

ANALYSIS OF THE HCl BANDS

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ABSTRACT

Wave-numbers for the two isotopes of hydrogen chloride in the bands at 3.5μ and 1.76μ have been fitted to formulae cubic in the rotational quantum number. From these formulae the constants of the molecule have been determined in accordance with the energy expression for the rotating dipole as derived by means of wave mechanics.

THE separation of the isotope components of the HCl infra-red bands and the accurate measurement of their positions as reported by Meyer and Levin in the preceding paper in this periodical have made it possible to test the success of formulae derived with the help of the new wave mechanics. In a recent paper,¹ Fues has discussed the case of the rotating vibrating dipole and has obtained an energy expression in the following form:

$$E = A + h\nu_0(n + \frac{1}{2}) [1 - B(j + \frac{1}{2})^2] + (h^2/8\pi^2J)(j + \frac{1}{2})^2 [1 - k^2(j + \frac{1}{2})^2] - (h^2/8\pi^2J)(n + \frac{1}{2})^2 C \quad (1)$$

n is the vibrational quantum number and j the rotational. B , C , ν_0 and k^2 contain constants of the force function but are independent of j and n . J is the moment of inertia of the molecule about an axis normal to the nuclear line. The entrance of the factors $(n + \frac{1}{2})$ and $(j + \frac{1}{2})$ throughout in place of n and j of the Kratzer formula gives a new interpretation to the experimental results.

The transitions involved in these bands are for n , $0 \rightarrow \Delta n$ for j , $j \rightarrow j \pm 1$ where $\Delta n = 1$ for the fundamental and $\Delta n = 2$ for the harmonic. For both of these bands the initial values of j in the positive branch begin with zero and for the negative branch with 1. It is more convenient however not to use initial values of j in numbering the lines but rather to number them on both sides starting with 1. This formulation allows one to write a single formula for both branches. We then have

$$\begin{aligned} \nu = & \nu_0 \Delta n - \frac{1}{4} \nu_0 B \Delta n - (h/8\pi^2J) C (\Delta n^2 + \Delta n) \\ & + (-\nu_0 B - \nu_0 B \Delta n + (2h/8\pi^2J) - (h/8\pi^2J) k^2) j \\ & - \nu_0 B \Delta n j^2 - (h/8\pi^2J) 4k^2 j^3 \end{aligned}$$

where j is the number of the line from the center of the band positive for the positive branch and negative for the negative. It has been possible

¹ Fues, Ann. d. Physik **80**, 367 (1926).

to fit the wave-numbers determined by Meyer and Levin very successfully to this cubic formula. The following four equations give the constants thus determined.

Fundamental

Major isotope component: $\nu = 2885.88 + 20.562j - 0.3030j^2 - 0.0020j^3$

Minor isotope component: $\nu = 2883.84 + 20.536j - 0.3022j^2 - 0.0020j^3$

Harmonic

Major: $\nu = 5667.96 + 20.291j - 0.6028j^2 - 0.0025j^3$

Minor: $\nu = 5663.97 + 20.259j - 0.6029j^2 - 0.0022j^3$

Tables I and II give the wave-numbers computed from these equations and the differences ($\Delta\nu$) between them and the observed values. It will be noticed that these differences lie satisfactorily within experimental error.

TABLE I. *Calculated frequencies of fundamental.*

| j | Major Component | $\Delta\nu$ | Minor Component | $\Delta\nu$ | j | Major Component | $\Delta\nu$ | Minor Component | $\Delta\nu$ |
|-----|-----------------|-------------|-----------------|-------------|-----|-----------------|-------------|-----------------|-------------|
| -12 | 2598.98 | 0.02 | 2597.40 | 0.03 | 1 | 2906.14 | 0.11 | 2904.07 | 0.09 |
| -11 | 2625.72 | .02 | 2624.08 | -.05 | 2 | 2925.78 | 0.00 | 2923.68 | .01 |
| -10 | 2651.98 | -.01 | 2650.29 | .07 | 3 | 2944.79 | .02 | 2942.67 | .04 |
| -9 | 2677.75 | -.02 | 2676.02 | -.12 | 4 | 2963.16 | .08 | 2961.01 | .07 |
| -8 | 2703.03 | .03 | 2701.25 | .04 | 5 | 2980.87 | .03 | 2978.70 | -.02 |
| -7 | 2727.79 | -.04 | 2725.97 | .04 | 6 | 2997.91 | -.13 | 2995.73 | -.07 |
| -6 | 2752.04 | -.01 | 2750.18 | .13 | 7 | 3014.28 | .01 | 3012.08 | .08 |
| -5 | 2775.75 | .04 | 2773.85 | -.08 | 8 | 3029.96 | 0.00 | 3027.74 | -.05 |
| -4 | 2798.92 | -.14 | 2796.99 | -.11 | 9 | 3044.93 | -.05 | 3042.69 | -.07 |
| -3 | 2821.52 | -.03 | 2819.56 | -.05 | 10 | 3059.19 | -.12 | 3056.93 | -.09 |
| -2 | 2843.56 | 0.00 | 2841.57 | .02 | 11 | 3072.73 | .03 | 3070.45 | .06 |
| -1 | 2865.02 | .07 | 2863.00 | -.01 | 12 | 3085.52 | .10 | 3083.23 | .05 |

TABLE II. *Calculated frequencies of harmonic.*

| j | Major Component | $\Delta\nu$ | Minor Component | $\Delta\nu$ | j | Major Component | $\Delta\nu$ | Minor Component | $\Delta\nu$ |
|-----|-----------------|-------------|-----------------|-------------|-----|-----------------|-------------|-----------------|-------------|
| -8 | 5468.33 | 0.22 | 5464.44 | 0.23 | 1 | 5687.65 | .16 | 5683.63 | .28 |
| -7 | 5497.24 | -.27 | 5493.37 | -.25 | 2 | 5706.11 | .10 | 5702.06 | -.05 |
| -6 | 5525.05 | -.01 | 5521.19 | .04 | 3 | 5723.34 | -.05 | 5719.26 | .16 |
| -5 | 5551.75 | -.07 | 5547.88 | -.14 | 4 | 5739.32 | -.03 | 5735.22 | .04 |
| -4 | 5577.31 | -.06 | 5573.43 | -.03 | 5 | 5754.04 | -.16 | 5749.92 | -.23 |
| -3 | 5601.73 | .32 | 5597.83 | .15 | 6 | 5767.47 | .03 | 5763.35 | -.07 |
| -2 | 5624.99 | -.17 | 5621.06 | -.14 | 7 | 5779.61 | -.07 | 5775.49 | -.09 |
| -1 | 5647.07 | -.04 | 5643.11 | -.01 | 8 | 5790.44 | .10 | 5786.34 | -.06 |
| | | | | | 9 | 5799.94 | 0.00 | 5795.87 | .17 |

In the energy Eq. (1) the constants B , C and k^2 have been used to replace somewhat inconvenient combinations of the constants of the force function which we are now in a position to evaluate from the empirical data for these four bands. In Kratzer's original paper the potential energy of the molecule was developed in the form

$$\phi = \phi_0 - (2\pi\nu_0)^2 J \left\{ 1/\rho - 1/(2\rho^2) + c_3\xi^3 + c_4\xi^4 + \dots \right\}$$

where $\rho = r/r_0$, the ratio of the distance between nuclei to the equilibrium distance. $\xi = \rho - 1$. ν_0 is the frequency of vibration for infinitesimal amplitude. In terms of the above constants

$$k = (h/4\pi^2\nu_0 J) ; \quad B = (3/2)k^2(1+2c_3) ; \quad C = 3+15c_3+(15/2)c_3^2+3c_4.$$

The constants ν_0 and J are easily found from the band data. To determine ν_0 both fundamental and harmonic band must be used. The two values for the two isotopes are given in the following table. Their ratio is satisfactorily equal to the inverse ratio of the square roots of the reduced masses. This is shown in the later computation of ϕ'' . Four values of J may be obtained, one for each band. With the help of the relation $J = \mu r_0^2$, r_0 has been computed and found to agree surprisingly well for the two isotopes. The small variation from fundamental to harmonic is typical of all the constants. It may be partly due to the fact that the harmonic has fewer lines and therefore less reliable constants. More probably it indicates that the energy expression is a closer approximation for the fundamental for which the amplitude of vibration is smaller. The value of k may be found directly from the coefficient of j^3 . This however is the least reliable of the coefficients. It has also been computed from the formula given above involving J and ν_0 . The latter values agree closely and do not differ much from the mean of the values found from the cubic term. The values of c_3 and c_4 have been calculated using the more satisfactory determination of k^2 . They are sensitive to small variations of the other constants but these relative variations are not important in the calculation of the derivatives of the force function. The constants are given in the following table.

TABLE III.

| | Fundamental Major | Harmonic Major | Fundamental Minor | Harmonic Minor |
|--|----------------------|-------------------|----------------------|-------------------|
| $(h/8\pi^2 J)/(1/3 \cdot 10^{10})$ | 10.5843 | 10.5980 | 10.5703 | 10.5817 |
| $J \cdot 10^{40}$ | 2.6126 | 2.6092 | 2.6161 | 2.6132 |
| $r_0 \cdot 10^8$ | 1.2765 | 1.2757 | 1.2764 | 1.2757 |
| $\nu_0(1/3 \cdot 10^{10})$ | | 2989.36 | | 2987.28 |
| C | | 4.8848 | | 4.8894 |
| $k^2 \cdot 10^6$ (cubic term) | 4.7499 | 5.8808 | 4.8107 | 5.1669 |
| $k^2 \cdot 10^6$ ($k = h/4\pi^2\nu_0 J$) | 5.0146 | 5.0276 | 5.0082 | 5.0193 |
| c_3 | 0.17370 | 0.16845 | 0.17342 | 0.17015 |
| c_4 | -0.31633 | -0.28942 | -0.31249 | -0.30000 |

Writing

$$\phi = \phi_0 + \frac{1}{2}\phi_0''(r-r_0)^2 + \frac{1}{3!}\phi_0'''(r-r_0)^3 + \frac{1}{4!}\phi_0^{IV}(r-r_0)^4 + \dots$$

and comparing with Kratzer's energy function, we have

$$\frac{1}{2}\phi'' = \frac{(2\pi\nu_0)^2 J}{2r_0^2} = 2\pi^2\nu_0^2\mu$$

$$\frac{1}{3!}\phi''' = -(1+c_3)\frac{(2\pi\nu_0)^2J}{r_0^3}$$

$$\frac{1}{4!}\phi^{IV} = \frac{3-2c_4}{2}\frac{(2\pi\nu_0)^2J}{r_0^4}$$

The derivatives of ϕ have been computed from these equations and are given in the following table.

TABLE IV.

| | Fundamental Major | Harmonic Major | Fundamental Minor | Harmonic Minor |
|---------------------------------|----------------------|-------------------|----------------------|-------------------|
| $\frac{1}{2}\phi''10^{-6}$ | | 2.5454 | | 2.5457 |
| $\frac{1}{3!}\phi'''10^{-13}$ | -4.6809 | -4.6628 | -4.6806 | -4.6701 |
| $\frac{1}{4!}\phi^{IV}10^{-21}$ | 5.6745 | 5.5835 | 5.6641 | 5.6313 |

The agreement of all the constants bears witness both to the high precision of this experimental work and to the success of the present theory of the rotating dipole.