



## Near infrared laser induced fluorescence spectroscopy of RuC

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## ARTICLE INFO

## Article history:

Received 3 December 2013

In revised form 8 January 2014

Available online 18 January 2014

## Keywords:

RuC

Electronic transition

LIF

Hyperfine structure

## ABSTRACT

Four electronic transition systems, namely, the  $[12.7]^3\Pi_2 - [0.1]^3\Delta_3$ , the  $[13.5]^3\Phi_3 - [0.9]^3\Delta_2$ , the  $[13.9]^3\Phi_4 - [0.1]^3\Delta_3$ , and the  $[13.9]^3\Pi_1 - [0.9]^3\Delta_2$  transitions of the ruthenium monocarbide molecule (RuC) were recorded and analyzed using laser vaporization/reaction supersonic free jet expansion and high resolution laser induced fluorescence spectroscopy. New vibrational bands of these transitions were observed and analyzed. Some of the observed bands show resolved hyperfine structure, which is caused principally by the unpaired  $5s\sigma$  electron interacting with large magnetic moment of the  $^{99}\text{Ru}$  and  $^{101}\text{Ru}$  nuclei with spin  $I = 5/2$ . The hyperfine width decreases rapidly as  $J$  increases suggesting that the hyperfine structure conforms to the Hund's case  $a_\beta$  coupling scheme. Accurate molecular constants for the seven RuC isotopic molecules were obtained and the hyperfine constants for the  $[0.1]^3\Delta_3$ ,  $[12.7]^3\Pi_2$  and  $[13.9]^3\Phi_4$  states of both  $^{99}\text{RuC}$  and  $^{101}\text{RuC}$  isotopes were also determined.

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## 1. Introduction

Spectroscopic study of the ruthenium monocarbide (RuC) molecule was first performed by Scullman and Thelin using a grating spectrograph and a King furnace molecular source [1,2]. Emission and absorption spectra of RuC were recorded in the near infrared and visible region. Due to the high temperature environment of the furnace, the RuC spectrum recorded was too congested for a detailed analysis and it was not possible to unambiguously determine the  $\Omega$  values involved in the observed transitions. Subsequently, Morse and coworkers [3–5] using resonant two-photon ionization (R2PI) spectroscopy and a laser ablation supersonic jet expansion (LA-SJE) molecular source investigated the electronic transition spectrum of RuC from the near infrared to the ultra-violet spectral region. Not only had they observed those bands recorded by Scullman and Thelin [1,2], numerous new transition bands were also recorded and analyzed. Rotational structure was generally resolved in their spectrum and the ground state of RuC was determined to be  $X^1\Sigma^+$  state. Accurate molecular constants for the ground and low-lying electronic states were reported. Using laser induced fluorescence spectroscopy and also the LA-SJE source, Steimle and coworkers [6,7] studied the Stark spectrum of RuC and reported the dipole moment of the ground and electronic states in the near infrared region. Recently, the same group performed pump/probe microwave-optical double resonance

(PPMODR) study of the ground  $X^1\Sigma^+$  state and reported the electric quadrupole coupling parameter for the  $^{101}\text{RuC}$  molecule [8]. Theoretical calculations on the electronic structure of RuC were first performed by Shim et al. [9], using the all-electron Hatree-Fock method at the valence configuration interaction level, predicted the energy order of 28 low-lying electronic states and also a  $^3\Delta$  state to be the ground state. However, in subsequent calculations using all-electron *ab initio* multi-configuration self-consistent-field (CASSCF) and multi-reference configuration interaction (MRCI) including relativistic corrections they have eventually correctly predicted the ground  $X^1\Sigma^+$  state [10]. Guo and Balasubramanian [11] using CASSCF and MRCI with relativistic effective pseudo potential (REPP) computed 29 low-lying electronic states of RuC with different spin multiplicities and spatial symmetries with energy separations less than  $38,000\text{ cm}^{-1}$ . The computed spectroscopic constants and dipole moments are generally in good agreement with experiment results.

In this paper, we report high-resolution spectroscopic study of the rotational and hyperfine structure of four electronic transition systems, namely the  $[12.7]^3\Pi_2 - [0.1]^3\Delta_3$ , the  $[13.5]^3\Phi_3 - [0.9]^3\Delta_2$ , the  $[13.9]^3\Phi_4 - [0.1]^3\Delta_3$ , and the  $[13.9]^3\Pi_1 - [0.9]^3\Delta_2$  transitions using laser vaporization/reaction supersonic free jet expansion and high resolution laser induced fluorescence (LIF) spectroscopy. For these transitions, due to the intense molecular source with enough number density all seven isotopic molecules from the ruthenium element with natural abundance were observed. In addition, resolved hyperfine structure of the  $^{99}\text{RuC}$  and  $^{101}\text{RuC}$  isotopic molecules has also been analyzed. Accurate molecular constants for

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the seven RuC isotopic molecules were obtained and the hyperfine constants for the  $[0.1]^3\Delta_3$ ,  $[12.7]^3\Pi_2$  and  $[13.9]^3\Phi_4$  states of both  $^{99}\text{RuC}$  and  $^{101}\text{RuC}$  isotopes were also determined.

## 2. Experimental

RuC molecule was produced by reacting laser ablated ruthenium atom with ethyl bromide ( $\text{C}_2\text{H}_5\text{Br}$ ) under supersonic free jet expansion. Our LIF spectrometer and the laser ablation system have been discussed in detail elsewhere [12]. Only a brief description of the experimental conditions is given here. Laser pulses of 1064 nm, 20 mJ from a Nd:YAG laser were focused onto the surface of a ruthenium rod to generate ruthenium atom, which was then allowed to react with a mixture of 2%  $\text{C}_2\text{H}_5\text{Br}$  in argon released from a pulsed valve to produce the RuC molecule. The operating cycle of the Nd:YAG laser-pulsed valve system was 10 Hz. The backing pressure at the pulsed valve was set to 5 atm and the background pressure of the vacuum chamber is around  $10^{-4}$  torr. Jet cooled RuC molecules were excited by a ring Ti-sapphire laser with short wavelength optics in the near infrared region. The ring laser was pumped by a diode pump solid state (DPSS) laser with the wavelength set at 532 nm. A lens system was used to collect the laser induced fluorescence signal, which was then sent through a monochromator, and detected by a photomultiplier tube (PMT). The monochromator was used as an optical filter for recording LIF spectrum and scanned to record the wavelength resolved fluorescence spectrum (WRF) of the RuC molecule. The Ti-sapphire laser wavelength was measured using a wavemeter with a repetition rate of 1 Hz and an accuracy of 1 part in  $10^7$ . The absolute accuracy of the measured line position is about  $\pm 0.002 \text{ cm}^{-1}$ .

## 3. Results and discussion

LIF spectrum of RuC in the near infrared region between 12,000 and  $14,060 \text{ cm}^{-1}$  has been studied. In a low resolution scan, 22 transition bands were observed; but, eventually, only 13 of them were further recorded under high resolution. Fig. 1 summarized the transitions identified and studied in this work, the thick lines represent transitions recorded under high resolution and studied. These bands belong to four electronic transition systems with the lower state originating from the meta-stable  $^3\Delta_i$  state, they are the  $[12.7]^3\Pi_2 - [0.1]^3\Delta_3$ ,  $[13.5]^3\Phi_3 - [0.9]^3\Delta_2$ ,  $[13.9]^3\Phi_4 - [0.1]^3\Delta_3$ , and  $[13.9]^3\Pi_1 - [0.9]^3\Delta_2$  transitions. Ruthenium element has seven naturally occurring isotopes and their abundance are as follows:  $^{96}\text{Ru}$ (5.5%),  $^{98}\text{Ru}$ (1.9%),  $^{99}\text{Ru}$ (12.7%),  $^{100}\text{Ru}$ (12.6%),  $^{101}\text{Ru}$ (17%),  $^{102}\text{Ru}$ (31.6%),  $^{104}\text{Ru}$ (18.7%). Except the  $^{99}\text{Ru}$  and  $^{101}\text{Ru}$  isotopes, with  $I = 5/2$ , all other isotopes have nuclear spin  $I = 0$ . In this work, the molecular source is very effective in producing the RuC molecule, we were able to observe LIF spectrum of all the seven RuC isotopic molecules. In addition, the hyperfine structures of the  $^{99}\text{RuC}$  and  $^{101}\text{RuC}$  isotopes have also been observed and analyzed, which arise from the interaction of the nuclear spin and the unpaired electrons in the valence orbital. The rotational assignment was straightforward and the observed line positions for individual isotopic molecule with no hyperfine structure were fit to a standard formula as follows [13]:

$$v = v_0 + B'J'(J' + 1) - D'[J'(J' + 1)]^2 - \left\{ B''J''(J'' + 1) - D''[J''(J'' + 1)]^2 \right\} \quad (1)$$

where the ' and '' refer to the upper and the lower states respectively. The least squares fits of the observed transition lines were performed in two stages for each RuC isotopic molecule. Initially each band was fit individually and, subsequently, all bands of the same transition system were merged together in the final fit to

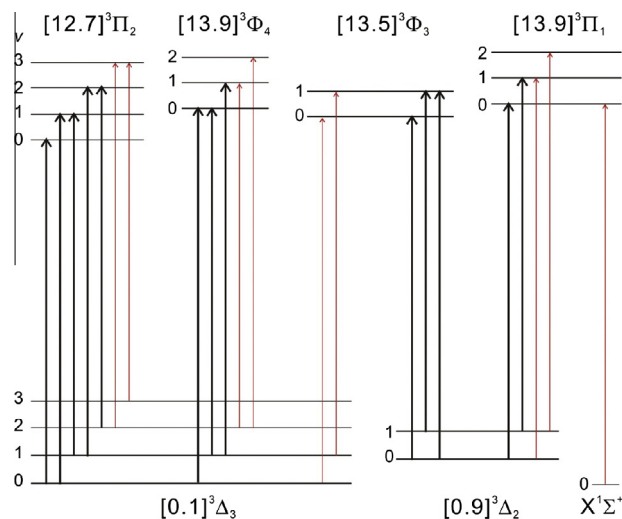


Fig. 1. Observed electronic transitions of RuC: rotationally resolved and analyzed bands are indicated with thick lines, and other observed transition bands but not analyzed are shown by red lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

determine only a single set of molecular constants for each vibrational level. The molecular constants determined for the  $[0.1]^3\Delta_3$ , the  $[0.9]^3\Delta_2$ , the  $[12.7]^3\Pi_2$ , the  $[13.5]^3\Phi_3$ , the  $[13.9]^3\Phi_4$  and the  $[13.9]^3\Pi_1$  states of the RuC isotopic molecules are listed in Tables 1–3. Electronic transition systems observed are discussed individually. A list of all the measured line positions of the observed bands of the four transition systems is available from the Journal archive.

### 3.1. The $[12.7]^3\Pi_2 - [0.1]^3\Delta_3$ transition and its hyperfine structure

Five vibrational bands have been analyzed for the  $[12.7]^3\Pi_2 - [0.1]^3\Delta_3$  transition system. Each vibrational band shows resolved P, Q and R branches and the first line of the branches are P(3), Q(3) and R(3) respectively, which confirms unambiguously that  $\Omega' = 2$  and  $\Omega'' = 3$  values for the electronic states involved. Furthermore, the P branches show greater intensity than the R branches, which is consistent with a  $\Lambda = -1$  transition. Fig. 2 shows the band head region of the (0,0) band, the transition lines of the isotopic molecules are crowded together under this condition, whereas in Fig. 3, which is the (1,0) band, transition lines of all the seven isotopic molecules are resolved. Table 1 listed the molecular constants for all the bands studied, it can be seen quickly that the isotopic shifts between the  $^{96}\text{RuC}$  and  $^{104}\text{RuC}$  for the (0,0) band is about  $-0.586 \text{ cm}^{-1}$  while this value for the (1,0) band is about  $4.073 \text{ cm}^{-1}$ . The equilibrium molecular constants obtained are listed in Table 4.

For (1,0) band of the  $^{99}\text{RuC}$  and  $^{101}\text{RuC}$  isotopic molecules, the low  $J$  lines of this band exhibit partially resolved hyperfine structure, which arises from the interaction of nuclear spin and unpaired electrons in the molecules. As shown in Fig. 3, it is easily noticed that the hyperfine structure decreases rapidly as  $J$  increases, which indicates the hyperfine interaction conforms to the Hund's case  $a_\beta$  scheme. The grand total quantum number  $F$  is the resultant from the coupling of the nuclear spin  $I$  with the total angular momentum  $J$  (i.e.,  $F = I + J$ ). In the spectrum, the molecular transitions with  $\Delta J = \Delta F = -1$  are expected to be strong. The assignment of the hyperfine components is straightforward. Since the hyperfine structure is dominated by the lower  $[0.1]^3\Delta_3$  state, it shows a nice pattern obeying the Landé interval rule [14], which suggests that the interval between successive components is proportional to the larger of their total angular momentum values (that is the separation is the largest for the highest  $F$  value). The

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