

Strong bonding in a doubly excited valence state of a van der Waals molecule

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Abstract

The results of ab initio calculations, using extended Gaussian basis sets and including correlation energy through a variety of means, provide strong support for the $\text{Mg}(3p\pi, 3p\pi^3P_J) \cdot \text{Ar}(^3\Sigma^-)$ electronic-state assignment made by Massick and Breckenridge to spectral features in the resonant two-photon photoionization spectrum of vibrationally cold $\text{Mg}(3s, 3p\pi^3P_J) \cdot \text{Ar}(^3\Pi)$ van der Waals complexes. The doubly excited $\text{Mg}(3p\pi, 3p\pi^3P_J) \cdot \text{Ar}(^3\Sigma^-)$ state is found to be much more strongly bound than the singly excited $\text{Mg}(3s, 3p\pi^3P_J) \cdot \text{Ar}(^3\Pi)$ state, which, in turn, is much more bound than the $\text{Mg}(3s^2\ ^1S_0) \cdot \text{Ar}(^3\Sigma^+)$ ground state.

1. Introduction

Massick and Breckenridge [1] reported the discovery and experimental characterization of an unusual doubly excited valence state of a van der Waals molecule to which they assigned $\text{Mg}(3p\pi, 3p\pi^3P_J) \cdot \text{Ar}(^3\Sigma^-)$ character. This state was found to be much more strongly bound than any known singly excited [2,3] state of MgAr (including Rydberg states), with a bond strength more than twice that of even the ground-state MgAr^+ cation [1,4], $\text{Mg}(3p\pi, 3p\pi^3P_J) \cdot \text{Ar}(^3\Sigma^-)$, $D_e = 2960\text{ cm}^{-1}$ at $R_e = 2.39\text{ \AA}$; $\text{MgAr}^+(^2\Sigma^+)$, $D_e = 1320\text{ cm}^{-1}$ at $R_e = 2.86\text{ \AA}$. This doubly excited $\text{Mg}(3p\pi, 3p\pi^3P_J) \cdot \text{Ar}(^3\Sigma^-)$ valence state is also seventeen times more strongly bound than the analogous singly excited $\text{Mg}(3s, 3p\pi^3P_J) \cdot \text{Ar}(^3\Pi)$ state, for which $D_e = 175 \pm 40\text{ cm}^{-1}$ at $R_e = 3.63\text{ \AA}$ [2,4,5]. Shown in Fig. 1 are (i) the potential curve for the weakly bound $\text{Mg}(3s, 3s\ ^1S) \cdot \text{Ar}(^1\Sigma^+)$ ground state, (ii) the singly

excited $\text{Mg}(3s, 3p\pi^3P_J) \cdot \text{Ar}(^3\Pi)$ state's curve computed in this work, and (iii) the potential energy of the doubly excited $\text{Mg}(3p\pi, 3p\pi^3P_J) \cdot \text{Ar}(^3\Sigma^-)$ deduced in Ref. [1] and calculated here.

Experimentally [1], a portion of the Mg atoms created by laser vaporization of a Mg rod are formed in the 3P_J states. These excited atoms were expanded into a supersonic jet, where they combined in three-body collisions with Ar to form metastable $\text{Mg}(3s, 3p\pi^3P_J) \cdot \text{Ar}(^3\Pi_{0^+,0^-})$ states. These states (cooled to $v'' = 0$) were then excited to various vibrational levels of the putative $\text{Mg}(3p\pi, 3p\pi^3P_J) \cdot \text{Ar}(^3\Sigma^-)$ state, and the resonant vibrational–rotational transitions were detected by R2PI (resonant two-photon photoionization) spectroscopy.

Because the observations reported in Ref. [1] were the first on such a doubly excited valence state of a van der Waals molecule, we thought it essential to attempt to verify or refute these assignments through the theoretical studies reported here. We present

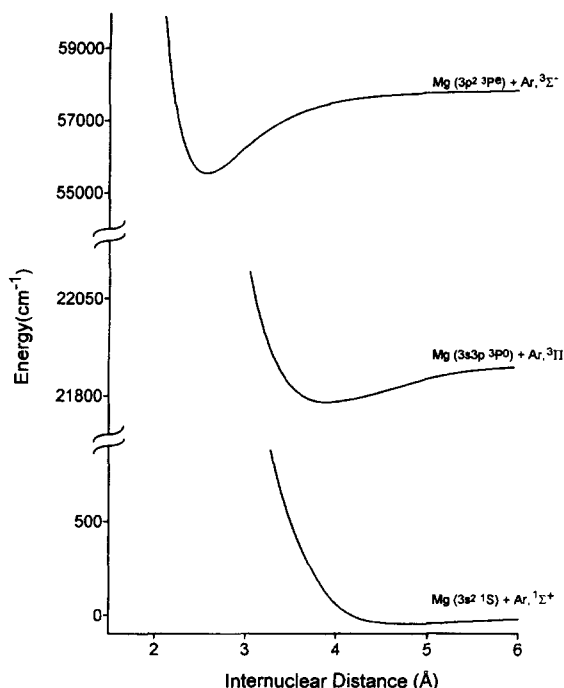


Fig. 1. Calculated potential curves of the $\text{Mg}(3s,3s \ ^1S_0) \cdot \text{Ar}(^1\Sigma^+)$ ground state [11], the singly excited $\text{Mg}(3s,3p\pi \ ^3P_J) \cdot \text{Ar}(^3\Pi)$ state (this work), and the doubly excited $\text{Mg}(3p\pi,3p\pi \ ^3P_J) \cdot \text{Ar}(^3\Sigma^-)$ state (this work).

results of high-level *ab initio* calculations of the potential energy curves for both the singly excited $\text{Mg}(3s,3p\pi \ ^3P_J) \cdot \text{Ar}(^3\Pi)$ and the doubly excited $\text{Mg}(3p\pi,3p\pi \ ^3P_J) \cdot \text{Ar}(^3\Sigma^-)$ states. Our calculations support the assignment of Massick and Breckenridge of the upper state in their R2PI spectra to the doubly excited $\text{Mg}(3p\pi,3p\pi \ ^3P_J) \cdot \text{Ar}(^3\Sigma^-)$ valence state because our most accurate theoretical curve closely approximates the RKR (Rydberg–Klein–Rees) potential derived from the data of Ref. [1].

The doubly excited asymptotic Mg atom state, $\text{Mg}(3p,3p \ ^3P_J)$ is quite high in energy, but still $\approx 3800 \text{ cm}^{-1}$ below the $\text{Mg}^+ + e^-$ ionization energy [6]. There are 24 excited valence and Rydberg atomic states below the $\text{Mg}(3p,3p \ ^3P_J)$ state. This means that there are a large number of attractive and repulsive MgAr molecular states in the energy region of the doubly-excited $\text{Mg}(3p\pi,3p\pi \ ^3P_J) \cdot \text{Ar}(^3\Sigma^-)$ state. However, *none* of the lower 24 asymptotic Mg atomic states can produce diatomic states of $^3\Sigma^-$ symmetry when interacting with $\text{Ar}(^1S)$. Thus, within

the Born–Oppenheimer approximation and neglecting spin–orbit coupling, our doubly excited state is not only unique but can also be computed reliably using *ab initio* methods.

2. Theoretical methods

2.1. Atomic basis sets and treatment of electron correlation

For both Mg and Ar, we employed a wide range of atomic orbital bases; specifically,

(i) for Mg, we used bases including 6-31 through 6-311⁺⁺, 6-311 + G(d), and 6-311 + G(2df) quality (more detail on the bases is provided in Tables 1 and 2 below);

(ii) for Ar, the Dunning [7] augmented correlation consistent polarized bases of quality aug-cc-pVDZ through aug-cc-pVQZ were employed.

Most of our calculations (in particular, those used to generate full potential energy curves) were carried out using the GAUSSIAN 94 program suite [8] and within the Møller–Plesset MP2, MP3, MP4, QCISD, and QCISD(T) progression of correlation treatment. However, we also performed multiconfiguration based studies on the Mg atom because this species is known to display significant non-dynamical correlation due to the near degeneracy of its 3s and 3p orbitals. In particular, we used the GAMESS program [9] to perform full-valence configuration interaction (FVCI) calculations on Mg with the 3s and 3p orbitals included in the valence space, followed by a singly and doubly excited configuration interaction (SDCI) calculation out of the reference configurations generated by the FVCI computation.

2.2. Calibration of atomic energy level findings

2.2.1. The Mg atom

In Table 1, we provide the total energies obtained for the 1S ground state of Mg, for its $3s^1 3p^1 \ ^3P^o$ state, its $3p^2 \ ^3P^e$ state, and for the $\text{Mg}^+(^2S)$ ion for a 6-311 + G(2df) quality basis and MP2 through QCISD correlation treatment of the 3s and 3p valence electrons, together with experimental values for the corresponding energy differences. Also included are total energies and energy differences ob-

Table 1

Total energies (au) and relative energies (cm^{-1}) of Mg and Mg^+ at various levels of valence correlation and basis sets

State	HF	MP2	MP3	MP4	QCISD	Expt. [6]
Mg(^1S)	-199.6066219	-199.6297256	-199.6358502	-199.6382228	-199.6401276	
Mg($^3\text{P}^o$)	-199.5408124	-199.5430473	-199.544033	-199.5445159	-199.5450589	
Mg($^3\text{P}^e$)	-199.3763837	-199.3811766	-199.3830883	-199.3839161	-199.3845674	
Mg $^+$ (^2S)	-199.3638927	-199.3638927	-199.3638927	-199.3638927	-199.3638927	
relative energies						
$^1\text{S} \rightarrow ^3\text{P}^o$	14445	19025	20153	20568	20867	21891
$^1\text{S} \rightarrow ^3\text{P}^e$	50537	54556	55481	55820	56095	57854
$^1\text{S} \rightarrow ^2\text{S}$	53279	58350	59694	60215	60633	61671
Basis set	HF(^1S)	HF($^3\text{P}^e$)	FVCI(^1S)	SDCI($^3\text{P}^e$)	$\Delta\text{HF}(^1\text{S} \rightarrow ^3\text{P}^e)$	$\Delta\text{CI}(^1\text{S} \rightarrow ^3\text{P}^e)$
6-31	-199.59521	-199.36461	-199.62761	-199.36588	50611	57442
6-31 +	-199.59533	-199.36497	-199.62771	-199.36636	50558	57359
6-311	-199.60656	-199.37622	-199.63914	-199.36519	50554	60124
6-311 +	-199.60662	-199.37633	-199.63923	-199.37776	50544	57385
6-311 + +	-199.60665	-199.37635	-199.63927	-199.37779	50544	57390
6-311 + G(d)	-199.60701	-199.37669	-199.64062	-199.38192	50550	56776

tained within the multiconfiguration based FVCI and MRCI approaches over a range of bases from 6-31 through 6-311 + G(d).

Our primary conclusions derived from these calibration studies are as follows:

(i) At the SCF (i.e. Hartree–Fock) level, the $^1\text{S} \rightarrow ^3\text{P}^e$ energy gap converges to between 50500 and 51000 cm^{-1} as the atomic basis is improved.

(ii) For the best bases, this same $^1\text{S} \rightarrow ^3\text{P}^e$ energy gap converges to between 56000 and 57400 cm^{-1} as the treatment of valence electron correlation is improved either through the MP2-QCISD or the FVCI-MRCI path, and these data compare well to the experimental excitation energy [6] of $\approx 57854 \text{ cm}^{-1}$.

(iii) At higher levels of correlation, the $^1\text{S} \rightarrow ^3\text{P}^o$ excitation energy of $\approx 20900 \text{ cm}^{-1}$ is close to the experimental value of 21891 cm^{-1} , and the ionization energy of 60633 cm^{-1} is also close to the experimental value [6] of 61671 cm^{-1} .

2.2.2. The Ar atom

In Table 2, we summarize our findings as functions of level of treatment of correlation using the aug-cc-pVQZ basis for the ^1S ground state of Ar and its $^2\text{P}^o$ cation. The agreement shown between our best ionization energy and the known experimental data [6] is excellent. Finally, we also computed the dipole polarizability of the Ar atom using the above basis and obtained 11.1 \AA^3 at the QCISD(T) level,

Table 2

Total energies (au) and relative energies (cm^{-1}) of Ar and Ar^+ at various levels of correlation with the aug-cc-pVQZ atomic basis

Species	HF	MP2	MP3	MP4SDQ	QCISD	QCISD(T)	Expt. [6]
Ar(^1S)	-526.8168049	-527.0489519	-527.0681387	-527.0667128	-527.066289	-527.075047	
Ar $^+$ ($^2\text{P}^o$)	-526.2820345	-526.4666876	-526.4890401	-526.490221	-526.490292	-526.496738	
relative energies							
$^1\text{S} \rightarrow ^2\text{P}^o$	117382	127807	127112	126539	126431	126938	127110

essentially in perfect agreement with the experimental value [10].

3. Findings for MgAr

3.1. Potential curve for the doubly excited $Mg(3p\pi, 3p\pi^3P_J) \cdot Ar(^3\Sigma^-)$ state

In Fig. 2 are shown the relative energies obtained as functions of internuclear distance for the doubly excited $p^2\ ^3P^e$ Mg interacting with 1S Ar in a $^3\Sigma^-$ fashion. All of these data were obtained using a pVTZ quality basis on Ar and a 6-311 + G(2df) basis for Mg, and only the two active electrons on Mg and the eight 3s and 3p electrons of Ar have been explicitly correlated. Corrections to these findings due to extending the bases or correlating more electrons have been obtained over a more limited range of internuclear distances and are discussed below. Also shown in Fig. 2 is the RKR potential curve derived from the data of Massick and Breckenridge [1,2].

At the SCF level of treatment, which ignores all electron correlation, the potential is far too shallow

($D_e = 732\text{ cm}^{-1}$ when basis set superposition errors (BSSE) are accounted for by applying the Boys counterpoise correction) and has too long a bond length ($R_e = 2.7\text{ \AA}$). However, as electron correlation is included, the curves seem to evolve toward convergence producing $D_e = 2314\text{ cm}^{-1}$ (BSSE correction of 120 cm^{-1}) and $R_e = 2.57\text{ \AA}$ at the above basis level.

Enhancing the Ar atomic basis by moving to a pVQZ quality basis and examining the region $R = 2.46\text{--}2.60\text{ \AA}$, we obtain an SCF potential minimum at $R_e = 2.60\text{ \AA}$ that is 777 cm^{-1} deep and a QCISD(T) minimum at $R_e = 2.55\text{ \AA}$ that is 2494 cm^{-1} deep (69 cm^{-1} BSSE correction).

Even with the larger basis and at the QCISD(T) level, our well depth differs significantly from the $2960 \pm 100\text{ cm}^{-1}$ shown in the RKR curve of Massick and Breckenridge. We therefore carried out a series of calculations in which more and more of the Mg and Ar electrons were explicitly correlated. As these calculations are extremely computer-time intensive, they were only performed near the R_e predicted by our 6-311 + G(2df) Mg, pVQZ Ar, QCISD(T) energies. We find that by correlating *all* but the 1s electrons on both atoms, the predicted D_e

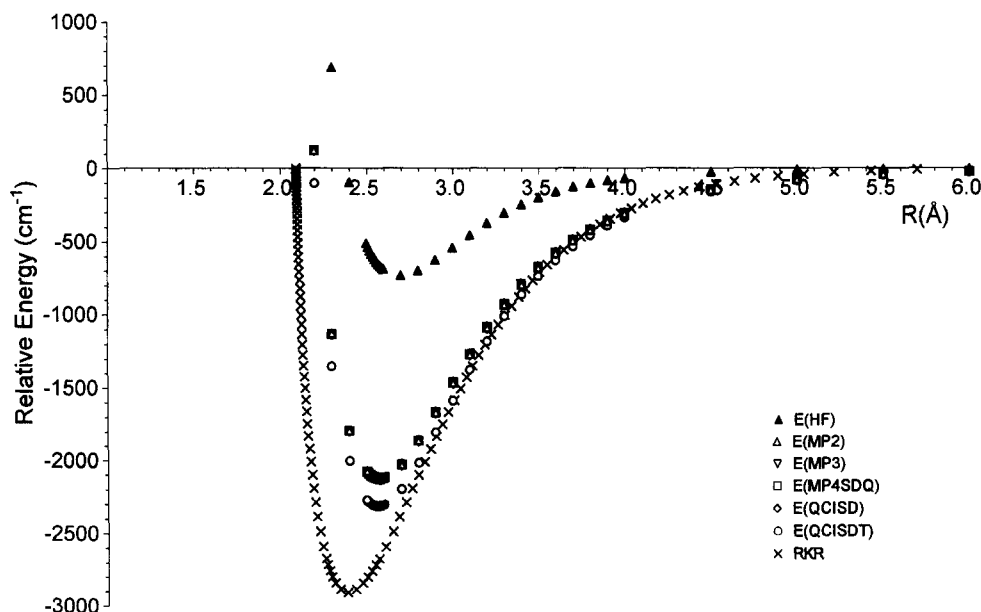


Fig. 2. Calculated potential curves for $Mg(3p\pi, 3p\pi^3P_J) \cdot Ar(^3\Sigma^-)$ at various levels of correlation using the 6-311 + G(2df) Mg basis and the aug-cc-pVTZ Ar basis. Also shown is the experimentally determined RKR curve of Ref. [1].

increases to 2573 cm^{-1} (271 cm^{-1} BSSE correction) at $R_e = 2.54 \text{ \AA}$, which represent our best estimates.

3.2. The singly excited $\text{Mg}(3s,3p\pi^3P_j) \cdot \text{Ar}(^3\Pi)$ state

We also examined the lower energy triplet state derived from the $3s^13p^1\ ^3P^o$ state of Mg and the 1S state of Ar. In Fig. 1, we display the potential curve obtained for this state of MgAr using the 6-311 + G(d) basis on Mg and the aug-cc-pVQZ basis on Ar and a MP4(SDTQ) treatment of correlation, which produces a D_e of 108 cm^{-1} (59 cm^{-1} BSSE correction) and $R_e = 3.9 \text{ \AA}$. Using the larger 6-311 + G(2df) basis on Mg and the aug-cc-pVQZ basis on Ar, and examining a more narrow range of internuclear distances, we obtain $D_e = 135 \text{ cm}^{-1}$ (18 cm^{-1} BSSE correction) and $R_e = 3.82 \text{ \AA}$, which are reasonably close to those values derived from the experimental data of Ref. [1] ($D_e = 175 \pm 40 \text{ cm}^{-1}$ and $R_e = 3.63 \text{ \AA}$). We should note that we find the potential well for this state to be especially “flat” in the range $R_e \pm 0.1 \text{ \AA}$.

3.3. Bonding in the ground and excited states

It is important to stress the very large differences among the $^1\Sigma^+$ ($\text{Mg}(^1S) + \text{Ar}(^1S)$), $^3\Pi$ ($\text{Mg}(^3P^o) + \text{Ar}(^1S)$), and $^3\Sigma^-$ ($\text{Mg}(^3P^e) + \text{Ar}(^1S)$) potential energy curves.

(i) The ground state is a weakly bound van der Waals complex with a long internuclear distance.

(ii) The singly excited state has a shorter bond length ($\approx 3.82 \text{ \AA}$) and a deeper well ($\approx 135 \text{ cm}^{-1}$).

(iii) In contrast, the doubly excited state, in which both 3s electrons have been removed, thus allowing the Ar atom to avoid their repulsion, is strongly bound ($D_e \approx 2573 \text{ cm}^{-1}$) and has an even shorter bond length ($R_e \approx 2.54 \text{ \AA}$).

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