

LABORATORY MEASUREMENTS OF NiH BY INTRACAVITY LASER ABSORPTION SPECTROSCOPY

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ABSTRACT

The visible electronic spectrum of the NiH $B^2\Delta_{5/2}-X^2\Delta_{5/2}$ transition has been recorded with rotational resolution by intracavity laser absorption spectroscopy. The gas-phase NiH molecules were produced in an electric discharge using a nickel cathode in a pure hydrogen atmosphere at 1–3 torr total pressure. Peak positions for the NiH isotopomers are presented. ^{58}NiH and ^{60}NiH have been observed in sunspots, and attempts to observe NiH in stellar spectra are underway.

Subject headings: methods: laboratory — molecular data — stars: chemically peculiar

Online material: color figures

1. INTRODUCTION

NiH was first observed spectroscopically by Gaydon & Pearce (1935). Vibrational bands in two separate electronic transitions were recorded and identified as members of the $B^2\Delta_{5/2}-X^2\Delta_{5/2}$ or $A^2\Delta_{5/2}-X^2\Delta_{5/2}$ transition. Heimer (1937) observed several additional vibrational bands. Åslund et al. (1964) identified both spin-orbit components and a cross component of a new ultraviolet $C^2\Delta_{5/2}-X^2\Delta_{5/2}$ transition.

The 1980s–1990s saw many groups working on the electronic spectrum (Gray et al. 1985, 1990; Gray & Field 1986; Li et al. 1987; Li & Field 1989; Hill & Field 1990; Adakkai Kadavathu et al. 1987, 1990; Scullman et al. 1982) and on the vibrational and rotational spectrum (Beaton et al. 1988; Steimle et al. 1990; Lipus et al. 1993; Nelis et al. 1988; Li et al. 1997). Several calculations pertaining to the electronic structure of NiH have been published (Marian 1987; Marian et al. 1989).

The low-lying electronic states with $T_0 < 5000\text{ cm}^{-1}$ are well understood. The $X^2\Delta$, $A^2\Sigma^+$, and $B^2\Pi$ states arise primarily from a covalent electron configuration, $\text{Ni}(3d^94s^1)\text{H}(1s^1)$ (Marian et al. 1989). A 15×15 supermultiplet Hamiltonian has been used to describe the following lower levels (Gray et al. 1990): $X^2\Delta$ ($v = 0, 1$), $A^2\Sigma^+$ ($v = 0, 1$), and $B^2\Pi$ ($v = 0, 1$). However, the only published data sets for the NiH $B^2\Delta_{5/2}-X^2\Delta_{5/2}$ transition are from Gaydon & Pearce (1935) and Heimer (1937), with peak position precisions of 0.1 and 0.02 cm^{-1} , respectively.

^{58}NiH and ^{60}NiH have been observed in sunspots (Lambert & Mallia 1971), and attempts to observe NiH in stellar spectra are underway. The $^{58}\text{NiH}/^{60}\text{NiH}$ isotopomer ratio in stellar spectra may be used to determine the neutron/proton ratio in other stars, with a view to probing models of supernovae and star formation. The $^{58}\text{Ni}/^{60}\text{Ni}$ ratio is sensitive to the neutron excess during the supernovae that produced the Ni atoms that are subsequently incorporated in the observed stars (Arnett 1996).

2. METHOD

The molecular absorption spectrum of NiH was measured at Doppler-limited resolution using intracavity laser absorption spectroscopy (ILS). The spectrometer, cathode source, and method of data analysis are described in previous publications (L. C. O'Brien et al. 2001, 2002; J. J. O'Brien 2002), although in this case spectra were recorded using a dye laser-based ILS system (Singh & O'Brien 1995). A brief synopsis is given here. A plasma discharge is formed in a 2 inch (5 cm) long nickel hollow cathode operated with a set pressure (1.4–2.3 torr) of pure hydrogen gas (H_2). The hollow cathode, located inside the cavity of a dye laser, is operated from a digital DC plasma generator operated at a specific current (0.26–0.30 A). The discharge is switched on just before ILS data acquisition occurs. Immediately following data acquisition, a background spectrum is obtained at the same H_2 pressure with the discharge switched off. The spectrum for NiH is 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 a much enhanced sensitivity: the effective path length employed for the NiH measurements is approximately 1 km.

Spectra are recorded as a series of overlapping, $\sim 5\text{ cm}^{-1}$ spectral segments. Calibration is accomplished by alternatively measuring the spectrum of the intracavity NiH species and an I_2 absorption spectrum recorded from an extracavity iodine cell. The widely used *Iodine Atlas* (Gerstenkorn & Luc 1982) is used as reference. Peak positions are 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 $\pm 0.005\text{ cm}^{-1}$.

3. RESULTS

The (0, 0) band of the $B^2\Delta_{5/2}-X^2\Delta_{5/2}$ transition of NiH has been recorded in the 15415–15905 cm^{-1} region. As illustrated in Figures 1–3, spectra with excellent signal-to-noise ratios (S/Ns) were obtained. The band origin region, 15905–16010 cm^{-1} , was

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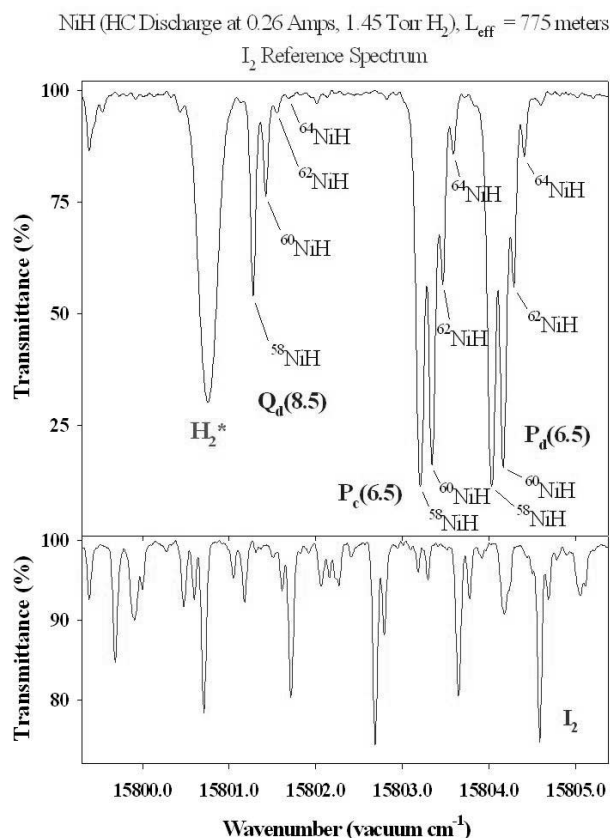


FIG. 1.—The (0, 0) band of the $B^2\Delta_{5/2}-X^2\Delta_{5/2}$ transition near 15803 cm⁻¹. [See the electronic edition of the Journal for a color version of this figure.]

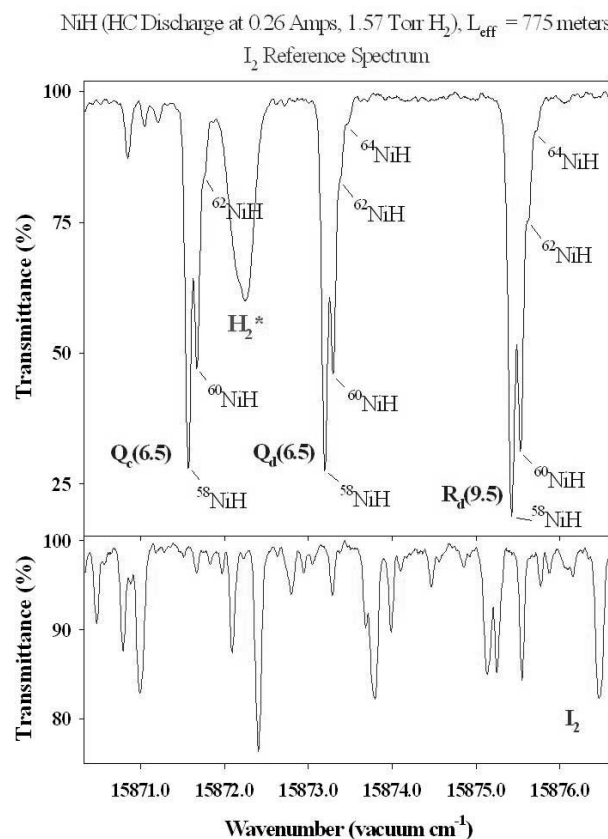


FIG. 3.—The (0, 0) band of the $B^2\Delta_{5/2}-X^2\Delta_{5/2}$ transition near 15873 cm⁻¹. [See the electronic edition of the Journal for a color version of this figure.]

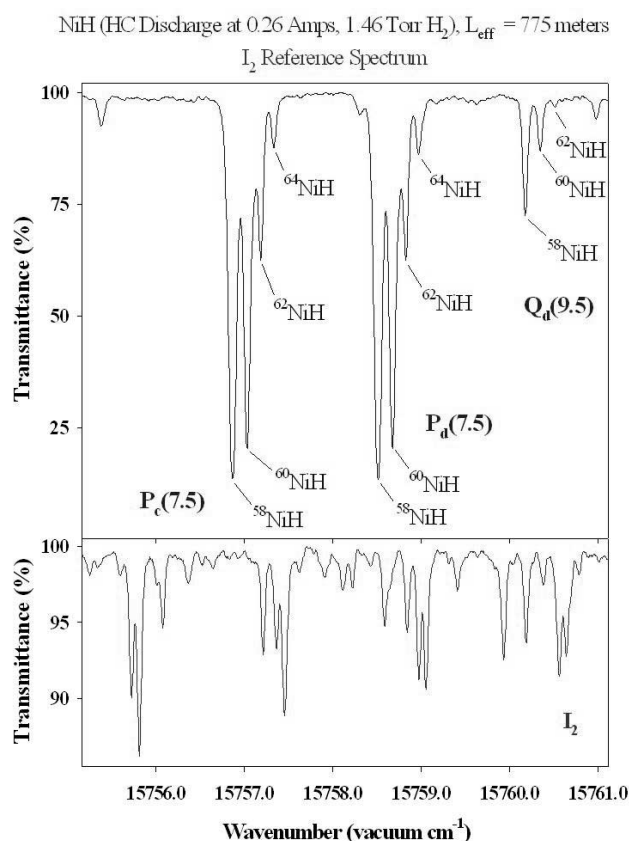


FIG. 2.—The (0, 0) band of the $B^2\Delta_{5/2}-X^2\Delta_{5/2}$ transition near 15758 cm⁻¹. [See the electronic edition of the Journal for a color version of this figure.]

not recorded, since it was outside the lasing region of the dye laser as configured in the experiment. Six branches, P_c , P_d , Q_c , Q_d , R_c , and R_d , resulting from the appreciable lambda doubling in the excited state, were observed in the spectrum. Rather than changing to the new e/f labeling of the lambda doublets (Brown et al. 1975), the original c/d labeling is retained for ease of comparison with the original observations. As expected for the $B^2\Delta_{5/2}-X^2\Delta_{5/2}$ transition, the Q branches are observable only at low J , $J'' \leq 9.5$ (see Figs. 1–3), while the P and R branches are readily observable up to $J'' = 17.5$. Excited-state transitions of molecular hydrogen (H_2^*) are also observed in the spectrum (Dieke 1972).

The nickel isotopomer structure (^{58}NiH 68%, ^{60}NiH 23%, ^{62}NiH 4%, and ^{64}NiH 1%) is identifiable in the $B-X$ transition. The isotopomer peaks are not fully resolved at low J , but rapidly become fully resolved at higher J . The P -branches show significant isotopomer structure even at low J . For instance, compare the clear isotopomer structure of the $P(7.5)$ lines (Fig. 2) with the compressed isotopomer structure of the $R(9.5)$ lines (Fig. 3).

The assignments were straightforward, using the data from Heimer (1937). Line positions and assignments are listed in Table 1. The peak positions of the minor isotopomers are listed in Table 1 only as they become resolved from the main isotopomer. Several lines that were overlapped or blended in the old data sets are clearly resolved in the new data set.

4. CONCLUSIONS

The (0, 0) band of the $B^2\Delta_{5/2}-X^2\Delta_{5/2}$ transition of NiH has been recorded at Doppler-limited resolution in the 15415–15905 cm⁻¹ region. Peak positions for NiH isotopomers are presented. This new data set is significantly more precise than

TABLE 1
LINE POSITIONS FOR THE (0, 0) BAND OF THE $B^2\Delta_{5/2}-X^2\Delta_{5/2}$ TRANSITION OF NiH ISOTOPOMERS (IN cm^{-1})

<i>J</i>	<i>R</i>				<i>Q</i>			<i>P</i>			
	^{58}NiH	^{60}NiH	^{62}NiH	^{64}NiH	^{58}NiH	^{60}NiH	^{62}NiH	^{58}NiH	^{60}NiH	^{62}NiH	^{64}NiH
4.5 <i>d</i>	15882.908	15883.004
4.5 <i>c</i>	15882.908	15883.004
5.5 <i>d</i>	15903.482	15903.559	...	15845.616	15845.722	15845.815	...
5.5 <i>c</i>	15902.638	15902.719	...	15845.271	15845.376	15845.473	...
6.5 <i>d</i>	15873.194	15873.292	...	15804.030	15804.163	15804.286	15804.406
6.5 <i>c</i>	15871.592	15871.674	...	15803.208	15803.343	15803.467	15803.389
7.5 <i>d</i>	15839.014	15839.135	...	15758.510	15758.671	15758.822	15758.968
7.5 <i>c</i>	15836.155	15836.283	...	15756.867	15757.031	15757.185	15757.332
8.5 <i>d</i>	15904.790	15904.881	15801.291	15801.435	...	15709.264	15709.452	15709.628	15709.792
8.5 <i>c</i>	15897.680	15897.756	15796.754	15796.902	15797.043	15706.409	15706.607	15706.788	15706.963
9.5 <i>d</i>	15875.425	15875.531	15760.178	15760.347	15760.514	15656.661	15656.884	15657.093	15657.287
9.5 <i>c</i>	15865.303	15865.425	15865.536	...	15753.103	15753.272	15753.436	15652.030	15652.257	15652.468	15652.669
10.5 <i>d</i>	15842.834	15842.960	15843.075	15600.770	15601.026	15601.266	15601.488
10.5 <i>c</i>	15829.046	15829.194	15829.328	15593.575	15593.829	15594.066	15594.283
11.5 <i>d</i>	15807.256	15807.402	15807.534	15541.824	15542.118	15542.385	15542.646
11.5 <i>c</i>	15789.117	15789.292	15789.453	15789.561	15531.636	15531.939	15532.221	... ^a
12.5 <i>d</i>	15768.822	15768.987	15769.138	... ^a	15480.000	15480.322	15480.624	15480.917
12.5 <i>c</i>	15745.670	15745.871	15746.056	15746.229	15466.102	15466.466	15466.767	15467.065
13.5 <i>d</i>	15727.658	15727.843	15728.000	15728.159	15415.458	15415.814	15416.148	15416.515
13.5 <i>c</i>	15698.930	15699.148	15699.373	15699.560
14.5 <i>d</i>	15683.874	15684.082	15684.258	15684.450
14.5 <i>c</i>	15649.100	15649.350	15649.578
15.5 <i>d</i>	15637.518	15637.743	15637.960
15.5 <i>c</i>	15596.491	15596.763
16.5 <i>d</i>	15588.711	15588.960
17.5 <i>c</i>	15537.650	15537.898

^a Blended line.

data from previous work: it was obtained at high resolution, with a much greater S/N, and line positions have been determined to better than $\pm 0.005 \text{ cm}^{-1}$.

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