Potential energy curve study on the $^3\Pi$ electronic states of GaX (X= F, Cl, and Br) molecules*

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The potential energy curves (PECs) of the $^3\Pi$ states of GaX (X = F, Cl, and Br) molecules are calculated using the multireference configuration interaction method with a large contracted basis set aug-cc-pV5Z. The PECs are accurately fitted to analytical potential energy functions (APEFs) using the Murrell–Sorbie potential function. The spectroscopic parameters for the states are determined using the obtained APEFs, and compared with the theoretical and experimental data available presently in the literature.

Keywords: potential energy curve, analytical potential energy function, spectroscopic parameters, multi-reference interaction configuration

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1. Introduction

Group (III) halides show many physical and chemical properties and broad prospects for application, therefore they have received much attention for a long time. For example, the gallium monohalide diatomic molecules GaX (X = F, Cl, Br, I) play an important role as intermediates in the production of new high-frequency and opto-electronic semiconductor devices.[1] Studies of gallium monohalides are currently being carried out both experimentally and theoretically, which have extended and deepened the comprehension of the properties of the electronic states of these molecules. The rotational analyses of bands of the $A^3\Pi_{0+}$ and the $B^3\Pi_1$–$X^1\Sigma$ systems of gallium monofluoride were studied by Barrow *et al.*,[2] and the results was notable. Hoeft and Nair[3,4] observed the microwave spectrum and reported on some accurate spectroscopic constants (SCs) of these molecules. With the development of computer technology, more and more theoretical studies on the electronic state structures of gallium monohalides have been reported. In the 1990s, Mahieu *et al.*,[5] Uehara *et al.*,[6] Dearden *et al.*,[7] Venkatasubramanian *et al.*,[8] Sunanda *et al.*,[9] and Saksena *et al.*[10] conducted some studies on the gallium monohalide diatomic molecules. They corrected some errors reported in early work, obtained more accurate SCs, and predicted the prospects of gallium monohalide molecules as an efficient excimer laser system. In 1992, Kim and Balasubramanian[11,12] obtained the SCs and potential energy curves (PECs) of GaCl and GaBr. In 1998, Mochizuki and Tanaka[13] calculated the GaF molecule and its positive ion by the coupled pair approximation and the configuration interaction method. In 1999, Barschlicher[14] studied the contribution of the scalar relativistic correction to the gallium halide bond energies. Yang *et al.*[15,16] calculated the spectroscopic constants of the ground state and the low-lying excited states of GaX (X = F, Cl, Br, and I) molecules using the density functional theory (DFT). In 2005, Singh[17] collected the available spectroscopic information on four gallium monohalides. In 2006, the high resolution Fourier transform spectrum of ^{69}GaCl was studied by Saksena *et al.*[18]

Some studies about diatomic molecules have been carried out through high-level *ab initio* calculations.[19–23] But as far as we know, there has been no report on the APEF for gallium monohalide diatomic molecules based on PECs with high-level *ab initio* calculations. The effect of the electronic shell of halogen elements on the spectroscopic properties of the GaX molecules has not been reported. Therefore, we first construct PECs containing dense energy points using high-level *ab initio* calculations. Then we fit APEFs from the PECs to conveniently perform further analysis or dynamical calculations. The spectroscopic parameters are determined by using the obtained APEF. The effect of the electronic shell of halogen elements is also investigated.

2. Computational method and basis sets

2.1. Technical details for PECs

In the calculations, highly accurate valence internally contracted multireference configuration interaction method (MRCI)[24,25] is used to calculate the PECs for the $^3\Pi$ electronic states of GaX (X = F, Cl, Br) complexes. MRCI is a way to systematically include those configuration state functions (CSFs) that contribute most significantly to the correlation en-

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ergy, and it is accurate in treating small systems, especially dimers. In the process of our calculation, these MRCI calculations are preceded by complete active space self-consistent field (CASSCF) calculations in which all valence molecular orbitals are optimized. The aug-cc-pV5Z basis sets are used. It means that (27s, 18p, 14d, 4f, 3g, 2h) primitive Gaussian functions are contracted to [9s, 8p, 6d, 4f, 3g, 2h] for Ga atom. As for F, Cl, Br atoms, the basis sets give (15s, 9p, 5d, 4f, 3g, 2h) → [7s, 6p, 5d, 4f, 3g, 2h] for F, (21s, 13p, 5d, 4f, 3g, 2h) → [8s, 7p, 5d, 4f, 3g, 2h] for Cl, and (27s, 18p, 14d, 4f, 3g, 2h) → [9s, 8p, 6d, 4f, 3g, 2h] for Br, respectively. The energies of PECs are calculated in the range of internuclear distances from 1.2 Å to 12.25 Å in steps of 0.05 Å. In order to obtain more accurate PECs, we take the effects of Davidson correction into account. All calculations are performed with the MOLPRO program package.[26]

2.2. Analytical potential energy function and spectroscopic parameters

The PECs are then fitted into APEFs in the form of Murrell–Sorbie (MS) potential energy function. The MS potential energy function can accurately reproduce interaction potential energies of many neutral and cationic diatomic molecules, and the general expression is

$$V(\rho) = -D_e\left(1+\sum_{i=1}^{n} a_i\rho^i\right)\exp(-a_1\rho), \tag{1}$$

where $\rho = R - R_e$, with R and R_e being the internuclear distance and equilibrium bond length respectively; D_e is the dissociation energy; α_i and D_e are the parameters that can be determined by fitting. After trying a series of fittings, we find that for the gallium monohalide diatomic molecules, reasonable APEFs of the $^3\Pi$ electronic states can be obtained when n equals 9.

As done in our previous work, D_e and R_e are equally treated as fitting parameters in order to obtain more accurate fitting results. We calculate their root-mean-square (RMS) error by judging the quality of the fitting results. The RMS can be represented as

$$\mathrm{RMS} = \frac{1}{N}\sqrt{\sum_{i=1}^{N}(V_{\mathrm{APEF}} - V_{ab\ initio})^2}, \tag{2}$$

where V_{APEF} and $V_{ab\,initio}$ are energies given by the fitting and *ab initio* calculations, respectively, and N is the number of points. RMS values are in cm^{-1}.

Based on the relationship equations among spectroscopic parameters and APEF, the spectroscopic parameters can be calculated. Furthermore, the precision and credibility of the APEF can be testified by comparing the calculated spectroscopic parameters with experimental counterparts directly. First of all, the force constants can be determined from the parameters of MS potential energy function as

$$\begin{aligned} f_2 &= D_e(a_1^2 - 2a_2),\\ f_3 &= 6D_e\left(a_1a_2 - a_3 - \frac{a_1^3}{3}\right),\\ f_4 &= D_e(3a_1^4 - 12a_1^2a_2 + 24a_1a_3 - 24a_4), \end{aligned} \tag{3}$$

where f_2, f_3, and f_4 are quadratic, cubic, and quartic force constants, respectively. Then the spectroscopic parameters are

$$B_e = \frac{h}{8\pi c\mu R_e^2}, \tag{4}$$

$$\omega_e = \sqrt{\frac{f_2}{4\pi^2\mu c^2}}, \tag{5}$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e}\left(1+\frac{f_3R_e}{3f_2}\right), \tag{6}$$

$$\omega_e\chi_e = \frac{B_e}{8}\left[-\frac{f_4R_e^2}{f_2} + 15\left(1+\frac{\omega_e\alpha_e}{6B_e^2}\right)^2\right]. \tag{7}$$

In the above equations, B_e is the rigid-rotational factor, α_e is the nonrigid-rotational factor, ω_e is the harmonic vibrational frequency, and $\omega_e\chi_e$ is the inharmonic vibrational factor.

3. Results and discussion

3.1. PECs for Ga*X* molecules

In order to display their characteristics clearly, all of the PECs of the $^3\Pi$ electronic states for Ga*X* molecule, obtained at MRCI /aug-cc-pV5Z, are shown in Fig. 1 with setting all dissociation limits of the PECs to be zero. It means that the energies of the lowest points on the PECs are the dissociation energies. From Fig. 1, one can find that from F to Br, the minimum positions of the PECs become larger and larger, while the dissociation energies become smaller and smaller. It means that the bonds become weaker with the increase of the electronic shells of the halide atoms.

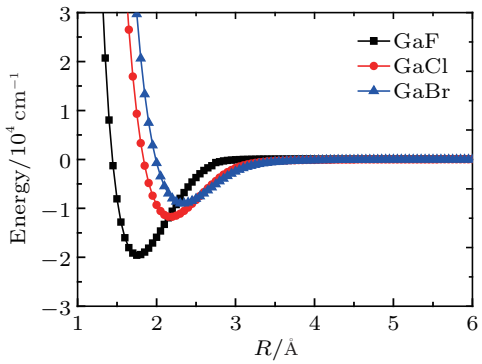


Fig. 1. (color online) PECs of the $^3\Pi$ electronic states of Ga*X*.

3.2. APEFs of the states

Based on the PECs, the APEFs are deduced using the MS function and nonlinear least square fitting method. The ob-

tained parameters are listed in Table 1. RMSs are also presented in order to evaluate the quality of the fitting process quantificationally. As can be seen in the table, all of the errors are tolerable. The largest RMS is 42.9 cm^{-1}, which is much smaller than the chemical accuracy (1.0 kcal/mol or 349.755 cm^{-1}). This indicates that the fitting processes and the deduced APEFs are creditable to be used for some further studies, for instance, to optimize stabilities of clusters, to induce polyatomic APEFs or to perform collisional calculations. Also, it confirms that MS function is very suitable for reproducing the PECs of GaX molecules.

Table 1. Parameters of MS potential energy function for the $^3\Pi$ electronic states of GaX.

	GaF	GaCl	GaBr
D_e/cm^{-1}	19585.13969	11805.01175	8968.45657
R_e/Å	1.76668	2.18247	2.32878
a_1/Å	2.95807	2.07014	2.28757
a_2/Å	–0.53225	–2.7914	–2.37198
a_3/Å	–1.88183	–1.3997	–1.23509
a_4/Å	–4.04512	1.08979	0.6254
a_5/Å	1.97755	2.30113	1.06335
a_6/Å	3.71997	–2.43899	–0.31704
a_7/Å	–3.16928	0.91071	–0.25041
a_8/Å	0.85454	–0.15069	0.11845
a_9/Å	–0.07676	0.00929	–0.01329
RMS/cm^{-1}	38.4	31.1	42.9

3.3. Spectroscopic properties

Using the fitted APEFs and Eqs. (4)–(7), we calculate the spectroscopic parameters of the states. The calculated spectroscopic parameters of the ground state of GaX molecules, and previous experimental and theoretical data, are listed in Table 2. As can be seen from the table, our present calculated values of the spectroscopic parameter R_es of GaX are close to the experimental values[2,27,30] and the theoretical values.[11,12,16,31] It is found that the electronic shells of X become bigger and the R_es of GaX turn bigger. The present D_es 2.43 eV, 1.46 eV, and 1.11 eV are close to the previous calculated values 2.09 eV, 1.40 eV, and 1.24 eV for GaF, GaCl, and GaBr,[16] respectively. However, the present D_e of 1.1 eV for GaBr is obviously larger than 0.851 eV given by Yang *et al.*[31] using MRCI with a smaller aug-cc- pVQZ basis sets. It shows that the basis sets play a significant role in the dissociation energy. Unfortunately, no experimental values of D_e have been found to date. We hope that the present calculated results can be used as a reference for further study. The data of D_e show that with the increase of X atomic mass, the D_e becomes smaller and smaller. From the fact that the R_es of GaX become longer and the D_es of GaX turn smaller, we can conclude that the increase of the electronic shells of GaX leads to the decrease of the energy stability of the molecules.

Table 2 also shows that the present values of ω_e are in agreement with the experimental data[10,17,30] and are better than theoretical data in the literature.[11,16] For GaBr, the present values of ω_e are larger than experimental values, but the results given by Yang *et al.*[31] at MRCI/aug-cc-pVQZ are closer to the experimental values. It implies the present high-level *ab initio* calculations are necessary to improve the computational values of ω_e, however, the aug-cc-pV5Z may overestimate the interaction between the atoms. For GaF, the experiment displays the spin–orbit split states $A^3\Pi_+$ and $B^3\Pi_1$. The present result with no spin–orbit coupling effect should be compared with the average value. Our ω_e of 658.825 cm^{-1} is very close to the average experimental value of $A^3\Pi_+$ and $B^3\Pi_1$[17] and is a little better than that given by Yang *et al.*[16] For GaCl and GaBr, our value of ω_e is 3% larger than the average experimental values of $A^3\Pi_+$ and $B^3\Pi_1$.[10,30] Carefully examining the table, one can find that the present B_es and α_es of the three molecules are in excellent agreement with experimental data.[2,17,28,29] These facts imply that the present PECs and APEFs are accurate and can safely be used for wider investigations.

Table 2. Spectroscopic parameters for the $^3\Pi$ electronic states of GaX.

			GaF	GaCl	GaBr
R_e/Å	present		1.7667	2.1824	2.3288
	expt.	$A^3\Pi_+$	1.7476 [a]	2.146 [b]	2.295 [h]
		$B^3\Pi_1$	1.7458 [a]	2.152 [b]	2.296 [h]
	theor.		1.7426 [i]	2.164 [e]	2.347 [d]
					2.2972 [j]
D_e/eV	present		2.4282	1.4636	1.1119
	theor.		2.09 [i]	1.40 [i]	1.24 [i]
					0.851 [j]
ω_e/cm^{-1}	present		658.825	408.814	284.651
	expt.	$A^3\Pi_+$	663.0 [k]	395.130 [c]	274.310 [h]
		$B^3\Pi_1$	662.1 [k]	394.710 [c]	274.980 [h]
	theor.		657.18 [i]	370 [e]	272.1 [j]
$\omega_e x_e$/cm^{-1}	present		2.50427	2.03775	1.44225
	expt.	$A^3\Pi_+$	2.18 [b]	2.278 [c]	1.560 [f]
		$B^3\Pi_1$	1.45 [b]	2.286 [c]	1.600 [f]
				2.3 [b]	
B_e/cm^{-1}	present		.361736	0.150598	0.0834882
	expt.	$A^3\Pi_+$	0.3705 [a]	0.158485 [g]	0.085830 [f]
		$B^3\Pi_1$	0.3715 [a]	0.158640 [g]	0.085710 [f]
α_e/cm^{-1}	present		0.002378	0.0007472	0.0004142
	expt.	$A^3\Pi_+$	0.0030 [k]	0.001917 [g]	0.000660409 [f]
		$B^3\Pi_1$	0.0030 [k]	0.00103528 [g]	0.000720144 [f]

[a] Ref. [2], [b] Ref. [27], [c] Ref. [10], [d] Ref. [12], [e] Ref. [11], [f] Ref. [28], [g] Ref. [29], [h] Ref. [30], [i] Ref. [16], [j] Ref. [31], [k] Ref. [17].

4. Conclusions

The APEFs of the $^3\Pi$ state of GaX (X = F, Cl, and Br) molecules are obtained based on the PECs at MRCI/aug-cc-pV5Z. It is found that the spectroscopic parameters determined with the APEFs are in agreement with experimental and theoretical results available in the literature. It is confirmed that the present APEFs accurately reproduce the interaction between the Ga and X (X = F, Cl, Br) atoms and can be used

for more investigations. It is also found that the energy stability of the GaX molecule decreases with the electronic shells of X atoms increasing.

References

[1] Grabandt O, Lange C A and Mooyman R 1989 *Chem. Phys. Lett.* **160** 359

[2] Barrow R F, Dodsworth P G and Zeeman P B 1957 *Proc. Phys. Soc. Lond. Sect. A* **70** 34

[3] Hoeft J and Nair K P R 1986 *Z. Phys. D: At. Mol. Clusters* **4** 189

[4] Hoeft J and Nair K P R 1993 *Chem. Phys. Lett.* **215** 371

[5] Mahieu E, Dubois I and Bredohl H 1991 *J. Mol. Spectrosc.* **150** 477

[6] Uehara H, Horiai K and Nakagawa K 1991 *Chem. Phys. Lett.* **178** 553

[7] Dearden D V, Johnson R D and Hudgens J W 1992 *J. Chem. Phys.* **97** 8880

[8] Venkatasubramanian R, Saksena M D and Singh M 1993 *Chem. Phys. Lett.* **210** 367

[9] Sunanda K, Saksena M D and Lakshminarayana G 1994 *J. Mol. Spectrosc.* **168** 158

[10] Saksena M D, Venkatasubramanian R and Singh M 1997 *Can. J. Phys.* **75** 191

[11] Kim G and Balasubramanian K 1992 *Chem. Phys. Lett.* **193** 109

[12] Kim G and Balasubramanian K 1992 *J. Mol. Spectrosc.* **152** 192

[13] Mochizuki Y and Tanaka K 1998 *Theor. Chem. Acc.* **101** 257

[14] Barschlicher C W 1999 *Theor. Chem. Acc.* **101** 421

[15] Yang X Z, Lin M R, Zou W X and Zhang B Z 2002 *Chem. Phys. Lett.* **362** 190

[16] Yang X Z, Lin M R, Zou W X and Zhang B Z 2004 *J. Mol. Struct. THEOCHEM* **668** 209

[17] Singh V B 2005 *J. Phys. Chem. Ref. Data* **34** 23

[18] Saksena M D, Deob M N, Sunandaa K and Khana H A 2006 *J. Mol. Spectrosc.* **235** 166

[19] Gao F, Yang C L, Hu Z Y and Wang M S 2007 *Chin. Phys.* **16** 3668

[20] Bai F J, Yang C L, Qian Q and Zhang L 2009 *Chin. Phys. B* **18** 549

[21] Wang J M and Sun J F 2011 *Acta Phys. Sin.* **60** 123103 (in Chinese)

[22] Wang J M, Sun J F and Shi D H 2010 *Chin. Phys. B* **19** 113601

[23] Tong X F, Yang C L, Xiao J, Wang M S and Ma X G 2010 *Chin. Phys. B* **19** 123102

[24] Werner H J and Knowles P J 1988 *J. Chem. Phys.* **89** 5803

[25] Knowles P J and Werner H J 1988 *Chem. Phys. Lett.* **145** 514

[26] MOLPRO, version 2010.1, a package of *ab initio* programs by Werner H J, Knowles P J, Lindh R, Manby F R, Schütz M, Celani P, Korona T, Lindh R, Mitrushenkov A, Rauhut G, Shamasundar K R, Adler T B, Amos R D, Bernhardsson A, Berning A, Cooper D L, Deegan M J O, Dobbyn A J, Eckert F, Goll E, Hampel C, Hesselmann A, Hetzer G, Hrenar T, Jansen G, Köppl C, Liu Y, Lloyd A W, Mata R A, May A J, McNicholas S J, Meyer W, Mura M E, Nicklaß A, O'Neill D P, Palmieri P, Peng D, Pflüger K, Pitzer R, Reiher M, Shiozaki T, Stoll H, Stone A J, Tarroni R, Thorsteinsson T and Wang M, see http://www.molpro.net

[27] Huber K P and Herzberg G 1979 *Spectroscopic Constants of Diatomic Molecules* Vol. 4 (New York: Van Nostrand Reinhold) p. 716

[28] Savithry T, Rao D V K, Murty A A N and Rao P T 1974 *Physica* **75** 386

[29] Venkatasubramanian R, Saksena M D and Singh M 1994 *J. Mol. Spectrosc.* **168** 290

[30] Borkowska-Burnecka J and Zyrnicki W 1994 *Bull. Pol. Acad. Sci.* **42** 63

[31] Yang X Z, Lin M R, Zou W X and Zhang B Z 2004 *J. Phys. Chem. A* **108** 4341