

## NOTES

The  $A(2)^1\Sigma^+$  State of NaK

Singlet and triplet states of the NaK molecule have been the subjects of experimental and theoretical work in recent years (1-5). However, the rotational structure in the first excited singlet state  $A(2)^1\Sigma^+$ , which correlates with  $\text{Na } (3s^2S_{1/2}) + \text{K } (4p^2P_{1/2})$  and which was first observed by Loomis and Arvin (6) in 1934, has not yet been described. In the course of our work on the ground state,  $X(1)^1\Sigma^+$ , and other low-lying singlet states, especially  $B(1)^1\Pi$  and  $C(3)^1\Sigma^+$ , we have assigned many lines to transitions involving  $A^1\Sigma^+$ , the first excited singlet state, and we now give a brief account of their analysis.

Visible and infrared laser-excited fluorescence spectra of NaK were recorded at high resolution by Fourier transform spectrometry; experimental details have already been given. Lines assigned to three systems,  $B(1)^1\Pi$ ,  $C(3)^1\Sigma^+$ , and  $D(2)^1\Pi-A(2)^1\Sigma^+$ , together with 58 lines of  $C(3)^1\Sigma^+-X^1\Sigma^+$  and 18 lines of a transition from an unidentified  $^1\Sigma^+$  state to  $C(3)^1\Sigma^+$  were fitted simultaneously to polynomials in the vibrational, rotational, and centrifugal distortion constants of  $A(2)^1\Sigma^+$ , using ground state constants fixed at values determined in a separate calculation (3). Levels of the  $A(2)^1\Sigma^+$  state are subject to many small perturbations by the lowest  $^3\Pi$  state,  $b(1)^3\Pi$ , and the estimates of the mean square errors of the fits are of the order of 50 times larger than those for typical fits to unperturbed lines. Details are given in Table I, and values of the derived molecular constants are given in Table II.

Isotope shifts between  $^{23}\text{Na}^{39}\text{K}$  and  $^{23}\text{Na}^{41}\text{K}$  are large compared with the observed perturbations, and the vibrational numbering in  $A(2)^1\Sigma^+$  followed from the analysis of 83 lines assigned to the  $C-A$  transition of  $^{23}\text{Na}^{41}\text{K}$ . It proved to be identical with that given by Loomis and Arvin from their vibrational analysis of the  $A-X$  system in absorption.

Experimental and calculated values of the constants for the state  $A^1\Sigma^+$  are given in Table III. The comparison affords an illustration of the quantitative success of modern ab initio methods in predicting the properties of the electronic states of small molecules.

TABLE I  
Transitions Involving the State  $A^1\Sigma^+$  of NaK

$B^1\Pi - A^1\Sigma^+$	327 P and R lines	$\sigma = 0.29 \text{ cm}^{-1}$
	357 Q lines	0.26
$C^1\Sigma^+ - A^1\Sigma^+$	640 P and R lines	0.19
	83 P and R lines*	0.20
$D^1\Pi - A^1\Sigma^+$	8 P and R lines	0.30
	6 Q lines	0.20
*lines of $^{23}\text{Na}^{41}\text{K}$		

TABLE II

Spectroscopic Constants for the State  $A^1\Sigma^+$  of NaK

	Coefficient ( $\text{cm}^{-1}$ )	$2\sigma(\text{cm}^{-1})$
$T_e$	12 137.272	0.127
$\omega_e$	81.250506	0.080
$\omega_e x_e$	0.27470815	$0.494 \times 10^{-2}$
$\omega_e y_e$	$0.41931994 \times 10^{-2}$	$0.273 \times 10^{-3}$
$\omega_e z_1$	$-0.7720508 \times 10^{-4}$	$0.726 \times 10^{-6}$
$\omega_e z_2$	$0.6932446 \times 10^{-6}$	$0.898 \times 10^{-7}$
$\omega_e z_3$	$-0.282698 \times 10^{-8}$	$0.412 \times 10^{-9}$
$B_e$	0.0661371	$0.370 \times 10^{-4}$
$\alpha_e$	$0.360162 \times 10^{-3}$	$0.330 \times 10^{-6}$
$\gamma_{e1}$	$0.3300504 \times 10^{-6}$	$0.144 \times 10^{-6}$
$\gamma_{e2}$	$-0.3409183 \times 10^{-7}$	$0.150 \times 10^{-8}$
$D_e$	$0.16600 \times 10^{-6}$	$0.428 \times 10^{-8}$
$\beta_e$	$-0.6343 \times 10^{-9}$	$0.158 \times 10^{-9}$

The polynomials are valid for  $0 \leq v \leq 75$ ,  $J \leq 3 \leq 70$  and allow calculation of the measured lines to within an r.m.s. error of about  $0.25 \text{ cm}^{-1}$ .

TABLE III

Comparison of Observed and Calculated Constants for the State  $A(2)^1\Sigma^+$  of NaK

$T_e/\text{cm}^{-1}$	$\omega_e/\text{cm}^{-1}$	$r_e/\text{\AA}$	reference
13700	100	4.10	(7)
12300	76	4.21	(8)
12011	86.2	4.066	(2)
12137	81.25	4.199	this work

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