Structure of Nickel Dichloride

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The energy levels and bonding in simple binary compounds of the d-block elements have provided intriguing problems for many years. One of the most extensively studied of this class of molecules is nickel dichloride, whose geometry has been a matter of debate for some time. In this communication we establish that the molecule is linear in an excited electronic state and provide compelling evidence that it is linear in its ground state also. We also report the unexpected result that the ground state of $NiCl_2$ is most probably $^3\Sigma$.

Nickel(II) chloride can be sublimed unchanged, is volatile below 1000 °C, and gives a vapor consisting predominantly of monomers. Both the gas-phase molecule and the discrete species isolated in cryogenic matrices have been studied by a variety of physical techniques including infrared,[1-11] Raman,[6] and electronic spectroscopies.[3,5,6,12-16] The disadvantage of gas-phase studies under equilibrium conditions at the required high temperatures is that the bands are broad and consist of unresolvable forests of lines because so many energy levels are populated. The matrix spectra are much sharper and simpler because of the low temperature and absence of rotational motion, but they suffer from "matrix effects", which are usually less serious for the vibrational spectra. However, it is becoming increasingly apparent that even inert gas matrices can affect the geometry of the isolated molecule quite markedly.[17,18] In the case of a nitrogen matrix, the well-tried isotope shift method using the antisymmetric (or asymmetric) stretching vibration gives a bond angle of 130° for $NiCl_2$.[10] This contrasts with the most recent measurements in an argon matrix,[8] which were interpreted in terms of a bond angle of 161°. The reliability of this conclusion has been questioned in ref 9, where it is pointed out that a change in bond angle from 180° to 160° results in a *difference* between the calculated isotope shifts of the order of 0.1 cm^{-1}, for either central or terminal atom substitution.[19] The reliability of theoretical calculations of these quantities can be judged from the observation that the discrepancy between observed and calculated isotope shifts for the diatomic molecule NiO is 0.12 cm^{-1}, again in an argon matrix.[20]

Table I. Vibrational Wavenumbers Determined for Nickel Dichloride in the Upper Electronic State of the 460-nm Band System

isotopomer	ω_1/cm^{-1}	ω_2/cm^{-1}
$^{60}Ni^{35}Cl_2$	356.0535(15)[a]	60.09810(59)[b]
$^{60}Ni^{37}Cl_2$	346.23(16)[b]	59.9130[c]
$^{58}Ni^{35}Cl_2$	356.0095(14)	60.66110(55)

[a] The numbers in parentheses represent one standard deviation of the least-squares fit, in units of the last quoted decimal place. Since the wavenumbers are not corrected for anharmonic effects due to the antisymmetric stretching vibration, q_3, the uncertainties in the harmonic wavenumbers are larger than these estimates. [b] Determined from measurements of the isotopic shifts of the R branches in the $1_0^1 2_0^1$ band. [c] Scaled from the $^{58}Ni^{35}Cl_2$ value assuming the molecule to be linear,

$$\frac{\omega_2^i}{\omega_2} = \frac{m_Y}{m_Y^i}\frac{(1 + 2m_Y^i/m_X^i)}{(1 + 2m_Y/m_X)}$$

It is apparent that measurements must be made on molecules in the gas phase under conditions where the rotational structure can be resolved to provide information on the moments of inertia. We have succeeded in recording rotationally resolved electronic spectra of nickel dichloride, using laser-induced fluorescence of samples in isentropically expanded "cold" beams.[21] A recent paper on the rotationally resolved infrared spectrum of BeF_2 reported "the first complete rotational analysis of a metal dihalide".[22] The interpretation of the electronic spectrum of $NiCl_2$ is a more difficult task,[21,23] but good progress has been made on the band system at 460 nm (Table I). This system can be interpreted as a $^3\Sigma-{}^3\Sigma$ transition. It seems likely that the ground state of $NiCl_2$ is $^3\Sigma_g^-$ rather than $^3\Pi_g$, the state expected from a consideration of the Ni d-orbital occupation according to simple molecular orbital theory.[24]

Figure 1 shows a portion of the $1_0^1 2_0^1$, $\Omega = 0 \leftarrow 0$ band at 22 070 cm^{-1} recorded at rotational resolution. The R branch, band origin, and start of the P branch are shown in this region. The branches arising from $^{58}Ni^{35}Cl_2$ and $^{60}Ni^{35}Cl_2$ are indicated; the 10:6 intensity alternation from these isotopomers, which are both symmetrical, is clearly visible. Several bands involving excitation of the symmetric stretching and bending vibrations in the upper electronic state have been recorded at rotational resolution and analyzed. These analyses provide values for the harmonic wavenumbers, ω_1' and ω_2', which are given in the accompanying table. The vibrational intervals determined refer to the upper electronic state as all the transitions which have been assigned

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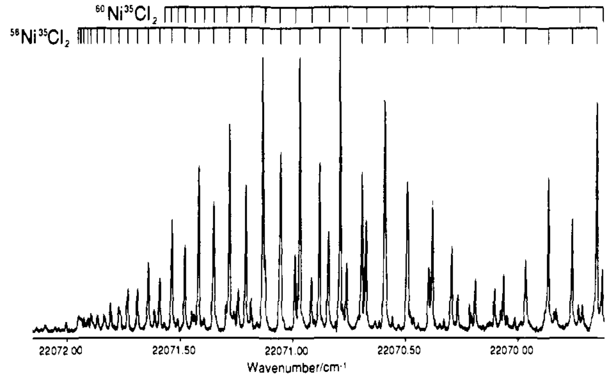

Figure 1. Part of the $1^1_0 2^1_0$, Ω = 0–0 band of the 460-nm band system of nickel dichloride recorded at rotational resolution by laser excitation spectroscopy. The region shown covers the R branch, the band origin, and the start of the P branch. The spectrum has been assigned to two isotopomers, $^{58}Ni^{35}Cl_2$ and $^{60}Ni^{35}Cl_2$. The rotational temperature is about 12 K. There is evidence that the electronic transition is induced by involvement of the bending coordinate.

so far arise from the ground vibrational level. Both the ^{58}Ni–^{60}Ni and ^{35}Cl–^{37}Cl shifts in these wavenumbers show that $NiCl_2$ is linear to within 4° in the upper electronic state involved in the 460-nm band system.

At present, we do not have such extensive information on the lower electronic state, but there are several pieces of information which strongly suggest that nickel dichloride is linear in its ground state also: (1) long progressions in the bending vibration are not observed in the 460-nm system;[23] (2) only bands which correspond to changes of even numbers of quanta of the bending vibration are seen in absorption and dispersed fluorescence; (3) coarse (K) structure, which would be expected even if the molecule were bent by 10°, is not seen in the rotationally resolved spectra; and (4) sequence bands in the bending vibration are very uniformly spaced. If the molecule were bent, the vibrational spacing would become nonuniform in the region at the top of the bending potential barrier.

If we accept that the molecule is linear in the two electronic states involved in the 460-nm system, we can use the rotational constants determined from our analysis to calculate the bond length. For $NiCl_2$ in the ground state, we obtain $r_0'' = 2.056\,07(13)$ Å, which is consistent with the vibrationally averaged value found by electron diffraction, $r_\alpha'' = 2.056(7)$ Å.[25] The value for the excited state is $r_0' = 2.0958(15)$ Å, which shows that there is a significant lengthening of the Ni–Cl bond distance on electronic excitation even though the wavenumbers ω_1' and ω_1'' are almost identical. The large change in bond length explains the long progression observed in the stretching vibration in the 460-nm system.[23]

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