SUPPORTING INFORMATION

PAPER TITLE: Rotationally resolved (1 + 1') resonance-enhanced multiphoton ionisation (REMPI) of *CaR* (*R*=*H*,*D*) in supersonic beams: CaR $X^2 \Sigma^+(v"=0) \rightarrow \text{CaR}^* B^2 \Sigma^+(v'=1,0) \rightarrow \text{CaR}^* X^1 \Sigma^+$

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Additional information on the CaR (X,v''=0 - B,v'=0,1) band spectra and on the determination of the rotational parameters B_v and D_v

In our experiments, as a compromise, the laser intensities were always adjusted to realise sufficiently strong ion signals, but at the same time to provide the best achievable signal-to-noise ratio for the weakest rotational transition lines of CaR.

Specifically, laser fluences for the first resonant excitation step were adjusted to normally reduce line broadening to values at which the line shape was still (nearly) Lorentzian.

The laser fluence for the ionisation step was normally far from saturation. An example for the effect of laser fluence on the intensity and width of spectral lines is shown in Figure S.1.



Figure S.1: Segment of RIMS spectra near 633.7nm, including overlapping lines from CaH(B-X, 0-0) and CaH(A-X, 1-0), recorded for different energy densities of the resonant excitation laser.

The narrowest line width value, which could be realised for any of the CaR rotational transition lines, was $\Delta \lambda \cong 0.008$ -0.009 nm; in most spectra line widths of $\Delta \lambda \cong 0.010$ -0.011 nm (or roughly $\Delta \nu \cong 0.3 \text{ cm}^{-1}$) were observed. This corresponds to roughly two to three times the line width of the dye laser (quoted by the manufacturer as $\Delta \lambda \cong 0.005$ nm, or $\Delta \nu \cong 0.125 \text{ cm}^{-1}$), at the wavelengths encountered in this study; most likely this is due to some residual power broadening. Typically, the wavelength tuning increment was $\lambda_{inc} = 0.002$ -0.004 nm, providing a sufficient number of data points over the line width of any transition to allow to apply standard peak fitting routines, to determine peak positions and line shapes. The spectrum for (X-B,0-0) band system of CaH exhibits overlap with the CaH (X,v"=0 – A,v'=1) band. In the bottom trace of Figure S.2 this spectral contribution from CaH (X,v"=0 – A,v'=1) has been subtracted, and only the CaH (X,v"=0 – B,v'=0) lines remain. Representative branches are indicated, to highlight (i) that R_2 and Q_{21} lines are not resolved and (ii) that (X-A) and (X-B) contributions strongly overlap for CaH. The latter is specifically true for the long wavelength section in which the dense line spectrum of the X ${}^{2}\Sigma^{+}$ (v"=0) – A ${}^{2}\Pi_{3/2}$ (v'=1) transition completely masks the P– lines with high rotational quantum numbers from the X ${}^{2}\Sigma^{+}$ (v"=0) – B ${}^{2}\Sigma^{+}$ (v"=0) transition.



Figure S.2: (1+1') REMPI spectra of CaH. Top trace: the $(X, \upsilon''=0 \rightarrow B, \upsilon'=0/A, \upsilon'=1)$ bands; bottom trace: extracted $(X, \upsilon''=0 \rightarrow B, \upsilon'=0)$ sub-system band. The intensities are normalised to the strongest rotational line.

Line positions are directly extracted from the calibrated spectra and tabulated in **Table S.1** below. The line positions (in units of nm) are converted into energy values (in units of cm^{-1}) based on Edlen's formula, using both temperature and pressure corrections.

From the line positions the rotational energy term values of the excited state B ${}^{2}\Sigma^{+}(v"=0,1 | N")$ are extracted, by subtracting the appropriate vibrational-rotational level energy of the ground state X ${}^{2}\Sigma^{+}(v"=0 | N")$. The ground state energies are calculated based on the spectroscopic parameters given by Petiprez *et al* (1989) and Frum and Pickett (1993). The excited state term values are tabulated in **Table S.2**; for comparison, the table includes term values for the F₂ sub-system of CaH B ${}^{2}\Sigma^{+}(v"=1 | N")$, extracted from the data tabulated in Martin (1984).

Table S.1: Transition lines for the CaD and CaH vibrational bands investigated in this study, listed in units wavelengths [nm] and wave numbers [cm^{-1}]. Line positions were fitted, with Lorentz line shape functions, using the GRAMS/32 Peak Fit module; lines with fit residual R² > 0.95 in normal font, lines with smaller residuals in italic font (for details see Table footnotes). *Transition lines of CaD (B-X,0-0)*

		R_1	P_1	/ Q ₁₂	R_2 / Q_{21}		P_2	
N "	λ [nm]	v [cm ⁻¹]	λ [nm]	$\nu \ [cm^{-1}]$	λ [nm]	v [cm ⁻¹]	λ [nm]	v [cm ⁻¹]
0	634.6132	15753.288	-	-	634.5892	15753.884	-	-
1	634.4374	15757.659	634.9609	15744.655	634.3934	15758.751	-	-
2	634.2455	15762.404	635.1408	15740.193	634.1896	15763.796	635.1128	15740.887
3	634.0537	15767.177	635.3126	15735.931	633.9777	15769.067	635.2635	15737.145
4	633.8538	15772.152	635.477	15731.870	633.7619	15774.441	635.4165	15733.356
5	633.6500	15777.230	635.6323	15728.034	633.5381	15780.019	635.5644	15729.717
6	633.438	15782.510	635.7882	15724.175	633.3263	15785.301	635.688	15726.649
7	633.210	15788.193	xxx	XXX	633.091	15791.160	xxx	xxx

italic = line fit converge R^{22} <0.5 – line positions questionable

xxx = line fit did not converge – line at or below noise limit

Transition lines of CaD (B-X,1-0)

		R_1	P_1	/ Q ₁₂	R_2 / Q_{21}		P_2	
N "	λ [nm]	$\nu \ [cm^{-1}]$	λ [nm]	$\nu \ [cm^{-1}]$	λ [nm]	$\nu \ [cm^{-1}]$	λ [nm]	v [cm ⁻¹]
0	600.2864	16654.124	-	-	600.2651	16654.707	-	-
1	600.1302	16658.453	600.5953	16645.556	600.0926	16659.480	-	-
2	599.9723	16662.840	600.7564	16641.095	599.9193	16664.312	600.7347	16641.677
3	599.8121	16667.285	600.9165	16636.636	599.7437	16669.175	600.8790	16637.688
4	599.6478	16671.843	601.0727	16632.319	599.5652	16674.151	601.0184	16633.841
5	599.4811	16676.487	601.2241	16628.141	599.3848	16679.158	601.1579	16629.967
6	599.3133	16681.162	601.3745	16623.966	599.199	16684.336	601.2881	16626.371
7	599.139	16686.010	601.5254	16619.821	599.014	16689.489	601.425	16622.584
8	598.967	16690.800	601.665	16615.926	XXX	xxx	600.735	16641.677

italic = line fit converge $R^2 < 0.5$ – line positions questionable

xxx = line fit did not converge – line at or below noise limit

Table S.1 ... continued.

Transition	lines	of CaH	(B-X, 0-0)
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		R_1	P_1/Q_{12} R_2/Q_{21}		$P_1/Q_{12} \qquad \qquad R_2/Q_{21} \qquad \qquad P_2$		P ₂	
N "	λ [nm]	v [cm ⁻¹]	λ [nm]	v [cm ⁻¹]	λ [nm]	v [cm ⁻¹]	λ [nm]	v [cm ⁻¹]
0	634.2584	15762.006	-	-	634.2078	15763.249	-	-
1	633.912	15770.759	634.9353	15745.199	633.8147	15773.122	-	-
2	633.536	15780.019	635.280	15736.749	633.4068	15783.257	635.2299	15737.987
3	633.153	15789.639	635.6110	15728.554	632.9832	15793.855	635.5122	15731.004
4	632.7530	15799.595	635.9194	15720.936	632.5528	15804.591	635.802	15723.829
5	632.3369	15809.990	636.220	15713.498	632.1062	15815.767	636.043	15717.871
6	631.9083	15820.723	636.480	15707.079	631.6485	15827.210	636.2851	15711.893
7	631.464	15831.847	XXX	XXX	631.1801	15838.970	636.510	15706.339
8	631.0151	15843.112	XXX	XXX	630.6964	15851.125	XXX	XXX
9	630.5475	15854.846	XXX	XXX	630.209	15863.450	XXX	XXX
10	630.070		xxx	xxx	xxx	xxx	xxx	xxx

italic = line fit convergence $0.65 < R^2 < 0.85$ – overlap with line from CaH(A-X,1-0), line position depends on components weighting xxx = line fit did not converge – line masked by a line from CaH(A-X,1-0), or at or below noise limit

Transition lines of CaH (B-X,1-0)

	ŀ	R ₁	P_1 / Q_{12}		
N "	λ [nm]	v [cm ⁻¹]	λ [nm]	v [cm ⁻¹]	
0	587.8632	17006.064	-	-	
1	587.5741	17014.428	588.4362	16989.504	
2	587.2812	17022.917	588.7392	16980.760	
3	586.9749	17031.791	589.0357	16972.199	
4	586.6674	17040.733	589.3258	16963.847	
5	586.3529	17049.858	589.6040	16955.849	
6	586.0334	17059.168	589.875	16948.059	
7	585.586	17072.190	590.157	16939.960	

	R_2/Q	Q_{21} (<i>i</i>)	R ₂	(ii)	P_2 (i)		P_2	(ii)
N "	λ [nm]	v [cm ⁻¹]	λ [nm]	v [cm ⁻¹]	λ [nm]	v [cm ⁻¹]	λ [nm]	v [cm ⁻¹]
0	587.8230	17007.221	-	-	-	-	-	-
1	587.5248	17015.847	-	-	XXX	XXX		
2	587.2866	17022.743	588.6958	16982.001	587.1036	17028.049	XXX	XXX
3	587.1116	17027.817	588.9802	16973.812	586.7951	17037.016	588.8015	16978.944
4	586.957	17032.314	589.3195	16964.020	586.4657	17046.573	589.1445	16969.059
5	XXX	XXX	589.7296	16952.226	586.1345	17056.200	589.4186	16961.170
6	XXX	XXX	XXX	XXX	585.716	17068.401	589.670	16953.951
7	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XXX

italic = line fit converge $R^2\!\!<\!\!0.5~$ – line positions questionable

xxx = line fit did not converge - line at or below noise limit

* = transition energies for (B-X,1-0), extracted (B-X,1-1) data tabulated in Martin [1984]

Table S.2: Rotational energy levels (in cm⁻¹) for the CaD and CaH transitions investigated in this study. The term values for the electronic ground state X ${}^{2}\Sigma^{+}$ are calculated from the rotational constants tabulated by **Frum and Picket (1992)** and the vibrational constants tabulated by **Petitprez** *et al* (1989). The term values T₁, T₂ for the electronic excited state B ${}^{2}\Sigma^{+}$ are derived from fits to the measured spectral line positions, utilising the constants for B_v, D_v and γ_v derived in this work.

 $CaD\left(X^{2}\Sigma^{+}, v^{\prime\prime}=0\right)$

N"	T ₁ calculated	T ₂ calculated
0	462.509	
1	466.874	466.841
2	475.591	475.536
3	488.658	488.582
4	506.072	505.974
5	527.828	527.709
6	553.920	553.779
7	584.341	584.178
8	619.083	618.899
9	658.137	657.930
10	701.491	701.263

 $CaD (B^{2}\Sigma^{+}, v'=0)$

N'	T ₁ experiment	T ₁ linear fit	T_1 quadratic fit	T ₂ experiment	T ₂ linear fit	T ₂ quadratic fit
0	16211.529	16211.509	16211.509			
1	16215.790	16215.837	16215.824	16216.408	16216.450	16216.438
2	16224.561	16224.656	16224.658	16225.660	16225.679	16225.681
3	16237.968	16237.988	16238.008	16239.331	16239.419	16239.439
4	16255.849	16255.831	16255.870	16257.537	16257.672	16257.710
5	16278.160	16278.187	16278.239	16280.422	16280.436	16280.488
6	16305.058	16305.054	16305.108	16307.728	16307.713	16307.767
7	16336.482	16336.433	16336.471	XXX	16339.501	16339.538
8	16372.534	16372.325	16372.317	16375.638	16375.802	16375.794
9	XXX	16412.729	16412.638	XXX	16416.614	16416.523
10	xxx	16457.644	16457.420	xxx	16461.939	16461.714

 $CaD(B^{2}\Sigma^{+}, v'=1)$

N'	T ₁ experiment	T_1 linear fit	T_1 quadratic fit	T ₂ experiment	T ₂ linear fit	T ₂ quadratic fit
0	17112.430	17112.420	17112.420			
1	17116.659	17116.661	17116.658	17117.215	17117.259	17117.257
2	17125.310	17125.321	17125.333	17126.296	17126.319	17126.331
3	17138.411	17138.412	17138.442	17139.832	17139.808	17139.838
4	17155.956	17155.932	17155.981	17157.716	17157.728	17157.776
5	17177.901	17177.883	17177.945	17180.138	17180.077	17180.139
6	17204.239	17204.263	17204.328	17206.814	17206.856	17206.921
7	17235.046	17235.074	17235.122	17238.115	17238.066	17238.114
8	17270.348	17270.314	17270.318	17273.667	17273.706	17273.710
9	17309.881	17309.984	17309.907	XXX	17313.775	17313.697
10	XXX	17354.085	17353.876	XXX	XXX	17358.066

xxx = at or below noise level, line fit did not converge

Table S.2: ... continued.

$Carr(\Lambda \mathbf{\Delta}, \mathbf{V} = 0)$	CaH ($(X^2\Sigma^+,$	v''=0)
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N"	T ₁ calculated	T ₂ calculated
0	644.409	
1	652.888	652.822
2	669.818	669.710
3	695.192	695.040
4	728.996	728.800
5	771.213	770.973
6	821.819	821.536
7	880.788	880.462
8	948.090	947.720
9	1023.689	1023.275
10	1107.545	1107.087

$CaH(B^{2}\Sigma^{+}, v'=0)$

N'	T ₁ experiment.	T_1 linear fit	T_1 quadratic fit	T ₂ experiment	T ₂ linear fit	T_2 quadratic fit
0	16398.087	16398.087	16398.004			
1	16406.491	16406.518	16406.461	16407.677	16407.709	16407.652
2	16423.697	16423.777	16423.768	16425.994	16425.762	16425.753
3	16449.885	16449.864	16449.914	16452.798	16452.643	16452.693
4	16484.771	16484.779	16484.884	16488.869	16488.352	16488.457
5	16528.745	16528.522	16528.658	16533.410	16532.889	16533.025
6	16581.203	16581.093	16581.209	16586.770	16586.254	16586.370
7	16642.542	16642.492	16642.508	16648.746	16648.447	16648.463
8	16712.635	16712.719	16712.519	16719.432	16719.468	16719.268
9	16791.202	16791.774	16791.200	16798.845	16799.317	16798.743
10	16878.499	16879.657	16878.507	16886.725	16887.994	16886.844

$CaH(B^{2}\Sigma^{+}, v'=1)$

N'	T ₁ experiment	T ₁ linear fit	T_1 quadratic fit	T ₂ (a) experiment	T ₂ (b) experiment	T ₂ (b) [1]
0	17642.292	17642.231	17642.232			
1	17650.526	17650.469	17650.488	17651.671	?	
2	17667.354	17667.328	17667.378	17668.761	17673.920	17673.874
3	17692.833	17692.808	17692.892	17692.636	17697.809	17697.846
4	17727.022	17726.910	17727.016	17723.028	17732.099	17732.118
5	17769.789	17769.633	17769.730	17761.114	17775.430	17775.385
6	17820.909	17820.978	17821.009	?	17827.171	17827.262
7	17880.987	17880.943	17880.825		XXX	17887.646
8	XXX	17949.531	17949.141		XXX	17956.511
9	XXX	18026.739	18025.920		XXX	18033.740
10	xxx	18112.569	18111.117		XXX	17673.874

xxx = at or below noise level, line fit did not converge

? = not observed / identified; intensity at or below noise level, or line fully masked by another stronger line

(a) , (b) = $\ \ perturbed$ rotational levels in the F_2- branch, with "extra" levels

[1] = term values derived from the transitions tabulated in Martin (1984)

The "pure" rotational energy, T_{rot} contribution associated with $B_v \cdot N \cdot (N+1)$ was determined from a plot of the rotational energy level terms T_I and T_2 versus $N \cdot (N+1)$, by first subtracting the spin splitting component, and then providing the zero-point for T_{rot} by subtracting $T_I(N'=0)$ from all T_I and T_2 values.

When comparing the T_1 and T_2 energy term values reconstructed using the fitted values for B_v , and γ_v with the experimental values, a discrepancy was observed for CaH (B,v'=0). For rotational quantum numbers up to $N' \cong 8$ the two values agreed to within the experimental uncertainty of about $\pm 0.2 \text{ cm}^{-1}$, while for $N' \cong 9,10$ the deviation was much larger. Not unusual for the relative ratio between B_v and D_v in general, the reported literature values for CaH / CaD are of the order $< 2 \times 10^{-4} \text{ cm}^{-1}$ (see Table 2 of the paper). However, since the energy correction changes as $D_v \cdot [N \cdot (N+1)]^2$, its contribution may become easily noticeable only with increasing rotational quantum number N; this is the case here for CaH.

Since the correction is quadratic in $N \cdot (N+1)$, a "quadratic fit" to the data points should return a sensible non-linear term. Indeed one obtains a reasonably-sized quadratic parameter c – associated with D_v , albeit with relatively large uncertainty. Reconstructing the energy term values T_1 and T_2 using the fitted values for B_v , D_v , and γ_v , the agreement for all observed rotational levels was now within the measurement accuracy. This approach of a quadratic fit to the rotational term energy values was also applied to the data for CaH (B,v'=1) and for the two vibrational levels of CaD. All respective parameters B_v , and D_v , are summarised in Table 2 of the paper.

One interesting aspect for CaH (B,v'=0) should be pointed out. The fit to the spin splitting values returned the indication of a perturbation at very low rotational levels. As for the other vibrational levels, this perturbation is expected in the F_2 level sub-set. When comparing the experimental data with the linear-fit and quadratic-fit reconstruction, complete agreement with experimental values for T_1 was found. However, for T_2 only the rotational term values for N' = 9,10improved significantly; at intermediate levels a noticeable discrepancy of the order ~0.4 cm⁻¹ remained, well outside the measurement errors but is in agreement with the offset of the same order of magnitude seen for the spin splitting data. An error in wavelength calibration can be excluded since the transition lines for the determination of T_1 and T_2 are from the same spectral segment, which was calibrated using three Ne lines (namely at 630.479 nm, 633.443 nm and 638.299 nm) recorded in an opto-galvanic resonance cell, and fringes from a Fabry-Perot etalon. Consequently, one can conclude with strong confidence, that – as suspected – the F_2 level sequence in *CaH* (B,v'=0) is perturbed at about N' = 0 or 1.

Finally, it should be noted that the reported literature values of B_v and D_v (for CaH) and those derived in this study exhibit a slight discrepancy (see Table 2). This can be attributed to the fact that much fewer and lower rotational energy levels were included in our (polynomial) fits.

References.

Petitprez, D.; Lemoine, B.; Demuynck, C.; Destombes, J.L.; Macke, B. J. Chem. Phys. **1989**, *91*, 4462. Frum, C.I.; Pickett, H.M. J. Mol. Spectrosc. **1993**, *159*, 329. Martin, H. J. Mol. Spectrosc. **1984**, *108*, 66.