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Spectroscopy of the NaH, NaD, KH, and KD $X^1\Sigma^+$ ground state by laser excited fluorescence in a high frequency discharge

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By laser excited fluorescence of the hydrides obtained in a discharge, the ground state vibrational levels of NaH, NaD, KH, and KD have been observed up to $v'' = 15, 20, 14,$ and 16 , respectively, instead of $v'' = 8, 2, 4,$ and 4 by conventional spectroscopy. Experimental values of $G_{v''}$, $B_{v''}$, and $D_{v''}$ are obtained. Spectroscopic parameters and RKR potential curves are calculated. In NaH and NaD, a comparison can be made with *ab initio* calculations.

INTRODUCTION

In alkaline hydrides, the internuclear distance in the ground $X^1\Sigma^+$ and in the first excited $A^1\Sigma^+$ states differ by a large amount, and the Franck-Condon principle allows excitation of many A vibrational states from the first X vibrational states which are most highly populated in these experiments. The A state has been studied by conventional spectroscopy¹⁻⁸ up to energies higher than 50% of the probable dissociation energy. However, the complexity of the spectra has prevented spectroscopists from analyzing the bands which decay to high v'' levels of the ground state.

In two recent experiments, the hydrides LiD⁹ and CsH¹⁰ have been obtained by heating the metal and the gas in an oven and have been excited by coincident lines of an argon ion laser. The selective excitation of a rovibrational level simplifies the spectra, making possible the identification of lines decaying to vibrational X states up to 60% (CsH) or 80% (LiD) of the dissociation energy. Spectroscopic constants and approximate dissociation energies were derived from these spectra.

We have made a similar study of the NaH, NaD, KH, and KD $X^1\Sigma^+$ ground states. In our experiment, the metal and the gas are excited by a high frequency discharge¹¹ which greatly increases the quantity of hydride obtained in the ground state, making it possible to obtain intense fluorescent light by dye-laser excitation.

The observed spectra consist of series of R and P doublets from the $v'J'$ excited level to several v'' , $J'' = (J' - 1)$ and $(J' + 1)$ ground state levels. They provide the rotational constants $B_{v''}$ and the vibrational energies $G_{v''}$. These values may be fitted to polynomials in $(v'' + \frac{1}{2})$, which are extrapolated to obtain an indication about the dissociation energy. By associating the values of $B_{v''}$ and $G_{v''}$, RKR potential curves may be calculated.

EXPERIMENT

The apparatus is very similar to that previously used in our laboratory to study hydrides and especially NaH.¹¹ A piece of metal of about 2 cm³ is placed at the end of a tube filled with H₂ or D₂ at about 1 Torr pressure. To obtain the hydride, a high frequency discharge provided by a magnetron at 2400 MHz, 150 mA is applied. The laser excitation and the observation are

made through windows carried by side tubes and heated to prevent deposition of metal. The cell may be operated for about 30 h after which all the metal has passed through the observation region. The cell has to be cleaned with water and refilled.

In the discharge, several reactions may provide the hydride in the ground electronic state: metal + atomic hydrogen, metal + vibrationally excited molecular hydrogen, or metal in the second resonant excited 2P level + molecular hydrogen. As the hydride is a stable molecule, it may deposit on the walls but its vapor pressure in thermal equilibrium is too small for the fluorescence to be observed: when the discharge is turned off the laser fluorescence disappears after a few ms.

We use an AVCO C 5000 Å N₂ laser at 150 Hz, to supply 10 ns 100 kW pulses, to pump a dye laser made in our laboratory which provides 0.2 Å linewidth.

The wavelengths may be measured within 0.1 Å with a Jobin-Yvon THR monochromator with 2.6 Å/mm dispersion which operates up to 9000 Å. Its temperature is kept constant to prevent wavelength shifts and the indicated wavelength are calibrated with several atomic lines. Its holographic grating is very effective in eliminating the scattered laser and discharge atomic light, compared to a ruled grating we previously used. The discharge need not be interrupted during the observation as its intensity is weak compared to the laser fluorescent light. The photomultiplier is the E.M.I. 9816, with a S 20 cathode and 14 dynodes. Lines have been observed up to 7600 Å.

The fluorescence is integrated by a Brookdeal boxcar with 500 ns gate width, much larger than the $A^1\Sigma^+$ lifetimes of about 30 ns. The output steady signal maximum is obtained by varying by hand the monochromator wavelength. The slit aperture is chosen according to the intensity of the signal, from 50 to 500 μ . The typical error is 0.2 Å, i.e., 1 cm⁻¹.

In order to observe lines decaying to the highest possible v'' levels, we excite the hydride from the highest possible v'' with the shortest possible wavelength, compatible with production of a fluorescence signal strong enough for the emission to be followed up to 7600 Å. With NaH (NaD), the BiBuQ at about 3850 Å was used. It gave no fluorescence in KH (KD) as the Franck-Con-

TABLE I. Exciting transitions, with dye laser light, and highest observed v'' in the fluorescent light.

	Exciting transitions $v''(J'') \rightarrow v'(J')$		Wavelengths (Å) in air	Highest observed v''
NaH	1 (1)	6 (2)	4309.2	8
	1 (8)	7 (7)	4286.0	10
	1 (8)	6 (9)	4340.5	11
	1 (6)	6 (5)	4335.6	11
	1 (8)	14 (7)	3871.5	15
	1 (11)	14 (12)	3886.8	15
NaD	2 (5)	11 (4)	4200.6	15
	1 (4)	10 (3)	4163.2	16
	1 (7)	10 (6)	4173.3	18
	1 (11)	10 (12)	4186.2	18
	0 (9)	14 (10)	3875.2	20
	0 (10)	15 (9)	3847.2	20
KH	0 (13)	15 (14)	3856.6	20
	0 (11)	12 (12)	4595.0	9
	0 (1)	12 (2)	4546.6	11
	0 (6)	12 (7)	4560.4	11
	0 (14)	12 (15)	4626.0	11
	1 (8)	22 (9)	4214.7	14
KD	0 (17)	16 (18)	4620.2	9
	0 (10)	16 (11)	4579.8	14
	0 (11)	23 (12)	4298.3	14
	0 (9)	22 (10)	4332.5	15
	0 (2)	16 (3)	4559.9	16

don factors were too small, and the shortest excitation wavelengths were obtained with popop (4200 Å) or dimethylpopop (4300 Å). Excitation from $v'' = 1$ or 2 is possible but the fluorescence is much less intense than

from $v'' = 0$ and in deuterides it has not given better results. The exciting transitions and the laser observed v'' are given in Table I. The measured wavelengths are available from the authors.

RESULTS

The measured energy separation between the R and P lines of a doublet arising from a (v', J') level is

$$\Delta_2 F''(J') = 2(2J' + 1) B_{v'', J'} - 4(2J'^3 + 3J'^2 + 3J' + 1) D_{v'', J'}. \quad (1)$$

It allows calculation of $B_{v'', J'}$ and $D_{v'', J'}$ if one observes the decay of at least two different J' to a given v'' . The results for each of the four molecules studied are as follows:

- (i) the $B_{v'', J'}$ decrease when v'' increases, as usual;
- (ii) the $D_{v'', J'}$, although imprecise, remain the same for all the v'' values.

To prevent the error of $D_{v'', J'}$ affecting the corresponding $B_{v'', J'}$ values, we make the calculations in two steps: First, we calculate the $D_{v'', J'}$ with Eq. (1) for all the available pairs of $J'(v'')$ and obtain a mean value $\overline{D_{v'', J'}}$ for each of the molecules; second, we use this value and Eq. (1) to obtain the $B_{v'', J'}$. As several $(v' - v'')$ transitions are observed, the obtained $B_{v'', J'}$ values are averaged over all the experiments.

When the $B_{v'', J'}$ and the $D_{v'', J'}$ are known, the measured energies $\nu_{v'', J' = 0}$ and $\nu_{v'', J'}$ of the lines arising from a given (v', J') level and decaying to $v'' = 0$ and to $v'' \neq 0$ provide the energy $G_{v'', J'} - G_{v'', J' = 0}$ of the v'' level:

$$G_{v'', J'} - G_{v'', J' = 0} = (\nu_{v'', J' = 0} - \nu_{v'', J'})_{R \text{ or } P} + F_{v'', J' = 0}(J' \pm 1) - F_{v'', J'}(J' \pm 1). \quad (2)$$

TABLE II. Values of $B_{v'', J'}$. Measurements compared with other experiments and with *ab initio* calculations.

v''	NaH			NaD			KH				KD		
	Present work	Other	Theory ^c	Present work	Other ^d	Theory ^c	Present work	Other ^e	Other ^f	Other ^g	Present work	Other ^h	Other ^f
0	4.825	4.831 ^a	4.6881	2.522	2.5315	2.4527	3.378	3.3730	3.371	3.373	1.744	1.652	1.740
1	4.687	4.701	4.5586	2.480	2.4795	2.4032	3.310	3.2960	3.293	3.292	1.715	1.624	1.706
2	4.566	4.571	4.4319	2.426		2.3559	3.217	3.2154	3.210	3.209	1.677	1.597	1.673
3	4.433	4.438 ^b	4.3068	2.376			3.131	3.127	3.130	3.122	1.635	1.567	1.636
4	4.313	4.302	4.1818	2.324			3.046	3.027	3.020	3.041	1.619		1.612
5	4.174	4.180	4.0566	2.277			2.963				1.603		
6	4.042	4.051	3.9331	2.234			2.879				1.548		
7	3.921	3.918	3.8069	2.190			2.782				1.526		
8	3.796	3.790	3.6796	2.147			2.730				1.503		
9	3.662		3.5515	2.089			2.642				1.470		
10	3.528			2.040			2.587				1.449		
11	3.389			1.992			2.484				1.418		
12	3.227			1.941			2.411				1.383		
13	3.110			1.887			2.317				1.350		
14	2.940			1.831			2.232				1.325		
15	2.770			1.783							1.290		
16				1.737							1.260		
17				1.672									
18				1.629									
19				1.572									
20				1.508									
B_e	4.890	4.886	4.748	2.550	2.5575	2.475	3.415	3.407	3.4123	3.415	1.753	...	1.753
α_e	0.131	0.129	0.126	0.049	0.0520	0.0474	0.081	0.0673	0.0817	0.083	0.030	...	0.031
r_e (Å)	1.889	1.890	1.918	1.889	1.886	1.918	2.24	2.24	2.24	2.24	2.24	...	2.24
$\overline{D} \times 10^4$	3.33	3.15	3.08	0.89	0.906	0.88	1.63	1.56	1.5	1.65	0.42	0.24	0.47

^aReference 1.

^bReference 2.

^cReference 15.

^dReference 4.

^eReference 5.

^fReference 8.

^gReference 6.

^hReference 7.

TABLE III. Values of $G_{v'',+1} - G_{v'',+1/2} = \Delta G_{v'',+1/2}$. Measurements compared with other experiments and with *ab initio* calculations.

v''	NaH			NaD		KH				KD		
	Present work	Other ^a	Theory ^b	Present work	Theory ^b	Present work	Other ^c	Other ^d	Other ^e	Present work	Other ^f	Other ^g
0	1134.0	1132.9	1104.62	825.3	804.28	956.0	954.5	955.6	955.9	690.6	691	692.8
1	1094.3	1094.6	1070.56	806.0	787.18	925.9	925.7	926.1	926.8	677.2	675	675.0
2	1057.9	1058.0	1034.34	787.8	767.82	897.3	899.0	898.8	898.0	661.1	661	662.5
3	1021.0	1021.2	1000.51	766.2	749.84	868.9	872.8	870.7	868.3	643.9	645	644.5
4	985.1	984.4	964.90	747.1	732.15	840.5				628.2		
5	948.8	948.8	930.09	729.7	713.58	813.7				619.9		
6	912.6	912.8	894.65	708.2	695.15	787.3				600.3		
7	876.8	876.9	858.29	690.9	677.29	755.8				586.9		
8	840.7		821.91	673.0	658.81	732.2				573.1		
9	804.1		785.40	653.4	640.07	703.1				559.3		
10	766.2		749.02	634.3	621.22	680.8				545.5		
11	728.2		710.77	616.5	602.16	649.8				532.9		
12	684.0		669.00	597.4	583.10	623.2				518.3		
13	639.1		623.89	578.4	564.24	597.2				502.5		
14	593.5		572.64	557.0	545.53					493.5		
15			514.21	538.0	525.95					477.2		
16			447.74	518.4	505.02							
17			373.63	494.8	483.34							
18			284.97	473.1	460.16							
19				455.3								
ω_e	1176.1	1172.2	1183.17	847.7	826.60	985.38	983.3	983.63	984.3	708.1	705.9	706.6
$\omega_e x_e$	21.19	19.72	21.23	10.62	9.44	15.08	14.4	14.32	14.5	8.27	7.6	7.73
$\omega_e y_e$	0.36	0.16		0.11		0.1				0.075		
$\omega_e z_e$	-0.014	-0.005	-	-0.003		-0.0022				-0.0015		

^aReference 2.^bReference 15.^cReference 5.^dReference 8.^eReference 6.^fReference 7.

$F_{v'',0}(J')$ and $F_{v'',0}(J'')$ are the rotational energies in the $v''=0$ and the v'' ground state, respectively. Calculations have been done with all the available measurements and averaged.

The values obtained for $G_{v''}$, $B_{v''}$, and $\overline{D_{v''}}$ are given in Tables II and III, with conventional spectroscopy data for comparison. In cases in which several authors have reported on the same experiment, the differences be-

tween their results are not smaller than our experimental uncertainty.

The vibrational energies, with the energy origin taken at the minimum of the potential energy curve, have been fitted to polynomials in $(v'' + \frac{1}{2})$ of degrees 2 to 6. The degree which provides the best physical description is such that the mean square difference with the measurements is equal to the estimated error square, in our

TABLE IV. RKR calculations of r_{\min} and r_{\max} .

v''	NaH		NaD		KH		KD	
	r_{\min}	r_{\max}	r_{\min}	r_{\max}	r_{\min}	r_{\max}	r_{\min}	r_{\max}
0	1.723	2.069	1.761	2.054	2.075	2.451	2.080	2.400
1	1.633	2.244	1.667	2.183	1.959	2.618	1.994	2.548
2	1.573	2.373	1.614	2.286	1.894	2.756	1.937	2.659
3	1.529	2.489	1.573	2.377	1.845	2.879	1.897	2.760
4	1.493	2.597	1.540	2.462	1.806	2.994	1.859	2.849
5	1.463	2.703	1.513	2.542	1.774	3.105	1.824	2.928
6	1.438	2.807	1.488	2.619	1.746	3.212	1.801	3.010
7	1.416	2.910	1.466	2.695	1.723	3.321	1.777	3.092
8	1.396	3.013	1.446	2.768	1.699	3.427	1.755	3.167
9	1.378	3.117	1.429	2.843	1.679	3.532	1.735	3.244
10	1.363	3.224	1.413	2.917	1.659	3.638	1.717	3.318
11	1.349	3.335	1.399	2.992	1.643	3.744	1.700	3.393
12	1.338	3.451	1.386	3.067	1.629	3.860	1.685	3.469
13	1.325	3.573	1.375	3.143	1.614	3.962	1.672	3.546
14	1.315	3.704	1.365	3.221			1.659	3.624
15	1.306	3.847	1.355	3.302			1.649	3.697
16			1.345	3.382				
17			1.337	3.467				
18			1.328	3.556				
19			1.320	3.646				
20			1.314	3.739				

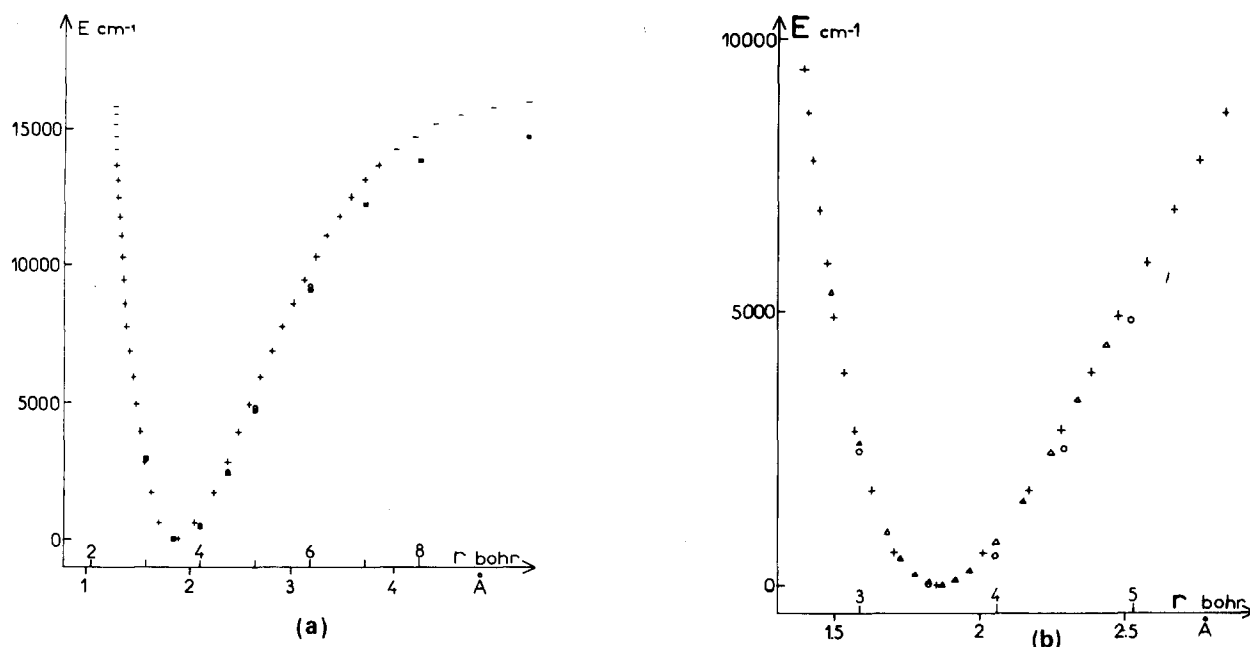


FIG. 1. NaH potential energy curve. +: RKR or "experimental"; —: extrapolation of RKR; o and □: calculations (a,d) and (a,e) of Ref. 16; Δ: calculations of Ref. 17. (a) General shape and Ref. 16 calculations; (b) bottom and Ref. 17 calculations.

case typically 1 cm^{-1} . A lower degree polynomial does not fit the experimental variation closely enough, whereas a higher degree polynomial fits the experimental discrepancies. In the four molecules studied, degree 4 gives the best fit and provides the four terms of the development¹²:

$$G_{v''} = \omega_e(v'' + \frac{1}{2}) - \omega_e x_e(v'' + \frac{1}{2})^2 + \omega_e y_e(v'' + \frac{1}{2})^3 + \omega_e z_e(v'' + \frac{1}{2})^4 + \dots \quad (3)$$

Of course, it is the set of the four terms which has a physical meaning.

The rotational constant $B_{v''}$ is well fitted by a first degree development, which may be obtained by a graphical determination:

$$B_{v''} = B_e - \alpha_e(v'' + \frac{1}{2}) + \dots \quad (4)$$

DISCUSSION

We find good agreement between our $G_{v''}$, $B_{v''}$, and $D_{v''}$ values and those reported in previous experimental papers for the first v'' values (except Imanishi's results in Table II). The calculated $\Delta G_{v''}$ ¹⁴ are greater for NaH (5%) and for NaD (2.5%). The calculated $B_{v''}$ ¹⁴ are smaller for NaH (3%) and for NaD (3%).

In the $G_{v''}$ development, the first two terms are most important and do not undergo large change when many more v'' values are considered: The values of ω_e and $\omega_e x_e$ given by several authors present a small dispersion which is similar to that we obtain by varying the degree of the polynomial fit. The same remark applies for $B_{v''}$, where more than two terms are not needed to fit the experimental values.

The extrapolation of the polynomial fit to $\Delta G_{v''} = 0$ (Birge-Sponer extrapolation) provides an approximate value of the dissociation energy. The chosen values

and their uncertainties are provided by the results of polynomial fits of degrees 4 ± 1 .

The $G_{v''}$, $B_{v''}$, and r_e are used to calculate the potential energy curves by the RKR method (Table IV). We notice no isotope effect: The hydride and corresponding deuteride curves are identical, i.e., the r_{\min} and r_{\max} values corresponding to the same energy differ by less than 0.003 \AA , which is close to the experimental uncertainty.

NaH and NaD

The energy of the last observed v'' is 83% of the dissociation energy which explains the satisfactory convergence of the results:

$$\text{NaH, } D_e(\text{extrap.}) = 16\,300 \pm 500 \text{ cm}^{-1}, \text{ last } v'' = 24 \pm 3;$$

$$\text{NaD, } D_e(\text{extrap.}) = 16\,700 \pm 500 \text{ cm}^{-1}, \text{ last } v'' = 35 \pm 4.$$

The result of Ref. 2 for NaH, extrapolated from eight v'' values instead of 15 in our case, is slightly higher: $17\,100 \text{ cm}^{-1}$.

The NaH RKR "experimental" potential curve is shown in Fig. 1 with the *ab initio* calculated potential curves for comparison. The energy origin has been taken at the bottom of the curves. Recently,¹³ RKR potential curves for NaH have been calculated from conventional spectroscopy data^{2,4} up to $v'' = 8$. The mean value of the difference between their r_{\min} and r_{\max} value and ours is less than 0.003 \AA .

There is no simple physical means¹⁹ to extrapolate the RKR curve beyond the experimental points as even at the last observed v'' there is strong configuration mixing.¹⁴ The extrapolation shown in Fig. 1 was obtained with the extrapolated values of $G_{v''}$, from the fourth order fit up to $\Delta G_{v''} = 0$, associated with $B_{v''}$, for which we do not extrapolate the linear variation with $v'' + \frac{1}{2}$ but rather adopt a

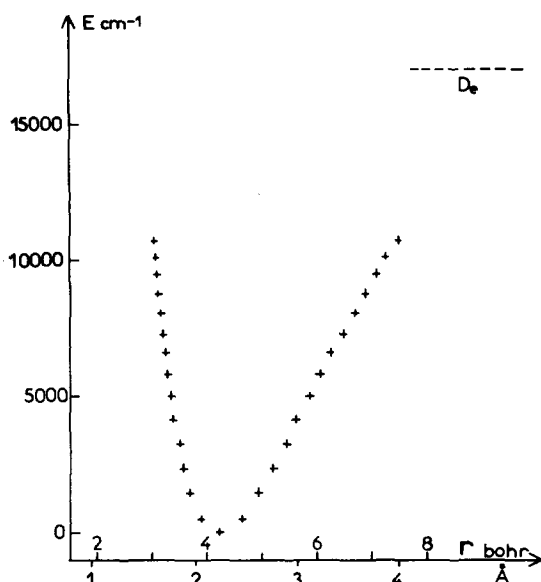


FIG. 2. KH RKR potential energy curve.

more rapid decrease such as $B_{v''} = 0$ for the dissociated v'' .

The calculated curve of Ref. 16 is lower than our "experimental" curve. The calculated curve of Ref. 17, given up to $v'' = 8$, agrees with the experimental curve. The calculated dissociation energies are lower than our values:

$$\text{NaH}, D_e(\text{calc.}, \text{Ref. 16}) = 15\,152 \pm 1400 \text{ cm}^{-1};$$

$$D_e(\text{calc.}, \text{Ref. 17}) = 15\,491 \text{ cm}^{-1}.$$

KH and KD

The dissociation energy for the $X^1\Sigma^+$ state of KH may also be approximated by the Birge-Sponer extrapolation

$$D_e(\text{extrap.}) = 17\,030 \pm 1500 \text{ cm}^{-1}.$$

For KD we obtained poor convergence of the results from the extrapolation of the 4 ± 1 degree polynomial fits.

The energies of the upper $A^1\Sigma^+$ state observed ($v' = 24$, $J' = 30$) have provided¹⁸ a lower limit for the energy at which $A^1\Sigma^+$ dissociates and subsequently a lower limit

for the $X^1\Sigma^+ D_e$ of $14\,000 \text{ cm}^{-1}$, which is not much lower than our result.

The RKR potential curve is shown in Fig. 2.

Note added in proof: The RKR results of Table IV have been obtained by introducing in the "Zare program" our experimental $B_{v''}$ and $G_{v''}$ values. When these values are replaced by those given by our fitted molecular developments the corresponding results of r_{\min} and r_{\max} vary by about 0.003 \AA due to the differences between the experimental and the fitted values. These last RKR results agree within 0.0001 \AA with those obtained by Stwalley using the "Tellinghuisen program," or by Bacis using the "Albritton-Zare program," where the molecular constants of our fitted developments are introduced. We acknowledge W. C. Stwalley for sending us his RKR results.

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