

Note

Fourier transform spectroscopy of NiCl: identification of a [9.1] $\Omega = 3/2$ state

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Received 29 October 2003; in revised form 4 March 2004

Available online 2 April 2004

1. Introduction

The ground state electronic configuration of $\text{Ni}^+(3d^9)\text{Cl}^-(3p^6)$ gives rise to five low-lying electronic states: ${}^2\Pi_{3/2}$, ${}^2\Pi_{1/2}$, ${}^2\Delta_{5/2}$, ${}^2\Delta_{3/2}$, and ${}^2\Sigma^+$. Excitation of one of the nickel $3d$ valence electrons to an unoccupied nickel $4s$ or $4p$ orbital leads to numerous electronic transitions throughout the visible and near-infrared spectral regions, identified in the literature as System A through to System J [1–9]. The low-lying electronic states with T_e s less than 3000 cm^{-1} are labeled $X^2\Pi$, $A^2\Delta$, and $B^2\Sigma^+$ [1–6]. The Bernath and Pinchemel groups [1–3] have identified five states with electronic term energies in the $20\,000$ – $25\,000\text{ cm}^{-1}$ range. In our laboratory two electronic states with term energies in the $10\,000$ – $13\,500\text{ cm}^{-1}$ range have been observed and identified [4–6].

This paper reports the observation of the [9.1] $\Omega = 3/2$ electronic state of NiCl. This state is identified for the first time through the analysis of an electronic band near 9100 cm^{-1} , namely the [9.1] $\Omega = (3/2)-X^2\Pi_{3/2}$ transition.

2. Experimental method

The near-infrared spectrum of NiCl was observed using the Fourier transform spectrometer associated with the McMath Pierce Solar Observatory at Kitt

Peak, AZ. The molecular emission from a carbon-type King Furnace loaded with NiCl_2 was observed at medium resolution (0.04 cm^{-1}). Approximately 25 g of NiCl_2 was loaded into a King Furnace and heated to 1500°C . The spectral region between 8000 and $14\,000\text{ cm}^{-1}$ was recorded using a UV quartz beam splitter and silicon diode detectors.

3. Results and discussion

Two vibrational bands were observed in the 8000 – $10\,000\text{ cm}^{-1}$ region with band heads at approximately 9100 and 9500 cm^{-1} ; the relative intensity for the two systems was approximately 4:1, respectively. Excited state vibrational frequencies for NiCl that have been observed to date are approximately 400 cm^{-1} [4,5], and thus, we concluded that the 9100 cm^{-1} system is the (0, 0) band and the 9500 cm^{-1} system is the (1, 0) band of a new electronic transition. Four branches were identified for the 9100 cm^{-1} system, and the branches appear to be two R branches and two P branches. The 9500 cm^{-1} system was too weak to identify branches. Only lines due to the strongest NiCl isotopomer, ${}^{58}\text{Ni}{}^{35}\text{Cl}$, were clearly identified in the 9100 cm^{-1} system, although several spectra show additional structure, probably due to the other NiCl isotopomers, around the strong features in the spectra [${}^{58}\text{Ni}{}^{35}\text{Cl}$ (51.58%), ${}^{60}\text{Ni}{}^{35}\text{Cl}$ (19.87%), ${}^{58}\text{Ni}{}^{37}\text{Cl}$ (16.50), and ${}^{60}\text{Ni}{}^{37}\text{Cl}$ (6.35%)].

Since the appearance of the 9100 cm^{-1} band was similar to what we had observed for the [13.0] ${}^2\Pi_{3/2}-X^2\Pi_{3/2}$ transition, namely two P branches and two R branches, we initially guessed that this transition could also be an $\Omega = (3/2)-X^2\Pi_{3/2}$ transition. Using the

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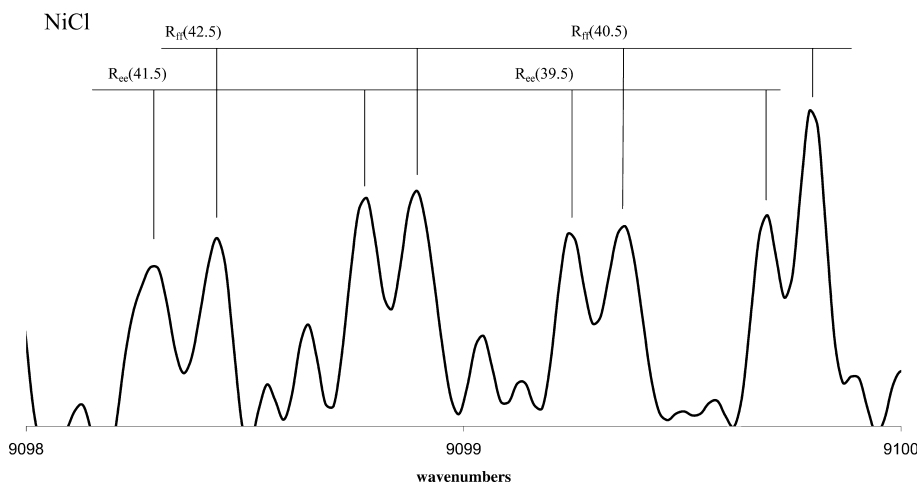


Fig. 1. A portion of the [9.1] $\Omega = (3/2)$ - $X^2\Pi_{3/2}$ transition of $^{58}\text{Ni}^{35}\text{Cl}$.

ground state parameters from our previous work [4,5], we calculated the ground state energy levels $F_e(J'')$ and $F_f(J'')$, and the values for $\Delta_2 F_e(J'')$ and $\Delta_2 F_f(J'')$, where $\Delta_2 F_e(J) = F_e(J+1) - F_e(J-1)$, and $\Delta_2 F_f(J) = F_f(J+1) - F_f(J-1)$ [10]. The method of combination differences [10] was used for the observed branches, and indeed, the four branches could be assigned definitively to P_{ee} , P_{ff} , R_{ee} , and R_{ff} branches connecting to the ground state. Rotational assignments were also obtained from this method. A portion of the spectrum is shown in Fig. 1.

A total of 205 lines were fitted in a non-linear least squares fitting program, using a standard $^2\Pi_{3/2}$ polynomial expression [1–6] for both the ground and excited states, $T = T_0 + B_0 J(J+1) - D_0 J^2(J+1)^2 + H_0 J^3(J+1)^3 \pm 0.5q_0 J(J+1)(J+0.5)$. Because the parameters for the $X^2\Pi_{3/2}$ state already are known quite accurately [4,5,11], only the parameters for the excited state were varied in the fit. The molecular parameters obtained in the fit are given in Table 1. The small value for the excited state λ -doubling parameter, $q_0 = -0.67565(96) \times 10^{-5} \text{ cm}^{-1}$, is consistent with the excited electronic state assignment of $\Omega = 3/2$. The line positions, assignments, and fit residuals are presented in Table 2.

The observed bandheads at 9104.4 and 9501.2 cm^{-1} can be used to estimate an excited state vibrational

frequency: $\Delta G_{1/2} = 396.8 \text{ cm}^{-1}$. This value is similar to the vibrational frequency observed for the [12.3] $^2\Sigma$ state, $\omega_e = 397.56 \text{ cm}^{-1}$ [4], and to that observed for the [13.0] $^2\Pi_{3/2}$ state, $\omega_e = 394.22 \text{ cm}^{-1}$ [5].

No theoretical calculations on the excited states (with $T_e > 3000 \text{ cm}^{-1}$) of NiCl are currently available. However, it is interesting to speculate on the nature of the excited [9.1] $\Omega = 3/2$ state. Since NiCl and NiH are ionic molecules which have metal-centered orbitals, NiH and NiCl should have a similar pattern of electronic states. A high-level ab initio calculation on the excited states of NiH was reported in 1982 by Blomberg et al. [12], and the excited states for NiH are shown below in Fig. 2. For comparison, the known states of the nickel halides [1–6,13–15] are presented in Fig. 3. For the excited $^2\Delta$, $^2\Phi$, $^2\Pi$, and $^2\Sigma$ states in the 10 000–15 000 cm^{-1} region, the nickel halides seem to follow a regular pattern of energy levels, which are a reasonable match with the NiH calculated energy levels of the doublet states from the $\text{Ni}^+[d^8\sigma^*(^3F)]\text{H}^- [s^2]$ configuration (see Fig. 2). We are confident that the excited state in the 9100 cm^{-1} band is an $\Omega = 3/2$ state but we are not sure whether this state is a $^2\Pi$ or $^4\Pi$ state. Using Fig. 3 as a guide, it is not unreasonable to consider that the $\Omega = 3/2$ state at 9100 cm^{-1} for NiCl is analogous to the NiH $^4\Pi_{3/2}$ state with an electron configuration of $\text{Ni}^+[d^8\sigma^*(^3F)]\text{Cl}^- [3p^6]$. In our spectrum, the intensity of the [9.1] $\Omega = (3/2)$ - $X^2\Pi_{3/2}$ transition is about one-third the intensity of the [13.0] $^2\Pi_{3/2}$ - $X^2\Pi_{3/2}$ transitions, based on the signal-to-noise ratio for the two bands, where the weaker intensity may be due to the large quartet nature of the [9.1] $\Omega = 3/2$ state. High-level, ab initio calculations on the excited states of NiCl could be very helpful in fully elucidating the electronic structure of this molecule.

Table 1
Molecular parameters of the [9.1] $\Omega = 3/2$ state of $^{58}\text{Ni}^{35}\text{Cl}$ (in cm^{-1})

	Value
T_0	9101.2610(63) ^a
B_0	0.1717728(59)
D_0	$0.1488(16) \times 10^{-6}$
H_0	$0.151(12) \times 10^{-11}$
q_0	$-0.67565(96) \times 10^{-5}$

^a Values in parenthesis are one standard deviation.

Table 2

Line positions, assignments, and fit residuals of the $[9.1] \Omega = 3/2 - X^2\Pi_{3/2}$ transition of $^{58}\text{Ni}^{35}\text{Cl}$ (in cm^{-1})

$J'' + 0.5$	P_{ee}	$o - c$	P_{ff}	$o - c$	R_{ee}	$o - c$	R_{ff}	$o - c$
27					9103.491	-0.017		
28	9084.129	0.022			9103.288	-0.016		
29	9083.195	-0.004			9103.052	-0.027		
30	9082.253	-0.018			9102.842	0.008		
31	*9081.287	-0.036			9102.575	0.006	9102.842	0.018
32	9080.371	0.016			9102.289	0.007	9102.575	0.012
33	*9079.398	0.032			9101.971	-0.005	9102.289	0.006
34	9078.368	0.011			9101.660	0.012	9101.978	-0.005
35	9077.306	-0.021			9101.304	0.004	9101.660	-0.005
36	9076.265	-0.012			9100.954	0.022	9101.304	-0.024
37	9075.202	-0.005			9100.553	0.011	9100.954	-0.017
38	9074.134	0.018			9100.127	-0.005	9100.620	0.024
39	9073.003	-0.002			9099.695	-0.006	9100.215	0.013
40	9071.876	0.003			9099.237	-0.013	9099.790	0.001
41	9070.719	-0.001			9098.770	-0.007	9099.371	0.014
42	9069.536	-0.011	9070.109	0.011	9098.279	-0.004	9098.894	-0.012
43	*9068.320	-0.034	9068.958	0.012	9097.764	-0.005	9098.436	0.000
44	9067.114	-0.025	9067.781	0.007	9097.234	0.000	9097.959	0.012
45	9065.883	-0.021	9066.580	-0.005	9096.681	0.004	9097.458	0.018
46	9064.639	-0.010	9065.378	0.002	9096.094	-0.006	9096.916	0.003
47	9063.367	-0.005	9064.157	0.008	9095.498	-0.003	9096.376	0.008
48	9062.059	-0.016	9062.898	-0.006	9094.875	-0.007	9095.804	0.000
49	9060.752	-0.005	9061.639	-0.001	9094.239	-0.002	9095.231	0.010
50	9059.407	-0.011	9060.361	0.004	9093.572	-0.007	9094.640	0.021
51	9058.053	-0.006	9059.064	0.008	9092.872	-0.024	9094.010	0.011
52	9056.660	-0.018	9057.748	0.011	9092.179	-0.013	9093.381	0.021
53	9055.268	-0.009	9056.398	-0.001	9091.449	-0.017	9092.713	0.011
54	9053.856	0.001	9055.058	0.016	9090.715	-0.005	9092.027	0.002
55	9052.387	-0.025	9053.672	0.005	9089.947	-0.005	9091.340	0.010
56	9050.923	-0.025	9052.273	-0.001	9089.146	-0.016	9090.634	0.018
57	9049.450	-0.013	9050.861	-0.002	9088.364	0.012	*9089.914	0.031
58	9047.976	0.019	9049.450	0.017	9087.525	0.005	9089.146	0.014
59	9046.448	0.018	9047.986	0.001	9086.647	-0.019	9088.364	0.002
60	9044.891	0.009	9046.522	0.003	9085.789	-0.003	9087.576	0.002
61	9043.307	-0.006	9045.043	0.009	9084.892	-0.003	9086.762	-0.005
62	9041.705	-0.018	9043.536	0.005	9083.958	-0.020	9085.922	-0.020
63	9040.103	-0.009	9042.010	-0.001	9083.023	-0.016	9085.102	0.004
64	9038.500	0.020	9040.484	0.012	*9082.012	-0.067	9084.244	0.008
65	*9036.860	0.033	9038.907	-0.008	*9081.025	-0.072	9083.341	-0.014
66	9035.143	-0.010	9037.337	-0.003	*9080.057	-0.036	9082.474	0.017
67	9033.445	-0.013	9035.734	-0.013	9079.074	0.005	9081.549	0.009
68	*9031.776	0.034	9034.137	0.001	9078.025	0.003	9080.610	0.006
69	9030.011	0.006	9032.501	-0.007	9076.950	-0.005	9079.627	-0.024
70	9028.276	0.030	9030.870	0.009	9075.876	0.010	9078.654	-0.025
71	9026.482	0.015	9029.217	0.020	9074.744	-0.011	9077.663	-0.026
72	9024.651	-0.016			9073.638	0.015	9076.652	-0.029
73	9022.858	0.012			9072.493	0.023		
74	9021.008	0.005			*9071.336	0.041		
75					9070.118	0.019		
76					*9068.926	0.045		
77					9067.667	0.025		
78					*9066.427	0.045		
79					9065.120	0.020		
80					9063.795	-0.002		
81					9062.497	0.024		
82					9061.124	-0.003		
83					9059.750	-0.011		
84					9058.367	-0.006		
85					9056.946	-0.018		
86					9055.535	0.001		

* Blended lines, deweighted in fit.

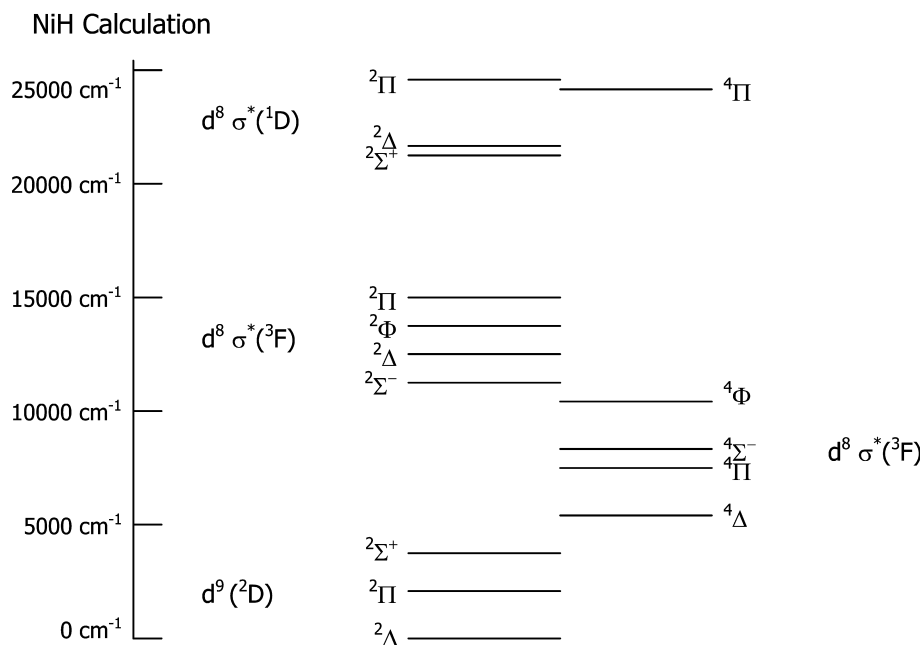


Fig. 2. Calculated energy levels of NiH, from Blomberg et al. [12].

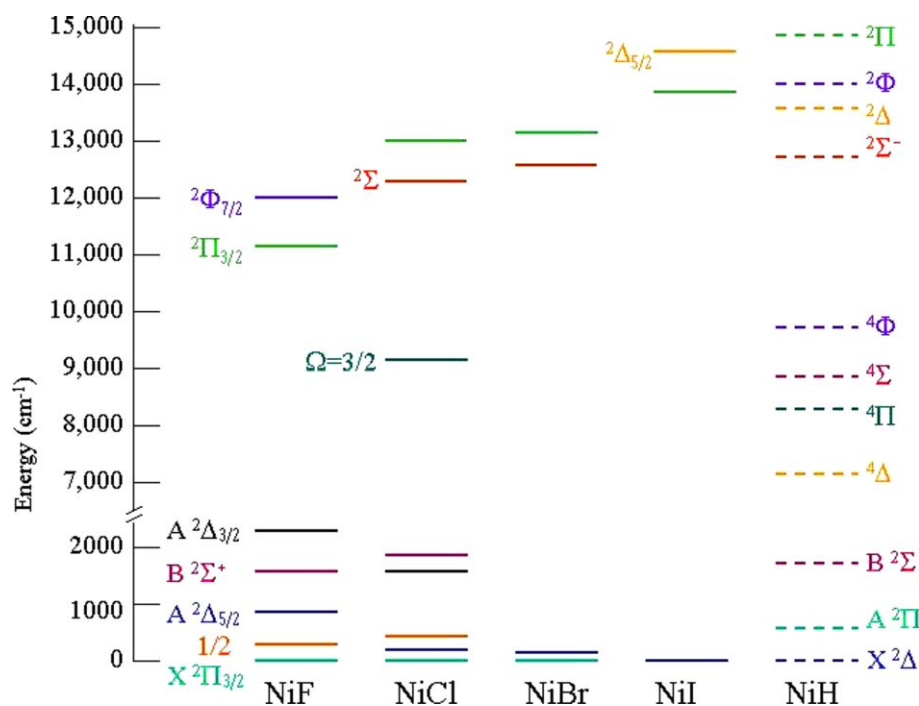


Fig. 3. Energy levels of observed states of nickel halides (solid) [1–6, 13–15] and predicted states of nickel hydride (dashed) [12] in the 0–15 000 cm^{-1} range.

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