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Theoretical investigation of the GaF molecule and its positive ion

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Abstract. Coupled pair approximation and configuration interaction calculations were carried out on the gallium fluoride molecule and its positive ion with flexible basis sets. Spectroscopic constants of these species were examined in detail through step-wise extensions of correlating space. The contribution from correlations of the semi-core 3*d* electrons in Ga was found to be sizable. The bonding character was revealed to be highly ionic even for the positive ion.

Key words: Gallium fluoride – Ionization – Semi-core electrons – Near-degeneracy – Size-consistency – Coupled pair approximation

1 Introduction

In our previous paper, we reported an ab initio molecular orbital (MO) investigation of the ground states of the gallium hydride (GaH) molecule ($^1\Sigma^+$) and its positive ion ($^2\Sigma^+$) [1]. Our goal was to see the role of the semi-core 3*d* electrons in the chemical bonds through correlations. Thus, the coupled pair approximation (CPA), which is a size-consistent extension of singly and doubly excited configuration interaction (CI) by perturbative inclusions of higher excitations and is applicable to multi-reference (MR) problems [2–5], was used with flexible basis sets. Evaluated spectroscopic constants of GaH were in quantitative agreement with experimental results, where the contribution from 3*d* electron correlations was shown to be substantial.

The gallium fluoride (GaF) molecule also has a single σ bond like GaH. Because of the pronounced electronegativity of the F atom, much higher ionic character of $Ga^+ - F^-$ is expected than in the case of GaH. The proper description of the GaH^+ bonding is given by mixing the Ga^+ atomic configurations of $4s^2$ and $4s4p$, and introducing 3*d* correlations. We would like to now extend the investigation to GaF^+.

In the present paper, we perform a series of extensive CPA calculations on the GaF molecule and its positive ion whose electronic ground states are formally similar to the GaH and GaH^+. The basis set for F is carefully set up to describe an F^- character in the bonding situation. For GaF, spectroscopic constants of the bond energy (D_e), bond length (R_e), and vibrational frequency (ω_e) will quantitatively agree with the experimental data [6]. An MRCPA treatment based on the complete active space self-consistent-field (CASSCF) [7] orbitals is essential to describe the delicate bonding in GaF^+. The qualitative difference between GaF^+ and GaH^+ will be shown.

2 Method of calculation

The Gaussian basis set for Ga was the same as used in our previous calculations [1]. Its contraction was $(15s12p7d4f2g)/[9s7p5d3f1g]$. The fundamental part of this set was given by Shäfer et al. [8]. The author's original augmentation was made to provide flexibility not only for the 4*s*4*p* valence shell but also for the 3*d* semi-core shell. The basis set for F was based on $(10s6p)/[6s3p]$ provided also by Shäfer et al. [8]. Diffuse functions were added to this contracted set, where the exponents are 0.1023 for *s* type and 0.0723 for *p* type, and these values were derived by multiplying the outermost functions in the above $[6s3p]$ by 1/3. The *d* and *f* functions to be augmented were taken from aug-cc-pVTZ set developed by Dunning et al. [9, 10]. The resulting $[7s4p3d2f]$ basis for F provides an acceptable electron affinity (EA) estimate, as will be shown in the next section. The numerical data for the basis sets were obtained from the

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internet database server of the US Pacific Northwest National Laboratory[1]. Cartesian contaminants for *d*, *f*, and *g* type functions were removed, and the total number of basis functions was 133.

The MO set for the neutral GaF molecule was prepared by the usual SCF procedure since its $^1\Sigma^+$ state can be described well by a single configuration. Note that the $4s^2$ shell looks like a lone-pair being polarized away from the F side. Electron correlations were introduced by the single-reference CPA wavefunction in the fourth-order treatment (CPA-4) for higher than double excitations [2–5]. Since the fluorine 2*s* level is energetically deeper than that of Ga 3*d*, both the 2*s* and 3*d* shells (−1.57 au for the former and −1.15 au for the latter [11]) were treated as the semi-core. Five 2*p* electrons of the F atom were considered to be valence. We considered three schemes for treating the correlation, as in our previous study [1]:

1. *V*: 8 valence shell electrons were correlated, whereas the semi-core shells were kept frozen.
2. *CV*: In addition to the correlation of the 8 valence shell electrons, 12 semi-core electrons were also correlated. However, simultaneous two-electron excitations were not involved from the semi-core shells. Namely, the valence/semi-core intershell correlation and the dynamical polarization in the semi-core shell were taken into account.
3. *C*: valence and semi-core electrons (total of 20) were correlated with equal weight.

In the following, the level of calculation will be abbreviated by these correlation schemes in combination with the method. For example, "*CV*-CPA-4" means "CPA-4 calculation *CV*" correlation schemes.

We found the dissociation limit, that is, the bond energy by two methods. In the first, the so-called supermolecule (SM), the dissociation limit defined as the energy of the $^3\Sigma^+$ state with an internuclear distance of 100 au. In the second method, the sum of the atomic energies (SAE) of the separate Ga and F atoms was calculated (by the respective correlation scheme). Note that, if the total wavefunction has "exact size-consistency", the SAE bond energy is the same as SM value. However, in general, the SM bond energy is more accurate than that of SAE because of the breakdown of "exactness", as symbolized by usual CI at the single and double excitation level. Davidson's quadruple correction (denoted as $+Q$) can partly remedy the problematic behavior of CI [12]. We will compare SM and SAE D_e values calculated both by CPA-4 and CI($+Q$).

For the GaF^+ case, the CASSCF procedure [7] was taken to generate the input MO set for the MR version of CPA-4 calculations. The active space was minimal, consisting of Ga 4*s* and $4p\sigma$, and F $2p\sigma$. Three electrons were distributed in these three σ orbitals which form the CAS natural orbitals (NO). The total number of configuration state functions (CSF) was eight. Three or four configurations (or four and five in the CSF unit, respectively) were taken as the reference set for MRCPA-4. The nature of these configurations will be described later. Although the MRCPA-4 is a "state-universal method" [2–5, 13], the lowest root, of which the reference (or zeroth-order) space was "pre-diagonalized", was used for the introduction of correlations since we were interested only in the ground state. Corresponding MRCI calculations were carried out in parallel to MRCPA-4 for comparison.

The actual calculations were carried out under the C_{2v} subgroup of $C_{\infty v}$. The five ($3 \times a_1, b_1$, and b_2) highest-lying MO, having radial nodes in the innermost core region of Ga and F, were deleted from the correlating MO space. The largest number of CSF in correlating expansions was 1 569 277 for the four-referenced case by the *C* scheme for GaF^+, where all the possible spin-couplings were included for each excited configuration. The present calculations were performed by using the Alchemy-II [14–17] suite of integrals, CASSCF, direct-CI programs and the direct CPA code (written by Tanaka [4]) interfaced with Alchemy-II, on IBM RS-6000 workstations.

A multiplicity-averaged spin-orbit splitting $\left(^2P_{1/2} - {}^2P_{3/2}\right)$ of −0.07 eV [18] was corrected in the evaluation of the GaF bond energy, as was done in the previous calculation for GaH [1]. The fitting procedure to obtain potential energy curves was also the same as in Ref. [1]. The atomic masses of Ga and F used for ω_e were 68.9256 and 18.998403, respectively.

3 Results and discussion

3.1 GaF

Prior to showing the calculated spectroscopic constants, we need to check the EA values for F since the Ga—F bond is ionic: Ga^+—F^-. Table 1 summarizes the results for EA. The notation *V*, *CV*, and *C* indicate the correlation treatment for the 2*s* shell. One can see that the CPA-4 calculation with the present [7*s*4*p*3*d*2*f*] basis provides a reasonable estimate of the experimental value of 3.40 eV [18]. Thus CPA-4 is confirmed to be better than $\mathrm{CI} + Q$. As has been well demonstrated by Feller and Davidson [19, 20] and Noro et al. [21, 22], calculations for EA of atoms and small molecules require huge basis sets to accurately describe differential correlation effects in wavefunctions. The quality of the F basis set used here is acceptable for evaluating the spectroscopic constants of GaF. We have already shown that the IP value obtained by a *C*-CPA-4 calculation for Ga of 5.98 eV, compares well with the experimental IP of 6.0 eV [18]. Thus, we can safely say that the quality of the basis sets we use for Ga and F is quite good.

The calculated spectroscopic constants are presented in Table 2. As noted in the previous section, the bond energy is found via SM and SAE. The *C*-CPA-4 result is in quantitative agreement with experiment [6], indicating a substantial contribution from semi-core electron correlations. Schwerdtfeger et al. [23, 24] calculated the GaF spectroscopic constants by using quadratic CI with single and double excitations corrected additionally by perturbative triple excitations [denoted QCI(T)] with semi-core correlations, where QCI(T) is size-consistent [25, 26]. However, the basis set that they used was less flexible than the present one; their D_e was much lower, 5.60 eV.

Table 1. Electron affinity of F atom [eV]. For the CI and CPA calculations the 2*s* shell is treated as semi-core

Scheme	*V*	*CV*	*C*	
CI	3.09	2.95	2.96	
CI + *Q*	3.23	3.13	3.14	
CPA-4	3.26	3.20	3.21	
SCF				1.32
Expt.				3.40

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[1] The numerical data of the [8*s*6*p*2*d*] basis set for Ga and [6*s*3*p*] for F [8] and also [3*d*2*f*] polarization functions for F [9, 10] were downloaded from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0 (http://www.emsl.pnl.gov:2080/forms/basisform.html), as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest National Laboratory, PO Box 999, Richland, Washington 99352, USA, and funded by the U.S. Department of Energy. The Pacific Northwest National Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Please contact Drs. D. Feller, K. Schuchardt, or D. Jones for further information.

Table 2. Spectroscopic constants for GaF

Method	D_e [eV]^{a,b}	R_e [au]	ω_e [cm^{-1}]
SCF	4.41	3.33	655
V			
CI	5.87(5.67)	3.37	643
CI + *Q*	5.99(5.93)	3.38	635
CPA-4	6.04(6.04)	3.38	631
CV			
CI	5.84(5.49)	3.31	643
CI + *Q*	5.99(5.85)	3.32	634
CPA-4	6.07(6.07)	3.33	623
C			
CI	5.69(5.00)	3.34	647
CI + *Q*	5.89(5.63)	3.35	637
CPA-4	6.00(6.00)	3.37	622
3*d*-correlated QCI(T)^c [23, 24]	5.60	3.42	585
Expt. [6]	6.02	3.35	622

[a] Average spin-orbit splitting for Ga of −0.07 eV [18], as in Ref. [1].
[b] Values in parentheses are calculated via SAE
[c] The contraction of the Ga basis was [11*s*8*p*5*d*]. 3*s*3*p* shells were also correlated

It is notable that in CPA-4 the SAE D_e values are almost the same as those found by SM. CPA-4 gives the proper energetic separability [5]. SM calculations can be more costly since the length of the correlation expansion will increase along with the number of open shells in the reference configuration at the dissociation limit: the lengths for the $^1\Sigma^+$ (bonding region) and $^3\Sigma^+$ (dissociation limit) states are 149 813 and 931 516, respectively, at the *C* level of correlation. Through CPA-4, one can evaluate D_e via SAE even if the SM calculation can not be performed due to computational limitations[2]. In contrast to CPA-4, the simple CI scheme can not hold such a separability. The $+Q$ correction helps somewhat but is apparently insufficient for the C scheme where a total of 20 electrons are correlated.

Table 2 shows that the bond length and vibrational frequency calculated by *C*-CPA-4 are also, in quantitative agreement with experimental data [6] and are better than the QCI(T) values reported by Schwerdtfeger et al. [24, 25]. As was found for GaH [1], the *CV*-CPA-4 treatment with valence/semi-core intershell correlations yields a slight overcontraction for R_e, although the ω_e value is good. More reliable results could be obtained by the *C* scheme if further intrashell correlations among semi-core electrons would be included. We also calculated the dipole moment, which reflects the charge distribution of a system, to be 2.26 Debye by *C*-CPA-4. The polarity of the $Ga^+ - F^-$ σ bond can be reduced by a delocalization of the $2p\pi$ lone-pairs toward the vacant $4p\pi$ orbital on Ga, and the resulting π MO enhance the overall bond stabilization between Ga and F. To provide a set of reference data for future calculations on GaF, the total energy and correlation energy calculated at each derived R_e are given in Table 3.

Table 3. Total energy and correlation energy for GaF, calculated at the respective R_e values from Table 2. Correlation energies are, taken as the difference to the SCF total energy (minus sign is omitted)

Method	Total energy [au]	Correlation energy [eV]
SCF	−2022.7378	
V		
CI	−2022.9635	6.14
CI + *Q*	−2022.9788	6.56
CPA-4	−2022.9836	6.69
CV		
CI	−2023.0801	9.31
CI + *Q*	−2023.1062	10.02
CPA-4	−2023.1161	10.29
C		
CI	−2023.4211	18.59
CI + *Q*	−2023.4769	20.11
CPA-4	−2023.5011	20.77

3.2 GaF^+

Two previous reports for GaF^+ have been published. Grabandt et al. [27] carried out Hartree-Fock-Slater (HFS) type density-functional theory (DFT) calculations with a pseudo-potential technique, in conjunction with experiments. Their experimental D_e much lower than our calculated values, was indirectly derived from an IP measurement (Table 4). This will be discussed below. Yoshikawa and Hirst [28] performed CASSCF/MRCI calculations with small basis sets in which the Ga $1s - 3d$ electrons were replaced by an effective potential.

It is instructive to discuss the bonding in GaF^+ by comparing it to that in GaH^+. Ionization of GaH occurs mainly from the σ bonding orbital which can be represented by $\lambda 4p\sigma + 1s$, where λ is a small mixing parameter. However, substantial screening by the 4*s* electrons, which form a lone-pair in the neutral state, occurs to retain some covalency in the ionized molecule. In other words, the Ga^+ site in the molecule can be represented as a mixture of $4s^2$ and $4s4p$, and the amount of mixing is affected by the 3*d* electron correlation. The $4s^2$ configuration is the ground state of Ga^+ and $4s4p$ excited configuration is responsible for the covalency in GaH^+.

The situation in GaF^+ is somewhat different, mostly because of the high electronegativity of F. The characters of the two occupied CAS-NO, denoted σ_a and σ_b, are $\lambda' 4p\sigma + 2p\sigma$ and 4*s*, respectively. The correlating NO, σ_c, is the anti-bonding σ_a. The occupation numbers around the minimum are 1.97, 1.01, and 0.02, respectively. Ionization is thus principally out of the 4*s* shell of Ga, while the Ga—F bonding orbital remains doubly occupied, although a mixing of the 4*s* and 4*p* orbitals certainly exists. Thus the Ga atom appears to be doubly charged even in GaF^+, as has been noted by Yoshikawa and Hirst [28]. Such high ionicity induced by F has also been noted by Glenewinkel-Meyer et al. [29] for AlF^+, based on their extensive all-electron CASSCF/MRCI calculations.

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[2] We have calculated spectroscopic constants for the GaN diatomic molecule using a CASSCF/MRCPA-4 scheme. The spin state around the minimum is a triplet. However, the SM approach needs the quintet state as the dissociation limit, which is hard to perform by the *C* scheme of treating the correlation. D_e is thus calculated from SAE.

Table 4. Spectroscopic constants for GaF$^+$

Method	D_e [eV][a]	R_e [au]	ω_e [cm^{-1}]	IP [eV][b]
3R				
V				
CI	1.81(1.65)	3.22	770	9.89
CI + *Q*	1.85(1.80)	3.23	746	10.03
CPA-4	1.85(1.85)	3.24	729	10.11
CV				
CI	1.59(1.27)	3.19	744	10.13
CI + *Q*	1.66(1.51)	3.22	714	10.29
CPA-4	1.68(1.63)	3.25	652	10.40
C				
CI	1.60(0.95)	3.18	789	9.89
CI + *Q*	1.70(1.47)	3.19	762	10.07
CPA-4	1.73(1.72)	3.24	683	10.26
4R				
V				
CI	1.85(1.69)	3.22	770	9.86
CI + *Q*	1.85(1.80)	3.23	752	10.03
CPA-4	1.82(1.83)	3.23	743	10.13
CV				
CI	1.64(1.32)	3.20	742	10.08
CI + *Q*	1.67(1.52)	3.21	720	10.28
CPA-4	1.64(1.60)	3.23	680	10.44
C				
CI	1.68(1.02)	3.18	784	9.81
CI + *Q*	1.73(1.49)	3.20	764	10.05
CPA-4	1.69(1.68)	3.22	713	10.29
HFS-DFT[c] [28]		3.27	655	10.45
CASSCF/ MRCI[d] [29]		3.29	669	
Expt. [28]	1.39	3.18	745 ± 25	10.64 ± 0.01

[a] SAE values in parentheses

[b] Adiabatic value relative to the energy obtained from each of the correlation schemes *V*, *CV*, or *C* for GaF (Refer to Table 2)

[c] A pseudo-potential technique was emloyed for the Ga $1s$–$2p$ shells

[d] Ga $1s$–$3d$ shells were replaced by an effective potential. The valence basis set was "double-zeta plus polarization" type

Two sets of MRCPA-4 (and MRCI) calculations on GaF$^+$ were carried out using the following four reference configurations:

1. $\sigma_a^2\sigma_b$: characterizing the total wavefunction (single-configurational SCF type),
2. $\sigma_a\sigma_b\sigma_c$: representing a dissociation channel toward Ga$^+(4s4p)$ + F$(2p^5)$,
3. $\sigma_a\sigma_b^2$: representing both a dissociation channel to Ga$^+(4s^2)$ + F$(2p^5)$ and screening of the $4s$ open shell by bonding electrons,
4. $\sigma_b\sigma_c^2$: representing a left-right correlation among the σ_a bonding electrons.

The three-reference (3R) calculation used the first three configurations while the four-reference (4R) used all of the configurations above. Table 4 summarizes spectroscopic constants calculated at a variety of levels of theory.

We will first focus on the results for the bond length and vibrational frequency. The 4R calculations yield the best agreement with experimental data [27, 28]. This is true for each of the *V*, *CV*, and *C* levels of correlation. This shows that the fourth, $\sigma_b\sigma_c^2$ reference configuration, which represents a left-right correlation in the bond and reduces the polarity in the Ga^{++}—F$^-$ bonding, is quite important. In GaH$^+$ this configuration is not important and thus a 4R calculation is not needed [1]. Although the R_e value does not change significantly between *V*- and *C*-4RCPA-4 calculations, the ω_e decreases when the correlations of semi-core electrons are included. The calculated D_e values also decrease slightly. The same situation is found for the 3R results. The *CV* scheme somewhat overestimates this behavior, as demonstrated by the 3RCPA-4 value of only 652 cm^{-1}. An equal inclusion of the valence and semi-core shells is desirable. The *C* scheme of correlation decreases the ω_e and D_e, indicating that the bond is weaker when modeled by the *V* scheme. The main source of covalent bonding is the formal combination of Ga$^+(4s4p)$ and F $(2p^5)$, but this actually leads to the ionic combination of Ga$^{++}(4s)$ and F$^-(2p^6)$. As given in Ref. [1], the excitation energy of the $4s^2 \rightarrow 4s4p$ transition for the Ga$^+$ atomic ion is calculated to be 5.49 eV by *V*-CPA4 and 5.77 eV by *C*-CPA-4, whereas the experimental value is 5.87 eV [18]. A reasonable separation between the $4s^2$ and $4s4p$ configurations in Ga$^+$ is reproduced by inclusion of $3d$ semi-core electron correlations. Thus, for GaF$^+$, a decrease in both D_e and ω_e in the *C* scheme could result from a proper reduction of $4s4p$ (covalent) and/or $4s$ (ionic) portions of the Ga site. For GaH$^+$, the D_e increases because of the increased dative stabilization between the Ga$^+(4s^2)$ and H [1]. The interaction between $4s^2$-like Ga$^+$ and F may be rather repulsive. The picture is qualitatively different for GaF$^+$ and GaH$^+$, although the correlations of the semi-core $3d$ electrons are non-negligible in both cases.

When we compare the R_e and ω_e values with those of neutral GaF (Tables 2, 4), we see a considerable decrease in R_e and increase in ω_e. The *C*-4RCPA-4 treatment shows that the shifts are as large as -0.15 au for R_e and $+91$ cm^{-1} for ω_e (Table 2). It is possible that electron removal mainly from the $4s^2$ shell, which is being repelled from the F side in the neutral state, could be reponsible for these shifts. In contrast to GaF$^+$, for GaH ionization a small decrease of -0.04 au is found, in R_e while ω_e decreases by -205 cm^{-1}. This is in accord with the fact that the electron is lost mainly not from the $4s^2$ shell but from the bonding MO in GaH [1]. The difference between GaF$^+$ and GaH$^+$ is again well evident in the shifts in R_e and ω_e.

MRCI calculations with and without the $+Q$ correction seem to provide good values for R_e, however, the ω_e results are considerably larger than those of corresponding MRCPA-4 calculations. This behavior reflects an artificial enhancement of bonding due to the lack of size-consistency. The $+Q$ treatment does not correct sufficiently at the *C* level of correlation. Thus, the CI picture for the bonding appears invalid.

We now compare our calculated D_e with the experimental value of 1.39 eV reported by Grabandt et al. [27]. MRCPA-4 calculations yield values converging around 1.7 eV. Note that again severe discrepancy between the SM and SAE values for the CI calculation exists but the separability is held well in MRCPA-4.

Grabandt et al. derived D_e from a measurement of the IP via the cyclic relation: (i) $Ga + F \rightarrow GaF$, (ii) $GaF \rightarrow GaF^+$, (iii) $GaF^+ \rightarrow Ga^+ + F$, (iv) $Ga^+ + F \rightarrow Ga + F$. The energy of step (iii) is just the D_e of interest [27]. The energy of step (ii) was observed by Grabandt et al. to be 10.64 ± 0.01 eV and the data for steps (i) and (iv) were taken from other experiments. Thus, they obtained 1.39 eV for D_e. Our calculations give an IP of around 10.3 eV, while calculated values for steps (i) and (iv), 6.0 eV and 5.98 eV, respectively, agree with the experimental numbers of 6.02 eV [6] and 6.0 eV [18]. Thus, a consistent difference of 0.3 eV for the IP and D_e exists between the present estimates and the experimental values [27].

We can try to resolve this discrepancy by surveying the data of similar systems. Glenewinkel-Meyer et al. carried out high-level CASSCF/MRCI calculations with extended basis sets on AlF^+ and $AlCl^+$ and obtained D_e values of 2.98 eV for the former and 1.72 eV for the latter [29], that is, the F bond to Al^+ is 1.7 times stronger than that of Cl to Al^+. The experimental D_e of AlF^+ is 3.14 ± 0.14 eV [30], verifying the reliability of Ref. [29]. Simple SCF/CI+Q calculations done by Mochizuki et al. [31] yielded estimates of 1.09 eV for D_e ($GaCl^+$) and 1.82 eV for D_e ($AlCl^+$). The closeness in the results for $AlCl^+$ with those in Ref. [29] may be coincidental. Thus Al^+ makes a bond with Cl that is 1.7 times stronger than Ga^+ bonds to Cl. We can thus argue that the GaF^+ D_e can be roughly 1.6–1.9 eV, in agreement with our calculations. A remeasurement of this bond energy is recommended. In conclusion we would like to note that the *C*-4RCPA-4 spectroscopic data reported in Table 4 should be taken as our best values.

4 Summary

We have performed a series of extensively correlated calculations on the gallium fluoride molecule and its positive ion. Using the size-consistent CPA-4 scheme, the contribution of the semi-core electron correlations was examined. For GaF, agreement between theory and experiment was quantitative when the correlation of semi-core electrons was taken into account. It was noted that new experimental data for the GaF^+ ion would be useful. The bond energy of GaF^+ was predicted to be as large as 1.7 eV, with strong ionic character, in contrast to GaH^+.

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