

## A MRCI comparative study of the electronic states of $\text{AsX}^+$ (X=F, Cl, Br and I)

Marcelo A. P. Pontes<sup>a</sup> (PG), Marcos H. de Oliveira<sup>a,b</sup> (PG), Luiz F. A. Ferrão<sup>a</sup> (PQ),  
 Joaquim D. Da Motta Neto<sup>c</sup> (PQ), Orlando Roberto-Neto<sup>d</sup> (PQ) e Francisco B. C. Machado<sup>a</sup> (PQ)

<sup>a</sup> Instituto Tecnológico de Aeronáutica, São José dos Campos, SP, Brazil

<sup>b</sup> Instituto Federal do Paraná, Curitiba, PR, Brazil

<sup>c</sup> Universidade Federal do Paraná, Curitiba, PR, Brazil

<sup>d</sup> Instituto de Estudos Avançados, São José dos Campos, SP, Brazil

e-mail: marceloapontes@gmail.com

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### INTRODUCTION

$\text{AsX}$  (F, Cl, Br and I) molecules belong to the halimino radical series, and their cations are isovalent with the  $\text{NF}^+$ ,  $\text{NCl}^+$ ,  $\text{PF}^+$  and  $\text{PCI}^+$  molecules.<sup>1-3</sup> The  $\text{AsCl}^+$  ion has been obtained in the eighties when Coxon *et al.*<sup>4,5</sup> observed the visible  $\text{A}^2\Pi_{1/2} \rightarrow \text{X}^2\Pi_{1/2}$  band. Later, Kim and Hirst<sup>6</sup> calculated spectroscopic constants for all states of the lowest dissociation asymptote at the CASSCF and MRCI levels. Recently, we have characterized the  $\text{AsCl}$  radical.<sup>7</sup>

### METHODS

We used CASSCF and MRCI to characterize the low-lying electronic states of the  $\text{AsX}^+$  radicals. The CASSCF (7,8) has 7 electrons in 8 active orbitals, consisting of the  $np$  electrons and orbitals plus one extra  $b_1$  and  $b_2$  virtual orbitals, within  $\text{C}_{2v}$  symmetry. The  $ns$  valence electrons and orbitals were kept doubly occupied for all atoms. The aug-cc-pV5Z basis set was used for all atoms, for As, Br and I the ECP was used. The CASSCF/MRCI calculations were carried out using the MOLPRO program and the molecular constants have been calculated by solving the radial equation using the INTENSITY code. The dissociation energies were calculated within the supermolecule approach with the asymptotic limit energies calculated at  $30.0 a_0$ .

### RESULTS AND DISCUSSION

Table 1 shows the energy order of the excited electronic states of  $\text{AsX}^+$  radicals.

**Table 1.** Energy order of the excited electronic states of  $\text{AsX}^+$  radicals.

Halogen	electronic state (increase order)
F	$\text{X}^2\Pi$ , $(1)^2\Sigma^+$ , $(1)^4\Pi$ , $(1)^2\Pi$ , $(1)^4\Sigma^-$
Cl, Br, I	$\text{X}^2\Pi$ , $(1)^4\Pi$ , $(1)^2\Pi$ , $(1)^4\Sigma^-$ , $(1)^2\Sigma^+$

The first excited state  $(1)^2\Sigma^+$  of  $\text{AsF}^+$  is the fourth excited state for the other molecules.

Table 2 shows the molecular constants of the  $\text{X}^2\Pi$  states of ionic molecules. Equilibrium distances are increasing, while vibrational frequencies and dissociation energies are decreasing monotonically in the order  $\text{F} \rightarrow \text{I}$ .

For  $\text{AsCl}^+$ , the experimental and theoretical equilibrium distance 2.031<sup>5</sup> and 2.055<sup>6</sup> Å, and the vibrational frequency 527.7<sup>5</sup> and 519.4<sup>6</sup>  $\text{cm}^{-1}$  are in very good agreement with our results (in bold).

**Table 2.**  $\text{X}^2\Pi$  molecular constants of  $\text{AsX}^+$ .

Halogen	F	Cl	Br	I
$r_e$ (Å)	1.669	<b>2.044</b>	2.192	2.397
$D_e$ (eV)	4.70	4.03	3.75	3.63
$\omega_e$ ( $\text{cm}^{-1}$ )	839.8	<b>520.3</b>	376.2	304.9
$\omega_e x_e$ ( $\text{cm}^{-1}$ )	3.65	1.47	0.93	0.73

### CONCLUSIONS

We characterized the low lying states of  $\text{AsX}^+$  (F, Cl, Br I) using CASSCF/MRCI method providing a set of molecular constants. For  $\text{AsCl}^+$ , the calculated molecular constants for the ground state are in good agreement with previous available experimental<sup>4,5</sup> and theoretical<sup>6</sup> results.

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