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The $[17.0]\,^2\Pi_{1/2} \leftarrow X\,^2\Pi_{1/2}$ system of AlCa

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Abstract

Laser-induced fluorescence spectroscopy has been used to study supersonically cooled AlCa. This study investigates under higher resolution (0.007 cm-1) a single band previously studied and tentatively assigned as the (0-0) vibrational transition of the $[17.0]\,^2\Delta_{3/2}(?) \leftarrow X\,^2\Pi_{1/2}$ system of AlCa. The resolution of the rotational structure in the present study enabled a definite assignment as a $^2\Pi_{1/2} \leftarrow {}^2\Pi_{1/2}$ transition. Analysis of the spectrum gives $B_0' = 0.096685(19)$ cm-1, $(p+2q)' = -0.013078(370)$ cm^{-1}, and $B_0'' = 0.105518(20)$ cm^{-1}. These convert to ground and excited state bond lengths of $r_0'' = 3.14942(30)$ and $r_0' = 3.29014(32)$ Å, respectively. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

As one of a series of experiments [1] on the 3d transition-metal aluminides, AlCa was investigated in 1994 by Behm, Morse, Boldyrev, and Simons [2]. Although calcium is an alkaline earth element, AlCa was investigated as an example of an aluminide of the same period without d electrons. Because of the difficulty in promoting calcium to a $4s^13d^1$ or a $4s^14p^1$ configuration, the AlCa molecule provides a prototype for understanding the chemical bonding between aluminum and transition metals with stable $3d^n4s^2$ configurations.

The investigation by Behm et al. provided the first experimental and theoretical studies to be performed on diatomic AlCa [2]. Ab initio calculations were also performed to ascertain the potential energy curves of seven low-lying states of AlCa. In the resonant two-photon ionization study of AlCa in a supersonic jet, the ground state of the molecule was determined to be of $^2\Pi_r$ symmetry, with a bond length of 3.1479 ± 0.0010 Å. This ground state originates from the interaction of ground state Al ($3s^23p^1$, $^2P^\circ_{1/2,3/2}$) and Ca ($4s^2$, $^1S_0$), with the Al 3p electron in the $p\pi$ orientation. Transitions to four excited states were observed in the wavenumber range from 13 500 to 17 900 cm^{-1}, with rotational analysis successfully performed on transitions to three of the four band systems. This rotational analysis yielded symmetries and bond lengths for the $[13.5]\,^2\Pi_r$, the $[15.8]\,^2\Sigma$, and the $[17.6]\,^2\Delta_{3/2}$ excited states. Transitions to the $[17.0]\,^2\Delta_{3/2}(?)$ excited state were not successfully rotationally resolved, but a tentative assignment was made based on the apparent intensities of the rotational branches at a resolution of 0.04 cm^{-1}. The present study was initiated to resolve the

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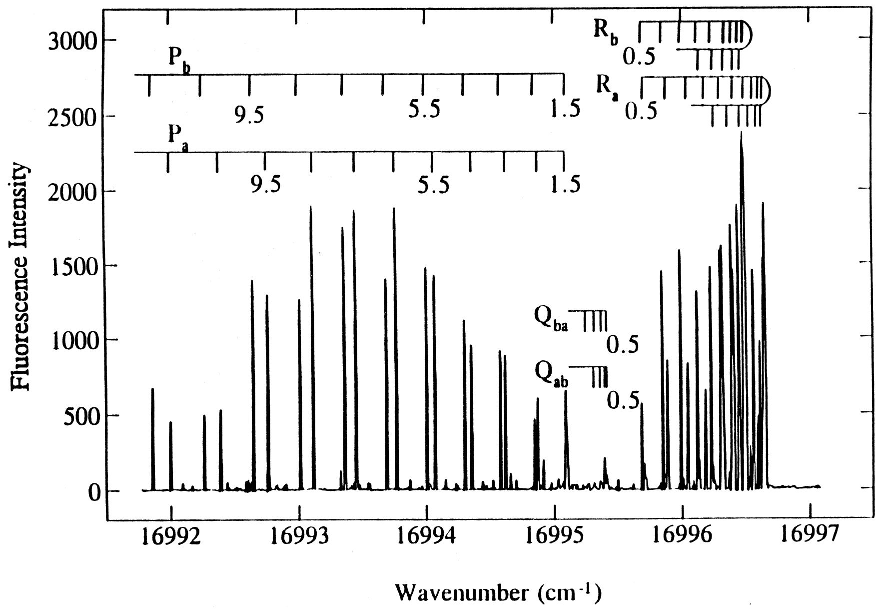

Fig. 1. Rotationally resolved 0-0 band of the $[17.0]^2\Pi_{1/2} \leftarrow X^2\Pi_{1/2}$ system of AlCa.

uncertainty in this assignment by investigating a transition to the $[17.0]^2\Delta_{3/2}$(?) state under much higher resolution (0.007 cm^{-1}) using laser-induced fluorescence with a cw ring dye laser employed for excitation.

2. Experimental

Laser-induced fluorescence spectroscopy of AlCa entrained in a supersonic jet was performed using an instrument that has been previously described [3].

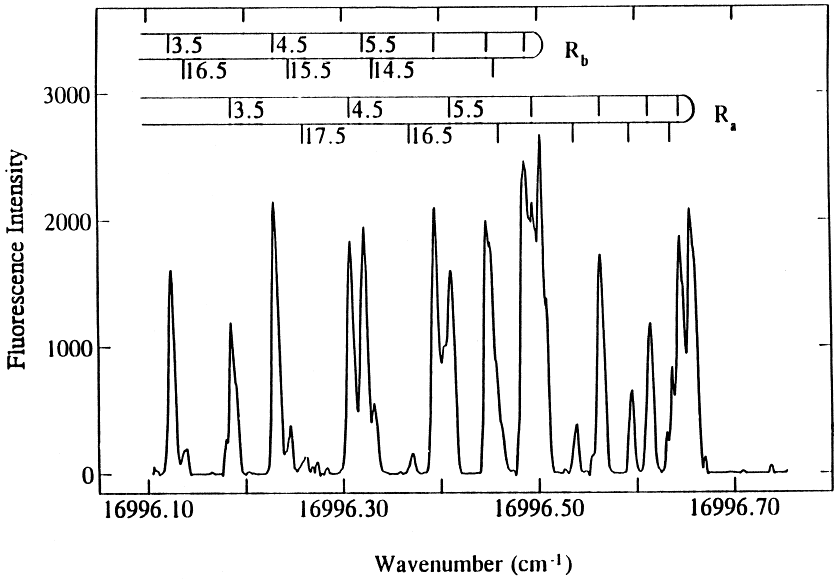

Fig. 2. *R* band head of the 0-0 band of the $[17.0]^2\Pi_{1/2} \leftarrow X^2\Pi_{1/2}$ system of AlCa.

The AlCa molecules were formed by pulsed laser ablation (Nd:YAG, 1064 nm) of an AlCa (2:1) alloy metal disk, followed by supersonic expansion in helium carrier gas (120 psi). The metal target used in the previous study [2] of AlCa was used in the present investigation. From the point of vaporization, the metal atoms and molecules were entrained in a pulse of carrier gas and traveled through a 6 cm long channel with a 2 mm exit orifice before expansion into vacuum. The resulting jet-cooled molecular beam was excited by an argon ion (Coherent, Innova 200-15) pumped cw ring dye laser (Coherent 899-21, ≈ 0.5 MHz linewidth) which crossed the molecular beam at right angles 1 cm downstream from the exit orifice. The fluorescence was detected using a Hammamatsu R3896 photomultiplier tube after being dispersed by a Spectral Energy GM252 monochromator (3.3 nm/mm linear dispersion), with an entrance slit width of 0.50 mm, and an exit slit width of 1.0 mm. Fluorescence in the 0-1 band at 595 nm was moni-

Table 1
Line positions of the 0–0 band of the $[17.0]^2\Pi_{1/2} \leftarrow X\,^2\Pi_{1/2}$ system of AlCa[a]

Label	J''	Frequency (cm^{-1})	Residual[b] (cm^{-1})	Label	J''	Frequency (cm^{-1})	Residual[b] (cm^{-1})
R_a	0.5	16995.7103	−0.0053	Q_{ab}	3.5	16995.3099	0.0027
R_b	0.5	16995.6888	−0.0011	P_a	1.5	16995.1003	−0.0020
R_a	1.5	16995.8876	−0.0012	P_b	1.5	16995.0901	0.0001
R_b	1.5	16995.8495	−0.0009	P_a	2.5	16994.8716	0.0005
R_a	2.5	16996.0454	0.0010	P_b	2.5	16994.8457	−0.0004
R_b	2.5	16995.9919	−0.0014	P_a	3.5	16994.6198	−0.0024
R_b	3.5	16996.1192	0.0007	P_b	3.5	16994.5813	−0.0033
R_a	4.5	16996.3035	0.0010	P_a	4.5	16994.3537	−0.0020
R_b	4.5	16996.2269	0.0009	P_b	4.5	16994.3023	−0.0031
R_a	5.5	16996.4063	0.0013	P_a	5.5	16994.0694	−0.0021
R_b	5.5	16996.3176	0.0017	P_b	5.5	16994.0057	−0.0028
R_a	6.5	16996.4904	0.0005	P_a	6.5	16993.7694	−0.0002
R_b	6.5	16996.3901	0.0020	P_b	6.5	16993.6924	−0.0016
R_a	7.5	16996.5591	0.0020	P_a	7.5	16993.4517	0.0016
R_b	7.5	16996.4447	0.0021	P_b	7.5	16993.3620	0.0002
R_a	8.5	16996.6093	0.0026	P_a	8.5	16993.1148	0.0019
R_b	8.5	16996.4827	0.0032	P_b	8.5	16993.0122	0.0003
R_b	12.5	16996.4531	0.0028	P_a	9.5	16992.7606	0.0025
R_a	13.5	16996.5899	0.0005	P_b	9.5	16992.6467	0.0023
R_a	14.5	16996.5335	0.0005	P_b	10.5	16992.2648	0.0056
R_b	14.5	16996.3277	−0.0020	P_a	11.5	16992.0003	0.0049
R_a	15.5	16996.4586	−0.0003	P_b	11.5	16991.8615	0.0052
R_b	15.5	16996.2415	−0.0014	P_a	12.5	16991.5924	0.0049
R_a	16.5	16996.3663	−0.0008	P_b	12.5	16991.4372	0.0014
R_a	17.5	16996.2547	−0.0029	P_a	13.5	16991.1605	−0.0015
Q_{ab}	0.5	16995.4139	−0.0055	P_b	13.5	16990.9958	−0.0018
Q_{ba}	0.5	16995.4139	0.0079	P_a	14.5	16990.7179	−0.0009
Q_{ab}	1.5	16995.3967	−0.0030	P_b	14.5	16990.5394	−0.0023
Q_{ba}	1.5	16995.3713	−0.0014	P_a	15.5	16990.2549	−0.0031
Q_{ab}	2.5	16995.3621	−0.0002	P_b	15.5	16990.0646	−0.0036
Q_{ba}	2.5	16995.3175	−0.0043				

[a] Rotational constants and band origin were determined by a least-squares fit of the measured line positions to the formula [6]$\nu = \nu_0 + B'J'(J'+1) \mp 1/2(p+2q)'(J'+1/2) - B''J''(J''+1) \pm 1/2(p+2q)''(J''+1/2)$,yielding the values $B' = 0.096685(19)$, $(p+2q)' = -0.013078(370)$, $B'' = 0.105518(20)$, $(p+2q)'' = -0.000402(367)$, and $\nu_0 = 16995.41932(50)$ cm^{-1}, with the 1σ error limit in units of the last reported digit provided in parentheses after each value. These rotational constants convert to bond lengths of $r_0'' = 3.14942 \pm 0.00030$ Å and $r_0' = 3.29014 \pm 0.00032$ Å for the dominant (96.9%) isotopic modification, ^{27}Al^{40}Ca.

[b] Defined as $\nu - \nu_{\text{calc}}$.

tored to avoid detecting scattered excitation laser light. The signal was processed by gated integration using a 10 μs gate width before being digitized and recorded using an IBM 386 compatible computer. Transmission fringes from a 250 MHZ confocal étalon were used to linearize the spectrum in frequency, with calibration accomplished by comparison of iodine absorption lines to the iodine absorption atlas of Gerstenkorn and Luc [4,5]. A Doppler limited FWHM resolution of approximately 230 MHz (0.007 cm^{-1}) was obtained for the spectrum of AlCa molecules in the jet-cooled beam.

3. Results and discussion

Fig. 1 displays the rotationally resolved 0-0 band of the $[17.0]^2\Pi_{1/2} \leftarrow X^2\Pi_{1/2}$ system as recorded in the present investigation. The presence of an R branch band head demonstrates that the bond length increases upon electronic excitation, and this is confirmed by the rotational constants obtained in this investigation. Because of the band head, the R branch region of the spectrum is particularly congested, but the cw ring laser provided sufficient resolution to assign the lines, as is illustrated in the expanded view shown in Fig. 2. The observation of the $R(0.5)$, $Q(0.5)$, and $P(1.5)$ lines leads to a definite assignment as an $\Omega = 0.5 \leftarrow \Omega = 0.5$ transition, and this in turn implies that the band corresponds to a $^2\Pi_{1/2} \leftarrow {}^2\Pi_{1/2}$ transition. The tentative assignment of $^2\Delta_{3/2} \leftarrow X^2\Pi_{1/2}$ obtained in the resonant two-photon ionization study [2] is shown to be incorrect with the higher resolution available in the present study. Line positions and residuals from the fit of the lines to the standard spectroscopic model [6] are listed in Table 1, with the resulting spectroscopic constants given in the footnotes of the table. As can be seen clearly in the P branch, the complexity of the spectrum results from a significant splitting of each P, Q, and R line into two lines due to lambda doubling in the ground and excited states. This effect was included in the fit of the spectrum, yielding lambda doubling parameters for both states. Because it is not known which of the levels correspond to e and f parity, the levels have been labeled a and b, with a being the higher energy level in the excited state.

The fit yielded the values $B'_0 = 0.096685(19)$, $(p+2q)'_0 = -0.013078(370)$, $B''_0 = 0.105518(20)$, and $(p+2q)''_0 = -0.000402(367)$ cm^{-1}, with the number in parentheses giving the 1σ error limit from the fit. The ground state rotational constant, B''_0, agrees well with that determined in the previous study by Behm et al. [2], but was determined with much greater precision in the present investigation due to the higher resolution obtained. From these values, r_0 values of $r''_0 = 3.14942 \pm 0.00030$ Å and $r'_0 = 3.29014 \pm 0.00032$ Å are obtained (1σ error limits). No lambda doubling in the $X^2\Pi_{1/2}$ ground state was observed in the previous study [2], and it is apparent that even with the higher resolution afforded in the present investigation the ground state lambda doubling constant, $(p+2q)''_0$, is not statistically significant. The rather large splitting observed in the rotational lines is almost entirely due to lambda doubling in the excited $[17.0]^2\Pi_{1/2}$ state. The electronic state or states that are responsible for this large lambda doubling parameter are at present unknown.

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