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Laser spectroscopy of the [17.9]4 – $X^3\Phi_4$ and [15.6]Ω – $X^3\Phi_4$ transitions of iridium monochloride (IrCl)

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ABSTRACT

Laser Induced Fluorescence (LIF) spectra of two electronic transitions, [17.9]4 – $X^3\Phi_4$ and [15.6]Ω – $X^3\Phi_4$, of IrCl have been obtained in a laser-ablation molecular beam source, at low resolution using a pulsed dye laser, and at high resolution using a single mode ring dye laser. The $^{193}Ir^{35}Cl$–$^{193}Ir^{37}Cl$ isotope shifts of the band heads in the low resolution spectra established the vibrational assignment of the 0-0, 1-0, 2-0 and 0-1 bands of the [17.9]4 – $X^3\Phi_4$ transition and the 0-0 and 1-0 bands of the [15.6]Ω – $X^3\Phi_4$ transition. High resolution spectra (linewidth $\sim$ 0.006 cm^{-1} FWHM) were obtained for the 0-0, 1-0 and 2-0 bands of the more intense [17.9]4 – $X^3\Phi_4$ transition. Rotational structure in the three bands of both $^{193}Ir^{35}Cl$ and $^{191}Ir^{35}Cl$ isotopologues was resolved and analyzed. The higher *J* rotational lines are observed to split into closely spaced doublets resulting from quadrupole hyperfine structure caused by the $I = 3/2$ nuclear spin in ^{191}Ir and ^{193}Ir. Examination of the spectra shows that the doublet separation of $\sim$0.008 cm^{-1} is similar to that observed in IrF (Linton et al., 2011) indicating that the quadrupole parameters, eQq_0, are similar in IrF and IrCl.

1. Introduction

In recent years, as part of a program in our laboratory at the University of New Brunswick (UNB) using laser spectroscopy to study the bonding properties of transition metals in small molecules, we have examined the spectroscopic properties of iridium (Ir)-containing molecules. Using the UNB laser ablation spectrometer, high-resolution spectra of IrF [1], IrH and IrD [2] and IrO [3] have been obtained and the electronic, vibrational and rotational structure analyzed. In addition, in collaboration with the group of T.C. Steimle at Arizona State University (ASU), we used the increased resolution of their laser ablation spectrometer to obtain a 5-fold improvement in resolution and (a) examine the hyperfine structure in IrF [4], IrH and IrD [5] and IrO [6] and (b) use the Stark effect to obtain the permanent electric dipole moment of IrF [7], and IrH [5]. In this article, as a continuation of our study of the Ir halides, we describe the first experiment, at UNB, to study the spectroscopy of iridium monochloride, IrCl.

Our previous study of an Ir – halide using the UNB apparatus [1] resolved the rotational structure of two transitions of IrF and showed that IrF, like CoF [8,9], has a $^3\Phi_4$ ground state. Hyperfine structure was not resolved but was observable as a broadening of the low *J* lines and a doubling of the higher *J* lines. The ASU experiments [4] resolved the hyperfine structure and the analysis showed that it originated primarily from the Ir atom ($I = 3/2$) with about a 5% contribution from the fluorine atom ($I = 1/2$).

The present work aims to follow the same pattern for IrCl as described above for IrF with the first experiment at UNB identifying the spectra and performing a rotational analysis to assign the electronic states, to be followed later by experiments at ASU to resolve the hyperfine structure and establish the electron configurations. The experiments described below first use a pulsed dye laser to scan the visible and near IR regions to obtain low resolution spectra in order to observe and identify IrCl bands. A cw ring dye laser is then used to obtain high resolution spectra of the bands observed in the low resolution spectra. The results are then compared with those of the other group 9 halides.

2. Experimental

The molecules were created in a pulsed laser ablation source where an iridium rod was ablated using the 3rd harmonic ultraviolet radiation from a Nd:YAG laser. The molecules were formed by reacting the vaporized Ir atoms with a 1% mixture of $CHCl_3$ in helium. For the low resolution survey scans, the molecular jet

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was excited approximately 5 cm downstream from the ablation source, using radiation from a pulsed dye laser with several dyes covering the region from 415 to 890 nm. A progression of strong bands, observed in the region 534–557 nm, was then studied at high resolution (FWHM ~ 0.006 cm^{-1} linewidth of strong unblended lines) using radiation from a CR699-29 ring dye laser operating in a single longitudinal mode with rhodamine 110 dye. The fluorescence was detected using a 0.25 m monochromator set at the laser wavelength and a photomultiplier. The spectra were calibrated using lines from the iodine atlas [10].

3. Results

3.1. Observation

Low resolution excitation spectra, obtained by scanning the pulsed laser through the visible and near infra-red regions, showed many bands. Dispersed fluorescence (DF) spectra, which were taken with the laser exciting each of the observed bands, showed progressions with two distinct vibrational frequencies. Excitation of most of the bands produced DFs with vibrational frequencies of ~1000 cm^{-1}, representative of IrC [11]. There were also six bands that we assigned to IrCl as the DFs showed vibrational progressions with spacings of ~400 cm^{-1}, which is typical of vibrational frequencies of transition metal chlorides [8,12–14]. The three most intense bands with heads at 534 nm, 545 nm, and 557 nm appear to form an upper state vibrational progression of an electronic transition and have been labeled as the 2-0, 1-0 and 0-0 bands. There was also a weak band at 570 nm which appears to be connected to the same band system. There were also two weaker IrCl bands in the red region at 626 nm and 640 nm. All the bands are red-degraded. Thus, we have observed two electronic transitions, which we have labeled the green and red systems, in the visible region. Fig. 1 shows 25 cm^{-1} segments of the pulsed laser excitation spectrum of each of the green system bands. Fig. 2 shows DFs that were obtained by setting the laser frequency to excite three of the four IrCl green system band heads in Fig. 1 (Fig. 2(a)–(c)) and both red system band heads (Fig. 2(d) and (e)). All show clear ground state vibrational progressions whose vibrational spacings are ~400 cm^{-1}. The DF from the 570 nm band is not shown as it was identical to that from the 0-0 band (Fig. 2(a)) of the green system and is therefore assigned as the 0-1 band of the green system.

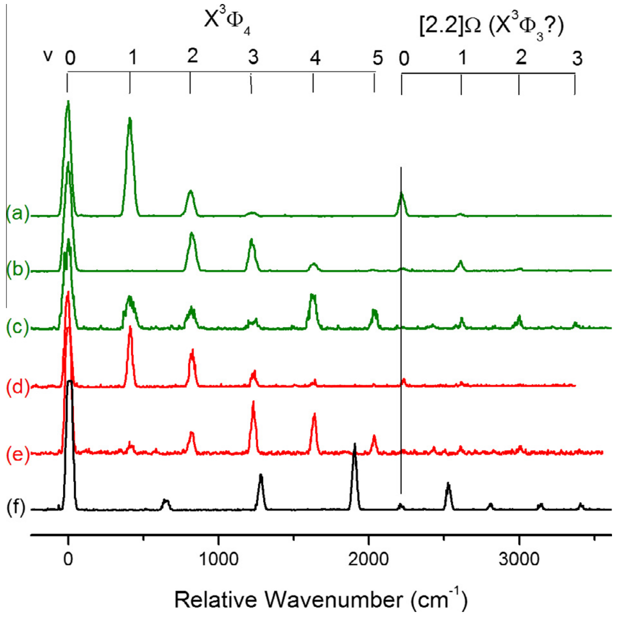

Fig. 2. Dispersed fluorescence spectra taken with the pulsed dye laser exciting band heads of the IrCl [17.9]4 – $X^3\Phi_4$ (green system) (a) 0-0 (b) 1-0 and (c) 2-0 bands, the IrCl [15.6]Ω – $X^3\Phi_4$ (red system) (d) 0-0 and (e) 1-0 bands, and (f) the IrF $A^3\Phi_4$–$X^3\Phi_4$ 1-0 band. Lower state vibrational progressions of the two lowest lying states, are labeled with their vibrational quantum numbers. The [2.2]Ω state at 2240 cm^{-1} is common to both IrCl and IrF and we believe this to be the $X^3\Phi_3$ spin–orbit component of the ground state.

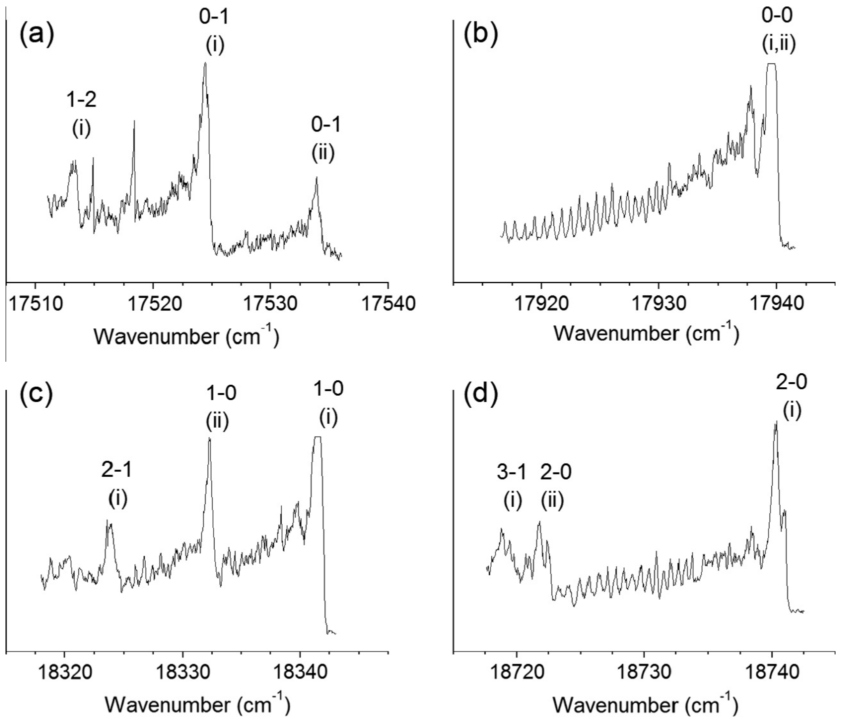

Fig. 1. 25 cm^{-1} segments of low resolution spectra showing the (a) 0-1 and 1-2, (b) 0-0, (c) 1-0 and 2-1, (d) 2-0 and 3-1 bands of the [17.9]4 – $X^3\Phi_4$ transition of IrCl. The band heads marked (i) and (ii) belong to the Ir^{35}Cl and Ir^{37}Cl isotopologues respectively.