Spectroscopic constants and potential energy curves of AsF

Lida Latifzadeh, K. Balasubramanian

Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287-1604, USA

Received 5 September 1995; in final form 5 December 1995

Abstract

Spectroscopic constants and potential energy curves of 21 electronic states of AsF are computed using the complete active space self-consistent field (CASSCF) followed by first- and second-order configuration interaction (FOCI, SOCI) and multireference singles and doubles configuration interaction (MRSDCI) methods. The computed spectroscopic constants agree with the experimental values for the observed states.

1. Introduction

The existence of metastable $^1\Delta$, and $^1\Sigma^+$ states for group VA diatomic halides has made them attractive candidates for chemical lasers [1-8]. All these halides share a common ground state, namely $X^3\Sigma^-$. Reactive ion etching (RIE) of a GaAs surface in a CCl$_4$F$_2$ discharge gives rise to the formation of volatile AsF$_3$ and AsF$_5$ molecules [9]. The AsF radical is generated by decomposition of the AsF$_3$ vapor in a microwave discharge at a pressure of about 30 µTorr [10-14].

The AsF radical was first studied by a Schuler-type discharge of AsF$_3$ vapor by Pannetier and co-workers [12]. The spectroscopic constants of the $X^3\Sigma^-$, $a^1\Delta$, $b^1\Sigma^+$, $c^3\Pi$ and $d^3\Pi$ electronic states have been obtained from the $d \rightarrow a$, $c \rightarrow a$, $d \rightarrow b$, and $c \rightarrow b$ transitions [10-14]. The electronic spectra of AsF attributed to the $^3\Pi \rightarrow X^3\Sigma^-$ transition have been reported by Yee and co-workers [10].

The dissociation energy of AsF corresponding to the $\text{AsF}(X^3\Sigma^-) \rightarrow \text{As}(^4S) + \text{F}(^2P)$ process has been determined [15-18]. Different measurements suggest the bond dissociation energy of AsF to lie between 4.3 ± 0.2 and 4.2 ± 0.2 eV.

O'Hare and co-workers [16] have computed the Hartree–Fock wavefunctions by the matrix expansion method of Roothaan for the $X^3\Sigma^-$ ground state of AsF at several internuclear separations. Liber- mann et al. [19] have obtained the potential energy curves of seven electronic states of AsF using a single configuration SCF followed by the MRDCI computations in the absence of spin–orbit coupling. They have included spin–orbit effects for the low-lying electronic states using the MRDCI-RCI technique. In the current study we employ a more extended basis set and full CASSCF followed by FOCI and SOCI schemes. We also study more electronic states in the current work. Theoretical studies of the AsF radical can provide an insight into the spectroscopic properties and the potential energy curves of this radical.

We carry out CASSCF followed by FOCI computations for the potential energy curves of 21 electronic states of AsF. The spectroscopic constants such as equilibrium bond lengths ($R_e$), energy separations ($T_e$), electric dipole moments ($\mu_e$), vibrational frequencies ($\omega_v$) and dissociation energies ($D_e$) of the bound electronic states were obtained using the CASSCF/FOCI/SOCI techniques.
2. Method of computations

The basic CASSCF/FOCI/SOCI techniques employed here for AsF are similar to those of PF described in a previous study [20]. All computations were made using the relativistic effective core potentials (RECPs). The outer-most 4s²4p³ shells for As and the 2s²2p⁵ shells for F were retained in the valence space, replacing the rest of the electrons by RECPs. Valence Gaussian (4s4p) basis sets for F taken from Ref. [21], were augmented with two sets of 3d polarization functions α₃ = 0.45 and α₄ = 0.1125, while for As, the (3s3p) valence Gaussian functions chosen from Ref. [22] were augmented with two sets of 3d-type functions α₃ = 0.3880 and α₄ = 0.1150. The valence Gaussian basis sets were contracted to the 3s3p2d sets for both atoms.

Analogous to the previous study on PF [20], we started with a CASSCF computation in which all of the valence electrons of AsF (12 electrons) were kept active. The CASSCF active space consisted of four a₁, two b₂, and two b₁ orbitals. The FOCI computations that were performed after the CASSCF computations, included all configurations in the CASSCF and configurations obtained by distributing 11 electrons in the internal space and one electron in the external space, in all possible ways. Subsequent to the FOCI method, the SOCI calculations that included second-order configurations also (10 electrons in the internal space and 2 electrons in the external space distributed in all possible way), were employed in order to compute the Rₑ value and energy separations of the bound electronic states of AsF. The CASSCF/MRSDCI calculations were employed for the d1Π(II) and c1Π(II) states. The electronic configurations in the CASSCF with coefficients > 0.1 were chosen as reference configurations in the MRSDCI computations. The results labeled SOCI + Q and MRSDCI + Q included the Davidson correction.

All of the calculations were carried out using Balasubramanian’s modified version of ALCHEMYII codes [23] to include the relativistic ECPs.

3. Results and discussions

3.1. Spectroscopic properties and potential energy curves of AsF

Table 1 shows a few possible low-lying electronic states of AsF and their dissociation limits together with the computed RECP-FOCI, SOCI and SOCI + Q energy separations at the asymptotic limit. As seen
Table 1

<table>
<thead>
<tr>
<th>Molecular state</th>
<th>Atomic states</th>
<th>FOCI (eV)</th>
<th>SOCI (eV)</th>
<th>Exp. (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As+F</td>
<td>$^3\Sigma^-$, $^3\Delta$, $^3\Pi$, $^3\Pi$</td>
<td>$^4S + ^2P$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$^2\Sigma^-$, $^2\Pi$, $^2\Pi$</td>
<td>$^4S + ^2P$</td>
<td>1.70</td>
<td>1.34</td>
</tr>
</tbody>
</table>

$a$ The value in parentheses includes the Davidson correction.

from Table 1, the computed As($^2D$)-As($^4S$) energy separation is 1.70 and 1.67 eV at the SOCI and SOCI + Q levels, respectively, in reasonable agreement with the experimental value of 1.34 eV [24]. In general, the results computed at the SOCI level are more reliable as these included the influence of the higher-order electron correlation effects more accurately.

Figs. 1 and 2 show the computed CASSCF/FOCI potential energy curves of AsF dissociating into As($^4S$) + F($^2P$) and As($^2D$) + F($^2P$) limits. Among these curves, the $X^3\Sigma^-$, $a^1\Delta$, $b^1\Sigma^+$, $A^3\Pi$, $c^1\Pi$, $d^3\Pi(III)$, and $e^3\Sigma^-$ (II) states exhibit potential minima. Many features of the potential energy curves of AsF are similar to those of PF studied by the authors before [20].

The ground electronic state of AsF is an $X^3\Sigma^-$ state arising from the $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2 2\pi^2$ electronic configuration [25–28]. The $1\pi$ orbital is mainly F(2p) and thus the $2\pi$ orbital is mainly As(4p). The $A^3\Pi$ and $c^1\Pi$ excited states arising from the $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 1\pi^4 2\pi^1$ electronic configuration are formed by transferring an electron from the $2\pi$ to $4\sigma$ orbitals. The crossing of the $a^1\Delta$ and $A^3\Pi$ curves at $R = 2.45 \text{ Å}$, and the $b^1\Sigma^+$ and $A^3\Pi$ curves at $R = 2.10 \text{ Å}$, could lead to spin–orbit coupling of the corresponding $\Omega$ states. Hence such interaction can lead to mixing of the $a^1\Delta$, and $A^3\Pi$ spin–orbit components as well as $b^1\Sigma^+(0^+)$ and $A^3\Pi(0^+)$ spin–orbit components.

The computed FOCI spectroscopic constants of the electronic states of AsF exhibiting potential minima are shown in Table 2. Although the $c^1\Pi(II)$, and $B^3\Pi(III)$ states do not exhibit pronounced minima at the FOCI level, further improvement in the basis set could yield a shallow potential well near the $R_c$ of the $d^3\Pi(II)$ state, and the FOCI and MRSDCI en-

Fig. 2. Potential energy diagram of the electronic states of AsF including $^1\Pi(IV)$ and $^3\Pi(IV)$ states.
Table 2
Spectroscopic constants of AsF at the FOCI level

<table>
<thead>
<tr>
<th>State</th>
<th>( R_e (\AA) )</th>
<th>( T_e (\text{eV}) )</th>
<th>Experimental ( T_e (\text{eV}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X^3\Sigma^- )</td>
<td>1.767</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( a^1\Delta )</td>
<td>1.761</td>
<td>1.17</td>
<td>0.88</td>
</tr>
<tr>
<td>( b^1\Sigma^+ )</td>
<td>1.761</td>
<td>2.08</td>
<td>1.69</td>
</tr>
<tr>
<td>( A^3\Pi )</td>
<td>1.971</td>
<td>3.39</td>
<td>3.19–3.37</td>
</tr>
<tr>
<td>( c^1\Pi )</td>
<td>1.977</td>
<td>4.44</td>
<td>4.03</td>
</tr>
<tr>
<td>( d^3\Pi(II) )</td>
<td>2.534</td>
<td>5.14</td>
<td>4.81</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( e^3\Sigma^- (II) )</td>
<td>2.765</td>
<td>5.45</td>
<td></td>
</tr>
<tr>
<td>( B^3\Pi(III) )</td>
<td>2.534 *</td>
<td>6.21</td>
<td>6.00</td>
</tr>
<tr>
<td>( c^1\Pi(II) )</td>
<td>2.534 *</td>
<td>6.28</td>
<td>6.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.89</td>
</tr>
</tbody>
</table>

* At the minimum of the \( d^3\Pi(II) \) state.
* Ref. [18].
* The energy separation has been calculated at the CASSCF/MRSDCI level of theory.
* The value in parentheses includes the Davidson correction.

As seen from Table 2, the energy separations of the excited electronic states of AsF such as \( A^3\Pi \), \( c^1\Pi \), and \( B^3\Pi(III) \) states are in good agreement with experiment.

More accurate spectroscopic constants obtained using the best methods here (SOCl, SOCl + Q) are shown in Table 3 and compared with the experimental and previous theoretical results. While the bond lengths do not change much at the SOCl level, the \( T_e \) values of the excited electronic states change considerably (see Table 3).

As seen from Table 3, our computed values are consistent with the values calculated by Liebermann et al. [19], except that their dipole moments are somewhat larger. Liebermann et al. have used a single set of 3d-type function for fluorine and arsenic, while we use two sets of 3d functions. Furthermore, Liebermann et al. use a single configuration method to generate the orbitals for their MRDCI computations, while we use the full CASSCF method. The electron correlation effects are also included to a higher-order in our technique as we use full SOCl schemes.

The \( T_e \) value of the excited \( 1\Delta \) state is computed as 1.06 eV at the SOCl + Q level, which is somewhat closer to the experimental value of 0.88 eV compared to the value of 1.25 eV reported by...
Liebermann et al. The equilibrium bond lengths computed by Liebermann et al. are in general agreement with our values for the low-lying states, although their result for the c'\,3\Pi state is longer than our value. It is thus anticipated that the lifetimes computed by Liebermann et al. would be in larger error. The differences are attributed mainly to the basis sets and the level of electron correlation effects.

Several researchers have studied the electronic spectra of AsF [10–15]. Several emission systems have been observed between 2050 Å (6.05 eV) and 5500 Å (2.25 eV) [11]. Our computed values of 3.23 (SOCI), and 3.14 eV (SOCI + Q) for the $T_e$ value of the A\,3\Pi state support the experimentally deduced $T_e$ value of 3.19–3.37 eV for the A\,3\Pi–X\,3\Sigma state and the theoretical value of 3.34 eV calculated by Liebermann and co-workers [19]. Our FOCI $T_e$ value of 6.21 eV for the B\,3\Pi(III) state is also in good agreement with the experimental value of 6.00 eV. The b'\,3\Sigma+-a\,\Delta energy separation has been determined from the spectral results, giving a value of 0.82 eV [11]. This value is in excellent agreement with our calculated values of 0.77 (SOCI) and 0.81 eV (SOCI + Q).

Three singlet–triplet transitions attributed to the b'\,3\Sigma+-X\,3\Sigma-, c'\,3\Pi–X\,3\Sigma-, d'\,3\Pi–X\,3\Sigma- systems and two triplet–triplet bands attributed to the \Pi–\Sigma- transitions have been observed by Liu and Jones [29]. The $T_e$ values obtained by these authors through the vibrational analysis of the observed spectra for the c'\,3\Pi–X\,3\Sigma- and d'\,3\Pi–X\,3\Sigma- systems are 6.03 and 6.29 eV, respectively. These bands were found to be extremely weak in intensity and were overlapping with other band systems. Our computed $T_e$ values of 6.28 eV at the FOCI level, 5.89 eV at MRSDCI level and 5.74 eV at MRSDCI + Q level reasonably support the observed energy separation of the c'\,3\Pi(II) state. We did not find an appreciable potential minimum in the d'\,3\Pi(III) curve (Fig. 1). However, it is clear from Fig. 1 that this state is close in energy to the c'\,3\Pi(II) state, thus supporting the experimental results. Two more complex systems were obtained in the 2050–2300 Å (6.05–5.39 eV) region without satisfactory rotational and vibrational structures, which were tentatively assigned to the \Pi–\Sigma- transition. The b'\,3\Sigma+-X\,3\Sigma- transition has been observed with a $T_e$ value of 1.69 eV [11,25,29], which is consistent with our computed value of 1.86 (SOCI) and 1.87 eV (SOCI + Q). Four singlet band systems involving d'\,1\Pi → a\,\Delta, c'\,1\Pi → a\,\Delta, d'\,\Pi → b'\,3\Sigma+, and c'\,1\Pi → b'\,3\Sigma+ transitions have been observed in the regions between 2290 Å (5.41 eV) and 2910 Å (4.26 eV) by Yee et al. [10]. According to the results from Table 2, at the FOCI level the energy separations of the c'\,1\Pi(II)–a\,\Delta and c'\,1\Pi(II)–b'\,3\Sigma+ systems are determined as 5.11 and 4.20 eV, respectively.

In order to determine the dissociation energy of AsF, the energy of AsF in the X\,3\Sigma- state with As–F internuclear distance of 8 Å was calculated, which gave the $D_0$ values of 3.81 and 3.91 eV at the SOCI and SOCI + Q levels, respectively. These results are in reasonable agreement with the experimental $D_0(AsF)=4.0 \pm 0.2$ eV determined from $\Delta\Pi(P)$ of AsF, by O’Hare and Hubbard [17] and with the value of 4.2 ± 0.2 eV reported by Pauling [30].

The dipole moments of the low-lying electronic states of AsF determined by the SOCI method are shown in Table 3. The largest dipole moment was computed for the A\,3\Pi state. The dipole moment polarity for all of the electronic states of AsF is As+F-. A theoretical value for the dipole moment of the ground state of AsF has been obtained by O’Hare and co-workers [16], as 2.25 D (upper limit) using the Hartree–Fock minimum.

### Table 4

Electronic leading configurations and their contributions to the low-lying electronic states of AsF

<table>
<thead>
<tr>
<th>State</th>
<th>$R_e$ (Å)</th>
<th>Electronic configuration (percentage contribution)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X,3\Sigma-</td>
<td>1.773</td>
<td>$1\sigma^22\sigma^23\sigma^21\pi^22\pi^2$ (91)</td>
</tr>
<tr>
<td>a,\Delta</td>
<td>1.768</td>
<td>$1\sigma^22\sigma^23\sigma^21\pi^22\pi^2$ (45)</td>
</tr>
<tr>
<td>b',3\Sigma+</td>
<td>1.765</td>
<td>$1\sigma^22\sigma^23\sigma^21\pi^22\pi^2$ (44)</td>
</tr>
<tr>
<td>A'\Pi</td>
<td>1.980</td>
<td>$1\sigma^22\sigma^23\sigma^24\alpha^1\pi^22\pi^1$ (88)</td>
</tr>
<tr>
<td>c',3\Pi</td>
<td>1.975</td>
<td>$1\sigma^22\sigma^23\sigma^24\alpha^1\pi^22\pi^1$ (88)</td>
</tr>
<tr>
<td>d',3\Pi(II)</td>
<td>2.534</td>
<td>$1\sigma^22\sigma^23\sigma^24\alpha^1\pi^22\pi^1$ (23)</td>
</tr>
<tr>
<td>c',3\Sigma- (II)</td>
<td>2.765</td>
<td>$1\sigma^22\sigma^23\sigma^24\alpha^1\pi^22\pi^1$ (40)</td>
</tr>
<tr>
<td>c',3\Pi(II)</td>
<td>2.534</td>
<td>$1\sigma^22\sigma^23\sigma^24\alpha^1\pi^22\pi^1$ (24)</td>
</tr>
<tr>
<td>B',3\Pi(III)</td>
<td>2.534</td>
<td>$1\sigma^22\sigma^23\sigma^24\alpha^1\pi^22\pi^1$ (27)</td>
</tr>
</tbody>
</table>

a At the minimum of the d'\,3\Pi(III) state.
Table 5
Mulliken population analysis of AsF

<table>
<thead>
<tr>
<th>State</th>
<th>As</th>
<th>F</th>
<th>As(s)</th>
<th>As(p)</th>
<th>As(d)</th>
<th>F(s)</th>
<th>F(p)</th>
<th>As-F</th>
</tr>
</thead>
<tbody>
<tr>
<td>X 3Σ -</td>
<td>4.47</td>
<td>7.53</td>
<td>1.97</td>
<td>2.45</td>
<td>0.041</td>
<td>1.93</td>
<td>5.45</td>
<td>0.254</td>
</tr>
<tr>
<td>a 1Δ</td>
<td>4.48</td>
<td>7.52</td>
<td>1.98</td>
<td>2.46</td>
<td>0.036</td>
<td>1.94</td>
<td>5.43</td>
<td>0.277</td>
</tr>
<tr>
<td>b 3Σ +</td>
<td>4.49</td>
<td>7.51</td>
<td>1.95</td>
<td>2.51</td>
<td>0.034</td>
<td>1.94</td>
<td>5.42</td>
<td>0.258</td>
</tr>
<tr>
<td>A 3Π</td>
<td>4.59</td>
<td>7.41</td>
<td>2.03</td>
<td>2.47</td>
<td>0.086</td>
<td>1.88</td>
<td>5.38</td>
<td>0.025</td>
</tr>
<tr>
<td>c' 1Π</td>
<td>4.59</td>
<td>7.41</td>
<td>2.04</td>
<td>2.45</td>
<td>0.095</td>
<td>1.90</td>
<td>5.35</td>
<td>0.070</td>
</tr>
</tbody>
</table>

F(d) population is between 0.150 and 0.156.

They suggested that the dipole moment of AsF is likely to be close to 1.75 D based on the experimental results of SF and SeF [31]. The calculated and estimated results determined by O’Hare and co-workers [16] for AsF dipole moment are consistent with our SOCI result of 1.88 D. AsF possesses a larger dipole moment compared to PF (1.04 D) because of the larger size of the As atom.

The leading configurations contributing to the electronic states of AsF are presented in Table 4. The leading configuration of the X 3Σ -, a 1Δ and b 1Σ + states is 1σ^2 2σ^2 3σ^2 1π^2 2π^2. Both the A 3Π and c' 1Π states have the same 1σ^2 2σ^2 3σ^2 4σ^1 1π^4 2π^1 leading configuration. Some of the excited electronic states are admixtures of several configurations (see Table 4).

The Mulliken populations for the low-lying electronic states of AsF are shown in Table 5. It can be seen that there is considerable charge transfer from As to F since the F atom is more electronegative. There is a slight increase in the As(p) population in the excited electronic states of AsF, but the F(p) character decreases in the excited states compared to the ground state. The contribution of the 3d polarization functions is not significant for As in all of the electronic states.

3.2. Comparison between AsF and PF

Although there are qualitative similarities between the electronic states of AsF and those of PF [20], quantitative differences are found. The bond length of the AsF radical in the ground X 3Σ - state is 1.773 Å compared to the corresponding bond length of PF, which is 1.645 Å. The \( T_e \) values of the excited states of AsF are slightly less than the corresponding values of PF. As an example, the \( T_e \) value for the A 3Π state of AsF is 3.14 eV, while the corresponding state of PF has the energy separation of 3.56 eV [20]. This may be a consequence of the fact that transfer of electronic charge into As(4p) would take less energy compared to the charge transfer into P(3p).

The overlap populations for the electronic states of AsF are generally larger compared to those of PF. The bonding for the AsF radical is somewhat more ionic because As is more electropositive than P and there are more charge transfer from As to F. This is also consistent with a larger dipole moment for AsF compared to PF.

4. Conclusions

In this research work, the RECP-CASSCF/FOCI computations of the potential energy curves of the 21 electronic states of AsF were performed. In order to compute the spectroscopic constants of the low-lying electronic states, the CASSCF/FOCI/SOCI levels of theories were employed. The bond dissociation energy of the AsF molecule was reported and compared with the other theoretical values. Our computed energy separations of the excited states agree reasonably with the experimental results.

Acknowledgements

This research was supported by the US National Science Foundation under grant CHE9417459.

References

[23] The major authors of ALCHEMYII are B. Liu, B. Lengsfield and M. Yoshimine.