Single vibronic level emission spectroscopy of the low-lying electronic states of NiI

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A B S T R A C T

Five low-lying \((T_e < 2200 \text{ cm}^{-1})\) electronic states of NiI have been observed using single vibronic level (SVL) emission spectroscopy, via three hitherto unobserved band systems in the range 21 150–22 410 cm\(^{-1}\). In addition to the previously characterized \(X^2\Delta_{5/2}\) and \(a^3\Pi_{1/2}\) states, the \(X^2\Delta_{3/2}\), \(a^3\Pi_{3/2}\), and \(b^3\Sigma_{1/2}^-\) states have been observed for the first time. The emission spectra yield term energies and vibrational constants that are in excellent agreement with recent \textit{ab initio} calculations. A number of perturbations in the vibrational level structure can be identified and are attributed to homogenous interactions under the selection rule \(\Delta \Omega = 0\).

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1. Introduction

Transition metal diatomics are model systems for probing details of metal–ligand bonding that aid in understanding larger transition-metal containing systems and provide rigorous benchmarks for theory, and the application of high resolution spectroscopic techniques such as laser-induced fluorescence (LIF) to these systems is a particularly powerful approach for investigation of their detailed structure, properties, and reactivity. Such systems play a vital role in areas from industrial [1] and biological [2] catalysts, to astrophysics [3]. Nickel monohalides (NiX; X = F, Cl, Br or I), have received much attention in recent years, and the electronic structure of NiF [4,5] and NiCl [6–11] is now relatively well understood, while the ground state of NiBr has also been identified [12,13]. The close proximity of the low-lying electronic states in these species results in many perturbations, and the application of high resolution spectroscopic techniques, together with thorough theoretical investigation, has resulted in an improved understanding of the electronic structure of these species.

In the nickel monohalide series, comparatively little is known about NiI. The limited experimental work has focused on the two lowest energy electronic states, observed using laser-induced fluorescence (LIF) [14,15] and microwave spectroscopy [16]. Indeed, the ground state has been unambiguously identified only in the last decade, in the high resolution studies of Cheung and co-workers [14,15]. Assignment of the ground state in that work as \(\tilde{2}\Delta_{5/2}\) is consistent with NiH, but differs from the lighter monohalide analogues, which feature a \(\tilde{2}\Pi_{3/2}\) ground state. Note that the estimated (experimental) splitting of the \(\tilde{2}\Delta_{5/2}\) and \(\tilde{2}\Pi_{3/2}\) states in NiBr is only 37 cm\(^{-1}\) [12,13]. The assignment of the NiI ground state was confirmed in the detailed theoretical study of Zou and Liu [17], who investigated the low-lying states of the nickel monohalides using multireference second-order perturbation theory with incorporation of relativistic effects. This work provided spectroscopic parameters for excited states up to 15 905 cm\(^{-1}\), although electronic states above this energy have yet to be characterized experimentally.

In the present study, three new band systems of NiI have been identified in the range 21 150–22 410 cm\(^{-1}\). Tentative assignments of the symmetries of the excited states have been made based upon rotational simulations and transitions observed in the emission spectra; however, the detailed rotational and vibrational analysis of these bands will be left to a future publication. Here we focus on the use of these new band systems to probe the vibrational structure of the five low-lying \((T_e < 2200 \text{ cm}^{-1})\) electronic states of NiI with single vibronic level (SVL) emission spectroscopy, a technique which measures the emission spectrum from a single laser-excited vibrational level in an excited electronic state. Three of these low-lying states are observed here for the first time, and the harmonic frequencies for all five low-lying states were derived from SVL emission spectra and are compared to recent \textit{ab initio} values [17].

2. Experiment

The apparatus, pulsed discharge nozzle and data acquisition procedures have been described in previous publications [18,19]. NiI was produced using a pulsed discharge source, wherein Ni atoms sputtered from stainless steel electrodes (Type 303 stainless contains 8–10% Ni) reacted with an appropriate iodine-containing precursor seeded in ~3 bar Ar (Airgas). Consistent with our previous study of CuOH using a similar source [20], a rotational temperature in the range of 50 K was determined from preliminary fits of
the fluorescence excitation spectra [21]. A variety of precursors, including CH₃I, CD₃I, and ¹³CD₃I, were employed in order to identify the species observed; the spectra presented herein were recorded using CD₃I (Sigma–Aldrich, 99.5+%). Typically, discharge was initiated by a ~1.3 kV pulse, with a width of ~1000 μs, through a current limiting 80 kΩ ballast resistor. In some experiments a smaller pulse width of 20 μs to reduce background emission from the discharge glow. The timing of laser, nozzle and discharge firing was controlled by an 8-channel pulse/digital delay generator (Berkeley Nucleonics).

The laser system used in this work consisted of a dye laser (lambda-physik, scanmate 2E) pumped by the third harmonic of Nd:YAG laser (continuum NY-61). The laser was operated on C₄₈₀ and C₄₆₀ dyes, giving typical pulse energies of ~4–5 mJ. In this dye range, the laser resolution is ~0.15 cm⁻¹. The unfocussed laser beam crossed the molecular beam 10 mm downstream, and the resulting fluorescence was collected by a two lens f/2.4 assembly and filtered via a combination of long-pass and short-pass cut-off filters (Corion or Edmund Scientific) prior to detection by a photomultiplier tube detector (orient) held at ~1000 V. Emission spectra were obtained using a 0.3 m spectrograph (action SR303i with ISTAR CCD) in photon counting mode, typically with a 160 μm slit width and integration over 15,000 laser shots, and were calibrated using the output of an Fe:Ne hollow cathode lamp (Photron). Bands in the emission spectra were fit to a Gaussian line shape function, using Origin 7.5 software; previous studies have shown the validity of this approach [19–21]. The uncertainty in the derived band positions is ±2 cm⁻¹.

### 3. Results and discussion

#### 3.1. Single vibronic level emission spectra

Three new band systems of NiI have been observed in the range 21 150–22 410 cm⁻¹, originating from the Ni⁺(3d⁴4s¹) configuration [17]. Excited state symmetries have been tentatively assigned based on preliminary rotational simulations [21] and analysis of the single vibronic level emission spectra. In the following discussion, these states will be identified using the nomenclature adopted by Tam et al. [14,15] with Tᵣ values given in square brackets: [21.1]²Π₄/2, [21.3]²Σ₃/2 and [21.9]²Π₃/2. A detailed rotational and vibrational analysis of these band systems will be discussed in a future publication.

SVL emission spectra were obtained from several bands in each of the three progressions; a total of 10 emission spectra were collected, each containing numerous bands extending up to 3746 cm⁻¹ above the X²Σ⁺₂ state origin. Examples are shown in Figure 1, which displays SVL emission spectra collected via the ν = 0 level of the [21.1]²Π₄/2 and [21.3]²Σ₃/2 bands. It is possible to identify five distinct vibrational progressions. In addition to the X²Σ⁺₂ and A²Π₅/2 states characterized in previous work [14–16], three additional electronic states have been identified. Based on the theoretical work of Zou and Liu [17], these are assigned as the A²Π₅/2, X²Σ⁺₃, and B²Σ⁺₁ states. Comparison of SVL spectra recorded via different vibrational levels in the excited states show consistent sets of levels with an intensity pattern reflecting the nodal structure of the vibrational wavefunction.

The calibrated emission spectra peak energies have been fitted to a Dunham expansion in order to derive term energies and vibrational constants for the five electronic states, and these are given in Table 1. Also included in Table 1 are the previous experimental [15,16] and theoretical [17] Tᵣ and V. Values. Note that previous experiments obtained vibrational information through the

<table>
<thead>
<tr>
<th>Table 1</th>
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<tbody>
<tr>
<td>Vibrational and term energies (in cm⁻¹) of the five low-lying electronic states observed in the present work.</td>
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<table>
<thead>
<tr>
<th></th>
<th>X²Σ⁺₂</th>
<th>A²Π₅/2</th>
<th>A²Π₅/2</th>
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<tbody>
<tr>
<td>T₀</td>
<td>0</td>
<td>162.7 (1.2)</td>
<td>787.8 (2.9)</td>
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<tr>
<td></td>
<td>164</td>
<td></td>
<td>1529.8 (1.8)</td>
</tr>
<tr>
<td></td>
<td>139</td>
<td>812</td>
<td>1332</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2210</td>
</tr>
<tr>
<td>v₀</td>
<td>278.5 (0.3)</td>
<td>273.2 (0.7)</td>
<td>260.0 (5.1)</td>
</tr>
<tr>
<td></td>
<td>271²</td>
<td>277.5 (1.4)</td>
<td>268.0 (2.2)</td>
</tr>
<tr>
<td></td>
<td>276.6²</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>283</td>
<td>274</td>
</tr>
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<td></td>
<td></td>
<td>287</td>
<td>281</td>
</tr>
<tr>
<td></td>
<td>274</td>
<td>274</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.02 (0.36)</td>
<td></td>
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* One standard error given in parenthesis.

*² Anharmonic values.
measurement of hot-band spectra, and therefore only anharmonic frequencies were reported. The experimental peak energies, their assignments and their deviation from the energies predicted by the Dunham expansion are provided in Table 15 in the supporting information. As expected, the theoretical values overestimate the experimentally derived harmonic frequencies; however, the trends in the two sets are in excellent agreement. This can be seen in Figure 2, where the experimental values are plotted with the ab initio values, which were scaled so that the $X^2A_e/2$ frequency is coincident with the experimental value. Experimental $T_0$ values are also in excellent agreement with the calculated $T_e$ values, with the exception of the $X^2A_e/2$ state, which appears $\sim 200$ cm$^{-1}$ higher than predicted.

The theoretical predictions of NiI $\Omega$ states up to $\sim 16,000$ cm$^{-1}$ predict a gradual if not monotonic decrease in vibrational frequency with increasing energy [17]. Following with this trend, our preliminary analysis indicates that the harmonic vibrational frequencies of the new states identified in this work in the region 21,000–22,000 cm$^{-1}$ are on the order of 220 cm$^{-1}$. We also note that the $X^2A_e/2$ and $A^\Pi_e/2$ states are observed in emission spectra recorded via the origin level of all three excited states observed in the present study, but with considerable variation in intensity. In SVL spectra recorded via the origin level of all three excited states observed in the present study, but with considerable variation in intensity. In SVL spectra recorded via the origin level of all three excited states observed in the present study, but with considerable variation in intensity. In SVL spectra recorded via the origin level of all three excited states observed in the present study, but with considerable variation in intensity.

3.2. Perturbations involving the low-lying electronic states

An examination of the residuals between the observed energies and those predicted by the Dunham expansion (Fig. 3) has identified the presence of homogenous perturbations in the low-lying electronic states. The ground $X^2A_e/2$ state is apparently free of perturbations, at least up to the $\nu = 8$ level, as all of the vibrational states can be fitted to the Dunham expansion within experimental error. The first obvious perturbation appears for the $\nu = 5$ and $\nu = 6$ levels of the $A^\Pi_e/2$ state at 1497.52 and 1773.53 cm$^{-1}$, which are shifted in energy by $-5.3$ and 7.8 cm$^{-1}$, respectively. Under the $\Delta \Omega = 0$ selection rule [22], the only candidate for the perturbing level is the $\nu = 0$ level of $X^2A_e/2$. Deperturbation analysis using analytical expressions appropriate for a three level system yield the following estimates for the matrix elements:

$$\langle A^\Pi_e/2; \nu = 5 | H | X^2A_e/2; \nu = 0 \rangle = 12 \text{ cm}^{-1},$$

$$\langle A^\Pi_e/2; \nu = 6 | H | X^2A_e/2; \nu = 0 \rangle = 43 \text{ cm}^{-1}.$$

At higher energies, another obvious perturbation involves the $B^2\Sigma_e/2$ $\nu = 1$ and $\nu = 2$ levels at 2415.76 and 2665.03 cm$^{-1}$, shifted by 7.6 and $-11.1$ cm$^{-1}$, respectively. Again, the magnitude of the shift is small, suggesting a weak interaction. Under the $\Delta \Omega = 0$ selection rule [22], the perturbing states must be vibrational levels of the $A^\Pi_e/2$ state. For example, the $\nu = 6$ level of $A^\Pi_e/2$ is predicted from the Dunham parameters to lie at 2329 cm$^{-1}$, and likely interacts with the $B^2\Sigma_e/2$ $\nu = 1$ level. As a consequence of this interaction, the former would be expected to appear in the emission spectra; however, we did not observe this level within our signal to noise. Note that the vibrational progression observed in the $A^\Pi_e/2$ state (up to $\nu = 3$) is significantly shorter than for any of the other four levels. As evident in Figure 3, the residuals between experimental and predicted peak positions become larger to higher energy, indicating significant perturbations in the level structure. Given the presence of five electronic states within roughly 2200 cm$^{-1}$ of the ground state, this is not surprising.

4. Conclusions

Five low-lying electronic states of NiI have been observed and vibrationally characterized (three for the first time) using single vibronic level emission spectroscopy, following the first observation of three excited state band systems in the range 21 150–22 410 cm$^{-1}$. The derived harmonic frequencies and term energies of the five low-lying electronic states are in good agreement with the theoretical values of Zou and Liu [17] and the trend in the calculated $\omega_k$ values is replicated extremely well by the experimental values determined in the present work. A number of perturbations have been identified, which arise from interactions between vibrational levels of the $A^\Pi_e/2$ and $X^2A_e/2$ states and $A^\Pi_e/2$ and $B^2\Sigma_e/2$ states. There are no other low-lying states with $\Omega = 5/2$, and the ground $X^2A_e/2$ state remains unperturbed up to the highest energies measured in this work.
Acknowledgments

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References

[21] Rotational Simulations were Generated Using P GOPHER, a Program for Simulating Rotational Structure, C.M. Western, University of Bristol, <http://pgopher.chm.bris.ac.uk>.