

Hyperfine spectrum of RbCl

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(Received 20 March 2006; accepted 16 May 2006; published online 27 June 2006)

The molecular beam electric resonance technique has been used to conduct a high precision examination of the hyperfine spectrum of the four isotopomers of RbCl. Coupling constants for the nuclear electric quadrupole interactions, the spin-rotation interactions, the tensor and scalar spin-spin interactions, and a rubidium nuclear octupole interaction, and their dependence on vibrational and rotational states have been determined. The dominant interaction, the rubidium nuclear electric quadrupole interaction, shows a small shift with substitution of the chlorine isotope. © 2006 American Institute of Physics. [DOI: 10.1063/1.2212413]

I. INTRODUCTION

In a recent paper¹ we reported a study of the hyperfine spectrum of ⁶LiI that showed a shift in the iodine nuclear electric quadrupole interaction constant when the lithium isotope was changed. We here report a similar study of the four isotopomers of RbCl, in which we determine the nuclear electric quadrupole and spin-rotation interactions of both Rb and Cl, the tensor and scalar spin-spin interactions, and a marginally significant rubidium magnetic octupole interaction (see Ref. 2 for the definition we use for the octupole interaction). We have measured a total of 210 transitions, with a precision that ranges between 0.5 and 250 Hz, including vibrational states $v=0-4$ and rotational states $J=1-7$. From these we have fit for the coefficients that describe the dependence of the interactions on v and J , including the four isotopomers together by using the expected dependence on atomic masses and magnetic moments.

As in LiI,¹ we find a small shift in the rubidium nuclear electric quadrupole coupling constant (NQCC) as the chlorine isotope is changed from 35 to 37. This shift measures 41.4 ± 5.6 Hz for the ⁸⁵Rb and an insignificant 16 ± 585 Hz for the ⁸⁷Rb.

The apparatus used and the theory of the hyperfine interactions will not be discussed here since they have been previously described.¹⁻⁶

II. DATA AND ANALYSIS

The pure hyperfine spectrum of RbCl is spread over the frequency range from zero to roughly 17 MHz. By adjusting the voltage applied to the quadrupole lenses we can optimize the spectrometer for any rotational state well beyond the $J=1-9$ we have included. We have not taken data on all possible lines for higher J values because the spectra become

very dense, making it difficult to identify and deconvolute overlapping lines. This is also the reason for concentrating on higher frequency lines, where the spectrum is more spread out. The lines for different vibrational states occur at different frequencies and can be identified by the sequences of nearly equally spaced lines with intensities dropping off in accordance with the Boltzmann factor for the vibrational energy differences.

An example of the data from a single run as fitted is shown in Fig. 1. It includes two lines from each of the ⁸⁵Rb³⁵Cl and ⁸⁵Rb³⁷Cl isotopomers, as split into their Stark components. Since the two pairs have the same quantum numbers, their Stark patterns are quite similar, with the intensities clearly showing the abundance ratio for the two Cl isotopes. The side lobes on the second highest frequency component are enhanced by its being overdriven. The quality of the fit indicates that our understanding of the quantum mechanical transition process is excellent. This particular run took over 5 days of running time, averaging 5000 passes back and forth through the 1100 bins of the frequency range. For each isotopomer shown, the transitions are from $v=0$,

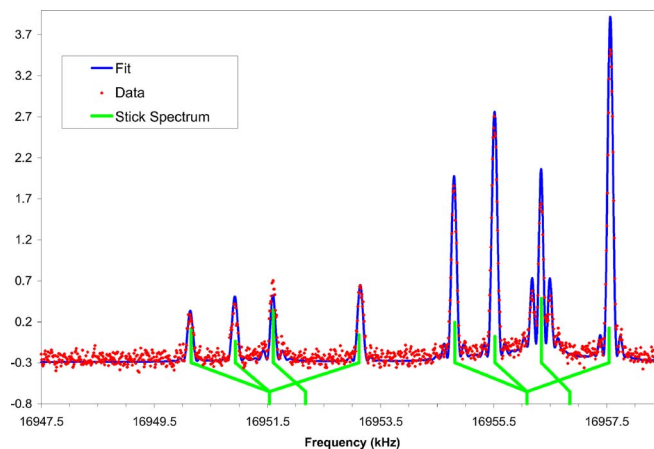


FIG. 1. Fitted data showing an example of two Stark-split pairs of lines from ⁸⁵Rb³⁷Cl (lower frequency pair) and ⁸⁵Rb³⁵Cl (higher frequency pair). The quantum numbers of the transitions are $v=0$, $J=2$, $F_1=1/2$, $F=1, 2$ to $F_1=7/2$, $F=2$. The relative abundance of the two Cl isotopes is evident in the line intensities of the two pairs.

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TABLE I. Molecular constants determined from fit (all frequencies in kHz).

i, j	$^{85}\text{Rb}^{35}\text{Cl}$ constants	$^{87}\text{Rb}^{35}\text{Cl}$ constants	$^{85}\text{Rb}^{37}\text{Cl}$ constants	$^{87}\text{Rb}^{37}\text{Cl}$ constants
Rubidium quadrupole (eQq_{Rbij})				
0,0	$-52\,884.585 \pm 0.028$	$-25\,587.2 \pm 1.2$	$-52\,884.543\,8 \pm 0.005\,6$	$-25\,587.2 \pm 1.2$
1,0	413.482 ± 0.074	199.387 ± 0.036	405.494 ± 0.073	195.508 ± 0.035
2,0	-1.597 ± 0.050	-0.768 ± 0.024	-1.536 ± 0.048	-0.738 ± 0.023
3,0	$-0.006\,0 \pm 0.009\,6$	$-0.002\,9 \pm 0.004\,6$	$-0.005\,7 \pm 0.009\,1$	$-0.002\,7 \pm 0.004\,4$
0,1	$0.080\,21 \pm 0.000\,74$	$0.038\,55 \pm 0.000\,36$	$0.077\,14 \pm 0.000\,72$	$0.037\,06 \pm 0.000\,34$
1,1	$-0.000\,75 \pm 0.000\,29$	$-0.000\,36 \pm 0.000\,14$	$-0.000\,71 \pm 0.000\,27$	$-0.000\,34 \pm 0.000\,13$
Chlorine quadrupole (eQq_{Clij})				
0,0	838.25 ± 0.046	838.226 ± 0.029	660.55 ± 0.16	660.55 ± 0.18
1,0	-138.17 ± 0.11	-137.71 ± 0.11	-106.752 ± 0.086	-106.379 ± 0.086
2,0	1.447 ± 0.068	1.438 ± 0.067	1.097 ± 0.051	1.089 ± 0.051
3,0	-0.059 ± 0.013	-0.059 ± 0.012	$-0.044\,0 \pm 0.009\,4$	$-0.043\,6 \pm 0.009\,3$
0,1	$-0.032\,36 \pm 0.000\,90$	$-0.032\,15 \pm 0.000\,89$	$-0.024\,52 \pm 0.000\,68$	$-0.024\,35 \pm 0.000\,67$
1,1	$-0.000\,14 \pm 0.000\,87$	$-0.000\,14 \pm 0.000\,86$	$-0.000\,11 \pm 0.000\,65$	$-0.000\,11 \pm 0.000\,64$
Rubidium spin-rotation (c_{Rbij})				
0,0	$0.394\,76 \pm 0.000\,77$	$1.328\,9 \pm 0.002\,6$	$0.379\,66 \pm 0.000\,74$	$1.277\,7 \pm 0.002\,5$
1,0	$-0.003\,8 \pm 0.001\,9$	$-0.012\,6 \pm 0.006\,5$	$-0.003\,5 \pm 0.001\,8$	$-0.011\,9 \pm 0.006\,1$
2,0	$0.000\,0 \pm 0.001\,3$	$0.000\,1 \pm 0.004\,3$	$0.000\,0 \pm 0.001\,2$	$0.000\,1 \pm 0.004\,0$
3,0	$0.000\,01 \pm 0.000\,25$	$0.000\,040 \pm 0.000\,84$	$0.000\,010 \pm 0.000\,23$	$0.000\,030 \pm 0.000\,76$
0,1	$0.000\,004 \pm 0.000\,014$	$0.000\,014 \pm 0.000\,047$	$0.000\,004 \pm 0.000\,013$	$0.000\,013 \pm 0.000\,043$
Chlorine spin-rotation (c_{Clij})				
0,0	$0.394\,3 \pm 0.001\,2$	$0.391\,6 \pm 0.001\,2$	$0.315\,63 \pm 0.000\,99$	$0.313\,43 \pm 0.000\,98$
1,0	$0.003\,1 \pm 0.002\,7$	$0.003\,0 \pm 0.002\,7$	$0.002\,4 \pm 0.002\,1$	$0.002\,4 \pm 0.002\,1$
2,0	$-0.004\,0 \pm 0.001\,7$	$-0.004\,0 \pm 0.001\,6$	$-0.003\,1 \pm 0.001\,3$	$-0.003\,1 \pm 0.001\,3$
3,0	$0.000\,66 \pm 0.000\,30$	$0.000\,65 \pm 0.000\,29$	$0.000\,5 \pm 0.000\,22$	$0.000\,49 \pm 0.000\,22$
0,1	$0.000\,019 \pm 0.000\,018$	$0.000\,018 \pm 0.000\,018$	$0.000\,014 \pm 0.000\,014$	$0.000\,014 \pm 0.000\,014$
Tensor spin-spin (c_{3ij})				
0,0	$0.033 \pm 0.001\,1$	$0.112\,0 \pm 0.003\,6$	$0.027\,51 \pm 0.000\,89$	$0.093\,2 \pm 0.003\,0$
1,0	$-0.000\,7 \pm 0.002\,3$	$-0.002\,2 \pm 0.007\,6$	$-0.000\,5 \pm 0.001\,8$	$-0.001\,8 \pm 0.006\,2$
2,0	$-0.000\,17 \pm 0.000\,76$	$-0.000\,6 \pm 0.002\,6$	$-0.000\,14 \pm 0.000\,61$	$-0.000\,5 \pm 0.002\,0$
Scalar spin-spin (c_{4ij})				
0,0	$0.026\,51 \pm 0.000\,63$	$0.089\,8 \pm 0.002\,1$	$0.022\,07 \pm 0.000\,52$	$0.074\,8 \pm 0.001\,8$
1,0	$-0.001\,3 \pm 0.001\,3$	$-0.004\,5 \pm 0.004\,2$	$-0.001\,1 \pm 0.001\,0$	$-0.003\,7 \pm 0.003\,4$
2,0	$-0.000\,61 \pm 0.000\,41$	$-0.002\,1 \pm 0.001\,4$	$0.000\,49 \pm 0.000\,33$	$-0.001\,6 \pm 0.001\,1$
Rubidium Octupole ($e\omega\Omega_{\text{Rbij}}$)				
0,0	$0.000\,202 \pm 0.000\,095$	0 ± 0	$0.000\,202 \pm 0.000\,095$	0 ± 0

$J=2$, $F_1=1/2$, $F=1,2$ to $F_1=7/2$, $F=2$. The three Stark components of the lower frequency triplet for each belong to $M_F=0, \pm 1$, and ± 2 , and the higher frequency singlet belongs to $M_F=\pm 1$, the $M_F=0$ component being forbidden.

The results of the fits for the observed lines are listed in tables filed with EPAPS.⁸ The Stark-corrected line frequencies are shown in the ‘‘Measured’’ column, along with our estimates for their one-sigma uncertainties.

The frequencies of the four isotopomers are fitted together to determine the molecular constants that are listed in Table I, with the frequencies predicted by the fitted constants shown in the ‘‘Predicted’’ column of the data tables. The values of the constants for the $^{85}\text{Rb}^{35}\text{Cl}$ isotopomer are used as the fitted parameters, with the other three isotopomers calculated from these using the expected dependence on B_e/ω_e and the known nuclear moments. In order to account for possible isotopomer shifts as well as refined values for the nuclear quadrupole moment ratios for the two Rb iso-

topes and the two Cl isotopes, eight additional parameters were included in the fit. These are (1) the ratio of the nuclear quadrupole moments of the two Rb isotopes, (2) the ratio of the quadrupole moments of the two Cl isotopes, [(3)–(5)] the possible shifts in the $i, j=0,0$ terms of the rubidium NQCC for the other three isotopomers, and [(6)–(8)] the possible shifts in the $i, j=0,0$ terms of the chlorine NQCC for the other three isotopomers. This procedure effectively means that the $i, j=0,0$ terms of both NQCCs are independent for all four isotopomers, while the nuclear moment ratios are determined from the other terms.

The question of which parameters to include in the fit is significant. One can certainly not include parameters for which the data give no information. For example, it would be meaningless to include any $i, j=3,0$ terms if there were no observations of vibrational states beyond $v=2$. The singular value decomposition method of fitting we used provides information about whether the parameters are determined by

the data. Beyond that simple consideration, however, there is the more subtle matter of whether the measurement uncertainty is larger than any reasonable range of the parameter value itself. We have included several parameters in our fit whose values came out to be not significantly different from zero. Forcing these to be zero and removing them from the fit would tighten up the fits of the other parameters. We believe it is appropriate to include them because we do not have reason to expect them to be small compared with their uncertainty, and the resulting larger uncertainties in the others are probably realistic. In the absence of a theoretical explanation of the isotopomer shifts in the NQCC values, we have retained the full freedom of all the $i, j=0, 0$ terms to avoid imposing any prejudice on the values.

The reduced χ value for the fit is about 2.0. This indicates that the parameters selected come close to fitting the data, but not quite within the range that would be expected on purely statistical grounds. As is customary in hyperfine spectroscopy, there are apparently small systematic errors that are not fully accounted for. Our quoted one-sigma uncertainties in the fitted parameters have been scaled by the χ value to take this into account.

III. RESULTS

In addition to the hyperfine coupling constants listed in Table I, our fit has given values of the nuclear electric quadrupole moments of the two Rb isotopes as $Q(^{87}\text{Rb})/Q(^{85}\text{Rb})=0.483\,837\pm 0.000\,022$, and for the two Cl

isotopes as $Q(^{37}\text{Cl})/Q(^{35}\text{Cl})=0.787\,82\pm 0.000\,24$. The Rb ratio is consistent with the ratio determined for the RbF molecule, as described in an accompanying paper,⁷ but the latter is more precise by an order of magnitude. Again, a successful theory for the isotopomer anomaly described in Ref. 1 would make it possible to extract more precise information for both molecules.

ACKNOWLEDGMENTS

The authors would like to thank the National Science Foundation for supporting this work as well as the Hardy Research Fellowship and St. Olaf College.

¹J. Cederberg, J. Nichol, E. Frodermann *et al.*, J. Chem. Phys. **123**, 134321 (2005).

²J. Cederberg, D. Olson, A. Nelson, D. Laine, P. Zimmer, M. Welge, M. Feig, T. Höft, and N. London, J. Chem. Phys. **110**, 2431 (1999).

³D. Olson, J. Cederberg, P. Soulen, H. Ton, K. Urberg, and B. Mock, J. Mol. Spectrosc. **166**, 158 (1994).

⁴J. Cederberg, J. Ward, G. McAlister, G. Hilke, E. Beall, and D. Olson, J. Chem. Phys. **111**, 8396 (1999).

⁵J. Cederberg, D. Olson, J. Larson, G. Rakness, K. Jarausch, J. Schmidt, B. Borovsky, P. Larson, and B. Nelson, Phys. Rev. A **57**, 2539 (1998).

⁶J. Cederberg, D. Olson, P. Soulen, K. Urberg, H. Ton, T. Steinbach, B. Mock, K. Jarausch, P. Haertel, and M. Bresnahan, J. Mol. Spectrosc. **154**, 43 (1992).

⁷J. Cederberg, E. Frodermann, H. Tøllerud, K. Huber, M. Bongard, J. Randolph, and D. Nitz, J. Chem. Phys. **124**, 244304 (2006), preceding paper.

⁸See EPAPS Document No. E-JCPA6-125-008625 for the tables of measured line frequencies. This document can be reached via a direct link in the online article's HTML reference section or via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>).