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Theoretical study of laser cooling of magnesium monofluoride using *ab initio* methods

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A theoretical investigation of the feasibility of laser-cooling the ^{24}Mg^{19}F molecule is performed using *ab initio* calculations. The low-lying electronic states are determined by the multireference configuration-interaction (MRCI) method, where the Davidson modification ($+Q$) with the Douglas-Kroll-Hess scalar relativistic correction is also taken into account. The calculated spectroscopic constants are in excellent agreement with the available experimental data. The Franck-Condon factors (FCFs), radiative lifetimes, and radiative widths are verified by calculating the potential energy curves and the transition dipole moment of the $A\,^2\Pi\,(\nu') \rightarrow X\,^2\Sigma^+(\nu)$ transition. Our calculation indicates that the $A\,^2\Pi(\nu'=0) \rightarrow X\,^2\Sigma^+\,(\nu=0)$ transition provides highly diagonally distributed FCFs ($f_{00} = 0.917$) and a short radiative lifetime ($\tau = 7.96$ ns) for the $A\,^2\Pi(\nu'=0)$ state, which is short enough for rapid laser cooling. The required cooling wavelengths are in the ultraviolet region. A comprehensive scheme demonstrates the possibility of laser-cooling MgF. Moreover, the $C\,^2\Sigma^+$ state is confirmed to be a Rydberg state at the MRCI level, which is in line with experimental conjecture. The $B\,^2\Pi$ and $D\,^2\Sigma^+$ states are also reported, but they have not been observed to date.

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I. INTRODUCTION

Cold and ultracold molecules are of considerable interest due to their prospective and wide range of applications [1]. For example, ultracold molecules can be used as attractive candidates for quantum systems [2], quantum computation [3], and the precise control over molecular degrees of freedom possible at ultracold temperatures due to their permanent electric dipole moments, which lead to long-range and controllable anisotropic dipole-dipole interactions. Ultracold molecules open up a route for research in chemical dynamics [4,5] and for controlling chemistry at low temperatures [6,7]. Therefore, theoretical and experimental investigations of the potential laser-cooling candidates are highly desirable.

As early as 2004, Di Rosa [8] conducted a brief survey of candidate molecules for laser cooling and identified a series of hydrides and halides, including CaH, AlH, AlF, AlCl, etc. However, laser cooling of molecules was thought to be a challenge in past decades because of their complex internal structure. Until recently, the laser cooling of molecules to ultracold temperatures was verified from the perspective of experiment [9–11]. Transverse laser cooling was applied to beams of SrF [9] and YO [10] molecules, and longitudinal laser cooling was applied to a supersonic beam of CaF molecules [11]. From a theoretical point of view, a series of diatomic polar molecules were considered to be potential molecules for laser cooling, such as the alkaline-earth-metal monofluorides (e.g., BeF [12] and RaF [13]), the alkaline-earth-metal monohydrides [14] (e.g., BeH, MgH, CaH, SrH, and BaH) and other polar molecules (e.g., CH [15] and AlF [16], etc.). According to previous research work [8], the molecule must meet the following criteria to be a promising laser-cooling candidate. The first criterion is strong one-photon transitions with highly diagonal Franck-Condon factors (FCFs). Highly diagonal FCFs could limit the number of lasers required to keep the molecule in a closed-loop cooling cycle. The second criterion is shorter lifetime to ensure high spontaneous-emission rates, which is highly desirable for rapid laser cooling. The last one is that there are nonintervening electronic states in the cycling transition. The alkaline-earth-metal monofluorides, such as BeF [12], CaF [11], SrF [9], and RaF [13], have been proposed to be laser-cooling molecules or potential laser-cooling candidates. Our original motivation for this work is to discuss the feasibility of laser-cooling the ^{24}Mg^{19}F molecule and provide a promising theoretical reference for further theoretical and experimental research on laser cooling of ^{24}Mg^{19}F.

Bands of the MgF molecule are found in disk and spot spectra in astrophysics [17]. The identification of the MgNC radical toward the carbon star IRC+10216 demonstrates that there is enough magnesium present in the gas phase to form simple molecules. Considering the relatively high cosmic abundance of magnesium (Mg :$H_2 \sim 6 \times 10^{-5}$), MgF seems a likely candidate for a circumstellar molecule [18]. The first quantum mechanical interpretations of the band spectra of MgF data back to the 1930s at least [19,20]. Subsequent early reports were concentrated on its rotational and vibrational structure [17,21], hyperfine interaction [22], and adsorption spectra [20]. The first rotational analysis of MgF was carried out by Barrow and Beale [21] in 1967. They recorded and analyzed the high-resolution spectrum of the 0-0 and 1-0 bands of the $A\,^2\Pi \rightarrow X\,^2\Sigma^+$ transition and also proposed that the $A\,^2\Pi$ state was inverted and the $C\,^2\Sigma^+$ state appeared to be a Rydberg state. This work was followed by several theoretical calculations and experiments [18,22–26]. Walker and Richards [23] computed the spin-orbit coupling constants and Λ-type doubling parameters for the MgF molecule, and explained that the $A\,^2\Pi$ state of MgF was regular from their calculated results. Based on Walker and Richards' conclusion,

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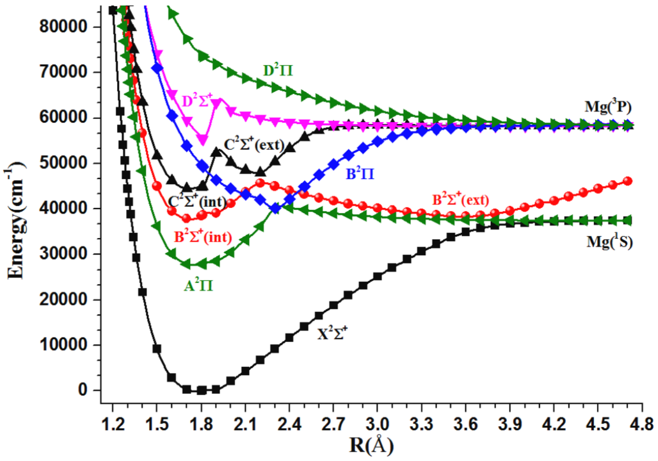

FIG. 1. (Color online) Potential energy curves of the low-lying doublet states of the molecule ^{24}Mg^{19}F at MRCI level.

Knight *et al.* [22] concluded by use of the ESR spectrum that the lowest $A\,^2\Pi$ excited state was regular from the evidence of the g tensor. The spectra of MgF have also been detected in the microwave- and millimeter-wave regions. Barber and co-workers [24] obtained the high-resolution infrared emission spectrum of MgF by using a Fourier transform spectrometer; they also determined some of the Dunham coefficients for the ground state $X\,^2\Sigma^+$ and the spin-rotation constants. Anderson *et al.* [18,25] used a direct absorption spectrometer in order to measure the pure rotational spectrum of MgF in its ground electronic state $X\,^2\Sigma^+$. Recently, the work of Pelegrini *et al.* [26] attracted considerable attention, diagonal transitions dominate the $A\,^2\Pi \rightarrow X\,^2\Sigma^+$ transition for the MgF molecule. They also calculated the spectroscopic constants, radiative transition probabilities, transition dipole moments (TDMs), and lifetimes for the $A\,^2\Pi \rightarrow X\,^2\Sigma^+$ transitions at the multireference configuration-interaction (MRCI) level.

Although a considerable amount of research has been done on MgF during the past decades, there appear to be only a few systematic studies of laser cooling of MgF in the public literature. The highly diagonally distributed Franck-Condon factors of MgF motivates us to further study the possibility of laser cooling of MgF. Compared to SrF [9] and CaF [11] molecules, the smaller mass of MgF is somewhat advantageous for laser cooling. Thus, the aim of the present work is to conduct a systematic theoretical investigation on the electronic structure and radiative properties, including the FCFs, the TDM, the radiative lifetimes, and the diode laser excitation wavelengths of the $A\,^2\Pi\,(v') \leftarrow X\,^2\Sigma^+\,(v)$ transitions of MgF. Moreover, a scheme for a viable laser-cooling cycle for MgF is also described briefly.

The paper is organized as follows. In Sec. II, we briefly describe the *ab initio* methods and basis sets used throughout the calculations. In the following Sec. III, the results and discussion are presented, outlining laser-cooling schemes for the MgF molecule. Finally, some conclusions and suggestions for further work are given in Sec. IV.

II. COMPUTATIONAL DETAILS

In the present work, we calculated the lowest electronic states of the ^{24}Mg^{19}F molecule using the complete active space self-consistent field (CASSCF) [27,28] and MRCI plus Davidson corrections (MRCI+Q) [29–31] methods. The contracted Gaussian-type all-electron correlation consistent cc-pwCV5Z-DK [32] basis sets are used for Mg and the relativistic ANO-RCC [33] basis sets (relativistic contracted atomic natural orbitals) for F. Scalar relativistic effects are also taken into account throughout the calculations using the Douglas-Kroll-Hess (DKH) [34,35] transformation of the relativistic Hamiltonian. Due to the limitation of the symmetry of the MOLPRO program package [36], the C_{2v} point group symmetry is adopted in the calculations, and all molecular orbitals are labeled by (a_1, b_1, b_2, a_2) irreducible representations. The active space consists of nine electrons and nine molecular orbitals (MOs) including five a_1, two b_1, and two b_2 symmetry MOs (5220), which correspond to the Mg $3s3p4s$ and F $2s2p$ shells. The active space is referred to as CAS (9,9). The 12 electrons in the Mg $1s2s2p$ and F

TABLE I. Spectroscopic constants for $X\,^2\Sigma^+$ and $A\,^2\Pi$ states of ^{24}Mg^{19}F calculated with cc-pwCV5Z-DK basis set on Mg and ANO-RCC basis set on F at MRCI level.

States	T_e (cm^{-1})	R_e (Å)	ω_e (cm^{-1})	B_e (cm^{-1})	D_e (eV)	Reference
$X\,^2\Sigma^+$	0	1.7611	555.0	0.5077	4.675	This work
	0	1.7500	721.6	0.5169	4.57 ± 0.1 [38]	Expt. [21]
		1.7529	720.1	0.5193		Expt [24].
	0	1.746	774.6		9.162	Ref. [26]
$A\,^2\Pi$	27834.1	1.7470	653.1	0.5239	1.596	This work
	27816.1 [22]	1.7469	746.0	0.5211 [22]		Expt. [21]
	27674	1.736	790.4		5.730	Ref. [26]
$B\,^2\Sigma^+$(int)	37679.7	1.7372	837.9	0.5317	1.730	This work
$B\,^2\Sigma^+$(ext)	38430.5	3.5848	263.6	0.1236	1.634	This work
	37187.5	1.7185	762.1	0.5359		Expt. [21]
$B\,^2\Pi$	40296.7	2.3000	1001.3	0.2993	2.280	This work
$C\,^2\Sigma^+$(int)	44624.8	1.7000	923.9	0.5388	3.891	This work
$C\,^2\Sigma^+$(ext)	47968.9	2.1776	898.5	0.3351	1.315	This work
	42589.6	1.6988	823.2	0.5488		Expt. [21]
$D\,^2\Sigma^+$	55394.4	1.8100	2066.0	0.4855	3.964	This work

1*s* shells are put in the closed spaces. The closed spaces are doubly occupied in all reference configuration state functions.

We calculate the spectroscopic constants, including the equilibrium bond distance (R_e), electronic transition energy (T_e), harmonic frequency (ω_e), rotational constant (B_e), and dissociation energy (D_e) for the $X\,^2\Sigma^+$, $A\,^2\Pi$, $B\,^2\Sigma^+$, $B\,^2\Pi$, $C\,^2\Sigma^+$, and $D\,^2\Sigma^+$ states of MgF using Le Roy's LEVEL8.0 program [37]. All the $^2\Sigma^-$ states are repulsive; therefore they are not discussed further. The permanent dipole moments (PDMs) and transition dipole moment (TDM) of MgF are computed at the MRCI level by taking the expectation and transition values.

III. RESULTS AND DISCUSSION

A. Potential energy curves and spectroscopic constants

The calculated potential energy curves (PECs) of MgF are shown in Fig. 1. Table I lists the corresponding spectroscopic constants, together with available theoretical and experimental values for comparison. Our results are in good agreement with experimental data [21,22,24,38] and previous theoretical calculations [26] ensuring the accuracy and reliability of our calculation.

As for the $X\,^2\Sigma^+$ state, the equilibrium bond distance R_e is calculated to be 1.7611 Å; the corresponding percentage error is only 0.47% with respect to the recent experiment data (1.7529 Å) [24]. The depth of the well is 4.675 eV for the ground state $X\,^2\Sigma^+$, which is in excellent agreement with the experimental D_e value 4.57 ± 0.1 eV [38]. Pelegrini *et al.* [26] calculated a shorter bond length (∼1.746 Å) and a larger dissociation energy (∼9.162 eV) using a smaller active space and different basis sets at the MRCI level. Concerning the first excited state $A\,^2\Pi$, the comparison with experimental data demonstrates that our calculations overestimate R_e(1.7470 Å) [21] by only 0.006%, T_e (27 834.1 cm^{-1}) [22] by only 0.065%, and B_e (0.5239 cm^{-1}) [22] by about 0.546%. The values of $B_e = 0.5077$ cm^{-1} and 0.5239 cm^{-1} for the $X\,^2\Sigma^+$ state and the state $A\,^2\Pi$ are also in good accordance with the experimental data 0.5169 cm^{-1} [21] and 0.5211 cm^{-1} [22], respectively. Although the values ω_{e} of the $X\,^2\Sigma^+$, $A\,^2\Pi$, $B\,^2\Pi$, and $C\,^2\Sigma^+$ states have some discrepancies with respect to experimental data, they are in a reasonable and acceptable range.

As is shown in Fig. 1, the $B\,^2\Sigma^+$ and $C\,^2\Sigma^+$ states exhibit similar behavior: they have two minima and two avoided crossings. In fact, this feature was found in $B\,^2\Sigma^+$ of BeF [12] and $C\,^2\Sigma^+$ of BeCl [39] molecules. The $B\,^2\Sigma^+$ state has two minima, the internal one with $R_e = 1.7372$ Å and $T_e = 37\,679.7$ cm^{-1}, and the external one with $R_e = 3.5848$ Å and $T_e = 38\,430.5$ cm^{-1}. The corresponding experimental value are $R_e = 1.7185$ Å and $T_e = 37\,187.5$ cm^{-1} for the $B\,^2\Sigma^+$ state [21]. The PEC of the $B\,^2\Sigma^+$ state exhibits two avoided crossings; one occurs with the $X\,^2\Sigma^+$ state, nearly at 3.9 Å and the other one with the $C\,^2\Sigma^+$ state close to 2.2 Å. In the case of the $C\,^2\Sigma^+$ state, it also has two minima, the internal one with $R_e = 1.7000$ Å and $T_e = 44\,624.8$ cm^{-1}, and the external one with $R_e = 2.1776$ Å and $T_e = 47\,968.9$ cm^{-1}. The corresponding experimental values are $R_e = 1.6988$ Å and $T_e = 42\,589.6$ cm^{-1} [21]. The $C\,^2\Sigma^+$ state has two avoided crossings; one occurs with $C\,^2\Sigma^+$ as mentioned above, and the other with with the $D\,^2\Sigma^+$ state at about 1.9 Å. Compared to the external section, the internal section has values ($B_e = 0.5317$ cm^{-1} and 0.5388 cm^{-1} for $B\,^2\Sigma^+$ and $C\,^2\Sigma^+$ states, respectively) closer to the experimental data ($B_e = 0.5359$ cm^{-1} and 0.5488 cm^{-1}) [21]. From Table I, it can furthermore be seen that the spectroscopic constants of the internal section are in good agreement with experimental data [21]. Nonetheless, it should be noted that the $B\,^2\Pi^+$ and $D\,^2\Sigma^+$ states have not been observed to date and their existence still awaits experimental confirmation.

It is noteworthy that the $C\,^2\Sigma^+$ state is found to be a Rydberg state. The $C\,^2\Sigma^+$ state is composed of the valence electronic configuration symbolized by $\ldots 5\sigma^2 6\sigma^2 2\pi^4 9\sigma$ and $\ldots 5\sigma^2 6\sigma^2 2\pi^4 8\sigma$ accounting for 79.6% and 12.4%, respectively. The 9σ state is localized mostly on the 4*s* orbital of Mg, which agrees with Barrow and Beale's experimental conjecture [21]. Thus, the lowest-energy $C\,^2\Sigma^+$ state is confirmed to be a Rydberg state at the MRCI level.

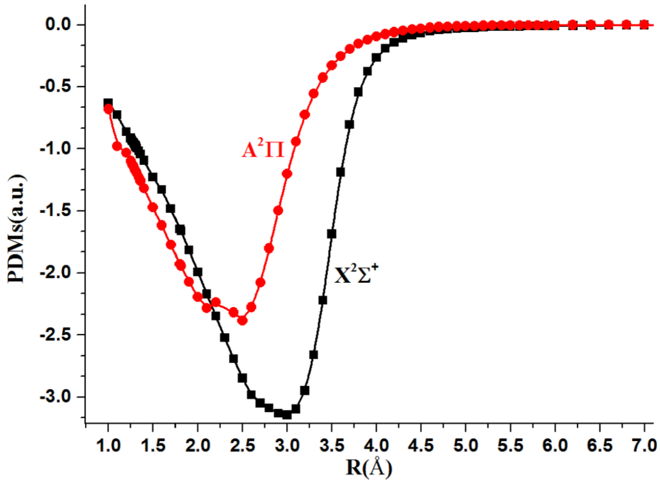

FIG. 2. (Color online) The permanent electronic dipole moments of the ground state $X\,^2\Sigma^+$ and the first excited state $A\,^2\Pi$ of ^{24}Mg^{19}F at MRCI level.

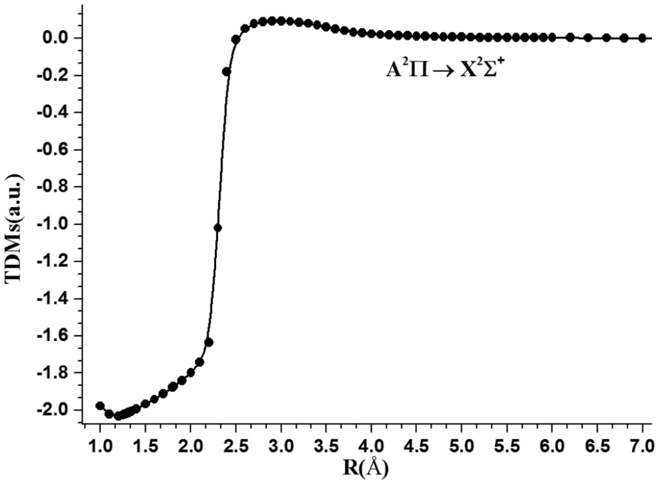

FIG. 3. The transition dipole moment for $A\,^2\Pi \rightarrow X\,^2\Sigma^+$ transitions of the molecule ^{24}Mg^{19}F at MRCI level.

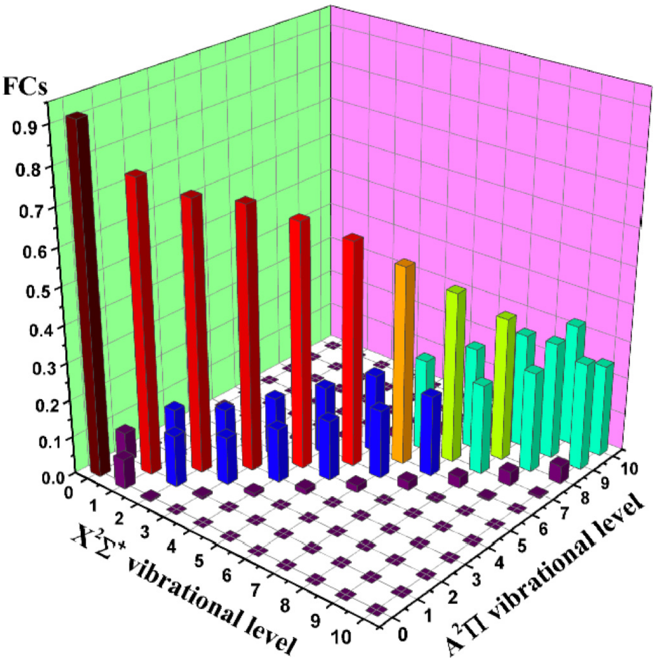

FIG. 4. (Color online) Calculated Franck-Condon factors (FCFs) in ^{24}Mg^{19}F for the lowest 11 vibrational levels of the cooling transition $A\,^2\Pi \rightarrow X\,^2\Sigma^+$ transition.

B. PDMs and TDM of the $X\,^2\Sigma^+$ and $A\,^2\Pi$ states

The PDMs as a function of the internuclear distance for the $X\,^2\Sigma^+$ and $A\,^2\Pi$ states of MgF are presented in Fig. 2. As shown in Fig. 2, the PDM functions of the $X\,^2\Sigma^+$ and $A\,^2\Pi$ states exhibit a similar behavior with respect to the internuclear distance R, wherein their absolute magnitudes demonstrate a linear behavior with the R for the short bond length indicating an ionic molecule. The magnitudes of the PDMs reach a maximum ($X\,^2\Sigma^+$ – 3.145 a.u. and $A\,^2\Pi$ – 2.382 a.u.) and drop thereafter. Then the dipole moments go to zero starting from the point about $R = 4.3$ Å at larger internuclear distances. As for the $A\,^2\Pi$ state, the PDM has an abrupt change in behavior observed at around its maximum probably due to an avoided crossing with the $B\,^2\Pi$ state at around the coincidence point.

The TDM between $A\,^2\Pi$ and $X\,^2\Sigma^+$ states of MgF as a function of the internuclear distance is depicted in Fig. 3. The absolute value of TDM shows a quasilinear behavior up to a distance of ∼2.8 Å at short bond lengths. Then the TDM reaches a maximum around 3.0 Å and trends to zero at large distances owing to spin-forbidden transitions at the atomic limits from Mg(^1S) to Mg(^3P). It should be noted that our calculations exhibit a very similar shape with respect to those in Ref. [27] within the calculation error in reasonable internuclear regions.

C. Franck-Condon overlap of the vibrational levels of the $A\,^2\Pi$ and $X\,^2\Sigma^+$ states

The calculated Franck-Condon factors of spontaneous radiative transitions are sketched in Fig. 4, which describes the overlap of the vibrational wave functions for the cooling transitions $A\,^2\Pi \rightarrow X\,^2\Sigma^+$. Figure 4 exhibits all possible transitions in the range $0 \leqslant \nu \leqslant 10$ and demonstrates the obvious characteristic that the transitions for $\Delta\nu = \nu' - \nu = 0$ (diagonal) have the largest probabilities. As mentioned in Sec. I, highly diagonal Franck-Condon factors represent the first criterion to be a potential laser-cooling candidate which could limit the number of lasers required to keep the molecule in a closed-loop cooling cycle. Several calculated FCF data and the wavelength $\lambda_{\nu\nu'}$ of the $A\,^2\Pi(\nu') \leftarrow X\,^2\Sigma^+(\nu)$ transition are presented in Table II. It can be clearly seen that the $A\,^2\Pi\,(\nu' = 0) \rightarrow X\,^2\Sigma^+(\nu = 0)$ transition has the strongest Franck-Condon factor $f_{00} = 0.917$, whereas the $A\,^2\Pi \rightarrow X\,^2\Sigma^+$ transitions for $\Delta\nu = \nu' - \nu \neq 0$ have very small values. Pelegrini *et al.* [26] obtained a larger FCF $f_{00} = 0.986$ than ours. By comparing with other molecules, our calculated value is slightly larger than that predicted in BeF ($f_{00} = 0.897$) [12] and smaller than that in SrF ($f_{00} = 0.98$) [9]. In spite of the fact that the FCFs in the present work have small differences with others reported in the literature, they are sufficiently large to be potentially viable for cooling. The proposed laser-driven transitions (solid red line) and spontaneous decay (dotted line) with calculated $f_{\nu'\nu}$ and $\lambda_{\nu\nu'}$ for the MgF molecule are plotted in Fig. 5. The calculated wavelength of the principal laser-driven cycling of the $A\,^2\Pi(\nu' = 0) \leftarrow X\,^2\Sigma^+(\nu = 0)$ transition λ_{00} is 358.7 nm which is in excellent agreement with the experimental value $\lambda_{00} = 359.4$ nm [21]. As shown

TABLE II. The calculated Franck-Condon factors (FCFs) $f_{\nu'\nu}$ together with other theoretical results (in italics) and wavelength $\lambda_{\nu\nu'}$ of the $A\,^2\Pi(\nu') \leftarrow X\,^2\Sigma^+(\nu)$ transition (experimental value in brackets). The diagonal FCFs $f_{\nu'\nu}(\nu' - \nu = 0)$ are in bold. Numbers in parentheses indicate the power of 10.

f_{00} f_{10} f_{20} f_{30}	f_{01} f_{11} f_{21} f_{31}	f_{02} f_{12} f_{22} f_{32}	f_{03} f_{13} f_{23} f_{33}	f_{04} f_{14} f_{24} f_{34}	λ_{00} (nm)	λ_{10} (nm)	λ_{21} (nm)
0.917	0.079	0.004	9.9(−5)	1.4(−5)			
0.986 [26]	*0.014* [26]	*0.000* [26]	*0.000* [26]	*0.000* [26]			
0.080	**0.776**	0.138	5.87(−3)	7.5(−5)	358.7	350.7	349.6
0.014 [26]	*0.961* [26]	*0.026* [26]	*0.000* [26]	*0.000* [26]	[359.4] [21]	[350.1] [21]	
0.003	0.139	**0.721**	0.127	0.010			
0.000 [26]	*0.026* [26]	*0.938* [26]	*0.035* [26]	*0.001* [26]			
8.5(−5)	0.005	0.133	**0.702**	0.144			
0.000 [26]	*0.000* [26]	*0.037* [26]	*0.917* [26]	*0.044* [26]			

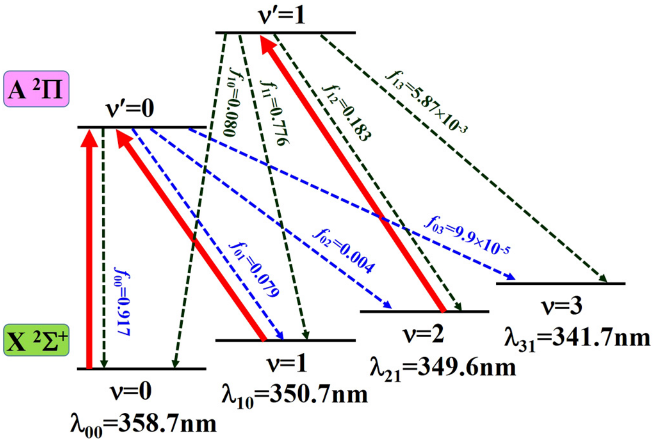

FIG. 5. (Color online) Proposed laser-cooling scheme for ^{24}Mg^{19}F using the $A\,^2\Pi \leftarrow X\,^2\Sigma^+$ transition (solid red) and spontaneous decay (dotted line) with calculated $f_{\nu'\nu}$ for the MgF molecule. Here $\lambda_{\nu\nu'}$ is the wavelength of the $A\,^2\Pi(\nu') \leftarrow X\,^2\Sigma^+(\nu)$ transition.

in Fig. 5, the first vibrational repump would be set up for the $A\,^2\Pi(\nu'=0) \leftarrow X\,^2\Sigma^+(\nu=1)$ transition, and the second one would be set up for the $A\,^2\Pi(\nu'=1) \leftarrow X\,^2\Sigma^+(\nu=2)$ transition. This pair of repumping lasers is required to reclaim molecules falling from $\nu'=0$ to $\nu=1$ ($f_{01}=0.079$) and from $\nu'=1$ to $\nu=2$ ($f_{12}=0.138$). As can be seen from both Fig. 5 and Table II, the first vibrational repump with the wavelength $\lambda_{10}=350.7$ nm and the second with $\lambda_{21}=349.6$ nm of the $A\,^2\Pi(\nu') \leftarrow X\,^2\Sigma^+(\nu)$ transition. The calculated $\lambda_{10}=350.7$ nm is also in perfect agreement with the experimental data $\lambda_{10}=350.1$ nm [21]. All of these three required laser-cooling wavelengths ($\lambda_{00}=358.7$ nm, $\lambda_{10}=350.7$ nm, $\lambda_{21}=349.6$ nm) are in the UV region, where it is difficult to generate continuous wave laser radiation. However, a frequency-doubled output of a Ti:sapphire laser should be capable of generating useful quantities of light at this wavelength. Note that the calculated off-diagonal f_{01} is about six times larger than the value measured by Pelegrini and co-workers. Due to the negligible probability ($f_{03+} < 10^5$) of decays to the $X\,^2\Sigma^+$ ($\nu \geqslant 3$) state from the $A\,^2\Pi$ state, a third repumping laser is not taken into account.

D. Spontaneous radiative lifetimes and radiative widths for the vibrational level of the $A\,^2\Pi$ state

The band system $A\,^2\Pi \rightarrow X\,^2\Sigma^+$ of the molecule MgF possesses highly diagonal Franck-Condon factors, meeting the first criterion to be a potential laser-cooling candidate. However, large FCFs alone are not enough to ensure a good cooling candidate. The rate of optical cycling must be significant as well ($10^5 - 10^8$ s^{-1}) to produce a strong spontaneous scattering force. The second criterion is a shorter lifetime which is highly desirable for rapid laser cooling due to the fact that it could provide a significant rate of optical cycling. The estimated spontaneous radiative lifetimes and radiative widths of the transition from the $A\,^2\Pi$ state in the lower vibrational levels to the ground state $X\,^2\Sigma^+$ of MgF are listed in Table III, together with the available theoretical work for comparison. The Einstein A coefficient for the primary cooling transition of the $A\,^2\Pi(\nu'=0)$ vibrational state is 1.26×10^8 s^{-1}, giving a lifetime of 7.96 ns (about 1/3 that of the transition in SrF) and therefore can offer better laser accessibility. The radiative lifetimes for the $A\,^2\Pi(\nu')$ vibrational states of the rest of the six vibrational levels ($\nu'=1-6$) are around 7.8 ns, smaller than the values calculated by Pelegrini *et al.* [26] to some extent. The orders of magnitude of these radiative lifetimes (nanometers) are still adequate to produce large spontaneous scattering forces. As for the third criterion, of course, there is no intervening electronic state between the $A\,^2\Pi$ state and the $X\,^2\Sigma^+$ state in the cycling transition.

E. Comparison with other molecules

In this section, we will compare the MgF molecule with other molecules studied previously and give some suggestions for further work. To apply large spontaneous accelerations for cooling, slowing, and trapping considerations, it is desirable to have a low mass, a short wavelength λ_{00}, and a short spontaneous radiative lifetime [40]. MgF as an equivalent molecule to SrF [9] and CaF [11] has a lower mass of Mg versus Sr and Ca, to some extent, and under the same conditions (e.g., the same initial velocity), this is somewhat advantageous to make the MgF molecule more suitable for laser cooling. The spontaneous radiative lifetime is slightly shorter and therefore can offer better laser accessibility: MgF (7.96 ns), CaF (∼19.2 ns) [11], SrF (∼23 ns) [9], and RaF (∼25 ns) [13]. Unfortunately, the wavelength is slightly shorter: MgF ($\lambda_{00} \sim 359$ nm), CaF ($\lambda_{00} \sim 606$ nm) [11], SrF ($\lambda_{00} \sim 663$ nm) [9], and RaF ($\lambda_{00} \sim 710$ nm) [13]; however a frequency-doubled output of a Ti:sapphire laser should be capable of generating useful quantities of light at this wavelength (350–475 nm). From an experimental standpoint, MgF possessed the advantage that its own favorable FCFs dictate that only three vibrational levels will be significantly populated after 10^5 photon scatters, which is more than sufficient to stop molecules in a cryogenic beam on principle, as is clearly shown in Fig. 5.

TABLE III. Estimated spontaneous radiative lifetimes (ns) and radiative width (cm^{-1}) (in italics) of the transitions from the $A\,^2\Pi$ state in the lower vibrational levels to the ground state $X\,^2\Sigma^+$ of ^{24}Mg^{19}F. Numbers in parentheses indicate the power of 10.

$\nu'=0$	$\nu'=1$	$\nu'=2$	$\nu'=3$	$\nu'=4$	$\nu'=5$	$\nu'=6$	Reference
7.96	7.90	7.87	7.88	7.90	7.93	7.95	This work
7.16	7.17	7.18	7.19	7.21	7.22		Ref. [26]
6.66(−4)	*6.71(−4)*	*6.73(−4)*	*6.73(−4)*	*6.71(−4)*	*6.68(−4)*	*6.67(−4)*	This work
7.40(−4)	*7.39(−4)*	*7.38(−4)*	*7.37(−4)*	*7.35(−4)*	*7.34(−4)*		Ref. [26]

TABLE IV. Estimated spontaneous radiative lifetimes τ (ns) ($\nu' = 0$) and wavelengths λ_{00} (nm) of the transitions from the $A\,^2\Pi$ state in the lower vibrational levels to the ground state $X\,^2\Sigma^+$ of the alkaline-earth-metal monofluorides and the alkaline-earth-metal monohydrides.

	λ_{00}	τ		λ_{00}	τ
BeF	305 [12]	7.9 [12]	BeH	497.2 [14]	82.0 [14]
MgF	359	7.96	MgH	525.5 [14]	48.6 [14]
CaF	606 [11]	19.2 [11]	CaH	675.4 [14]	33.3 [14]
SrF	663 [9]	22.6 [9]	SrH	740.3 [14]	33.2 [14]
RaF	710 [13]	25 [13]	BaH	952.6 [14]	68.6 [14]

SrF [9] and CaF [11] have been proved to be laser-cooling molecules using the transverse laser beam cooling and longitudinal laser beam cooling, respectively. BeF [12] and RaF [13] are predicted to be candidate laser-cooling molecules. We have conducted a detailed investigation on the alkaline-earth-metal monohydrides using the same method, indicating that MH (M = Be,Mg,Ca,Sr,Ba) species are laser-cooling candidates [14]. The alkaline-earth-metal monofluorides (BeF [12], MgF, CaF [11], SrF [9], and RaF [13]) and monohydrides all display diagonal FCFs and short spontaneous radiative lifetimes. From an atomic theoretical standpoint, the nondegenerate ground state and zero nuclear spin make alkaline-earth-metal atoms good candidates for the construction of ultracold molecules. Unfortunately, the alkaline-earth-metal monooxides are do not have diagonal FCFs nor short spontaneous radiative lifetimes [40]. Because Yb has an electronic structure similar to that of the alkaline-earth-metal atoms (a $^1S_0$ ground state and first excited state $^3P_1$), we can infer from the above content that the equivalent molecules BaF, YbF, and YbH seem to be potential laser-cooling candidates. Tarbutt *et al.* [41] have experimentally demonstrated laser cooling of the polar molecule YbF. In this paper, we present MgF, a similar Group-II alkaline-earth-metal monofluoride molecule, as a potential laser-cooling molecule candidate. MgF is a likely circumstellar molecule which is usually at low temperature [18]. This work is useful for investigating chemical reactions for the cold interstellar molecule MgF.

In addition, we compare the laser cooling parameters of the alkaline-earth-metal monofluorides with those the alkaline-earth-metal monohydrides in Table IV. As for the alkaline-earth-metal monofluorides, the spontaneous radiative lifetimes τ (ns) and wavelengths λ_{00} (nm) display a monotone increasing tendency as the molecule goes from light atoms to heavy atoms. For the alkaline-earth-metal monohydrides, the spontaneous radiative lifetimes τ (ns) present a similar trend; nevertheless, the wavelengths exhibit an initially decreasing and later increasing trend. Comparing the τ (ns) of the alkaline-earth-metal monofluorides to that of the alkaline-earth-metal monohydrides, we see that those of the alkaline-earth-metal monofluorides are shorter and therefore might offer better laser accessibility than the alkaline-earth-metal monohydrides in theory. The wavelengths are in the IR (CaH, SrH and BaH) red visible (BeH, MgH, CaF, SrF, and RaF), or UV (BeF, MgF) region. From the standpoint of certain applications, hydride compounds are undesirable because of their rotational transitions exceed 100 GHz [40].

IV. CONCLUSIONS

To investigate the feasibility of laser cooling the low-lying electronic states of MgF were calculated at the CASSCF/MRCI+Q level of theory, where Davidson modification with the Douglas-Kroll-Hess scalar relativistic correction was also taken into account. All the results are summarized as follows:

(1) The calculated spectroscopic constants (R_e,D_e,ω_e, B_e,T_e) are in good agreement with the available experimental data. The PDMs and TDM for the first excited $A\,^2\Pi$ state and the ground state $X\,^2\Sigma^+$ are also investigated.

(2) Using the PECs and TDM, the FCFs, radiative lifetimes, and radiative widths for the first seven vibrational levels ($\nu' = 0-6$) of the $A\,^2\Pi$ state as well as the wavelengths of the laser-driven cycling of the $A\,^2\Pi(\nu') \rightarrow X\,^2\Sigma^+(\nu)$ transition are determined. The transition provided highly diagonally distributed Franck-Condon factors. The radiative lifetimes are also sufficiently short to produce large spontaneous scattering forces. In summary, these results suggest that MgF is a promising laser-cooling molecule candidate.

(3) At the MRCI level, the $C\,^2\Sigma^+$ state is found to be a Rydberg state. The $B\,^2\Pi$ and $D\,^2\Sigma^+$ states are also reported, but still await experimental confirmation.

(4) The lower mass and shorter spontaneous radiative lifetimes make the MgF molecule more suitable for laser cooling than SrF and CaF molecules in principle.

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[1] L. D. Carr, D. DeMille, R. V. Krems, and J. Ye, New J. Phys. **11**, 055049 (2009).

[2] A. Micheli, G. Brennen, and P. Zoller, Nat. Phys. **2**, 341 (2006).

[3] D. DeMille, Phys. Rev. Lett. **88**, 067901 (2002).

[4] S. Eckel, P. Hamilton, E. Kirilov, H.W. Smith, and D. DeMille, Phys. Rev. A **87**, 052130 (2013).

[5] J. Baron *et al.* (The ACME Collaboration), Science **343**, 269 (2014).

[6] N. Balakrishnan and A. Dalgarno, Chem. Phys. Lett. **341**, 652 (2001).

[7] R. V. Krems, Phys. Chem. Chem. Phys. **10**, 4079 (2008).

[8] M. D. Di Rosa, Eur. Phys. J. D **31**, 395 (2004).

[9] E. S. Shuman, J. F. Barry, and D. DeMille, Nature (London) **467**, 820 (2010).

[10] M. T. Hummon, M. Yeo, B. K. Stuhl, A. L. Collopy, Y. Xia, and J. Ye, Phys. Rev. Lett. **110**, 143001 (2013).

[11] V. Zhelyazkova, A. Cournol, T. E. Wall, A. Matsushima, J. J. Hudson, E. A. Hinds, M. R. Tarbutt, and B. E. Sauer, Phys. Rev. A **89**, 053416 (2014).
[12] I. C. Lane, Phys. Chem. Chem. Phys. **14**, 15078 (2012).
[13] T. A. Isaev, S. Hoekstra, and R. Berger, Phys. Rev. A **82**, 052521 (2010).
[14] Y. F. Gao and T. Gao, Phys. Rev. A **90**, 052506 (2014).
[15] N. Wells and I. C. Lane, Phys. Chem. Chem. Phys. **13**, 19036 (2011).
[16] N. Wells and I. C. Lane, Phys. Chem. Chem. Phys. **13**, 19018 (2011).
[17] T. V. Ramakrishna Rao and S. V. J. Lakshman, Physica (Amsterdam) **46**, 609 (1970).
[18] M. A. Anderson, M. D. Allen, and L. M. Ziurys, Astrophys J. **425**, L53 (1994).
[19] F. A. Jenkins and R. Grinfeld, Phys. Rev. **45**, 229 (1934).
[20] C. A. Fowler, Jr., Phys. Rev. **59**, 645 (1941).
[21] R. F. Brarrow and J. R. Beale, Proc. Phys. Soc, London **91**, 483 (1967).
[22] L. B. Knight, Jr., W. C. Easley, W. Weltner, Jr., and M. Wilson, J. Chem. Phys. **54**, 322 (1971).
[23] T. E. H. Walker and W. G. Richards, J. Phys. B: At. Mol. Phys. **3**, 271 (1970).
[24] B. E. Barber, K.-Q. Zhang, B. Guo, and P. F. Bernath, J. Mol. Spectrosc. **169**, 583 (1995).
[25] M. A. Anderson, M. D. Allen, and L. M. Ziurys, J. Chem. Phys. **100**, 824 (1994).
[26] M. Pelegrini, C. S. Vivacqua, O. Roberto-Neto, F. R. Ornellas, and F. B. C. Machado, Braz. J. Phys. **35**, 950 (2005).
[27] H.-J. Werner and P. J. Knowles, J. Chem. Phys. **82**, 5053 (1985).
[28] P. J. Knowles and H.-J. Werner, Chem. Phys. Lett. **115**, 259 (1985).
[29] H. -J. Werner and P. J. Knowles, J. Chem. Phys. **89**, 5803 (1988).
[30] P. J. Knowles and H.-J. Werner, Chem. Phys. Lett. **145**, 514 (1988).
[31] S. R. Laughoff and E. R. Davidson, Int. J. Quantum Chem. **8**, 61 (1974).
[32] B. P. Prascher, D. E. Woon, K. A. Peterson, T. H. Dunning, Jr., and A. K. Wilson, Theor. Chem. Acc. **128**, 69 (2011).
[33] B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov, and P. -O. Widmark, J. Phys. Chem. A **108**, 2851 (2005).
[34] N. Douglas and N. M. Kroll, Ann. Phys (NY) **82**, 89 (1974).
[35] B. A. Hess, Phys. Rev. A **33**, 3742 (1986).
[36] H. -J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, P. Celani, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll *et al.*, *ab initio* computer program MOLPRO, version 2009.1, http://www.molpro.net.
[37] R. J. Le Roy, LEVEL 8.0, *A Computer Program for Solving the Radial Schrödinger Equation for Bound and Quasibound Levels*, Chemical Physics Research Report No. 663, University of Waterloo, Waterloo, ON, 2007.
[38] A. G. Gaydon, *Dissociation Energies* (Chapman and Hall, London, 1968).
[39] J. C. B. de Lima and F. R. Ornellas, J. Mol. Spectrosc. **283**, 22 (2013).
[40] J. F. Barry, Ph.D. thesis,Yale University, 2013.
[41] M. R. Tarbutt, B. E. Sauer, J. J. Hudson, and E. A. Hinds, New J. Phys. **15**, 053034 (2013).