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Spectroscopy of nickel chloride: Identification of the [15.0] $^2\Pi_{3/2}$ and [15.0] $^2\Delta_{5/2}$ states

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Abstract

Vibrational bands belonging to the [15.0] $^2\Delta_{5/2}$–A $^2\Delta_{5/2}$, [15.0] $^2\Delta_{5/2}$–X $^2\Pi_{3/2}$, and [15.0] $^2\Pi_{3/2}$–X $^2\Pi_{3/2}$ electronic transitions of NiCl have been observed in the 14000–16000 cm^{-1} region. The [15.0] $^2\Delta_{5/2}$ and [15.0] $^2\Pi_{3/2}$ states are identified for the first time. The observed bands have been recorded at high spectral resolution using several techniques, which include intracavity laser spectroscopy (ILS), Fourier transform emission spectroscopy (FTS), and laser induced fluorescence (LIF) spectroscopy. For the ILS absorption spectra, NiCl molecules were produced in a nickel hollow cathode operated with a small amount of CCl_4. For the FTS emission spectra, excited NiCl molecules were produced in a King-type carbon tube furnace loaded with $NiCl_2$ and heated to 1600 °C. In the LIF work, NiCl molecules were produced by reacting laser-ablated nickel with PCl_3 seeded in argon. Detailed analysis of rotational transition lines indicates that the observed [15.0] $^2\Delta_{5/2}$ and [15.0] $^2\Pi_{3/2}$ states are only separated by 10 cm^{-1} and are interacting with each other. Molecular constants for these newly observed electronic states are reported.
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1. Introduction

The electronic structure of NiCl has received much recent attention. The ground state electronic configuration of $Ni^+(3d^9)$ $Cl^-(3p^6)$ gives rise to three low-lying electronic states: X $^2\Pi$, A $^2\Delta$ and B $^2\Sigma^+$ [1–3]. Excitation of one of the various nickel 3d electrons to an unoccupied nickel 4s or 4p orbital leads to numerous electronic transitions throughout the near-infrared and visible regions of the spectrum [1–8]. The pure rotational spectrum of the X $^2\Pi_{3/2}$ state was observed by Yamazaki et al. [9], and rotational transitions for the A $^2\Delta_{5/2}$ state also have been observed [10]. The Pinchemel and Bernath groups [1–3] have investigated the visible spectrum of NiCl via high-resolution laser-induced fluorescence and Fourier transform (FT) spectroscopy. They established the ground state of NiCl to be a X $^2\Pi_{3/2}$ state, and identified other low-lying states: the A $^2\Delta_{5/2}$ state at 161.55 cm^{-1}, the X $^2\Pi_{1/2}$ state at 382 cm^{-1}, the A $^2\Delta_{3/2}$ state at 1646 cm^{-1}, the B $^2\Sigma^+$ state at 1768 cm^{-1}, and a state at 1385 cm^{-1} which is possibly a quartet state. They have identified several excited electronic states in the 20000–26000 cm^{-1} region. The pattern of low-lying states is in reasonably good agreement with the known low-lying states of the isovalent molecule NiF [11–15]. Our research projects have focused on the NiCl transitions that occur in the near-IR, and we have identified a $^2\Sigma^+$ state at 12259 cm^{-1} [4,5], a $^2\Pi_{3/2}$ state at 12961 cm^{-1} [6], and a $\Pi_{3/2}$ state (probable quartet state) at 9100 cm^{-1} [7].

In the visible and near-IR, several electronic transitions for NiCl have been observed [8]. In the red and near-IR (6350–8750 Å), the bands recorded with vibrational resolution were classified into band systems designated as F, G,

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H, I and J [16]. The identification of the band systems has progressed significantly from recent analysis with rotational resolution: System G is the [13.0] $^2\Pi$–$X\ ^2\Pi_{3/2}$ transition [6], System H is the [12.3] $^2\Sigma^+$–$X\ ^2\Pi_{3/2}$ transition [4], and System I is the [12.3] $^2\Sigma^+$–$X\ ^2\Pi_{1/2}$ transition [17]. This paper reports on the spectrum of NiCl in the area of System F, which is now identified as containing three separate electronic transitions, the [15.0] $^2\Delta_{5/2}$–$A\ ^2\Delta_{5/2}$, [15.0] $^2\Delta_{5/2}$–$X\ ^2\Pi_{3/2}$ and [15.0] $^2\Pi_{3/2}$–$X\ ^2\Pi_{3/2}$ systems.

2. Experimental method

High resolution spectra of NiCl in the region 14 000–16 000 cm^{-1} were recorded using three different techniques: Fourier transform (FT) emission spectroscopy, intracavity laser absorption spectroscopy and laser induced fluorescence spectroscopy. For the FT experiment, the NiCl molecules were produced in a King-type carbon tube furnace and heated to 1600 °C. The emission from the King furnace was focused onto the entrance slit of the 1-m FT spectrometer associated with the McMath-Pierce Solar Observatory at Kitt Peak, AZ. The FT spectrometer was configured with a UV-quality quartz beamsplitter and silicon diode detectors. The spectrometer integrated 10 scans over 100 minutes, with a resolution of 0.02 cm^{-1}. Peak positions were measured using the *Gremlin* program developed by Jim Brault (National Solar Observatory).

The molecular absorption spectrum of NiCl was measured at Doppler-limited resolution using intracavity laser absorption spectroscopy (ILS). In this technique, the dye laser was operated in a time-modulated fashion so that the absorption spectrum of the intra-cavity species was amplified and superimposed on the spectrally broad output of laser. The spectrometer, cathode source, and method of data analysis were described in previous publications [5,6,18]. A brief synopsis is given here. A plasma discharge was formed in a 2-in.-long nickel hollow cathode operated with a set pressure (1.3–2.7 Torr) of argon. Immediately before the discharge potential was applied, a burst of CCl_4 vapor (a few mTorr) was introduced manually from a side vial of CCl_4 liquid by opening the vial to the cathode chamber for approximately 2 s. The hollow cathode, located inside the cavity of a dye laser, was operated from a digital DC plasma generator operated at a specific current (0.60 A). The discharge was switched on just before ILS data acquisition occurs. Immediately following data acquisition a background spectrum was obtained with the discharge switched off. The spectrum for NiCl was obtained by dividing the dark-current corrected data spectrum by the dark-current corrected background spectrum. The ILS technique enables absorption spectra to be observed at much enhanced sensitivity: the effective path length employed for the NiCl measurements is in the range of 0.6–0.9 km. ILS spectra were recorded as a series of overlapping, $\sim$5 cm^{-1} spectral segments. Calibration was accomplished by alternatively measuring the spectrum of the intracavity NiCl species and an I_2 absorption spectrum recorded from an extra-cavity iodine cell. The widely used iodine atlas [19] was used as a reference. Peak positions were determined from the zero crossing-points of the first derivative spectra using Savitzky–Golay polynomial smoothing. The procedure enables the positions for isolated, unblended lines to be determined to an accuracy of better than $\pm$0.005 cm^{-1}.

The laser induced fluorescence spectrum of NiCl was obtained using the laser vaporization/reaction free jet expansion laser induced fluorescence spectrometer. Descriptions of the spectrometer and the laser ablation system are given in detail elsewhere [20,21]. Only a brief description of the experimental conditions will be given here. Pulses of 532 nm light (5–6 mJ, and 10 ns) from a Nd:YAG laser were focused onto the surface of a nickel rod to obtain metal atoms in a plasma. A pulsed valve, synchronized with an appropriate delay, released gas mixtures of 2% PCl_3 in argon into the reaction zone. The production of NiCl was achieved by the reaction of Ni atoms with PCl_3 in the gas phase. The Nd:YAG laser/valve system was operated at 10 Hz. The jet-cooled NiCl molecules were excited by an argon ion laser pumped cw ring dye laser using DCM dye. The laser induced fluorescence signal was collected by means of a lens system and detected by a photomultiplier tube (PMT). The PMT output was fed into a boxcar integrator for averaging. Low-resolution data was obtained by removing the intracavity assembly (ICA) of the dye laser. For high resolution scans, the laser scanning speed was set to about 9 min per 0.8 cm^{-1}. The wavelength of the dye laser was measured by a wavemeter with an accuracy of about 1 part in 10^7. The accuracy of the wavemeter was calibrated using iodine lines in the near-infrared region [19]. The absolute accuracy of a measured line position is about $\pm$0.002 cm^{-1}.

3. Results and discussion

A low-resolution laser excitation spectrum of NiCl in the 14 500–16 200 cm^{-1} region recorded using LIF is presented in Fig. 1. Vibrational progressions of three separate electronic transitions were observed. Transitions originating from the $v = 0$ level of the lowest two electronic states, namely the $X\ ^2\Pi_{3/2}$ and $A\ ^2\Delta_{5/2}$ states to the same [15.0] $^2\Delta_{5/2}$ upper state were observed. The separation between two of the (0,0) origin bands matched the separation of 157.7 cm^{-1} between the $X\ ^2\Pi_{3/2}$ and $A\ ^2\Delta_{5/2}$ states, which indicates possibility of bands sharing a common upper state. Another new transition labeled as [15.0] $^2\Pi_{3/2}$–$X\ ^2\Pi_{3/2}$ was also identified.

3.1. The [15.0] $^2\Delta_{5/2}$–$X\ ^2\Pi_{3/2}$ and [15.0] $^2\Delta_{5/2}$–$A\ ^2\Delta_{5/2}$ systems

The high-resolution spectrum of the (0,0), (1,0), and (2,0) bands for the [15.0] $^2\Delta_{5/2}$–$X\ ^2\Pi_{3/2}$ transition was recorded using the LIF spectroscopy. (0,0), (1,0), and (2,0) bands of the [15.0] $^2\Delta_{5/2}$–$A\ ^2\Delta_{5/2}$ transition were

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