

Will Ballard
Mawhorter
Physics 199RA
16 May 2019

Summary of “Molecular Ion Spectroscopy” Independent Study

This spring, I participated in an independent study entitled “Molecular Ion Spectroscopy” under the guidance of Professor Richard J. Mawhorter. The primary objective of this research assistantship was to calculate the line frequencies of the three $J = 1 \leftarrow 0$ hyperfine transitions in the ground vibrational states of $^{179}\text{HfF}^+$ and $^{177}\text{HfF}^+$.

There is particular experimental interest in these two molecular ions due to the ongoing search for the electron’s electric dipole moment (eEDM) at the Joint Institute for Laboratory Astrophysics (JILA) in Boulder, CO. The team at JILA, led by Dr. Eric Cornell, has selected HfF^+ as its molecule of choice to probe the electron for a non-zero EDM. Although the Cornell group has initially fixed its attention on $^{180}\text{HfF}^+$, recent theoretical papers demonstrate that the odd isotopologues also provide optimal testing grounds for investigating parity non-conserving (PNC) effects [2]. For this reason, Professor Mawhorter and I believe that accurate predictions of the frequencies of the aforementioned transitions in $^{179}\text{HfF}^+$ and $^{177}\text{HfF}^+$ would be of experimental value to the team at JILA.

I utilized the spectral analysis package SPCAT/SPFIT to predict the line frequencies of interest. In order for this program to calculate predictions, one must provide it with the correct parameters for the given molecule. In the case of $^{179}\text{HfF}^+$ and $^{177}\text{HfF}^+$, these parameters consist of B (rotational constant), D (centrifugal distortion constant), and eQq_0 (electric quadrupole hyperfine structure constant). In addition, we spent some time considering the importance of lambda doubling parameters but concluded that they were not relevant to our study of HfF^+ .

Unlike other eEDM candidates such as $^{180}\text{HfF}^+$, there has not been a comprehensive study on the odd isotopologues of HfF^+ , and therefore the relevant parameters are not readily available. As a result, I spent the majority of the semester calculating B and D for $^{179}\text{HfF}^+$ and $^{177}\text{HfF}^+$. As for eQq_0 , I relied on theoretical calculations of this parameter by Dr. Alexander Petrov, one of Professor Mawhorter’s collaborators at the St. Petersburg Nuclear Physics Institute [3]. To calculate B and D for $^{179}\text{HfF}^+$ and $^{177}\text{HfF}^+$, I took advantage of the known scaling of rotational parameters across the various isotopologues of a given molecule. In particular, I calculated B and D for $^{180}\text{HfF}^+$ by analyzing data from a comprehensive spectroscopic study of this molecule performed by the group at JILA in 2012 [4]. This exercise provided a valuable introduction to the use of statistical weights in the analysis of experimental data. Once I arrived at values for these parameters for $^{180}\text{HfF}^+$, I was in theory ready to calculate B and D for $^{179}\text{HfF}^+$ and $^{177}\text{HfF}^+$ by means of the scaling relationships and produce our desired predictions.

However, prior to inputting our new parameters into SPCAT for HfF^+ , Professor Mawhorter and I felt it was important to evaluate the accuracy of this scaling technique in a familiar system: HfO . Using past spectroscopic studies of HfO , I was able to apply the same

scaling technique to $^{180}\text{Hf}^{16}\text{O}$ and predict the three $J = 1 \leftarrow 0$ hyperfine transitions in the ground vibrational states of $^{179}\text{Hf}^{16}\text{O}$ and $^{177}\text{Hf}^{16}\text{O}$ [5,6]. Since these transitions have been measured to a high degree of precision, I could then compare my predicted values with the experimental values. I found that the differences between these values were on the order of tens of kHz. Therefore, we gained greater confidence that our predictions for $^{179}\text{HfF}^+$ and $^{177}\text{HfF}^+$ — using the same technique — would achieve reasonable accuracy.

Having completed my analysis of HfO , I was at last ready to input my calculated values for B and D , as well as the theoretical eQq_0 values from Dr. Petrov, into SPCAT. My predictions for the the three $J = 1 \leftarrow 0$ hyperfine transitions in the ground vibrational states of $^{179}\text{HfF}^+$ and $^{177}\text{HfF}^+$ are shown in Table I.

TABLE I. Calculated hyperfine frequencies for the $J = 1 \leftarrow 0$ transition of $^{177}\text{HfF}^+$ and $^{179}\text{HfF}^+$.

| $^{177}\text{HfF}^+ (I = 7/2)$ | | $^{179}\text{HfF}^+ (I = 9/2)$ | |
|--------------------------------|--------------------------|--------------------------------|--------------------------|
| Hyperfine component | Calculated frequency MHz | Hyperfine component | Calculated frequency MHz |
| $5/2 \leftarrow 7/2$ | 18 533.428 | $7/2 \leftarrow 9/2$ | 18 508.704 |
| $9/2 \leftarrow 7/2$ | 18 412.768 | $11/2 \leftarrow 9/2$ | 18 408.110 |
| $7/2 \leftarrow 7/2$ | 18 007.878 | $9/2 \leftarrow 9/2$ | 17 968.116 |

In closing, this independent study has served as an invaluable introduction to the analytical and quantitative methods of molecular spectroscopy. In addition to becoming more familiar with the SPCAT/SPFIT package, I also developed my ability to dissect recent publications and make sense of graduate-level texts on molecular spectroscopy. Lastly, I hope that these skills will prove useful in the coming weeks, as I participate in Professor Mawhorter's research in Hannover, Germany as a SURP recipient.

-
- [1] W. Cairncross, et al., Phys. Rev. Lett. **119**, 153001 (2017).
 - [2] L. V. Skripnikov et al., Rev. A **99**, 012517 (2019).
 - [3] A. N. Petrov et al., Evaluation of CP violation in HfF^+ , Phys. Rev. A **98**, 042502 (2018).
 - [4] K. C. Cossel et. al, Chem. Phys. Lett. **546**, **1** (2012).
 - [5] R. D. Suenram et al., J. Chem. Phys. **92**, 4724 (1990).
 - [6] A. Lessari et al., J. Chem. Phys. **117**, 9651 (2002).