# Prediction of vibrational spectra from microwave spectra

## T A MATHAI and V BALASUBRAMANIAN

Department of Physics, University College of Science, Osmania University, Hyderabad 500 007, India

**Abstract.** Explicit and simple relations are derived for the Kivelson–Wilson parameters which can directly generate the vibrational spectrum of $XY_2$ bent type molecules. These relations are also shown to generate the above parameters for the different isotopes of a parent molecule. These predictions are verified in the case of some molecules of the above symmetry for which experimental microwave studies have been made.

**Keywords.** Microwave spectrum; Kivelson–Wilson parameters; vibrational spectrum.

## 1. Introduction

The detailed study of the microwave spectra of polyatomic molecules yields the values of the Kivelson–Wilson (1953) parameters $\tau_{\alpha\beta\gamma\delta}$ which account for the influence of the centrifugal force on the rotational motion of molecules. The $\tau$ parameters can be used to predict the vibrational spectrum of a molecule as was shown by Kirchhoff and Lyde (1973). In this procedure the $\tau$'s are first related to the harmonic force constants which then yield the vibrational frequencies. Davis and Gerry (1977) have given explicit relations for the harmonic force constants in terms of the $\tau$ parameters in the case of $XY_2$ bent type molecules. But this procedure, as Kirchhoff *et al* (1973) himself points out leads to slightly different sets of vibrational frequencies and in the absence of infrared or Raman spectra to confirm, the correct set of frequencies cannot be ascertained. In this paper we develop relations for the $\tau$ parameters directly in terms of vibrational frequencies and show how the vibrational spectrum can be very reliably predicted without any ambiguity in the case of $XY_2$ bent, symmetric molecules. One can also see how the present set of equations are simple enough to predict the $\tau$ parameters of different isotopic modifications of a parent system.

## 2. Theory

Considering a bent symmetric $XY_2$ molecule, let $xz$ be its molecular plane with the $z$-axis bisecting the interbond angle. Then the two cartesian symmetry coordinates pertaining to $a_1$ species can be written as

$$S_1 = 1/[2(m_x + 2m_y)]^{1/2} \{2\sqrt{m_x}z_2 - \sqrt{m_x}(z_1 + z_3)\}, \tag{1}$$

225

$$S_2 = 1/\sqrt{2}\,(x_1 - x_3), \tag{2}$$

where the subscripts 1 and 3 refer to the two Y atoms. The two normal coordinates can be given as:

$$Q_1 = (S_1 + aS_2)/(1 + a^2)^{1/2}, \tag{3}$$

$$Q_2 = (S_2 - aS_1)/(1 + a^2)^{1/2}, \tag{4}$$

where $a$ is known as the mixing parameter. The above relations define the transformation

$$Q = lq, \tag{5}$$

$q$'s being the mass weighted cartesian coordinates. DeWames and Wolfram (1964) have given the complete transformation matrix $l$ for $XY_2$ bent molecules.

The distortion constants $\tau_{\alpha\beta\gamma\delta}$ are given by the well-known relation (Wilson and Howard 1936; Kivelson–Wilson 1952, 1953)

$$\hbar^4\,\tau_{\alpha\beta\gamma\delta} = -\frac{K}{I^0_{\alpha\alpha}\,I^0_{\beta\beta}\,I^0_{\gamma\gamma}\,I^0_{\delta\delta}}\sum_i \frac{a_i^{\alpha\beta}\,a_i^{\gamma\delta}}{\omega_i^2}, \tag{6}$$

where $a_i^{\alpha\beta}$ are given as,

$$a_i^{\alpha\alpha} = 2\sum_k m_k^{1/2}\,(\beta_k^0\,l_{ki}^\beta + \gamma_k^0\,l_{ki}^\gamma), \tag{7}$$

$$a_i^{\alpha\beta} = -2\sum_k m_k^{1/2}\,\alpha_k^0\,l_{ki}^\beta. \tag{8}$$

In the above $\alpha_k^0$, $\beta_k^0$ and $\gamma_k^0$ are the equilibrium coordinates of the $k$th atom of mass $m_k$ and $l_{ki}$'s are the $l$ matrix elements given by equation (5). From the above the following relations can be obtained :

$$\hbar^4\,\tau_{xxxx} = -\frac{K}{(I^0_{xx})^4}\frac{2d^2\,c_a^2}{(1+a^2)}\frac{(m_x^{3/2}+2m_y^{3/2})^2}{(m_x+2m_y)^3}\left(\frac{1}{\omega_1^2}+\frac{a^2}{\omega_2^2}\right) \tag{9}$$

$$\hbar^4\,\tau_{yyyy} = -\frac{K}{(I^0_{yy})^4}\frac{2d^2}{(1+a^2)}\left\{\left[\frac{(m_x^{3/2}+2m_y^{3/2})}{(m_x+2m_y)^{3/2}}c_a - aS_a\right]^2\frac{1}{\omega_1^2}\right.$$

$$\left. +\left[\frac{(m_x^{3/2}+2m_y^{3/2})}{(m_x+2m_y)^{3/2}}ac_a + S_a\right]^2\frac{1}{\omega_2^2}\right\}, \tag{10}$$

$$\hbar^4\,\tau_{xzxz} = -\frac{K}{(I^0_{zz})^4}\frac{2d^2\,S_a^2}{(1+a^2)}\left(\frac{a^2}{\omega_1^2}+\frac{1}{\omega_2^2}\right), \tag{11}$$

$$\hbar^4\,\tau_{xzxz} = -\frac{K}{(I^0_{xx}\,I^0_{zz})^2}\frac{2m_x}{(m_x+2m_yS_a^2)}\frac{d^2\,S_a^2\,c_a^2}{\omega_3^2}, \tag{12}$$

where the $I$'s are moments of inertia expressed in amu $\mathring{A}^2$, $K = 5\cdot7498 \times 10^{11}$ Kc/sec, $\omega_i$'s the vibrational frequencies in cm$^{-1}$, $a$, half the interbond angle and $d$, the equilibrium bond length. Similar expressions can be developed for other constants also. Equations (9) to (11) contain the three unknown parameters $\omega_1$, $\omega_2$ and $a$. Hence they can be solved independently. One can first solve for the mixing parameter $a$ knowing the experimental values of $\tau_{\alpha\beta\gamma\delta}$'s and $I$'s. This

immediately helps to calculate $\omega_1$ and $\omega_2$. Equation (12) gives the value of $\omega_3$, the $b_2$ species frequency if $\tau_{aaaa}$ is known. Thus the complete vibrational spectrum can be calculated from the microwave spectral data.

## 3. Vibrational spectra

Table 1 presents the predicted spectra along with the experimental and literature values. The solution of equations (9) to (11) leads to two different values of $a$ corresponding to two different possible assignments of $\omega_1$ and $\omega_2$ to $Q_1$ and $Q_2$. For each molecule we give that value of $a$ corresponding to designating $Q_1$ as the stretching and $Q_2$ as the bending modes. Both values of $a$ predict the same spectrum. Among the molecules considered the frequency data from infrared or Raman studies are not available only for $SF_2$ : Except in $H_2S$ and $NF_2$, the predicted frequencies agree with the experimental values to within 5%. In $H_2S$, the discrepancy persists even after correcting the rotational constants $A$, $B$ and $C$ as suggested by Cook *et al* (1974) in $H_2O$. In $NF_2$, though our values differ by more than 5% from the infrared values, they are in excellent agreement with those deduced by Brown *et al* (1974) from his microwave studies. Summing up we can say that our equations are basically sound and the revised microwave data for $H_2S$ and $NF_2$ will definitely reproduce the experimentally observed vibrational frequencies to a fair degree of accuracy. Also for those molecules for which only microwave data are available, our equations help in predicting the vibrational spectra.

## 4. Prediction of $\tau$ parameters for isotopes

DeWames and Wolfrom (1964) have given the isotopic rules relating the frequencies of two different isotopes of $XY_2$ bent molecules. Knowing $H_2O$ frequencies and its $a$ value $D_2O$ frequencies can be determined. The same isotopic rules can again be used to get the mixing parameter for $D_2O$. Thus, knowing the frequencies and mixing parameter, the various $\tau$ parameters can be calculated for $D_2O$ and $T_2O$. A similar procedure yields the $\tau$ parameters for the various isotopes of ozone. The predicted values are presented in table 2 along with experimental values wherever available. It is seen that the $\tau$'s for $D_2O$ and $T_2O$ differ slightly from the experimental values. This is due to the experimental difficulty in getting accurately the $\tau$'s for a light molecule like $H_2O$ free from vibrational contributions, as admitted by Cook *et al* (1974). In fact this experimental difficulty and the resulting errors in the $\tau$ parameters are responsible for the rather large deviation of $\omega_2$ and to a slight extent that of $\omega_1$ from the experimentally observed frequencies as shown in table 1 for water. As these $\tau$'s are used to generate the parameters of $D_2O$ and $T_2O$, the basic error propagates itself and hence the differences in table 2.

As for ozone, the other molecule presented in table 2, the experimental values are from Depannemaecker and Bellet (1977) and again some of the $\tau$ parameters differ from the experimental values. These discrepancies arise because our equations generate equilibrium values of the parameters for the different isotopes whereas

Table 1. Predicted and observed frequencies of $XY_2$ bent molecules.

| Molecule | Data Used | Mixing parameter $a$ | Predicted | | | Experimental (Literature) | | | Reference |
|---|---|---|---|---|---|---|---|---|---|
| | | | $\omega_1$ | $\omega_2$ | $\omega_3$ | $\omega_1$ | $\omega_2$ | $\omega_3$ | |
| $SO_2$ | $\tau_{ssss}$ $\tau_{zzzz}$ $\tau_{sszz}$ $\tau_{szsz}$ | $-1.17$ | 1153·6 | 518 | 1364·5 | 1151 | 519 | 1361 | 1 |
| $CF_2$ | $\tau_{ssss}$ $\tau_{yyyy}$ $\tau_{zzzz}$ $\tau_{szsz}$ | $-0.45$ | 1222·3 | 663·3 | 1128·6 | 1222 | 663 | 1128 | 2 |
| $SCl_2$ | $\tau_{sszz}$ $\tau_{yyyy}$ $\tau_{zszz}$ $\tau_{zzzz}$ | $-0.61$ | 517·1 | 202·4 | 527·5 | 518 | 211 | 525·5 | 3 |
| $H_2O$ | $\tau_{ssss}$ $\tau_{yyyy}$ $\tau_{zzzz}$ | $-1.45$ | 3626·8 | 1537·3 | | 3656·7 | 1594·6 | | 4,5 |
| $SF_2$ | $\tau_{ssss}$ $\tau_{yyyy}$ $\tau_{zzzz}$ | $-0.69$ | 823·9 | 351·9 | | 852 | 350 | | 6 |

Vibrational frequencies in $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $O_3$ | $\tau_{xxxx}$ $\tau_{yyyy}$ $\tau_{zzzz}$ | $-0.65$ | 1128·5 | 712·1 | 1110 | 705 | 7 |
| $H_2S$ | $\tau_{xxxx}$ $\tau_{yyyy}$ $\tau_{zzzz}$ | $-1.06$ | 2923·6 | 1149·1 | 2721·9 | 1214·5 | 8 |
| $NF_2$ | $\tau_{xxxx}$ $\tau_{xxzz}$ $\tau_{xxzz}$ $\tau_{x:xz}$ | $-0.38$ | 1001·7 | 580·9 | 1097·6 | 1074·3 1003·7 | 573·4 575·9 | 9 |

For $NF_2$: 930·7 1086·2

1. Kivelson (1954).
2. Kirchhoff and Lyde (1973).
3. Davis and Gerry (1977).
4. Cook et al. (1974).
5. Herzberg (1966).
6. Kirchhoff et al. (1973).
7. Depannenaecker and Bellet (1977).
8. Speirs and Spirko (1975).
9. Brown et al. (1974).

**Table 2.** Predicted and observed values of distortion constants.

| Isotopes | $\tau_{\alpha\beta\gamma\delta}$ in MHz | | | | | | Reference |
|---|---|---|---|---|---|---|---|
| | Predicted | | | Observed (Literature) | | | |
| | $\tau_{xxxx}$ | $\tau_{yyyy}$ | $\tau_{zzzz}$ | $\tau_{xxxx}$ | $\tau_{yyyy}$ | $\tau_{zzzz}$ | |
| $D_2O$ | $-1088\cdot925$ | $-7\cdot59$ | $-65\cdot354$ | $-966\cdot5$ | $-7\cdot87$ | $-67\cdot12$ | 1 |
| $T_2O$ | $-662\cdot628$ | $-3\cdot539$ | $-25$ | $-504\cdot977$ | $-3\cdot704$ | $-29\cdot461$ | 1 |
| $18_0 18_0 18_0$ | $-26\cdot49$ | $-0\cdot029$ | $-0\cdot0539$ | $-19\cdot868$ | $-0\cdot0297$ | $-0\cdot0562$ | 2 |
| $16_0 18_0 16_0$ | $-21\cdot28$ | $-0\cdot0384$ | $-0\cdot0737$ | $-21\cdot59$ | $-0\cdot0362$ | $-0\cdot07117$ | 2 |
| $18_0 16_0 18_0$ | $-26\cdot92$ | $-0\cdot0277$ | $-0\cdot0497$ | $-23\cdot37$ | $-0\cdot03102$ | $-0\cdot05623$ | 2 |

1. Cook *et al* (1974).
2. Depannenaecker and Bellet (1977).

experimentally only effective values of the $\tau$'s can be obtained. As pointed out by the above authors the effective and equilibrium values are different and the equilibrium values can be obtained only when the rotational spectra of the vibrationally excited states are studied along with that of the ground state. Only for $^{16}O_3$ such a study is possble among the different isotopes.

## 5. Conclusion

The equations for the distortion constants $\tau_{\alpha\beta\gamma\delta}$ derived by us enable prediction of the vibrational spectra directly from the rotational spectra of $XY_2$ bent molecules. These equations also generate the distortion constants of the different isotopes of a parent molecule. The accuracy of such a prediction increases with increase in the accuracy of the experimental data and the results obtained are without any ambiguity and as such is an improvement over earlier procedures.

## References

Brown R D, Burden F R, Godfrey P D, and Gillard I R 1974 *J. Mol. Spectrsc.* **52** 301
Cook R L, Delucia F G and Helminger P 1974 *J. Mol. Spectrosc.* **53** 62
Davis R W and Gerry M C L 1977 *J. Mol. Spectrosc.* **65** 455
Depannenaecker J C and Bellet J 1977 *J. Mol. Spectrosc.* **66** 106
DeWames R E and Wolfram T 1964 *J. Chem. Phys.* **40** 853
Herzberg G 1966 *Electronic spectra of polyatomic molecules* (New York : Van Nostrand)
Kirchhoff W H, Johnson D R Jr. and Powell P X 1973 *J. Mol. Spectrosc.* **48** 157
Kirchhoff W H and Lyde D H 1973 *J. Mol. Spectrosc.* **47** 491
Kivelson D 1954 *J. Chem. Phys.* **22** 904
Kivelson D and Wilson E B Jr 1952 *J. Chem. Phys.* **20** 1575
Kivelson D and Wilson E B Jr 1953 *J. Chem. Phys.* **21** 1229
Speirs G K and Spirko V 1975 *J. Mol. Spectrosc.* **56** 104
Wilson E B Jr and Howard J B 1936 *J. Chem. Phys.* **4** 260