Available online at www.sciencedirect.com
ScienceDirect
Journal of Molecular Spectroscopy 240 (2006) 64–68
Journal of MOLECULAR SPECTROSCOPY
www.elsevier.com/locate/jms

Fourier transform spectroscopy of NiCl: Identification of the [10.3] $^4\Phi_{7/2}$ state

Krystal D. Gibbs [b], Darci J. Trader [b], Leah C. O'Brien [b,*], James J. O'Brien [a]

[a] *Department of Chemistry and Biochemistry and Center for Molecular Electronics, University of Missouri—St. Louis, St. Louis, MO 63121-4499, USA*
[b] *Department of Chemistry, Southern Illinois University Edwardsville, Edwardsville, IL 62026-1652, USA*

Received 24 July 2006; in revised form 11 August 2006
Available online 22 August 2006

Abstract

This paper reports the observation of the [10.3] $^4\Phi_{7/2}$ electronic state of NiCl. This state is identified for the first time through the analysis of an electronic band near 10168 cm^{-1}, namely the [10.3] $^4\Phi_{7/2}$–A $^2\Delta_{5/2}$ transition. Molecular parameters for the newly identified [10.3] $^4\Phi_{7/2}$ state are presented. Excited NiCl molecules were produced in a King furnace using $NiCl_2$ heated to 1600 °C. Emission spectra were recorded using the Fourier transform spectrometer associated with the McMath Pierce Solar Telescope at Kitt Peak.

Keywords: Nickel chloride; Diatomics; High resolution spectroscopy; Fourier transform spectroscopy; Quartet Φ

1. Introduction

This paper reports the observation of the [10.3] $^4\Phi_{7/2}$ electronic state of NiCl. This state is identified for the first time through the analysis of an electronic band near 10168 cm^{-1}, namely the [10.3] $^4\Phi_{7/2}$–A $^2\Delta_{5/2}$ (0,0) transition.

The ground state electronic configuration of $Ni^+(3d^9)Cl^-(3p^6)$ 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 $^2\Sigma^+$. The low-lying electronic states with term energies less than 3000 cm^{-1} are labeled X $^2\Pi$, A $^2\Delta$, and B $^2\Sigma^+$ [1–9]. Excitation of one of the nickel 3*d* valence electrons to an unoccupied nickel 4*s* or 4*p* 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 [1–12]. The Bernath and Pinchemel groups have identified five states with electronic term energies in the 20000–25000 cm^{-1} range [1–3]. In our laboratory five electronic states with term energies in the 9000–15000 cm^{-1} range have been observed and identified [4–9].

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 14000 cm^{-1} was recorded using a UV quartz beam splitter and silicon diode detectors.

3. Results and discussion

Two red-degraded vibrational bands were observed in the 10000–12000 cm^{-1} region with band heads at approximately 10168 and 10561 cm^{-1}. The relative intensity for the two systems was approximately 4:1, respectively. The vibrational frequencies of the five low-lying states are all approximately 430 cm^{-1} [1–3], whereas the excited state vibrational frequencies for NiCl that have been observed to date are approximately 395 cm^{-1} [4–9]. Thus, we concluded that the two new bands are a vibrational progression in the excited state.

* Corresponding author. Fax: +1 618 650 3556.
E-mail address: lobrien@siue.edu (L.C. O'Brien).

0022-2852/$ - see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jms.2006.08.009

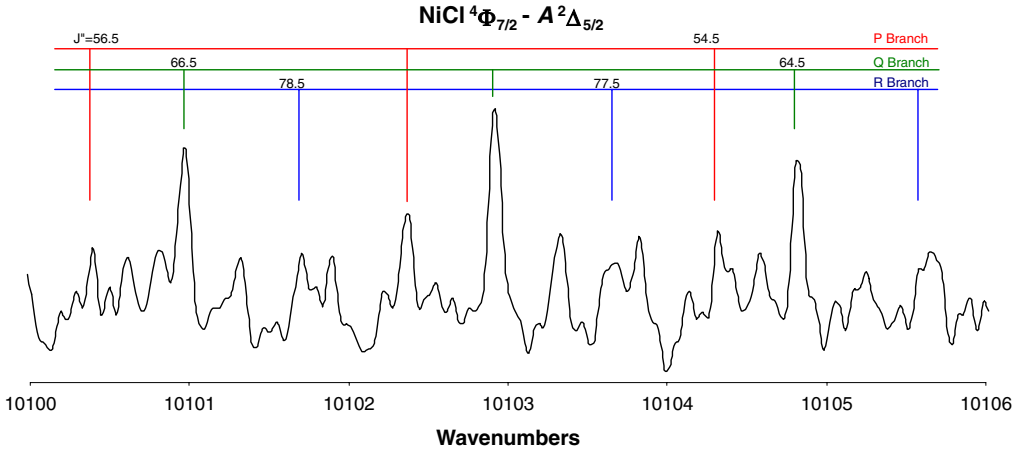

Fig. 1. A portion of the [10.3] $^4\Phi_{7/2}$–$A\,^2\Delta_{5/2}$transition of $^{58}Ni^{35}Cl$.

Table 1
Molecular parameters (in cm^{-1}) for the [10.3] $^2\Phi_{7/2}$ and $A\,^2\Delta_{5/2}$ states of $^{58}Ni^{35}Cl$ (all uncertainties are 1σ)

	T_0	B_0	$D_0 \times 10^6$	$\Delta G_{1/2}$
[10.3] $^2\Phi_{7/2}$	10327.3563(9)	0.16888776(86)	0.12459(15)	393.05[a]
$A\,^2\Delta_{5/2}$, $v=0$	161.550[b]	0.1837527[b]	0.1311[b]	431.72[b]

[a] Estimated from bandheads.
[b] Held fixed in fit, from Ref. [1].

Three branches were identified for the 10 168 cm^{-1} system: these appeared to be one *R*-, one *P*-, and one *Q*-branch. The 10 561 cm^{-1} system was too weak to identify branches. Only lines due to the strongest NiCl isotopomer, $^{58}Ni^{35}Cl$ (51.58% abundance), were clearly identified in the 10 168 cm^{-1} system, although the spectra show additional structure, probably due to other NiCl isotopomers ($^{60}Ni^{35}Cl$ [19.87%], $^{58}Ni^{37}Cl$ [16.50], and $^{60}Ni^{37}Cl$ [6.35%]). Using the published parameters for the low-lying levels from previous work [1–9], we calculated the energy levels $F_e(J'')$ and $F_f(J'')$, and the values for $\Delta_2F_e(J'')$ and $\Delta_2F_f(J'')$, where $\Delta_2F_e(J) = F_e(J+1) - F_e(J-1)$, and $\Delta_2F_f(J) = F_f(J+1) - F_f(J-1)$ for all five of the low-lying states. The method of combination differences [13] was used for the observed branches, and indeed, the three observed branches could be assigned definitively as one *P*-, one *Q*-, and one *R*-branch connecting to the $A\,^2\Delta_{5/2}$ $v=0$ state. No omega-doubling was observed at high *J*. A portion of the spectrum is shown in Fig. 1.

A total of 216 lines were fitted in a least squares fitting program, using a standard polynomial expression [1–9] for both the ground and excited states, $T = T_0 + B_0J(J+1) - D_0J^2(J+1)^2$. All lines were weighted equally in the fit. Because the parameters for the $A\,^2\Delta_{5/2}$ state already are known quite accurately [1], only the parameters for the excited state were varied in the fit. The molecular parameters obtained from the fit are given in Table 1. The line positions, assignments and fit residuals are presented in Table 2.

We initially assigned the 10 168 cm^{-1} system as the (0, 0) band and the 10 561 cm^{-1} system is the (1, 0) band of a new electronic transition. The observed bandheads at 10167.85 and 10560.90 cm^{-1} can be used to estimate an excited state vibrational frequency: $\Delta G_{1/2} = 393.05\ cm^{-1}$. This value is similar to the vibrational frequency observed for the [12.3] $^2\Sigma$ state ($\omega_e = 397.56\ cm^{-1}$ [4]), the [13.0] $^2\Pi_{3/2}$ state ($\omega_e = 394.22\ cm^{-1}$ [5]), and to that observed for the [9.1] $\Omega = 3/2$ state ($\omega_e = 396.8\ cm^{-1}$ [7]).

Although the lower state vibrational assignments are secure, the excited state vibrational assignments were, as this point, not definitive. To confirm our assignment, we searched the 9700–9800 cm^{-1} region of the spectrum, looking either for another band in the progression, or for emission near 9736 cm^{-1} which would be emission associated with the (0, 1) vibrational band ($\Delta G_{1/2}$ for the $A\,^2\Delta_{5/2}$ state is 431.72 cm^{-1}). Indeed, a bandhead was observed at 9735.87 cm^{-1}, which confirmed our initial vibrational assignments.

The three observed branches in this band indicate a transition with $\Delta\Omega = \pm 1$. With the lower state of $^2\Delta_{5/2}$ symmetry, the upper state should have $\Omega = 7/2$ or 3/2. If the excited state is $\Omega = 3/2$, emission to the other low-lying electronics states should also be observable, which was not the case. The absence of observable transitions to any of those other four low-lying states provides support for the upper state assignment as $\Omega = 7/2$. Accordingly, the upper state is presumed to be $\Omega = 7/2$.

Assignment of the upper state to $^4\Phi_{7/2}$ symmetry is based on results of a recent high level *ab initio* calculation of NiCl by Zou and Liu [14]. Fig. 2 shows a comparison of known electronic states for Ni^+ [15], predicted electronic states of NiCl [14], and observed states of NiCl [1–9]. A