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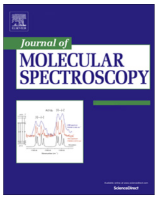

Hyperfine structure in the X8, A[19.1]9 and B[21.68]8 states of HoF and X8 and A[15.6]9 state of HoCl

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ABSTRACT

High resolution spectra of holmium monofluoride, HoF and holmium monochloride, HoCl, prepared in a laser ablation source, have been obtained using laser induced fluorescence. Spectra of the A[19.1]9–X8 0-0 and 1-0 and B[21.68]8–X8 0-0 bands of HoF and the A[15.6]9–X8 0-0 band of HoCl all show resolved hyperfine structure. Analysis of the spectra yielded magnetic hyperfine parameters, $h = 0.2240(5)$, 0.2210(6), 0.2177(6) and 0.2488(5) cm^{-1} for the X ($v = 0$), A ($v = 0$ and 1) and B ($v = 0$) states of HoF and 0.2355(32) and 0.2448(29) cm^{-1} for the X ($v = 0$) and A ($v = 0$) states of HoCl, respectively. The following quadrupole coupling constants were obtained for the above six states; $eQq_0(HoF) = -0.0874(67)$, $-0.0586(44)$, $-0.0579(56)$, $-0.0840(64)$ cm^{-1} and $eQq_0(HoCl) = -0.082(11)$, $-0.060(11)$ cm^{-1}. Comparison with previously determined values for HoO and HoS show that the ground state magnetic hyperfine structure in HoF and HoCl is entirely due to the Ho 4f electron and is consistent with the ground state, X8, configuration of $Ho^+\{4f^{10}(^5I_8)6s^2\}X^-$ (X = F, Cl). Calculations of the ground state magnetic, h(X8), and quadrupole, eQq_0(X8) hyperfine parameters from atomic hyperfine parameters are found to be consistent with the observed values for both molecules.

1. Introduction

Over the past three decades, in our laboratory at the University of New Brunswick (UNB), we have conducted an extensive series of experiments, using laser induced fluorescence (LIF) to study the spectroscopic properties of lanthanide-containing diatomic molecules. One of the primary goals is to determine the extent to which the lanthanide 4f electrons participate in the molecular bonding. Of the many spectroscopic parameters that contribute toward building an understanding of molecular properties, a study of hyperfine structure of molecules with unpaired nuclear spin is particularly valuable in elucidating finer details of the electron structure, electron configuration and bonding. Holmium (Ho) is a prime candidate among the lanthanides as it has a single isotope with nuclear spin $I = 7/2$ and a very large magnetic moment. An important portion of these studies has therefore been devoted to holmium-containing molecules, HoO [1–4], HoS [5,6] and the halides HoF [7,8] and HoCl [9,10]. For HoO and HoS, the eight hyperfine components of the rotational lines in the observed electronic transitions were well resolved even at the Doppler limited resolution (~900 MHz) in a Broida oven. The hyperfine structure in HoO [1,2] and HoS [6] was studied and confirmed that the low lying electronic states originate from the metal centered $Ho^{2+}(4f^{10}6s\ ^6I_{8.5})O^{2-}$ (or S^{2-}) configuration. The analysis led to determination of the relative contributions of the 4f and 6s electrons.

Rotationally resolved spectra of HoF, recorded on photographic plates, were first observed and analyzed by Robbins and Barrow [11]. They observed two electronic transitions, A–X in the 490–570 nm region and B–X from 450–490 nm. They were able to analyze several bands in the A–X system. The B–X transition was heavily perturbed and, although several bands were observed and assigned, only the 2-0 band could be rotationally analyzed. They suggested assignments of $\Omega = 9$, 8 and 8 for the A, B and X states, respectively. Using LIF techniques, we recorded many bands of the A–X system at higher resolution [7] and the analysis supported the previous Ω assignments. In a second LIF experiment [8], we examined the B–X region and observed and rotationally analyzed several bands which we assigned to three separate electronic transitions. Although hyperfine structure was not resolved at the Doppler limited resolution (~900 MHz) of the Broida oven, there was considerable broadening of the rotational lines, especially at low J, in some of the bands. The rotational lines of the band

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assigned as B–X 1-0 by Robbins and Barrow [11] showed considerable hyperfine broadening whereas the 2–0 band showed very little, indicating that the two bands belong to two different $\Omega = 8$–8 electronic transitions. As a result, the old B–X 1-0 band was reassigned as B[21.68]8–X8 0-0 and the 2-0 band was assigned as the 0-0 band of a new B′[21.65]8–X8 transition. A third $\Omega = 7$–7 transition was observed which did not involve the ground state and was labeled C[22.3]7–$X_2$7 [8].

LIF experiments on HoCl yielded three electronic transitions, A[15.6]9–X8 [9], B[17.7]8–X8 and C[19.3]9–X8 [10]. The A and B states in HoCl are analogous to those in HoF whereas the C states with $\Omega = 9$ in HoCl and $\Omega = 7$ in HoF are obviously different. The rotational structure in HoCl is much more congested than in HoF and the low J lines in all three transitions show broadening due to hyperfine structure. Dispersed fluorescence (DF) experiments showed the existence of several unassigned electronic states between 900 and 2500 cm^{-1} above the ground state of HoCl [10] and between 4300 and5500 cm^{-1} above the ground state of HoF [8].

There have been extensive theoretical calculations of the properties of all the lanthanide halides by Kaledin et al. [12] using ligand field theory (LFT) in which the molecular electronic states are derived from the states of the lanthanide ion, Ln^+, perturbed by the field of the halide ion, X^- (X = F, Cl, Br, I). Among other properties, they calculated the energies for the lowest-lying states of all the lanthanide halides. They showed that the ground and low lying electronic states of the halides arise from three possible Ln^+ configurations $4f^{N-1}6s^2$, $4f^N6s$, $4f^{N-1}5d6s$. For the Holmium halides, the ground configuration was predicted to be $\text{Ho}^+(4f^{10}6s^2)X^-$ leading to an $\Omega = 8$ ground state. In a Hund's case c coupling scheme, the total angular momentum of the f-electron core, $\boldsymbol{J_c} = \boldsymbol{L_c} + \boldsymbol{S_c}$ is coupled with that of the s-electrons, $\boldsymbol{j_s} = \boldsymbol{l_s} + \boldsymbol{s_s}$ to give a total atomic angular momentum, $\boldsymbol{J_a} = \boldsymbol{J_c} + \boldsymbol{j_s}$. This interacts with the ligand field of the halide ion, F^- or Cl^- which couples it to the internuclear axis to give molecular states with angular momentum $\boldsymbol{\Omega}$ which is the projection of $\boldsymbol{J_a}$ on the internuclear axis. For HoF and HoCl, the Ho^+ f^{10} core gives a ${}^5I_8$ ground state with $L_c = 6$, $S_c = 2$, $J_c = 8$. The closed s^2 shell with $j_s = 0$ adds no angular momentum, leaving the ground state of Ho^+ as ${}^5I_8$ with $J_a = 8$ whose projection on the internuclear axis gives a ground state with $\Omega = J_a = 8$. The lowest state of each of the other low lying configurations, $f^{11}s$ and $f^{10}ds$ would have $\Omega = 0$ [12]. The observation of $\Omega = 8$ ground states for HoF and HoCl thus establishes the ground state configuration as $f^{10}s^2$ in agreement with the LFT predictions. Dolg and Stoll [13] calculated the properties of the lanthanide fluorides using pseudopotentials and also predicted a $f^{10}s^2$ ground state configuration for HoF.

As the hyperfine structure was not resolved in the Broida oven spectra, we used the laser ablation source at UNB to obtain higher resolution spectra and resolve the hyperfine structure in the A–X and B–X transitions of HoF and the A–X transition of HoCl. In the following sections we describe the analysis of the hyperfine structure and discuss the insights provided by the hyperfine parameters into the finer details of the electron configuration and bonding in the ground state.

2. Experimental details

The molecules were created in a pulsed laser ablation source where a holmium rod was ablated using the 3rd harmonic ultraviolet radiation from a Lumonics HY-400 Nd:YAG laser. The molecules were formed by reacting the vaporized Ho atoms with a 5% mixture of SF_6 in helium for HoF or 0.8% $CHCl_3$ vapor in helium for HoCl. Approximately 5 cm downstream from the ablation source, the molecular jet was excited using radiation from a CR699-29 ring dye laser operating in a single longitudinal mode. For the HoF A–X transition, the laser was scanned using coumarin 521 dye in the region of 524 nm for the 0-0 band and 509 nm for the 1-0 band. For the HoF B–X 0-0 band, S420 dye was used in the region of 460 nm. For the HoCl A–X 0-0 band, DCM dye was used in the 640 nm region. The fluorescence was detected using a 0.25 m monochromator set at the laser wavelength and a photomultiplier. The HoF and HoCl A–X transitions were calibrated using iodine lines [14] while the HoF B–X 0-0 band was calibrated using uranium lines [15] from a hollow cathode lamp.

3. Results

3.1. Observations

In the ablation source, the spectra that had shown broad lines with unresolved hyperfine structure in the Broida oven [8–10] now showed clearly resolved hyperfine structure in some of the branches. All the rotational assignments were already known from our previous work [7–10] so the assignment of the F quantum numbers for the hyperfine lines was straightforward. Spectra were obtained for the HoF A[19.1]9–X8 0-0 and 1-0 and B[21.68]8–X8 0-0 bands and for the HoCl A[15.6]9–X8 0-0 band.

Fig. 1 shows the start of the Q branch of the (a) B–X 0-0 (b) A–X 0-0 and (c) A–X 1-0 bands of HoF. Hyperfine structure is clearly resolved in each of the bands with each rotational transition split into 8 main components due to the $I = 7/2$ nuclear spin of the Ho nucleus. The A–X 0-0 band is, by far, the most intense. The hyperfine structure in the R branch was resolved only for the lowest J transitions which are in the region of the band head where the spectra are overlapped and impossible to assign. In the higher J region away from the band head, the R branch transitions appeared as single lines. This is clearly seen in Fig. 1(b) where the R branch transitions, R(31)–R(36), appear as intense narrow lines with no observable structure. For the Q and P branches, the hyperfine structure was well resolved with the Q branch considerably more intense than the P branch (there are no P branch transitions in the spectral regions shown in Fig. 1). The detailed hyperfine structure in the Q branch is demonstrated in Fig. 2 which shows the structure of the Q(16) transition. As well as the eight main components with $\Delta F = \Delta J = 0$ (q type), there are weaker satellite lines with $\Delta F = +1$ (r type) at higher wavenumber and $\Delta F = -1$ (p type) at lower wavenumber. The r type lines are seen in Fig. 2 to be well resolved whereas the p type lines are not resolved and appear as a single broad line. There were several upper state perturbations, starting at $J' \sim 17$, in which the hyperfine structure was irregular.

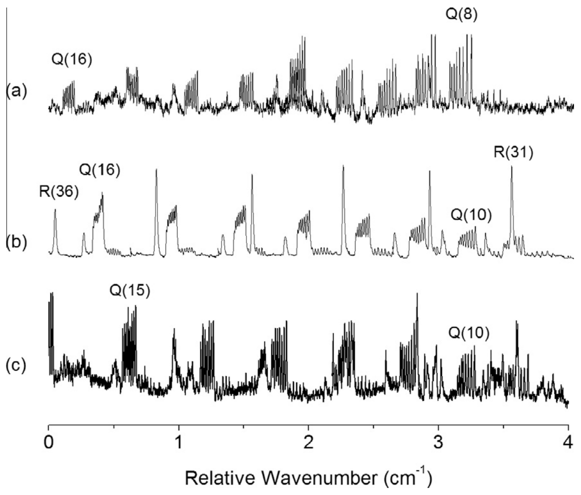

Fig. 1. Spectra showing hyperfine structure in the low J transitions in the Q branch of the B[21.68]8–X8 0-0, (b) A[19.1]9–X8 0-0 and (c) A[19.1]9–X9 1-0 bands of HoF.