

Nuclear electric quadrupole moments of Rb from the hyperfine spectrum of RbF

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The molecular beam electric resonance technique has been used to examine the hyperfine spectrum of RbF. The Rb nuclear electric quadrupole interaction, the spin-rotation interactions, and tensor and scalar spin-spin interactions have been measured for both Rb isotopes, including their dependence on vibrational and rotational states. Transition frequencies have been determined to a precision of better than 1 Hz in many cases. The magnetic interactions in the two isotopomers are consistent with what is expected from the known masses and magnetic dipole moments. In the case of the Rb nuclear electric quadrupole interaction, adjustments have been made for a small isotopomer shift, and for the ratio of the effective nuclear electric quadrupole moments, $Q(^{87}\text{Rb})/Q(^{85}\text{Rb}) = 0.483\,830\,1 \pm 0.000\,001\,8$. The effective quadrupole interaction includes a pseudoquadrupole interaction that may be significant at this level of precision, but cannot be distinguished experimentally. © 2006 American Institute of Physics. [DOI: 10.1063/1.2212414]

I. INTRODUCTION

The technique of molecular beam spectroscopy is a very precise method of measuring molecular hyperfine interactions. In this paper we report our measurements for both isotopomers of RbF. We have measured a total of 153 transitions for $^{85}\text{Rb}^{19}\text{F}$ and 108 for $^{87}\text{Rb}^{19}\text{F}$, with a precision that ranges between 0.3 and 50 Hz, including vibrational states $v=0-6$ and rotational states $J=1-10$. From these we have fitted for the coefficients that describe this dependence, including the two isotopomers together, by using the expected dependence on atomic masses and magnetic moments.

The Rb nuclear electric quadrupole coupling constant (NQCC) consists of two factors, written as eQq , where Q is the moment of the nucleus and q is the field gradient produced by the rest of the molecule. In principle, the ratio of the $i, j=0, 0$ term of the NQCC for the two isotopomers would be the ratio of the nuclear electric quadrupole moments of the two isotopes of Rb, because at the equilibrium distance the field gradients should be independent of the isotope located there.

One problem with this is that we cannot experimentally distinguish between the true nuclear quadrupole interaction and a pseudoquadrupole (PSQ) interaction that arises from the perturbation of the atomic orbitals by the magnetic mo-

ment of the nucleus. This PSQ is possibly larger than the experimental uncertainty we have been able to achieve for RbF.

A second problem is suggested by our recently reported observation of a shift (Ref. 1) in the NQCC of one nucleus when the isotope of the other is changed. Until theoretical calculations of the PSQ and this shift can be made and corrections applied for them, we cannot extract a value for the nuclear moment ratio that takes full advantage of our experimental precision. Therefore we report here only the experimentally determined values of the expansion coefficients and a value of the nuclear moment ratio based on the higher terms of the vibration-rotation expansion.

The details of the theory and the techniques used for the experiment and analysis will not be discussed here since they have been described previously.¹⁻⁶

II. DATA AND ANALYSIS

The pure hyperfine spectrum of RbF is spread out over the frequency range from zero up to nearly 23 MHz. By adjusting the voltage applied to the quadrupole lenses, we can optimize the spectrometer for any rotational state from $J=1$ to well beyond the $J=10$ that we have included. The difficulty with the higher rotational states is that the spectrum becomes quite congested, with overdriven lower J transitions being particularly difficult to deconvolute when they overlap with the higher J transitions. The lines for different vibrational states simply 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.

The 2 m long transition plates in our spectrometer give a linewidth of 100–200 Hz that fits nicely to a Rabi line shape averaged over a velocity distribution that we have calculated

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Data Fitted with Common Stark Amplitudes

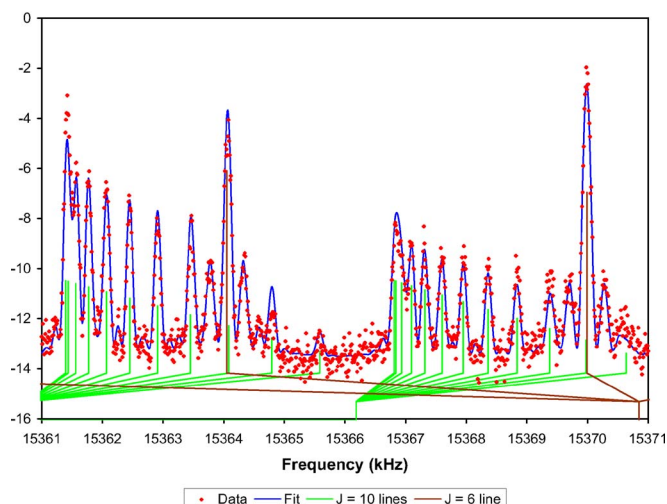


FIG. 1. Fitted data showing an example of a pair of Stark-split $J=10$ lines overlapping with a $J=6$ line. The vertical scale is in arbitrary units, proportional to the number of molecules thrown out of the beam by the transition.

from the dimensions of the rods forming the quadrupole lenses. The pure hyperfine transitions violate the familiar $\Delta J = \pm 1$ selection rule of infrared and microwave spectroscopies, but by using a combination of dc and rf fields of sufficient size, we can achieve nearly complete saturation of the transitions. These second order transitions follow a $\Delta F = 0, \pm 1, \pm 2$ selection rule. In our configuration the dc and rf

fields are parallel so that there is a $\Delta M_F = 0$ selection rule. It is the strong-field Stark effect that determines whether a hyperfine state is focused or defocused by the lenses. The close match of our experimental lines to the theory makes it possible for us to determine line frequencies to a small fraction of the linewidth, and also deconvolute overlapping lines.

The dc and rf fields needed to produce the transitions also give rise to a Stark splitting of the levels, which is a function of the sum of the squares of the dc and rf (rms) fields. For some transitions these shifts can be small compared to the linewidth, but are rarely negligible compared to our fitted precision. For this reason we need to correct for the Stark shifts in order to achieve the full precision of the experimental data. This, in turn, requires that we know the fields with reasonable accuracy. The dc field is fairly straightforward to determine, but the rf field is more problematic because of standing wave effects in the cables and the plates themselves. A rf probe located on the plates gives a useful measurement, but still does not tell us what the effective average of the field is over the length of the plates. We have turned to the molecules themselves to tell us what the effective field is, by using fields that are just large enough to fully resolve the Stark components of each line and then fitting for the rf amplitude that corresponds to this splitting.

An example of such a fit is shown in Fig. 1. Here the solid curve uses just ten fitting parameters: a baseline (which happens to be negative for this run), a root frequency and one amplitude describing each of the three transitions, and

TABLE I. Molecular Constants Determined from Fit (all in kHz).

i, j	^{85}RbF constants		^{87}RbF constants	
	Rubidium quadrupole (eQq_{Rbij}) ^a			
0,0	-70 739.184 9	$\pm 0.003 7$	-34 225.75	± 0.13
1,0	796.780 2	$\pm 0.007 2$	384.695 4	$\pm 0.003 5$
2,0	-5.164 3	$\pm 0.003 6$	-2.488 2	$\pm 0.001 7$
3,0	0.027 05	$\pm 0.000 48$	0.013 01	$\pm 0.000 23$
0,1	0.191 337	$\pm 0.000 035$	0.092 186	$\pm 0.000 017$
1,1	-0.002 111	$\pm 0.000 032$	-0.001 015	$\pm 0.000 015$
	Rubidium spin-rotation (c_{Rbij})			
0,0	0.497 668	$\pm 0.000 037$	1.679 49	$\pm 0.000 12$
1,0	-0.008 695	$\pm 0.000 073$	-0.029 28	$\pm 0.000 25$
2,0	0.000 069	$\pm 0.000 035$	0.000 23	$\pm 0.000 12$
3,0	-0.000 001 0	$\pm 0.000 004 5$	-0.000 003	$\pm 0.000 015$
	Fluorine spin-rotation (c_{Fij})			
0,0	10.638 7	$\pm 0.000 38$	10.594	$\pm 0.000 38$
1,0	-0.112 54	$\pm 0.000 54$	-0.111 83	$\pm 0.000 53$
2,0	0.000 7	$\pm 0.000 13$	0.000 7	$\pm 0.000 13$
	Tensor spin-spin (c_{3ij})			
0,0	0.797 57	$\pm 0.000 29$	2.702 92	$\pm 0.000 99$
1,0	-0.007 54	$\pm 0.000 4$	-0.025 5	$\pm 0.001 4$
2,0	0.000 111	$\pm 0.000 097$	0.000 37	$\pm 0.000 33$
	Scalar spin-spin (c_{4ij})			
0,0	0.237 08	$\pm 0.000 24$	0.803 46	$\pm 0.000 80$
1,0	-0.002 00	$\pm 0.000 32$	-0.006 8	$\pm 0.001 1$
2,0	-0.000 057	$\pm 0.000 075$	-0.000 19	$\pm 0.000 25$

^a X_{ij} denotes the coefficient in the expansion $X(v, J) = \sum_{i,j} X_{ij} (v+1/2)^i [J(J+1)]^j$.

three parameters relating to the rf field amplitude averages and the velocity distribution. A slightly better fit is obtained if the amplitudes of the different Stark components of each transition are fitted independently, but this shows how well it works even with common amplitudes.

The results of the fits for the observed lines are listed in tables filed with the Electronic Physics Auxiliary Publication Service (EPAPS).⁸ The Stark-corrected line frequencies are shown in the “Measured” column, along with our estimates of their one-sigma uncertainties. These are fitted, both isotopes 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. Independent runs on many of the transitions are listed (and fitted) as separate lines in the tables. While this greatly expands the size of the tables, it does serve to show the consistency that we obtain in the measurements. The values of the constants for ⁸⁷RbF are not fitted independently from those for ⁸⁵RbF (except for the nuclear electric quadrupole interaction), but are calculated using the expected dependence on B_e/ω_e and the known nuclear magnetic moments. The $i, j=0, 0$ term of NQCC is fitted separately for the two isotopomers in order to allow for an isotopomer shift like that reported in Ref. 1. The value of this shift as determined from fitting our data turned out to be an insignificant -0.004 ± 0.125 kHz, but allowing for it in the fit still has a realistic effect on the uncertainties of the other parameters. The nuclear moment ratio was determined as a separate fitting parameter, which effectively means that it is determined by the higher expansion terms. This ratio, $Q(^{87}\text{Rb})/Q(^{85}\text{Rb})=0.483\,830\,1 \pm 0.000\,001\,8$, is consistent

with, but an order of magnitude more precise than the value obtained for RbCl as reported in an accompanying paper.⁷

The fitting of the molecular constants to these line frequencies has been done utilizing the singular value decomposition method. This method separates the fitted parameters and the associated errors. The reduced χ value for the fit is about $\chi=1.40$. The molecular parameters resulting from this fit are listed in Table I, with the one-sigma uncertainties scaled by χ to account for the fact that it is a bit larger than 1.

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⁸See EPAPS Document No. E-JCPSA6-125-009625 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>).