**Identification of Two New Excited Electronic States of NiCl:
Analyses of the (1,0) & (0,0) bands of the [13.5] $^2\Phi_{7/2}$ – [0.16] $A\ ^2\Delta_{5/2}$
and (0,0) band of the [13.8] $^2\Pi_{1/2}$ - [0.38] $X\ ^2\Pi_{1/2}$ Transitions**

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Abstract

The near-infrared spectrum of NiCl has been recorded at high resolution in the 13,200 - 13,500 cm^{-1} and 13,600 - 13,750 cm^{-1} regions using Intracavity Laser Spectroscopy (ILS). The NiCl molecules were produced in the plasma discharge of a Ni-lined copper hollow cathode with 0.3 -0.6 torr of argon as the sputter gas, and a trace amount of CCl_4 . Several electronic transitions were observed, including three transitions involving two previously unreported excited electronic states. The (0,0) and (1,0) bands of the [13.5] $^2\Phi_{7/2}$ – [0.16] $A\ ^2\Delta_{5/2}$ transition were observed near 13,318 cm^{-1} and 13,709 cm^{-1} , respectively. The (0,0) band of the [13.8] $^2\Pi_{1/2}$ – [0.38] $X\ ^2\Pi_{1/2}$ transition was observed near 13,480 cm^{-1} . With analysis of these transitions, molecular constants have been obtained for eleven of the twelve predicted NiCl doublets states with term energies less than 16,000 cm^{-1} . Comparison of experimentally observed transitions with the theoretical work is presented.

Keywords

Nickel monochloride, NiCl, Intracavity spectroscopy, gas-phase spectroscopy, diatomic radicals, absorption spectroscopy, molecular parameters, bond lengths, electronic spectroscopy, and theoretical calculations of excited states

1. Introduction

There have been several experimental investigations into the electronic spectrum of NiCl. The visible region was examined at high resolution using Laser Induced Fluorescence (LIF) and Fourier-Transform Emission Spectroscopy,¹⁻³ definitively identifying five excited electronic states 20,000-25,000 cm⁻¹ above the ground state and all five expected low-lying electronic states predicted from the 3d⁹ configuration of Ni⁺, all within 2000 cm⁻¹ of the ground state. The near-infrared region has been studied using Intracavity Laser Absorption Spectroscopy (ILS) and Fourier-Transform Emission Spectroscopy.⁴⁻¹⁰ Thirty-two transitions were observed in the 9,000-15,000 cm⁻¹ region, and thirteen of those transitions were rotationally analyzed. Yamazaki *et al.*¹¹ investigated the millimeter- and submillimeter-region and were able to obtain ground state constants for six isotologues of NiCl. Figure 1 provides an energy level diagram of the known electronic states and the experimentally observed transitions.

Theoretical studies into NiCl also have been reported. Zou and Liu¹² presented a theoretical investigation into the low-lying states of NiX molecules (X = F, Cl, Br, I), including relativistic effects. Jon Hougen¹³ developed an effective Hamiltonian model describing the electronic states of Ni⁺X⁻ molecules and the five electronic states resulting from the 3d⁹ configuration of Ni⁺ by the bonded, closed-shell X⁻ ion. Hougen also described in detail the Λ -type doubling of the $|\Omega_e| = \frac{1}{2}$ states of Ni⁺X⁻. The treatment indicated that the initial Λ -doubling parameter used by Hirao *et al.*¹³ was inverted and that the *e/f* parity of all assigned lines needed to be reversed in the prior NiCl literature. In light of these theoretical studies, Dahms *et al.*¹⁴ reassigned the *e/f* levels of the [12.3] ² Σ^+ - X ² $\Pi_{3/2}$, [12.3] ² Σ^+ - X ² $\Pi_{1/2}$, and [12.3] ² Σ^+ - [1.7] B ² Σ^+ transitions, by converting the [12.3] ² Σ^+ state to the [12.3] ² Σ^- state and inversion of fine structure constants for the B ² Σ^+ and X ² $\Pi_{3/2}$ states. The presence of the ² Σ^- state at ~12,000 cm⁻¹ is consistent with the calculations by Zou and Liu.¹²

Several vibrational bandheads of the [13.0] ² $\Pi_{3/2}$ - X ² $\Pi_{3/2}$ transition were reported in 2002 by O'Brien *et al.*,⁵ but many could not be rotationally analyzed due to thermal broadening associated with the high temperature King Furnace emission method used to obtain the spectra. A more recent publication (2016) from our laboratory reported the ILS spectra and rotational analyses of the (2,0) and (1,0) bands of the [13.0] ² $\Pi_{3/2}$ - X ² $\Pi_{3/2}$

transitions at 13,742 cm⁻¹ and 13,353 cm⁻¹ : the identity of these two bands was confirmed, and molecular constants for the $v=1,2$ levels of the [13.0] $^2\Pi_{3/2}$ state have been published.¹⁵ Our 2016 paper reported that the (2,1) and (3,1) bandheads (assigned in 2002) were not part of the [13.0] $^2\Pi_{3/2} - X^2\Pi_{3/2}$ transition.¹⁵

In this study, the analyses of three new near-infrared bands of NiCl occurring in the 13,200 - 13,500 cm⁻¹ and 13,600-13,750 cm⁻¹ regions are presented. The new bands connect to previously unidentified excited states of NiCl. Two new bands near 13,709 cm⁻¹ and 13,318 cm⁻¹ were recorded at high resolution, analyzed, and identified as the (0,0) and (1,0) bands of the [13.5] $^2\Phi_{7/2} - [0.16] A^2\Delta_{5/2}$ transition. A new transition with a bandhead at 13,480 cm⁻¹ was analyzed and is identified as the (0,0) band of the [13.8] $^2\Pi_{1/2} - [0.38] X^2\Pi_{1/2}$ transition. Analyses of the transitions and obtained molecular constants are presented and compared with theoretical studies.

2. Experimental method

The near-IR spectrum of NiCl was collected in the 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 been described in detail.^{4,16} Briefly, a Verdi-V10 laser is used to pump a Ti:Sapphire crystal, the gain medium for the ILS system. As indicated in Figure 2, the resonator cavity of this laser includes a high reflector (HR), two fold mirrors (FM), an intracavity hollow cathode, two Brewster-angle prisms, an adjustable slit, and an output coupler (OC). Molecules are created inside the hollow cathode, allowing the resonator cavity to act a laser-amplified, multi-pass cell over the generation time, t_g , of laser gain prior to detection. The transmittance due to interaction with a particular absorber, $I_{obs}(\nu)$, for ILS is described by the following expression¹⁶

$$I_{obs}(\nu) = I_0(\nu) \exp \left[- \sigma(\nu) N \left(\frac{l}{L} \right) c t_g \right] = I_0(\nu) \exp \left[- \sigma(\nu) N L_{eff} \right] \quad (1)$$

where $I_0(\nu)$ is the broadband output of the laser, $\sigma(\nu)$ is the absorption cross-section, N is the number density of molecules, l is the length of the hollow cathode, L is the length of the resonator chamber of the laser, c is the speed of light, t_g is the generation time, and L_{eff} is the effective pathlength. For this study, a t_g of 90 μ sec was used, resulting in an effective pathlength of ~ 0.7 km for a 5 cm hollow cathode and ~ 1.9 m resonator chamber. The laser

pulse, generation time, and viewing window are controlled with two acousto-optic modulators (AOM1, AOM2). AOM1 is used to control the pump beam so the Ti:sapphire crystal is held just above and below the lasing threshold, setting the laser on-laser off timing cycle. At t_g , AOM2 is used to divert $\sim 70\%$ of the Ti:sapphire output to the spectrograph, where it is dispersed by a diffraction grating onto a 1024 channels of a diode array detector, allowing a $\sim 5 \text{ cm}^{-1}$ wide segment of spectrum to be collected.

The NiCl molecules were produced in the radio-frequency plasma discharge (ENI RPG-50) 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 regions of intense Ar plasma lines, ~ 1.8 torr of He was used instead as a sputter gas in place of Ar. Various plasma discharge currents were used in order to enhance spectral features at different locations. The set currents used for this study ranged from 0.3 - 0.7 A. It was found that a steady 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 used for calibration with the well-known iodine atlas.¹⁷ 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 positions for isolated, unblended lines to be determined to better than $\pm 0.003 \text{ cm}^{-1}$.

3. Results and discussion

The $[13.5] \ ^2\Phi_{7/2} - [0.16] \ A \ ^2\Delta_{5/2}$ Transition

Electronic bands at $13,317.96 \text{ cm}^{-1}$ and $13,709.22 \text{ cm}^{-1}$ have been recorded at rotational resolution by ILS. These two bands were originally assigned in 2002 as the (2,1) and (3,1) bands $[13.0] \ ^2\Pi_{3/2} - X \ ^2\Pi_{3/2}$ transition,⁵ and are the same bands that were shown in our 2016 paper to originate from a band other than the $[13.0] \ ^2\Pi_{3/2} - X \ ^2\Pi_{3/2}$ transition.¹⁵ Three rotational branches were identified in each band, which suggested electronic symmetry with $\Delta\Lambda \neq 0$ and were a possible vibrational progression of a different electronic system. Indeed, the lower state of these two bands was confirmed using the method of combination differences to be the $v = 0$ level of the $A \ ^2\Delta_{5/2}$ state based on the constants reported by Hirao *et al.*¹

There are four Ω -states predicted by Zou and Liu¹² between 13,000 and 15,000 cm^{-1} , namely the $(\text{II})^2\Pi_{3/2}$, $(\text{I})^2\Phi_{7/2}$, $(\text{II})^2\Pi_{1/2}$, and $(\text{II})^2\Delta_{5/2}$ states. Only the $[13.0] ^2\Pi_{3/2}$ state has been experimentally observed in the 13,000 - 14,000 cm^{-1} region. Absorption from the low-lying $A ^2\Delta_{5/2}$ state could connect to the excited $(\text{II})^2\Pi_{3/2}$ state or the $(\text{I})^2\Phi_{7/2}$ state. The term energy and vibrational constants for the $(\text{II})^2\Pi_{3/2}$ state, aka $[13.0] ^2\Pi_{3/2}$ state, are known and this state could be eliminated from further consideration. However, treatment of the transitions as the (1,0) and (0,0) bands of the $[13.5] ^2\Phi_{7/2} - [0.16] A ^2\Delta_{5/2}$ transitions was very promising. The experimentally determined T_e values were consistent with the theoretical predictions, and the experimental $\Delta G_{1/2}$ value of 391 cm^{-1} was very close to the predicted ω_e value of 403 cm^{-1} for the $(\text{I})^2\Phi_{7/2}$ state. Thus, the transitions observed near 13,709 cm^{-1} and 13,318 cm^{-1} , respectively, are newly reassigned as the (0,0) and (1,0) bands of the $[13.5] ^2\Phi_{7/2} - [0.16] A ^2\Delta_{5/2}$ transition. Secure vibrational assignments for the excited state could not be confirmed using isotopologue shifts because no clear isotopologue bandheads were observed; the strong (2,0) and (1,0) bands of the $[13.5] ^2\Pi_{3/2} - X ^2\Pi_{3/2}$ transition overlap these transitions resulting in spectra that are quite congested. Figure 3 present a comparison between the experimental spectrum (black) and the PGOPHER¹⁵ simulation (blue) of the (1,0) band of the $[13.5] ^2\Phi_{7/2} - [0.16] A ^2\Delta_{5/2}$ transition of NiCl. The (2,0) band of $[13.0] ^2\Pi_{3/2} - X ^2\Pi_{3/2}$ transition for NiCl overlaps this transition, as can be seen from the PGOPHER¹⁵ simulation for $^{58}\text{Ni}^{35}\text{Cl}$ included in the figure (red).

For the final fit, the reported line positions of the (1,0) and (0,0) bands of the $[21.9] ^2\Delta_{5/2} - [0.16] A ^2\Delta_{5/2}$ transition from Hirao *et al.*¹ were included with the line positions for the (1,0) and (0,0) bands of the $[13.5] ^2\Phi_{7/2} - [0.16] ^2\Delta_{5/2}$ transition. The transitions were fit using PGOPHER.¹⁸ The line positions, assignments, and residuals for the (1,0) and (0,0) bands of the $[13.5] ^2\Phi_{7/2} - [0.16] ^2\Delta_{5/2}$ transition are available in the Supplementary Materials. The obtained molecular constants are displayed in Table 1, with the values from Hirao *et al.*¹ shown in italics.

The $[13.8] ^2\Pi_{1/2} - [0.38] X ^2\Pi_{1/2}$ Transition

While scanning in the 13,000 – 14,000 cm^{-1} region, an additional electronic band was observed with a bandhead near 13,480 cm^{-1} , as shown in Figure 4. The exact position of the bandhead was obscured by the presence of a strong Cl atomic line and a weak Ni

atomic line, but red-degraded branches were clearly visible. Upon inspection, four branches were identified; two R-branches and two P-branches. No Q-branch was observed, and the overall branch pattern was consistent with a $\Delta\Lambda = 0$ transition. As stated above, only the $X^2\Pi_{3/2}$ state and the relatively low-lying [0.16] $A^2\Delta_{5/2}$ the [0.38] $X^2\Pi_{1/2}$ states are expected to be populated for our absorption studies. The appearance of large Λ -doubling constants excluded the possibility of a $^2\Delta_{5/2} - ^2\Delta_{5/2}$ transition. Combination differences between the four branches of the observed transition were compared to the Δ_2F levels calculated from the constants for the [0.38] $X^2\Pi_{1/2}$ state reported by Rice *et al.*,⁸ and a secure rotational assignment for the transition was obtained. The transition was fit using PGOPHER.¹⁸ Line positions for the [12.3] $^2\Sigma^- - X^2\Pi_{3/2}$ transition reported by O'Brien *et al.*⁵ and for the [12.3] $^2\Sigma^- - [0.38] X^2\Pi_{1/2}$ transition reported by Rice *et al.*⁸ were included in the fit in order to eliminate any ambiguity in the reported constants due to the inversion of the Λ -doubling parameters that was described in the introduction. The obtained constants for the fit of the newly assigned [13.8] $^2\Pi_{1/2} - [0.38] X^2\Pi_{1/2}$ transition are provided in Table 2. The line positions, assignments, and residuals for the fit are available in the Supplementary Materials.

An attempt was made to fit the excited [13.8] $^2\Pi_{1/2}$ and [13.0] $^2\Pi_{3/2}$ as a combined $^2\Pi$ state using a Hund's case (a) treatment, incorporating the line positions from the (0,0) band of [13.5] $^2\Pi_{3/2} - X^2\Pi_{3/2}$ transition.⁵ However, the experimental data could not be fit in PGOPHER¹⁸ without incorporating a large γ -parameter in the excited state. This result indicates strong interactions of the [13.8] $^2\Pi_{1/2}$ state with the nearby [12.3] $^2\Sigma^-$ state, and validates the *Hund's case (c)* treatment suggested by Zou and Lou¹² for the (VIII) $\Omega = \frac{1}{2}$ state which is predicted to be 71% $^2\Pi$ and 28% $^2\Sigma^-$ in character.

Experimentally Observed and Theoretically Predicted States of NiCl.

With the observation of these two new electronic states, the $v=0$ vibrational level for eleven of the twelve predicted¹² doublet spin-orbit components for NiCl below 15,000 cm^{-1} have been rotationally analyzed. In general, the experimental data shows an excellent agreement with the predictions of this theoretical study, predicting the energy of the observed state within 500 cm^{-1} in all but two observed cases. Additionally, in all but one case, the predicted energy was higher than the observed energy, showing a clear trend. A

comparison of the observed and calculated spin-orbit components of $^{58}\text{Ni}^{35}\text{Cl}$ is shown in Figure 5. It should be noted that only $v = 2$ of the $[14.2] \ ^2\Delta_{5/2}$ state has been observed and analyzed.⁹ The analysis performed in this work was greatly assisted by these valuable calculations.

4. Conclusion

Two new electronic states for $^{58}\text{Ni}^{35}\text{Cl}$ have been identified and a mis-assignment in the previous literature have been corrected: the (3,1) and (2,1) bands of the $[13.0] \ ^2\Pi_{3/2} - X \ ^2\Pi_{3/2}$ transition have been reassigned as the (1,0) and (0,0) bands of the $[13.5] \ ^2\Phi_{7/2} - [0.16] \ A \ ^2\Delta_{5/2}$ transition and the $[13.8] \ ^2\Pi_{1/2} - [0.38] \ X \ ^2\Pi_{1/2}$ transition has been observed and rotationally analyzed. Molecular constants have been obtained for the new $[13.5] \ ^2\Phi_{7/2}$ and $[13.8] \ ^2\Pi_{1/2}$ states. The good agreement between the experimental data and the theoretical predictions of Zou and Liu¹² underscores how valuable contributions from computational investigations can be in experimental analysis.

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Appendix A. Supplementary material

The line positions, assignments, and residuals for the reported transitions as well as the matrix elements utilized by PGOPHER¹⁸ for the various transitions can be found in the supplementary materials. For the online version, they can be found at <http://dx.doi.org/j.jms.2016.xx.xxx>.

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Figure captions

Figure 1: Energy Level diagram for the previously reported states of NiCl. (a) Hirao *et al.*¹, (b) Poclet *et al.*², (c) Krouti *et al.*³ (d) O'Brien *et al.*⁴, (e) O'Brien *et al.*⁵, (f) Rice & O'Brien⁶, (g) Tunturk *et al.*⁷, (h) Rice *et al.*⁸, (i) Leung *et al.*⁹, (j) Gibbs *et al.*¹⁰, and (k) this work.

Figure 2: Schematic of the ILS system. [HR=High Reflector, FM=Fold Mirror, OC=Output Coupler, AOM=Acousto-Optic Modulator]

Figure 3: Overlay of the experimental spectrum (black) and PGOPHER¹⁸ simulation (blue) of the (1,0) band of the $[13.5] \ ^2\Phi_{7/2} - [0.16] \ A \ ^2\Delta_{5/3}$ transition of NiCl. The (2,0) band of System G for NiCl overlaps this transition, as can be seen from the PGOPHER¹⁵ simulation for $^{58}\text{Ni}^{35}\text{Cl}$ included in the figure (red).

Figure 4: A sample spectrum of the $[13.8] \ ^2\Pi_{1/2} - [0.48] \ X \ ^2\Pi_{1/2}$ transition with branch patterns identified. This figure is composition of 3 spectra that were collected under the same plasma discharge conditions. Other conditions were used to determine positions of the R-bandhead, which is obscured by nickel ($13,483.35 \text{ cm}^{-1}$) and chlorine ($13,484.08 \text{ cm}^{-1}$) atomic lines in this figure.

Figure 5: A comparison of the experimentally observed electronic states [Right: (a) O'Brien *et al.*⁴, (b) O'Brien *et al.*⁵, (c) Rice & O'Brien⁶, (d) Tunturk *et al.*⁷, (e) Rice *et al.*⁸, (f) Leung *et al.*⁹, (g) Gibbs *et al.*¹⁰ and (h) this work.] and the doublet states of NiCl predicted by Zou and Liu.¹²

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Table 1

Molecular Constants for (1,0) and (0,0) bands the [13.5] $^2\Phi_{7/2}$ – [0.16] $A\ ^2\Delta_{5/2}$ transition of $^{58}\text{Ni}^{35}\text{Cl}$. The values in parentheses correspond to one standard deviation.

[13.5] $^2\Phi_{7/2}$	T_v	B_v	$D_v \times 10^6$	r_v (Å)
$v' = 1$	13869.0142(15)	0.167633(13)	0.1461(20)	2.1474
$v' = 0$	13477.6790(21)	0.168305(13)	0.1375(21)	2.1432
[0.16] $^2\Delta_{5/2}$				
$v'' = 0$	161.550 ^a	0.183891(13)	0.1507(20)	2.0503
$v'' = 0^b$	161.550(4) ^b	0.1837527(46) ^b	0.1311(10) ^b	

^a All units in cm^{-1} unless otherwise noted

^b Values reported by Hirao *et al.*¹

Table 2

Molecular Constants for the [13.8] $^2\Pi_{1/2}$ – [0.38] $X\ ^2\Pi_{1/2}$ transition of $^{58}\text{Ni}^{35}\text{Cl}$. The line positions from Rice *et al.*⁸ were included in the fit, and the parameters for the $X\ ^2\Pi_{1/2}$ state were allowed to float. Deviations arise from differences in the polynomial used by Rice *et al.*⁸ and the matrix elements utilized by PGOPHER,¹⁵ which are listed in the Supplementary Materials. The values in parentheses correspond to one standard deviation.

	T_v	B	$D \times 10^6$	$H \times 10^{12}$	r_0 (Å)
[13.8] $^2\Pi_{1/2}$	13866.4667 (20)	0.1687286 (17)	0.11869 (34)		2.1405
[0.38] $X\ ^2\Pi_{1/2}$	384.8740 (13)	0.1807680 (14)	0.16237 (46)	-1.410 (51)	2.0680
	385.666(2) ^b	0.180778 ^b (2)	0.1652 (3) ^b	-0.34 (3) ^b	

	p	$p_D \times 10^6$	$p_H \times 10^{10}$
[13.8] $^2\Pi_{1/2}$	0.74266 (11)	0.145 (36)	
[0.38] $X\ ^2\Pi_{1/2}$	0.837910 (92)	-2.548 (59)	-7.119 (84)
	0.8391 (1) ^b	3.90 (7) ^{b,c}	4.0 (1) ^{b,c}

^a All values reported in cm^{-1} unless otherwise noted

^b Values reported by Rice *et al.*⁸

^c Sign convention in PGOPHER is inverted relative to polynomial used for this fit

Table 3

Comparison of Theoretical and Experimental Molecular Constants for the Doublet States of $^8\text{Ni}^{35}\text{Cl}$ (in cm^{-1}). The values in parentheses correspond to one standard deviation.

Ω State	Composition	Expt. Λ -S State	Theor. $T[\text{e}]$	Expt. T_{e}	Theor. ω_{e}	Expt. ω_{e}	Theor. B_{e}	Expt. B_{e}
(I) 3/2	(I) $^2\Pi(87)$ +(I) $^2\Delta(13)$	$X^2\Pi_{3/2}^{\text{a}}$	0	0	433	425.63 (3)	0.185	0.181421 (12) ⁱ
(I) 5/2	(I) $^2\Delta(99)$	$A^2\Delta_{5/2}^{\text{a}}$	268	157.70 (5)	440	435.52 (3)	0.185	0.18431 (1)
(I) 1/2	(I) $^2\Pi(81)$ +(I) $^2\Sigma^+(19)$	$X^2\Pi_{1/2}^{\text{b}}$	473	385.666 (2) ^h	420		0.183	0.180778 (2) ⁱ
(II) 3/2	(I) $^2\Delta(87)$ +(I) $^2\Pi(13)$	$A^2\Delta_{3/2}^{\text{c}}$	1549	1645.834 (5) ^h	439		0.185	0.182295 (4) ⁱ
(II) 1/2	(I) $^2\Sigma^+(79)$ + (I) $^2\Pi(13)$	$B^2\Sigma^+^{\text{c}}$	2002	1768.066 (5) ^h	433		0.179	0.179935 (10) ⁱ
(VII) 1/2	(I) $^2\Sigma^-(72)$ +(II) $^2\Pi(27)$	$[12.3]^2\Sigma^-^{\text{d,e}}$	12924	12273.18 (12) ^d	407	397.56 (20) ^d	0.169	0.1708924 (86) ^e
(VII) 3/2	(II) $^2\Pi(91)$ + (II) $^2\Delta(7)$	$[13.0]^2\Pi_{3/2}^{\text{e}}$	13386	12762.201	404	394.84	0.168	0.1681106 (27)
(III) 7/2	(I) $^2\Phi(98)$	$[13.5]^2\Phi_{7/2}^{\text{f}}$	13916	13477.6790 (21) ^h	403	391.3352(26) ⁱ	0.169	0.168305 (13) ⁱ
(VIII) 1/2	(II) $^2\Pi(71)$ + (I) $^2\Sigma^-$	$[13.8]^2\Pi_{1/2}^{\text{f}}$	14264	13866.4667 (20) ^h	408		0.169	0.1687286 (17) ⁱ
(V) 5/2	(II) $^2\Delta(68)$ + (I) $^2\Phi_{7/2}$	$[\sim 14.2]^2\Delta_{5/2}^{\text{g}}$	14355	~ 14165	392		0.166	0.162603 (4) ^k
(VI) 5/2	(I) $^2\Phi(68)$ + (II) $^2\Delta(31)$	$[15.0]^2\Delta_{5/2}^{\text{g}}$	15279	14792.372	407	401.535	0.168	0.170320 (8) ⁱ
(VIII) 3/2	(II) $^2\Delta(92)$ + (II) $^2\Pi(8)$	$[15.0]^2\Pi_{3/2}^{\text{g}}$	15526	14782.224	398	390.435	0.165	0.161598 (9) ⁱ

^a Hirao *et al.* (2000); ^b Rice *et al.* (2006); ^c Krouti *et al.* (2001); ^d O'Brien, Homann, *et al.* (2002); ^e Harms *et al.* (2016); ^f This work; ^g Leung *et al.* (2006); ^h T_0 Value; ⁱ $\Delta G_{1/2}$ Value; ^j B_0 Value; ^k B_2 Value

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