

l-Type Doubling Transitions in HCN and DCN*

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Direct transitions between levels split by *l*-type doubling have been observed for $J=9, 10$, and 11 in HCN and for $J=10, 11$, and 12 in DCN. The *l*-type doubling coefficient calculated from the observed line frequencies shows a slight decrease with increasing J for both molecules. While the observed values of the *l*-type doubling coefficient q are in good agreement with those calculated theoretically, the slight variation of q with J was not expected. This variation of q with increasing J involves a negative term in q proportional to $J(J+1)$ and may therefore be related to the effects involved in centrifugal stretching of the rotating molecule.

A LINEAR triatomic molecule is capable of a doubly degenerate perpendicular mode of vibration. When this mode of vibration is excited, the resulting component of angular momentum along the molecular axis is given by¹

$$L_z = \pm l_2 \hbar,$$

where

$$l_2 = V_2, \quad V_2 - 2, \quad V_2 - 4, \quad \dots, 1 \text{ or } 0.$$

In this expression V_2 is the total vibrational quantum number associated with the degenerate mode of vibration ν_2 .

To the degree of approximation ordinarily considered, the energy of the rotating vibrating molecule is a function of l_2^2 and is therefore independent of the sign of l_2 . There are, however, terms in the Hamiltonian which remove this degeneracy. These terms can be interpreted as largely the result of Coriolis forces acting on atoms which are vibrating in a rotating coordinate system. Their effect is to split each rotational energy level into two levels. The magnitude of this splitting has been calculated by Nielsen,² who gives the following value:

$$\Delta\nu = qJ(J+1). \quad (1)$$

For the case $V_2 = l_2 = 1$,

$$q = q_0(V_2 + 1) = \frac{B_e^2}{\omega_2} \left[1 + 4 \sum_{s'} \xi_{2s'}^2 \frac{\lambda_2}{\lambda_{s'} - \lambda_2} \right] (V_2 + 1). \quad (2)$$

In this expression ω_2 is the degenerate vibration frequency, B_e is the equilibrium rotational constant, $\xi_{2s'}$ are the Coriolis coupling factors, and $\lambda_s = 4\pi^2 c^2 \omega_s^2$. The Coriolis coupling factors as given by Nielsen³ for the linear XYZ molecule are

$$\xi_{21} = - \left[\frac{M_1 M_3}{\sigma I^e} \right]^{\frac{1}{2}} (z_1^0 - z_3^0) \cos \gamma - \left[\frac{M_2 \Sigma}{\sigma I^e} \right]^{\frac{1}{2}} z_2^0 \sin \gamma$$

and

$$\xi_{23} = \left[\frac{M_1 M_3}{\sigma I^e} \right]^{\frac{1}{2}} (z_1^0 - z_3^0) \sin \gamma - \left[\frac{M_2}{\sigma I^e} \right]^{\frac{1}{2}} z_2^0 \cos \gamma,$$

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

$$\tan 2\gamma = 2k_4 / (k_1 - k_3).$$

The constants k_i are defined as follows:

$$k_1 = [K_1(M_3/\sigma)^2 + K_2(M_1/\sigma)^2] / \mu_1,$$

and

$$k_3 = (K_1 + K_2) / \mu_3,$$

$$k_4 = [-K_1(M_3/\sigma) + K_2(M_1/\sigma)] / (\mu_1 \mu_3)^{\frac{1}{2}},$$

where

$$\mu_1 = M_1 M_2 / (M_1 + M_3), \quad \mu_3 = M_2 \sigma / \Sigma,$$

and the K_i are the valence force constants. The quantity q as defined by Eq. (2) is a constant for a particular molecule and is called the *l*-type doubling coefficient.

Direct transitions between levels split by *l*-type doubling were first observed by Shulman and Townes⁴ for HCN. For this type of transition there is no change in either the rotational or the total vibrational quantum number. The absorption frequency is given directly by Eq. (1). The results of these observers indicated a slight dependence of q on the rotational level involved. The reported variation was positive with increasing J . The present work was undertaken with the purpose of investigating further this variation of q with J for the molecules HCN and DCN.

The lines were observed with a recording microwave spectrograph using 6 kc/sec square-wave Stark modulation. Frequencies were measured by the method of Rogers, Cox, and Braunschweiger⁵ using ammonia lines as standards. The observed line frequencies, measured q -values, and calculated q -values are given in Table I. The measured q -value is 0.9 percent lower than the calculated value for HCN, and 1.2 percent higher

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¹ D. M. Dennison, *Revs. Modern Phys.* **3**, 280 (1931); Wave H. Shaffer, *Revs. Modern Phys.* **16**, 245 (1944).

² H. H. Nielsen, *Phys. Rev.* **78**, 296 (1950).

³ A. H. Nielsen, *J. Chem. Phys.* **11**, 160 (1943).

⁴ R. G. Shulman and C. H. Townes, *Phys. Rev.* **77**, 421 (1950).

⁵ Rogers, Cox, and Braunschweiger, *Rev. Sci. Instr.* **21**, 1014 (1950).

TABLE I. *l*-type doubling constants for HCN and DCN.

Rotational quantum number J	Observed line frequency $\Delta\nu$ Mc/sec	$q = \frac{\Delta\nu}{J(J+1)}$ Mc/sec	$\frac{\Delta q}{\Delta J}$
HCN			
9	20,181.39±0.15	224.238±0.0015	-0.053
10	24,660.40±0.10	224.185±0.0010	-0.055
11	29,585.12±0.20	224.130±0.0020	
Calculated $q = 226.2$ Mc/sec.			
DCN			
10	20,454.58±0.15	185.951±0.0015	-0.048
11	24,539.20±0.10	185.903±0.0010	-0.053
12	28,992.55±0.20	185.850±0.0020	
Calculated $q = 183.6$ Mc/sec.			

for DCN. Both molecules show a slight decrease of q with increasing J .

It was suggested⁶ that this small difference between the observed and calculated values of q might be explained by taking into account certain Hamiltonian matrix elements nondiagonal in V_2 which were neglected in the original treatment of the problem.² When these elements are included, one finds that both levels are shifted downward slightly with no change in their spacing. Therefore the predicted line frequency and q -value are unaffected.

There is, however, a reason to expect that q would decrease with increasing J . The value of q is affected by centrifugal stretching, which was not considered in the theory of *l*-type doubling.^{1,2} The rotational energy of a molecule is usually written

$$F_v(J) = B_v J(J+1) - D_v J^2(J+1)^2,$$

where D_v is the centrifugal stretching coefficient. This equation can be written

$$F_v(J) = B_{vJ} J(J+1),$$

where

$$B_{vJ} = B_v - D_v J(J+1).$$

Here centrifugal stretching has been included in the rotational constant rather than separated from it, as is ordinarily done. If now one replaces B_v [by B_{vJ} in the expression for q the result is

$$q = \frac{[B_v - D_v J(J+1)]^2}{\omega_2} \left[1 + 4 \sum \xi_{2s'}^2 \frac{\lambda_2}{\lambda_{s'} - \lambda_2} \right] (V_2 + 1).$$

⁶ H. H. Nielsen (private communication).

For a small change ΔJ in J the approximate change in q is

$$\Delta q = -(2q/B_{vJ})D_v(2J+1)\Delta J.$$

From the value of D_v determined by infrared spectroscopy,⁷ Δq can be calculated. For HCN and $J=10$, this equation gives $\Delta q = -0.021$ Mc/sec for $\Delta J=1$. The observed Δq in this case was -0.055 Mc/sec.

That this predicted value of Δq does not agree with the observed value is not surprising. The fact that it is of the correct order of magnitude is significant. There are several factors in the expression for q which may be affected by centrifugal stretching, and only the rotational constant has been corrected. In order to predict the variation of q accurately it would be necessary to include in the Hamiltonian terms which represent the effect of centrifugal stretching on *l*-type doubling, and to solve the resulting 4th-order perturbation problem.⁸

The change of q with increasing J reported here does not agree with that found by Shulman and Townes. One discrepancy lies in the frequency measurement of the HCN, $J=10$ line. The frequency reported here has been carefully checked and is believed to be correct.

The nuclear quadrupole coupling constant of N^{14} in the HCN molecule has been measured by Simmons, Anderson, and Gordy.⁹ Using their value of 4.58 Mc/sec, one can predict the splitting of the HCN, $J=10$ rotational level due to the interaction of the N^{14} quadrupole moment and the molecular electric field. On the basis of the selection rule $\Delta F=0, \pm 1$, one might expect the observed line for HCN, $J=10$ to consist of several components spread over a spectral range of 3.5 Mc/sec. However, by reducing pressure to approximately 10^{-3} mm of Hg, it was possible to record a single line less than 1 Mc/sec in width. This result is to be expected on the basis of general rules for line intensities, which show that $\Delta F=\pm 1$ transitions are extremely weak for high J -values.

Each of the six lines observed showed a Stark effect, but resolution of the individual components was not accomplished.

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⁷ Gerhard Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945), p. 393.

⁸ This problem is being investigated by H. H. Nielsen.

⁹ Simmons, Anderson, and Gordy, *Phys. Rev.* **77**, 77 (1950).