YU ISSN 0015—3206
FZKAAA 12 (2) 131 (1980)

LETTERS TO THE EDITOR

ON THE LOW-LYING ELECTRONIC STATES OF STRONTIUM MONOIODIDE

S. S. MURTY

Indian Institute of Astrophysics, Kodaikanal 624 103, *India*

Received 20 January 1980

UDC 539.19

Original scientific paper

Published vibrational analysis on the A and B systems of SrI is reinterpreted. Proposed new assignments of bands of the two systems result in the identification of the electronic energy states for $B^2\Sigma^+$, $A^2\Pi_{3/2}$ and $A^2\Pi_{1/2}$ at 14815.9, 14748.8 and 14422.7 cm^{-1}, respectively, with a spin-orbit coupling constant of 326 cm^{-1} for the $A^2\Pi$ state, as against the reported value of 393 cm^{-1}.

In recent years, studies on the electronic spectra of diatomic alkaline earth halides and oxides have received increasing attention, in view of the search for possible visible chemical laser candidates.

All the alkaline earth monohalide molecules have $^2\Sigma^+$ ground states (i.e. one unpaired electron), and it appears that the electronic spectra are characterized by the promotion of a nonbonding electron in a molecular orbital, to an excited nonbonding orbital (both the electrons being principally centered on the metal atoms). The character of the ground state of these molecules is known to be extremely ionic[1]. Vibrational frequencies and internuclear separations for all the low-lying excited states of these molecules are nearly the same as those of the ground state, resulting in appearance of very strong $\Delta v = 0$ vibrational sequence and with much weaker $\Delta v = \pm 7$ and ± 2 sequences. The relative positions of the energy

levels of low-lying states are similar; the energy values of $A^2\Pi$ and $B^2\Sigma^+$ states are known to decrease gradually in going from Ca to Ba and from F to I.

Based upon some of the above characteristic features of the spectra of alkaline earth halides, we were led to examine the published vibrational analysis of the $A - X$ and $B - X$ band systems of SrI[2] (to be referred to as *ARR*), as a qualitative difference between the states of strontium halides is not expected.

From high dispersion spectrograms of SrI, *ARR* assigned the double headed bands in the region 650—720 nm as due to the $A^2\Pi - X^2\Sigma^+$ and $B^2\Sigma^+ - X^2\Sigma^+$ transitions, by analogy with similar systems in remaining halides of calcium and strontium. Derived vibrational constants of the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states of SrI were compared with the corresponding states of SrF, SrCl and SrBr. However, as seen from Table 4 of *ARR*, we believe, contrary to their conclusion that the reported values of T_e and $A^2\Pi$ interval, are not in keeping with those of the remaining halides, for the following reasons:

(1) There is no reason to believe that the T_e value of the B state should be smaller than that of the A state, since this is not observed in any of the other remaining halides, as can be seen from Table 4 of *ARR*.

(2) The reported value (393 cm^{-1}) for the $A^2\Pi$ interval, appears to be too high to be reasonable, because it is known that the splittings of the $^2\Pi$ states and the corresponding ^2p states, follow closely.

We believe that the identification of the sequence at 674.5 nm as the $\Delta v = 0$ sequence of the $A^2\Pi_{3/2} - X^2\Sigma^+$ transition, is not convincing (see Figs. 1 and 2 of *ARR*) for the following reason:

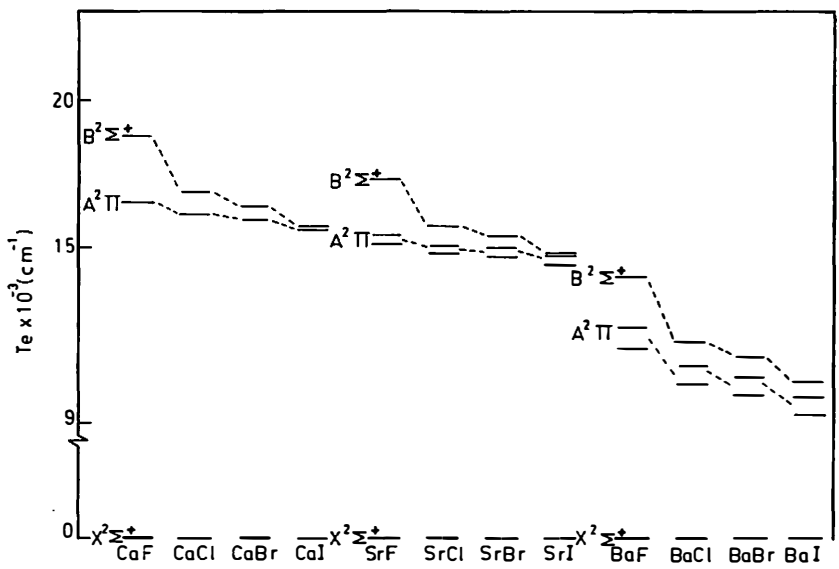

Fig. 1. Observed term values for the lowest-lying electronic states ($X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$) of the calcium, strontium and barium monohalides. (The spin — orbit splitting $^2\Pi$ states of calcium monohalides is too small to be shown).

It is known that (0,0) sequences of the $AA-X$ transitions of all the alkaline earth halides, are the most intense parts of the systems. Further, recent measurements of photon yields of several reactions producing diatomic alkaline earth halides have shown 3—5 that the $A - X$ transition should be the strongest, followed by $B - X$ and $C - X$ transitions.

It appears reasonable to propose that the strong sequences at 677.7 and 692.9 nm may be identified as the $\Delta v = 0$ sequences of the two subsystems of the $A^2\Pi - {}^2\Sigma^+$ transition and the weak sequence at 674.5 nm may be identified as the $\Delta v = 0$ sequence of the $B^2\Sigma^+ - X^2\Sigma^+$ transition. These proposed modifications bring about a change in the identification of the band systems. The band system previously assigned to the $B - X$ transition is to be reassigned as the $A^2\Pi_{3/2} - X^2\Sigma^+$ sub-system and the assigned $A^2\Pi_{3/2} - X^2\Sigma^+$ sub-system is to be identified as the $B^2\Sigma^+ - X^2\Sigma^+$ system. Consequently, the assigned P_1 and P_2 head (of $B - X$) are to be identified as the Q_2 and P_2 heads respectively (of $A^2\Pi_{3/2} - X^2\Pi_{3/2}$) and similarly, the Q_2 and P_2 heads are to be identified as the P_1 and P_2 heads respectively. Following this reinterpretation of the systems, the electronic energy states for the $B^2\Sigma^+$, $A^2\Pi_{3/2}$ and $A^2\Pi_{1/2}$ states are identified at 14815.9, 14748.8. and 14422.7 cm^{-1}, respectively., with a spin-orbit coupling constant of 326 cm^{-1}. In Table 1, the vibrational and spinorbit coupling constants of the $A^2\Pi$ and $B^2\Sigma^+$ states of strontium monohalides are compared. These new values of T_e and spin-orbit coupling constant, fit very well with the values observed in the other homologous molecules, as illustrated in Fig. 1.

TABLE 1.

Molecule	State	T_e (T_0)	ω_e	$\omega_e x_e$	A
SrF	$B^2\Sigma^+$	(17303.4)	488.9	1.86	
	$A^2\Pi$	(15352.0)	505.1	2.18	
		(15071.6)	505.7	2.20	+280.4
	$X^2\Sigma^+$	0.0	498.0	2.15	
SrCl	$B^2\Sigma^+$	(15779.5)	306.4	0.98	
	$A^2\Pi$	(15112.6)	309.1	0.97	
		(14818.5)	309.6	0.99	+294.1
	$X^2\Sigma^+$	0.0	302.3	0.95	
SrBr	$B^2\Sigma^+$	15352.0	222.0	0.55	
	$A^2\Pi$	15000.7	222.1	0.53	
		14694.4	222.2	0.53	+306.3
	$X^2\Sigma^+$	0.0	216.5	0.51	
SrI	$B^2\Sigma^+$	14815.9	179.5	0.32	
	$A^2\Pi$	14748.8	182.2	0.37	
		14422.7	182.3	0.54	+326.1
	$X^2\Sigma^+$	0.0	173.8	0.29	

Comparison of the vibrational and spin-orbit coupling constants of the $A^2\Pi$ and $B^2\Sigma^+$ states of strontium monohalides (in cm^{-1}).

In conclusion, it may be noted that recently, Dagdigian et al.[6] during their measurements of the radiative lifetimes for a number of electronic states of the alkaline earth monohalides, reported their disagreement with the assignments of *ARR* for the $B - X$ system. The present report, explains the reason for their disagreement and thus, provides an explanation for the existing uncertainty regarding the assignments of the low-lying states of the SrI molecule. However, the «final confirmation of the proposed new assignments should await a rotational analysis of the $A - X$ and $B - X$ systems of SrI.

Acknowledgments

The author is thankful to Drs R. F. Barrow and W. Weltner, Jr., for helpful correspondence, Dr. M. K. V. Bappu for his interest in this report and Mr. S. Duraikannu for typing the manuscript.

References

1) L. B. Knight jr., W. C. Easley, W. Weltner jr. and M. Wilson, J. Chem. Phys. **54** (1971) 322;
2) Ashrafunnisa, D. V. K. Rao and P. T. Rao, J. Phys. B: Atom. Molec. Phys. **6** (1973) 1503;
3) G. A. Capelle, C. R. Jones, J. Zorskie and H. P. Broida, J. Chem. Phys. **61** (1974) 4777;
4) G. A. Capelle, H. P. Broida and R. W. Field, J. Chem. Phys. **62** (1975) 2121;
5) R. S. Brasford jr., C. R. Jones, L. A. Southall and H. P. Broisa, J. Chem. Phys. **62** (1975) 2060;
6) P. J. Dagdigian, H. W. Cruse and R. N. Zare, J. Chem. Phys. **60** (1974) 2330.

O NISKOLEŽEĆIM ELEKTRONSKIM STANJIMA STRONCIJEVA MONOJODIDA

P. S. MURTY

Indian Institute of Astrophysics, Kodaikanal 624 103, *India*

UDK 539.19

Originalni znanstveni rad

Učinjena je reinterpretacija dosadašnjih objavljenih vibracijskih ispitivanja A i B sistema SrJ. Nove predložene oznake vrpci dvaju sistema vode na identifikaciju elektronske energije stanja za $B^2\,\Sigma^+$, $A^2\,\pi_{1/2}$ i $A^2\pi_{1/2}$ na vrijednostima 14815.9, 14748.8 i 14422.7 cm^{-1}, respektivno, sa spin-orbitalnom konstantom veze 326 cm^{-1} za $A^2\pi$, što je suprotno objavljenoj vrijednosti od 393 cm^{-1}.