JULY 15, 1938 PHYSICAL REVIEW VOLUME 54

Spectra of the Monochlorides of Nickel, Cobalt and Iron

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(Received May 21, 1938)

Emission spectra in the region 3800 to 6000A which are attributed to the molecules NiCl, CoCl, and FeCl have been excited by means of high frequency discharges in silica tubes containing $NiCl_2$ $CoCl_2$, and $FeCl_2$, respectively. Vibrational analyses of four systems of NiCl and three systems of CoCl are given. No regularities were found among the FeCl bands.

INTRODUCTION

EMISSION spectra attributed to the chlorides of iron, cobalt, and nickel were reported by Mesnage[1] in 1935. Mesnage suggests that most of the bands are due to the diatomic chlorides. Many of the bands reported form sequence-like structures. In the case of one group of bands attributed to NiCl Mesnage suggests a provisional assignment of vibrational quantum numbers. This quantum assignment is untenable because it leads to a value of about 1400 cm^{-1} for the ground state vibrational frequency of the NiCl molecule. This value is much too high for a molecule as heavy as NiCl.

In the present investigation the spectra in question were excited in a high frequency discharge and were photographed with a grating which gives much higher dispersion than did the spectrograph used by Mesnage. The data obtained lead to quite a different interpretation of the NiCl spectrum.

EXPERIMENTAL

The spectra under investigation were excited by the passage of a high frequency discharge through a fused silica tube which contained a small amount of $NiCl_2$, $CoCl_2$, or $FeCl_2$. The power was supplied by a radiofrequency oscillator having a two kilowatt power tube. The materials used were of the highest purity obtainable commercially. The silica tube was 1.5 cm in diameter and 25 cm in length. It was provided with external electrodes which were placed 12 cm apart. The discharge tube was evacuated with a Hyvac pump. In order to maintain a suitable pressure of the chloride vapor in the discharge the tube was heated externally by means of a Mecker burner. The tube was pumped while the discharge was in operation in order to prevent the pressure from becoming too high for the passage of the high frequency discharge. This was necessary because chlorine was formed by the dissociation of the triatomic chlorides.

The spectra were photographed in the second order of a 21-foot grating which was in a stigmatic mounting. The dispersion was about 2.5A per mm. Exposure times varied from fifteen minutes to two hours. Iron arc comparison spectra were recorded on all plates. Nickel and cobalt arc spectra were also recorded on the NiCl and CoCl plates, respectively. The latter served for the identification of the nickel and cobalt lines which were excited in the discharge.

DATA

The spectrum of nickel chloride extends from 3900 to 4800A, with the strongest bands in the region 4050 to 4450A. Most of the heads reported by Mesnage are found, together with many others. The bands all degrade to the red. Several groups of strong bands form rather closely spaced sequences. Partially resolved rotational structure extends for a considerable distance from the strong heads.

The cobalt chloride spectrum extends from 3800 to 5700A. As in the case of nickel chloride nearly all the bands reported by Mesnage are found, along with several others. The cobalt chloride bands also degrade to the red. Some of the bands form very closely spaced sequences, while many of the heads are not part of any obvious sequence array. Partially resolved rotational structure is observed in all the bands.

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[1] P. Mesnage, Comptes rendus **200**, 2072 (1935); **201**, 389 (1935).

Bands of iron chloride are observed in the region 4000 to 6000A. These bands do not resemble the NiCl and CoCl bands in appearance, inasmuch as few distinct heads and no rotational structure are found. Some of the heads degrade to the red, some to the violet, and some do not degrade definitely in either direction. None of the bands form obvious sequence arrays.

ANALYSIS

Nickel chloride

Four prominent groups of heads are arranged in vibrational arrays and a fifth group in a sequence of double heads. The other bands present seem to be single heads, unrelated to the other heads observed. The wave numbers of the four systems analyzed, and the wave numbers of the other bands observed, are given in Tables I and II, respectively. It is found that for all the systems analyzed the $\Delta v=0$ sequence is strong and the $\Delta v=\pm 1$, ± 2 sequences are weak. The intensity distribution thus follows a rather narrow Condon parabola. In the case of the systems analyzed the strong $\Delta v=0$ sequences consist of single strong heads which are probably Q heads. Weak heads which may be R heads are observed in some cases. For the $\Delta v=\pm 1$, ± 2 sequences only Q heads are observed. The fifth system, for which only one sequence has been identified, consists of double heads of about equal intensity.

TABLE I. *Wave numbers of analyzed bands of* NiCl.

v'' / v'	0	1	2	3	4
			System 1		
0	22738.3				
1		22718.2	22302.6	21888.2	
2		23112.8	22697.3	22283.4	21871.3
3		23504.0		22676.3	
			System 2		
0	23222.7				
1		23200.7	22785.3		
2		23593.9	23177.7	22762.8	
3			23567.9	23152.7	22738.3
4					23125.9
5					23511.6
			System 3		
0	24129.6	23712.8			
1		24112.0	23697.6		
2			24094.7		
			System 4		
0	24614.7	24199.6			
1	25012.5	24596.7	24181.8		
2	25406.5	24991.3	24577.5		
3		25382.2	24968.8		

TABLE II. *Wave numbers of unanalyzed bands of* NiCl.

24417.7	24494.5	21246.1	21747.4
410.7			
	476.4	237.7	
387.6			
382.8	460.0	230.1	23333.3
359.1			
354.9			
	21911.0	21639.3	23757.6
331.9			
327.8	890.7	627.1	
305.4	871.3		24214.6
301.5			
		22289.8	
		283.4	

The Q heads of the four systems analyzed are represented by the following equations:

$$\nu=22747.6+400.2u'-1.35u'^2-419.2u''+0.88u''^2, \quad (1)$$

$$\nu=23232.7+397.3u'-1.18u'^2-417.2u''+0.35u''^2, \quad (2)$$

$$\nu=24138.5+401.3u'-1.05u'^2-419.2u''+1.20u''^2, \quad (3)$$

$$\nu=24623.2+400.7u'-1.58u'^2-416.6u''+0.55u''^2, \quad (4)$$

where $u=v+\frac{1}{2}$.

The electronic interval 484 cm^{-1} occurs between system 1 and system 2, and also between system 3 and system 4. This equality of intervals suggests that these systems arise from transitions involving a common doublet term. It is probable that this common doublet state is the ground state. If this is the case the two doublet systems arise from transitions to the ground state from two upper states which are either single or have practically the same electronic doubling.

The vibrational constants also suggest that systems 1 and 3 have a common lower state, as have systems 2 and 4. With this interpretation 1 and 2 must have a common upper state, and also 3 and 4, if the upper states are single. The differences between the vibrational constants which should thus be equal are within the limits to be expected because the constants are derived from head data. In the case of systems for which the frequencies of the upper and lower state are nearly equal, the use of head data instead of origin data reduces the accuracy with which the constants may be determined. It has already been pointed out that the upper states may be electronic doublets with nearly equal splittings. In this case 1 and 2, and also 3 and 4, do not have common initial levels. The upper state vibrational frequencies are thus not necessarily equal.

A vibrational isotope effect due to the chlorine isotopes is found in only a few cases, probably because of the weakness of the bands for which the effect should be appreciable and because of the blending of weak heads with rotational structure. No isotope effect due to the nickel isotopes is observed.

The bands discussed are all attributed to the diatomic NiCl molecule. The appearance and arrangement of the bands support this interpretation. The observation of strong line spectra of Ni I and Cl I and only a very weak spectrum of molecular chlorine indicates that the high frequency discharge produces a considerable amount of complete dissociation of the $NiCl_2$ into atomic fragments. Under such conditions of excitation it is probable that the bands observed are due to the diatomic molecule NiCl rather than to the triatomic molecule $NiCl_2$. It is of course possible that some of the bands are due to impurities in the compounds used, but none of them have been identified as being due to any known spectrum. The partially resolved rotational structure has the same appearance in all the bands, indicating that all are due to the same molecule.

Since the low lying terms of Ni I are $3d^84s^2$, ^3F and $3d^94s$, ^3D, and the ground state term of Cl I is $3p^5$, ^2P, any Λ value from zero to four is possible for the ground state of the NiCl molecule. The multiplicity may be either doublet or quartet, with doublet the more probable. If the excited states of the NiCl molecule are built by the combination of a Cl I atom in the ground state with a Ni I atom in an excited state, as is probable, doublet terms of Λ values from zero to five are possible, together with terms of higher multiplicity.

A doublet interval of the order of 484 cm^{-1} in the ground state is reasonable for a $^2\Pi$ state, considering the multiplet splittings of the ground states of Ni I and Cl I. It is moreover a rather high value for a $^2\Delta$ or $^2\Phi$ state. Hence it is probable that the ground state of NiCl is $^2\Pi$. The two upper states involved in the four systems analyzed may have either negligible electronic doublet intervals or nearly identical intervals which are not zero. If the first is the case the terms are probably $^2\Sigma$, though a $^2\Delta$ term might have a negligible doublet interval. The appearance of the bands, with strong Q and very weak R heads, indicates transitions of the type $^2\Sigma \rightarrow {}^2\Pi$ or $^2\Delta \rightarrow {}^2\Pi$. The fact that slightly different values of ω are found for the apparently common upper state in both cases suggests that the upper terms may be $^2\Delta$, with different values of ω for the two members of a given doublet term. This evidence is not conclusive, however, because the observed differences in the ω' values may be due entirely to the errors which may arise when band head data are used. The fifth system mentioned has double heads of about equal intensity. This has the appearance of a $^2\Pi \rightarrow {}^2\Pi$ transition. If this is so only one member of the doublet is observed. The other bands reported are weaker than those discussed and do not fit any vibrational array. These unrelated bands suggest the existence of several excited electronic states of the NiCl molecule.

TABLE III. *Wave numbers of analyzed bands of* CoCl.

v' \ v''	0	1	2	3	4	5	6
				System 1			
0	22014.0						
1	22432.5	22012.0					
2		22426.9	22008.9				
3		22840.0		22005.5			
4			22832.6	22416.4	22001.2	21587.4	21174.8
5				22825.1	22408.4	21994.2	21581.4
6					22814.8	22401.0	21988.1
				System 2			
0	22402.7	21984.0	21565.6				
1		22398.8	21980.6	21562.9			
2		22812.6	22394.1	21976.5	21559.3		
3				22388.0	21971.2		
4				22798.1		21966.6	
				System 3			
0	22966.2	22546.2					
1	23383.4	22964.1					
2	23795.5	23378.0	22961.5				
3		23786.9	23371.8	22956.7			
4			23777.3	23362.1	22951.1		
5					23354.6		
6					23755.5	23347.5	

TABLE IV. *Wave numbers of unanalyzed bands of* CoCl.

22074.9	22182.4	23497.2	26079.5

Cobalt chloride

The three groups of bands which form closely spaced sequences are fitted to vibrational arrays which are given in Table III. Each band in these arrays consists of a single head. The cobalt chloride bands for which no analysis is made are given in Table IV. These bands seem to be single with no sequence structure like that which is so prominent in the case of the other bands. The heads of the three systems analyzed are given by the following equations:

$$\nu = 22014.6 + 420.0u' - 1.14u'^2 - 421.2u'' + 0.74u''^2, \quad (1)$$

$$\nu = 22404.3 + 416.6u' - 0.82u'^2 - 419.4u'' + 0.28u''^2, \quad (2)$$

$$\nu = 22967.3 + 420.0u' - 1.66u'^2 - 421.8u'' + 1.34u''^2, \quad (3)$$

where $u = v + \frac{1}{2}$.

The ground state electronic term of the CoCl molecule is probably a triplet with a Λ value of 0, 1, 2, 3, or 4, because the ground state of Co I is $3d^7 4s^2$, ^4F. Terms of singlet, triplet, and higher multiplicities are possible for the excited states of CoCl. No obvious electronic multiplets are observed in the spectrum. The three systems analyzed may be members of an electronic triplet, with intervals of 390 and 563 cm^{-1}. Usually the two intervals in a molecular triplet are more nearly equal than are these.

Iron chloride

On account of the absence of distinct heads in the spectrum of FeCl attempts at analysis have failed. It is probable that the lack of heads indicates that the rotational constants of the upper and lower states are nearly equal, while the lack of sequence structure suggests that the vibrational constants are also nearly equal. The fact that this equality is indicated for both the rotational and vibrational constants is consistent with the Mecke rule. In cases where the vibrational constants are nearly equal the bands for Δv not zero are usually weak. It is thus likely that the FeCl bands for which Δv is not zero are weak as well as diffuse, and are readily masked by other bands.

DISCUSSION

It is of interest to compare the vibrational frequencies of the monochlorides of the elements of the first transition group of the periodic table. The frequencies are now known for TiCl,[2] CoCl, NiCl, and CuCl,[3] being 456, 421, 418, and 417 cm^{-1} respectively for the ground states. In addition the bands of TiCl degrade to the violet while the bands of CoCl, NiCl, and CuCl degrade to the red. The differences between the lower and upper state frequencies are approximately -47, $+3$, $+18$, and $+20$ cm^{-1} for TiCl, CoCl, NiCl, and CuCl, respectively. The difference is called positive if ω'' is greater than ω'. This trend indicates that ω' and ω'' may well be nearly equal for the FeCl molecule, since Fe is the element immediately preceding Co in the periodic table.

The decrease in the ground state frequency from the 456 cm^{-1} value for TiCl to the 418 cm^{-1} value for NiCl is greater than that expected from the mass change alone. It is thus evident that the force constant of the molecule must decrease somewhat with the addition of electrons to the incomplete $3d$ shell.

In conclusion the author wishes to express his appreciation to Professor W. W. Watson for stimulating discussions of this work.

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[2] K. R. More and A. H. Parker, Phys. Rev. **52**, 1150 (1937).

[3] R. Ritschl, Zeits. f. Physik **42**, 172 (1927).