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Franck-Condon Factors and Band Origins for MgH in the $A^2\Pi$-$X^2\Sigma^+$ System

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We measure the dispersed spectrum of the $A^2\Pi$-$X^2\Sigma^+$ system of MgH using laser ablation/laser induced Fluorescence method and obtain the Frank-Condon factors and related transition frequencies of the $A^2\Pi(v'=0)$-$X^2\Sigma^+(v''=0,1)$ system by analyzing the experimental spectrum. Also, we calculate the Franck-Condon factors and transition frequencies of the $A^2\Pi$-$X^2\Sigma^+$ system of MgH. A comparison of our theoretical calculation and experimental results with other reported theoretical results was carried out as well.

Key words: Franck-Condon factors, Energy curve, Vibrational frequencies, Dispersed fluorescence

I. INTRODUCTION

Magnesium hydride, MgH, is a molecule of considerable astrophysical importance which exsits in the photosphere of the sun and the atmosphere of cool stars [1, 2]. It has prominent features in the spectra of certain galaxies and is used as an indicator of relative magnesium isotopes abundance in stellar atmosphere [3]. Efforts have also been made to search for MgH in interstellar clouds [4].

A bunch of experimental investigations on the $A^2\Pi$ and $X^2\Sigma^+$ states of MgH were made. The first high resolution absorption spectra of $A^2\Pi$-$X^2\Sigma^+$ were measured by Balfour in 1970 [5, 6]. Then, the high resolution Fourier transform spectroscopy was carried out by Bernath and his coworkers [7]. Five years later, several of the lower rotational transitions of MgH were observed by Zink *et al.* [8]. Then Ziury *et al.* studied the millimeterwave spectrum of the ground electronic state of MgH in 1993 [9].

As one of the quite simple three valence electrons molecules, the potential energy curves of the ground and several low excited states of MgH have been investigated [10–13]. Popkie gave the MgH ($A^2\Pi$-$X^2\Sigma^+$) energy curves based on Hartree-Fock (HF), multi-configuration (MC) and Rydberg-Klein-Rees (RKR) methods [10]. Kirby *et al.* [11] and Mestdagh *et al.* [12] used the state-averaged MRCI and MCSCF+MRCI methods to get the ground and excited energy curves of the MgH. Shayesteh *et al.* got the potential energy curves of the $A^2\Pi$ and $X^2\Sigma^+$ states of MgH using MRCISD method [13].

Since the first diatomic molecule SrF was successfully cooled in experiment by using laser cooling method in DeMille's group [14, 15], laser cooling was applied to beams of YO [16] and CaF [17]. Other promising molecules for laser cooling are searched. One of the requirements for possible laser cooling molecules is that the molecules should have a perfect closed molecular cycling transition. But there is no completely closed transition in a real molecule system because of their complex internal structures. Secondly, a molecule which can be successful cooled by laser cooling requires that its excited state has a relative short lifetime, so it can complete enough absorption and emission cycles before leaving the laser interaction region. Also, a highly-diagonal Frank-Condon array is required for the band system [18]. Some possible laser cooling molecules of TiF [19], AlH and AlF [20] were proposed.

Here, we measure and analysize the dispersed fluorescence spectrum of MgH $A^2\Pi(v'=0)$-$X^2\Sigma^+(v''=0,1)$ transition, calculate the Franck-Condon factors (FCF) and transition frequencies in the $A^2\Pi$-$X^2\Sigma^+$ system of MgH. We also compare our experimental results and theoretical calculation with other theoretical results for exploring the possibility of laser cooling of MgH using Robert J. Le Roy's LEVEL program [21].

II. EXPERIMENTS

The experimental setup was similar to that used in studies of the visible bands [22, 23]. A pulsed neodymium-doped yttrium aluminum garnet laser ablated a continuously rotating magnesium sample rod in a supersonic expansion of pure H_2 to generate MgH molecule. A relatively high backing pressure of approximately 20 atm was used to cool the molecules to a rotational temperature of less than 20 K. Charged par-

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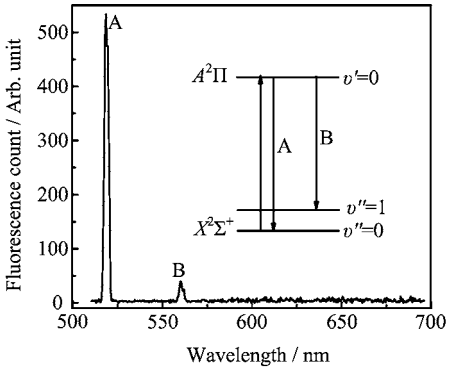

FIG. 1 A portion of the dispersed LIF signal resulting from the excitation of the MgH R(1/2) line in the (0,0) band of the $A^2\Pi$-$X^2\Sigma^+$ system at 19287.365 cm^{-1}. The monochromator had a spectral resolution of 10 Å. A: $A^2\Pi(v'=0)\rightarrow X^2\Sigma^+(v''=0)$ transition, B: $A^2\Pi(v'=0)\rightarrow X^2\Sigma^+(v''=1)$ transition.

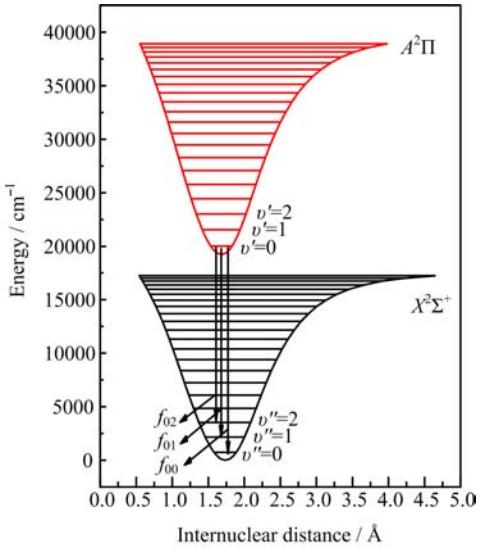

FIG. 2 The potential energy curves together with the vibrational levels of the $X^2\Sigma^+$ and $A^2\Pi$ states of MgH, the down arrows indicating the vibronic transitions.

ticles generated in the ablation process were removed by exposing the supersonic expansion to a electrostatic field just prior to the skimmer. The molecular beam was crossed by a single frequency dye laser approximately 15 cm downstream from the source. The dispersed fluorescence of the (0,0) band in the $A^2\Pi$-$X^2\Sigma^+$ system near 520 nm was selected for measurements. The resulting dispersed fluorescence signal was viewed through a 2/3 m monochromator, detected with a water-cooled photomultiplier tube and finally processed with a photon counter (SRS 400). The monochromator had a spectral resolution of 10 Å. The absolute wavenumbers were determined by simultaneously recording the sub-Doppler absorption spectrum of I_2 [24, 25].

A portion of the observed dispersed LIF signal, resulting from excitation of the R(1/2) line in the (0,0) band of the $A^2\Pi$-$X^2\Sigma^+$ system at 19287.365 cm^{-1} (518.47 nm), is presented in Fig.1. The slits of the monochromator were adjusted to give a spectral resolution of 10 Å. No spectrum in the blue of the excitation wavelength was observed, confirming that the lower state associated with the transition is the $X^2\Sigma^+$ ground state. The observed feature in the red excitation wavelength at 560.20 nm shown in Fig.1 belongs to $A^2\Pi(v'=0)$-$X^2\Sigma^+(v''=0,1)$. No other feature is seen in current experimental condition.

III. RESULTS AND DISCUSSION

In this work, potential energy curves of the ground ($X^2\Sigma^+$) and first excited ($A^2\Pi$) states of the MgH molecule are calculated using RKR method, which was developed by RKR methods [26–28].

The potential energy of interaction between Mg and H atom can be written as

$$U(R,L) = V(R) + \frac{K^2}{R} \tag{1}$$

$$K = \frac{L^2}{2\mu} \tag{2}$$

where μ is reduced mass, L is orbital angular momentum.

The resulting potential energy curves of the $X^2\Sigma^+$ and $A^2\Pi$ states of MgH are shown in Fig.2.

Table I lists the calculated FCFs and their related band origins of the $A^2\Pi$-$X^2\Sigma^+$ system of MgH. The FCF matrix is highly diagonal, the $A^2\Pi(v'=0)$-$X^2\Sigma^+$ (v''=0,1) transitions could provide a good cycling transition and the leakage to other vibraional levels is very similar to that of SrF molecules [14, 15]. The band origins of the (0,0) and (0,1) bands in the $A^2\Pi$-$X^2\Sigma^+$ system are experimentally determined to be 518.47 and 560.20 nm respectively. Our theoretical calculation gives the corresponded frequencies as 19278.676 cm^{-1} (518.70 nm) and 17847.254 cm^{-1} (560.31 nm) which are in good agreement with the experimental values.

Evidently, both the experimental and the calculated FCFs data (listed in Table II) indicate that the (0,0) band of $A^2\Pi$-$X^2\Sigma^+$ system of MgH has the largest FCF, while the (0,1), (0,2) and (0,3) bands are all much less, at least an order of magnitude less. In experimental conditions, the v'=0→v''=2,3 transition probabilities are too weak to be measured. Popkie's theoretical multiconfiguration (MC) and RKR methods give the FCF of v'=0→v''=0 of 0.962 and 0.944, respectively. Our experimental and calculated results are 0.94 and 0.944. Our results are in good agreement with those of Popkie *et al.* [31].

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TABLE I The Franck-Condon factors and band origins in the $A^2\Pi(v')$-$X^2\Sigma^+(v'')$ system of MgH calculated using RKR potential derived from the spectroscopic parameters of Ref.[29].

v'	v''=0	v''=1	v''=2	v''=3	v''=4	v''=5
			FCF			
0	$9.44(6)\times10^{-1}$	$5.51(0)\times10^{-2}$	$1.45(1)\times10^{-4}$	$1.28(2)\times10^{-4}$	$4.49(5)\times10^{-6}$	$9.55(6)\times10^{-7}$
1	$5.09(9)\times10^{-2}$	$8.45(3)\times10^{-1}$	$1.02(6)\times10^{-1}$	$5.08(6)\times10^{-4}$	$4.82(7)\times10^{-4}$	$3.10(1)\times10^{-5}$
2	$4.27(3)\times10^{-3}$	$8.80(2)\times10^{-2}$	$7.61(6)\times10^{-1}$	$1.43(5)\times10^{-1}$	$1.18(3)\times10^{-3}$	$1.11(6)\times10^{-3}$
3	$1.15(8)\times10^{-4}$	$1.11(7)\times10^{-2}$	$1.15(1)\times10^{-1}$	$6.90(0)\times10^{-1}$	$1.78(8)\times10^{-1}$	$2.28(4)\times10^{-3}$
4	$1.06(6)\times10^{-7}$	$3.41(4)\times10^{-4}$	$1.97(9)\times10^{-2}$	$1.35(0)\times10^{-1}$	$6.27(6)\times10^{-1}$	$2.09(0)\times10^{-1}$
5	$7.24(7)\times10^{-7}$	$1.46(0)\times10^{-6}$	$6.26(1)\times10^{-4}$	$2.96(7)\times10^{-2}$	$1.50(0)\times10^{-1}$	$5.72(1)\times10^{-1}$
			Band origin/cm^{-1}			
0	19278.7	17847.2	16479.6	15175.8	13935.6	12759.3
1	20814.7	19383.3	18015.6	16711.7	15471.7	14295.4
2	22288.5	20857.1	19489.5	18185.6	16945.5	15769.2
3	23700.2	22268.8	20901.2	19597.3	18357.2	17180.9
4	25049.8	23618.3	22250.7	20946.8	19706.7	18530.4
5	26337.1	24905.7	23538.1	22234.2	20994.1	19817.8

TABLE II The Franck-Condon factors in the $A^2\Pi(v')$-$X^2\Sigma^+(v'')$ system of MgH calculated.

	FCF			
	(0,0)	(0,1)	(0,2)	(0,3)
Expt.	0.94	0.06		
Calc.	0.944	0.055	0.145×10^{-3}	0.128×10^{-3}
Ref.[10]	1.000[a]	0.546×10^{-1}	0.405×10^{-2}	0.396×10^{-3}
Ref.[10]	1.000[b]	0.376×10^{-1}	0.207×10^{-2}	0.145×10^{-3}

[a] RKR $q_{v'v''}/q_{00}$ (q_{00}=0.944).
[b] Theoretical $q_{v'v''}/q_{00}$ (q_{00}=0.962).

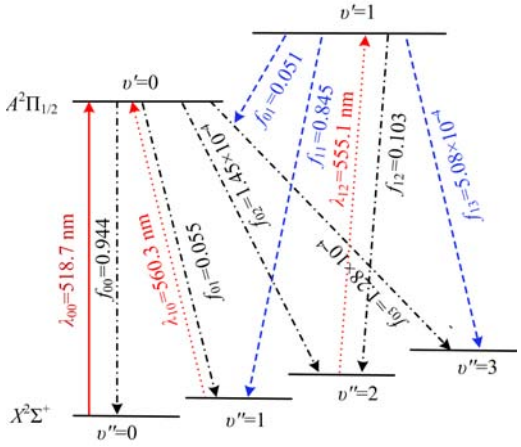

FIG. 3 The possible laser cooling scheme for $A^2\Pi\rightarrow X^2\Sigma^+$ system of MgH molecule. Upward lines indicate the laser-driven transitions with wavelengths $\lambda_{v''v'}$. Downward lines indicate spontaneous decay from the excited state $A^2\Pi$ to ground state $X^2\Sigma^+$ with the calculated FCFs $f_{v''v'}$. Upward solid line means the main cooling cycle, and upward dotted lines are the proposed repump lasers.

Following the argument of DeMille [15] we would propose a three-laser-cyclic system involving the v''=0−2 of the $X^2\Sigma^+$ state, and v'=0,1 of the $A^2\Pi_{1/2}$ state, as shown in Fig.3. The main cooling transition is set up for the $A^2\Pi(v'=0)\leftarrow X^2\Sigma^+(v''=0)$ transition with FCF of 0.944. A couple of repump lasers are required to reclaim molecules decay from $A^2\Pi(v'=0)\rightarrow X^2\Sigma^+(v''=1)$ (FCF≈0.056) and $A^2\Pi(v'=1)\rightarrow X^2\Sigma^+(v''=2)$ (FCF≈0.103) respectively. Our experimental and calculated results show the $A^2\Sigma(v'=0)\leftarrow X^2\Sigma^+(v''=0)$ FCF of 0.944 is not as large as that predicted in SrF (0.98) [15], CaF (0.972) [18] and AlH (0.965) [20], but it is much larger than that of TiF (0.89) [19]. So, the FCF of $A^2\Pi(v'=0)\leftarrow X^2\Sigma^+(v''=0)$ is still sufficiently large to be possible for laser cooling.

The lifetime of the $A^2\Pi(v'=0)$ state of MgH was measured in experiment as 43.6±3 ns by Dufayard [29]. Pokie [10, 31] gives the theoretical value of the $A^2\Pi(v'=0)$ lifetime is 41 ns which is in agreement with Dufayard's experimental result [30]. So the excited state $A^2\Pi$ of MgH has a relative short lifetime, it can complete enough absorption and emission cycles before leaving the laser interaction region. It is suitable for laser cooling experiment.

IV. CONCLUSION

The dispersed fluorescence spectrum of the MgH R(1/2) line in the (0,0) band of the $A^2\Pi$-$X^2\Sigma^+$ system has been measured to obtain the FCFs of v'=0→v''=0 and v'=0→v''=1. The potential energy of MgH have

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been calculated using RKR method. And the FCFs of the $A^2\Pi(v'=0-5)$-$X^2\Sigma^+(v''=0-5)$ of the MgH has been calculated using LEVEL program. The theoretical calculation demonstrates a highly diagonal transition. By comparing the experimental results and the calculated ones, we can see that the $A^2\Pi \rightarrow X^2\Sigma^+$ transition of MgH looks quite promising for laser cooling. According to the experimental and theoretical results, the main laser and two repump lasers are 518.7, 560.3, and 555.1 nm, respectively. All of these lasers source are in visible range, and can be obtained easily.

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[1] A. Fowler, Mon. Not. R. Astron. Soc. **67**, 530 (1907).
[2] P. F. Weck, A. Schweitzer, P. C. Stancil, P. H. Hauschildt, and K. Kirby, Astrophys. J. **582**, 1059 (2003).
[3] S. M. Faber, *The Evolution of Galaxies and Stellar Population*, B. Tinsley and R. Larson Eds., New Haven: Yale Univ. Obs., 157 (1977).
[4] T. E. Sharp and H. M. Rosenstock, J. Chem. Phys. **41**, 3453 (1964).
[5] W. J. Balfour, Astrophys. J. **162**, 1031 (1970).
[6] W. J. Balfour, J. Phys. B **3**, 1749 (1970).
[7] P. F. Bernath, J. H. Black, and J. W. Brault, Astrophys. J. **298**, 375 (1985).
[8] L. R. Zink, D. A. Jennings, K. M. Evenson, and K. R. Leopold, Astrophys. J. Lett. **359**, L65 (1990).
[9] L. M. Ziurys, W. L. Jr. Barclay, and M. A. Anderson, Astrophys. J. Lett. **402**, 21 (1993).
[10] H. E. Popkie, J. Chem. Phys. **54**, 4597 (1971).
[11] R. P. Saxon, K. Kirby, and B. Liu, J. Chem. Phys. **69**, 5301 (1978).
[12] J. M. Mestdagh, P. de Pujo, B. Soep, and F. Spiegelman, Chem. Phys. Lett. **471**, 22 (2009)
[13] M. Mostafanejad and A. Shayesteh, Chem. Phys. Lett. **551**, 13 (2012)
[14] E. S. Shuman, J. F. Barry, D. R. Glenn, and D. DeMille, Phys. Rev. Lett. **103**, 223001 (2009)
[15] E. S. Shuman, J. F. Barry, and D. DeMille, Nature **467**, 820 (2010).
[16] M. T. Hummon, M. Yeo, B. K. Stuhl, A. L. Collopy, Y. Xia, and J. Ye, Phys. Rev. Lett. **110**, 143001 (2013).
[17] 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).
[18] M. D. Di Rosa, Eur. Phy. J. D. **31**, 395 (2004).
[19] L. R. Hunter, S. K. Peck, A. S. Greenspon, and S. Saad Alam, Phys. Rev. A **85**, 012511 (2012).
[20] N. Wells and I. C. Lane, Phys. Chem. Chem. Phys. **113**, 1918 (2011).
[21] R. J. Le Roy, *LEVEL 7.1: A Computer Program for Solving the Radial Schrödinger Equation for Bound and Quasibound Levels*, University of Waterloo Chemical Physics Research Report CP-642 R (2000).
[22] T. C. Steimle, Int. Rev. Phys. Chem. **19**, 455 (2000).
[23] H. Wang, T. C. Steimle, C. Apetrei, and J. P. Maier, Phys. Chem. Chem. Phys. **11**, 2649 (2008).
[24] A. L. Schawlow, Rev. Mod. Phys. **54**, 697 (1982).
[25] IODINESPEC4, Toptica Photonics, Munich, Germany (http://www.toptica.com).
[26] R. Rydberg, Z. Phys. **73**, 376 (1931).
[27] O. Klein, Z. Phys. **76**, 226 (1932).
[28] A. L. G. Rees, Prog. Phys. Soc. **59**, 998 (1947).
[29] http://webbook.nist.gov/cgi/cbook.cgi?ID=C14332537&Units=SI&Mask=100♯Diatomic
[30] O. Nedelec and J. Dufayard, J. Chem. Phys. **69**, 1833 (1978).
[31] W. H. Henneker and H. E. Popkle, J. Chem. Phys. **54**, 1763 (1971).

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