



# The spectrum of nickel monoxide between 410 and 510 nm: laser-induced fluorescence and dispersed fluorescence measurements

Walter J. Balfour<sup>\*</sup>, Jianying Cao, Roy H. Jensen<sup>1</sup>, Runhua Li

*Department of Chemistry, University of Victoria, P.O. Box 3055, Victoria, BC, Canada V8W 3P6*

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## Abstract

The products from the reaction of laser-ablated Ni atoms with CH<sub>4</sub>, O<sub>2</sub> and NO have been studied via laser-induced and dispersed fluorescence spectroscopies. NiC, NiH and NiO species have been detected between 410 and 510 nm. Twenty NiO bands have been rotationally analyzed for the first time and, in most instances, measurements of the <sup>58</sup>NiO/<sup>60</sup>NiO isotopic shifts have been made. Dispersed fluorescence data have been collected at two excitation wavelengths, corresponding to two prominent LIF bands – near 479.1 and 474.5 nm. Vibrational energies for all ground state levels up to  $v = 9$  have been determined.

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## 1. Introduction

In the course of examining excitation spectra between 410 and 510 nm in the reaction of laser-ablated nickel and helium doped with methane, we inadvertently observed bands of NiO. These bands have been briefly mentioned in the literature but no analyses have been given hitherto.

Because of their importance in many fields, from materials science to interstellar chemistry, 3d transition metal monoxides have been the subject of many experimental [1–3] and theoretical studies [4–6]. While the database for ground and excited electronic states is expanding it remains far from complete. In the case of nickel monoxide, its ground state and several low-lying excited states have been characterized but observations at energies beyond 20 000 cm<sup>-1</sup> are only qualitative.

The emission spectrum of NiO was first observed in 1945 in the infrared and visible by Rosen [7,8] who arranged the numerous bands into six systems, labeled I through VI, and suggested vibrational assignments [9]. Investigations by Srdanov and Harris [10], by Fried-

man-Hill and Field [11], and by Ram and Bernath [12] have established the ground state to be a case a  $^3\Sigma^-$  state with a spin-splitting of  $\sim 50$  cm<sup>-1</sup>, and identified excited states of  $^3\Pi$  and  $^3\Sigma^-$  symmetries, near 4300 and 16 000 cm<sup>-1</sup>, respectively. The NiO pure rotation spectrum has been observed [13] and three independent reports of negative ion photoelectron studies of NiO<sup>-</sup> have been published [14–16].

In this Letter we present detailed observations on 25 vibronic bands of NiO whose upper state levels lie between 19 600 and 23 400 cm<sup>-1</sup>.

## 2. Experimental procedure

The apparatus and methods used to observe spectra of NiO were not fundamentally different from those of recent experiments in our laboratory [17]. The NiO molecules were produced in a standard laser vaporization molecular beam source, following reaction of a laser ablation nickel plasma with  $\sim 5\%$  O<sub>2</sub> or NO doped in helium. The nickel was in the form of a rotating and translating rod, 5-mm in diameter  $\times$  30-mm, 99.9% purity, from Strem Chemicals. Excitation (LIF) spectra in the range 410–510 nm were generated using a Nd:YAG pumped dye laser (Lumonics HY600 and HD300) with

<sup>\*</sup> Corresponding author. Fax: +1-250-721-7147.

E-mail address: [balfour@uvvm.uvic.ca](mailto:balfour@uvvm.uvic.ca) (W.J. Balfour).

<sup>1</sup> Present address: Department of Chemistry, Grant MacEwan College, Edmonton, AB, Canada T5J 5J5.

Exalite 416 and Coumarin 440, 460, 480 and 500 dyes. The fluorescence was collected through a Jobin-Yvon H20 monochromator and converted to an electrical signal by a Hamamatsu R106UH photomultiplier tube.

Opto-galvanic signals from an Fe/Ne hollow cathode lamp, known features in NiH, NiC and C<sub>2</sub> spectra, and the atomic spectrum of vanadium were used to calibrate internally the probe laser. The band positions reported are expected to be accurate within  $\pm 1 \text{ cm}^{-1}$ . Peaks separated by  $0.1 \text{ cm}^{-1}$  at 500 nm were clearly resolved in our spectra and this resolution was sufficient to enable all low  $J$  lines in each band to be identified.

The NiO LIF bands are red-degraded and dispersed fluorescence (DF) spectra were obtained by fixing the probe laser frequency at or near a strong R-head and scanning the monochromator. The uncertainty in our measurement of DF intervals is of the order of  $15 \text{ cm}^{-1}$ .

### 3. LIF results

An overview of the spectrum, obtained by co-adding many separate scans, is shown in Fig. 1. Between 400 and 480 nm, a mixture of Ni + CH<sub>4</sub>/He was used so that features due to NiC and NiH can be seen. The NiC observations are in perfect agreement with spectra recorded using resonant two-photon ionization spectroscopy [18]. A weak band, with head at  $434.97 \text{ nm}$  and  $\nu_0 = 22980 \text{ cm}^{-1}$ , lies  $869 \text{ cm}^{-1}$  lower in energy than Brugh and Morse's NiC [23.8] $\Omega = 0^+ - X^1\Sigma^+0-0$  band and is clearly the accompanying 0–1 band. The  $B^2\Delta_{5/2} - X^2\Delta_{5/2}$  system of NiH [19] was observed strongly when either CH<sub>4</sub>/He or H<sub>2</sub>/He gas mixtures were used. Features near  $448 \text{ nm}$  may also arise from

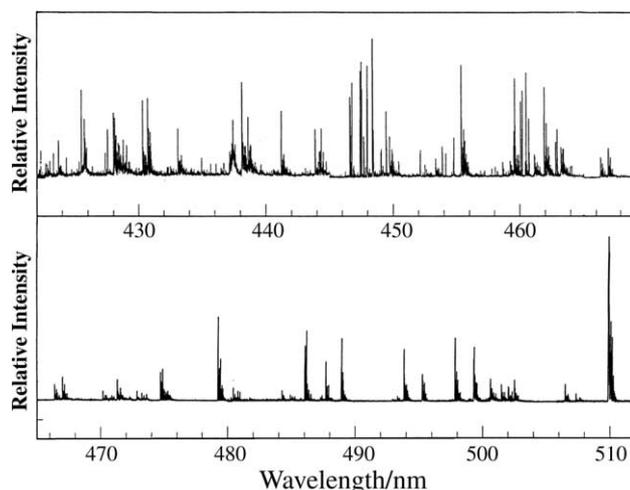


Fig. 1. Low resolution survey LIF spectra. The upper spectrum, while obtained with Ni + CH<sub>4</sub>/He, contains NiO bands due to small traces of O<sub>2</sub>. The lower spectrum was recorded using Ni + O<sub>2</sub>/He. These spectra show data collected under differing conditions and using a range of laser dyes. Consequently relative intensities are only approximate.

NiH and these observations are being investigated further.

<sup>58</sup>NiO band heads are listed in Table 1. In most instances they can be identified with bands listed previously [9] although, as observed by Friedman-Hill and Field [11], some discrepancies in positions over [9] measurements are noted. All the NiO bands show a similar R–P rotational structure as may be seen in the  $474.54 \text{ nm}$  band in Fig. 2. In most instances an accompanying weaker <sup>60</sup>NiO band of similar structure is discernible slightly to the red of the main band. The <sup>58</sup>Ni/<sup>60</sup>Ni natural abundance is 2.6/1.

Rotational combination differences for the ground  $X^3\Sigma^-(\Omega = 0^+)$ ,  $v = 0$  level were available [10,11] making analysis straightforward. Within the precision of our measurements, all NiO bands studied gave matching lower state combination differences. Because data from the jet-cooled source rarely gave measurable lines for  $J > 15$ , the rotational lines were fitted, band by band, using least squares to determine only a band origin  $\nu_0$  and  $\Delta B = B' - B''$ . A fitting of published data for the  $0^+$  component of  $X^3\Sigma^-$  gave  $B''_{\text{eff}} = 0.474882 \text{ cm}^{-1}$ . These parameters, together with the isotope shifts  $\nu_0(^{58}\text{NiO}) - \nu_0(^{60}\text{NiO})$ , are included in Table 1. Table 2 lists rotational assignments for the  $479.08$  and  $474.54 \text{ nm}$  bands. Similar data for other bands are available on request (WJB).

Experimental conditions and rotational analyses confirm that all save perhaps the weakest features of our NiO spectrum have the  $X^3\Sigma^-(\Omega = 0^+)$ ,  $v = 0$  level as the lower level. The vibronic assignments suggested in [9] then require substantial revision. Unfortunately, despite the details from isotopic shifts and rotational constants provided by the present study, a comprehensive classification of bands is far from obvious. The conclusion is that perturbations between excited states are widespread.

A focus on position and isotopic shift suggests three groupings of bands: (i) a progression from  $479.08 \text{ nm}$ , namely bands at  $479.08$ ,  $466.85$ ,  $455.29$ ,  $443.79$  and  $433.02 \text{ nm}$ . Their corresponding isotopic shifts are  $7.49$ ,  $7.65$ ,  $9.61$ ,  $16.7$  (doubtful) and  $10.50 \text{ cm}^{-1}$ , and consecutive intervals of  $547$ ,  $544$ ,  $568$ , and  $562 \text{ cm}^{-1}$  represent plausible vibrational spacings. This series had been identified by Rosen [8] as a  $v - 1$  progression; (ii) a progression from  $474.54 \text{ nm}$ , namely bands at  $474.54$ ,  $461.77$ ,  $449.63$ , and  $438.05 \text{ nm}$ , showing isotopic shifts of  $7.28$ ,  $7.38$ ,  $9.3$ , and  $12.2 \text{ cm}^{-1}$ , respectively. These bands occur at intervals of approximately  $585 \text{ cm}^{-1}$ ; and (iii) a progression from  $466.22$ , namely bands at  $466.22$ ,  $453.26$ ,  $441.14$ , and  $430.24 \text{ nm}$ , with corresponding isotopic shifts of  $6.94$ ,  $9.03$ ,  $10.1$ , and  $11.52 \text{ cm}^{-1}$ . Here the vibrational intervals are progressively  $613$ ,  $606$ , and  $573 \text{ cm}^{-1}$ . The magnitudes of the isotopic shifts in all three series suggest reasonably high upper level  $v$  quantum numbers, e.g.  $v' \geq 3$  for the  $479.08 \text{ nm}$  band. However, in

Table 1  
NiO band heads (nm), rotational constants ( $\text{cm}^{-1}$ ) and  $^{58}\text{NiO}$ – $^{60}\text{NiO}$  isotopic shifts ( $\text{cm}^{-1}$ ) observed in LIF between 420 and 510 nm<sup>a</sup>

$\lambda_{\text{head}}$ (nm)	$\nu_0$ ( $\text{cm}^{-1}$ )	$B'$ ( $\text{cm}^{-1}$ )	$B'-B''$ ( $\text{cm}^{-1}$ )	$\Delta\nu_0^i$ ( $\text{cm}^{-1}$ )
509.85	19604.9	0.41762	-0.06726	1.65
506.46	19736.2	0.40529	-0.06959	Very small
502.48	19891			Very small
502.00	19912			
501.45	19933			9.5?
500.57	19968			
499.24	20021.6	0.41782	-0.05706	2.24
497.76	20082	–	–	9.3
495.19	20185.0	0.40100	-0.07388	1.33
493.75	20245.1	0.38582	-0.08906	8.52
488.83	20448.5	0.40989	-0.06499	3.20
487.60	20500			
485.93 <sup>b</sup>	20570.8	0.40878	-0.06610	4.82
479.08	20865.0	0.40090	-0.07398	7.49
474.54	21064.5	0.40574	-0.06914	7.28
471.14	21217			11.3
466.85	21411.9	–	–	7.65
466.22	21440.7	0.40191	-0.07297	6.94?
461.77	21646.5	0.40692	-0.06796	7.38
461.01	21683.4	–	–	–
455.29	21955.5	0.40841	-0.06647	9.61
453.26	22053.9	0.39239	-0.08249	9.03
449.63	22231.4	0.40827	-0.06661	9.3
443.79	22523.5	0.42433	-0.05055	16.7?
441.14	22659.9	0.39165	-0.08717	10.1
438.54	22793.9	–	–	–
438.05	22819.2	0.37232	-0.10256	12.2
433.02	23085.3	0.38913	-0.08575	10.50
430.62	23213.9	0.38285	-0.09203	9.8
430.24	23233.1	0.38909	-0.08579	11.52
427.93	23359.5	0.38684	-0.08804	

<sup>a</sup>  $B''$  was fixed at  $0.474882 \text{ cm}^{-1}$  (see text).

<sup>b</sup> Not certain that NiO  $X^3\Sigma^-(0^+)$  is the lower state.

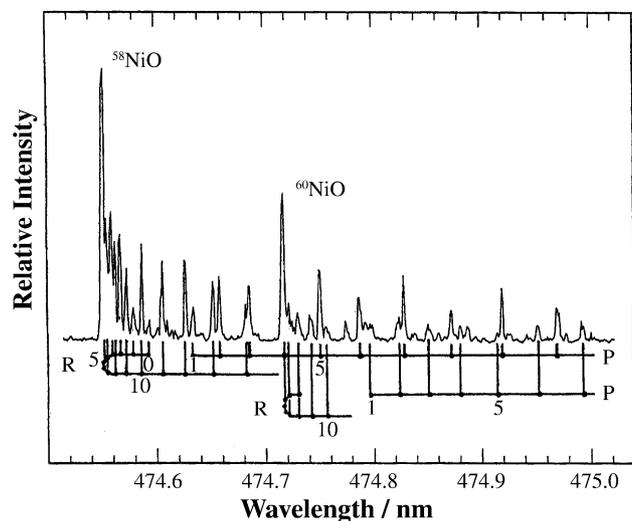


Fig. 2. The LIF spectrum of NiO near 474.6 nm. The  $^{58}\text{NiO}$  and  $^{60}\text{NiO}$  band centers are separated by  $7.28 \text{ cm}^{-1}$ .

none of the series are lower energy members evident. The question of upper level  $\nu$  numbering has been probed further using DF (vide infra). Correlations among other

NiO bands of Table 1 remain speculative at best. The following groupings have separations of  $550\text{--}600 \text{ cm}^{-1}$ :  $517.45 \text{ nm}$  ( $19\,326 \text{ cm}^{-1}$ ) [10],  $502.48 \text{ nm}$  ( $19\,891 \text{ cm}^{-1}$ ) and  $488.83 \text{ nm}$  ( $20\,449 \text{ cm}^{-1}$ );  $509.85 \text{ nm}$  ( $19\,605 \text{ cm}^{-1}$ ) and  $495.19 \text{ nm}$  ( $20\,185 \text{ cm}^{-1}$ ); and  $438.54 \text{ nm}$  ( $22\,794 \text{ cm}^{-1}$ ) and  $427.93 \text{ nm}$  ( $23\,360 \text{ cm}^{-1}$ ).

Three features in the Ni + CH<sub>4</sub> spectrum show a common but very different profile from the R-headed, rotationally resolved bands of NiO and NiC. These three features lie centered at  $418.06$ ,  $425.65$  and  $437.35 \text{ nm}$ . The latter two are seen in Fig. 1. They show the high density of lines typical of a polyatomic species. Ni-CH<sub>3</sub> is a possibility. Similar observations have been made using Fe + CH<sub>4</sub> and Cr + CH<sub>4</sub> [20]. Better spectra than currently obtained are needed before a definite identification of the carrier can be made.

#### 4. Dispersed fluorescence results

In two of the progressions identified above, the lead bands, specifically those at  $479.08$  and  $474.54 \text{ nm}$ , are

Table 2  
Rotational assignments ( $\text{cm}^{-1}$ ) in the 479.08 and 474.54 nm bands of  $^{58}\text{NiO}$  and  $^{60}\text{NiO}$

$J$	$^{58}\text{NiO}$		$^{60}\text{NiO}$	
	$R(J)$	$P(J)$	$R(J)$	$P(J)$
(a) 479.08 nm band				
0	20 865.77 (−0.03)	–		
1	866.47 (0.02)	20 864.03 (0.01)		20 856.55 (0.00)
2	866.86 (−0.09)	862.94 (−0.01)	20 859.42 (0.00)	855.42 (−0.04)
3	867.29 (−0.02)	861.73 (0.03)	859.77 (0.00)	854.20 (−0.02)
4	867.51 (0.00)	860.29 (−0.01)	859.98 (0.02)	852.94 (0.12)
5	867.60 (0.03)	858.72 (−0.04)	859.98 (−0.02)	851.24 (−0.04)
6	867.521 (0.05)	857.07 (0.01)		849.59 (0.02)
7	867.29 (0.08)	855.24 (0.04)		847.72 (0.00)
8	866.73 (−0.06)	853.16 (−0.03)		845.64 (−0.07)
9	866.21 (−0.01)	850.98 (−0.04)		843.47 (−0.06)
10	865.51 (0.03)	848.64 (−0.05)		841.21 (0.02)
11	864.61 (0.04)	846.16 (−0.01)		838.69 (0.00)
12	863.55 (0.06)	843.51 (−0.02)		836.09 (0.08)
13	862.29 (0.06)	840.64 (−0.06)		
14	860.90 (0.10)	837.65 (−0.03)		
15		834.39 (−0.09)		
16		831.01 (−0.09)		
(b) 474.54 nm band				
0	21 065.27 (0.04)	–		
1	065.93 (0.03)	21 063.49 (0.00)		21 056.27 (0.03)
2	066.47 (0.04)	062.43 (0.01)	21 059.24 (0.07)	055.07 (−0.08)
3	066.82 (−0.01)	061.23 (0.03)	059.59 (0.04)	053.87 (−0.06)
4	067.04 (−0.04)	059.81 (−0.04)	059.81 (0.03)	052.59 (0.03)
5	067.13 (−0.07)	058.35 (0.00)	059.81 (−0.07)	051.04 (−0.02)
6	067.13 (−0.04)	056.71 (0.00)	059.81 (−0.01)	049.40 (0.00)
7	067.04 (0.04)	054.89 (−0.02)	059.59 (−0.03)	047.63 (0.03)
8	066.69 (0.01)	052.94 (−0.03)	059.24 (−0.02)	045.68 (0.03)
9	066.20 (0.00)	050.86 (−0.01)	058.75 (0.01)	043.55 (0.00)
10	065.58 (0.01)	048.64 (0.04)	058.08 (0.01)	041.25 (−0.04)
11	064.74 (−0.03)	046.16 (0.00)	057.29 (0.06)	
12	063.85 (0.04)	043.55 (0.00)	056.18 (−0.04)	
13	062.70 (0.03)		055.07 (0.03)	
14	061.36 (0.01)			
15	059.81 (−0.03)			

the strongest members. DF spectra were recorded with probe laser excitation fixed to coincide with the most intense R-head region in the  $^{58}\text{NiO}$  isotopomer of each band. Excitation at 479.080 nm gave the DF spectrum shown in Fig. 3. At 474.714 nm, the result was qualitatively similar. Both DF spectra are readily interpreted in terms of emission solely into the vibrational manifold of the electronic ground state,  $v = 0-9$ . Somewhat surprisingly we find no sign of the low-lying electronic levels near 2525, 3910, 4325 and 5225  $\text{cm}^{-1}$  present in the negative ion photoelectron spectra of NiO [14–16].

Measured vibrational energies are given in Table 3. Also included in Table 3, for comparison, are level predictions based on the  $\omega_e = 839.1 \text{ cm}^{-1}$  and  $\omega_e x_e = 5.4 \text{ cm}^{-1}$  vibrational constants of Srdanov and Harris [10] determined from  $v = 0, 1$  and 2 data. Since agreement between the two set of data is excellent a dissociation energy given by  $\omega_e^2/4\omega_e x_e = 32600 \text{ cm}^{-1}$  may be reasonable.

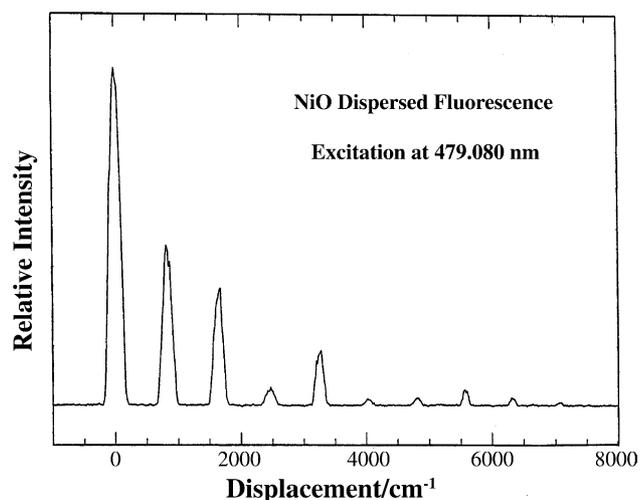


Fig. 3. The dispersed fluorescence spectrum of  $^{58}\text{NiO}$  obtained using a probe laser wavelength of 479.080 nm.

Table 3  
Ground state  $^{58}\text{NiO}$  vibrational levels ( $\text{cm}^{-1}$ ) observed in dispersed fluorescence at two excitation wavelengths

$v$	$\lambda_{\text{exc}}$ at 479.080 nm	$\lambda_{\text{exc}}$ at 474.714 nm	From [10]
0	0	0	0
1	830	820	828
2	1645	1635	1646
3	2460	2440	2453
4	3255	3240	3248
5	4030		4034
6	4810	4795	4808
7	5575	5560	5571
8	6325		6324
9	7070		7066

We have attempted to match the variations in intensity displayed in Fig. 3 by Franck–Condon calculations using established vibrational and rotational constants for the ground state, together with  $B' = 0.405 \text{ cm}^{-1}$  for the excited state and the estimated parameters  $\omega'_e = 548 \text{ cm}^{-1}$  and  $\omega'_e x'_e = 1 \text{ cm}^{-1}$ . Trial simulations with  $v'$  successively 2, 3, 4, 5 and 6 gave best and good results with  $v' = 4$  for both 479.08 and 474.54 nm bands. These results are in agreement with the observed isotopic shifts.

## 5. Conclusions

The jet-cooled electronic spectrum of NiO has been studied between 410 and 510 nm where twenty bands have been observed and rotationally analyzed. Earlier vibronic assignments have had to be revised,  $v_0(^{58}\text{NiO})$ – $v_0(^{60}\text{NiO})$  isotopic shifts have been measured and tentative new assignments of several upper state vibrational progressions are suggested. Dispersed fluorescence spectra map ground state vibrational levels up to  $v = 9$ .

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