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Velocity modulation spectroscopy of molecular ions I: The pure rotational spectrum of $TiCl^+$ ($X^3\Phi_r$)

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Abstract

The pure rotational spectrum of the $TiCl^+$ ion in its $X^3\Phi_r$ ground state has been measured in the frequency range 323–424 GHz, using a combination of direct absorption and velocity modulation techniques. The ion was created in an AC discharge of $TiCl_4$ and argon. Ten, eleven, and nine rotational transitions were recorded for the $^{48}Ti^{35}Cl^+$, $^{48}Ti^{37}Cl^+$, and $^{46}Ti^{35}Cl^+$ isotopomers, respectively; fine structure splittings were resolved in every transition. The rotational fine structure pattern was irregular with the $\Omega = 4$ component lying in between the $\Omega = 2$ and 3 lines. This result is consistent with the presence of a nearby $^3\Delta_r$ state, which perturbs the $\Omega = 2$ and 3 sub-levels, shifting their energies relative to the $\Omega = 4$ component. The data for each isotopomer were analyzed in a global fit, and rotational and fine structure parameters were determined. The value of the spin–spin constant was comparable to that of the spin–orbit parameter, indicating a large second-order spin–orbit contribution to this interaction. The bond length established for $TiCl^+$, $r_0 = 2.18879(7)$ Å, is significantly shorter than that of TiCl, which has $r_0 = 2.26749(4)$ Å. The shorter bond length likely results from a $Ti^{2+}Cl^-$ structure in the ion relative to the neutral, which is thought to be represented by a Ti^+Cl^- configuration. The higher charge on the titanium atom shortens the bond.

Keywords: Spectroscopy; Ions; Rotational

1. Introduction

The technique of velocity modulation (VM) has traditionally been used only in optical and infrared ion spectroscopy (i.e., 600–17 000 cm^{-1}) [1,2]. However, it is not limited to these spectral regions and has recently been shown to work at much longer wavelengths. Stephenson and Saykally [3] have demonstrated that velocity modulation can be applied at terahertz frequencies, and Savage, Apponi, and Ziurys [4,5] extended the scope of VM to the millimeter/sub-millimeter regime. At the longer wavelengths, the VM technique is not quite as powerful as in the infrared, for example, because the lines are somewhat undermodulated [3,4]. Nevertheless, the ion selectivity of this method is still a major advantage in eliminating neutral signals [4].

The first molecule studied with the mm/sub-mm VM instrument in the Ziurys group was SH^+ [5]. The measurement of the pure rotational spectrum of this open-shell ion demonstrated the potential of the spectrometer system to preferentially detect such species. Naturally obtaining the rotational spectrum of other ionic species using this instrument is of interest, in particular metal-containing compounds. One such ion is $TiCl^+$.

Titanium chloride cation has been the subject of various studies over the past 15 years. It was observed initially by Balfour and Chandrasekhar [6] in 1990, who measured P-branch bandheads from 559 to 564 nm and assigned the spectrum as a $^3\Pi$–$X^3\Delta$ transition. Following this work, Kaledin et al. [7] used ligand field theory (LFT) to calculate the electronic states of $TiCl^+$.

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Their computations indicated that a $^3\Phi_r$ term was the ground state, and therefore these authors suggested that the transition observed by Balfour and Chandrasekhar was the $[17.9]^3\Delta_r$–$X^3\Phi_r$ system. Kaledin and Heaven [8] subsequently confirmed this assignment experimentally using direct laser absorption methods, and determined preliminary spectroscopic constants for the $^3\Delta$ and ground $^3\Phi$ states, as well. At the same time, Focsa et al. [9] used laser absorption/velocity modulation techniques to also measure the $[17.9]^3\Delta_r$–$X^3\Phi_r$ band of $TiCl^+$ with 0.005 cm^{-1} resolution, establishing effective rotational, spin–orbit, and spin–spin parameters for both states. These authors also suggested that the $\Omega = 4$ spin–orbit component in the $X^3\Phi_r$ state was perturbed relative to the other two Ω components. Kaledin and Heaven [10] then conducted further measurements of the $[17.9]^3\Delta_r$–$X^3\Phi_r$ and $[17.9]^3\Delta_r$–$(1)^3\Delta_r$ transitions with associated LFT calculations, which predicted nearby $^3\Sigma$ and $^3\Pi$ states. The most recent work is by Focsa et al. [11,12] and Focsa and Pinchemel [13]. In the Focsa et al. [11] study, the $[17.9]^3\Delta_r$–$X^3\Phi_r$ ($v = 0$ and 1) and the $[17.9]^3\Delta_r$–$A^3\Delta_r$ systems were measured. Here, the $\Omega = 2$ and 3 ladders of $TiCl^+$ in its $X^3\Phi_r$ ($v = 0$ and 1) and $A^3\Delta_r$ ($v = 0$) states were found to interact with each other, while the $\Omega = 4$ sub-level ($X^3\Phi_r$) remained free of any perturbations [11]. An analysis combining the data of the $X^3\Phi_r$ ($v = 0$ and 1) and $A^3\Delta_r$ ($v = 0$) states was then performed to establish "deperturbed" spectroscopic constants for these states [11]. Focsa et al. [12] additionally performed density functional theory (DFT) and LFT calculations on TiCl and $TiCl^+$, and determined that the ionization potential of titanium chloride was ~7.06 eV.

In this study, we report the first measurement of the pure rotational spectrum of $TiCl^+$ in its $X^3\Phi_r$ ($v = 0$) state. The ion was synthesized in an AC discharge of $TiCl_4$. All three spin components were observed for the isotopomers $^{48}Ti^{35}Cl^+$, $^{48}Ti^{37}Cl^+$, and $^{46}Ti^{35}Cl^+$. This study was conducted using a combination of velocity modulation (for ion selectivity) and direct absorption (for sensitivity in scanning). Here, we present our results, spectral analysis, and a discussion of the data.

2. Experimental

The pure rotational spectrum of $TiCl^+$ was measured using the velocity modulation spectrometer of the Ziurys group, which has been described in detail elsewhere [4]. Briefly, the instrument consists of a radiation source, gas cell, and detector. Gunn oscillators/Schottky diode multipliers are used to generate frequencies between 65 and 650 GHz. The reaction chamber is a single-pass glass cell containing ring discharge electrodes, and a cooling jacket chilled to −65 °C by methanol. The radiation is launched from a scalar feedhorn and is propagated through the system quasi-optically using a series of Teflon lenses, two of which seal off the ends of the gas cell. The detector is an InSb hot electron bolometer, and the system is under computer control.

Titanium chloride cation was created in an AC discharge of gas-phase $TiCl_4$ and argon. The strongest signals of $TiCl^+$ occurred using 20 mTorr of Ar and less than 1 mTorr of $TiCl_4$; this mixture produced a bright blue–white plasma that dominated the normal purple discharge glow from the argon. The discharge was modulated at a rate of 20 kHz with a power level of 200 W at 600 Ω.

Signals arising from $TiCl^+$ were initially found by recording scans 100 MHz in coverage. First, scans were taken in source modulation mode with 2f detection for a higher signal-to-noise ratio. If lines were present, the data were then retaken in velocity modulation mode to select those signals arising from ions. Precise rest frequencies were obtained by averaging scans 5 MHz wide, taken in increasing and decreasing frequency, using source modulation. Typically, 1–4 scan pairs were needed to obtain a sufficient signal-to-noise ratio. Gaussian profiles were fit to the line shapes to obtain the center frequency and line width, which varied from 1.0 to 1.4 MHz from 323 to 424 GHz. The experimental accuracy is estimated to be ±40 kHz.

3. Results and analysis

The transitions frequencies of $^{48}Ti^{35}Cl^+$ and $^{48}Ti^{37}Cl^+$ were initially predicted using the effective rotational parameters of Focsa et al. [9,11]. These constants were sufficiently accurate that signals from these ions were found within 100 MHz of the predictions. Previous estimates of rotational constants for $^{46}Ti^{35}Cl^+$ did not exist, so these were obtained from the ^{48}Ti isotopomer by scaling by molecular mass.

The observed rotational transitions of the three $TiCl^+$ isotopomers are listed in Table 1. Ten, eleven, and nine transitions were measured for $^{48}Ti^{35}Cl^+$, $^{48}Ti^{37}Cl^+$, and $^{46}Ti^{35}Cl^+$, respectively. As shown in the table, each rotational transition is split into three fine structure components due to spin–orbit/spin–spin coupling and is labeled by the quantum number Ω. As is also evident in Table 1, the pattern of the spin–orbit splittings deviates considerably from a typical case (a) coupling scheme. For a given rotational transition, the $\Omega = 2$ and 3 components are both shifted to significantly higher frequency as compared to the $\Omega = 4$ line, such that the ordering of these features in increasing frequency is $\Omega = 2$, 4, and 3, not $\Omega = 2$, 3, and 4 as in a "normal" Φ_r state. This pattern can be seen in Fig. 1, which displays spectra of the $J = 37 \rightarrow 38$ transition of $^{48}Ti^{35}Cl^+$ near 395 GHz (top panel), and the $J = 36 \rightarrow 37$ transition of $^{46}Ti^{35}Cl^+$ near 392 GHz (bottom panel). These