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Note

The observation of hot bands in the 288 nm system of the $FeCl_2$ radical

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Abstract

The 288 nm band system of $FeCl_2$ has been recorded with a sample produced in a warmed, free-jet expansion at moderately high resolution (with a linewidth of 0.28 cm^{-1}). Under these conditions, several hot bands are observed involving excitation of the symmetric and antisymmetric stretching vibrations. The wavenumbers determined as a result for $FeCl_2$ in its ground $^5\Delta_{g,4}$ state are $\nu_1'' = 352.34(12)$ cm^{-1} and $\nu_3'' = 504.8(2)$ cm^{-1}. No hot, sequence bands in the bending vibration ν_2'' were observed. The most likely explanation is that the wavenumber for ν_2 is essentially the same in both the electronic states involved (88 cm^{-1}). Additional strong hot bands are observed that are unrelated to the previously assigned electronic transitions; they appear to emanate from a low-lying electronic state of $FeCl_2$.

Keywords: Electronic spectroscopy; Transition metal compounds; Iron dichloride; Hot bands; Vibrational intervals

The electronic transition of $FeCl_2$ at 288 nm has been assigned as $\Omega = 5$–4, emanating from the lowest spin component of the $^5\Delta_g$ ground state [1]. In two recent publications, we reported vibrational parameters for $FeCl_2$ in its ground electronic state [2] and in the excited state [1]. The molecule was formed in a sample at low vibrational temperatures (<100 K) in a free-jet expansion, and no hot bands were observed in the excitation spectrum [1]. The least-squares fits of the ground-state vibrational bands observed in dispersed emission measurements [2] were supplemented by measurements of some hot band features in an early study of the spectrum recorded at higher vibrational temperature by Ashworth and Brown [3]. Since the calibration of this spectrum (by means of the optogalvanic effect) was slightly less reliable than expected, we have made a new recording of the spectrum and obtained more accurate vibrational parameters.

The experimental setup is the same as that described in the previous publications [1,2], except that we have reintroduced the "light shield" [4] that was designed to prevent blackbody radiation from the heated nozzle swamping the photomultiplier tube. The light shield consists of a stainless steel disc mounted beyond the alumina nozzle. It contains a small hole of diameter 4 mm, through which the molecular beam emerges. In previous experiments with the light shield [4,5], the sample was formed at an increased rotational temperature, possibly due to backscatter from the molecular beam striking the edge of the small exit hole. In the present experiments, effective warming was observed when a 25 mm spacer was inserted before the light shield, such that the 4 mm hole in the shield was 40 mm from the nozzle exit hole.

A portion of the warm vibrationally resolved excitation spectrum of $FeCl_2$ is shown in Fig. 1, and at higher resolution (with a linewidth of 0.28 cm^{-1}) in Fig. 2. The spectrum was calibrated against the accurately determined positions of the *R*-branch heads of bands recorded at rotational resolution [1]. As usual, the dye laser scanning system was found to be highly linear in wavelength.

The vacuum wavenumbers of the origins of assigned vibronic bands observed in excitation [1] and dispersed emission [2], and the hot bands assigned from the present experiments (1^0_2, 3^0_1, 1^0_1, $1^1_0 3^0_1$, 1^1_1, $1^0_2 3^0_1$, 1^2_1, $1^0_1 3^1_0$, 1^3_1) are given in Table 1. For vibronic bands that have not been recorded at rotational resolution, the position of the band origin has

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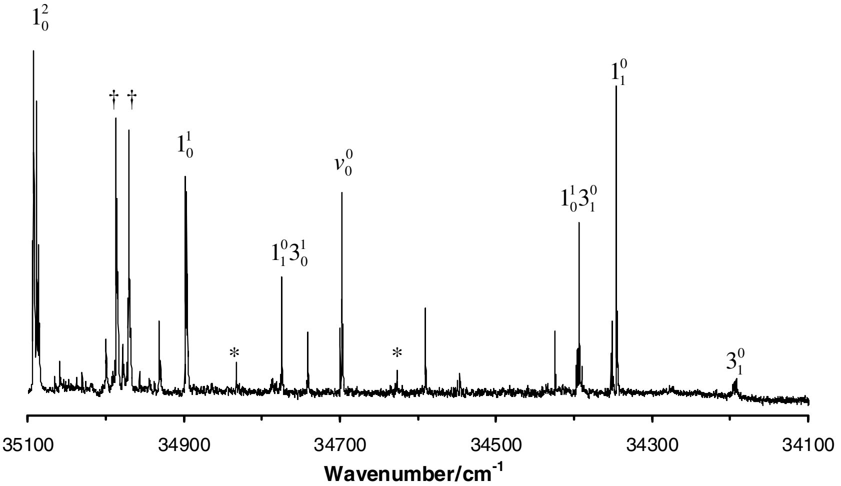

Fig. 1. A portion of the vibrationally resolved spectrum of the $FeCl_2$ band system at 288 nm, recorded under "warm" conditions. The bands marked with asterisks have been tentatively assigned to transitions between the second lowest spin components in both electronic states ($\Omega = 4$–3). The bands marked with daggers are thought to correspond to a strong, separate transition from a low-lying electronic state of $FeCl_2$.

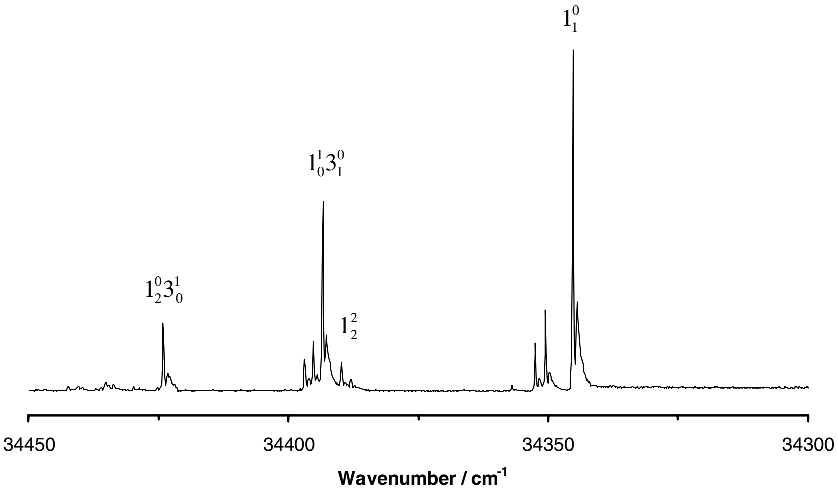

Fig. 2. A portion of the "warm" vibrationally resolved spectrum of the $FeCl_2$ band system at 288 nm, recorded under "warm" conditions with a laser linewidth of 0.28 cm^{-1}. The chlorine isotope splittings are clearly visible in these bands.

been calculated from the measured position of the *R*-branch head in the vibrationally resolved spectrum, using rotational constants predicted from Ref. [1]. The wavenumbers for the bands observed in dispersed emission are quoted to the nearest integer and are estimated to be accurate to ±10 cm^{-1}. The table also includes residuals from a least-squares fit to vibrational parameters for the totally symmetric stretching vibration, v_1. The results of the fit are given in Table 2. Table 3 lists known vibrational wavenumbers for a number of transition metal dichlorides. This table first appeared in our recent publication concerning the $CoCl_2$ radical [6]. It has been amended to include the results from the present work.

The observation of two progressions in the symmetric stretching vibration in the excitation spectrum has been explained [1] in terms of allowed transitions to an electronic state of *gerade* symmetry, and vibronically induced transitions (through the antisymmetric stretching vibration) to a nearby state of *ungerade* symmetry. The resultant value of excited-state v_3 was tentatively declared to be 429.5 cm^{-1}. The assignment was said to be speculative because the differences between the values of v_1 and v_3 in the ground and excited states appeared to be inconsistent with a valence force field model. In the warm spectrum reported here, a progression in excited state v_1 based on the 3^0_1 hot band is observed; the value determined for v_3 of 504.8(2) cm^{-1} is in good agreement with that determined by dispersed fluorescence spectroscopy [2] but considerably more accurate and precise. The observation of this complementary progression built on one quantum of v_3 in the ground state reinforces our assignments of the vibronically induced progression referred to as Progression B in Ref. [1]. Additional support comes from the observation of $1^0_1 3^1_0$ and $1^0_2 3^1_0$ hot bands.