The Near-Infrared Spectrum of NiCl: Analysis of Vibrational Components of System G and System H between 12,500 cm⁻¹ and 13,750 cm⁻¹

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Abstract

The near-infrared spectrum of nickel chloride, NiCl, has been recorded at high resolution from 12,400-12,600 cm⁻¹, 13,200-13,500 cm⁻¹, and 13,600-13,750 cm⁻¹ using intracavity laser absorption spectroscopy, ILS. The NiCl molecules were produced in the plasma discharge of a nickel-lined, copper hollow cathode with ~1.8 torr of Ar as the sputter gas and a trace amount of CCl₄ as the chloride source. Several transitions were observed and analyzed, including the (2,0), (1,0), and (0,1) bands of the [13.0] ²Π_{3/2} – X ²Π_{3/2} transition, System G, and the (1,0) band of the [12.3] ²Σ⁺ – X ²Π_{3/2} transition, System H. The transitions were analyzed using PGOPHER and obtained molecular parameters are reported. A potential energy curve for the [13.0] ²Π_{3/2} state has been constructed using the vibrational information from the analyzed transitions.

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INTRODUCTION

There have been several prior investigations into the electronic spectrum of NiCl. Experimentally, the visible region was examined at high resolution using Laser Induced Fluorescence (LIF) and Fourier-Transform Emission Spectroscopy,¹⁻³ definitively identifying 5 excited electronic states 20,000-25,000 cm⁻¹ above the ground state and the 3 expected low-lying electronic states predicted from the 3d⁹ configuration of Ni⁺, all within 2000 cm⁻¹ of the ground state.³ Yamazaki *et al.*⁴ investigated the millimeter- and submillimeter-region and were able to obtain ground state constants for 6 isotopologues of NiCl. The near-infrared region has been studied using Intracavity Laser Absorption Spectroscopy and Fourier-Transform Emission Spectroscopy.⁵⁻¹¹ Two of these studies included reassignment of System G as the [13.0] ²Π_{3/2} - X ²Π_{3/2} transition⁵ and System H as the [12.3] ²Σ⁺ - X ²Π_{3/2} transitions.⁶ Several vibrational components of these systems were observed in the Fourier-transform data, but the high-temperature King Furnace method used to produce the emission spectra lead to spectral broadening that made rotational analysis impossible.

Theoretical studies for NiCl also have been reported. Zou and Liu¹² presented a theoretical investigation of the low-lying states of NiX molecules (X = F, Cl, Br, I), including relativistic effects. Additionally, Jon Hougen¹³ developed an effective Hamiltonian describing the electronic states of Ni⁺X⁻ molecules and the 5 spin-orbit states resulting from the distortion of the 3d⁹ configuration of Ni⁺ by the bonded, closed-shelled X⁻ ion. Both of these studies suggested that the [12.3] ²Σ state reported by O'Brien *et al.*⁶ was ²Σ⁻ in character. In light of these theoretical studies, Dahms *et al.*¹⁴ reassigned the *e/f* levels of the [12.3] ²Σ⁺ - X ²Π_{3/2}, [12.3] ²Σ⁺ - X ²Π_{1/2}, and [12.3] ²Σ⁺ - [1.7] B ²Σ⁺ transitions, resulting in conversion of the [12.3] ²Σ⁺ state to the [12.3] ²Σ⁻ state and inversion of the Λ-doubling parameters of the X ²Π states and the spin-rotation parameters of the B ²Σ⁺ state.

In this study, several vibrational bands of Systems G and H, the [13.0] ²Π_{3/2} - X ²Π_{3/2} and [12.3] ²Σ⁻ - X ²Π_{3/2} transitions, have been observed in high resolution and analyzed, namely the (2,0), (1,0), and (0,1) bands of System G and the (1,0) band of System H. Molecular constants have been obtained via simultaneous fit of these transitions using PGOPHER.¹⁵ In addition, a potential energy curve has been constructed for the [13.0] ²Π_{3/2}

state with the RKR-method using a program from J. Tellinghuisen¹⁶ and the T_e , B_e , α_e , ω_e , and $\omega_e x_e$ values obtained from the constants for the (2,0), (1,0) and (0,0) bands of System G. The obtained constants, line assignments and residuals, potential energy curve, and portions of the experimental spectrum are presented.

EXPERIMENTAL METHOD

The near-IR spectrum of NiCl was collected in the 12,400-12,600 cm^{-1} , 13,200-13,500 cm^{-1} , and 13,600-13,750 cm^{-1} regions using Intracavity Laser Spectroscopy (ILS). The ILS system used in this study has previously been described in detail.^{5,6,17} Briefly, a tunable Ti:sapphire crystal pumped by a Verdi V-10 laser is used as the light source for detection of an intracavity species. The NiCl molecules were produced in the plasma discharge of a nickel-lined copper hollow cathode in the presence of 0.3-0.6 torr of Ar as sputter gas, and a trace amount of CCl_4 . In spectral regions where intense Ar plasma lines occur, ~ 1.8 torr of He was used as a sputter gas in place of Ar. It was found that a flow of CCl_4 suppressed the observed transitions, but a chamber “seeded” by small, intermittent additions of CCl_4 greatly enhanced the absorption intensity of the transitions. Plasma spectra were recorded alternatively with I_2 spectra, so that line positions could be calibrated using the well-known Iodine Atlas.¹⁹ A portion of the plasma spectrum overlaid with the I_2 spectrum is shown in Figure 1. Peak positions are determined from the zero-crossing points of the first- and second-derivative spectra using Savitzky-Golay polynomial smoothing. This allows the line position of smooth, unblended lines to be determined to better than $\pm 0.003 \text{ cm}^{-1}$.

RESULTS AND DISCUSSION

O'Brien *et al.*^{5,6} reported several vibrational bandheads associated with System G and System H between 12,000 cm^{-1} and 14,000 cm^{-1} . For this work, the reported (2,0), (1,0), (3,1), (2,1), and (0,1) bands of System G and the (1,0) band of System H were observed at high resolution using ILS, and the transitions were rotationally resolved. The spectra confirmed the red-degraded bandheads near the positions reported by O'Brien *et*

al.^{5,6} The primary focus of this work is on the (2,0), (1,0), and (0,1) bands of System G and the (1,0) band of System H, as analysis indicated the transitions near the (2,1) and (3,1) bands of System G belong to a different electronic transition. Vibrational assignments were confirmed via comparison of bandhead positions for ⁵⁸Ni³⁵Cl (52%) and ⁶⁰Ni³⁵Cl (20%). The relationship between the vibrational energies of different isotopologues within an electronic state¹⁹ is given by equation 1,

$$\frac{v_1}{v_2} = \sqrt{\frac{\mu_2}{\mu_1}} \quad (1)$$

where $v_{1,2}$ refer to the vibrational constants and $\mu_{1,2}$ refer to the reduced masses of the isotopologues. For the typical NiCl vibrational frequency of $\sim 400 \text{ cm}^{-1}$ for the electronic states involved in these transitions,, the expected isotope shift in origin is roughly $\pm 2.5 \text{ cm}^{-1}$ from ⁵⁸Ni³⁵Cl to ⁶⁰Ni³⁵Cl for each increase in vibrational level. The bandhead shift from ⁵⁸Ni³⁵Cl to ⁶⁰Ni³⁵Cl for the (2,0) band of System G was -4.89 cm^{-1} ; for the (1,0) band of System G, it was -2.41 cm^{-1} ; for the (1,0) band of System H, it was -2.50 cm^{-1} ; and for the (0,1) band of System G, it was $+2.66 \text{ cm}^{-1}$. The labeled isotopologue bandheads for the (1,0) band of System H are shown in Figure 1 and for the (2,0) band of System G in Figure 2. The ⁵⁸Ni³⁷Cl (16%) peaks were also observed shifted $\sim 6 \text{ cm}^{-1}$ for each change in vibrational level, but were much less apparent amongst the dense clusters of lines present in the NiCl spectrum. However, the ⁵⁸Ni³⁷Cl peak for the (2,0) band of System G can be seen clearly in Figure 2, when the experimental data is overlaid with the simulation for ⁵⁸Ni³⁵Cl using PGOPHER,¹⁵ an open-source, spectral simulation program.

The transitions belonging to System G of NiCl had 4 clear branches, 2 P-type and 2 R-type. The (1,0) band of System H of NiCl showed clear P- & Q-bandheads and a total of 6 branches, consistent with a $^2\Sigma - ^2\Pi$ transition. The R-bandhead was obstructed by interfering species in the plasma that remained under various discharge conditions. Assignments for the (2,0) and (1,0) bands of System G and the (1,0) band of System H of NiCl were confirmed using combination differences and $\Delta_2 F''$ values calculated from parameters of the $X \ ^2\Pi_{3/2}$ ground state reported by Hirao *et al.*¹ Assignment for the (0,1) band of System G of NiCl was confirmed using combination differences and $\Delta_2 F'$ values calculated from parameters of the $[13.0] \ ^2\Pi_{3/2}$ state reported by O'Brien *et al.*⁶ All transitions were fit simultaneously using PGOPHER.¹⁶ The line positions^{4,5} for the (0,0)

bands of Systems G and H also were included in the fit to avoid the confusion over the sign of fine splitting parameters present in the NiCl literature. In total, over 1500 lines were fit to 30 molecular parameters.

Line positions, assignments, and residuals of the NiCl transitions are available in the Supplemental Materials depository for this Journal. Obtained molecular constants for $^{58}\text{Ni}^{35}\text{Cl}$ are shown in Table 1. It should be noted that the matrix element of the Λ -doubling parameter for a $^2\Pi_{3/2}$ state in PGOPHER, q_D , has the reverse sign of the matrix element of the q_J Λ -doubling parameter used by Hirao *et al.*,¹ accounting for the positive value of q_D after treating the (0,0) bands of Systems G and H in the manner suggested by Hougen.¹⁴ Equilibrium constants obtained from the fit are provided in Table 2, and vibrational intervals of the states are provided in Table 3.

Our work reports the first high resolution analysis of the $v=1$ level of the $X^2\Pi_{3/2}$ ground state. It is interesting to note that the sign of q_D in $v=1$ has changed from that in $v=0$. This is understandable when comparing the energies of the relevant levels: $T_0(X^2\Pi_{3/2})=0\text{ cm}^{-1}$; $T_0(X^2\Pi_{1/2})=382\text{ cm}^{-1}$; and $T_1(X^2\Pi_{3/2})=423\text{ cm}^{-1}$. The $v=1$ $X^2\Pi_{3/2}$ level is *higher* in energy than the $v=0$ $X^2\Pi_{1/2}$ level. The change in sign for q_D of the $v=1$ $X^2\Pi_{3/2}$ level thus provides evidence of interactions between the $X^2\Pi_{3/2}$ and $X^2\Pi_{1/2}$ states summed over vibrational states. Remembering that the Hougen model and previous experimental work have shown considerable mixing between the low-lying $X^2\Pi_{1/2}$ and $B^2\Sigma^+$ states, the negative sign of q_D for the $v=1$ $X^2\Pi_{3/2}$ ground state is thus consistent with the expected interactions among the low-lying electronic states associated with the $\text{Ni}^+(\text{d}^9)$ electron configuration. Furthermore, in a recent article Arsenault *et al.*²⁰ have examined the origin of the doubling in $\Omega=3/2$ states by extending the model developed by Hougen.¹³ They show that third order perturbation theory must be invoked to account for Ω -doubling in the $\Omega=3/2$ states. The doubling in the $X^2\Pi_{3/2}$ state results from terms in the rotational Hamiltonian that mix this state with the two $\Omega=3/2$ states and the $\Omega=5/2$ state associated with the $\text{Ni}^+(\text{d}^9)$ electron configuration.²⁰

The equilibrium constants shown in Tables 2 and 3 were used to construct a potential energy curve for the [13.0] $^2\Pi_{3/2}$ state of NiCl with the RKR-method using a program supplied by Joel Tellinghuisen.¹⁶ The constructed curve is shown in Figure 3. While this curve is accurate for $v=0-2$ levels, there may be some irregularities in the

potential energy surface at $v=3$ and $v=5$, which nearly overlap the [14.2] $^2\Delta_{5/2}$ state near $14,165\text{ cm}^{-1}$ and the [15.0] $^2\Pi_{3/2}$ and [15.0] $^2\Delta_{5/2}$ states at $14,782\text{ cm}^{-1}$ and $14,792\text{ cm}^{-1}$.¹⁰ As both the excited vibrations of the [13.0] $^2\Pi_{3/2}$ state and their near overlapping states can be reached from both the $X\text{ }^2\Pi_{3/2}$ and [0.16] $A\text{ }^2\Delta_{5/2}$ states, future investigation into the spectrum of NiCl in the $13,750\text{--}15,000\text{ cm}^{-1}$ region could yield more interesting information from this spectrally dense species.

CONCLUSION

Several new NiCl electronic transitions have been identified in the near-infrared and rotationally analyzed. A simultaneous fit of the (2,0), (1,0), (0,0), & (0,1) bands of System G and the (1,0) & (0,0) bands of System H has been performed, fitting 1500 lines to 30 parameters. The reported constants have fine splitting parameters adjusted in accordance with the suggestion from Jon Hougen.¹³ A potential energy curve has been produced for the [13.0] $^2\Pi_{3/2}$ state based on the equilibrium constants obtained from the rotational constants for the $v=0\text{--}2$ levels.

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Figure 2: (2,0) band of [13.0] ²Π_{3/2} – X ²Π_{3/2} transition. Isotopologue peaks consistent with (2,0) transition (top) and PGOPHER simulation from fit (bottom).

Figure 3: Potential energy curve for the [13.0] ²Π_{3/2} state of NiCl. The experimentally observed states from Leung *et al.*⁹ nearly overlap the v=3 and v=5 levels.

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Figure 2: (2,0) band of [13.0] $^2\Pi_{3/2} - X^2\Pi_{3/2}$ transition. Isotopologue peaks consistent with (2,0) transition (top) and PGOPHER simulation from fit (bottom).

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Table Titles

Table 1: Molecular constants for $^{58}\text{Ni}^{35}\text{Cl}$.

Table 2: Equilibrium constants for $^{58}\text{Ni}^{35}\text{Cl}$.

Table 3: $\Delta G_{1/2}$ values and vibrational constants for states of $^{58}\text{Ni}^{35}\text{Cl}$.

Table 1: Molecular constants (in cm^{-1}) and bond lengths for $^{58}\text{Ni}^{35}\text{Cl}$.^a

$[13.0] \ ^2\Pi_{3/2}$	T_v	B_v	$D_v \times 10^6$	$H_v \times 10^{12}$	$q_D \times 10^5$	r_v (Å)
$v'=2$	13740.0965(12)	0.1659064(60)	0.11964(68)		-0.1095(10)	2.1586
$v'=1$	13351.1462(13)	0.1667857(61)	0.11873(76)		-0.0915(11)	2.1529
$v'=0$	12959.2518(13)	0.1676705(59)	0.11910(64)		0.30604(84)	2.1472
$v'=0$ ^b	<i>12959.2556(13)</i>	<i>0.167697(20)</i>	<i>0.12757(74)</i>	<i>0.855(76)</i>	<i>0.08135(71)</i> ^c	
$[12.3] \ ^2\Sigma^-$	T_v	B_v	$D_v \times 10^6$	γ	$\gamma_D \times 10^5$	r_v (Å)
$v'=1$	12647.2249(14)	0.1695539(62)	0.11857(82)	-0.740523(87)	-0.1240(31)	2.1353
$v'=0$	12252.0495(19) ^d	0.1704462(60)	0.12694(64)	-0.746539(39)	0.04590(58)	2.1297
$v'=0$ ^b	<i>12252.1867(13)</i>	<i>0.17045427(87)</i>	<i>0.127910 (96)</i>	<i>-0.746635(24)</i>	<i>0.04758(27)</i>	
$X \ ^2\Pi_{3/2}$	T_v	B_v	$D_v \times 10^6$	$H_v \times 10^{12}$	$q_D \times 10^5$	r_v (Å)
$v''=1$	422.5856(28)	0.1806398(83)	0.0978(28)		-0.2404(45)	2.0687
$v''=0$	0.00	0.18149280(59)	0.12549(70)	-0.133(24)	0.11519(23)	2.0638
$v''=0$ ^b	<i>0.00</i>	<i>0.18150389(12)</i>	<i>0.16704(41)</i>	<i>-0.1004(45)</i>	<i>0.115225(14)</i> ^c	

^a All values in cm^{-1} unless otherwise noted; one standard deviation given in parenthesis

^b Values in italics are from Ref. 15.

^c Literature values converted to q_D , where $q_I = -q_D$

^d This value was determined from a PGOPHER fit of the previously reported line positions. The difference in origin is due to variations between fitting programs, not transition assignment.

 Table 2: Equilibrium constants for $^{58}\text{Ni}^{35}\text{Cl}$.^a

	T_e	B_e	$\alpha_e \times 10^3$	r_e (Å)
$[13.0] \ ^2\Pi_{3/2}$	12762.201	0.1681106(27)	0.8820(16)	2.1444
$[12.3] \ ^2\Sigma^-$	12054.462	0.1708924(86)	0.892(86)	2.1269
$X \ ^2\Pi_{3/2}$		0.1819193(59)	0.8530(83)	2.0614

^a All units in cm^{-1} unless otherwise noted, one standard deviation given in parenthesis

 Table 3: $\Delta G_{1/2}$ values and vibrational constants for states of $^{58}\text{Ni}^{35}\text{Cl}$.^a

	$\Delta G_{1/2}$	ω_e	$\omega_e x_e$
$[13.0] \ ^2\Pi_{3/2}$	391.8944(18)	394.84	1.47
$[12.3] \ ^2\Sigma^-$	395.1754(24)		
$X \ ^2\Pi_{3/2}$	422.5856(28)		

^a All units in cm^{-1} unless otherwise noted, one standard deviation given in parenthesis