

On the Infrared and Raman Spectra of Methyl Compounds

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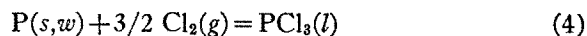
$$\Delta F^\circ_T = -11,300 + 16.48 T \log_e T + 0.0028 T^2 - 3.4 \times 10^{-6} T^3 - 41.3 T$$

$$\Delta H_{298} = -16,400 \text{ cal.} \quad \Delta F^\circ_{298} = 5155 \text{ cal.}$$

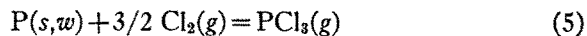
From these equations and the heat and free energy of vaporization of white phosphorus given above, a second value of 15.5 cal./deg. for the entropy of solid white phosphorus may be calculated. The close agreement between the two independent values is, in some measure, fortuitous, and, judging from the entropies of other solid substances of similar nature, both values are possibly too high. Until more accurate data are available we shall take 15.0 cal./deg. as the entropy of solid white phosphorus at 25°.

It is now possible to calculate the thermody-

namic constants for phosphorus trichloride. The heats of formation¹⁴ and vaporization¹⁵ of $\text{PCl}_3(l)$ are 75,900 cal. and -7620 cal., respectively, and the free energy of vaporization at 25° is 1080 cal. The following free energy equations may then be written:



$$\Delta H = -75,900 \text{ cal.} \quad \Delta F^\circ_{298} = -63,300 \text{ cal.}$$



$$\Delta H = -68,280 \text{ cal.} \quad \Delta F^\circ_{298} = -62,220 \text{ cal.}$$

¹⁴ Berthelot and Longuinine, *Ann. d. chim. phys.* (5) **6**, 307 (1875); Thomsen, *Ber.* **16**, 37 (1883); J. Ogier, *Comptes rendus* **87**, 210 (1878).

¹⁵ Regnault, *Mem. de l'acad. Sciences, France* **26**, 339 (1862).

On the Infrared and Raman Spectra of Methyl Compounds

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An analysis of the resonance interaction between the vibrations ν_1 and $2\nu_4$ in the methyl halide molecules explains the appearance of the very intense extra band in the infrared and Raman spectra of these molecules. This degeneracy is evidently characteristic of the methyl group. A number of molecules involving the methyl group and exhibiting the phenomenon of the extra band are listed.

THE infrared spectra of the methyl halides has been found by Bennett and Meyer¹ to consist of four single or parallel bands and three double or perpendicular ones. The frequency and intensity relations between them seem to preclude the possibility that any one is an harmonic; nevertheless, the molecule must have only nine degrees of freedom for vibration, and not ten as apparently indicated. The Raman spectra do not resolve this difficulty, but rather tend to emphasize it. Methyl chloride and methyl bromide each have strong Raman lines corresponding to the four single frequencies. Only a few of the double frequencies appear in Raman observations, and these lines are weak as would be expected from Placzek's theory.

The positions of the infrared bands observed in gaseous absorption, and of the Raman lines ob-

tained from the liquid, are listed in Table I. The designations by letter in the first column follow Bennett and Meyer, while the numerical subscripts are those of Dennison's analysis,² the even numbers corresponding to the double frequencies. Motions primarily involving the halogen atom are responsible for the frequencies ν_5 and ν_6 , while in first approximation ν_3 and ν_4 correspond to oscillations of the carbon and ν_1 and ν_2 to those of the three hydrogen atoms. Consequently, ν_4 , ν_2 and ν_1 are very insensitive to changes in mass of the fifth atom, and may be said to characterize the methyl radicle. There is no difficulty about the identification of *D* and *G* as ν_4 and ν_2 , respectively, but either *E* or *F* seems at first superfluous.

Analysis indicates that the harmonic of a perpendicular band consists of two components,

¹ Bennett and Meyer, *Phys. Rev.* **32**, 888 (1928).

² Dennison, *Rev. Mod. Phys.* **3**, 280 (1931).

one parallel and one perpendicular, and the table shows that the harmonic of D should fall almost midway between E and F . This suggests that the parallel component of $2\nu_4$ may be in close resonance with ν_1 , introducing an interaction which gives rise to a mixed wave function and a displacement of the two levels in opposite directions from their unperturbed positions. A similar situation has already been described in detail for CO_2 .³ Hence it seems quite natural to suppose that the bands E and F represent the set $(\nu_1, 2\nu_4)$, their intensities being comparable both in infrared and in Raman transitions, and considerably exceeding the expected intensity of a simple harmonic, as indicated by the absence of all such bands including the perpendicular component of $2\nu_4$ which does not partake of the interaction.

To determine the degree to which the vibrational levels ν_1 and $2\nu_4$ interact, and therefore the extent to which the resonance calculations must be introduced in the correlation of the infrared spectra of these molecules, we shall assume that in zeroth order approximation the degeneration is complete so that $\nu_1 = 2\nu_4$. The separation between the interacting frequencies will then be introduced as a part of the first order perturbing function, the remainder of which will consist of the terms of the cubic anharmonic potential giving the coupling between the two modes of vibration ν_1 and ν_4 .

Accordingly, the zeroth order system of the modes of vibration is given by:

$$H_0 = \frac{2\pi^2\nu_4}{h} \left[2p_\sigma^2 + p_\rho^2 + \frac{1}{\rho^2} p_\varphi^2 \right] + \frac{h\nu_4}{2} [2\sigma^2 + \rho^2],$$

where σ , ρ and φ are the dimensionless counterparts of the normal coordinates. σ specifies the single vibration ν_1 , while ρ and φ measured in a plane perpendicular to the symmetry axis of the molecule describe the motion ν_4 . Examination shows that the potential energy of vibration is an even function of ρ .

Forming and solving the wave equation, we find the zeroth order solution described by the energy

$$E_0 = h\nu_4 [2V_1 + V_4 + 2],$$

³ Adel and Dennison, Phys. Rev. **43**, 716 (1933); **44**, 99 (1933).

and by the wave function

$$\Psi_0 = \Psi^{V_1(\sigma)} \Psi^{V_4 l(\rho)} e^{\pm i l \varphi}.$$

V_1 , V_4 , and l are the quantum numbers of vibration; and $\Psi^{V_1(\sigma)}$ and $\Psi^{V_4 l(\rho)}$ are, respectively, the Hermitian orthogonal function with argument σ and the associated Laguerre orthogonal function with argument ρ^2 .

Setting $\Delta = \nu_1 - 2\nu_4$ we have, since the potential energy is an even function of ρ ,

$$\lambda H_1 = \frac{2\pi^2\Delta}{h} p_\sigma^2 + h \left[\frac{\Delta\sigma^2}{2} + b\sigma\rho^2 \right].$$

Replacing p_σ by $(h/2\pi i)(d/d\sigma)$, and making the substitution

$$d^2\Psi^{V_1(\sigma)}/d\sigma^2 = -[2V_1 + 1 - \sigma^2]\Psi^{V_1(\sigma)},$$

we have, finally:

$$\lambda H_1 = h[\Delta\{V_1 + \frac{1}{2}\} + b\sigma\rho^2].$$

Applying the first order perturbation to the system E_0 , Ψ_0 , the new description of the pair of interacting levels is set forth in Fig. 1, where the ψ 's are the stabilized wave functions of the resultant levels.

The above analysis yields the solution

$$\Delta = \bar{R} - 2\nu_4, \quad b^2 = (\Lambda^2 - \Delta^2)/2,$$

where \bar{R} is the mean of the two infrared band

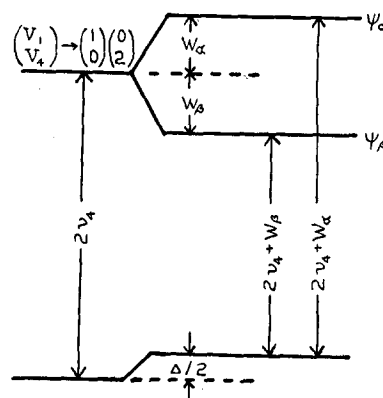


FIG. 1. Resonance splitting of energy levels.

$$W_\alpha = \Delta + [\Delta^2/4 + b^2/2]^{1/2}$$

$$W_\beta = \Delta - [\Delta^2/4 + b^2/2]^{1/2}$$

$$\psi_\alpha \sim [\Delta/2 - W_\alpha]\psi_\sigma^{V_1=1}\psi_\rho^{V_4=0} + (b/2^{1/2})\psi_\sigma^{V_1=0}\psi_\rho^{V_4=2}$$

$$\psi_\beta \sim (b/2^{1/2})\psi_\sigma^{V_1=1}\psi_\rho^{V_4=0} + [3\Delta/2 - W_\beta]\psi_\sigma^{V_1=0}\psi_\rho^{V_4=2}.$$

centers (ν_1 , $2\nu_4$), or the mean of the two corresponding Raman lines for the gas; and where Δ is the interval between the two band centers.

Employing the data given in the first part of Table I, we find the values for Δ and $|b|$ which

TABLE I. *Infrared and Raman spectra of methyl halides.* Infrared band centers⁴ in *italics*, for gaseous absorption. Raman lines⁵ for scattering by liquids.

| | | CH ₃ I | CH ₃ Br | CH ₃ Cl | CH ₃ F |
|------------------------------|-------------------|-------------------|--------------------|--------------------|-------------------|
| A | ν_5 | 534 | 610 | 734 | 1049 |
| | | 522 | 594 | 712 | |
| B | ν_6 | 885 | 957 | 1020 | 1200 |
| C | ν_3 | 1252 | 1305 | 1355 | 1476 |
| | | 1239 | 1296 | 1357 | 1462 |
| D | ν_4 | 1445 | 1450 | 1460 | 1476 |
| | | 1416 | | | |
| E | $(\nu_1, 2\nu_4)$ | 2855 | 2861 | 2880 | 2862 |
| | | 2889 | | 2815 | |
| F | $(\nu_1, 2\nu_4)$ | 2971 | 2972 | 2967 | 2965 |
| | | 2947 | 2956 | 2955 | |
| G | ν_2 | 3074 | 3061 | 3047 | 2987 |
| | | 3046 | 3050 | 3024 | |
| Δ in cm ⁻¹ | | 23 | 16 | 4 | -38 |
| $ b $ in cm ⁻¹ | | 80 | 78 | 62 | 68 |
| $(3\nu_4, \nu_1 + \nu_4)$ | | 4286 | 4288 | 4322 | 4322 |
| predicted | | 4440 | 4444 | 4446 | 4458 |

are tabulated in the second part of Table I. These values are in a class with those found for the carbon dioxide molecule, and it is thus apparent that a precise correlation of the infrared and Raman data for the methyl halide molecules will demand a treatment similar to the one accorded CO₂; namely, an analysis based upon the resonance interaction. An extended calculation of this type must be projected for the future when there will be more data available on the harmonic and combination bands in these spectra. The foregoing analysis can be employed to compute the expected positions of these bands correct to the first order; for example, the pair of bands

($3\nu_4, \nu_1 + \nu_4$) may be expected at approximately the positions listed in the last line of Table I.

Raman data are available for many other methyl compounds and the pair of lines corresponding to bands *E* and *F* occur quite generally. However, because of the lack of observations in the infrared, ν_4 cannot always be determined. Table II indicates a few more examples.

TABLE II.

| | ν_4 | $(\nu_1, 2\nu_4)$ | |
|---|---------|-------------------|------|
| CH ₃ OH | — | 2835 | 2943 |
| CH ₃ SH | — | 2871 | 2972 |
| CH ₃ C ₂ H ⁶ | — | 2871 | 2928 |
| C ₂ H ₆ | 1460 | 2890 | 2950 |
| C ₆ H ₁₄ | 1455 | 2862 | 2941 |
| C ₈ H ₁₈ | 1448 | 2870 | 2934 |

There is also an indication of resonance in CH₄, but here the band *D* (now designated ν_2) is inactive both for infrared and Raman excitation, and cannot be located directly. With Dennison's value, $\nu_2 \approx 1520$ cm⁻¹,⁷ and the observed Raman lines at 2915 and 3072 as $(\nu_1, 2\nu_2)$, we find for methane

$$\Delta = \bar{R} - 2\nu_2 = \frac{1}{2}(2915 + 3072)$$

$$-2 \times 1520 = -46 \text{ cm}^{-1},$$

$$|b| = +[(\Lambda^2 - \Delta^2)/2]^{\frac{1}{2}} = +[(22,533/2)^{\frac{1}{2}}] = 107 \text{ cm}^{-1}.$$

The large value of Δ is significant. It shows that the resonance interaction is weak, and thereby accounts for the observation that the 3072 cm⁻¹ Raman line is but one-tenth as strong as the one at 2915 cm⁻¹. The weakness of this interaction is also indicated by observations on the combination bands of methane. Several bands are known which involve ν_1 , but none involving $2\nu_2$ have been observed.⁸

⁴ Infrared measurements from (1) and from Barker and Plyler (to be published).

⁵ Raman data from Kohlrausch, *Der Smekal-Raman-Effekt*, where original references may be found.

⁶ Glockler and Davis, *Phys. Rev.* **41**, 370 (1932).

⁷ Dennison, *Astrophys. J.* **62**, 84 (1925).

⁸ Adel and Slipher, *Phys. Rev.* **46**, 240 (1934).