MgH Rydberg Series: Transition Energies from Electron Propagator Theory and Oscillator Strengths from the Molecular Quantum Defect Orbital Method

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Abstract

Vertical excitation energies belonging to several Rydberg series of MgH have been inferred from 3+ electron-propagator calculations of the electron affinities of MgH^+ and are in close agreement with experiment. Many electronically excited states with n>3 are reported for the first time and new insight is given on the assignment of several Rydberg series. Valence and Rydberg excited states of MgH are distinguished respectively by high and low pole strengths corresponding to Dyson orbitals of electron attachment to the cation. By applying the Molecular Quantum Defect Orbital method, oscillator strengths for electronic transitions involving Rydberg states also have been determined.

1. Introduction

MgH is a molecule of great astrophysical importance. Electronic transitions of MgH have been observed in the atmosphere of the Sun, in F-K giants in the Milky Way halo and halos of other Local Group galaxies and in bright L dwarfs [1-4]. In particular, the $A^2\Pi$-$X^2\Sigma$ green system, one of the objects of the present study, has been detected in absorption in solar disk and sunspot spectra, in the spectra of M-type stars, in nearby galaxies and in four nearby L dwarfs and sub-dwarfs [5-11]. MgH is also most likely to be present in the atmospheres of exoplanets [12]. Thus, MgH becomes relevant for stellar atmospheric models, for example PHOENIX [13]. Furthermore, as MgH is a trace molecule, the knowledge of its spectroscopic properties is important for spectral classification and to estimate magnesium isotope abundances in stellar atmospheres [1,14] and surface gravity in late-type stars [15].

Since the visible spectrum of MgH was photographed in 1907 [16], it has been extensively studied by experimentalists and theoreticians. A list of early spectroscopic studies has been given by Huberg and Herzberg [17]. Balfour and coworkers [18-20] have studied the low-lying $^2\Pi$ and $^2\Sigma$ excited states of MgH up to about 6 eV. In 2007, Shayesteh *et al.* [21] have reported a summary of studies of the visible and ultraviolet spectra of MgH. Moreover, these authors provided new, high-resolution, visible-emission spectra of MgH, including several bands of the $A^2\Pi$-$X^2\Sigma^+$ and $B'^2\Sigma^+$-$X^2\Sigma^+$ systems. Parallel to the experimental work, accurate *ab initio* calculations of potential energy functions have also been made, from which experimental assignments of the low-lying excited states have been confirmed. Bruna and Grein [22] have calculated excitation energies and oscillator strengths for MgH with multi-reference configuration-interaction (MRCI) wave functions. These authors have reported excitation energies for low-lying states of $^2\Sigma^+$, $^2\Pi$, $^2\Delta$, $^4\Sigma^+$ and $^4\Pi$ symmetries. Metsdagh *et al.* [23] have analyzed the electronic structure of MgH using a pseudopotential description of the Mg^{2+} core, complemented by a core polarization operator and an internally contracted (IC) MRCI method. Later, Guitou *et al.* [24] have reported a consistent set of molecular data for the lowest states of $^2\Sigma^+$, $^2\Pi$, $^2\Delta$, $^4\Sigma^+$ and $^4\Pi$ symmetries by using the MRCI method. More recently, this methodology has also been employing by Mostafanejad and Sayesteh [25] to report potential curves for the $X^2\Sigma^+$, $A^2\Pi$ and $B'^2\Sigma^+$ states of MgH and corresponding transition dipole moments.

In spite of the considerable body of experimental and theoretical studies of the MgH spectrum, important molecular data, such as energy levels, are known for some low-lying states. To the best of our knowledge, no further attempt has been made to analyze the Rydberg manifold of MgH. In view of this lack of spectroscopic data, we feel motivated to perform highly accurate calculations with the aim of reexamining the electronic spectrum of MgH and to supply new vertical excitation energies for electronic states, including higher Rydberg states than previously reported in the literature. In the present work, we have calculated vertical excitation energies for ns, np, nd and nf Rydberg series covering the 2-7 eV energy range, by using the 3+ electron propagator method [26-28].

It is well known that the interpretation of observational data for some bands of MgH requires accurate data of oscillator strengths. Unfortunately, these molecular properties of MgH are only poorly known through theory and reliable laboratory estimations are still lacking, as has been pointed out by Sinha [29]. The only available data of oscillator strengths for electronic transitions of MgH are those calculated by Chan & Davidson [30] with the limited CI method and more recently by Bruna and Grein [22] with MRCI wave functions. These studies are limited to some lower-lying states. Therefore, another aim of the present study was to estimate oscillator strengths for electronic dipole-allowed transitions from the ground state to higher excited states of MgH. These calculations have been carried out by using the Molecular-Quantum-Defect-Orbital (MQDO) method, for it has produced reliable intensities for Rydberg transitions in previous studies of similar metal hydrides, BeH [31] and CaH [32].

2. Methods of calculation

2.1 Electron propagator theory

Electron propagator theory (EPT) provides a reliable, *accurate and efficient ab-initio* approach to the calculation of electron binding energies of atoms and molecules [26-28]. In EPT, ionization energies or electron affinities may be calculated by solving the Dyson equation [26,27], whose solutions read,

$$[F + \Sigma(E)]\varphi_i^{Dyson} = \varepsilon_i \, \varphi_i^{Dyson} \, ,$$

where F is the one-electron Fock operator with the usual Coulomb and exchange components and Σ(E) is known as the energy-dependent, self-energy operator. This operator describes electron-correlation and orbital-relaxation effects that are neglected by the Fock operator. Solutions of the Dyson equation may be obtained through an iterative self-consistent process that converges when E is equal to an electron binding energy. At convergence, the eigenfunctions of the Dyson equation, $\phi^{Dyson}{}_{n,N\pm1}$, are the Dyson orbitals,

$$\phi^{Dyson}{}_{n,N-1}(x_1) = N^{0.5} \int \Psi_N(x_1,x_2,x_3,\ldots,x_N)\, \Psi_{N-1,n}{}^*(x_2,x_3,x_4,\ldots,x_N)dx_2dx_3dx_4\ldots dx_N$$

$$\phi^{Dyson}{}_{n,N+1}(x_1) = (N+1)^{0.5} \int \Psi_{N+1,n}(x_1,x_2,x_3,\ldots,x_{N+1})\, \Psi_N{}^*(x_2,x_3,x_4,\ldots,x_{N+1})dx_2dx_3dx_4\ldots dx_{N+1}$$

Dyson orbitals may be interpreted as overlap functions between states with N and N±1 electrons. The eigenvalues of the Dyson equation, ε_i, are electron binding energies of the molecular system.

The values of the norm of the Dyson orbital corresponding to a given electron binding energy, or pole strengths (PS), are commonly used to diagnose the validity of an approximate electron propagator method or to distinguished final states that differ from initial states by one-electron (Koopmans-like) or more complicated (correlated) processes. EPT methods may be systematically improved to the exact limit by incorporating more terms in the self-energy operator. In the present study, the 3+ self-energy approximation was used for the calculation of the vertical attachment energies (electron affinities) of MgH^+. Final states with pole strengths close to unity correspond to Rydberg series of the MgH molecule and conform qualitatively to the single-configuration assumption of Koopmans's theorem. The 3+ EPT method is a non-diagonal self-energy approximation of EPT that employs a Hartree-Fock reference state, retains all terms in the self-energy through third order and includes higher-order self-energy terms that arise from couplings between h (hole or occupied orbital), p (particle or virtual orbital), 2h1p, and 2p1h operators [26,33,34]. In the present calculations of MgH^+ electron affinities, pole strengths that are close to unity correspond to dominance by the p operators, which represent simple addition of an electron to a virtual orbital of the cation. However, when pole strengths fall below 0.85, 2p1h operators (wherein two electrons are added to virtual orbitals and one electron is removed from an occupied orbital of the cation) become significant or even dominant as the pole strength approaches zero.

For the MgH molecule, all electronic-structure calculations have been carried out with the Development Version of the Gaussian package of programs [35]. Bond distances between the Mg and H nuclei were obtained by geometry optimizations of MgH and MgH^+ using the CCSD(T) [36] method in combination with the augmented, correlation-consistent quadruple ζ basis set (aug-cc-pvqz) [37,38]. Electron attachment energies of MgH^+ were computed using the

3+ method in combination with the correlation-consistent quadruple ζ basis set (cc-pvqz) [37, 39] plus 9s9p9d7f extra diffuse functions centered on the Mg nucleus. Exponents of the extra diffuse functions were generated by successively applying a multiplicative factor of one third to the least diffuse s, p, d and f members of the Mg cc-pvqz set.

2.2 Molecular Quantum Defect Orbital theory

In the MQDO methodology, the molecular Rydberg electron is described by an orbital in this form,

$$\psi(r,\theta,\varphi)_{nl\mu\nu} = r^{-1} R(r)_{nl}\, \Xi(\theta,\varphi)_{l\mu\nu} ,$$

where n and l are the principal and orbital angular momentum quantum numbers, respectively, μ labels the irreducible representation of the molecular symmetry group and ν identifies the basis function of this representation. The function $\Xi(\theta,\varphi)_{l\mu\nu}$ refers to the angular part of the MQDO wave functions. The radial quantum defect orbital $R(r)_{nl}$ are the analytical solutions of the one-electron Hamiltonian with a parametric potential that accounts for electron correlation and has been previously described in several papers [40, 41].

The absorption oscillator strength for a transition between two electronic states *i* and *f*, is expressed as follows:

$$f = (2/3)\,(E_f - E_i)Q_{i\to f}\ |R_{if}|^2$$

where $Q_{i\to f}$ is the angular factor resulting from the integration of the angular part of the MQDO wave function and that of the transition operator. R_{if} is the radial electric dipole transition moment which turns out to have a closed-form, analytical expression, and therefore offers a significant computational advantage.

3. Results and discussion

The electronic configuration of the $X^2\Sigma^+$ ground state of MgH is $(1\sigma)^2(2\sigma)^2(1\pi)^4(3\sigma)^2(4\sigma)^2(5\sigma)$ in the $C_{\infty v}$ symmetry group. Our calculations indicate that the outermost, singly-occupied, 5σ molecular orbital (MO) is dominated by Mg basis functions. A Mulliken population analysis of the Dyson orbital of electron attachment to MgH^+ at the equilibrium geometry of MgH (1.724 Å) shows 51% s and 41% p character for this MO. Whereas 1σ through 3σ are 1s, 2s and 2p Mg core orbitals, 4σ is chiefly a bonding combination of H 1s and Mg s and p functions. In the unrestricted Hartree-Fock calculation that precedes the evaluation of the CCSD(T) total energy of MgH, the expectation value of S^2 is 0.76 and indicates that spin-contamination is negligible.

The adiabatic ionization energy (IE) of MgH has been determined to be 6.897 eV with harmonic, zero-point-corrected, coupled-cluster energies. Vertical electron affinities of MgH^+ calculated at the CCSD(T) MgH or MgH^+ inter-nuclear distances (1.724 and 1.655 Å, respectively) are 6.951 and 6.900 eV, respectively.

Rydberg MOs in MgH will be denoted as $nl\Gamma_i$, where Γ_i is the irreducible representation of the molecular point group. In the present work, we have inferred vertical excitations energies (VEE) from differences of vertical electron affinities for the $ns\sigma(^2\Sigma^+)$, $np\sigma(^2\Sigma^+)$, $np\pi(^2\Pi)$, $nd\sigma(^2\Sigma^+)$, $nd\pi(^2\Pi)$, $nd\delta(^2\Delta)$ and $nf\sigma(^2\Sigma^+)$, $nf\pi(^2\Pi)$, $nf\delta(^2\Delta)$ and $nf\varphi(^2\Phi)$ Rydberg series. The data are collected in Table I. Assignments of the quantum number n to Rydberg states have been made through a careful review of the quantum defects. In this analysis, we have taken into account the fact that the quantum defects of metal hydrides are expected to have the same magnitude as those of the corresponding metal atom [42]. Specifically, the quantum defects for the Mg atom are about 1.5, 1.0, 0.4 and 0.0 for the s, p, d and f series, respectively [43]. The most important contributions by Mg basis functions for each of the Dyson orbitals of electron attachment to the cation are listed in Table I. For Dyson orbitals with pole strengths that are close to unity, the MgH states have a single important configuration in which a diffuse electron is outside the MgH^+ core. In those cases where the pole strength is less than 0.85, qualitatively important configuration mixing takes place.

In order to assess the accuracy of our results, the presently calculated vertical excitation energies are compared with experimental values available in the literature in Table II. It seems apparent in Table II that our study reproduces well the experimental spectrum. Our energies are in close agreement with experiment except for the state designed as $B'^2\Sigma^+$, where the difference amounts to ~0.9 eV. However, it should be noted that, for this state, our VEE cannot be compared with the experimental data of T_e, because of the different inter-nuclear distances of the ground and $B'^2\Sigma^+$ states. Nonetheless, our VEE of 3.679 eV compares well with the most recent IC-MRCI vertical excitation energy equal to 3.769 eV, given by Mestdagh *et al.* [23]. The low pole strength (0.24) for the corresponding electron affinity indicates that substitutions from the 4σ MO to higher, virtual orbitals are important in the wave function of $B'^2\Sigma^+$. Therefore, $B'^2\Sigma^+$ is a valence, excited state and does not belong to a Rydberg series. At higher energy lies the $B^2\Sigma^+$ state, where the present calculation and experiment are in closer (within approximately 0.1 eV) agreement. Here, the larger pole strength indicates that this state has a diffuse electron of mixed s-p-d character and that valence-excited configurations also are present to a minor extent.

We have assigned the first excited state, $A^2\Pi$, observed at 2.39 eV [17], to an excitation from the 5σ of MgH in its ground state to a 3pπ Rydberg orbital. This assignment is in good agreement with that made by Bruna and Grein [22] using the all-electron, multi-reference single and double configuration interaction method (MRSDCI). Our results also confirm the assignments made by these authors for the $C^2\Pi$ state, observed at 5.11 eV, to be a $4p\pi(^2\Pi)$ Rydberg state and for the $3^2\Pi$ state, experimentally found at 5.28 eV, to be the first member of the $nd\pi(^2\Pi)$ Rydberg series.

Regarding the observed $E^2\Sigma^+$ state at 4.41 eV, it has been presently assigned to a $4s\sigma(^2\Sigma^+)$ Rydberg state, whereas Bruna and Grein [22] have considered this state as an excitation to a mixed $3d\sigma/3p\sigma$ orbital. These authors have predicted the excitation to the state denoted as $6^2\Sigma^+$ to belong a $4s\sigma$ Rydberg state and to occur at a higher energy of 6.20 eV. However, our assignment leads to a quantum defect equal to 1.66, in consistency with the expected value for an s state of the Mg atom. On the other hand, according to our calculations, the $5s\sigma$ Rydberg state lies at higher energy, 5.725 eV (see Table I), close to the energy associated by Bruna and Grein [22] to the $4s\sigma$ state, with an associated quantum defect equal to 1.6, which conforms to that expected for a 5s state in the Mg atom. Thus, the present calculations hint at characterizing the $E^2\Sigma^+$ state as a $4s\sigma(^2\Sigma^+)$ Rydberg state and $6^2\Sigma^+$ as a $5s\sigma$ Rydberg state.

The present calculations predict the first member of the Rydberg series $nd\delta(^2\Delta)(n=3)$ at 5.235 eV, in fairly good agreement with previous *ab initio* calculations of Bruna and Grein [22] (5.43 eV) and of Mestdagh *et al.* [23] (5.33 eV). No earlier theoretical or experimental data as regards the nf Rydberg series seem to exist in the literature for comparison. In Table I, we have given the VEE for the $nf\sigma$, $nf\pi$, $nf\delta$ and $nf\varphi$ Rydberg series of MgH with n = 4 - 6. As can be seen, for a given quantum number, all these states fall together in a small range of ~0.03 eV, which is smaller than the precision of our methodology.

In this work, we have also calculated the intensities corresponding to dipole-allowed excitations from the outermost MO in the ground state of MgH radical to the ns($^2\Sigma^+$), npσ($^2\Sigma^+$), npπ($^2\Pi$), ndσ($^2\Sigma^+$) and ndπ($^2\Pi$) Rydberg series. Absorption oscillator strengths, or f-values, are collected in Table III. For calculations, we have used as inputs the presently calculated ionization energy and vertical excitation energies. The f-values have been grouped according to the $nl\Gamma_i$ values, rather than by increasing excitation energies. As we have mentioned in the introduction, there is very little known about electronic oscillator strengths of MgH. Previous *ab initio* theoretical values have been reported by Chan and Davidson, [30] who performed limited configuration interaction (CI) calculations, and by Bruna and Grein, [22] who used MRSDCI wave functions. For comparative purposes, these data have been included in Table III.

As can be seen in Table III, our results are in reasonably good agreement with the *ab initio* oscillator strength reported by Bruna and Grein [22]. It should be noted that our results and those of the latter authors [22] for transitions to nsσ($^2\Sigma^+$) and npπ($^2\Pi$) states reproduce the expected decrease of the f-value as n increases in a Rydberg series, while those reported by Chan and Davidson [30] do not. The values given by Chan and Davidson, in general, seem to be lower than our results and those given by Bruna and Grein. *f*-values for transitions to the ndσ($^2\Sigma^+$) Rydberg states have been reported for the first time, as far as we know. Globally, from Table III, it is found that our results are in better agreement with the more sophisticated *ab initio* calculations due to Bruna and Grein [22]. Furthermore, the MQDO values show the expected decrease in the magnitude of the oscillator strength as the transition energy increases along a given Rydberg series.

4. Conclusions

In the present work, the assignment of the MgH spectrum has been performed by using electron-propagator methods together with the MQDO approach. Vertical excitation energies for a large number of excited Rydberg states, including those of *f* character, and oscillator strengths for transitions from the ground state of MgH have been determined. It may be remarked that both vertical excitation energies and oscillator strengths show consistency with the comparative data, when they are available. In this work, new data of excitation energies and transition intensities are given. Thus, our results are, to our knowledge, the most complete series of theoretical excitation energies and electronic oscillator strengths of the MgH radical. We expect that the data provided by the present work will help in future analysis and interpretation of the electronic spectrum of MgH in the 2-7 eV excitation range.

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Table I. Vertical excitation energies (eV) of MgH

MO	Irrep.[1]	AO[2]	Δ_{3+}^{3}	PS[4]
7	σ	3s	0.000	0.957
8, 9	π	3p	2.416	0.959
10	σ	4s	4.411	0.961
11	σ	3d	4.666	0.814
11	σ	3d	3.679	0.243
12, 13	π	4p	5.130	0.979
14, 15	δ	3d	5.235	0.987
16, 17	π	3d	5.309	0.949
18	σ	4p	5.358	0.973
19	σ	5s	5.725	0.991
20	σ	4d	5.790	0.980
21, 22	π	4d	5.985	0.837
23, 24	δ	4d	6.016	0.994
25, 26	φ	4f	6.093	0.999
27, 28	π	5p	5.961	0.658
27, 28	π	5p	6.141	0.621
29	σ	5p	6.068	0.991
30, 31	δ	4f	6.108	0.999
32, 33	π	4f	6.113	0.973
34	σ	4f	6.117	0.999
35	σ	6s	6.241	0.994
36	σ	5d	6.269	0.989
37, 38	π	5d	6.357	0.988
39, 40	δ	5d	6.372	0.997

41, 42	π	6p	6.410	0.979
43, 44	φ	5f	6.413	1.000
45	σ	6p	6.404	0.996
46, 47	δ	5f	6.420	0.999
48, 49	π	5f	6.423	0.996
50	σ	5f	6.423	0.999
51	σ	7s	6.505	0.985
52	σ	6d	6.520	0.996
53, 54	π	6d	6.574	0.993
55, 56	δ	6d	6.579	0.999
57, 58	φ	6f	6.604	1.000
59	σ	6f	6.602	0.998
60, 61	δ	6f	6.607	1.000
62, 63	π	7p	6.609	0.997
64, 65	π	6f	6.607	0.997
66	σ	7p	6.607	0.998
67	σ	7f	6.630	0.987
68	σ	8s	6.686	1.000
69, 70	φ	7f	6.713	0.999
71, 72	π	7d	6.721	0.997
73, 74	δ	7d	6.719	0.999
75	σ	7d	6.720	0.999
76, 77	δ	7f	6.722	0.998
78, 79	π	7f	6.711	0.978
80, 81	π	8p	6.743	1.000

[1] Irreducible representation

[2] Approximate atomic orbital type

[3] Excitation energy = difference between electron affinities

[4] Pole strengths of the electron affinities

Table II: Vertical excitation energies (eV) of MgH

	This work		Expt.[a]	
		ΔE		T_e
$1^2\Pi$	3pπ($^2\Pi$)	2.416	$A^2\Pi$	2.39
$2^2\Sigma^+$	Valence ($^2\Sigma^+$)	3.679	$B'^2\Sigma^+$	2.78
$3^2\Sigma^+$	4sσ($^2\Sigma^+$)	4.411	$E^2\Sigma^+$	4.41
$4^2\Sigma^+$	3d-4s-4pσ($^2\Sigma^+$)	4.666	[$B^2\Sigma^+$]	4.77
$2^2\Pi$	4pπ($^2\Pi$)	5.130	$C^2\Pi$	5.11
$3^2\Pi$	3dπ($^2\Pi$)	5.309	$3^2\Pi$	5.28

[a] Refs. 18 and 19

Table III: Oscillator strengths for transitions from the ground state to nsσ, npπ, npσ, ndπ and ndσ Rydberg series of MgH.

Transition	MQDO[a]	Previous
$X^2\Sigma^+$ - 4sσ($^2\Sigma^+$)	0.0941	0.13[b],0.03[c]
$X^2\Sigma^+$ - 5sσ($^2\Sigma^+$)	0.0169	0.01[b], 0.08[c]
$X^2\Sigma^+$ - 6sσ($^2\Sigma^+$)	0.0076	
$X^2\Sigma^+$ - 7sσ($^2\Sigma^+$)	0.0036	
$X^2\Sigma^+$ - 8sσ($^2\Sigma^+$)	0.0023	
$X^2\Sigma^+$ - 3pπ($^2\Pi$)	0.1794	0.17[b], 0.11[c]
$X^2\Sigma^+$ - 4pπ($^2\Pi$)	0.1432	0.14[b], 0.03[c]
$X^2\Sigma^+$ - 6pπ($^2\Pi$)	0.0132	
$X^2\Sigma^+$ - 7pπ($^2\Pi$)	0.0026	
$X^2\Sigma^+$ - 4pσ($^2\Sigma^+$)	0.0509	0.12[b], 0.14[c]
$X^2\Sigma^+$ - 5pσ($^2\Sigma^+$)	0.0176	
$X^2\Sigma^+$ - 6pσ ($^2\Pi$)	0.0069	
$X^2\Sigma^+$ - 3dπ($^2\Pi$)	0.0527	0.06[b], 0.02[c]
$X^2\Sigma^+$ - 4dπ($^2\Pi$)	0.0202	
$X^2\Sigma^+$ - 5dπ($^2\Pi$)	0.0084	
$X^2\Sigma^+$ - 6dπ($^2\Pi$)	0.0029	
$X^2\Sigma^+$ - 7dπ($^2\Pi$)	0.0006	

$X^2\Sigma^+$ - $4d\sigma(^2\Sigma^+)$	0.0146
$X^2\Sigma^+$ - $5d\sigma(^2\Sigma^+)$	0.0064
$X^2\Sigma^+$ - $6d\sigma(^2\Sigma^+)$	0.0033
$X^2\Sigma^+$ - $7d\sigma(^2\Sigma^+)$	0.0004

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[a] This work
[b] Bruna and Grein [22]
[c] Chan and Davidson [30]