

Direct *l*-Type Doubling Transitions in ClCN†

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Direct *l*-type doubling transitions have been observed in Cl<sup>35</sup>C<sup>12</sup>N<sup>14</sup> for  $J=17, 18, 19,$  and  $23$ . A formula has been constructed for the *l*-type doubling constant:  $q=7.467467-1.327\times 10^{-6}J(J+1)$ . The absolute value of the asymmetry parameter  $\eta$  was determined to be  $0.0101\pm 0.0004$ .

WITH  $\Delta J=0$  ( $J\neq 0$ ), transitions are possible between the upper and lower *l*-type doublet levels that belong to the first excited vibrational bending mode of a linear molecule. The frequency of such a transition is given by the formula  $\nu=qJ(J+1)$ ,<sup>1</sup> where  $q$  is very nearly constant. Such transitions have been previously observed for only HCN and DCN simply because their *l*-type doubling constants are of the order of 200 Mc/sec, whereas most other linear molecules<sup>1</sup> have  $q$ 's smaller by a factor of 50. This paper reports on such transitions for Cl<sup>35</sup>C<sup>12</sup>N<sup>14</sup>. The  $J$  values observed are 17, 18, 19, and 23.

The signal sources for these lines were harmonics of the output of the lighthouse tube oscillator T-85/APT-5. A description of the Stark-modulated spectrometer used is found elsewhere.<sup>2</sup>

Each of the observed lines was split (see Fig. 1). This splitting is of the  $\Delta F=0$  transitions and is the result of an asymmetry of the electric field gradient at the chlorine nucleus. A further splitting due to the presence of N<sup>14</sup> occurs but is too small to have been observed with the present resolution. Removal of the degeneracy of the  $\Delta F=0$  transitions theoretically produces four lines when, as in chlorine, the spin is  $\frac{3}{2}$ . Only two were observed because in both the high-frequency pair and the low-frequency pair the separation was approximately 20 kc/sec and not resolvable with this spectrometer.

For large  $J$  the intensities of these four split lines are equal to within a few percent. This makes it impossible to distinguish between the two unresolved lines. As a result only the absolute value of the asymmetry parameter  $\eta$  could be determined.

Table I lists the frequencies of the lines observed, the calculated center frequencies, the *l*-type doubling constant, the separation between the split lines, and the absolute value of  $\eta$  calculated from this difference. Included in the table are values for the absorption coefficient calculated in the usual way.<sup>1</sup> From the table the average value of  $|\eta|$  is  $0.0101\pm 0.0004$ . This value falls in line with those for HCN ( $-0.081$ ),<sup>3</sup> DCN ( $-0.080$ ),<sup>3</sup> BrCN ( $+0.0095$ ),<sup>4</sup> and ICN ( $+0.0087$ ).<sup>4</sup> The value of the *l*-type doubling constant compares favorably with the early measurement of Townes *et al.*,<sup>5</sup>  $q=7.50$ , and with the recent Burrus and Gordy<sup>6</sup> value of  $q=7.46$ .

As in HCN,<sup>7</sup>  $q$ , the *l*-type doubling constant, has a slight dependence on  $J$ . Measurements made by Townes *et al.*<sup>5</sup> and Burrus and Gordy<sup>6</sup> were not accurate enough to determine such a dependence because both groups measured  $\Delta J=1$  transitions where  $q=\nu_0/2(J+1)$ . Transitions herein observed were for  $\Delta J=0$  with  $q=\nu_0/J(J+1)$ . This, plus the high  $J$  values used accounts for the improved value of  $q$  obtained. From the data in Table I the following formula was constructed:  $q_{\text{ClCN}}=7.467467-1.327\times 10^{-6}J(J+1)$ .

TABLE I. Cl<sup>35</sup>C<sup>12</sup>N<sup>14</sup> data and evaluated constants.

$J$	Measured frequency Mc/sec	Center frequency $\nu_0$ Mc/sec	$q = \left( \frac{\nu_0}{J(J+1)} \right)$ Mc/sec	Separation between split lines kc/sec	Absolute value of asymmetry parameter $\eta$	Absorption coefficient $\text{cm}^{-1}$
17	2283.698±0.010	2283.802	7.463405	208	0.00998	4.4×10 <sup>-9</sup>
	2283.906±0.010					
18	2552.224±0.010	2552.336	7.462971	224	0.0107	5.1×10 <sup>-9</sup>
	2552.448±0.010					
19	2835.622±0.010	2835.726	7.462436	207	0.00993	5.9×10 <sup>-9</sup>
	2835.829±0.010					
23	4117.869±0.020	4117.968	7.460087	198	0.00950	9.3×10 <sup>-9</sup>
	4118.067±0.020					

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<sup>1</sup> C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955).

<sup>2</sup> Weisbaum, Beers, and Herrmann, *J. Chem. Phys.* **23**, 1601 (1955).

<sup>3</sup> R. L. White, *J. Chem. Phys.* **23**, 249 (1955). L. Yarmus, *Phys. Rev.* **104**, 365 (1956).

<sup>4</sup> A. Javan, *Phys. Rev.* **99**, 1302 (1955).

<sup>5</sup> Townes, Holden, and Merritt, *Phys. Rev.* **74**, 1113 (1948).

<sup>6</sup> C. A. Burrus and W. Gordy, *Phys. Rev.* **101**, 599 (1956).

<sup>7</sup> J. F. Westerkamp, *Phys. Rev.* **93**, 716 (1954).

TABLE II.  $l$ -type doubling constant for C1CN.

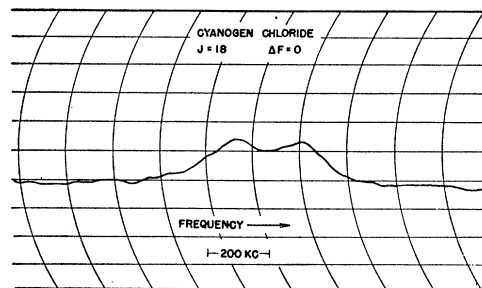
$J$	$q$ from formula <sup>a</sup>	$q = \nu_0/[J(J+1)]$ experimental	Difference
17	7.463406 <sup>b</sup>	7.463405	+ $1 \times 10^{-6}$
18	7.462929	7.462971	- $42 \times 10^{-6}$
19	7.462424	7.462436	- $12 \times 10^{-6}$
23	7.460142	7.460087	+ $55 \times 10^{-6}$

<sup>a</sup>  $q_{\text{C1CN}} = 7.467467 - 1.327 \times 10^{-5} J(J+1)$ .

<sup>b</sup> All values in Mc/sec.

The values obtained from this formula are compared with the experimentally determined values,  $q = \nu_0/[J(J+1)]$ , in Table II. Nielsen,<sup>8</sup> using a fourth order perturbation calculation, estimates the correction term to have a value slightly larger than  $2B_s(B_s/\omega_s)^3(V_s+1)J(J+1)$ , where  $B_s$  is the rotational constant and  $\omega_s$  the vibrational frequency of the degenerate bending mode. This expression (using  $B_s = 5970.821$  Mc/sec,  $\omega_s = 1191 \times 10^4$  Mc/sec, and  $V_s = 1$ ) yields a value of  $0.3 \times 10^{-5}$  as compared with the  $1.327 \times 10^{-5}$  determined above. For HCN the above

<sup>8</sup> H. H. Nielsen, Phys. Rev. **78**, 296 (1950).

FIG. 1. Recorder trace of the  $J=18, \Delta F=0$  transition in  $\text{C}^{135}\text{C}^{12}\text{N}^{14}$ .

expression equals  $16 \times 10^{-4}$  and the experimental value  $26 \times 10^{-4}$ .<sup>7</sup> Thus in both cases the theoretical estimate is the right order of magnitude.

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## Collection of Ions Produced by Alpha Particles in Air\*

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An investigation of the effects of pressure and collector potential on ion collection in air indicates that recombination of ions may occur even when the ionization current is independent of the collecting field. A  $\text{Po}^{210}$  source of reduced-range alpha particles was used as the central electrode in a cylindrical ionization chamber of sufficiently large dimensions that the residual energy of the particles was absorbed by the gas at pressures greater than 4.5 cm of mercury. Apparently complete ion collection was achieved by reducing the pressure until at 10 cm of mercury a maximum ionization current was obtained which was independent of the collecting field and of further reduction in pressure. The ionization current at atmospheric pressure, though independent of the collecting potential over a large range of voltages, was 3.3% lower. Since field independence has been the usual criterion of saturation, undetected recombination is suggested as a possible cause for the apparent increase of average energy expended per ion pair formed in air ( $W$ ) by alpha particles of decreasing energy as well as the reported difference between  $W$  values for alpha and beta particles.

### INTRODUCTION

KIMURA *et al.*<sup>1</sup> have shown that for ionization measurements in air using alpha particles, very large collecting fields are necessary to prevent recombination of ions, especially at low alpha energies where the ion density is greatest. Lack of saturation due to insufficient potential is suggested as one possible cause of the anomalous air ionization-energy curve for alpha particles of low energy reported by Jesse,<sup>2</sup> who has stated that his experimental conditions did not exclude

this possibility. We would like to report another difficulty in achieving saturation, that is, collection of all the ions produced in the chamber, which may exist even when an ionization plateau is observed over a large potential range, and to suggest that an additional condition must be satisfied to insure saturation.

### EXPERIMENTAL

When the entire energy of the ionizing particles is expended inside the chamber and when ion collection is complete, further increase of the collector potential or the gas pressure should not alter the ionization current. We have investigated the effects of both pressure and voltage on the ion collection in air using

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<sup>1</sup> Kimura, Ishiwari, Yusa, Yamashita, Miyake, and Kimura, J. Phys. Soc. Japan **7**, 111 (1952).

<sup>2</sup> Jesse, Forst, and Sadauskis, Phys. Rev. **77**, 782 (1950).