

NiI [14.6] ²Δ_{5/2} - X ²Δ_{5/2} (9 0) 带的超精细结构

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摘 要: 在可见光范围内, 用激光蒸发/反应、超声射流和激光诱导荧光光谱方法, 对 NiI [14.6] ²Δ_{5/2} - X ²Δ_{5/2} 跃迁的 (9 0) 带进行了高分辨研究. 80 MHz 分辨的光谱显示超精细结构是由于激发态中未成对电子与碘 (I = 5/2) 核大磁矩相互作用引起的. 在 v = 9 能级上低 J 谱线的超精细线宽快速下降, 表明在 [14.6] ²Δ_{5/2} 态中超精细耦合适合 Hund a_β 耦合情况. [14.6] ²Δ_{5/2} 态的精确转动参数和超精细参数已得到, 而且显示 v = 9 能级被微扰了.

关键词: 激光诱导荧光光谱; 激光蒸发/反应; Ni 的超精细结构

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Hyperfine Structure of the [14.6] ²Δ_{5/2} - X ²Δ_{5/2} (9 0) Band of NiI

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Abstract The (9 0) band of the [14.6] ²Δ_{5/2} - X ²Δ_{5/2} transition of NiI in the visible region has been studied at high resolution using laser vaporization/reaction supersonic free jet expansion and laser induced fluorescence spectroscopy. Spectrum taken at a resolution of about 80 MHz shows the resolved hyperfine structure which is caused by an unpaired electron in the excited state interacting with the large magnetic moment of the I nucleus with nuclear spin I = 5/2. The rapid decrease in hyperfine width of the low J lines in the v = 9 level suggests that the hyperfine coupling in the [14.6] ²Δ_{5/2} state conforms to the Hund's Case a_β coupling scheme. Accurate rotational and hyperfine parameters for the [14.6] ²Δ_{5/2} state have been obtained, which indicate that the v = 9 level is perturbed.

Keywords Laser induced fluorescence spectroscopy, Laser vaporization/reaction, Hyperfine structure of NiI

1 Introduction

Spectroscopic studies of transition metal diatomic halides have been an active area of research for many years^[1-4]. Amongst the first transition metal period, there has been considerable interest in the spectroscopic properties of nickel monohalides. Through years of hard work of many workers, good knowledge of electronic structure of the ground and some excited states of the monofluoride^[5] and monochloride^[6] has been obtained. However, only recently the monobromide^[7]

and monoiodide^[8] have been studied.

The observation of magnetic hyperfine structure in optical spectra of transition metal molecules is common, which is caused by the interaction of the unpaired electron with magnetic moment of the nucleus with non-zero nuclear spin. The magnetic hyperfine structure provides specific information about the nature of chemical bonding in a molecule. This is because hyperfine parameters are related to expectation values of the coordinates of the electrons near the spinning nuclei^[9]. It is commonly known that the hyperfine

structure arises from transition metal nucleus with the non-zero nuclear spin^[10,11], however, this is not the case in NiI. Since nickel atom has the zero nuclear spin, the observed hyperfine structure is expected to be caused by an unpaired electron interacting with the large magnetic moment of the iodine nucleus with nuclear spin $I = 5/2$.

In this paper, we report the high-resolution spectroscopic study of NiI and rotational and hyperfine analysis of the $[14.6]^2\Delta_{5/2} - X^2\Delta_{5/2}(9,0)$ band of NiI in the visible region. Accurate rotational and hyperfine constants for the $v = 9$ level of the $[14.6]^2\Delta_{5/2}$ state have been obtained.

2 Experiment

A laser vaporization/reaction supersonic free jet-laser induced fluorescence (LIF) experimental apparatus similar to the one used in this experiment has been discussed in our earlier publications^[12,13]. Figure 1 shows schematically the arrangement of the optical components, the tunable continuous wave laser system and the vacuum chamber system. In this experiment, a two-chamber vacuum system was used which consisted

of a source chamber and a detection chamber was separated by a 3 mm diameter skimmer. Each chamber was individually pumped by a 600 L/s turbo molecular pump backed by a rotary pump. Pulses of 532 nm, 9 ~ 10 mJ from a Nd:YAG laser were focused onto the nickel metal rod surface for generating nickel atoms. A pulsed valve with an appropriate delay, released a gas mixture of 3% CH₃I in argon into the reaction region. The operating cycle of the Nd:YAG pulsed valve was 10 Hz. Jet-cooled NiI molecules were excited by an argon ion laser pumped continuous wave ring-dye laser system operating with the DCM dye in the visible region. Laser induced fluorescence signal from the NiI molecule was collected by a lens system and detected by a photomultiplier tube (PMT). The PMT signal was fed into a boxcar integrator for averaging. The width of the molecular transition lines measured was about 80 MHz. The wavelength of the dye laser output was measured by a wavemeter with a repetition rate of 1 Hz and an accuracy of 1 part in 10⁷. The absolute calibration of the wavemeter reading was checked against I₂ absorption lines that were estimated to be accurate to about $\pm 0.002 \text{ cm}^{-1}$.

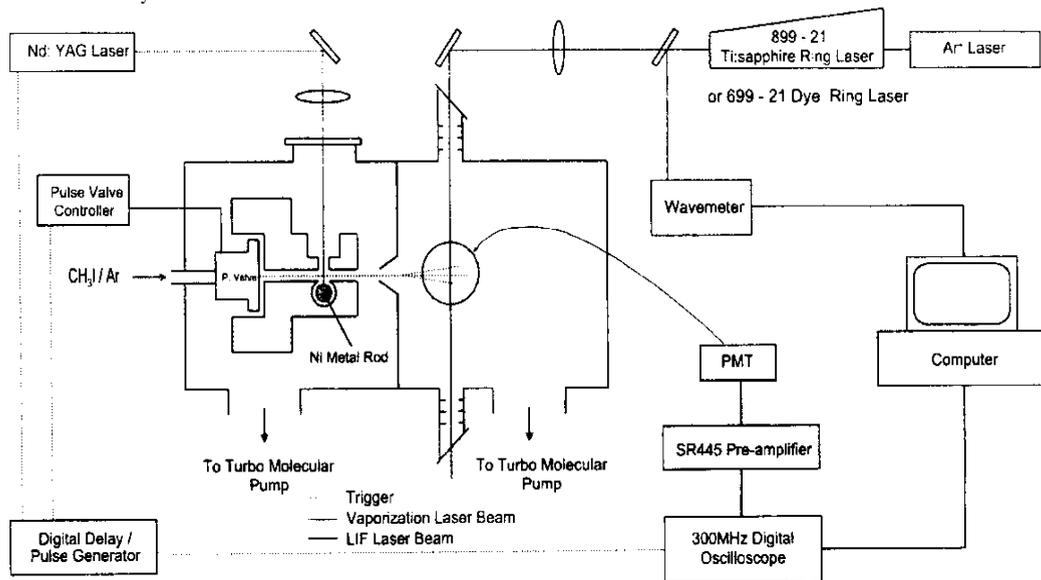


Fig. 1 Schematic diagram for the laser vaporization/reaction free jet expansion/ laser induced fluorescence spectroscopy

3 Results and discussion

The laser induced fluorescence spectrum of the $(9,0)$ band of the $[14.6]^2\Delta_{5/2} - X^2\Delta_{5/2}$ transition system has been observed and analyzed. Figure 2

shows the band head region of this band. As already discussed in our earlier paper^[8], the $[14.6]^2\Delta_{5/2} - X^2\Delta_{5/2}$ transition system with bands consist of resolved P, Q and R branches. One can easily notice from Fig. 2 that transition lines less than $J = 10$ are all with size-

able linewidth and these linewidths collapse rapidly as J increases. The large width in these lines is the unresolved hyperfine structure that arises from the interaction between the magnetic moment of unpaired electrons and the magnetic moment of a nucleus in the molecule. Given sufficient resolutions, it is quite common to study the hyperfine structure in transition metal compounds, which usually arises from the non-zero nuclear

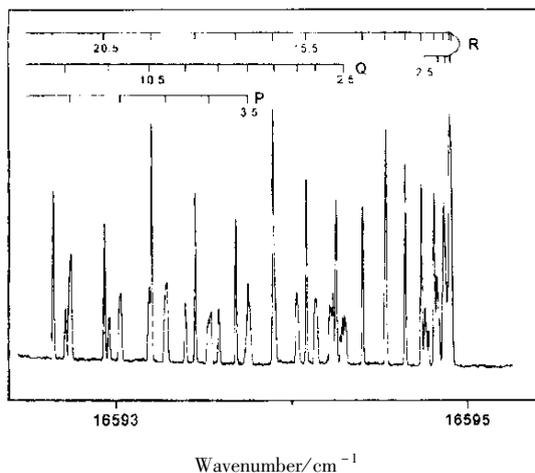


Fig.2 The(9 0) band of the [14.6]² Δ_{5/2} - X² Δ_{5/2} transition of NiI

spin of the metal atom. However, this is not the case in NiI. The fact is that we could not observe any hyperfine structure in the (v 0) bands with $v = 0 \sim 6$, which indicates that the hyperfine splitting can be confined to the higher vibrational levels of the [14.6]² Δ_{5/2} upper state^[8]. The rapid decrease in linewidth as J increases in a vibronic level suggests that the hyperfine splitting in the [14.6]² Δ_{5/2} state conforms to the Hund's Cases a_β coupling scheme^[10]. Fig. 3 shows the Q(3.5) line of the (9 0) band with hyperfine components well resolved.

A ² Δ state has two spin components, due to large spin-orbit interaction in NiI^[8], and only one substate, namely $\Omega = 5/2$, has been observed. For only one substate, rotational energy level is easily represented by the following expression,

$$F(J) = T_0 + B\mathcal{K}(J + 1) - DJ^2(J + 1)^2 \quad (1)$$

and the hyperfine Hamiltonian can be expressed by

$$\hat{H}_{\text{hfs}} = a\hat{L}_z + b\hat{I}\hat{S} + c\hat{L}_z\hat{S}_z \quad (2)$$

where B and D are the rotational constant and its centrifugal distortion, and the three terms in the hyperfine

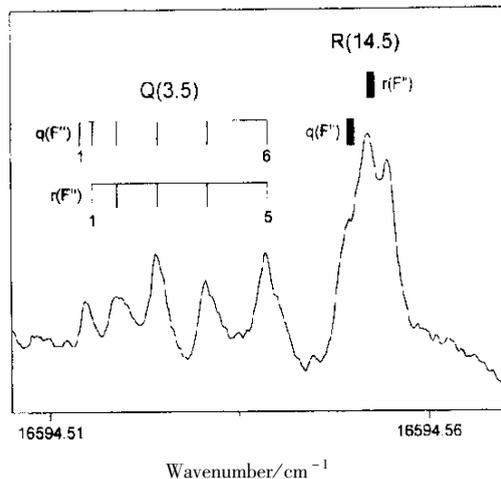


Fig. 3 High resolution spectrum of the Q(3.5) and R(14.5) lines of the (9 0) band of the [14.6]² Δ_{5/2} - X² Δ_{5/2} transition of ⁵⁸NiI showing resolved hyperfine components.

Hamiltonian a , b and c parameters are the same as those defined by Frosch and Foley^[15]. The ² Δ state can be appropriately described by the Hund's Case a_β coupling scheme^[10]. In such a coupling scheme, the grand total quantum number \mathbf{F} results from coupling the nuclear spin \mathbf{I} with the angular momentum \mathbf{J} , where $\mathbf{F} = \mathbf{I} + \mathbf{J}$. Matrix elements of a ² Δ state in Hund's Case a_β coupling scheme can be found in Azuma *et al*^[16]. The matrix elements of concern in this analysis are:

$$J\Omega F \langle \hat{H}_{\text{hfs}} \rangle J\Omega F = \Omega h/2\mathcal{K}(J + 1) \times [F(F + 1) - \mathcal{K}(I + 1) - \mathcal{K}(J + 1)] \quad (3)$$

$$J\Omega F \langle \hat{H}_{\text{hfs}} \rangle J - 1 \Omega F = \frac{h\sqrt{J^2 - \Omega^2}}{2J\sqrt{(2J + 1)(2J - 1)}} \times \sqrt{(J + I + F + 1)(F + J - 1)(J + I - F)(F + I - J + 1)} \quad (4)$$

where $h = a\Lambda + (b + c)\Sigma$, for the ² Δ_{5/2} substate (i. e. with $\Lambda = 1$ and $\Sigma = 1/2$) than $h = 2a + (b + c)/2$.

The observed rotation-hyperfine line positions were fit in two steps. Initially, line positions of the lower resolution spectrum were fit to obtain rotational constants and band origin and subsequently, a least squares fit with all the measured hyperfine transition lines was performed using the molecular constants determined from the lower resolution spectrum as initial parameters. In view of the fact that our free jet expansion source produced relatively low temperature NiI molecules, we observed only low J lines and it was legitimate to set the centrifugal distortion constant, D , to

zero in our least squares fit. The rotational constant of the ground state was set to the value determined by Tam *et al*^[8]. Due to the observation that the hyperfine structure arises only from the upper state, the ground state h constant was set to 0. The root-mean-squares error of our final least squares fit was 0.002 cm^{-1} , which is about the limit of our experimental accuracy. The molecular constants determined from our fit for the $v=9$ level of the $[14.6]^2\Delta_{5/2}$ state are as follows: $\nu_0 = 16594.680(1)$, $B = 0.067029(2)$, $h = 0.0066(2)$

Our analysis indicated that the hyperfine transition lines observed in the $(9,0)$ band were explainable in terms of the interaction between the magnetic moments of the unpaired electron and the iodine nucleus with the nuclear spin $I=5/2$. Using molecular constants reported by Tam *et al*^[8], we calculated the projected band origin, $\nu_0 = 16579.66 \text{ cm}^{-1}$ and the rotational constant, $B = 0.064922 \text{ cm}^{-1}$ for the $v=9$ level. Comparing with the experimentally determined values, we notice the observed band origin is shifted upward by 15 cm^{-1} and the observed B value is also larger by 0.0021 cm^{-1} , which suggest clearly that the whole $v=9$ level is perturbed. Together with our earlier measurements of the rotational structure of the $v=0\sim 6$ vibrational levels that show no noticeable hyperfine structure^[8], we can conclude comfortably that the hyperfine structure results from a perturbation between the $v=9$ level and a perturbing state with the large hyperfine structure. However, due to insufficient knowledge of the excited states of NiI, it is not possible at this stage to confidently characterize the perturbing state that gives rise to the observed hyperfine structure. The experimentally determined h value could be compared to the theoretical value estimated using *ab initio* results for atom to understand the various atomic contributions to the molecule. However, in view of the hyperfine structure, which arises from a perturbing state that has large hyperfine splitting and much about this perturbing state is not known, we would like to reserve the discussion of this parameter to a later stage when more information is available. In this situation, theoreticians performing high level *ab initio* calculations incorporating various spin-orbit interactions could compute the ener-

gy of low-lying excited states to provide a better understanding of the electronic structure and the nature of this perturbation in NiI. Further work concerning high vibrational levels of the $[14.6]^2\Delta_{5/2}$ state is necessary to characterize the perturbing state. We have work in progress to study other higher vibrational levels of the $[14.6]^2\Delta_{5/2}$ state to understand the hyperfine structure and the perturbation.

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References

- [1] Bauschlicher Jr C W, Walch S P, Langhoff S R. *Quantum Chemistry :The Challenge of Transition Metals and Chemistry*, NATO ASI Series C, edited by Veillard A. Reidel Dordrecht, 1986.
- [2] Langhoff S R, Bauschlicher Jr C W. *Annu. Rev. Phys. Chem.*, 1988, **39**:181
- [3] Hirota E. *Annu. Rep. Prog. Chem. Sect. C : Phys. Chem.*, 2000, **96**:95
- [4] Bernath P F. *Annu. Rep. Prog. Chem. Sect. C : Phys. Chem.*, 2000, **96**:177
- [5] Pinchemel B, Hirao T, Bernath P F. *J. Mol. Spectrosc.*, 2002, **215**:262
- [6] Krouti Y, Poclet A, Hirao T, Pinchemel B, Bernath P F. *J. Mol. Spectrosc.*, 2001, **210**:41
- [7] Leung J W H, Wang X, Cheung A S C. *J. Chem. Phys.*, 2002, **117**:3694
- [8] Tam W S, Leung J W H, Hu S M, Cheung A S C. *J. Chem. Phys.*, 2003, **119**:12245
- [9] Townes C H, Schawlow A L. *Microwave Spectroscopy*, Dover, New York, 1995.
- [10] Dunn T M. in *Molecular Spectroscopy :Modern Research*, Ed. by Narahari Rao K, Academic Press, New York, 1973
- [11] Merer A J. *Annu. Rev. Phys. Chem.*, 1989, **40**:407
- [12] Ran Q, Tam W S, Ma C, Cheung A S C. *J. Mol. Spectrosc.*, 1999, **198**:175
- [13] He S G, Tam W S, Leung J W H, Cheung A S C. *J. Chem. Phys.*, 2002, **117**:5764
- [14] Gerstenkorn S, Luc P. *Atlas der Spectra d absorption de la Molecule d'iode*, Editions du CNRS, Paris 1978; *Rev. Phys. Appl.*, 1979, **14**:791
- [15] Frosch R A, Foley H M. *Phys. Rev.*, 1952, **88**:1339
- [16] Azuma Y, Barry J A, *et al.* *J. Chem. Phys.*, 1989, **91**:1