The Normal Frequencies of Vibration of the Plane Square Molecule AB4 with Reference to the Structure of Nickel Carbonyl

E. Bright Wilson Jr.

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Duncan and Murray[1] have recently studied the normal vibrations of the plane square molecule AB_4, using the method of mechanical models devised by Andrews.[2] They also applied their results to the interpretation of the Raman spectrum of $Ni(CO)_4$, considering the CO groups as dynamic units, and came to the conclusion that this molecule has the plane structure. Whereas it is certainly possible that this is the structure, I do not believe that their arguments in support of it are correct.

In the first place it seems very doubtful if any conclusions can be drawn by treating the CO groups as dynamic units, as they have done. Furthermore, it is unnecessary to do so, since the complete molecule can be treated by analytical methods without great difficulty. However, if we grant the validity of this approximation, their results are nevertheless incorrect because they did not take account of the selection rules[3] in the Raman effect. They correlated every mode of vibration of their models with an observed Raman line, whereas the vibrations ω_2, ω_3, ω_4 and ω_6 of their figure can be shown to be forbidden in the Raman effect. Their assignment of frequencies is consequently not valid and cannot therefore be used either directly as an argument for the plane structure or as a basis for the calculation of the symmetry number.

Although the model AB_4 is probably not a good approximation to $Ni(CO)_4$, it is so easy to treat analytically that I have done so and given the results below. The application of group theory leads to normal modes of vibration in agreement with those given by Duncan and Murray in Fig. 1 of their paper. The symmetry requirements[3b] also show that ω_1, ω_2, ω_5, ω_6 and ω_7 are obtainable from linear factors of the secular equation, while ω_3 and ω_4 are the roots of a quadratic factor.

The most general quadratic potential function for this model has eight independent force constants.[4] Since there is no way in which so many constants can be evaluated, the potential energy has been expressed in terms of the three constants K, H and h of stretching and bending of the valence bonds. Experience has shown that these are usually sufficient to give a rough fit of observed spectra and at present it is not certain which of the other constants are the most important.

$$\therefore 2V = K\sum_{i=1}^{4}\Delta R_i{}^2 + HR_0{}^2\sum_{i=1}^{4}\Delta\gamma_i{}^2 + hR_0{}^2\sum_{i=1}^{4}\Delta\beta_i{}^2.$$

ΔR_i is the extension of the bond $A - B_i$ from its equilibrium length, R_0, $\Delta\gamma_i$ is the angle of bending of the same bond in the plane of the molecule, and $\Delta\beta_i$ is the angle of bending of the ith bond out of this plane. K, H and h are the force constants.

This expression, by means of the methods previously described,[4] leads to the following formulas for the seven normal frequencies of vibration.

$\lambda_1 = K/m$, $\lambda_2 = h/m$, $\lambda_5 = H/m$,
$\lambda_6 = (1 + 4m/M)h/m$, $\lambda_7 = K/m$,
$\lambda_{3\ 4} = (1/2m)\{(1 + 2m/M)(H + K)$
$$\pm[(1 + 2m/M)^2(H + K)^2 - 4(1 + 4m/M)KH]^{\frac{1}{2}}\},$$

where

$$\omega_i{}^2 = \lambda_i/4\pi^2 C^2.$$

m, M are the masses of atoms B and A, respectively, in grams; c is the velocity of light, and ω is the frequency in wave numbers if K, H and h are in dynes per cm.

Except for the undesired effect of the masses of the springs, etc., these formulas should give the frequencies of the mechanical models when the proper values are inserted for K, H and h. Since it is a matter of a few hours at most to obtain these formulas and since they permit the variation of the force constants whereas the mechanical models require new springs for every such change, the analytical method seems to me very much simpler and more useful than the model method, at least for such symmetrical molecules.

The complete nine-atom model of $Ni(CO)_4$ is now being treated analytically. The number of fundamental frequencies which may appear in the Raman, the infrared, and in both spectra for this complete model are listed in Table I for the two configurations. Definite conclusions

TABLE I. *Selection rules for fundamental frequencies of $Ni(CO)_4$.*

No. of frequencies	Raman active	Infrared active	Active in both	Inactive
Plane	7	6	0	3
Tetrahedron	8	4	4	1

regarding the structure will require a careful comparison of the infrared and Raman lines in terms of the formulas for the normal frequencies. Frequencies listed in the third column are also enumerated in the first two columns.

<div align="right">E. Bright Wilson, Jr.*</div>

Mallinckrodt Chemical Laboratory,
Harvard University,
November 15, 1934.

* Junior Fellow of the Society of Fellows.
1 A. B. F. Duncan and J. W. Murray, J. Chem. Phys. 2, 636 (1934).
2 D. H. Andrews and J. W. Murray, J. Chem. Phys. 2, 634 (1934).
3 (a) G. Placzek, *The Structure of Molecules* (edited by P. Debye). Blackie and Sons, London, 1932. (b) E. B. Wilson, Jr., J. Chem. Phys. 2, 432 (1934). Table III, No. 4.4b.
4 J. B. Howard and E. B. Wilson, Jr., J. Chem. Phys. 2, 630 (1934), Footnote 4.

The Raman Spectrum of 1,3-Cyclohexadiene

In order to study the changes in the Raman spectrum which accompany the progressive introduction of double bonds into the cyclohexane ring, the Raman spectrum of 1,3-cyclohexadiene has been investigated. The Raman spectra of cyclohexane, cyclohexene, and benzene are well known, and 1,3-cyclohexadiene constitutes a hitherto missing member of this interesting series of spectra. The material used was prepared from cyclohexene by the method described by Crossley.[1] The sample was fractionated several times with a small column and boiled at 80–81°C. The technique employed to obtain the spectrum was that described by Murray and Andrews.[2] Spectra were excited by the 4358 and 4046 mercury lines separately using filters.

The following Raman frequencies were found: 298(4), 394(2), 458(1), 505(0), 559(1), 618(1), 823(10), 848(8), 945(4b), 992(15), 1060(2), 1174(4), 1220(3), 1240(2), 1266(1), 1324(1), 1411(1), 1432(5), 1576(20), 1615(3), 2823(8b), 2864(8b), 2908(4), 2936(8), 3018(5), 3041(10), 3056(7). The figures given in parentheses are visually estimated relative intensities.

The chemical behavior of 1,3-cyclohexadiene is very different from that of benzene or that of cyclohexane as there are two double bonds of distinctly ethylenic character. In view of this fact, it is interesting to note that most of the strong lines in the benzene spectrum have counterparts in the spectrum of 1,3-cyclohexadiene. Because of the lower symmetry, there are more strong lines in the latter spectrum, the number being nearly the same as in the spectrum of cyclohexene which has the same degree of symmetry. The low frequency line at 176 in cyclohexene is not found in the spectrum of 1,3-cyclohexadiene. Two lines are found in this spectrum in the region associated with double bond vibrations both of which have lower frequencies than the lines in this region of the cyclohexene spectrum and are rather close to the positions of the benzene lines in this region. This appears to support the assignments of these benzene lines to vibrations involving double bonds.   JOHN W. MURRAY

Chemistry Laboratory,
    The Johns Hopkins University,
        November 26, 1934.

[1] Crossley, J. Chem. Soc. (1904), 1416.
[2] J. W. Murray and D. H. Andrews, J. Chem. Phys. 1, 406 (1933).

The Oxidation of Fe^{++} to Fe^{+++} by the Irradiation with X-Rays of Solutions of Ferrous Sulfate in Sulfuric Acid

In earlier work[1] we have studied the chemical effect of x-rays on ferrous sulfate in 0.8N sulfuric acid. This work has now been extended by a study of the influence of the hydrogen ion in this reaction. Solutions of ferrous sulfate in sulfuric acid, gas-free or containing oxygen at different pressures, were irradiated and analyzed for the ferrous ion, hydrogen and oxygen. The temperature was 30°C. For the wavelength used, the x-ray absorption for all irradiated solutions was practically the same as for water. The ferrous ion concentration was determined by electrometric titration with potassium dichromate. Analysis for hydrogen and oxygen was made by means of a van Slyke apparatus.

In gas-free solutions, hydrogen is produced, the number of moles being slightly larger than one-half the number of ferrous ions oxidized. In solutions containing oxygen, none, or a very small quantity of hydrogen is produced. The number of moles of oxygen consumed is slightly less than one-fourth the number of ferrous ions oxidized. The lack of exact equivalence may be due to the action of the rays on traces of organic impurities in the solutions, resulting in the production of a small quantity of hydrogen and the binding of a small quantity of oxygen.

The number of ferrous ions oxidized per unit of dosage depends on the hydrogen ion concentration, and is within certain limits independent of the concentration of the ferrous and the sulfate ions, and, for solutions containing oxygen, of the oxygen pressure. The ferrous ion concentration has been changed from 50 micromoles per liter to such concentrations as can be obtained in solution, but not over one millimole per liter. In the earlier work[1] at pH equal to 0.5, the independence was established up to 10.0 millimoles per liter of ferrous sulfate. The oxygen pressure has been changed from 70 to 1 cm of mercury. The sulfate ion concentration has been varied by the addition of sodium sulfate in concentrations up to 0.4 molar. The results obtained show that the oxidation of the ferrous ion is due to a primary activation of the water by the x-rays.

The dependence on the hydrogen ion concentration is shown in Fig. 1, where the number of microequivalents of
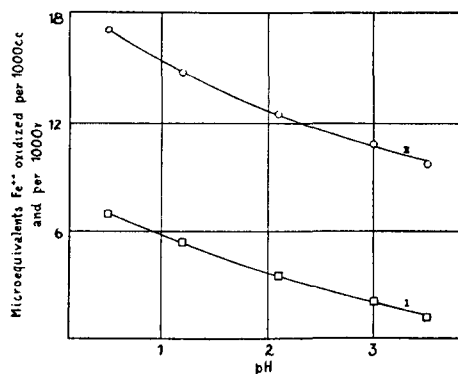

FIG. 1. The oxidation of ferrous sulfate in sulfuric acid as a function of the pH of the irradiated solution. I. gas free; II. oxygen present.

ferrous ion oxidized per 1000 cc of solution and per 1000 r of dosage is given as a function of the pH, for gas-free solutions (I) and for solutions containing oxygen (II). The two curves have a constant difference of 8.8 microequivalents.

The reaction occurring in gas-free solution may be written:

$$Fe^{++}+H^{+}=Fe^{+++}+\tfrac{1}{2}H_2. \tag{1a}$$
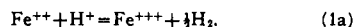
In solutions containing oxygen, it would appear that this same reaction occurs, but the hydrogen evolved is oxidized to water in a secondary reaction, giving as the complete reaction:

$$Fe^{++}+H^{+}+\tfrac{1}{4}O_2=Fe^{+++}+\tfrac{1}{2}H_2O. \tag{2a}$$
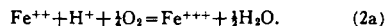
Furthermore, the additional reaction, which is independent of the pH, takes place:

$$Fe^{++}+\tfrac{1}{4}O_2+\tfrac{1}{2}H_2O=Fe^{+++}+OH^{-}, \tag{2b}$$

this reaction being represented by the difference between curves I and II. The continuous rise of curve I is rather