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Laser cooling of BH and GaF: insights from an *ab initio* study

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The feasibility of laser cooling BH and GaF is investigated using *ab initio* quantum chemistry. The ground state $X^1\Sigma^+$ and first two excited states $^3\Pi$ and $^1\Pi$ of BH and GaF are calculated using the multireference configuration interaction (MRCI) level of theory. For GaF, the spin-orbit coupling effect is also taken into account in the electronic structure calculations at the MRCI level. Calculated spectroscopic constants for BH and GaF show good agreement with available theoretical and experimental results. The highly diagonal Franck-Condon factors (BH: $f_{00} = 0.9992$, $f_{11} = 0.9908$, $f_{22} = 0.9235$; GaF: $f_{00} = 0.997$, $f_{11} = 0.989$, $f_{22} = 0.958$) for the $^1\Pi$ ($v' = 0-2$) \rightarrow $X^1\Sigma^+$ ($v = 0-2$) transitions in BH and GaF are determined, which are found to be in good agreement with the theoretical and experimental data. Radiative lifetime calculations of the $^1\Pi$ ($v' = 0-2$) state (BH: 131, 151, and 187 ns; GaF: 2.26, 2.36, and 2.48 ns) are found to be short enough for rapid laser cooling. The proposed laser cooling schemes that drive the $^1\Pi$ ($v' = 0$) \rightarrow $X^1\Sigma^+$ ($v = 0$) transition use just one laser wavelength λ_{00} (BH: 436 nm, GaF: 209 nm). Though the cooling wavelength of GaF is deep in the UVC, a frequency quadrupled Ti:sapphire laser (189–235 nm) could be capable of generating useful quantities of light at this wavelength. The present results indicate that BH and GaF are two good choices of molecules for laser cooling.

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1. Introduction

In recent years, the interest in laser cooling and magneto-optical trapping (MOT) of diatomic molecules has grown with the evolution of the experimental techniques.^{1–7} Compared with atoms, molecules possess rotational and vibrational degrees of freedom resulting in decays to unwanted sublevels, thus finding a quasi-closed-level system with a very high Franck-Condon factor (FCF) is a challenge. However, most recent experimental demonstrations^{2,4–6} have shown that certain molecules can be amenable to traditional laser cooling because their highly-diagonal FCFs suppress decays to excited vibrational states. The theoretical and experimental studies of cold and ultra-cold molecules are motivated by a variety of prospective applications.⁸ So far, laser cooling of diatomic molecules SrF,^{2,6} YO⁴ and CaF⁵ have been experimentally demonstrated. Since there are more than 90 elements in the periodic table, in principle, it is possible to form more than 4000 different diatomic molecules. Therefore, we have reason to believe that there could be others that exist which are appropriate for molecular laser cooling. As early as 2004, Di Rosa presented a brief survey⁹ of

candidate molecules for laser cooling and identified a number of hydrides and aluminum compounds (BeH, MgH, CaH, SrH, BaH, NH, BH, AlH, AlF and AlCl). As with atomic systems, molecules must meet certain criteria to be potential laser cooling candidates. The first criterion, highly-diagonal FCFs, describes the overlap of the vibrational wave functions for different electronic states. From a practical standpoint, highly-diagonal FCFs limit the number of lasers required to keep the molecule in a quasi-closed-loop cooling cycle. The second, a shorter lifetime (*i.e.* high spontaneous-emission rates) is highly desirable for rapid laser cooling. The third criterion, is that there is no intervening electronic states to which the upper state could radiate and terminate the cycling transition.

Very recently, polar molecules (such as RaF,¹⁰ AlH,¹¹ AlF,¹¹ TlF¹² and BeF¹³) have been theoretically investigated for the laser cooling of molecules. The theoretical calculations¹⁰ indicate that the RaF molecule appears very well suited for laser cooling. The RaF molecule possesses (i) highly diagonal FCFs between the electronic ground state and the energetically lowest electronically excited state and (ii) the properties that (a) the corresponding electronic transition frequency is in the visible region with a reasonable lifetime and (b) isotopes with nuclear-spin quantum number $I = 1/2$ are available. The FCFs of AlF¹¹ are equal to 0.99992, and the excited state lifetime is extremely short at 1.8 ns. Unfortunately, the laser excitation wavelength is 227 nm for AlF and there is a low-lying triplet state a $^3\Pi$. Hunter *et al.*¹² measured the B-state lifetime (99(9) ns) and two ratios of

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vibrational branching fractions $f_{\nu'\nu}$ on the $B^3\Pi_1(\nu')-X^1\Sigma^+(\nu)$ transition of TlF ($f_{01}/f_{00} < 2 \times 10^{-4}$ and $f_{02}/f_{00} = 1.10(6)\%$). Laser cooling of TlF has been proposed for high-precision searches for the Schiff moment and the proton electric dipole moment. The calculated FCF of BeF¹³ is 0.897, and the laser excitation wavelength is ~ 300 nm, which is not currently accessible by diode laser.

Although SrF^{2,6} has a $X^2\Sigma \rightarrow A^2\Pi$ quasi-cycling transition, there are benefits to choosing a molecule with a $^1\Sigma \rightarrow ^1\Pi$ quasi-cycling transition instead.¹⁴ BH and GaF both possess highly diagonal FCFs, display the desirable $^1\Sigma \rightarrow ^1\Pi$ cycling transition, have extremely short excited state lifetimes, have no spin-rotational structure, and display small or unresolved hyperfine structures due to their closed electron shells. In addition, the smaller masses of BH and GaF *versus* SrF are also somewhat advantageous. It is worth noting that our previous theoretical calculations show that BF ($f_{00} = 0.798$) and GaH ($f_{00} = 0.732$) molecules don't have as highly diagonal FCFs as that of our current calculations on BH ($f_{00} = 0.9992$) and GaF ($f_{00} = 0.997$). We, therefore, now would like to focus on the feasibility of laser cooling BH and GaF using *ab initio* quantum chemistry and briefly design a scheme for a viable laser cooling cycle for BH and GaF.

A number of theoretical calculations^{15–23} have been performed on the BH molecule with *ab initio* quantum mechanical methods based on Born–Oppenheimer (BO) and non-BO approaches. The BH molecule has been the object of many *ab initio* calculations, mainly focusing on the X-state and low lying excited states, because the BH molecule is one of the smaller and simpler diatomic molecules. The $X^1\Sigma^+$, $A^1\Pi$, and $B^1\Sigma^+$ potential energy curves (PECs) and spectroscopy of BH has been studied by Luh *et al.*¹⁵ The radiative lifetimes ($\tau(\nu' = 0) = 121$ ns, $\tau(\nu' = 1) = 129$ ns, and $\tau(\nu' = 2) = 137$ ns) of the $A^1\Pi$ state of BH were calculated by Dierksen *et al.*¹⁶ In 1994, the spin-forbidden dipole-allowed radiative decay process BH ($a^3\Pi$) \rightarrow BH ($X^1\Sigma^+$) was studied by Pederson *et al.*¹⁷ A value for the ground state ($X^1\Sigma^+$) dissociation energy (D_0) of 81.5 kcal mol^{−1} was given by Curtiss and Pople¹⁸ through singles and doubles quadratic configuration interaction with a quasi-perturbative treatment of connected triple substitutions [QCISD(T)] calculations correlating all six electrons of BH. Martin *et al.*¹⁹ give a predicted value for D_0 of 82.4 ± 0.12 kcal mol^{−1}. A more accurate D_0 (81.5 – 81.7 kcal mol^{−1}) value has been obtained by Feller *et al.*²⁰ at the singles and doubles coupled-cluster method including perturbative connected triple excitations [CCSD (T)]-complete basis set (CBS) limit level. The most accurate dissociation energy seems to be that of Miliordos and Mavridis²¹ who obtained $D_0 = 81.43$ kcal mol^{−1} with multi-reference configuration interaction (MRCI) calculations including scalar relativistic effects and the basis set superposition error (BSSE) correction. This value (81.43 kcal mol^{−1}) is in excellent agreement with the best experimental estimate of 81.6 ± 0.6 kcal mol^{−1} (or $28\,535 \pm 210$ cm^{−1}) suggested by Bauschlicher Jr. *et al.*²² The most recent non-BO calculation of the BH molecule by Bubin *et al.*²³ is currently the reliable theoretical study and reports the D_0 as 81.20 ± 0.43 kcal mol^{−1} (or $28\,400 \pm 150$ cm^{−1}).

Some experimental investigations for the $A^1\Pi-X^1\Sigma^+$ transition of BH have been reported based on vibrational and rotational

electronic spectroscopy. The spectrum of BH was examined in the near ultraviolet both in absorption and also in emission by Johns *et al.*²⁴ The Fourier transform spectroscopy of the $A^1\Pi-X^1\Sigma^+$ transitions of BH and BD were recorded in emission near 4330 Å by Fernando *et al.*²⁵ Improved line positions and molecular constants were also determined from the analysis of the data for BH. In 1989, the radiative lifetimes²⁶ of the $\nu' = 0$, 1 and 2 levels of the $A^1\Pi$ state of BH were measured to be 127 ± 10 , 146 ± 12 , and 172 ± 14 ns, respectively. In 2001, the $A^1\Pi-X^1\Sigma^+$ (2, 0) transition in ¹¹BH and ¹⁰BH was observed by (1 + 2)-photon resonance-enhanced multiphoton ionization spectroscopy by Clark *et al.*²⁷ Very recently, the branching ratios for the decay of the $A^1\Pi(\nu' = 0)$ state to vibrational levels of the ground $X^1\Sigma^+$ state were measured by Hendricks *et al.*²⁸ They also verified that the branching ratio for the spin-forbidden transition to the intermediate $a^3\Pi$ state is inconsequential small. Their results show that the BH molecule is exceedingly favorable for laser cooling.

The first report of the electronic spectrum in GaF was by Welti and Barrow,^{29–31} who identified the ultra-violet emission spectra of the transitions A–X, B–X and C–X of ⁶⁹GaF. Then, Barrow³² and Murad *et al.*³³ measured the dissociation energy ($D_0 = 143.9$ kcal mol^{−1} and 138 ± 3.5 kcal mol^{−1}) of the $^1\Pi$ state for GaF. Hoeft *et al.*³⁴ later measured the microwave spectra of the isotopic species ⁶⁹GaF and ⁷¹GaF. In 1974, the Zeeman effect for the low rotational transitions of GaF was reported by Honerjäger *et al.*³⁵ Ten years later, Griffith *et al.*³⁶ analyzed the rotational structure of the C $^1\Pi-X^1\Sigma^+$ band system of GaF. In 1990, Grabandt *et al.*³⁷ measured the ionization energy of GaF using He(I) photoelectron spectroscopy. In 1991, the infrared emission spectrum of $\Delta\nu = 1$ bands of GaF was observed at 1000 °C with a resolution of 0.1 cm^{−1} by Uehara *et al.*³⁸ In 1993, the millimeter wave rotational spectrum of GaF was studied in the 250–300 GHz frequency region by Hoeft *et al.*³⁹ In 1995, new measurements of vibration-rotational absorption spectra of ⁶⁹Ga¹⁹F and ⁷¹Ga¹⁹F were reported by Ogilvie *et al.*⁴⁰

From a theoretical point of view, numerous theoretical calculations^{41–47} have been performed on the electronic structure of the GaF molecule. In 1990, the Hartree–Fock–Slater type density-functional theory (DFT) calculations with a pseudo-potential technique were carried out for GaF by Grabandt *et al.*³⁷ In 1995, a comparison of the finite basis set with the finite difference Hartree–Fock (HF) calculations were performed on GaF by Kobus *et al.*⁴¹ In 1999, the contribution from correlations of the semi-core 3d electrons in Ga was studied by Mochizuki *et al.*⁴² In the same year, the scalar relativistic contribution to the atomization energies of GaF_{*n*} were studied by Bauschlicher.⁴³ In 2000, dipole, quadrupole, octupole, and hexadecapole moments were calculated for the ground states of sixteen diatomic species (including GaF) by Kobus *et al.*⁴⁴ In 2002, the ground and the first excited states of gallium monohalides (GaX, X = F, Cl, Br, I) were calculated using DFT with different local density approximation (LDA) and general gradient approximations (GGA) by Yang *et al.*⁴⁵ In 2004, the ground and valence excited states of GaF were studied by using the MRCI method with all-electronic basis sets and Douglas–Kroll scalar relativistic correction by Yang *et al.*⁴⁶ In 2013, the ground

electronic states of GaX (X = F, Cl, and Br) molecules were computed by Cao *et al.*⁴⁷

As mentioned above, BH and GaF have been extensively studied in the past. In the present work, we focus on the theoretical studies of the laser cooling of BH and GaF molecules, though neither has yet been cooled. The electronic structure and radiative properties associated with the laser cooling of BH and GaF are calculated, including radiative lifetimes, FCFs and diode laser excitation wavelengths of the $^1\Pi-X^1\Sigma^+$ electronic transitions of the BH and GaF molecules. Also, we briefly design a scheme for a viable laser cooling cycle for BH and GaF. It is worth noting, our study is concerned with the vibrational cooling, so the rotational degrees of freedom can be neglected in the first approximation. The main transition of laser cooling is the $^1\Pi(\nu' = 0, J' = 1) \leftarrow X^1\Sigma^+(\nu = 0, J = 1)$ electric dipole transition, labeled Q(1). Due to the selection rules for the change in parity and angular momentum in an electric dipole transition, the excited state decays exclusively on the Q(1) branch, always returning the molecule to $X^1\Sigma^+(\nu = 0, J = 1)$.

The paper is organized as follows. In Section II, we detail our *ab initio* method and the basis sets used in the present calculations for the included electronic states of BH and GaF molecules. A discussion of the results is presented in Section III, and the laser cooling schemes for BH and GaF molecules are outlined. Finally, a brief conclusion is given in Section IV.

2. Computational details

For all the calculations in this study, the MOLPRO⁴⁸ program was used. Due to the limitation of symmetry of the MOLPRO program package, C_{2v} point-group symmetry has been considered for BH and GaF molecules although they belong to a higher symmetry group. The complete active space self-consistent field (CASSCF)^{49,50} and MRCI plus Davidson correction (MRCI + Q)^{51–53} methods were performed for the calculations of adiabatic PECs of the BH and GaF. For GaF, the scalar relativistic effect was accounted for using the Douglas–Kroll–Hess (DKH)^{54,55} transformation of the relativistic Hamiltonian.

To minimize the errors caused by basis set truncation, rather large augmented consistent polarized core-valence correlation basis set aug-cc-pCV5Z (=ACV5Z)⁵⁶ and correlation consistent polarized valence quintuple zeta aug-cc-pV5Z (=AV5Z)⁵⁶ are chosen for B and H, respectively. The CASSCF calculations of BH are constructed by allotting the six active electrons (core + valence) to 10 orbitals: one 1s, one 2s, three 2p, one 3s, three 3p on B, plus one 1s on H, and the active space is referred to as CAS (6, 10). In the CASSCF and subsequent MRCI calculations, the reference configurations were all generated from $[1\sigma^{0-2}, 2\sigma^{0-2}, 3\sigma^{0-2}, 1\pi^{0-4}, 4\sigma^{0-2}, 5\sigma^{0-2}, 2\pi^{0-4}, 6\sigma^{0-2}]$. The ground $X^1\Sigma^+$ state of BH is characterized mainly by the closed-shell electronic configuration $1\sigma^2 2\sigma^2 3\sigma^2$. The leading electronic configuration of the excited state $A^1\Pi$ is described by $1\sigma^2 2\sigma^2 3\sigma^\alpha 1\pi^\beta$ (where α and β represent spin up and spin down, respectively). That excitation involves the shifting of an electron from one non-bonding molecular orbital (MO) to another. The AVQZ⁵⁷ and AV5Z⁵⁸ all-electron basis sets are used for the Ga and F atoms in

the calculations of the Λ -S states, respectively. In the CASSCF and MRCI calculations, nine MOs ($9\sigma^2 10\sigma^2 4\pi^4 11\sigma^2 5\pi^0 12\sigma^0 13\sigma^0$) are selected as the active space, including five a_1 , two b_1 and two b_2 symmetry MOs, which correspond to the Ga 4s4p5s and F 2s2p shells. The ten active (valence) electrons are put into the active space. In this case, the active space is referred to as CAS (10, 9). The ten electrons in the 3d shell of the Ga atom are put into the closed spaces, but they are still optimized ($7\sigma^2 8\sigma^2 3\pi^4$). The rest of the inner electrons are kept frozen in the core orbitals. The ground state ($X^1\Sigma^+$) of GaF is dominated by a closed shell configuration ($\dots 9\sigma^2 10\sigma^2 4\pi^4 11\sigma^2$), and the leading configuration describing the excited state ($C^1\Pi$) of GaF is $9\sigma^2 10\sigma^2 4\pi^4 11\sigma^1 5\pi^1$, where 5π is weakly antibonding localized mostly on the p orbitals of Ga. That is, for the excited state $C^1\Pi$, an electron is excited from a non-bonding σ type MO to a weakly antibonding π type MO. There is a negligible change in the bond lengths between ground state $X^1\Sigma^+$ (1.774 Å) and excited state $C^1\Pi$ (1.778 Å).

For the heavier Ga atom, spin–orbit coupling (SOC) becomes important for the valence electronic structure. Thus, SOC effects are also taken into account for the GaF molecule with the SOC operator H_{SO} defined within the Breit–Pauli approximation.⁵⁹ The active space is the same as those used above ($5a_1, 2b_1, 2b_2, 0a_2$). The smaller basis sets AVTZ⁵⁷ and AVQZ⁵⁸ are used for Ga and F atoms in the SOC calculations.

Ro-vibrational energies and wavefunctions of the bound states of these PECs were determined by solving the nuclear Schrödinger equation using the LEVEL8.0 program.⁶⁰ With the PECs and transition dipole moments (TDMs) of different electronic states, the FCFs and radiative lifetimes of the various vibrational levels can be obtained from LEVEL8.0.

3. Results and discussion

3.1 BH molecule

Fig. 1 shows the PECs of these bound states ($X^1\Sigma^+$, $a^3\Pi$ and $A^1\Pi$) acquired at the MRCI level. In Table 1 we report the three bound states' spectroscopic constants of BH using the ACV5Z

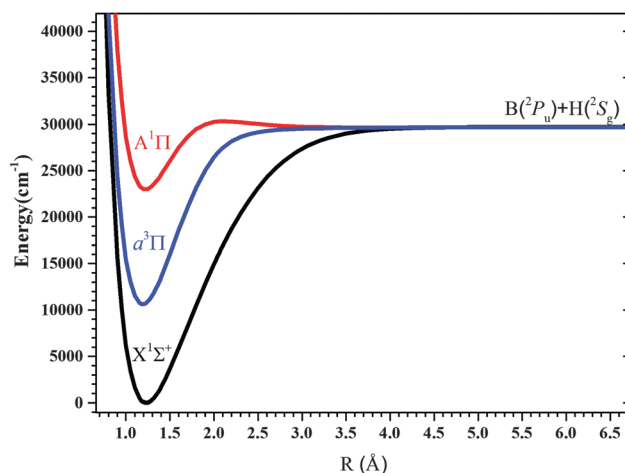


Fig. 1 Potential energy curves of the first three electronic states of the BH molecule at the MRCI level of theory.

Table 1 Spectroscopic constants for the first three states of BH and GaF molecules at the MRCI level of correlation

Molecule	States	T_e (cm ⁻¹)	R_e (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	B_e (cm ⁻¹)	D_e (eV)	Ref.
BH	X ¹ Σ ⁺	0	1.2290	2352.0	44.0	12.086	3.6863	This work
		0	1.2349	2349	50			17
		0	1.230	2359	48.8		3.6773	21
		0	1.23218	2366.7	49.39	12.021	3.5775	Exp. ^a
	a ³ Π	10 645.0	1.1900	2961.0	109.6	12.904	2.3806	This work
		10 643	1.1939	2612	63			17
		10 583	1.190	2625	60.4		2.3677	21
			1.2006 ^b	2625.1	55.8	12.667 ^c		Exp. ^d
	A ¹ Π	22 997.9	1.2210	2404.6	147.3	12.2795	0.9098	This work
		23 401	1.2266	2314	138			17
		23 144	1.222	2341	129.6		0.8109	21
		23 105.1 ^e	1.2186	2250.9	127.8 ^e	12.295		Exp. ^b
GaF	X ¹ Σ ⁺	0	1.7730	635.52	2.77	0.3601	6.1941	This work
		0	1.7830	614.01				45
		0	1.7741	631.8	2.87		6.20	46
		0	1.7744	622.2	3.2	0.3595	6.02	Exp. ^b
	³ Π	32 945.5	1.7450	676.59	3.82	0.3719	2.1216	This work
		33 767.6	1.7634	626.13				45
		33 706.4	1.7440	672.0	2.74		2.02	46
		33 105.5	1.7467	663.0	2.18	0.3719	2.07	Exp. ^b
	C ¹ Π	47 829.6	1.7680	619.45	21.95	0.3624	0.4233	This work
		48 446.6	1.7695	545.6	14.01		0.28	46
		47 365.7	1.778	542.3	9.55	0.358		Exp. ^b

^a Ref. 61. ^b Ref. 62. ^c Ref. 63. ^d Ref. 64. ^e Ref. 27.

(B) and AV5Z (H) basis sets at the MRCI level. Previous theoretical^{17,21} and experimental data^{27,61–64} of BH are also listed together for comparison. Because our main interest is in the first three electronic states that are relevant for laser cooling, we have restricted our calculations to the three states (X ¹Σ⁺, a ³Π and A ¹Π) only.

Overall, the agreement between the calculations and the correspondence with the experimental and other theoretical results, are reasonably good. Pederson *et al.*¹⁷ provided a slightly larger equilibrium distance R_e for the X ¹Σ⁺ (2.3337 a₀) and A ¹Π (2.3179 a₀) states compared to the experimental data.^{61,62} The calculated dissociation energy for X ¹Σ⁺ of $D_e = 3.6863$ eV is slightly larger than the observed value of 3.5775 eV. Recently, Miliordos *et al.*²¹ also obtained a larger calculated value of $D_e = 3.6773$ eV. The present calculation yields a T_e value for a ³Π of

10 645.0 cm⁻¹, which is in good agreement with the theoretical value (10 643 cm⁻¹).¹⁷ Our calculations yield a shorter equilibrium distance (1.1900 Å) for a ³Π compared to the observed value (1.2006 Å).⁶² The depth of the well is 2.3806 eV for the a ³Π state of BH, and the result is in reasonable agreement with the recent theoretical value (2.3677 eV).²¹ The computational results presented here are in good agreement with the recent results of Miliordos *et al.*²¹ Larger reference spaces (18 orbitals: one 2s, three 2p, one 3s, three 3p, five 3d, one 4s, and three 4p on B, plus one 1s on H) were used in their MRCI calculations for BH. Comparing our results with experimental values,^{61–64} shows ω_e and B_e to be accurate to better than 6.8% and 0.54% for the X ¹Σ⁺ and A ¹Π states of BH.

The FCFs of the A ¹Π → X ¹Σ⁺ transition were evaluated by the LEVEL program and are tabulated in Table 2. For the A ¹Π state, it is clear that the $\Delta v = 0$ bands have the strongest transition probability. That is to say, BH has highly diagonal FCFs ($f_{00} = 0.9992$, $f_{11} = 0.9908$, $f_{22} = 0.9235$ and $f_{33} = 0.6289$). (Here f_{ji} is the Franck–Condon factor of the A ¹Π ($v' = j$) → X ¹Σ⁺ ($v = i$) transition.) This is the first criterion to be a good candidate molecule for direct laser cooling. Compared to the theoretical¹⁷ and experimental data,¹⁵ a good agreement can be found for our present results.

However, large FCFs are not enough to ensure a good laser cooling candidate, when the rate of optical cycling must also be significant (10⁵–10⁸ s⁻¹) to produce larger spontaneous scattering forces. The second criterion is a sufficiently short lifetime, which is desirable for rapid laser cooling, because it could provide a significant rate of optical cycling. The computed radiative lifetimes of the $v' = 0, 1, 2$ and 3 levels of the A ¹Π state are collected in Table 3 along with other available experimental^{26,65–67} and theoretical^{15,16,68} results for comparison. The radiative lifetimes

Table 2 Calculated Franck–Condon factors (FCFs) $f_{v'v}$ ($J = 0$) of the BH A ¹Π → X ¹Σ⁺ transition at MRCI/ACV5Z(B), AV5Z(H)^a

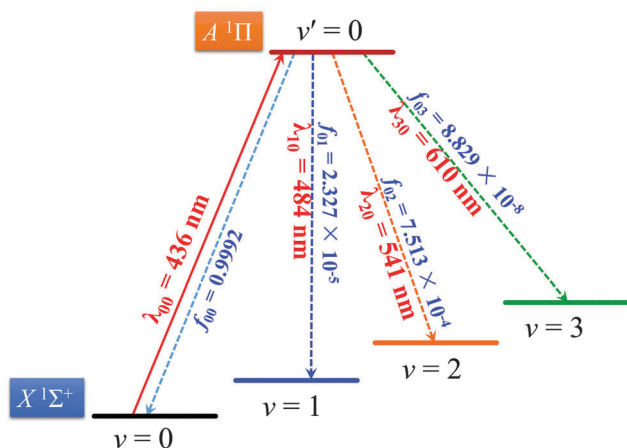
$v' = 0$	1	2	3	Ref.
$\nu = 0$	0.9992	0.7946(−5)	0.7252(−3)	0.4028(−4)
	0.9987	0.2075(−3)	0.9858(−3)	0.5643(−4)
	0.9990	0.3372(−4)	0.8785(−3)	—
1	0.2327(−4)	0.9908	0.7057(−2)	0.1333(−2)
	0.2718(−3)	0.9911	0.6074(−2)	0.1631(−2)
	0.7756(−5)	0.9852	0.1255(−1)	—
2	0.7513(−3)	0.5104(−2)	0.9235	0.6715(−1)
	0.9827(−3)	0.4177(−2)	0.9209	0.7020(−1)
	0.9883(−3)	0.8892(−2)	0.8821	—
3	0.8829(−7)	0.3997(−2)	0.4705(−1)	0.6289
	0.2335(−7)	0.4430(−2)	0.4787(−1)	0.6164

^a Characteristic base 10 given parenthetically.

Table 3 The spontaneous radiative lifetimes τ (ns) for the lowest vibronic bands of the BH $A^1\Pi$ ($J' = 1, 3$) \rightarrow $X^1\Sigma^+$ transition

Level	Experimental			Calculated				
	Douglass <i>et al.</i> ^a	Gustafsson and Rittby ^b	Others	This work $J' = 1, 3$	Luh and Stwalley ^e	Cimiraglia and Persico ^f	Diercksen <i>et al.</i> ^g	Combined ^h
$\nu' = 0$	127 \pm 10	152 \pm 6	125 \pm 5 ^c 159 \pm 16 ^d	131/131	85	90	121	114
$\nu' = 1$	146 \pm 12	167 \pm 7		151/152	99	96	129	133
$\nu' = 2$	172 \pm 14	198 \pm 8		187/187	124	103	137	166
$\nu' = 3$				261/265				

^a Ref. 26. Values for $J' = 3$. ^b Ref. 65. Values for $J' = 3$ in $\nu' = 0$ and $\nu' = 1$ and $J' = 5$ in $\nu' = 2$. ^c Ref. 66. ^d Ref. 67. ^e Ref. 15. ^f Ref. 68. ^g Ref. 16. ^h Ref. 15 and 16.

**Fig. 2** Proposed laser cooling scheme for BH using the $X^1\Sigma^+$ (ν) \rightarrow $A^1\Pi$ (ν') transition and spontaneous decay with calculated $f_{\nu\nu'}$. Here $\lambda_{\nu\nu'}$ is the wavelength of the $X^1\Sigma^+$ (ν) \rightarrow $A^1\Pi$ (ν') transition.

of the $A^1\Pi$ ($\nu', J' = 1, 3$) vibrational states are computed to be 131/131 ns, 151/152 ns, 187/187 ns and 261/265 ns for the first four vibrational levels ($\nu' = 0-3$) of BH, respectively. We found that our radiative lifetimes for $\nu' = 0-2$ agree well with the experimental results ($\nu' = 0$, 127 \pm 10/125 \pm 5 ns, $\nu' = 1$, 146 \pm 12 ns, $\nu' = 2$, 172 \pm 14 ns) of Douglass *et al.*²⁶ and Dufayard *et al.*⁶⁶ Thus, our lifetime value (261/265 ns) for $\nu' = 3$ should be credible.

In general, other theoretical results^{15,16,68} are somewhat smaller than the experimental lifetimes.

Fig. 2 shows the proposed laser driven quasicycling transitions and spontaneous decay with calculated FCFs. With this scheme, only one cooling laser (the main pump laser, with $\lambda_{00} = 436$ nm) is required (here λ_{ij} is the wavelength of the $X^1\Sigma^+$ ($\nu = i$) \rightarrow $A^1\Pi$ ($\nu' = j$) transition), and the molecule will scatter an average of 1000 photons before being optically pumped to a higher vibrational state. In recent experimental measurements,²⁸ a scheme with only two cooling lasers (one main pump laser addressing the $\nu = 0$ branch at 433 nm and the other re-pumping the $\nu = 1$ branch at 481 nm) is required, as shown in Fig. 1 of ref. 28. In their study, the theoretical values ($f_{00} = 0.99054$, $f_{01} = 0.00888$, $f_{02} = 0.00057$ and $f_{03} = 9.46 \times 10^{-6}$) were derived from Luh and Stwalley.¹⁵ Examining carefully the FCFs between our present results and the above theoretical values, we can find that the main differences concern f_{01} , which is two orders of magnitude larger than our value ($f_{01} = 0.00002327$).

One possible problem with the above laser cooling scheme, is the presence of the intervening $a^3\Pi$ state between the two states ($X^1\Sigma^+$ and $A^1\Pi$) that would be lost from the laser cooling cycle. Thus it is important to know the rate for this transition ($A^1\Pi \rightarrow a^3\Pi$). There are no experimental measurements or theoretical calculations of this rate, though Hendricks *et al.*²⁸ expected it to be of a similar magnitude to the rate for the $a^3\Pi \rightarrow X^1\Sigma^+$ transition, which is calculated to be less than 0.06 s⁻¹.¹⁷ In the present work, we calculated this rate ($A^1\Pi_1 \rightarrow a^3\Pi_1$) to be less than 0.011 s⁻¹. So the shortest radiative lifetime for $\nu' = 0-3$ will be longer than 90 s and the wavelength of the $A^1\Pi_1 \rightarrow a^3\Pi_1$ transition was computed to be 796 nm ($J' = 1, \nu' = 0 \rightarrow \nu = 0$). However, this transition is very weak because it is spin-forbidden and indeed there has been no experimental observation of the $A^1\Pi_1 \rightarrow a^3\Pi_1$ transition. Also the FCFs ($f_{00} = 0.9467$, $f_{01} = 9.81 \times 10^{-4}$, $f_{02} = 3.60 \times 10^{-5}$ and $f_{03} = 6.38 \times 10^{-7}$) are slightly weaker than those for the $A^1\Pi \rightarrow X^1\Sigma^+$ vibronic lines, so the latter transition $A^1\Pi$ ($\nu' = 0$) \leftrightarrow $X^1\Sigma^+$ ($\nu = 0$) is more promising for laser cooling in the BH molecule.

3.2 GaF molecule

In Fig. 3, we present the PECs ($X^1\Sigma^+$, $^3\Pi$ and $C^1\Pi$) of GaF at the spin-free MRCI electron correlation level. Table 1 reports the corresponding spectroscopic constants for the $X^1\Sigma^+$, $^3\Pi$ and $C^1\Pi$ states and compares them with available theoretical^{14,45} and experimental⁶² results.

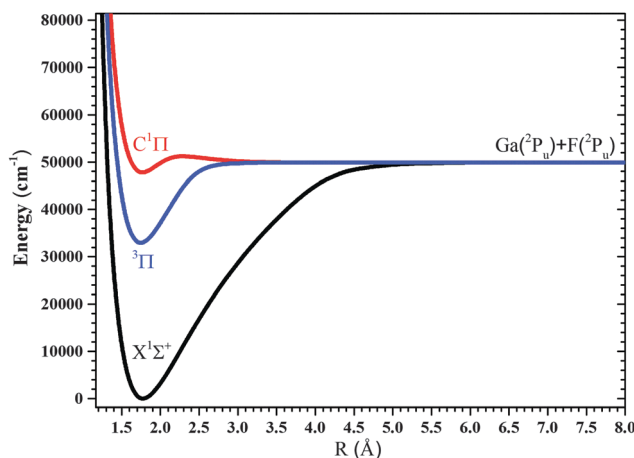
**Fig. 3** Potential energy curves of the first three electronic states of the GaF molecule at the MRCI/AVQZ_{Ga}, AV5Z_H level of theory.

Table 4 Spectroscopic constants of the first six Ω states of GaF at MRCI level

Ω states	T_e (cm ⁻¹)	R_e (Å)	ω_e (cm ⁻¹)	$\omega_e\chi_e$ (cm ⁻¹)	B_e (cm ⁻¹)	D_e (eV)	Ref.
$X^1\Sigma_0^+$	0	1.7680	643.5	2.70	0.362	5.95	This work
	0	1.7741	634.6	2.13		6.13	Ref. 46
	0	1.7744	622.2	3.2		6.02	Exp. ^a
$^3\Pi_{0-}$	32 079.9	1.7400	681.8	4.16	0.374	2.00	This work
	33 370.6	1.7445	668.9	2.00		1.98	Ref. 46
$A^3\Pi_{0+}$	32 082.0	1.7400	681.8	4.16	0.374	2.06	This work
	33 376.8	1.7443	674.8	2.88		2.03	Ref. 46
	33 105.5	1.7467	663.0	2.18			Exp. ^a
$B^3\Pi_1$	32 352.3	1.7400	682.5	4.18	0.374	1.98	This work
	33 673.4	1.7440	675.0	2.89		1.95	Ref. 46
	33 427.8	1.7444	662.1	1.45			Exp. ^a
$^3\Pi_2$	32 632.6	1.7390	683.2	4.19	0.374	2.02	This work
	33 993.3	1.7438	675.1	2.85		1.92	Ref. 46
$C^1\Pi_1$	48 530.4	1.7710	560.6	22.10	0.361	0.28	This work
	48 451.1	1.7693	579.9	16.80		0.29	Ref. 46
	47 365.7	1.778	542.3	9.55			Exp. ^a

^a Ref. 62.

Comparison of our present results with existing theoretical calculations, and experimental measurements of the molecular constants shows that our T_e , R_e , B_e and D_e are in good agreement with those results.^{14,45,62} For example, in comparison with experiments,⁶² the calculated T_e , R_e , B_e and D_e are found to be accurate to better than 0.98%, 0.57%, 1.3% and 2.90%, respectively. The basis sets and CAS used in our calculations and those used in the results obtained by Yang *et al.*⁴⁶ are almost the same; we find close agreement (~ 0.0015 Å for R_e) with all the three electronic states ($X^1\Sigma^+$, $^3\Pi$ and $C^1\Pi$) computed in our present work. Overall, our present calculated spectroscopic constants give a good agreement with earlier theoretical and experimental data.

The SOC effect was also taken into account for the GaF molecule. The corresponding spectroscopic constants of six Ω states are given in Table 4 along with other available experimental⁶² and theoretical⁴⁶ results for comparison. Examining carefully the spectroscopic constants without (Table 1) and with the SOC (Table 4) of GaF, we can find that the influence of spin-orbit coupling on the spectroscopic properties is generally weak. The properties of the $X^1\Sigma_0^+$ ground state are almost identical to those of their $X^1\Sigma^+$ parent, and the variation is very small ($\delta R_e = 0.005$ Å, $\delta\omega_e = 7.98$ cm⁻¹, $\delta\omega_e\chi_e = 0.07$ cm⁻¹). In the case of the $^3\Pi_{2,1,0^+,0-}$ and $C^1\Pi_1$ states, the spectroscopic constants for R_e , ω_e , and generally show only small deviations with respect to their $^3\Pi$ and $C^1\Pi$ parent states ($\delta R_e = 0.005$ – 0.006 Å, $\delta\omega_e = 5.21$ – 6.61 cm⁻¹, $\delta\omega_e\chi_e = 0.34$ – 0.37 cm⁻¹ for $^3\Pi_{2,1,0^+,0-}$ and $\delta R_e = 0.003$ Å, $\delta\omega_e = 58.85$ cm⁻¹, $\delta\omega_e\chi_e = 0.15$ cm⁻¹ for $C^1\Pi_1$).

These results suggest that the effect of spin-orbit coupling on the spectroscopic parameters of all-electron calculations did not show a significant impact with respect to the results of a spin-free scalar relativistic DKH-MRCI approach.

Like BH, GaF also has highly diagonal FCFs ($f_{00} = 0.997$, $f_{11} = 0.989$, $f_{22} = 0.958$ and $f_{33} = 0.863$) for the $C^1\Pi$ ($\nu' = j$) $\rightarrow X^1\Sigma^+$ ($\nu = i$) transition, and the corresponding FCFs are presented in Table 5. Our computed FCFs are in good agreement with those

Table 5 Calculated Franck–Condon factors (FCFs)^a $f_{\nu'\nu}$ of the GaF $A^1\Pi \rightarrow X^1\Sigma^+$ transition at MRCI level

	$\nu' = 0$	1	2	3	4
$\nu = 0$	9.97(−1)	4.12(−4)	2.73(−3)	4.60(−5)	5.63(−6)
1	4.73(−4)	9.89(−1)	1.59(−3)	7.93(−3)	6.48(−4)
2	2.70(−3)	8.63(−4)	9.58(−1)	2.31(−2)	1.12(−2)
3	3.04(−6)	9.26(−3)	1.27(−2)	8.63(−1)	9.76(−2)
4	1.45(−5)	2.85(−5)	2.33(−2)	4.62(−2)	6.57(−1)
5	2.18(−8)	9.66(−5)	6.94(−4)	5.18(−2)	9.61(−2)
6	1.08(−7)	6.38(−7)	4.82(−4)	4.91(−3)	1.03(−1)

^a Characteristic base 10 given parenthetically.**Table 6** Radiative lifetimes of the $C^1\Pi$, $A^3\Pi_{0+}$, $B^3\Pi_1$, and $C^1\Pi_1$ states at lower vibrational levels to the ground state transition

Transitions	Radiative lifetimes					
	$\nu' = 0$	1	2	3	4	
$C^1\Pi \rightarrow X^1\Sigma^+$	(ns)	2.26	2.36	2.48	2.64	2.85
$A^3\Pi_{0+} \rightarrow X^1\Sigma_0^+$	(ms)	29.0	30.2	30.9	30.8	29.7
$B^3\Pi_1 \rightarrow X^1\Sigma_0^+$	(μs)	27.7	27.9	28.2	28.5	28.8
$C^1\Pi_1 \rightarrow X^1\Sigma_0^+$	(ns)	2.15	2.28	2.44	2.70	3.17
$C^1\Pi_1 \rightarrow X^1\Sigma_0^+{}^a$	(ns)	2.56	2.47	2.39	2.31	2.24

^a Ref. 46.

of the results predicted by Yang *et al.*⁴⁶ Thus, GaF meets the first criterion to be a potential laser cooling candidate.

However, large FCFs are not enough to ensure a good laser cooling candidate. The sufficiently short lifetimes are highly desirable for rapid laser cooling. The calculated spontaneous radiative lifetimes for the $C^1\Pi \rightarrow X^1\Sigma^+$ transition are given in Table 6 for $\nu' = 0$ –4 and $J' = 1$. Lifetimes increase with increasing ν' ($\nu' = 0$ –4: 2.26, 2.36, 2.48, 2.64, and 2.85 ns, respectively). This result shows that the $C^1\Pi$ is a rather short lifetime state. Thus, GaF also meets the second criterion for direct laser cooling. Fig. 4 shows the proposed laser-driven transition (solid red) and spontaneous decay (dotted line) with calculated $f_{\nu'\nu}$ for the $C^1\Pi \rightarrow X^1\Sigma^+$ transition.

The calculated f_{00} of 0.997 is larger than that predicted in SrF ($f_{00} = 0.98$);² thus it is sufficiently large to be potentially viable for cooling. With this proposed cooling scheme, only one cooling laser (the main pump laser, with $\lambda_{00} = 209$ nm) is required. But the required cooling wavelength of 209 nm is located in the short-wavelength ultraviolet light (UVC) range [*i.e.*, 400–320 (or 315) nm = UVA; 320 (or 315)–280 nm = UVB; 280–190 nm = UVC], which is a difficult region to generate continuous wave laser radiation in. However, a frequency quadrupled Ti:sapphire laser (189–235 nm) should be capable of generating useful quantities of light at this wavelength (209 nm).

As in BH, there is an intervening $^3\Pi$ state between the two states ($X^1\Sigma^+$ and $C^1\Pi$) of GaF. Fig. 5 shows the computed TDMs of the $A^3\Pi_{0+}$, $B^3\Pi_1$, and $C^1\Pi_1$ states to the ground state $X^1\Sigma_0^+$ transitions as functions of the internuclear distance R .

Because the $^3\Pi \rightarrow X^1\Sigma^+$ transition is spin-forbidden, the TDMs of the $A^3\Pi_{0+} \rightarrow X^1\Sigma_0^+$ and $B^3\Pi_1 \rightarrow X^1\Sigma_0^+$ transitions are much weaker than that of the $C^1\Pi_1 \rightarrow X^1\Sigma_0^+$ transition.

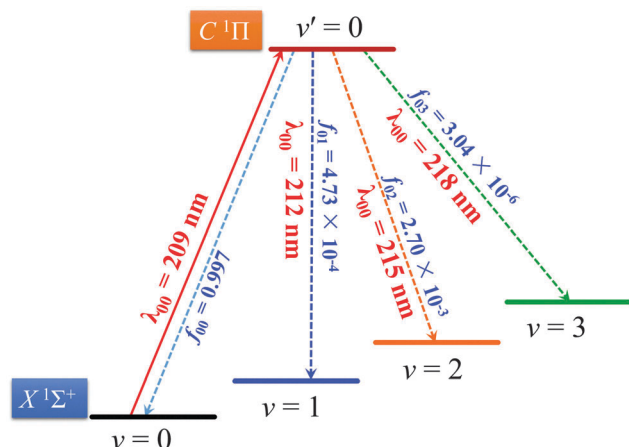


Fig. 4 Proposed laser cooling scheme for GaF using the $X^1\Sigma^+(v) \rightarrow C^1\Pi(v')$ transition and spontaneous decay with calculated $f_{v'v}$. Here $\lambda_{v'v}$ is the wavelength of the $X^1\Sigma^+(v) \rightarrow C^1\Pi(v')$ transition.

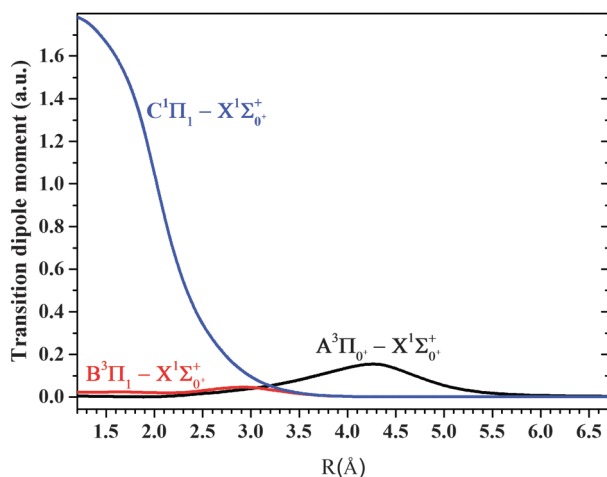


Fig. 5 Calculated TDMs of the $A^3\Pi_0^+$, $B^3\Pi_1$, and $C^1\Pi_1$ states as functions of the internuclear distance R .

The present results are consistent with those of Yang *et al.*⁴⁶ and the radiative lifetimes of the $A^3\Pi_0^+ \rightarrow X^1\Sigma_0^+$ and $B^3\Pi_1 \rightarrow X^1\Sigma_0^+$ transitions are much longer than that of the $C^1\Pi_1 \rightarrow X^1\Sigma_0^+$ transition. The corresponding radiative lifetimes are presented in Table 6. These radiative lifetimes are in reasonable agreement with those obtained by Yang *et al.*,⁴⁶ except for the $A^3\Pi_0^+ \rightarrow X^1\Sigma_0^+$ transition. Thus, the transition $C^1\Pi(v'=0) \leftrightarrow X^1\Sigma^+(v=0)$ is more promising for laser cooling in the GaF molecule.

4. Conclusions

In the present work, *ab initio* PECs of the $X^1\Sigma^+$, $A^3\Pi$ and $A(C)^1\Pi$ states of BH and GaF have been calculated at the MRCI + Q level of theory. The spectroscopic constants (T_e , R_e , D_e , ω_e , $\omega_e x_e$, B_e) were calculated for the $X^1\Sigma^+$, $A^3\Pi$ and $A(C)^1\Pi$ states of BH and GaF. The comparison between our present work and available theoretical and experimental data in literature shows a good agreement.

The spin-orbit coupling effect was also taken into account in the electronic structure calculations of GaF at MRCI level. The results indicate that the influence of spin-orbit coupling on the spectroscopic properties is generally weak.

The theoretical results indicate that BH and GaF both have highly diagonally distributed $f_{v'v}$ for transitions between the $A(C)^1\Pi(v') \rightarrow X^1\Sigma^+(v)$ and short lifetimes for the $A(C)^1\Pi(v')$ states. The two criteria are highly desirable for rapid and efficient laser cooling. The proposed laser cooling schemes that drive the $A(C)^1\Pi(v'=0) \rightarrow X^1\Sigma^+(v=0)$ transition using just one laser wavelength (BH: 436 nm, GaF: 209 nm), though the cooling wavelength of GaF is deep in the UVC, a frequency quadrupled Ti:sapphire laser (189–235 nm) could be capable of generating useful quantities of light at this wavelength.

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