

less than the drift mobility for re-entrant energy surfaces like those possible for degenerate energy bands<sup>6</sup> and, in fact, may even change sign.

Further evidence that the energy bands are not spherical is furnished by the large and anisotropic magneto resistance effects in germanium single crystals.<sup>7</sup>

We are indebted to Drs. J. Bardeen and F. Seitz for helpful discussions of the theory.

<sup>1</sup> J. R. Haynes and W. Shockley, Phys. Rev. **75**, 691 (1949).

<sup>2</sup> Shockley, Pearson and Haynes, Bell Sys. Tech. J. **28**, 344 (1949).

<sup>3</sup> G. L. Pearson, Phys. Rev. **76**, 179 (1949).

<sup>4</sup> W. C. Dunlap, Jr., Phys. Rev. **77**, 759 (1950).

<sup>5</sup> Pearson, Struthers and Theurer, Phys. Rev. **75**, 344 (1949); **77**, 809 (1950).

<sup>6a</sup> A. H. Wilson, *The Theory of Metals* (Cambridge University Press, London, 1936), Eq. (362).

<sup>6b</sup> W. Shockley, Phys. Rev. **78**, 173 (1950).

<sup>7</sup> G. L. Pearson and H. Suhl, to be reported at Oak Ridge meeting.

### *l*-Type Doubling in OCS and HCN

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THE two components of the rotation-vibration states of a linear molecule in an excited perpendicular vibration level are separated by *l*-type doubling, *l* being the quantum number of angular momentum so that *l* = *V*, *V* - 2, ... 0 or 1). The doubling is predicted by theory<sup>1</sup> to be  $\Delta\nu = qJ(J+1)$  where  $q = q_0(V_s+1) = (B_s^2/\omega_s)[1 + 4 \sum_{s'} \xi_{ss'}^2 \lambda_s / (\lambda_{s'} - \lambda_s)](V_s+1)$  when  $|l| = 1$ ,  $\omega_s$  being the degenerate vibration frequency and  $\xi_{ss'}$  the Coriolis coupling factors. Recent measurements by Shulman and Townes<sup>2</sup> have shown that *q* is, indeed, proportional to  $(V_s+1)$ , thereby verifying one phase of the theory of *l*-type doubling. Calculations on the quantities  $q_0$  for comparison with experimental values have been impeded largely because of the complicated nature of  $\xi_{ss'}$ . We shall report in this letter on the evaluation of  $q_0$  for two molecules, namely OCS and HCN.

The quantities  $\xi_{ss'}$  have been determined by A. H. Nielsen<sup>3</sup> for the linear XYZ molecule. He gives the following values

$$\xi_{21} = -[M_1 M_3 / \sigma I^{(e)}]^{1/2} (Z_1^0 - Z_3^0) \cos \gamma - [M_2 \Sigma / \sigma I^{(e)}]^{1/2} Z_2^0 \sin \gamma$$

and

$$\xi_{23} = [M_1 M_3 / \sigma I^{(e)}]^{1/2} (Z_1^0 - Z_3^0) \sin \gamma - [M_2 \Sigma / \sigma I^{(e)}]^{1/2} Z_2^0 \cos \gamma,$$

where  $M_2$  is the central atom,  $\sigma = M_1 + M_3$ ,  $\Sigma = M_1 + M_2 + M_3$ ,  $Z_i^0$ , the equilibrium values of the coordinates and

$$\frac{\sin \gamma}{\cos \gamma} = \pm 2^{-1/2} \{ 1 \pm [(k_1 - k_3)^2 (4k_4^2 - (k_1 - k_2)^2)]^{1/2} \}.$$

The constants  $k_i$  are defined as follows:  $k_1 = \mathfrak{R}_1 / \mu_1^{1/2}$ ,  $k_3 = \mathfrak{R}_3 / \mu_3^{1/2}$ ,  $k_4 = \mathfrak{R}_4 / (\mu_1 \mu_3)^{1/2}$  with  $\mu_1 = M_1 M_3 / (M_1 + M_3)$  and  $\mu_3 = M_2 \sigma / \Sigma$  and  $\mathfrak{R}_1 = \{ K_1 (M_3 / \sigma)^2 + K_2 (M_1 / \sigma)^2 \}$ ,  $\mathfrak{R}_3 = K_1 + K_2$ ,  $\mathfrak{R}_4 = \{ -K_1 (M_3 / \sigma) + K_2 (M_1 / \sigma) \}$ , where  $K_i$  are the valence force constants of  $2V = K_1 \delta Q_1^2 + K_2 \delta Q_2^2$  in which  $\delta Q_1 = Z_2 - Z_1$ , and  $\delta Q_2 = Z_3 - Z_2$ . One may, moreover, quickly show that  $\sum_{s'} \xi_{ss'}^2 = 1$ .

The force constants  $K_1$  and  $K_2$  used in this calculation have been taken from the tables of Herzberg<sup>4</sup> and are the following:  $K_1 = 8 \times 10^5$  dynes/cm,  $K_2 = 14.2 \times 10^5$  dynes/cm for OCS and  $K_1 = 5.8 \times 10^5$  dynes/cm,  $K_2 = 17.9 \times 10^5$  dynes/cm for HCN. Computation of the quantities  $\xi_{ss'}$  for these molecules is now a simple matter. These in turn lead to values of  $q_0 = 3.17$  Mc/sec. for OCS which is in complete agreement with the measured value<sup>1</sup> and  $q_0 = 113.6$  Mc/sec. for HCN which is about 2 percent in excess of the measured value 111.8 Mc/sec. given by Shulman and Townes. When one considers that the  $K_1$  and  $K_2$  were determined from the band centers and not from the harmonic frequencies this agreement must be regarded as satisfactory.

Shulman and Townes have, moreover, reported a higher order effect in the *l*-type doubling of HCN. This manifests itself in a deviation of the quantity  $q/J(J+1)$  which is proportional to *J* and of the order of magnitude  $q(B_s/\omega_s)$ . We have attempted to

calculate this effect which involves a fourth-order perturbation calculation. We find a correction to the  $(l/l \pm 2)$  components of the energy matrix of a little more than  $2B_s(B_s/\omega_s)^3(V_s+1)J^2(J+1)^2$ . The following argument which is of a symmetry nature, may be used to support this. The correction required must be a correction to the  $(l/l)$  or the  $(l/l \pm 2)$  elements, and since for linear molecules  $l = K$ , also to the  $(K/K)$  and  $(K/K \pm 2)$  elements of the energy matrix. The matrix components must contain terms proportional to  $J^3$  if the deviation to  $q/J(J+1)$  is to be proportional to *J*. Such terms can arise only from terms in the Hamiltonian of the molecule proportional to  $P_x$  and  $P_y$  to some odd power. Such terms have only  $(K/K \pm 1)$ ,  $(K/K \pm 3)$  ... elements and, therefore, only  $(l/l \pm 1)$ ,  $(l/l \pm 3)$  ... elements.

The differences between the deviations in the states  $J = 8$  and  $J = 10$ , and  $J = 10$  and  $J = 12$  have been calculated by our method. One obtains 0.13 Mc/sec. and 0.16 Mc/sec. respectively compared to 0.18 Mc/sec. measured for both of these instances. While the data of Shulman and Townes certainly fit a linear relation better than the one derived here, it is suggested that the next approximation may bring the two into agreement and that to this approximation our expression is substantially correct.

<sup>1</sup> H. H. Nielsen, Phys. Rev. **77**, 130 (1950).

<sup>2</sup> R. G. Shulman and C. H. Townes, Phys. Rev. **77**, 421 (1950).

<sup>3</sup> A. H. Nielsen, J. Chem. Phys. **11**, 160 (1943).

<sup>4</sup> G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945), p. 174.

### Proton Groups from the Alpha-Particles Bombardment of Beryllium\*

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BOMBARDMENT of a 0.23 mg/cm<sup>2</sup> surface density metallic beryllium target with 21.94 Mev alpha-particles from the cyclotron has produced four proton groups. We have calculated *Q*-values for the reaction  $\text{Be}^9(\alpha, p)\text{B}^{12}$  and three energy levels of  $\text{B}^{12}$  and have obtained a value for the mass of  $\text{B}^{12}$ .

Protons emerging from the target at 90° from the incident beam were counted by means of a dual proportional counter in a coincidence and discriminator circuit as described by Brolley, Sampson, and Mitchell.<sup>1</sup> The pulse discriminator was adjusted so that only pulses were counted which corresponded to the peak of the Bragg curve. Proton energies were calculated from aluminum absorption using unit absorber foils of 1.06 mg/cm<sup>2</sup> surface density. The alpha-particle beam energy was measured by aluminum absorption after scattering from a gold foil of 0.17 mg/cm<sup>2</sup> surface density. The residual range of the counter and the surface density of the beryllium target were measured with the aid of thorium C' alpha-particles. The beryllium target was prepared by vacuum evaporation from a tungsten filament. Smith's calculations<sup>2</sup> were used in determining proton energies from aluminum absorption.

Proton groups, relative intensities and calculated *Q*-values and excitations are given in Table I.

The -7.02 Mev *Q*-value of our end group gives a calculated atomic mass of 12.01839 for  $\text{B}^{12}$  which may be compared with the value 12.01827 ± 0.00009 calculated by Hornyak and Lauritsen.<sup>3</sup>

A low intensity proton group of 2.98 Mev energy was observed with variable intensity with different beryllium targets and is

TABLE I. Proton groups from  $\text{Be}^9(\alpha, p)\text{B}^{12}$ .

Proton energy Mev	Relative intensity	<i>Q</i> -value (Mev)	$\text{B}^{12}$ energy level (Mev)
7.02	1	-7.02	0
6.06	2	-8.06	1.04
5.26	25	-8.93	1.91
3.25	40	-11.11	4.09