the constants. From Fig. 137, in which the S^+ and O^- branches are shown by dotted lines, one can see easily that the following relation must hold:

$$S^+(J) - P^+(J+3) = R^-(J) - O^-(J+3) = F''(J+3) - F''(J) = 6B''(J+2). \quad \text{(IV, 89)}$$

When the data of Dickinson, Dillon, and Rasetti (287) for the Raman band and of Nielsen and Nielsen (656) for the infrared band ν_3 of CH_4 are used, it is found that the agreement of $S^+(J) - P^+(J+3)$ with $R^-(J) - O^-(J+3)$ is not very satisfactory. This may be due to insufficient accuracy of the Raman measurements, or to the second-order Coriolis splitting of the levels with larger J values in the upper vibrational state.