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Determination of the normal A²II state in MgF with application to direct laser cooling of molecules

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ABSTRACT

We report high resolution electronic spectroscopy of cold magnesium monofluoride (MgF) molecules in the gas phase, which are created by a combination of laser ablation, chemical reaction, and 6 K helium buffer-gas cooling. Thanks to the sufficient population in the low-lying rotational states, the P, Q, and R branches in the electronic transition of the $X^2\Sigma^+$ to $A^2\Pi$ state are able to be measured unambiguously by in-cell absorption spectra. For the first time, we show that the $A^2\Pi$ state of MgF is actually a normal state, not an inverted one. The laser cooling relevant transitions $X^2\Sigma^+(v = 0, 1, N = 1) \rightarrow A^2\Pi_{1/2}(v = 0, J' = 1/2)$ are also identified, along with the hyperfine structure of the $X^2\Sigma^+(v = 0, N = 1)$ state. This study provides an important step for ongoing laser cooling experiments of MgF molecules.

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I. INTRODUCTION

Cold molecules are increasingly important for discovering new physics and chemistry, such as in the fields of ultracold collisions and controlled chemistry,¹⁻⁴ precision measurement,^{5.6} complex quantum systems under precise control,⁷⁻⁹ and so forth. Over the past 20 years, development of the cold molecule physics has progressed from traditional methods by taming molecules with electric and magnetic fields via the Stark decelerator¹⁰⁻¹² and the Zeeman decelerator¹³⁻¹⁵ to the laser cooling technique. Direct laser cooling, as a relatively new way to achieve ultracold molecules, has indeed progressed rapidly. For example, a few polar diatomic molecules as SrF,¹⁶ YO,¹⁷ and CaF^{18,19} have been successfully cooled and trapped by lasers, while other candidates (such as BaF,^{20,21} YbF,²² and BaH²³) are working in progress. Moreover, polyatomic molecules (such as $\rm SrOH,^{24}$ $\rm CH_3F,^{25}$ and $\rm H_2CO^{26})$ have also received significant attention.

In our group, we have found that magnesium monofluoride (MgF) molecule is also a good candidate, among others. This molecule has the following promising characteristics: (i) the Franck-Condon factors (FCFs) of the vibrational main transitions are very close to unity, that is to say, only two laser frequencies are required to construct the quasicycling transition; (ii) a strong spontaneous radiation decay ($\Gamma = 2\pi \times 22$ MHz) due to the short lifetime of the $A^2\Pi_{1/2}$ state; (iii) the pumping laser can be modulated into two sidebands through an electro-optic modulator (EOM) to cover the four sublevels of the $X^2\Sigma_{1/2}^+(v = 0, N = 1)$ state since the interval between the upper F = 2 and F = 1 levels of the $X^2\Sigma_{1/2}^+$ ground state is ~0.4 Γ ; and (iv) there is no intervening electronic state in the quasi-cycling transition.²⁷ used in laser cooling. In 1934, Jenkins and Grinfeld first measured the band heads and the partially resolved rotational structure for MgF in a high temperature heat pipe oven.²⁸ From their data, the spin orbit coupling constant could only be pinned down to two values A = -34.3 and A = +38.3 instead of one. This raises the question that which $A^2\Pi$ state is lower in energy. In 1967, Barrow and Beale analyzed the rotational structures in the 0-0, 1-0, and 0-1 vibrational bands of the two lowestlying electronic states of MgF molecules. The variation of the A-type doubling in the one component of the $A^2\Pi - X^2\Sigma^+$ transition suggested that the A²Π was an inverted state.²⁹ However, in 1969, Walker and Richards argued in theory that the $A^2\Pi$ state of MgF molecule was normal while they computed the spin-orbit coupling constants and Λ -type doubling parameters from Hartree-Fock wave functions.³⁰ Until now, the debate on whether the $A^2\Pi$ state is normal or inverted remains to be resolved, due to the lack of a good MgF sample. Fortunately, using the buffer gas cooling technique, an MgF molecular beam with low enough internal temperature can be obtained.

Herein, we report a solid and definitive study to clarify the long lasting issue–whether the $A^2\Pi$ state is normal or inverted. We first demonstrate the efficient creation of cold MgF molecules and then measure the P, Q, and R rotational branches in the $A^2\Pi - X^2\Sigma^+$ transition, so to confirm the assignment of the $A^2\Pi$ state. In Sec. II, we describe the experimental setup, including the 6 K cryogenic apparatus and the absorption measurement. In Sec. III, we analyze the absorption signal. We also calculate the P, Q, and R branches, which are related to laser cooling. Our results conclude that the $A^2\Pi$ state is a normal state. The main laser cooling transition and the repumping laser frequency are also identified. In Sec. IV, we give the measured hyperfine structure of the X (v = 0, N = 1) state, which reinforces our analysis.

II. CRYOGENIC SETUP AND ABSORPTION SIGNAL IN CELL

Figure 1(a) shows a portion of our cryogenic apparatus used in the experiment.³¹ We use a closed-cycle pulse tube refrigerator (Cryomech PT415), which consists of a 33 K first cold plate and a 6 K second cold plate. To prevent room temperature radiation from impinging directly upon the charcoal shields, a cylindrical copper is used to shield thermal radiation from the first stage. Inside the first radiation shield, surrounding the cell and attached to the 6 K cold head, are two half copper cylinders. The inner surface of the cylinders is attached with activated charcoal, which can efficiently absorb helium gas when being cooled down below 8 K. At a

distance of 40 mm away from the exit aperture of the cell, a charcoal-covered copper plate with 5 mm aperture is used to reduce the helium gas load into the rest of the system. The whole beam setup is placed into a stainless vacuum chamber, where a vacuum pressure of $\sim 2 \times 10^{-6}$ Pa under cryogenic temperature condition is maintained by a 1000 liter/s turbo pump.

We follow the cell design in Ref. 32 As illustrated in Fig. 1(b), cold MgF molecules are produced inside the cell by laser ablation of an Mg metal target (purity of 99.95%) in the presence of the SF_6 gas, which is found to be better than using an ablation target formed from a mixture of powders. Helium gas enters the cooling cell through an angled tube and is directed toward the laser ablation target. Before being injected into the cell, the helium gas is sequentially precooled to 33 K and 6 K through two copper cylinders which are mounted on the first and second cold plates, respectively. A pulsed Nd:YAG laser producing 10 ns duration and 17-19 mJ per pulse at 532 nm was used. The laser is focused to a $1/e^2$ diameter of 0.6 mm onto the Mg target by a lens of f = 75 cm. The room temperature SF_6 gas is fed into the vacuum chamber through a copper tube. At an atmospheric pressure, the melting point of SF₆ is 222 K. To prevent the gas from freezing, the SF_6 gas line is thermally insulated from the cooling cell by a polyimide spacer. Temperature sensors are directly attached to the cell and the point where SF_6 gas enters the cell to monitor the temperature. It takes roughly 1.5 h to cool the cell from room temperature to 6 K, and the polyimide spacer can maintain the SF_6 gas line to above 200 K, as shown in Fig. 1(c). During experiments, a heater is wrapped around the capillary to warm it up to 240 K, which has little influence on the temperature of the cell. The flow rate of the helium buffer gas can be adjusted from 1 to 10 sccm (standard cubic centimetres per minute) by using a flow meter. For SF_6 , a range of 0.035-2 sccm can be obtained. In a typical experiment, the flow rates for helium and SF_6 are 2 and 0.05 sccm, respectively.

An absorption spectrum was taken to detect and optimize the experimental conditions. The probe beam passes through the cell and is detected by using a photodetector (PD). Once the laser matches the molecular transitions in $A^2\Pi - X^2\Sigma^+$, a dip appears at the time trace of the PD signal. We normalized the absorption signal to the absorption fraction $c = 1 - I_{abs}/I_{avg}$, where I_{avg} is the mean value of the background signal. Figure 1(d) shows a typical absorption signal from a single shot of the ablation laser with the depletion efficiency ~50% at 834.290 295 THz (359.3 nm). According to our calculation, the Doppler broadening of MgF molecules at 6 K is 223 MHz, which is much larger than the hyperfine splitting of X (v = 0, N = 1) state.²⁷ However, for measurements of P, Q, and R transitions and finding the exact frequency for laser cooling, absorption spectroscopy is enough.

The ultraviolet (UV) laser used in our experiment is generated by doubling the frequency of a commercial Ti:sapphire laser (Matisse TS), which has a large tuning range (700–1030 nm) and high output power.³³ To stabilize the UV frequency, we locked the laser to a reference cavity. The absolute value of the wavelength is determined from an



FIG. 1. (a) A portion view of the cryogenic apparatus. Two shielding layers are attached to the first and the second stages of a pulse tube refrigerator, respectively. The buffer gas is precooled by using the 33 and 6 K copper cylinders before sending into the cell. The SF₆ line is thermally insulated from the cell with a polyimide spacer. Charcoal is used to pump helium gas at 6 K. (b) Scheme for absorption spectroscopy measurement. (c) The cooling process from room temperature to 6 K for the cell, along with the temperature curve of SF₆ line. (d) Normalized flipped absorption signal in cell at 359.3 nm.

ultrahigh-resolution wavemeter (HighFinesse WS-U), with an uncertainty of 30 MHz. We performed a wide range of frequency scan around 359.3 and 358.8 nm at a rate of 40 MHz/s and acquired the signal by using an oscilloscope (DSO 7062A) at a repetition of 2 Hz. These data were transferred to a computer system and processed for real time monitoring using Labview software.

III. P, Q, AND R TRANSITIONS OF THE A-X STATES

A. Theoretical model

The specific energy levels within the $A^2\Pi - X^2\Sigma^+$ electronic transition is labeled T_{ab} . T depends on the transition, ΔJ , a is for the excited state (either the $A^2\Pi_{1/2}$ or $A^2\Pi_{3/2}$ state), and b is for the initial value of J in the ground state. The transitions with $\Delta J = -1, 0, 1$ are assigned as T = P, Q, and R, respectively. For the normal $A^2\Pi$ state, if the transition reaches the $A^2\Pi_{1/2}$ state, a = 1; if the transition reaches the $A^2\Pi_{3/2}$ state, then a = 2. For the inverted $A^2\Pi$ state, the results are opposite. For the $X^2\Sigma$ state, if the transition originates from the J = N + 1/2 state, then b = 1; if the transition originates from the J = N - 1/2

state, then b = 2. If a = b, the second subscript is sometimes omitted. Transitions between the $A^2\Pi_{1/2}$ and the $A^2\Pi_{3/2}$ states are forbidden based on the selection rule of $\Delta\Sigma = 0$ in Hund's case (a).

The transitions of the A-X states can be expressed by

$$v = v_0 + F' - F, \tag{1}$$

$$F'_{1}(J) = B'_{\nu} \left[\left(J + \frac{1}{2} \right)^{2} - \Lambda^{2} - \frac{1}{2} \sqrt{4 \left(J + \frac{1}{2} \right)^{2} + Y(Y - 4) \Lambda^{2}} \right] - D_{\nu} J^{4}, \quad (2a)$$

$$F'_{2}(J) = B'_{\nu}\left[\left(J + \frac{1}{2}\right)^{2} - \Lambda^{2} + \frac{1}{2}\sqrt{4\left(J + \frac{1}{2}\right)^{2}} + Y(Y - 4)\Lambda^{2}\right] - D_{\nu}(J + 1)^{4},$$
(2b)

$$F_1(N) = B_v N(N+1) + \frac{1}{2} \gamma N,$$
 (3a)

$$F_2(N) = B_v N(N+1) + \frac{1}{2}\gamma(N+1),$$
(3b)

where $Y = A/B'_{\nu}$ and subscripts 1 and 2 represent the J = N + 1/2 and J = N - 1/2 states, respectively. B_{ν} , D_{ν} , Λ , and γ accordingly correspond to the molecular rotational constant, the



FIG. 2. (a) Diagram of energy levels for the $A^2\Pi - X^2\Sigma^+$ transitions for a normal $A^2\Pi$ state of MgF molecules. The ± labels indicate the parity quantum numbers of each state. (b) The corresponding calculated bands of the $A^2\Pi - X^2\Sigma^+$ system, with the constant A = 38.30 cm⁻¹; the other relevant parameters used in equations can be found in the context.

centrifugal distortion constant, the axial components of the electronic orbital angular momentum, and the spin-rotational coupling constant, respectively. Since the constant D_v is negligible compared with B'_v , the last term in Eq. (2) is skipped in the following calculation. With A > 0, the $A^2\Pi$ state is a normal state. With A < 0, it forms an inverted state. For a normal state, F'_1 and F'_2 represent the $A^2\Pi_{1/2}$ and $A^2\Pi_{3/2}$ states, respectively.

For an inverted state, they represent the $A^2\Pi_{3/2}$ and $A^2\Pi_{1/2}$ states, respectively.

Figure 2(a) shows the transitions from the $X^2\Sigma$ state to a normal $A^2\Pi$ state and their labeling. For simplicity, only transitions from the first rotational state of the P, Q, and R branches are shown. For an inverted $A^2\Pi$ state, a similar energy level diagram can be seen in Fig. 3(a) except that the initial rotation



FIG. 3. (a) Diagram of energy levels for the $A^2\Pi - X^2\Sigma^+$ transitions for an inverted $A^2\Pi$ state of MgF molecules. The \pm labels indicate the parity quantum numbers of each state. (b) The corresponding calculated bands of the $A^2\Pi - X^2\Sigma^+$ system, with the constant A = -34.3 cm^{-1} ; the other relevant parameters used in equations can be found in the context.

quantum numbers of the same branches are different from the normal ones. These differences are attributed to the different initial spin-rotation quantum numbers between the $A^2\Pi_{1/2}$ and $A^2\Pi_{3/2}$ states and the selection rule. The experimental spectroscopic constants in Ref. 28 are used, which includes $v_0 = 27\ 846.5\ \text{cm}^{-1}$, $A = 38.3\ \text{or} -34.3\ \text{cm}^{-1}$, $B'_v = 0.5287\ \text{cm}^{-1}$, $B_v = 0.5180\ \text{cm}^{-1}$, and $\gamma = 0.001\ \text{691}\ \text{cm}^{-1}$.

Figures 2(b) and 3(b) show the calculated spectra of the normal and inverted states, respectively. In the figures, the y axis is the rotational quantum numbers of the ground state, N, and the x axis is the frequency of the $A^2\Pi - X^2\Sigma^+$ transitions. If we assume the A state as normal, we do not see these branches such as $P_1(0)$, $P_{12}(0)$, and $P_{12}(1)$ associated with the $A^2\Pi_{1/2}-X^2\Sigma_{1/2}$ transitions, as well as P₂(0), P₂(1), P₂(2), Q₂(0), Q₂(1), and R₂(0) with the $A^2\Pi_{3/2}-X^2\Sigma_{1/2}$ transitions. The P₁, Q1, Q2, and R2 branches accordingly overlap with the Q12, R_{12} , P_{21} , and Q_{21} branches, which are not resolved in our experiments. On the other hand, if we assume the A state as inverted, in fact we do not observe the branches such as $P_1(0)$, $P_1(1)$, $P_{12}(0)$, $P_{12}(1)$, $P_{12}(2)$, and $Q_1(0)$ of the $A^2\Pi_{3/2} - X^2\Sigma_{1/2}$ transitions, as well as P₂(0), P₂(1), and Q₂(0) of the $A^2\Pi_{1/2}-X^2\Sigma_{1/2}$ transitions. The difference in the unseen branches associated with the normal or inverted state case can be used to determine the characteristic of the A state.

B. A normal or inverted $A^2\Pi$ state?

Figure 4(a) shows the measured absorption spectrum of MgF around 359.3 nm with transitions in blue vertical line and the simulated ones in red point. With an offset of 0.074422 THz, the spectra lines agree well with the calculated ones. This shift may be because the constants used in the equations are determined by measuring the high-lying rotational states. Taking the P₁(1) line, its peak width is 463 MHz. There are also a series of weaker absorption lines between the main peaks, which may be from the isotopes of magnesium since the abundance ratios of 24 Mg, 25 Mg, and 26 Mg are 7:1:1. Here, we focus on 24 Mg. The sequences in the P₁ and Q₁ branches are nearly

the same, with a space of ~15 GHz. As the angular momentum (N) increases, the sequence in the P₁ branch gets smaller, while the sequence in the Q₁ branch becomes bigger. The sequences in the P₁₂ and R₁ branches are also close to each other, which are ~46 GHz. When the angular momentum (N) increases, the sequence in the P₁₂ branch gets smaller, while the sequence in the R₁ branch becomes bigger. This trend is consistent with the characteristics of the vibration-rotation spectra of ${}^{2}\Pi {-}^{2}\Sigma$ transition of a diatomic molecule. The frequency difference between P₁(1) and Q₁(0) is quite large, around 31 GHz. The most intense peak is Q₁(2). This shows that most molecules populate at the N = 2 state in the 6 K cell. We only measured the transitions up to N = 8 because the signal becomes much worse at higher rotational numbers.

For the electronic transition near 358.8 nm, after a correction of -0.006113 THz, the results between calculations and measurements agree well, as shown in Fig. 4(b). The sequence in the Q₂ branch varies from 13 to 8 GHz as N increases. This is because the sequence is gradually close to the band head of the branch and finally is reversed, seen in red squares of the theoretical results. When N increases, the sequence in the R₂ branch varies from 18 to 24 GHz, while the sequence in the R₂₁ branch varies from 49 to 55 GHz. For the P₂ branch, we only measured the two lines [P₂ (3) and P₂ (4)] and the spacing between the two lines is about 44 GHz. The frequency difference between Q₂ (2) and R₂ (1) is also quite large, around 62 GHz.

Which of the two components of the upper state is $A^2\Pi_{1/2}$ and which is $A^2\Pi_{3/2}$ -that is, whether the $A^2\Pi$ term is normal or inverted-can be decided in which one can use the fact that the missing lines in the neighborhood of the zero gap are different for the two sub-bands.³⁴ We simulate the spectrum with the A state as an inverted state, we find that the agreement between the measured spectral lines (the blue lines in Fig. 5) and simulated ones (red points in Fig. 5) becomes much worse, especially for the P₁₂ and R₁ branches associated with the $A^2\Pi_{3/2}-X^2\Sigma_{1/2}$ transitions and the P₂ and



FIG. 4. Measured and calculated spectra of the $A^2\Pi - X^2\Sigma^+$ transition in the cryogenic cell. (a) around 834.3 THz (359.3 nm) and (b) around 835.5 THz (358.8 nm). Blue lines show the measured spin-rotation transitions, while red points represent the calculated ones assuming the normal *A* state. The overlapped branches have the same shape, like P_1/Q_{12} of squares, which cannot be resolved from our experiments.



FIG. 5. Measured and calculated spectra of the $A^2\Pi - X^2\Sigma^+$ transition in the cryogenic cell. (a) around 834.3 THz (359.3 nm) and (b) around 835.5 THz (358.8 nm). Blue lines show the measured spin-rotation transitions, while red points represent the calculated ones assuming the inverted A state. The overlapped branches have the same shape, like P₁/Q₁₂ of squares, which cannot be resolved from our experiments.

 R_{21} branches with the $A^2\Pi_{1/2}-X^2\Sigma_{1/2}$ transitions, as shown in Fig. 5. For Q_1/R_{12} branches with the $A^2\Pi_{3/2}-X^2\Sigma_{1/2}$ transitions in Fig. 5(a), there are additional observed lines, 834.321 391 THz and 834.336 941 THz, which cannot be assigned, while for R_2/Q_{21} branches with the $A^2\Pi_{1/2}-X^2\Sigma_{1/2}$ transitions in Fig. 5(b), there are unobserved lines, such as 835.367 169

THz and 835.384 407 THz, which are actually predicted by theory. All these features further confirm that the A state is not inverted. So, according to the criteria of Herzberg,³⁴ the $A^2\Pi$ state shall be a normal state.

The exact frequency values by experiments in Fig. 4 for P, Q, and R branches are listed in Tables I and II. N represents the rotational quantum number of the ground state, which

TABLE I. Measured and calculated transitions for P, Q, and R branches for the transition $X^2\Sigma$ to $A^2\Pi_{1/2}$. The column on the right summarizes the energy differences between the observed and calculated lines.

	N	Obs. (THz)	Cal. (THz)	O-C
P_1/Q_{12}	1	834.290 295	834.215 873	0.074 422
	2	834.274 986	834.200 620	0.074366
	3	834.259756	834.185 570	0.074186
	4	834.244729	834.170725	0.074004
	5	834.229734	834.156 090	0.073644
	6	834.214772	834.141667	0.073105
	7	834.200 095	834.127 463	0.072632
	8	834.185405	834.113 484	0.071921
Q_1/R_{12}	0	834.321391	834.246 957	0.074 434
C - <i>7</i>	1	834.336941	834.262762	0.074179
	2	834.352714	834.278771	0.073943
	3	834.368 630	834.294 985	0.073 672
	4	834.384606	834.311407	0.073199
	5	834.400 684	834.328 043	0.072 641
	6	834.417 003	834.344 898	0.072105
	7	834.433 427	834.361977	0.071450
	8	834.450 007	834.379288	0.070719
R _I	0	834.368 012	834.293 846	0.074166
1	1	834.414 625	834.340 913	0.073712
	2	834.461391	834.388186	0.073205
	3	834.508 575	834.435676	0.072 899
	4	834.555744	834.483 361	0.072 383
P ₁₂	2	834.228 356	834.153 875	0.074 481
	3	834.182137	834.107597	0.074540
	4	834.135 968	834.061539	0.074429
	5	834.089972	834.015686	0.074286

hetween the cheered and calculated lines
sition $X^2\Sigma$ to $A^2\Pi_{3/2}$. The column on the right summarizes the energy differences
TABLE II . Measured and calculated transitions for P, Q, and R branches for the tran-

	Ν	Obs. (THz)	Cal. (THz)	O-C
P ₂	3	835.243 244	835.249141	-0.005 897
-	4	835.199 508	835.205 281	-0.005773
Q ₂ /P ₂₁	2	835.336178	835.342291	-0.006 113
	3	835.323 298	835.329490	-0.006192
	4	835.311458	835.317767	-0.006309
	5	835.300 847	835.307118	-0.006271
	6	835.291261	835.297540	-0.006279
	7	835.282 544	835.289 025	-0.006481
	8	835.274799	835.281569	-0.00677
R_2/Q_{21}	1	835.398206	835.404382	-0.006176
	2	835.416 307	835.422 640	-0.006333
	3	835.435 454	835.441976	-0.006522
	4	835.455 687	835.462386	-0.006699
	5	835.476 928	835.483 865	-0.006937
	6	835.499215	835.506 409	-0.007194
	7	835.522 566	835.530 012	-0.007446
	8	835.547 098	835.554666	-0.007568
R ₂₁	0	835.429203	835.435390	-0.006187
	1	835.478 293	835.484656	-0.006363
	2	835.528 421	835.534999	-0.006578
	3	835.579 671	835.586 417	-0.006746
	4	835.631737	835.638904	-0.007167
	5	835.685 015	835.692456	-0.007441
	6	835.739286	835.747 066	-0.00778
	7	835.794 561	835.802728	-0.008167

TABLE III. The fitted parameters by the methods of Ref. 34, in contrast with the results of Refs. 28 and 29.

	B_{v}^{\prime} (cm ⁻¹)	B_v (cm ⁻¹)	A (cm ⁻¹)	$v_0 ({ m cm}^{-1})$
Our results Previous results	0.526 4 0.519 41 ²⁹ 0.528 7 ²⁸	0.5171 0.516 87 ²⁹ 0.518 0 ²⁸	36.406 -34.3 ²⁹ 38.3/-34.3 ²⁸	27 830.0 27 829.6 ²⁹ 27 846.5 ²⁸

is from 0 to 8, and O–C represents the frequency difference between the observed and calculated lines. From the tables, these three branches are located near 834 and 835 THz, which corresponds to the electronic transition of X to A states. The measured values are away from the calculated ones only by about 0.074 540 and -0.008167 THz when we consider A as the normal state. If we assume A as the inverted state, the measured values are much further away from the calculated ones.

From Table I, the transition of $X^2 \Sigma_{1/2}(v = 0, N = 1)$ $\rightarrow A^2 \Pi_{1/2}(v = 0, J' = 1/2, e)$ for laser cooling of MgF is the P₁(1) branch, and the exact frequency is 834.290 295 THz. Similarly, we also measure the transition of $X^2 \Sigma_{1/2}(v = 1, N = 1) \rightarrow A^2 \Pi_{1/2}(v = 0, J' = 1/2, e)$, which is 812.959 242 THz. Now, we obtained the two values of frequency for constructing the quasi-closed cycling transitions of MgF, that is, one cooling laser $\lambda_{00} = 359.3$ nm and one repumping laser λ_{10} = 368.7 nm. Thanks to the favorable FCFs ($f_{00} = 0.9978$, $f_{01} = 0.0022, f_{03} < 10^{-4}$), only two laser beams can obtain more than 10⁴ photons, which is sufficient to stop and cool the MgF beam extracted from the buffer gas source.²⁷

Table III lists a set of new fitting parameters (the rotational constant of the $A^2\Pi$ state B'_v , the rotational constant of the $X^2\Sigma^+$ state B_v , the spin orbit coupling constant A, and the zero lines v_0) obtained from our measured spectral data, along with the experimental results of Refs. 28 and 29. The specific fitting formula can be found in spectral theory of diatomic molecules.³⁴ With the fitted spin orbit coupling constant A = 36.406, the $A^2\Pi$ state is a normal state, and the diagram of energy levels for the $A^2\Pi - X^2\Sigma^+$ transitions is shown in Fig. 2(a).

IV. HYPERFINE STRUCTURE MEASUREMENTS

To support our conclusion that the A state of MgF is a normal state, we measured the laser induced fluorescence (LIF) of the molecules with a low-power Doppler insensitive probe beam at 90° with respect to the molecular beam propagation. The laser beam is about 30 cm away from the exit of the cell. We focus on the main cooling transitions of $X^2\Sigma_{1/2}(v = 0, N = 1)$ to $A^2\Pi_{1/2}(v = 0, J' = 1/2, e)$, which are the P₁(1)/Q₁₂(1) branches in Table I. Figure 6(a) shows the energy levels. The hyperfine splitting of the $X^2\Sigma_{1/2}$ ground state with J = 1/2 is ~120 MHz, while the splitting between the F = 0 (J = 1/2) and the F = 1 (J = 3/2) levels is ~110 MHz. The splitting of J = 3/2 is ~9 MHz, which is within the spontaneous emission rate and cannot be resolved in our experiments. The hyperfine splitting within the excited $A^2\Pi_{1/2}$ state is only a few MHz, which is not resolvable. Figure 6(b) shows the LIF spectra of the transition $X^2\Sigma_{1/2}(v = 0, N = 1) \rightarrow A^2\Pi_{1/2}(v = 0, J' = 1/2, e)$. There are three observed peaks, which are labeled p1, p2, and p3, respectively. The p1 peak is the most intense peak and is assigned from the transition of X (J = 3/2, F = 1, 2) \rightarrow A (v = 0, J' = 1/2). The p2 peak is from the transition of X (J = 1/2, F = 0) \rightarrow A (v = 0, J' = 1/2); although it is weak, it is also resolvable. The remaining peak with moderate intensity is from the transition of X (J = 1/2, F = 1) \rightarrow A (v = 0, J' = 1/2). The spacing between the p1 and p2 peaks is ~112 MHz, which is consistent with the theoretical values.²⁷



FIG. 6. (a) Hyperfine-structure levels of the main cooling transition of MgF molecule. The hyperfine levels for N = 1 are shown. Because of the parity selection rule, the transitions from X(N = 1) to A(J' = 1/2, e) is allowed. (b) LIF spectra of the transition from X(N = 1) to A(J' = 1/2, e). The red curve is from a Gaussian fitting.

V. CONCLUSIONS AND PERSPECTIVES

In summary, we have generated the cold MgF molecules by combining the laser ablation and chemical reaction, and cryogenic buffer-gas cooling. The P, Q, and R branches of the electronic transition of $A^2\Pi - X^2\Sigma$ have been measured. The $A^2\Pi$ state of MgF is determined to be a normal state. The laser cooling relevant transition $X^2\Sigma_{1/2}(v = 0, 1, N = 1)$ to $A^2\Pi_{1/2}(v = 0, J' = 1/2, e)$ and the hyperfine splitting of X (v = 0, N = 1) are also measured.

As far as we know, the monofluorides formed by group II atoms and fluorine are the suitable candidates for direct laser cooling and trapping, such as MgF,²⁷ CaF,^{18,19} SrF,¹⁶ and BaF.²⁰ There are not enough spectral data to prove that RaF can be directly laser cooled. For the nature of the $A^2\Pi$ state relevant to laser cooling, the structures of CaF, SrF, and BaF are normal states,³⁵ but for BeF, it is inverted state.³⁶ Here, we report the direct observation of spectroscopy of MgF in the low-lying rotational states to conclude that the $A^2\Pi$ state is a normal state. This leads us to further push for achieving laser cooling of MgF molecules.

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