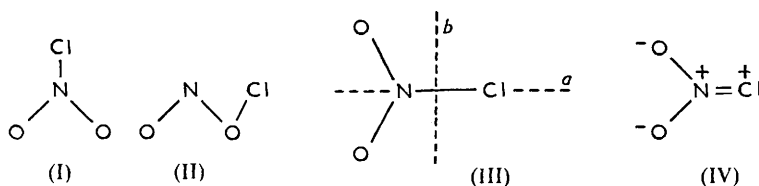


### 64. *The Microwave Spectrum, Structure, and Dipole Moment of Nitril Chloride.*

By D. J. MILLEN and K. M. SINNOTT.

Rotational transitions in the microwave spectra of  $\text{NO}_2^{35}\text{Cl}$  and  $\text{NO}_2^{37}\text{Cl}$  have been assigned and molecular rotational constants evaluated. Structural parameters  $r_{\text{NCl}} = 1.840 \text{ \AA}$ ,  $r_{\text{NO}} = 1.202 \text{ \AA}$  and  $\angle \text{ONO} = 130^\circ 35'$  are obtained. From the hyperfine structure of the spectra, chlorine nuclear quadrupole coupling parameters  $eQ \cdot \partial^2 V / \partial a^2 = -94.28 \text{ Mc./sec.}$ ,  $eQ \cdot \partial^2 V / \partial b^2 = 51.23 \text{ Mc./sec.}$ , and  $eQ \cdot \partial^2 V / \partial c^2 = 43.05 \text{ Mc./sec.}$  were obtained for  $\text{NO}_2^{35}\text{Cl}$ ; the corresponding values for  $\text{NO}_2^{37}\text{Cl}$  are  $-74.45$ ,  $40.98$ , and  $33.47 \text{ Mc./sec.}$  These coupling parameters have been interpreted to give information about the double-bond character of the nitrogen-chlorine bond. From a study of the Stark effect of the  $0_{00}^{3/2} \rightarrow 1_{01}^{5/2}$  transition the molecular dipole moment has been evaluated as  $0.42 \pm 0.01 \text{ D}$ .

SEVERAL compounds of the type  $\text{NO}_2\text{X}$  are well known. Crystalline salts<sup>1</sup> with ionic structures<sup>2</sup>  $\text{NO}_2^+\text{X}^-$  are obtained for  $\text{X} = \text{NO}_3^-$ ,  $\text{HS}_2\text{O}_7^-$ ,  $\text{FSO}_3^-$ ,  $\frac{1}{2}\text{S}_2\text{O}_7^{2-}$ , and  $\frac{1}{2}\text{S}_3\text{O}_{10}^{2-}$ . By contrast, for  $\text{X} = \text{Cl}$  or  $\text{F}$  the compounds are gaseous at room temperature. For nitril chloride chemical evidence<sup>3</sup> has at different times been interpreted to support both structures (I) and (II).



The infrared spectrum<sup>4</sup> was interpreted on the basis of structure (I) although no decision between planar and non-planar possibilities was reached. The present study of the microwave spectrum has provided a clear argument<sup>5</sup> establishing the planar structure (I). We have now analysed the spectra of  $\text{NO}_2^{35}\text{Cl}$  and  $\text{NO}_2^{37}\text{Cl}$  to give values for internuclear distances and angles, and information about bond properties from nuclear quadrupole fine structure and the molecular dipole moment.

*The Spectrum.*—Many lines were observed in the region 8000—26,000 Mc./sec.; those which have been assigned to low- $J$  transitions are listed in Tables 1 and 2. The spectrum has the features expected for the isotopic asymmetric rotors  $\text{NO}_2^{35}\text{Cl}$  and  $\text{NO}_2^{37}\text{Cl}$  with hyperfine structure due to quadrupole interaction of a single nucleus in each case. The magnitude of the splitting makes it clear that the chlorine nuclei are involved. No further splitting of these lines could be resolved; nuclear quadrupole interaction with  $^{14}\text{N}$  was therefore ignored and the problem treated as one of rotational coupling with a single nucleus.

The multiplet 8876.26, 8899.90, and 8918.70 Mc./sec. was identified as a  $J, 0 \rightarrow 1$  transition for  $\text{NO}_2^{35}\text{Cl}$ , the outer lines being displaced from the middle one in very nearly the ratio 4 : 5 expected for this transition when the splitting arises through rotational coupling with a single quadrupolar nucleus of spin  $I = \frac{3}{2}$ . Rotational transitions  $J, 1 \rightarrow 2$  and  $J, 2 \rightarrow 3$  having appropriate hyperfine structure were also identified. The

<sup>1</sup> Goddard, Hughes, and Ingold, *J.*, 1950, 2559.

<sup>2</sup> Millen, *J.*, 1950, 2610.

<sup>3</sup> Schmiesser and Gregor-Haschke, *Z. anorg. Chem.*, 1948, **255**, 33; Seel and Nogradi, *ibid.*, 1952, **269**, 188; Batey and Sisler, *J. Amer. Chem. Soc.*, 1952, **74**, 3408.

<sup>4</sup> Ryason and M. K. Wilson, *J. Chem. Phys.*, 1954, **22**, 2000.

<sup>5</sup> Millen and Sinnott, *Chem. and Ind.*, 1955, 538.

assignments are listed in Table 1,  $F_i$  and  $F_f$  being the initial and final values of the resultant angular momentum quantum number,  $F = I + J$ .

In the same way the multiplet 8644·60, 8663·20, and 8678·10 Mc./sec. was identified as the  $J, 0 \rightarrow 1$  transition of the heavier isotopic species,  $\text{NO}_2^{37}\text{Cl}$ . The rotational lines assigned are given in Table 2.

TABLE 1. *Spectrum of  $\text{NO}_2^{35}\text{Cl}$ . Assignments, intensities, and comparison of observed and calculated frequencies.*

$J$	$J'$			Frequency (Mc./sec.)		Intensity ( $\text{cm.}^{-1}$ )
		$F_i$	$F_f$	Observed	Calculated	
$0_{00}$	$1_{01}$	3/2	3/2	8876·28	8876·27	$5 \times 10^{-8}$
		3/2	5/2	8899·90	8899·87	$7.5 \times 10^{-8}$
		3/2	1/2	8918·70	8918·75	$2.4 \times 10^{-8}$
$1_{01}$	$2_{02}$	1/2	3/2	17,587·70	17,587·62	$1.0 \times 10^{-7}$
		5/2	5/2	17,589·88	17,589·94	$1.1 \times 10^{-7}$
		1/2	1/2	17,610·80	17,610·81	$1.0 \times 10^{-7}$
		5/2	7/2	17,612·98	17,613·12	$4.8 \times 10^{-7}$
		3/2	5/2	17,613·52	17,613·54	$2.5 \times 10^{-7}$
		3/2	3/2	17,629·90	17,630·10	$1.2 \times 10^{-7}$
$2_{02}$	$3_{03}$	3/2	1/2	17,653·20	17,653·29	$1.8 \times 10^{-8}$
		7/2	7/2	25,964·70	25,964·86	$1.5 \times 10^{-7}$
		1/2	3/2	25,981·40	25,981·35	$4.2 \times 10^{-7}$
		3/2	5/2	25,982·15	25,981·99	$6.6 \times 10^{-7}$
		7/2	9/2	25,987·44	25,987·39	$1.5 \times 10^{-6}$
		5/2	7/2	25,988·15	25,988·04	$1.0 \times 10^{-6}$
$6_{24}$	$6_{25}$	5/2	5/2	25,998·40	25,998·65	$2.1 \times 10^{-7}$
		3/2	3/2	26,004·63	26,004·56	$1.5 \times 10^{-7}$
		13/2	13/2	9973·90	9974·00	$4.9 \times 10^{-8}$
		11/2	11/2		9974·51	$4.4 \times 10^{-8}$
		15/2	15/2	9976·40	9976·16	$5.5 \times 10^{-8}$
		9/2	9/2		9976·65	$4.0 \times 10^{-8}$

TABLE 2. *Spectrum of  $\text{NO}_2^{37}\text{Cl}$ . Assignments, intensities, and comparison of observed and calculated frequencies.*

$J$	$J'$			Frequency (Mc./sec.)		Intensity ( $\text{cm.}^{-1}$ )
		$F_i$	$F_f$	Observed	Calculated	
$0_{00}$	$1_{01}$	3/2	3/2	8644·60	8644·59	$1.7 \times 10^{-8}$
		3/2	5/2	8663·20	8663·22	$2.5 \times 10^{-8}$
		3/2	1/2	8678·10	8678·12	$8.0 \times 10^{-9}$
$1_{01}$	$2_{02}$	5/2	7/2	17,161·32	17,161·24	$1.6 \times 10^{-7}$
		3/2	5/2		17,161·54	$8.0 \times 10^{-8}$
$2_{02}$	$3_{03}$	7/2	7/2	25,337·90	25,338·00	$5.0 \times 10^{-8}$
		1/2	3/2	25,351·20	25,351·09	$1.4 \times 10^{-7}$
		3/2	5/2	25,351·20	25,351·57	$2.2 \times 10^{-7}$
		7/2	9/2	25,356·00	25,355·85	$5.0 \times 10^{-7}$
		5/2	7/2	25,356·50	25,356·33	$3.5 \times 10^{-7}$
		5/2	5/2	25,364·30	25,364·66	$7.0 \times 10^{-8}$
$2_{21}$	$3_{21}$	3/2	3/2	25,369·80	25,369·42	$5.0 \times 10^{-8}$
		3/2	3/2	25,978·50	25,978·49	$3.7 \times 10^{-8}$
		3/2	5/2		25,978·49	$1.3 \times 10^{-7}$
		7/2	7/2	25,983·48	25,983·52	$3.4 \times 10^{-8}$
		7/2	9/2		25,983·52	$3.1 \times 10^{-7}$

Intensities in Tables 1 and 2 were evaluated for 300° K, pressure broadening of 5 Mc./sec. per mm. being assumed, since contributions to line breadth from unresolved nitrogen nuclear quadrupole effects made experimental determination difficult.

*Molecular Structure.*—The rotational constants  $A$ ,  $B$ , and  $C$  for each molecule can in principle be determined from the frequencies of the three low- $J$  transitions. This procedure is not entirely satisfactory here since none of these frequencies is very sensitive to changes in  $A$ , so it was important to include in the calculation another transition which would overcome this insensitivity. The transition  $6_{24} \rightarrow 6_{25}$  was identified for this purpose.

The frequency of this transition is readily related to the rotational constants of the molecule through the equation

$$E_{J_r} = \frac{A - C}{2} \cdot E_r(\kappa) + \frac{A + C}{2} \cdot J(J + 1)$$

in which the asymmetry parameter  $\kappa = (2B - A - C)/(A - C)$  and values of  $E_r(\kappa)$  can be obtained from Turner, Hicks, and Reitwiesner's tables.<sup>6</sup>

The nuclear quadrupole coupling constants were evaluated from the first-order interaction energy which is given<sup>7</sup> in terms of the nuclear quadrupole moment  $Q$  and the field gradients along the inertial axes  $a$ ,  $b$ , and  $c$  by

$$E_Q(J, F) = \frac{eQ}{J(J+1)} \left\{ \left( \frac{\partial^2 V}{\partial a^2} \right) \left[ J(J+1) + E(\kappa) - (\kappa+1) \left( \frac{\partial E(\kappa)}{\partial \kappa} \right) \right] \right. \\ \left. + 2 \left( \frac{\partial^2 V}{\partial b^2} \right) \left( \frac{\partial E(\kappa)}{\partial \kappa} \right) + \left( \frac{\partial^2 V}{\partial c^2} \right) \left[ J(J+1) - E(\kappa) + (\kappa-1) \left( \frac{\partial E(\kappa)}{\partial \kappa} \right) \right] \right\} Y(F)$$

where

$$Y(F) = \frac{\frac{3}{4}C(C+1) - I(I+1)J(J+1)}{2(2J+3)(2J-1)(2I-1)(I)}$$

with

$$C = F(F+1) - I(I+1) - J(J+1)$$

Making use of the condition

$$\frac{\partial^2 V}{\partial a^2} + \frac{\partial^2 V}{\partial b^2} + \frac{\partial^2 V}{\partial c^2} = 0$$

and writing  $\chi_{aa} = eQ \left( \frac{\partial^2 V}{\partial a^2} \right)$ , etc., we can put the expression in a convenient form for computation:

$$E_Q(J, F) = \left\{ (\chi_{aa} + \chi_{cc}) \left[ J(J+1) - 3 \left( \frac{\partial E(\kappa)}{\partial \kappa} \right) \right] \right. \\ \left. + (\chi_{aa} - \chi_{cc}) \left[ E(\kappa) - \kappa \left( \frac{\partial E(\kappa)}{\partial \kappa} \right) \right] \right\} \cdot \frac{Y(F)}{J(J+1)}$$

The rotational constants, and nuclear quadrupole coupling parameters calculated for the two isotopic species, are given in Table 3. The frequencies calculated from these six

TABLE 3. *Rotational constants and nuclear quadrupole coupling constants for NO<sub>2</sub><sup>35</sup>Cl and NO<sub>2</sub><sup>37</sup>Cl (all values are given in Mc./sec.).*

	A	B	C	$\chi_{aa}$	$\chi_{bb}$	$\chi_{cc}$
NO <sub>2</sub> <sup>35</sup> Cl .....	13,239.9 <sub>8</sub>	5173.78	3721.37	-94.28	51.23	43.05
NO <sub>2</sub> <sup>37</sup> Cl .....	13,240.0	5019.00	3640.49	-74.45	40.98	33.47

TABLE 4. *Parameters relating to the momental ellipsoids of NO<sub>2</sub><sup>35</sup>Cl and NO<sub>2</sub><sup>37</sup>Cl. I<sub>a</sub>, I<sub>b</sub>, I<sub>c</sub>, and  $\Delta$  are expressed in atomic mass units  $\times \text{\AA}^2$ .*

	I <sub>a</sub>	I <sub>b</sub>	I <sub>c</sub>	$\Delta$	$\kappa$
NO <sub>2</sub> <sup>35</sup> Cl .....	38.1822	97.710 <sub>1</sub>	135.845 <sub>4</sub>	-0.046 <sub>9</sub>	-0.694827
NO <sub>2</sub> <sup>37</sup> Cl .....	38.1821	100.723 <sub>5</sub>	138.863 <sub>4</sub>	-0.041 <sub>6</sub>	-0.712807

parameters for each species are listed in Tables 1 and 2 for comparison with the observed frequencies. The agreement is satisfactory.

The rotational constants lead directly to molecular principal moments of inertia. These are listed in Table 4, which also includes the values calculated for the asymmetry parameter  $\kappa$  and the inertial defect  $\Delta = I_a - I_b - I_c$ .

<sup>6</sup> Turner, Hicks, and Reitwiesner, Ballistics Research Laboratories Report No. 878, reproduced in Townes and Schawlow, "Microwave Spectroscopy," McGraw-Hill, New York, 1955.

<sup>7</sup> Bragg and Golden, *Phys. Rev.*, 1949, **75**, 735.

For both isotopic species  $\Delta$  is nearly zero, as required for a rigid planar body. The values of  $\Delta$  are comparable with those observed for other planar molecules and can be safely attributed to zero-point motion. A further simple argument confirms planarity and establishes structure (I) conclusively. From the values of the rotational constants of  $\text{NO}_2^{35}\text{Cl}$  it was calculated that the  $1_{10} \rightarrow 2_{11}$  and  $2_{12} \rightarrow 3_{13}$  transitions would be expected at 19,230 and 24,380 Mc./sec. respectively, both transitions being allowed by that component of dipole moment which permits the observed transitions. A careful search failed to reveal any lines which could be assigned to these transitions. Their absence is easily understood in terms of the planar structure (I), for which rotation about the two-fold axis along the nitrogen-chlorine bond interchanges identical oxygen atoms. In order that the total wave function be symmetric to this operation, the rotational wave functions must also be symmetric with respect to this operation for a molecule in even electronic and vibrational states. Thus the rotational states  $1_{10}$ ,  $2_{11}$ ,  $2_{12}$ , and  $3_{13}$  do not occur for planar structure (I) in its ground vibrational and electronic state, since they belong to the forbidden classes  $J_{0e}$  and  $J_{0o}$ .

Internuclear distances and angles for the planar structure were evaluated from the rotational constants and are as follows:  $r_{\text{NCl}} = 1.840 \text{ \AA}$ ,  $r_{\text{NO}} = 1.202 \text{ \AA}$ , and  $\angle \text{ONO} = 130^\circ 35'$ . The inertial axes are shown in (III). Some idea of the uncertainties in the structural parameters due to zero-point vibrations can be obtained from the inertial defect. By assigning the whole of the inertial defect for  $\text{NO}_2^{35}\text{Cl}$  to each principal moment of inertia in turn, it was found possible to fit any pair of principal moments by a structure falling in the range  $r_{\text{NCl}} = 1.840 \pm 0.002 \text{ \AA}$ ,  $r_{\text{NO}} = 1.202 \pm 0.001 \text{ \AA}$  and  $\angle \text{ONO} = 130^\circ 35' \pm 15'$ .

Further information about the nitrogen-chlorine bond has been obtained by interpreting the nuclear quadrupole fine structure. Nitryl chloride provides a particularly clear case for the estimation of double-bond character in this way. The analysis of the spectrum leads directly to the coupling coefficients along and perpendicular to the nitrogen-chlorine bond, and the usual assumptions about transformation of axes to evaluate coupling components along a bond direction from values along inertial axes are not required. Table 3 shows that the coupling constants along the  $b$  and  $c$  axes [see (III);  $c$  is orthogonal to  $a$  and  $b$ ] are not identical. Thus there are different field gradients along the  $b$  and  $c$  axes at the chlorine nucleus. Evidently there is not axial symmetry about the nitrogen-chlorine bond as would be expected for an unperturbed  $\sigma$  bond.<sup>8</sup> The departure of the field gradient from axial symmetry is in the direction expected for electron loss from the  $3p_c$  chlorine orbital. Such an electron loss is represented by a contribution to the ground state from the resonance structure (IV). The quantitative importance of this resonance structure has been calculated on the assumption that so far as chlorine nuclear quadrupole interactions are concerned the structure is equivalent to loss of an electron from the  $3p_c$  chlorine atomic orbital.

The observed coupling coefficients  $\chi_{aa}$ ,  $\chi_{bb}$ , and  $\chi_{cc}$  along the directions of the inertial axes are given in Table 3. If the electron loss along the direction of the  $c$  axis contributes  $\chi_{cc}^e$  to  $\chi_{cc}$  then, according to Laplace's theorem, it makes a contribution of  $-\frac{1}{2}\chi_{cc}^e$  to each of  $\chi_{bb}$  and  $\chi_{aa}$ . Thus  $\chi_{cc}^e = \frac{2}{3}(\chi_{cc} - \chi_{bb})$  may be evaluated as  $-5.45 \text{ Mc./sec.}$  for  $\text{NO}_2^{35}\text{Cl}$ . Since the complete removal of an electron from a  $3p_c$  atomic orbital for the chlorine atom leads to a coupling coefficient of  $-109.6 \text{ Mc./sec.}$ , the value for  $\chi_{cc}^e$  can be interpreted as indicating 5.0% electron deficit for the chlorine  $3p_c$  orbital.

The interpretation of the coupling coefficient along the nitrogen-chlorine axis is not so clear because of the usual difficulty of separating contributions from ionic character  $\text{O}_2\text{N}^+\text{Cl}^-$  and  $s$  character in the chlorine atomic orbital used in bond formation.<sup>9</sup> If the chlorine orbital is taken to be a pure  $p$  orbital, then, making the usual assumptions, we obtain a value of 11.6% ionic character.

<sup>8</sup> Goldstein and Bragg, *Phys. Rev.*, 1950, **78**, 347; Goldstein, *J. Chem. Phys.*, 1956, **24**, 106.

<sup>9</sup> Townes and Dailey, *ibid.*, 1949, **17**, 782; 1955, **23**, 118; Gordy, *Discuss. Faraday Soc.*, 1955, **19**, 14.

### 354 Microwave Spectrum, Structure, and Dipole Moment of Nitryl Chloride.

*Dipole Moment.*—The Stark effect of the transition  $J, 0_{00} \longrightarrow 1_{01}$ ;  $F, 3/2 \longrightarrow 5/2$ , at 8899.90 Mc./sec. was studied quantitatively. The line is expected to give rise to two Stark components corresponding to  $M_F = \pm \frac{1}{2}$  and  $M_F = \pm \frac{3}{2}$  for the upper state. These were not resolved, their calculated separation at the highest voltage used being only 0.2 Mc./sec. The frequencies of the Stark component for various field strengths are given in Table 5.

TABLE 5. Stark effect for the  $0_{00}^{3/2} \longrightarrow 1_{01}^{5/2}$  transition.

Field strength $V$ (v/cm.)	0	723	822	907	988	1070
Frequency of Stark component (Mc./sec.)	8899.90	8900.90	8901.30	8901.75	8902.30	8902.80

The frequency displacements  $\Delta\nu$  (Mc./sec.) of the single Stark component observed are fitted moderately well by  $\Delta\nu = 0.203\epsilon^2$ , values of  $\epsilon$  in e.s.u. being obtained by calibration of the equipment by use of the Stark effect of the  $J, 1 \longrightarrow 2$  transition of carbonyl sulphide OCS which has a dipole moment<sup>10</sup> of  $0.7085 \pm 0.004 \times 10^{-18}$  e.s.u.

Second-order perturbation theory<sup>11</sup> gives the following expressions for the two unresolved components:

$$M_F = \pm \frac{1}{2} \quad \Delta\nu = 1.24 \times 10^{36} \mu^2 \epsilon^2$$

$$M_F = \pm \frac{3}{2} \quad \Delta\nu = 1.09 \times 10^{36} \mu^2 \epsilon^2$$

where both  $\mu$  and  $\epsilon$  are in e.s.u. Both expressions satisfy the experimental result for  $\mu = 0.42 \pm 0.01$  D.

#### EXPERIMENTAL

Spectra were observed by using a Stark-modulated spectrometer.<sup>12</sup> Absorption cells were made of 10 ft. lengths of copper  $X$ - and  $K$ -band waveguide, with a central strip electrode insulated by Teflon tape. Stark modulation voltages were applied by a 100 kc./sec. square-wave generator. Microwave power was detected by IN26 or CV253 crystals, and the 100 kc./sec. component amplified by a H.R.O. communications receiver. The output signal was either displayed on an oscilloscope or fed into a Brown recorder.

As microwave sources, 2K33 klystrons were used in the region 21,000—27,000 Mc./sec. and CV129 klystrons with modified cavities for the region 8000—11,000 Mc./sec. For observing spectra in the region 16,000—21,000 Mc./sec. a crystal doubler was constructed. A CV364 crystal was mounted in a holder across the  $X$ -band waveguide and provided with probes on either side of the crystal for matching. It was found important to adjust the depth of insertion of the crystal as well as the probe positions in order to obtain best operation. The method provided a simple and adequate source of power of the doubled frequency, and was found also to generate smaller amounts of the tripled frequency. The fundamental frequency was removed by use of appropriately-dimensioned filter sections. These and the necessary microwave transformer sections were prepared by electrodeposition of copper on machined formers, which were prepared from polystyrene coated with silver by evaporation. Finally the polystyrene was dissolved by sulphur-free benzene.

Approximate values of frequencies were obtained with wavemeters, several of which, utilising the  $TE_{011}$  mode and the coupling system suggested by Bleaney, Loubser, and Penrose,<sup>13</sup> were constructed. Three such meters were found to operate well over the ranges 7.5—9.5, 9.5—12.5, and 19—23 kMc./sec. The frequencies of lines were measured with a frequency standard constructed to have an accuracy of about 1 part in  $10^7$ . The first stage consists of a 5 Mc./sec. electron-coupled oscillator, controlled by a quartz crystal operated at its inversion temperature in a thermostatically controlled oven. The frequency of this stage can be reduced by about 0.0001% by a trimming condenser in parallel with the crystal, and in this way the output can be adjusted to zero-beat with the standard 5 Mc./sec. signal from station MSF (operated by the National Physical Laboratory of Rugby). Successive stages of frequency multipliers raise the frequency through 20, 60, 180, to 540 Mc./sec. The multipliers are conventional

<sup>10</sup> Shulman and Townes, *Phys. Rev.*, 1950, **77**, 500.

<sup>11</sup> Golden and E. B. Wilson, jun., *J. Chem. Phys.*, 1948, **16**, 669; Fano, *J. Res. Nat. Bur. Stand.*, 1948, **40**, 215.

<sup>12</sup> McAfee, Hughes, and E. B. Wilson, jun., *Rev. Sci. Instr.*, 1949, **20**, 821.

<sup>13</sup> Bleaney, Loubser, and Penrose, *Proc. Phys. Soc.*, 1947, **59**, 185.

except for the last stage which employs a QQVO3—20 valve operated with a quarter-wave parallel-line tuned input circuit, and in the plate circuit a butterfly resonant circuit of the type described by Karplus.<sup>14</sup> In order to obtain spectra of nitryl chloride it was necessary for the gas to flow through the cell continuously and to surround the wave-guide cell in solid carbon dioxide.

We thank Professor C. K. Ingold, F.R.S., for his interest.

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[Received, August 7th, 1957.]

<sup>14</sup> Karplus, *Proc. Inst. Radio Eng.*, 1945, **33**, 426.

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