Ab initio calculations of infrared transition probabilities in the electronic ground states of AlF and AlF$^+$

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Electric dipole moment functions and radiative transition probabilities have been calculated for the electronic ground states of AlF and AlF$^+$ from highly correlated CEPA electronic wavefunctions. The dipole moments in $v = 0$ are calculated to be 1.56 D (experimental value is 1.53 ± 0.1 D) for AlF and 5.49 D for AlF$^+$. Intense transitions in the microwave and infrared spectral region are predicted for both species.

Key words: Electric dipole moment functions – correlated electronic wavefunctions – infrared transition probabilities

1. Introduction

The large absorption strengths and emission rates [1, 2] in the electronic ground state of BF makes it feasible for infrared absorption and chemiluminescent studies of reaction kinetics. Like BF, the valence isoelectronic AlF molecule has a large dissociation energy, namely 6.89 eV [3], and it is formed in various exothermic reactions. Recently, Ishikawa and Parson [4] investigated the chemiluniscent spectra produced in the reaction Al with F_2 in a crossed-beam experiment. The exothermicity of 5.29 ± 0.05 eV allowed to populate the $a^3\Pi$ state of AlF, the emission spectrum of which has been investigated. But the channel producing AlF in the electronic ground state has not been directly monitored. High-resolution infrared absorption gas phase spectra of AlF in the $X\,^1\Sigma^+$ electronic ground state have been measured by Maki and Lovas [5]. AlF has also been observed to give stimulated infrared emission in an exploding wire experiment [6]. So far no infrared transition probabilities in the electronic ground state of AlF are known, which are required for a quantitative interpretation of the chemiluminescent spectra.

Previously, we have calculated the electric dipole moment functions (EDMF) of BF and BF^+ from correlated electronic wavefunctions and derived the vibrational transition probabilities in their electronic ground states [2]. Similar calculations are now reported for the valence isoelectronic AlF and AlF^+ molecules. Near Hartree–Fock limit calculations for AlF have been published by McLean and Yoshimine [7] and So and Richards [8]. The EDMF's of fluorine-containing diatomics like BF, CF, FO etc. exhibit two extrema in the avoided-crossing regions of internuclear distances [2, 9, 11]. Therefore, depending on the position of the classical turning points of the vibrational ground states, unusual polarities of the dipole moments may arise. In the vibrational ground state of BF the polarity is B^-F^+ [2], and similarly, in CF and OF at equilibrium distances C^-F^+ [10] and O^-F^+ [11], respectively. The dipole moment of OF in $v = 0$ amounts to only 0.0043 Debye [11, 12], and the polarity is O^+F^- [11]. Therefore, it is of interest to compare the EDMF's for the $X^1\Sigma^+$ state of AlF with similar functions of valence-isoelectronic compounds like BF, CO or SiO.

The AlF molecule has been subject of numerous visible, microwave and matrix spectroscopic studies [3]. Recently Dyke et al. [13] obtained information on the position of several electronic states of AlF^+ from the PE-spectrum. Like BF^+, AlF^+ has a repulsive $A^2\Pi$ state and unfavourable Franck–Condon factors for the $X^2\Sigma^+ \to B^2\Sigma^+$ transitions [12, 13]. Hence the AlF^+ ion is spectroscopically probably best monitored by its vibration-rotation spectrum. In the present work such infrared transition probabilities in the $X^2\Sigma^+$ state have been calculated for AlF^+ and compared with those of BF^+ and CO^+.

2. Methods and potential energy functions

In the calculations a GTO basis set [14] with $12\,s, 9\,p, 2\,d$ functions for Al and $10\,s, 6\,p, 2\,d$ functions for F was employed. Only the innermost $5s$ and $4p$ functions for Al and $4\,s$ and $3\,p$ for F were contracted. The electronic wavefunctions have been calculated by the pseudonatural orbital CI (PNO-CI) method [15] with coupled electron pair approximation (CEPA) [15] or with the selfconsistent electron pair approach (SCEP) [16]. In the SCEP method all singly and doubly substituted configurations with respect to the leading Hartree–Fock configuration are considered. In the PNO-CI method these configurations are selected according to an energy threshold. The dipole moments were calculated as expectation values or as first derivatives of the energy with respect to the strength of an external electric field [17, 18].

The calculated spectroscopic constants for AlF and AlF^+ are compared with available experiments in Table 1. The ω_e value for the $X^1\Sigma^+$ state of AlF obtained from SCEP/CEPA results deviates by only 2 cm^{-1} from experiment. Also the SCEP/CEPA equilibrium distance is calculated to be only 1 pm larger than the experimental value. This is due to the fact that the Hartree–Fock results for ω_e agree with the empirical values already within about 50 cm^{-1} and the R-dependent correlation contributions to the PEF are covered to a large extent in the SCEP/CEPA calculations. Also for AlF^+ the R_e and ω_e values are in good

Table 1. Spectroscopic constants of AlF and AlF$^+$

Species	Method	E^a (a.u.)	R_e (pm)	B_e (cm^{-1})	α_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	μ_e (D)	$\mu_e'^b$ (D/pm)
AlF $X^1\Sigma^+$	HF	-341.471933	164.1	0.561	0.005	838	5.0	1.134	-0.588×10^{-1}
	SCEP/CEPA	-341.734090	166.4	0.546	0.005	805	4.3	1.543	-0.543×10^{-1}
	exp.		165.4	0.552	0.00498	802.26	4.77		
AlF$^+$ $X^2\Sigma^+$	HF	-341.158880	157.6	0.609	0.004	1019	4.2	5.517	-0.584×10^{-1}
	PNO/CEPA	-341.380474	160.1	0.590	0.004	960	3.7	5.466	-0.555×10^{-1}

[a] Total energies at calculated equilibrium distances
[b] Dipole moments and first derivatives of the dipole moment functions at calculated equilibrium distances

agreement with the data obtained by Dyke et al. [13] from the PE-spectrum and the Franck–Condon analysis of the vibrational envelope for the $X^2\Sigma^+$ state. The vibrational wavefunctions and the dipole matrix elements were calculated from the numerical solutions of the radial Schrödinger equation of nuclear motion with the theoretical PEF's as an input.

3. Vibrational transition probabilities in the $X^1\Sigma^+$ state of AlF

The only experimental study dealing with the dipole moment of AlF has been reported by Lide [19]. The dipole moment in the vibrational ground state of 1.53 ± 0.1 Debye was determined from Stark measurements. No vibrational dependence and transition dipole matrix elements are so far known from experiments. McLean and Yoshimine [7] obtained a dipole moment of 1.34 Debye from the Hartree–Fock wavefunction at R_e. The EDMF's of AlF calculated from the correlated SCEP/CEPA wavefunctions as an expectation value and as the first derivative of the energy with respect to the strength of an external field are given in Table 2. For molecules with single bonds the CEPA dipole moments calculated as an expectation value yields the dipole moments with an accuracy of about ± 0.05 D, but the correlation contributions to the dipole moment for molecules with multiple bonds have often been calculated to be too large [20, 21]. Recently, we calculated the infrared transition probabilities for SiO and HOSi$^+$ [21] from the SCEP/CEPA wavefunctions and found that the dipole moments calculated

Table 2. Potential energy and dipole moment functions for the electronic ground states of AlF and AlF$^+$

R (pm)	AlF ($X^1\Sigma^+$)			AlF$^+$ ($X^2\Sigma^+$)	
	$E^a + 341$ (a.u.)	$\mu(D)^b$	$\mu(D)^c$	$E^d + 341$ (a.u.)	$\mu(D)^e$
127.00	−0.564427	−0.3019	−0.3055	−0.228404	1.2522
137.58	−0.660498	0.1771	0.1634	−0.325046	1.5450
148.17	−0.710616	0.6105	0.6153	−0.368042	1.8787
158.75	−0.730667	1.1046	1.1285	−0.380346	2.2417
169.33	−0.733753	1.6477	1.6924	−0.376317	2.6216
179.92	−0.727440	2.2279	2.2966	−0.360912	3.0026
190.50	−0.716123	2.8339	2.9307	−0.341558	3.3684
211.67	−0.687695	4.0775	4.2472		

[a] SCEP/CEPA total energies.
[b] SCEP/CEPA dipole moments calculated as expectation values.
[c] Dipole moments calculated from the SCEP/CEPA total energies; positive sign indicates the polarity Al$^+$F$^-$.
[d] PNO/CEPA total energies.
[e] PNO/CEPA dipole moments calculated as expectation values (Al atom in the origin of the coordinate system); positive sign indicates that the center of positive charge is closer to the Al atom than the center of mass

Table 3. Calculated rotationless dipole matrix elements[a] R_v^{v+i} for the $X\,^1\Sigma^+$ state of AlF (in Debye)

v	R_v^v	R_v^{v+1}	R_v^{v+2}	R_v^{v+3}
0	1.562	0.246	-0.8×10^{-2}	$\leq 10^{-3}$
1	1.624	0.350	-0.16×10^{-1}	$\leq 10^{-3}$
2	1.691	0.431	-0.24×10^{-1}	0.1×10^{-2}
3	1.761	0.500	-0.32×10^{-1}	0.2×10^{-2}
4	1.831	0.561	-0.40×10^{-1}	0.3×10^{-2}
5	1.902	0.617	-0.48×10^{-1}	0.4×10^{-2}
6	1.974	0.669	-0.56×10^{-1}	0.6×10^{-2}
7	2.045	0.719	-0.65×10^{-1}	0.7×10^{-2}
8	2.117	0.766	-0.74×10^{-1}	
9	2.190	0.811		
10	2.263			

[a] From the dipole moment function obtained from SCEP/CEPA energies; positive sign indicates the polarity Al^+F^-

from energies are more reliable than those from the density matrices. As can be recognized from the values presented in Table 2 both approaches yield relatively small differences in the case of AlF. For instance, the first derivatives at R_e are calculated to be 0.501×10^{-1} D/pm (expectation value) and 0.543×10^{-1} D/pm (dE/dF). Nevertheless, the EDMF of AlF calculated from the energy derivatives is considered to be more accurate and has therefore been used in further analysis.

In Table 3 some diagonal and off diagonal vibrational dipole matrix elements are listed up to $v = 10$. For $v = 0$ we obtained a value of 1.56 D (*cf.* Table 3) which is in good agreement with the value of 1.53 ± 0.1 D derived by Lide [19].

In Fig. 1 the near equilibrium EDMF's of AlF, SiO, BF and CO are compared. Since all these molecules dissociate diabatically to the ionic asymptotes the dipole moment functions exhibit extrema caused by crossings of states of the same symmetry which leads to the correct asymptotic behavior. Close to the equilibrium distances these functions change their sign (cf. Fig. 1). The AlF EDMF resembles the function of BF and also has a region with a polarity Al^-F^+ (*cf.* Fig. 1), but due to the large R_e the polarity in the vibrational ground state is Al^+F^-. The first derivatives of the EDMF's at R_e's are 0.523×10^{-1} D/pm (BF) [2], 0.543×10^{-1} D/pm (AlF), 0.314×10^{-1} D/pm (CO) [9] and $(0.25 \pm 0.05) \times 10^{-1}$ D/pm (SiO) [22]. The nearly linear form of the BF and AlF functions and their large first derivatives at R_e lead to large dipole transition matrix elements for the fundamentals and much smaller values for the first overtone sequence in low lying vibrational states. In CO and SiO the first overtones are relatively more intense due to the maxima on their EDMF's lying closer to the R_e's. The Einstein coefficients of spontaneous emission for AlF (*cf.* Table 4) are of the same magnitude as those of CO [9] or OH [18], the infrared emissions of which have been investigated experimentally many times.
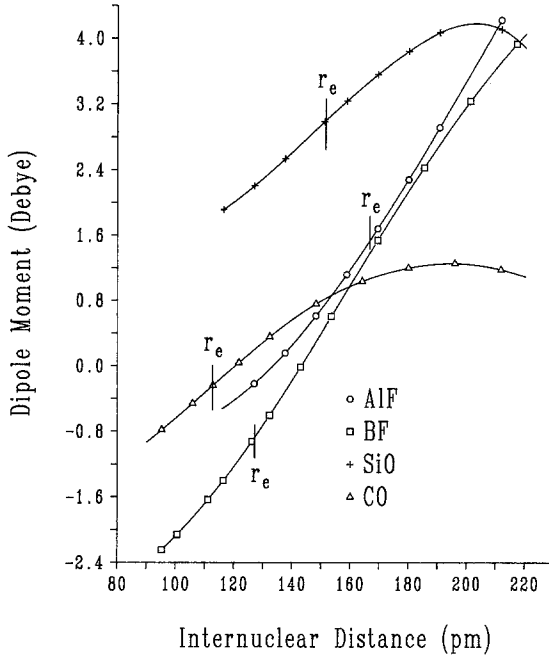
Fig. 1. The electric dipole moment functions of the electronic ground states of AlF (this work), BF (Ref. [2]), CO (Ref. [9]) and SiO (Ref. [24]). The equilibrium distances are quoted as r_e

Table 4. Calculated rotationless dipole matrix elements[a] R_v^{v+i} for the $X^2\Sigma^+$ state of AlF$^+$ (in Debye)

v	R_v^v	R_v^{v+1}	R_v^{v+2}	R_v^{v+3}
0	5.491	0.220	-0.10×10^{-1}	$\leqq 10^{-3}$
1	5.542	0.311	-0.18×10^{-1}	$\leqq 10^{-3}$
2	5.593	0.382	-0.24×10^{-1}	$\leqq 10^{-3}$
3	5.640	0.441	-0.30×10^{-1}	0.3×10^{-2}
4	5.685	0.493	-0.37×10^{-1}	0.4×10^{-2}
5	5.731	0.541	-0.44×10^{-1}	0.4×10^{-2}
6	5.780	0.585	-0.54×10^{-1}	0.5×10^{-2}
7	5.834	0.626	-0.66×10^{-1}	0.5×10^{-2}
8	5.896	0.666	-0.82×10^{-1}	
9	5.966	0.704		
10	6.046			

[a] From the PNO/CEPA dipole moment function (see also footnote[c] of Table 2).

4. Vibrational transition probabilities in the $X^2\Sigma^+$ state of AlF$^+$

The $X^2\Sigma^+$ state dissociates diabatically to Al$^+$ (^3P) + F(^2P). At the equilibrium distance the 7σ orbital of this state is mainly described by the $3s2p_\sigma$ functions of Al, whereas at larger distances it changes its character to $3s^2$. Therefore, an avoided crossing of the $X^2\Sigma^+$ and the $B^2\Sigma^+$ states of AlF$^+$ occurs at larger internuclear distances (3.8 to 4 Bohr). This effect has been discussed in detail for BF$^+$ previously [2]. In the present work we restricted the calculations of the
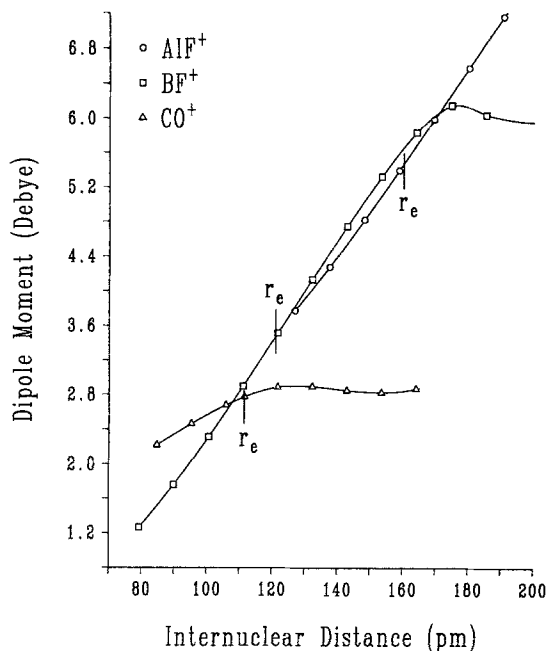
Fig. 2. The electric dipole moment functions of the electronic ground states of AlF$^+$ (this work), BF$^+$ (Ref. [2]) and CO$^+$ (Ref. [23])

EDMF to the region of low lying vibrational levels, i.e. for internuclear distances outside of this crossing region, where the wavefunctions are strongly dominated by one leading configuration in the CI expansion. At larger distances the CEPA method, which is biased towards one leading configuration, would be unable to reproduce the EDMF correctly. In Fig. 2 the AlF$^+$ function is compared with those of the $X^2\Sigma^+$ states of BF$^+$ and CO$^+$. The EDMF of CO$^+$ [23] and also SiO$^+$ [24] are very flat. The resulting vibrational-rotational transition probabilities in these states are therefore very small. We have shown previously that the radiative transitions to the lower lying vibrational levels of the $A^2\Pi$ states are much more probable, i.e. a reversed infrared emission of the type $X^2\Sigma^+ \rightarrow A^2\Pi$ and not the emission in the X state will radiatively depopulate high vibrational states of the electronic ground states of CO$^+$ and SiO$^+$ [23, 24]. A different situation is found in the isoelectronic BF$^+$ and AlF$^+$ ions. The $A^2\Pi$ states are repulsive and the Franck–Condon factors for the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transitions are very small due to the large shifts of the equilibrium distances of the B states relative to the X states. For this reason the vibrational-rotational transitions in the electronic ground states of BF$^+$ and AlF$^+$ might be of interest for optical studies of reaction kinetics with these ions. As for their neutral counterparts the steep EDMF's of BF$^+$ and AlF$^+$ (*cf.* Fig. 2) give rise to large dipole matrix elements, which are listed up to $v' = 10$ in Table 4. The Einstein transition probability coefficients of spontaneous emission are given in Table 5. In the vibrational ground states the dipole moments of BF$^+$ (3.49 D) and AlF$^+$ (5.46 D) are much larger than in BF (1.09 D) and AlF (1.56 D). Also their first derivatives of the EDMF's are large: 0.523×10^{-1} D/pm (BF), 0.584×10^{-1} D/pm (BF$^+$),

Table 5. Calculated rates of spontaneous emission (in $\sec^{-1}$) for AlF $(X^1\Sigma^+)$ and AlF$^+$ $(X^2\Sigma^+)$

v	AlF $(X^1\Sigma^+)$		AlF$^+$ $(X^2\Sigma^+)$.	
	A_v^{v+1}	A_v^{v+2}	A_v^{v+1}	A_v^{v+2}
0	9.1	0.08	13.2	0.22
1	17.8	0.27	25.5	0.64
2	26.1	0.61	37.4	1.20
3	34.2	1.07	49.1	1.85
4	41.9	1.65	60.5	2.67
5	49.3	2.34	71.3	3.77
6	56.3	3.15	81.1	5.38
7	62.9	4.07	88.9	7.71
8	69.8	5.10	94.4	11.0
9	74.8		97.0	

0.543×10^{-1} D/pm (AlF) and 0.554×10^{-1} D/pm (AlF$^+$). Therefore, both ions have large transition dipole matrix elements and intense microwave and infrared transitions in their electronic ground states. Experimental detection of these transitions could help to establish accurate spectroscopic constants of the $X^2\Sigma^+$ state of AlF$^+$, which are also of importance for the interpretation of Rydberg transitions in AlF [25].

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