High-resolution visible laser spectroscopy of the $\tilde{B}^2 B_1 - \tilde{X}^2 A_1$ transition of CaNH₂

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(Received 16 January 1998; accepted 23 February 1998)

The $0_0^0 \tilde{B} {}^2B_1 - \tilde{X} {}^2A_1$ band of CaNH₂ has been recorded at high resolution with a laser ablation molecular beam spectrometer. This $\tilde{B} {}^2B_1$ state is the last of the low-lying electronic states of CaNH₂ to be characterized. The pure precession model, which has previously been used to describe the spin-rotation interactions in this family of molecules was used to interpret and correctly assign the spectrum. The detailed analysis of the high resolution spectrum and energy level structure of the $\tilde{B} {}^2B_1$ state is presented. @ 1998 American Institute of Physics. [S0021-9606(98)00121-4]

I. INTRODUCTION

The analysis of the $\tilde{B}^{2}B_{1}-\tilde{X}^{2}A_{1}$ transition completes the high resolution spectroscopic study of the low-lying electronic states of CaNH₂.^{1,2} The monovalent derivatives of the alkaline-earth molecules (MX, M=Mg, Ca, Sr, Ba) have an electronic structure that can be described by a one-electron hydrogenic picture. This rather unique property is partly responsible for the many research papers devoted to this family of molecules.^{3,4} The study of the metal-ligand bond is an important aspect of modern chemistry and the alkaline-earth molecules have given researchers^{3,4} ample opportunity to study the metal-halide, metal-oxygen, metal-carbon, metal-sulfur, and metal-nitrogen bonds. Molecules with metal-oxygen bonds are important in atmospheric and combustion chemistry,^{5,6} while metal-carbon and metalnitrogen bonds are found in biological systems,^{3,4} such as the active sites of enzymes, while metal-sulfur systems have applications in industrial chemical processes.

While the spectroscopy of the low-lying electronic states of alkaline-earth molecules is fairly well understood, the reactions which generate them are not. Studies to date have been concerned with the reaction of an alkaline-earth atom with water or alcohols. In the two mechanisms that have been proposed, the rate limiting step is the insertion of the metal atom into the H-OR bond. This step forms an intermediate species such as H–Ba–OR (R=H, CH₃, $C_2H_5\cdots$). Different products can be generated from this reaction where BaH, BaO or BaOR have all been observed under widely different experimental conditions. The dynamics of a few reactions of H₂O and ROH with alkaline earths have been studied in detail and they show that the reactivity is strongly dependent on the electronic state of the alkaline-earth atom⁷⁻⁹ and also on the size of the reacting species.¹⁰⁻¹² For example, ground state Ba atoms react with H₂O to give predominantly the BaO product while ${}^{1}D$ Ba atoms favor the BaOH product, even though BaO is favored on energetic grounds.¹³ There is a great need for experimental work on the kinetics and dynamics of the reactions before a good understanding of the reaction mechanisms can be achieved.

The spectroscopy of the high-lying or Rydberg electronic states of the alkaline-earth molecules has also not been extensively studied. Rydberg states of CaF and more recently CaOH^{14,15} and CaOD¹⁵ have been studied mainly by optical–optical double resonance (OODR) techniques. The theoretical calculations of Ortiz¹⁶ are in good agreement with the experimentally observed electronic states. The work of Pereira and Levy, OODR in a molecular beam detected by R2PI, has shown that one excited electronic state ($\tilde{F}'' \, {}^{2}\Pi''$) has a bent geometry while the next higher-lying electronic state, $\tilde{G} \, {}^{2}\Pi$, is linear.¹⁵ It is well known that the bonding in the low-lying electronic states is predominantly ionic leading to linear geometries. Further theoretical and experimental work needs to be done to determine what dictates the geometry in the excited state.

We have previously reported the high resolution analysis of the $\tilde{C}-\tilde{X}$ system of CaNH₂² and this work was preceded by a high resolution analysis of the $\tilde{A}-\tilde{X}$ system by Marr *et al.*¹ Other work on CaNH₂ has included low resolution studies in a Broida oven^{17,18} and a moderate resolution study using a laser ablation molecular beam spectrometer.¹⁹ In this paper we discuss the spectroscopy of the \tilde{B} ² $B_1-\tilde{X}$ ² A_1 system and the details of the pure precession model that helped us to correctly assign the spectrum.

II. EXPERIMENT

The experimental apparatus consists of a source compartment containing a Smalley-type laser ablation source and a second detection chamber. The experimental arrangement has been described in previous publications.^{2,20} Briefly, a 10 ns pulse of 532 nm radiation from a Nd:YAG (Continuum: Surelite) laser is gently focused onto a rotating calcium rod. The laser-produced metal plasma reacts with ammonia gas coexpanded with an inert carrier (5% NH₃ in Ar) which is held at 50–60 psi behind a pulsed valve (10 Hz). The CaNH₂

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FIG. 1. Some of the assigned branches of the 0–1 subband in the $0_0^0 \tilde{B} \,^2 B_2 - \tilde{X} \,^2 A_1$ transition of CaNH₂. This spectrum corresponds to a $^2\Sigma$ -case (b) $^2\Pi$ electronic transition of a linear molecule. The *Q*-branch lines are not labeled for clarity.

molecules are subsequently probed by the output of a singlemode (1 MHz) CW ring dye laser (Coherent 699-29) about 15 cm downstream from the nozzle. Detection of the CaNH₂ species was carried out by averaging the laser-induced fluorescence (LIF) signal in the time window between 175–205 μ s after the laser ablation pulse. This is the time required for the CaNH₂ molecules to travel the 15 cm to the detection region. The LIF passes through a 630±5 nm bandpass filter and is collimated with a 1.5 in. lens and focused onto a photomultiplier tube with a 7 in. lens. A 5 mm aperture is used to limit the field of view and it reduces the Doppler linewidth to approximately 150–200 MHz. The laser was calibrated by splitting off a small fraction of the beam to record the LIF spectrum of I₂ in a static gas cell.^{21,22}

III. RESULTS AND ANALYSIS

The $\tilde{A}-\tilde{X}$ and $\tilde{C}-\tilde{X}$ band systems of CaNH₂ have previously been recorded and analyzed at high resolution. A detailed analysis of $\tilde{B} {}^{2}B_{1}-\tilde{X} {}^{2}A_{1}$ transition, which occurs near 629 nm, has not been carried out. However, the low resolution laser excitation spectrum has been studied, ini-



FIG. 2. The assigned branches of the 1–0 subband in the $0_0^0 \tilde{B} \,^2 B_2 - \tilde{X} \,^2 A_1$ transition of CaNH₂. Note the intermediate case (a)–(b) behavior in the excited state (see the text for details).



FIG. 3. The 2–1 subband of the $\tilde{B}^2 B_2 - \tilde{X}^2 A_1$ electronic transition of CaNH₂. The origins and band gap are evident for the F_1 and F_2 spin components.

tially in a high temperature source (Broida oven)¹⁸ and later with a laser ablation/molecular beam spectrometer¹⁹ using a pulsed dye laser as a probe.

CaNH₂ is a planar (C_{2v}) , near prolate asymmetric top molecule, and thus the electronic transitions can be classified as parallel (a-type) or perpendicular (b- or c-type). The $\tilde{B}-\tilde{X}$ transition corresponds to the promotion of an electron from a ground state metal-centered *s*-type orbital to a predominantly metal-centered p_x -type orbital (see Figs. 1 and 2 of Ref. 2), where the p_x orbital is perpendicular to the plane of the molecule. A $p_x \leftarrow s$ electronic transition is therefore a c-type perpendicular transition. The spectrum will consist of subbands separated by approximately 2A (A is the largest of the three rotation constants), where each subband originates



FIG. 4. The energy level diagram for the 1–0 subband of the $\tilde{B}^2 B_2 - \tilde{X}^2 A_1$ transition.



FIG. 5. The energy level diagram for the 0–1 subband of the $\tilde{B}^2 B_2 - \tilde{X}^2 A_1$ transition.



FIG. 6. The energy level diagram for the 2–1 subband of the $\tilde{B}^{2}B_{2}-\tilde{X}^{2}A_{1}$ transition.



FIG. 7. The energy level diagram for the 1–1 subband of the $\tilde{C}^2 A_1 - \tilde{X}^2 A_1$ transition using the labeling scheme adopted in this paper, see the text for details.

from a different K''_a value of the molecule. The selection rule for a c-type transition is, $\Delta K_a = \pm 1$ ($\Delta K_c = 0$) giving rise to $(K'_a \leftarrow K''_a)$ 0–1, 1–0, and 2–1, etc., subbands. As was found with the $\tilde{C} - \tilde{X}$ transition of CaNH₂, the free jet expansion cools all of the ortho (odd K''_a) rotational levels into $K''_a = 1$ and the para (even K''_a) levels into $K''_a = 0$. But, unlike the parallel $\tilde{C} - \tilde{X}$ transition, where all of the subbands are overlapped due to the $\Delta K_a = 0$ selection rule, the subbands of the $\tilde{B} - \tilde{X}$ transition are separated by approximately 26 cm⁻¹. Therefore, the high resolution analysis of this band system is somewhat simpler than the spectrum of the $\tilde{C} - \tilde{X}$ transition.

The appearance of the high resolution spectrum can be related to analogous transitions of a diatomic or linear molecule. The 0–1 (Fig. 1) subband has the appearance of a ${}^{2}\Sigma$ –[Hund's case (b)] ${}^{2}\Pi$ transition while the 1–0 (Fig. 2)

TABLE I. The spectroscopic constants for $CaNH_2$ in cm^{-1} .

	$\tilde{X}^2 A_1$	$\tilde{B}^2 B_1$		
T_{0-0}	0	15 885.281 096(869)		
Α	13.057 452(598)	14.364 92(132)		
$\frac{1}{2}(B+C)$	0.296 657 2(126)	0.301 719 9(194)		
$\frac{1}{4}(B-C)$	$1.891\ 67(436) \times 10^{-3}$	$3.6947(536) \times 10^{-3}$		
ϵ_{aa}	0	-7.541 63(157)		
$\frac{1}{2}(\epsilon_{bb}+\epsilon_{cc})$	$8.525(601) \times 10^{-4}$	$2.053\ 16(992) \times 10^{-2}$		
$\frac{1}{4}(\epsilon_{bb}-\epsilon_{cc})$	0	$8.321(161) \times 10^{-2}$		
$\dot{\Delta}_{K}$	-	$-4.0843(275) \times 10^{-2}$		
Δ_N	-	$-4.69(103) \times 10^{-7}$		
δ_{K}	-	$2.0053(462) \times 10^{-3}$		
Δ_{K}^{S}	-	$-1.632(132) \times 10^{-2}$		
Δ_{KN}^{S}	-	$-6.629(121) \times 10^{-2}$		
Δ_{NK}^{S}	-	$5.857(133) \times 10^{-3}$		

TABLE II. Line positions of the $\tilde{B}^{2}B_{1}-\tilde{X}^{2}A_{1}$ of CaNH₂ (cm⁻¹).

		$\Delta \times 10^{-5}$	<i>J</i> ″		
T !!	Observed P D	0 1 0 1		Observed	1 > 10-5
<i>J</i> "	· P ₁₁	0–1 Su	bband	${}^{e}Q_{22}$	$\Delta \times 10^{-5}$
1.5	15 871.919 95	-341	1.5	15 872.509 62	- 33
2.5	15 871.336 22	-610	2.5	15 872.518 63	-58
3.5	15 870.764 15	-350	3.5	15 872.534 08	-74
4.5	15 870.198 76	- 59	4.5	15 872.556 09	-78
5.5	15 869.643 38	591	5.5	15 872.584 75	- 67
6.5	15 869.082 53	48	6.5	15 872.620 16	-42
7.5	15 868.542 62	946	7.5	15 872.662 39	-3
8.5	15 867.997 24	636	8.5	15 872.711 48	42
9.5	15 867.451 08	-424	9.5	15 8/2./6/46	83
10.5	15 866.928 17	159	10.5	15 872.830 29	102
11.5	15 866.401 14	- 364	11.5	15 872.899 85	14
12.5	15 865.890 78	/1	12.5	15 8/2.9/5 91	-45
13.5	15 805.582 10 Rp	- 50		⁰ 0	
2.5	κ ₁₁ 15 974 279 22	- 172	1.5	$^{\sim}Q_{11}$	92
2.5	15 875 005 42	-1/2	1.5	15 872.557 90	63 06
5.5	15 875 644 20	- 685	2.3	15 872.500 41	90
4.5	15 876 207 08	- 085	3.5	15 872 624 22	99 80
5.5	15 876 951 77	358	4.5	15 872.024 52	69
0.5	15 877 607 22	358 45	5.5 6.5	15 872 713 68	40
85	15 878 272 68	40 53	7.5	15 872 768 15	40
9.5	15 878 944 81	35	85	15 872 829 34	-24
10.5	15 879 621 95	- 189	9.5	15 872 897 43	-46
11.5	15 880 310 76	32	10.5	15 872 972 61	- 54
12.5	15 881 004 57	15	11.5	15 873 055 08	-40
12.5	10 001.001.07	15	12.5	15 873 145 05	2
	$^{P}P_{22}$		12.5	$^{P}O_{12}$	-
2.5	15 870.714 12	-510		£ 12	
3.5	15 870.132 05	70	1.5	15 871.345 21	91
4.5	15 869,548 31	-154	2.5	15 870.771 80	110
5.5	15 868.971 25	-356	3.5	15 870.204 59	117
6.5	15 868.405 86	-42	4.5	15 869.643 65	112
7.5	15 867.848 80	445	5.5	15 869.089 06	97
8.5	15 867.290 08	95	6.5	15 868.540 91	74
9.5	15 866.743 04	233	7.5	15 867.999 32	46
10.5	15 866.195 99	- 324	8.5	15 867.464 45	19
11.5	15 865.663 96	-86	9.5	15 866.936 49	1
	${}^{R}R_{22}$			${}^{R}Q_{21}$	
1.5	15 874.304 94	-500	1.5	15 873.702 30	-42
2.5	15 874.920 36	-233	2.5	15 874.307 24	-72
3.5	15 875.540 79	-105	3.5	15 874.918 71	-92
4.5	15 876.169 56	207	4.5	15 875.536 76	-101
5.5	15 876.803 33	361	5.5	15 876.161 47	- 96
6.5	15 877.440 44	180	6.5	15 876.792 94	-74
7.5	15 878.087 55	319	7.5	15 877.431 22	-41
8.5	15 878.741 34	435	8.5	15 878.076 37	-1
9.5	15 879.393 46	-321	9.5	15 878.728 40	36
10.5	15 880.068 93	537	10.5	15 879.387 27	50
11.5	15 880.736 05	-177	11.5	15 880.052 87	17
		1 0 5.46	and		
	$Q_{\mathbf{p}}$	1-0 Subb	anu	R_{R}	
2.5	15 894 691 98	97	0.5	15 895 879 46	162
3.5	15 894 375 00	221	1.5	15 896 149 65	60
4.5	15 894 048 20	- 39	2.5	15 896 413 17	405
5.5	15 893 721 30	173	3.5	15 896 660 00	152
6.5	15 893 384 41	- 286	4 5	15 896 896 83	- 64
7.5	15 893 050 84	-231	5.5	15 897 123 66	- 305
8.5	15 892 717 28	-131	6.5	15 897 343 81	- 320
9.5	15 892.390 38	545	7.5	15 897.557 29	-200
10.5	15 892.053 38	-1	8.5	15 897.763 91	- 64
11.5	15 891.723 11	-201	5.0		51
			$^{Q}O_{22}$		
	${}^{S}R_{21}$		1.5	15 894.696 43	304
1.5	15 897.343 81	342	2.5	15 894.377 56	135

TABLE II. (Continued.)

	Observed	$\Delta \times 10^{-5}$	<i>J</i> ″	Observed	
J''	${}^{P}P_{11}$	0-1 Sub	band	${}^{Q}Q_{22}$	$\Delta \times 10^{-5}$
2.5	15 898.204 41	171	3.5	15 894.052 39	- 49
3.5	15 899.058 33	- 192	4.5	15 893.722 81	-200
4.5	15 899.912 25	-225	5.5	15 893.390 80	-266
5.5	15 900.766 18	-70	6.5	15 893.058 36	- 193
6.5	15 901.616 77	-202	7.5	15 892.727 42	74
7.5 8.5	15 902.407 30	-418 -102	8.5	15 892.399 75	578
0.5	15 905.524 44	- 192		0	
	⁰ P ₁₂			$^{\varrho}Q_{11}$	
2.5	15 901.196 48	844	1.5	15 904.151 77	-45
3.5	15 900.375 91	626 286	2.5	15 904.519 93	46 57
4.J 5.5	15 898 824 84	- 165	3.5 4 5	15 905 346 15	- 138
3.5	15 905 346 01	- 581	5.5	15 905 801 04	- 685
4.5	15 905.803 01	-1012	010	10 9 00 100 1 0 1	000
5.5	15 906.283 33	-2133		${}^{P}Q_{21}$	
6.5	15 906.823 51	-220	1.5	15 895.881 06	295
7.5	15 907.373 94	- 153	2.5	15 896.154 50	121
			3.5	15 896.421 63	- 66
	${}^{P}P_{11}$		4.5	15 896.684 33	-222
2.5	15 902.991 05	568	5.5	15 896.944 59	-293
3.5	15 902.770 90	562	6.5	15 897.204 40	-224
4.5	15 902.574 10	247	7.5	15 897.465 67	37
5.5 6.5	15 902.400 64	-243 -100	8.5	15 897.730 21	538
0.5	15 902.237 21	-100 -857		^{P}P	
1.5	13 902.127 12	057	25	15 892 914 08	184
	$R_{R_{11}}$		3.5	15 892.000 11	336
0.5	15 904.772 28	602	4.5	15 891.069 47	- 87
1.5	15 905.736 28	349			
2.5	15 906.726 97	123			
3.5	15 907.741 00	-276			
4.5	15 908.778 39	-705			
5.5	15 909.845 62	- 381			
6.5	15 910.933 01	-142			
	$P_{\mathbf{D}}(N-1)$	2–1 Subba	ind	$O_{\mathbf{D}}(N-1)$	
3.5	P ₁₁ 15 037 145 61	36	35	15 034 757 20	- 315
3.5 4 5	15 936 902 11	30	3.5 4 5	15 933 920 04	- 85
5.5	15 936.671 95	-223	5.5	15 933.096 14	-104
6.5	15 936.468 47	607	6.5	15 932.290 03	73
7.5	15 936.275 01	860			
8.5	15 936.094 88	871			
9.5	15 935.921 43	- 19		$Q_{R_{12}}^{(N-1)}$	
			1.5	15 938.936 85	-219
	p (N-1)		2.5	15 939.291 54	-218
	${}^{R}R_{11}^{(N-1)}$		3.5	15 939.664 02	- 19
1.5	15 940.131 01	-80	4.5	15 940.045 39	-511
2.5	15 941.085 00	253	5.5	15 940.454 56	199
3.5 4.5	15 942.049 00	-2	0.5	15 940.871 52	115
4.5	15 944 033 71	414	7.5 8.5	15 941 751 02	- 194
6.5	15 945 044 41	93	9.5	15 942 219 12	153
7.5	15 946.075 12	205	10.5	15 942.695 00	-267
8.5	15 947.119 17	90	11.5	15 943.189 79	- 328
	${}^{P}P_{11}^{(N)}$		-	${}^{O}P_{21}^{(N)}$	
3.5	15 937.190 08	-56	3.5	15 934.836 23	14
4.5	15 936.977 71	29	4.5	15 934.032 34	-202
5.5 6.5	15 936.785 36	- 227	5.5 6.5	15 933.250 69	- 535
0.3 7.5	13 930.028 38 15 936 475 14	/30	0.3	13 932.493 72	- 538
1.5	13 730.473 14	502	15	15 938 961 31	-42
	$R^{(N)}$		2.5	15 939.339 35	24
1.5	15 940.141 01	164	3.5	15 939.737 40	-246

TABLE II. (Continued.)

		$\Delta \times 10^{-5}$	J″	01 1	
J''	$^{P}P_{11}$	0–1 Sub	band	$^{Q}Q_{22}$	$\Delta \times 10^{-5}$
2.5	15 941.105 01	-15	4.5	15 940.158 80	-517
3.5	15 942.095 70	131	5.5	15 940.612 45	102
4.5	15 943.106 40	-61	6.5	15 941.084 33	215
5.5	15 944.147 12	414	7.5	15 941.569 78	-640
6.5	15 945.205 63	339			
7.5	15 946.288 60	386		${}^{R}Q_{21}^{(N)}$	
8.5	15 947.393 81	341	2.5	15 922.006 01	-167
			3.5	15 922.311 47	-560
	${}^{Q}P_{21}^{(N)}$		4.5	15 922.637 51	694
3.5	15 920.243 19	462	5.5	15 922.952 97	496
4.5	15 919.959 66	121	6.5	15 923.270 04	86
5.5	15 919.682 80	36	7.5	15 923.594 48	65
6.5	15 919.409 28	-108	8.5	15 923.924 81	312
7.5	15 919.139 09	-292	9.5	15 924.251 11	-134
8.5	15 918.878 91	176	10.5	15 924.588 09	232
9.5	15 918.616 51	100	11.5	15 924.924 51	321
	${}^{S}R_{21}^{(N)}$			${}^{R}Q_{21}^{(N-1)}$	
1.5	15 923.187 81	51	2.5	15 921.991 08	610
2.5	15 924.085 10	-108	3.5	15 922.273 22	154
3.5	15 924.986 83	-237	4.5	15 922.552 90	-203
4.5	15 925.896 35	20	5.5	15 922.831 95	-260
5.5	15 926.801 42	-541	6.5	15 923106 17	-416
6.5	15 927.714 27	-673	7.5	15 923.383 69	167
7.5	15 928.634 91	- 345	8.5	15 923.649 81	44
8.5	15 929.562 22	360	9.5	15 923.910 12	- 193
9.5	15 930.479 52	- 192	10.5	15 924.174 39	466
	0 (11 1)		11.5	15 924.424 37	232
	${}^{Q}P_{21}^{(N-1)}$		12.5	15 924.670 98	237
3.5	15 920.199 83	665	13.5	15 924.915 88	690
4.5	15 919.882 94	14	14.5	15 925.138 36	-436
5.5	15 919.569 39	42		G (N 1)	
6.5	15 919.251 39	-12		${}^{S}R_{21}^{(N-1)}$	
7.5	15 918.932 28	207	2.5	15 924.062 86	-63
8.5	15 918.606 50	167	3.5	15 924.942 36	- 145
9.5	15 918.282 94	783	4.5	15 925.817 41	-310
			5.5	15 926.688 01	- 536
			6.5	15 927.557 50	- 464
			7.5	15 928.425 88	- 68
			8.5	15 929.284 25	-205
			9.5	15 930.145 96	491

and 2–1 (Fig. 3) subbands appear like case (a) ${}^{2}\Pi({}^{2}\Delta) - {}^{2}\Sigma$ (case (b) ${}^{2}\Pi$) transitions. This is because the spin–rotation constant, ϵ_{aa} , in CaNH₂ has a similar effect as the spin–orbit constant (A^{SO}) of a hypothetical linear molecule. The rotational energy levels of a near prolate doublet asymmetric top are approximately given by

$$E(N,K_a) = AK_a^2 \pm \frac{1}{2}\epsilon_{aa}K_a + \frac{1}{2}(B+C)[N(N+1) - K_a^2] + \cdots,$$
(1)

where A, B, C are the rotational constants, and K_a and N are angular momentum quantum quantum numbers. Thus for a subband with $K'_a = 0$ (0–1 subband) in the $\tilde{B} {}^2B_1$ state, the excited state energy levels will approximate a ${}^2\Sigma$ state of a linear molecule. The value of ϵ_{aa} in the ground state is small because the \tilde{X} state originates from an s orbital which does not have any spin-orbit coupling. The $K''_a = 1$ levels behave as a Hund's case (b) ${}^{2}\Pi$ state and the spectrum appears like a ${}^{2}\Sigma$ -case (b) ${}^{2}\Pi$ transition.

For the 1–0 subband, the excited state is like an intermediate Hund's case (a)–case (b) ² Π state. This is because the term, $|\epsilon_{aa}/(B+C)J| \leq 1$ ($\epsilon'_{aa} \approx -7.5 \text{ cm}^{-1}$) for low Jvalues (i.e., $J \leq 15$). The \tilde{A} and \tilde{B} states of CaNH₂ differ from the corresponding states of SrNH₂, where $|\epsilon_{aa}| \approx 30 \text{ cm}^{-1}$. The splitting of the F_1 and F_2 spin components in the excited electronic state is approximately given by, $\epsilon_{aa}K_a$, so the term $|\epsilon_{aa}/(B+C)J| \geq 1$, even for low $J(\leq 20)$ in SrNH₂. Thus the $K_a \geq 1$ levels will approximate case (a) behavior in SrNH₂ because of the large value of ϵ_{aa} in the \tilde{A} and \tilde{B} states. The transition from pure case (a) behavior to intermediate case (a)–(b) behavior begins at high rotational angular momentum ($J \approx 50$). Some spin uncoupling was observed in the $\tilde{A} - \tilde{X}$ and $\tilde{B} - \tilde{X}$ transitions of SrNH₂, since high *J* rotational levels were populated in the Broida oven source.²³ High *J* rotational transitions were not observed in the cold spectrum of CaNH₂ recorded in this work.

The difference between case (a) and intermediate case (a)–(b) behavior can clearly be seen by comparing the spectra of the 1–0 (Fig. 2) and 2–1 (Fig. 3) subbands. The 2–1 subband corresponds to a case (a) ${}^{2}\Delta$ –case (b) ${}^{2}\Pi$ transition of a linear molecule. The separation between F_{2} and F_{1} spin–rotation components in the excited state is roughly 17 cm⁻¹ ($|\epsilon_{aa}K_{a}|=15.1$ cm⁻¹), while the corresponding splitting in the 1–0 band ($\nu({}^{Q}Q_{22})-\nu({}^{Q}Q_{11})$) is 7.1 cm⁻¹. A clear separation of the band origins of the F_{1} and F_{2} components is quite evident in the spectrum of the 2–1 subband but is not clearly observed in the 1–0 subband.

The fine structure of the $K_a=0$ rotational levels arises from spin-rotation interactions, where the splittings are proportional to $\frac{1}{2}(\epsilon_{bb} + \epsilon_{cc})$. These levels are labelled F_1 and F_2 according to the total angular momentum J ($=N\pm\frac{1}{2}$, + for F_1 , - for F_2). In rotational levels with $K_a \neq 0$, the splitting of the F_1 and F_2 components are equivalent to a "spinorbit" splitting which is proportional to $\epsilon_{aa}K_a$. This is because the spin-rotation interactions are dominated by second order spin-orbit effects rather than first order coupling between electron spin and nuclear rotation. The second order nature of the spin-rotation interaction allows one to derive simple formulas (pure precession model,² Coriolis interaction¹⁹) for the spin-rotation parameters. The small splitting within each component is due to slight asymmetry in the molecule.

The energy level diagram for a 1-0 subband is given in Fig. 4, the transitions are labeled according to the recommendations of Marr *et al.*, ${}^{1} \Delta N \Delta J_{F'_i F''_i}$. There are a total of 12 allowed branches in the 0-1 and 1-0 subbands and 8 were observed for the 0-1 subband while 11 were observed for the 1-0 subband. In the 2-1 subband 14 of the 24 possible branches were observed. Energy level diagrams for the 0-1, 1-0, and 2-1 subbands are depicted in Figs. 4-6. The labeling of the F_1 and F_2 components in a case (a) electronic state of an asymmetric top molecule can lead to some confusion. One can choose F_1 and F_2 according to the sign of ϵ_{aa} [ϵ_{aa} >0 regular case (a), ϵ_{aa} <0 inverted case (a)], or, the conventional spectroscopic method based on a Hund's case (a)-case (b) correlation diagram between N and Jwhich leads to the identification of the F_1 and F_2 spin labels.²⁴ In the paper by Marr *et al.*, they chose F_1 and F_2 based on the sign of ϵ_{aa} , we, however, choose the conventional scheme. The choice of the labeling scheme, however, does not effect the molecular constants or the J assignment. For example, fitting the data of Marr et al. using our nonlinear least squares program gave identical constants to those in the published literature.¹ The differences arise in the label of each rotational level (N_{KaKc}) and the spin labels, F_1 and F_2 . Using the notation adopted here, the F_1 and F_2 labels for the assigned branches of the 1-0 and 2-1 subbands in the $\tilde{A}^{2}B_{2}-\tilde{X}^{2}A_{1}$ transition should be interchanged and the N (and K_c) quantum number label should be increased by 1 for the F_1 component and reduced by 1 for F_2 , For example, the ${}^{P}P_{22}^{N}$ branch becomes ${}^{O}P_{12}^{N}$, since the rotational transitions are relabeled, $(F_1)2_{21} \leftarrow (F_2)4_{14}$, from $(F_2)3_{22} \leftarrow (F_2)4_{14}$ in Fig. 5 of Ref.1. In the paper of the $\tilde{C}-\tilde{X}$ band system of CaNH₂,² we had labeled the rotational levels of the excited state in the 1–1 subband using the scheme of Marr *et al*. For consistency we reproduce the energy level diagram using the scheme adopted in this paper (see Fig. 7). The 0–0 energy level diagram depicted in Fig. 3 of Ref. 2 does not change since $K_a = 0$ levels approximate a ${}^{2}\Sigma$ states of a diatomic (linear) molecules.

The assignment of the $\tilde{B} - \tilde{X}$ spectrum was carried out in a using a color Loomis-Wood program²⁵ to sort the branches, and ground state combination differences were calculated with the constants of Marr et al. There were, however, problems in fitting the assigned lines. There was difficulty in simultaneously fitting all the branches with the inclusion of the highest J lines. It was reasoned that there were perturbations in the B state similar to those found in the \tilde{B} state of SrNH₂.²³ Here a Coriolis coupling between one quanta in the ν_3 Sr–N stretch (a_1 symmetry) of the $\tilde{A}^2 B_2$ state was found to interact with v=0 of the $\tilde{B}^{2}B_{1}$ state. Another possibility for a Coriolis interaction is between ν_6 (NH bend b_2 symmetry) of the $\tilde{A}^2 B_2$ state with the $\tilde{B}^2 B_1$ state. The estimated location of the energy levels of the excited stretching and bending modes in the $\overline{A}^{2}B_{2}$ state were found to be $\sim 50 \text{ cm}^{-1}$ away (to the blue and red, respectively) from v = 0 of the energy levels of the $\tilde{B}^{-2}B_1$ state in CaNH₂. This eliminated the possibility of a local Coriolis interaction causing the problems in fitting the line positions of the $\tilde{B}^{2}B_{1}-\tilde{X}^{2}A_{1}$ transition. It was found that adding higher order (quartic) centrifugal distortion constants to the fit, both rotational^{26,27} and spin-rotational,²⁸ alleviated the difficulties associated with fitting all the branches of each subband simultaneously. Perhaps these high order constants take into account the interactions with distant vibronic levels of the A state.

The molecular constants for the $\tilde{B} \,^2 B_1$ and $\tilde{X} \,^2 A_1$ states are reported in Table I. These constants are obtained from fitting the data of all three low-lying electronic transitions $(\tilde{A} \,^2 B_2 - \tilde{X} \,^2 A_1, {}^1 \tilde{B} \,^2 B_1 - \tilde{X} \,^2 A_1, \tilde{C} \,^2 A_1 - \tilde{X} \,^2 A_1^2)$. A version of this table was published in the $\tilde{C} - \tilde{X}$ paper, but since then we have investigated the spin–rotation parameters more carefully. In the pure precession model, the spin–rotation parameters can be predicted using a simple formula, for example, the interacting pair of states due to rotation about the *b* axis (\tilde{B} and \tilde{C} states), gives the following formula for the second order correction to ϵ_{bb} :²

$$\boldsymbol{\epsilon}_{bb}^{(2)} = \pm \frac{2l(l+1)BA^{\mathrm{so}}}{E_{\tilde{C}} - E_{\tilde{B}}},\tag{2}$$

where the top sign refers to the lower lying electronic state and l=1 for p orbitals. This model also predicts that $\epsilon_{cc}^{(2)}=0$ for the $\tilde{B}^{2}B_{1}$ state. In the previous paper, the observed value of the spin-rotation constants derived from a global fit of the dataset are $\epsilon_{bb}^{obs}=0.00351 \text{ cm}^{-1}$ and $\epsilon_{cc}^{obs}=0.0389 \text{ cm}^{-1}$ while the pure precession model predicted the following values: $\epsilon_{bb}^{(2)}=0.0539 \text{ cm}^{-1}$ and $\epsilon_{cc}^{(2)}=0 \text{ cm}^{-1}$. At the time of

publication we believed the large discrepancy between the observed values and the predicted values were due to the failure of the pure precession model which assumed that the unpaired electron belongs in an pure p-type orbital. It was suggested to us²⁹ that perhaps the values of ϵ_{bb} and ϵ_{cc} could be interchanged to improve the agreement with the predictions of the pure precession model. In terms of fitted constants, this would mean that the observed value of the term, $\frac{1}{4}(\epsilon_{bb}-\epsilon_{cc})$, would have to change sign in the $\tilde{B}^{2}B_{1}$ state. This term is a correction term due to the slight asymmetry (indicated by $\gamma = 1$ or $\gamma = 0$) of the molecule in a particular rotational level $(N_{K_aK_a})$ with $K_a \neq 0$. By simply changing the sign of this term and leaving all other constants unchanged, it was found that the residuals of the fit in the 1-0 subband were more than an order of magnitude larger than the uncertainty of their line positions. This is because the asymmetry splitting in $K_a=1$ is significantly larger than in $K_a=2$. We then interchanged the assignment of the asymmetry components in the 1-0 subband and refit the data. This reassignment reduced the residuals down to the experimental uncertainty of the line positions and the sign of the term, $\frac{1}{4}(\epsilon_{bb})$ $-\epsilon_{cc}$) became positive. From these fits we find the values for the spin-rotation parameters are now $\epsilon_{bb}^{obs} = 0.0372 \text{ cm}^{-1}$ and $\epsilon_{cc}^{obs} = 0.003 \text{ 89 cm}^{-1}$, which is in much better agreement with the pure precession model. This was further confirmed by finding the first lines in the spectrum of the 1-0 subband. The first line of the ${}^{P}P_{11}(1.5)$ branch is predicted to occur at 15 903.2289 cm⁻¹. The observed line was found at 15 903.2224 cm⁻¹ confirming the correctness of the new assignment of the 1-0 subband. We have also confirmed the assignment of the asymmetry components of the C-X transition. In this case, the prediction for the first line of the ${}^{P}P_{11}^{1}(1.5)$ is 17 374.5830 cm⁻¹ which should be compared to the observed position at 17 374.5765 cm^{-1} . The usefulness of the simple pure precession model is illustrated by this example.

IV. CONCLUSION

Laser ablation sources coupled with supersonic expansions have provided researchers with a powerful technique for the analysis of the electronic spectra of polyatomic molecules. These spectra could not be recorded easily in any other way regardless of the resolution of the probe laser. High temperature sources such as the Broida oven was the most widely used method to generate the alkaline earth containing diatomic and polyatomic molecules. This method is not suitable for the rotational analysis of larger polyatomic molecules. It is only from high resolution studies that we can elucidate the details of structure and bonding in molecular systems. The pure precession model has been used to describe the spin–rotation interactions in the alkaline-earth family of molecules.^{3,4} We have presented a case where the model can be used to help correctly assign the spectrum of an open shell asymmetric molecule. The utility of this model for other polyatomic molecules with more complex spectra should be of considerable interest.

ACKNOWLEDGMENTS

This work is supported by the Natural Sciences and Engineering Research Council of Canada (NSERC). We wish to thank Professor John Brown and Professor Tim Steimle for their helpful discussions.

- ¹A. J. Marr, M. Tanimoto, D. Goodridge, and T. C. Steimle, J. Chem. Phys. **103**, 4466 (1995).
- ²Z. Morbi, C. Zhao, and P. F. Bernath, J. Chem. Phys. **106**, 4860 (1997).
 ³P. F. Bernath, Science **254**, 665 (1991).
- ⁴P. F. Bernath, in *Spectroscopy and Photochemistry of Polyatomic Alkaline Earth-Containing Molecules*, Vol. 23 of Advances in Photochemistry, edited by D. H. Volman and D. C Neckers (Wiley, New York, 1997).
- ⁵E. Murad, W. Swider, and S. W. Benson, Nature (London) **289**, 273 (1981).
- ⁶P. A. Bonczyk, Combust. Flame 67, 179 (1987).
- ⁷M. D. Oberlander and J. M. Parson, J. Chem. Phys. 105, 5806 (1996).
- ⁸H. F. Davis, A. G. Suits, H. Hongtao, and Y. T. Lee, Ber. Bunsenges. Phys. Chem. **94**, 1193 (1990).
- ⁹J. P. Visticot, C. Alcaraz, J. Berlande, J. Cuvellier, T. Gustavsson, J. M. Mestdagh, P. Meynadier, P. de Pujo, and O. Sublemontier, J. Chem. Phys. **94**, 4913 (1991).
- ¹⁰ M. Esteban, M. Garay, J. M. Garcia-Tijero, E. Verdasco, and A. Gonzalez, Chem. Phys. Lett. **230**, 525 (1994).
- ¹¹J. M. Mestdagh, J. P. Visticot, and P. F. Bernath, Chem. Phys. Lett. 237, 568 (1995).
- ¹²A. Gonzalez Urena and M. Garay, Chem. Phys. Lett. 237, 570 (1995).
- ¹³ H. F. Davis, A. G. Suits, Y. T. Lee, C. Alcaraz, and J. M. Mestadagh, J. Chem. Phys. **98**, 9595 (1993).
- ¹⁴R. Pereira and D. H. Levy, J. Chem. Phys. 105, 9733 (1996).
- ¹⁵R. A. Hailey, C. N. Jarman, and P. F. Bernath, J. Chem. Phys. **107**, 669 (1997).
- ¹⁶ J. V. Ortiz, J. Chem. Phys. **92**, 6728 (1990).
- ¹⁷ R. F. Wormsbecher, R. E. Penn, and D. O. Harris, J. Mol. Spectrosc. **97**, 65 (1983).
- ¹⁸A. M. R. P. Bopegedera, C. R. Brazier, and P. F. Bernath, J. Phys. Chem. 91, 2779 (1987).
- ¹⁹C. J. Whitham and Ch. Jungen, J. Chem. Phys. **93**, 1001 (1990).
- ²⁰C. Zhao, P. G. Hajigeorgiou, P. F. Bernath, and J. W. Hepburn, J. Mol. Spectrosc. **176**, 268 (1996).
- ²¹ S. Gerstenkorn and P. Luc, Atlas du Spectre d' Asorption de la Molécule d'Iode (CNRS II, 91405 Orsay, France, 1978).
- ²²S. Gerstenkorn and P. Luc, Rev. Phys. Appl. 14, 791 (1978).
- ²³C. R. Brazier and P. F. Bernath (unpublished).
- ²⁴G. Herzberg, Spectra of Diatomic Molecules (Van Nostrand Reinhold, New York, 1950).
- ²⁵C. N. Jarman and P. F. Bernath (unpublished).
- ²⁶J. K. G. Watson, J. Chem. Phys. 46, 1935 (1967).
- ²⁷ J. K. G. Watson, in Aspects of Quartic and Sextic Centrifugal Effects on Rotational Energy Levels, Vol. 6 of Vibrational Spectra and Structure, edited by J. R. Durig (Elseiver Scientific, Amsterdam, 1977).
- ²⁸ J. M. Brown and T. J. Sears, J. Mol. Spectrosc. **75**, 111 (1979).
- ²⁹ John Brown (private communication).