Theor Chem Acc (1998) 99:88–94

Theoretical
Chemistry Accounts

Regular article

Theoretical investigation on the GaH molecule and its positive ion

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Received: 25 July 1997 / Accepted: 13 November 1997

Abstract. The gallium monohydride (GaH) molecule and its positive ion were theoretically investigated by abinitio molecular orbital calculations with a flexible basis set including *g*-type functions on the Ga atom. Electron correlations among not only the valence electrons of Ga 4*s*4*p* and H 1*s* but also the semi-core electrons of Ga 3*d* were incorporated by a size-consistent scheme of the coupled pair approximation. The contribution of the 3*d* electron correlation was found to be considerable on spectroscopic constants of both GaH and GaH^+, especially on the bond length.

Key words: Gallium monohydride – Ionization potential – 3*d* Semi-core electrons – Size consistency – Coupled pair approximation

1 Introduction

Gallium containing systems are of interest to the compound semi-conductor industry. Thus, they have been extensively investigated not only by experimental but also theoretical methods. The ground state of the Ga atom is a ^2P, having the electronic configuration $(1s-3p)^{18}\,(3d)^{10}4s^24p$. In many theoretical calculations, only the valence shell 4*s*4*p* has been explicitly treated, using the technique of so-called effective potential replacement for inner-core electrons. However, such a potential replacement up to the 3*d* shell can lead to considerable errors in the calculated properties, suggesting the importance of relaxations of the 3*d* electron distribution. Furthermore, the correlation contribution from 3*d* cannot be negligible in certain cases. The 3*d* orbital energy, calculated by the atomic self-consistent field (SCF) scheme [1], is −1.15 a.u. and the Ga 3*d* shell is characterized as the semi-core, while the corresponding 4*s* and 4*p* energies are −0.42 a.u. and −0.20 a.u., respectively. Based on the all-electron calculation by coupled cluster singles and doubles with perturbative triples [abbreviated CC(T) without a default symbol of SD], Richards et al. [2] have reported that there is an error of more than 1 eV in the energetics of the GaOH → HGaO isomerization reaction if the 3*d* electrons are not correlated. In plane-wave density-functional (DF) calculations of GaN surfaces, the necessity of careful treatment of 3*d* was pointed out [3]. Actually, the 2*s* levels of O and N atoms are fairly close to that of Ga 3*d* (−1.24 a.u. for O and −0.93 a.u. for N [1]).

In the present paper, we perform extensive ab initio calculations on the GaH molecule and its positive ion (GaH^+). They are the simplest heteronuclear species involving the Ga atom. The ground state of GaH is of $^1\Sigma^+$ symmetry and has a single σ bond. The bonding orbital is characterized by the combination of Ga 4*p* and H 1*s* with the polarity $Ga^+{-}H^-$. The Ga 4*s* orbital is composed primarily of a lone-pair, the direction of which is polarized away from the H side. Although the ionization formally occurs from the Ga—H bonding orbital to produce the $^2\Sigma^+$ state of the GaH^+ ion, a certain amount of hole-screening by Ga 4*s* electrons may take place.

The spectroscopic constants computed by previous molecular orbital (MO) calculations for GaH [4–11] are not in satisfactory agreement with the experimental data [12, 13]. To our knowledge, no experimental spectroscopic data are available for GaH^+. There are only two papers on this system but the calculated dissociation energies were quite different from each other [7, 14]. The principal purpose of this paper is to obtain accurate spectroscopic constants of GaH and GaH^+, where the correlation contribution from the semi-core 3*d* electrons is of special interest. A large Gaussian basis of the all-electron type is carefully set up, where the contracted set used for Ga is [9*s*7*p*5*d*3*f*1*g*]. Pettersson and Langhoff [4] have reported calculations including 3*d* correlation with an extended Slater-type basis up to the *f*-type function and thus a comparison with our results may be interesting. Correlations are described by the coupled pair approximation (CPA) scheme, which takes higher excitations into account to satisfy the size consistency and can handle the multireference (MR) cases [15–17]. The

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present investigation can be considered as a touchstone for more complicated molecular systems containing Ga.

2 Method of calculation

2.1 Basis set

The Gaussian basis set for Ga was based on a valence triple-zeta (TZ) set of (6,2,1,1,1,1,1,1/3,3,1,2,1,1/4,1)/[8*s*6*p*2*d*] which was provided by Shäfer et al. [18]. To this fundamental set, we first determined the *f*– and *g*–type polarization functions, which are more important actually in describing the angular correlations in the 3*d* semi-core shell. For this purpose, a series of singly and doubly excited configuration interaction (SDCI) calculations was carried out on the Ga$^+$ atomic ion represented by the $4s^2$ configuration of ^1S. Hereafter, we simply denote SDCI as CI. The reason why the ionized state was used is that the ionization potential (IP) of Ga is as small as 6.0 eV [19] and thus the Ga$^+$ character may play an important role even in the neutral GaH molecule. A total of 12 electrons of 4*s* and 3*d* shells were correlated in the atomic CI. Before the augmentation of polarization functions, we divided the 3*d* shell originally of (4,1) and contracted it to (3,1,1). This relaxation was necessary to obtain the node position of the 4*d* type natural orbital (NO), which accounts for the most important $3d^2 \rightarrow 4d^2$ radial correlation, and this indicates the necessity of TZ flexibility. For *f* polarization, we prepared three primitive *f* functions the exponents of which were 10.612, 3.5372 and 1.1791, where the second function was adjusted so that the radial extension of the function, $\langle r_f \rangle$, matched $\langle r_{3d} \rangle$ the numerical value of which was 0.7758 given by Huzinaga et al. [1], and the first and third ones were simply derived by scaling factors of 3 and 1/3. With the basis set thus obtained, [8*s* 6*p*3*d*3*f*], we carried out an atomic CI calculation to determine the contraction coefficients for the first and second *f*-type primitive functions according to the atomic NO (ANO) contraction scheme [20]. The resulting coefficients were 0.1933 and 0.5529. Furthermore, a single *g* polarization function, which consists of two primitives in an ANO manner, was added. These exponents were roughly optimized by trial CI calculations and they were 8.25 and 2.75. Their ANO coefficients were 0.3271 and 0.8083. To improve the flexibility of the description for the valence 4*s*4*p* region, a primitive function was augmented to each of the *s*, *p*, *d* and *f* set, where each exponent was derived by multiplying a factor of 1/3 to the outermost functions in the above [8*s*6*p*3*d*2*f*1*g*] set. The exponents for *s*, *p*, *d* and *f* were 0.0235, 0.0212, 0.2223 and 0.3930, respectively. A set of *d* functions was further added, and its exponent was 0.0741. The final contraction of Ga basis set was (15*s*12*p*7*d*4*f*2*g*)/[9*s*7*p*5*d*3*f*1*g*].

The H basis was based also on the (3,1,1) TZ set provided by Shäfer et al. [18]. An *s* function (exponent: 0.0344) was added. As for the *p*– and *d*–type augmentation, we used the 3*p*2*d* exponents of the "aug-cc-pVTZ" set developed by Dunning et al. [21, 22]. The contraction scheme for H was denoted as (6*s*3*p*2*d*)/[4*s*3*p*2*d*].

Only pure spherical-harmonic components of *d*, *f* and *g* functions were used. The total number of the basis for GaH was thus 108. The basis functions except for the author's augmentation were down-loaded from the Internet server at the United States Pacific Northwest National Laboratory [23].

2.2. Treatment of electron correlation

Electron correlations were introduced by CPA, which was proposed by the second author (K.T.) [15–17]. CPA is an approximate MR size-consistent method. Technically, CPA has the merit that its implementation is fairly easy using the usual MRCI calculation scheme. The dimension of the Hamiltonian matrix and of most of the associated elements are common between CI and CPA. A new CPA program recently developed by K.T. has been interfaced with the integrals and energy expressions for the matrix elements generated by Alchemy-II, which is a suite of integral, multiconfiguration self-consistent-field (MCSCF), MRCI programs [24–27]. CPA has two levels of approximations at the second order (CPA-2) and fourth order (CPA-4) according to the perturbational inclusion of higher excitations. A brief description of the method and implementation is given elsewhere [17]. We will only show results of CPA-4 in the present paper, since the CPA-2 results did not notably differ from those of CPA-4. To illustrate the importance of size consistency, CI results with/without Davidson's correction (denoted as $+Q$ [28]) will be compared with the CPA-4 results.

A set of SCF MO was used for the CI and CPA-4 calculations for the $^1\Sigma^+$ ground state of GaH. The state is well described by the single closed-shell determinant, as noted in Ref. [4] in which the coupled pair functional (CPF) method [29] was applied to the state. CPF is a size-consistent modification of single SCF reference CI. The CPA-4 wave function is also well represented by a single reference function and may show similar behaviour to CPF. In contrast, the positively ionized state or $^2\Sigma^+$ of GaH$^+$ required MR treatment. Thus, a complete-active-space type MCSCF (CASSCF) [30] was employed to make an MO set for the successive MRCI and MRCPA-4. The active MO space, which was designed to be minimal for the generation of reference, consisted of Ga 4*s*, 4*pσ* and H 1*s*. Three valence electrons were distributed among these three *σ* orbitals, leading to eight functions of CAS space. Two or three important configurations among CASCI were selected from the CASSCF wave function as the reference set in MRCI and MRCPA-4. In actual MRCPA-4 calculations, an approximated scheme was employed [17]; the reference space is pre-diagonalized and only the lowest state function was used in the introduction of correlations. Further details for GaH$^+$ will be described in the next section.

The Ga 3*d* semi-core shell was treated in the following three levels:

1. *V*: 3*d* electrons were kept frozen. Namely, only the valence Ga 4*s*4*p* and H 1*s* electrons are correlated.

Table 1. Ionization potential for the process ^2P ($4s^24p$) Ga $\rightarrow$ ^1S ($4s^2$) Ga$^+$ and energy for the excitation ^1S ($4s^2$) Ga$^+$ $\rightarrow$ ^3P ($4s4p$) Ga$^+$. Units are in eV. An average spin-orbit splitting was taken into account for the calculated values. Corrections are 0.07 eV for the ionization potential and 0.11 eV for the excitation energy [19]

Scheme		*V*	*CV*	*C*	
^2P ($4s^24p$) Ga $\rightarrow$ ^1S ($4s^2$) Ga$^+$					
SCF	5.54				
CI		5.87	5.91	5.83	
CI + *Q*		5.90	5.96	5.91	
CPA-4		5.91	5.97	5.98	
Expt. [19]					6.0
^1S ($4s^2$) Ga$^+$ $\rightarrow$ ^3P ($4s4p$) Ga$^+$					
SCF	4.53				
CI		5.44	5.70	5.41	
CI + *Q*		5.49	5.80	5.63	
CPA-4		5.49	5.80	5.77	
Expt. [19]					5.87

2. *CV*: simultaneous two electron excitations from the 3*d* shell were not included. Only polarization-type correlation, which is induced by valence electrons, was incorporated for 3*d* electrons. Single excitations of 3*d* were, of course, allowed to dynamically relax the electron distribution.
3. *C*: double excitation from 3*d* were added. Thus, a 3*d*–3*d* pair correlation was introduced as usually done for valence electrons. The total number of correlated electrons is 14 for GaH.

In generating configuration state functions (CSFs), all possible spin-coupling functions were taken into account.

The actual calculations were carried out under the C_{2v} or subgroup of $C_{\infty v}$ symmetry. The four highest-lying MOs (two a_1, b_1 and b_2 types), which have the radial nodes at the 1*s* and 2*p* region of Ga, were deleted from the correlating MO space. The largest number of CSFs (or dimension of the Hamiltonian matrix) was 374 280 for GaH^+ by the *C*-level calculation with three reference configurations. All calculations were carried out by the Alchemy-II system [24–27] and an MRCPA program [17] on IBM RS-6000 workstations.

Although relativistic effects were not explicitly considered in the calculations, an average spin-orbit splitting of the ^2P state of the free Ga atom was taken into account in the evaluation of the dissociation energy (D_e), as done by Pettersson and Langhoff [4]. The correction derived from Moore's table [19] was −0.07 eV. The equilibrium bond length (R_e) and vibrational frequency (ω_e) were obtained by fourth-order polynomial fittings around the minimum, where the step sizes were less than 0.03 a.u. The scanned range for bond length was 2.9–3.3 a.u. The atomic masses of Ga and H used in the ω_e evaluation were 68.9256 amu and 1.0078 amu, respectively.

3 Results and discussion

3.1 Ga

Before discussing the results on GaH and GaH^+, we show the results of the Ga atom itself. The purpose is to demonstrate the high quality of the [9*s*7*p*5*d*3*f*1*g*] basis. Table 1 summarizes the IP for the process ^2P ($4s^24p$) Ga → ^1S ($4s^2$) Ga^+ and the energy for the excitation ^1S Ga^+ → ^3P (4*s*4*p*) Ga^+. The corrections used for the spin-orbit splitting are 0.07 eV for the former and 0.11 eV for the latter [19].

The IP calculated by the SCF method is insufficient to discuss quantitatively. Inclusion of correlation improves the calculated IP and the agreement with the experimental data [19] is very good. Especially, the *CV* and *C* levels of CPA-4 treatment provide very good values, indicating that the basis set is accurate and the correlation correction for the 3*d* semi-core electrons is effective in predicting IP even for the Ga atom. For the energy of excitation 4*s* → 4*p*, the 3*d* correlation through the CPA-4 calculations presents a more significant improvement than that in the IP case. The contribution amounts to 0.28 eV for the *C* level. The size inconsistency in CI deteriorates results by proceeding from *V* to *C* schemes. The $+Q$ correction presents an improvement but the difference from CPA is not negligible. The use of a size-consistent method like CPA is highly desirable.

3.2 GaH

Now, we focus on the calculated spectroscopic constants of GaH. The results of D_e, R_e and ω_e are listed in comparison with the experimental data [13, 14] in Table 2. The table contains other calculated results [4–11].

One can see that the SCF theory does not provide a reliable result for D_e; we note also that Ref. [5] reported a similar value of 2.30 eV. In other words, inclusion of electron correlation is significant in describing the Ga—H σ bond. Even at the *V* level, in which only four valence electrons are correlated, the improvement is as large as 0.7–0.8 eV. The introduction of 3*d* correlation presents a further increase in D_e. In the CPA-4 calculation, the increase is 0.06 eV from *V* to *C* levels. This is comparable with 0.05 eV, obtained by the CPF method using an extended Slater-type basis set [4]. Schwerdtfeger et al. [9, 10] also reported almost the same increase by using a size-consistent quadratic CI calculation with singles, doubles and perturbative triples [QCI(T)] [31], although the flexibility of their basis [11*s*8*p*5*d*] (see their paper for details) was restricted for the 3*d* shell relative to the present one. The present value of 2.99 eV calculated by *C*-CPA-4 (that is a simple notation of "the *C*-level calculation by CPA-4") is in good agreement with the experimental data [13, 14] and is comparable with the values of CPF [4] and QCI(T) [9, 10]. Balasubramanian used an effective core potential (ECP) replacement up to 3*d* shells of Ga and treated the valence electron correlation by an extensive second-order CI (SOCI) after a CASSCF calculation [6, 7]. As is shown in Table 2, his D_e value was 2.81 eV, which is smaller than those obtained by other correlated calculations with all-electron treatment. This implies that inclusion of electron relaxation and correlation in the 3*d* shell is important in describing bond formation. Explicit treatment of 3*d* electrons is recommended for Ga-containing systems which are larger than GaH, if possible.

The correlation contribution from 3*d* is also found to be important for R_e and ω_e, as shown in Table 2. The best agreement with the experimental data [13] was obtained by the *C* level of CPA-4 among the present calculations. When we compare the R_e and ω_e calculated by CPA-4, the *C*-level treatment provides a contraction in R_e of 0.04 a.u. and an increase in ω_e of 35 cm^{-1} relative to the *V* level. The CPF [4] and QCI(T) [10] calculations also reported a bond contraction after including the semi-core correlation. Comparison between the *C* and *CV* levels by CPA-4 suggests that the *CV* scheme tends to enhance the 3*d* correlation effect and the *C* level of 3*d* treatment is desired to obtain a more reliable result.

The weight of the SCF-reference configuration by the *V* level CPA-4 is 0.91 and that by the *C* level is 0.88. In contrast, the reference weights for the *V* and *C* levels by CI were 0.93 and 0.94, respectively, although the length of expansion at the *C* level is larger than *V* level due to the increase of correlated electrons (4–14). The weight of the correlation part of the total wavefunction should be increased as the number of correlating electrons increases if the wave function is obtained by a size-consistent method. This illustrates the size inconsistency in limited CI expansions.

The dipole moment was evaluated with the NO set of the *C*-level CPA-4 at the R_e of 3.15 a.u. and the result was 0.46 debye with a polarity of Ga^+—H^-. This value is

Table 2. Spectroscopic constants for GaH

Method	D_e[a] (eV)	R_e (a.u.)	ω_e (cm^{-1})
SCF	2.10	3.15	1674
V			
CI	2.84	3.18	1616
CI + *Q*	2.91	3.19	1595
CPA-4	2.93	3.19	1589
CV			
CI	2.89	3.13	1659
CI + *Q*	2.97	3.13	1632
CPA-4	3.01	3.13	1623
C			
CI	2.76	3.12	1701
CI + *Q*	2.90	3.13	1674
CPA-4	2.99	3.15	1624
Other calculations			
3*d*-correlated CPF, Slater-type basis [4]	2.90	3.14	1626
SCF, 3-21G* [5]	2.30	3.20	
CASSCF/SOCI, [4*s*4*p*2*d*] for 4*s*4*p* shells[b] [6–7]	2.81	3.14	1612
SCF, [6*s*4*p*2*d*] [8]		3.17	1685
3*d*-correlated QCI(T)[c], [11*s*8*p*5*d*] [9–10]	2.87	3.16	1567
CC(T), [5*s*4*p*1*d*] with some augmentations [11]		3.17	1569
Exptl.			
[12]	<2.94	3.14	1605
[13]	2.89–3.04		

[a] An average spin-orbit splitting was taken into account for the present calculations. See text
[b] An effective core potential (ECP) was used for Ga 1*s*–3*d* shells
[c] 3*s*3*p* shells were correlated

Table 3. Total energy and correlation energy for GaH

Method	Total energy (a.u.)[a]	Correlation energy (eV)[b]
SCF	−1923.7459	
V		
CI	−1923.8227	2.09
CI + *Q*	−1923.8280	2.23
CPA-4	−1923.8291	2.26
CV		
CI	−1923.8716	3.42
CI + *Q*	−1923.8802	3.65
CPA-4	−1923.8826	3.72
C		
CI	−1924.2160	12.79
CI + *Q*	−1924.2460	13.61
CPA-4	−1924.2591	13.96

[a] Each value was evaluated at the respective R_e
[b] Energy difference from the SCF total energy. The minus sign was omitted

comparable with 0.369 debye provided by the 3*d*-correlated CPF [4]. The dipole moment calculated by the *C*-CI scheme was only 0.14 debye, which is again similar to 0.111 debye obtained by the CI approach reported in Ref. [4]. The dipole moment at the *V* level was calculated to be 0.41 debye for CPA-4, and 0.34 debye for CI. The dipole moment is slightly increased by inclusion of 3*d* correlation for the CPA-4 case. However, the situation is quite the opposite for CI. This may reflect the size inconsistency in CI. The size-consistency problem can appear in electronic properties such as dipole moment, as well as in the spectroscopic constants of $D_{e,}$ R_e and ω_e.

As has been seen, the present calculations are reasonably accurate. Thus, the total energies may be used as a reference for future investigations. We show the set of total energy at each R_e for GaH in Table 3. For convenience, the correlation energies, which are the differences from the SCF energy are also listed. The energy lowering due to 3*d* correlation is as large as 10 eV in the present calculations.

3.3 GaH$^+$

In this section, we first discuss the necessity of a MR treatment for GaH$^+$ by the following two methods. The first method is based on the concept of hole-screening. The first ionized state, $^2\Sigma^1$, is formally described as a one-electron ionization from the σ-bonding MO of GaH, which is characterized by the polarized combination of λ4p + 1s. But, a screening of a 4*s*-like lone-pair takes place to compensate the large energy loss by ionization. Thus, these two orbitals should mix with each other. The single-configurational SCF procedure for GaH$^+$ takes into account this mixing by a certain amount to relax the hole orbital. However, the introduction of dynamical correlation dynamically changes the balance in mixing and the character of the resultant hole-type MO significantly differs from the SCF-hole MO. This means that the single-configurational correlated approach does not work well.

The second method to explain why the MR scheme is needed stems from the consideration of two attractive potentials. The Ga$^+$ ion having the closed-shell ground state of ^1S ($4s^2$) cannot form covalent bond with H and thus the interaction should be ligatic with a small stabilization having a wide and shallow well. As an example, the D_e of KH$^+$ is less than 0.1 eV [32, 33]; the molecule is regarded as a standard for ligatically stabilized molecular ions. The second state of Ga$^+$ is the $4s \rightarrow 4p$ excited state (^3P), which is higher in energy by 5.87 eV [19] than the ground state. But the interaction with H provides a strong covalent bond to stabilize the system. As both ligatic and covalent potentials for Ga$^+$ + H belong to $^2\Sigma^+$, configurational mixing is expected in the wave function. Balasubramanian [7] obtained 0.32 eV for the D_e of GaH^+ by valence-electron CASSCF/SOCI calculations with an ECP technique for 1*s*–3*d* shells. On the other hand, Gutowski et al. [14] reported 0.65 eV by the QCI(T) calculation, in which the core potential technique was also used but the 3*d* shell was explicitly taken into account. The difference between these two estimates suggests the need for further calculations to obtain a more reliable D_e.

We performed two types of MRCPA-4 calculation (denoted as 2RCPA-4 and 3RCPA-4) using the MO set generated by the σ-space CASSCF. To describe the reference configurations, the characteristics of the CASSCF results are summarized here. The CASSCF active NOs are simply labelled σ_a, σ_b and σ_c. The σ_a NO is roughly characterized by Ga 4*s*. The σ_b and σ_c are bonding and anti-bonding combinations of Ga 4*p* and H 1*s*, respectively. The occupation numbers for active NOs are 1.96, 1.00, and 0.04 around the minimum. In the CASSCF calculation the dimension is eight, the weight of the single-configurational SCF-type configuration of $\sigma_a^2\sigma_b$ is 0.97 and the singly excited configuration of $\sigma_a\sigma_b\sigma_c$ dominates the remaining portion with the weight of 0.02, where two CSFs associate with the latter configuration due to the linearly independent spin-coupling functions. The 2RCPA-4 calculation was based on these two configurations, and its reference CI dimension is three. The contribution of $\sigma_a\sigma_b\sigma_c$ was also noted in Ref. [7]. The $\sigma_a\sigma_b^2$ configuration, which describes the hole-screening, was augmented for 3RCPA-4 (the dimension of the reference CI is four). This third configuration does not notably contribute to the CASSCF wave function but has a weight range of 0.005–0.01 are the 2RCPA calculations. Thus, the configuration is moved to the reference space.

Table 4 lists the calculated spectroscopic constants for GaH^+, where the single SCF-reference (explicitly denoted as 1R) results are included to illustrate the necessity of MR treatment. For simplicity, only the $+Q$-corrected values of CI are compared with the CPA-4 results. The V-3R (representing the *V*-level treatment by CI or CPA-4 with three reference configurations) results are not included since they are the same as the results from the *V*-2R scheme within the decimals shown in the table. Note that the dissociation limit for D_e was set to ^1S $Ga^+ + H$.

As seen from the table, the 2R(CASSCF) and 3R(CASSCF) treatments of CPA-4 provide almost the same values for D_e, R_e and ω_e in each of the *V*, *CV* and *C* levels. However, the calculated results by 1R(SCF) CPA-4 deviate greatly from those of the MR scheme. This resulted from the fact that the weight of $\sigma_a\sigma_b^2$ excited configuration was unexpectedly large in the 1RCPA-4 wave function due to the perturbational nature of CPA [14, 15]. SCF values are far from the MR-correlated results. Inclusion of correlation through 1RCPA-4 does not correct the poor description of SCF. 1RCI + *Q* results also show unreliable behaviour.

Hereafter, we discuss the MR results shown in Table 4. The V-2RCPA-4 provides a D_e of 0.47 eV, which falls in the interval between 0.32 eV from CASSCF/SOCI [7] and 0.65 eV from QCI(T) [14]. The potential replacement even for the semi-core 3*d* shell in Ref. [7] could be responsible for the smaller value of 0.32 eV as discussed in the previous section. The QCI(T) value [14] might be an overestimate since the calculation was

Table 4. Spectroscopic constants for GaH^+

Method	D_e (eV)	R_e (a.u.)	ω_e (cm^{-1})
SCF	0.09	2.98	1935
1R(SCF) *V*			
CI + *Q*	0.49	3.15	1380
CPA-4	0.50	3.16	1401
1R(SCF) *CV*			
CI + *Q*	0.51	3.13	1380
CPA-4	0.59	3.17	1544
1R(SCF) *C*			
CI + *Q*	0.44	3.05	1498
CPA-4	0.60	3.17	1585
2R(CASSCF) *V*			
CI + *Q*	0.47	3.12	1476
CPA-4	0.47	3.12	1449
2R(CASSCF) *CV*			
CI + *Q*	0.49	3.12	1394
CPA-4	0.50	3.12	1376
2R(CASSCF) *C*			
CI + *Q*	0.54	3.09	1434
CPA-4	0.52	3.12	1404
3R(CASSCF) *CV*			
CI + *Q*	0.49	3.11	1401
CPA-4	0.47	3.12	1401
2R(CASSCF) *C*			
CI + *Q*	0.55	3.10	1438
CPA-4	0.50	3.11	1419
Other calculations			
CASSCF/SOCI, [4*s*4*p*2*d*] for 4*s*4*p* shells[b] [7]	0.32	3.12	1299
QCI(T), [4*s*4*p*3*d*] for 3*s*3*p*3*d*4*s*4*p* shells[c] [14]	0.65	3.12	

[a] The method used to prepare the MO set is indicated in parentheses

[b] An ECP was used for 1*s*–3*d* shells

[c] A pseudo-potential technique was employed for Ga 1*s* –2*p* shells

Table 5. Adiabatic ionization potential of GaH. Units are in eV

2R(CASSCF) *V*	
CI + *Q*	8.34
CPA-4	8.37
2R(CASSCF) *CV*	
CI + *Q*	8.43
CPA-4	8.48
3R(CASSCF) *C*	
CI + *Q*	8.27
CPA-4	8.45
3R(CASSCF) *CV*	
CI + *Q*	8.44
CPA-4	8.51
3R(CASSCF) *C*	
CI + *Q*	8.26
CPA-4	8.47
Other calculations [7]	8.28

based on a single SCF-reference function although the connected triple excitations were taken into account [34]. The increase in D_e is 0.05 eV from V to C at the 2RCPA-4 level. The 2RCI + Q shows a similar increase, implying that the MR scheme reduces the size inconsistency by a certain amount. The D_e value of C-3RCPA-4 is smaller than that of 2R by 0.02 eV. The 3RCI + Q presents a rather larger value of 0.55 eV. Accepting the level of approximation, it is safe to note that the best D_e estimate is 0.50 eV provided by the C-3RCPA-4 calculation.

The frequency lowering, or ω_e decrease by 30–40 cm^{-1} from V to C is noteworthy, in spite of the increase in D_e and no significant change in R_e. The situation is in contrast to the neutral GaH case. This illustrates that the ligatic interaction is well accounted for by the inclusion of correlation of semi-core 3*d* electrons. Recall that the C-level CPA-4 calculation considerably enlarged the excitation energy of $4s^2 \rightarrow 4s4p$ to give better agreement with the experimental data than that of V (refer to Table 1). We again recommend the C-3RCPA-4 results as the better estimates. These values are 3.11 a.u. for R_e and 1419 cm^{-1} for ω_e. The R_e is shortened by 0.04 a.u. relative to the value of GaH (see Table 2). This may reflect the situation that 4*s* is more compact than 4*p* and the contribution of 4*s* to the bonding is larger in GaH$^+$ than in GaH. The smaller ω_e value for GaH$^+$ than GaH is consistent with the fact that the principal removal of electron takes place at the Ga—H bonding MO as a whole.

Finally, adiabatic IP values for GaH → GaH$^+$ are shown in Table 5. The 3*d* correlation increases the IP by about 0.1 eV. The value of 8.47 eV provided by C-3RCPA-4 is compared with 6.0 eV [19] of the free Ga atom for the 4*p* electron removal. The increase of 2.5 eV correlates with a difference in the bonding nature between GaH and GaH$^+$.

4 Summary

We have performed a series of CPA-4 calculations with a large Gaussian basis set of [9*s*7*p*5*d*3*f*1*g*]/[4*s*3*p*2*d*] to investigate GaH and GaH$^+$. The contribution of correlation among the semi-core 3*d* shell was found to be substantial for both systems. Overall agreement with the experimental data was excellent for GaH. The necessity of a MR treatment for GaH$^+$ is discussed in detail. The spectroscopic constants have not been experimentally observed yet and the constants just predicted for GaH$^+$ are 0.50 eV for D_e, 3.11 a.u. for R_e, and 1419 cm^{-1} for ω_e.

Acknowledgements. The present work has been performed under a contract for collaborative investigations between The University of Electro-Communications (UEC) and NEC Fundamental Research Laboratories. Y.M. has been a visiting researcher at K.T.'s laboratory. His warm hospitality is gratefully acknowledged. Finally, the authors wish to thank the referees for their valuable suggestions.

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