



A study of the X $^2\Sigma^+$ and A $^2\Pi$ states of MgAr $^+$ and MgKr $^+$

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Abstract

The ground $^2\Sigma^+$ and lowest excited $^2\Pi$ states of MgAr $^+$ and MgKr $^+$ are studied using the singles and doubles configuration-interaction (SDCI) approach, in conjunction with large basis sets. The effect of Mg core correlation and core polarization are accounted for using the core-polarization potential (CPP) approach. Franck–Condon factors, oscillator strengths, radiative lifetimes, dissociation energies, bond lengths, and excitation energies are reported. The computed results are in good agreement with the available experimental data.

1. Introduction

We have studied [1–6] the ground and excited states of several MgL $^+$ systems. For those cases where the bonding is electrostatic, the ground state of MgL $^+$ is derived from Mg $^+ 2S(3s^1)$. The bonding is enhanced by polarization of the 3s electron away from the ligand, by mixing in Mg 3p. The two lowest excited states arise from an excitation of the 3s-like electron into one of the two Mg 3p orbitals perpendicular to the Mg–L axis. The excited states have a shorter Mg–L distance and are more strongly bound than the ground state, because these Mg 3p orbitals have a smaller overlap (and hence repulsion) with the ligand than does the Mg 3s orbital. This effect can be quite large, so that the MgL $^+$ transition energies are very different from the Mg $^+ 2P \leftarrow 2S$ transition from which they are derived. In fact one of our first calculations was performed to predict the transition energy for MgH $_2$ O $^+$ to simplify the experimental search [7] for the band origin. The calculations were successful [1] in this regard and, in addi-

tion, they gave some insight [2] into the identification of the vibrational modes [8].

Pilgrim et al. studied [9] the $^2\Pi \leftarrow ^2\Sigma^+$ transition in the Mg $^+$ –rare gas (Rg) systems, for Rg = Ar, Kr, and Xe. The very weak charge-induced dipole bonding results in an even larger difference between the ground and excited state binding energies and bond lengths than was found for the more strongly bound systems [7,8,10,11]. This large difference in geometry between the two states results in a very weak 0–0 transition. In order to identify the vibrational levels, Pilgrim et al. were forced to fit the spectra treating the upper vibrational numbering as an unknown. This was possible because they had spectra for several isotopic substitutions and were able to determine $\Delta G''_{1/2}$ from the spectra with some guidance from previous ab initio calculations [12]. For MgAr $^+$ they observed the 0 \leftarrow 0 transition, but for MgKr $^+$ they assigned the first observed transition as 1 \leftarrow 0. By extrapolating the vibrational levels in the upper state they were able to estimate the binding energy for the $^2\Pi$ states. Using the $^2\Pi$ binding energies and the

differences between the ${}^2\Pi-{}^2\Sigma^+$ and the ${}^2P-{}^2S$ transition energies, they were able to estimate the binding energies in the ground states.

Le Roy [13] extended this work by performing a detailed analysis of the extrapolation of the vibrational levels and obtained more accurate dissociation energies for MgAr^+ and MgKr^+ . In addition, Scurlock and Duncan [14] have rotationally resolved data for MgAr^+ that allowed them to determine the r_0 value of the ground state and the bond length of the $v = 5$ level of the ${}^2\Pi$ state. They are analyzing the results of similar experiments on MgKr^+ .

In this work we report on calculations of MgAr^+ and MgKr^+ . The comparison of the computed and experimental results will allow a calibration of the theoretical methods. Overall, the calculations compare very favorably with the available experimental results. Thus, theory supports the analysis of the existing spectra, and should aid in the interpretation of the current experiments [14] on MgKr^+ .

2. Methods

The Mg and Ar basis sets are the (17s12p5d4f)/[7s6p4d3f] sets developed by Widmark, Persson, and Roos [15]. The Kr basis set is derived from the (20s15p9d) primitive set optimized by Partridge [16]. For polarization, three even-tempered ($\beta = 2.5$) 3d and five 4f functions (the most diffuse f exponent is 0.1303) are added. This primitive set is contracted to [7s6p5d3f], using the atomic natural orbital procedure [17]. The outermost s and p primitives are uncontracted and even-tempered s and p functions are added, yielding a final basis set of the form (21s16p12d5f)/[(7 + 2)s(6 + 2)p5d3f]. Only the pure spherical harmonic components of the basis functions are used.

Mg core–valence correlation and core-polarization effects are accounted for using the core-polarization potential (CPP) approach suggested by Müller et al. [18]. The cut-off (0.7485) and core polarizability (0.4814) are taken from Müller et al. [18].

The orbitals are optimized using a state-averaged self-consistent-field (SA-SCF) approach. The ${}^2\Sigma^+$ and ${}^2\Pi$ states are included in the SA-SCF calculations. More extensive correlation is added using the singles and doubles configuration-interaction (SDCI)

approach. Nine electrons are correlated in the SDCI calculations; these correspond to the eight valence electrons of the rare gas atom and the one valence electron of Mg^+ .

The lifetimes and oscillator strengths are computed using the SDCI potentials and transition moments. The calculations are performed using MOLECULE–SWEDEN¹, which has been extended² to include the CPP operator. The calculations were performed using the NASA Ames Central Computer Facility CRAY C90 computer.

3. Results and discussion

The computed SA-SCF ${}^2P-{}^2S$ separation of 35642 cm^{-1} for Mg^+ is in excellent agreement with the experimental value [19] of 35746 cm^{-1} . Thus we expect our computed excitation energies to agree well with experiment. The polarizability of Ar is computed to be 10.99 a_0^3 at the SDCI level. This is in good agreement with the experimental result of 11.07 [20] and the value of 11.08 derived from dipole oscillator strength distributions [21]. The polarizability at the coupled-cluster singles and doubles level, including a perturbational estimate of the connected triples [CCSD(T)], is 11.15 a_0^3 ; thus part of the difference with experiment is a result of level of correlation treatment and not due to limitations in the basis set. However, it should be noted that previous work [22] for Ar has shown that the CCSD(T) result in a very large spdf basis set is close to 11.3 a_0^3 and that the inclusion of higher angular momentum functions and core correlation reduce the polarizability. The SDCI result for Kr (16.2 a_0^3) agrees well with the recommended value of Miller and Bederson [23] (16.7 a_0^3).

The potential curves are plotted in Fig. 1 and the computed spectroscopic constants are summarized in Table 1 along with the experimental results [9,13,14].

¹ MOLECULE–SWEDEN is an electronic structure program written by J. Almlöf, C.W. Bauschlicher Jr., M.R.A. Blomberg, D.P. Chong, A. Heiberg, S.R. Langhoff, P.-Å. Malmqvist, A.P. Rendell, B.O. Roos, P.E.M. Siegbahn, and P.R. Taylor.

² The CPP operator programs were written and interfaced with MOLECULE–SWEDEN by L.G.M. Pettersson.

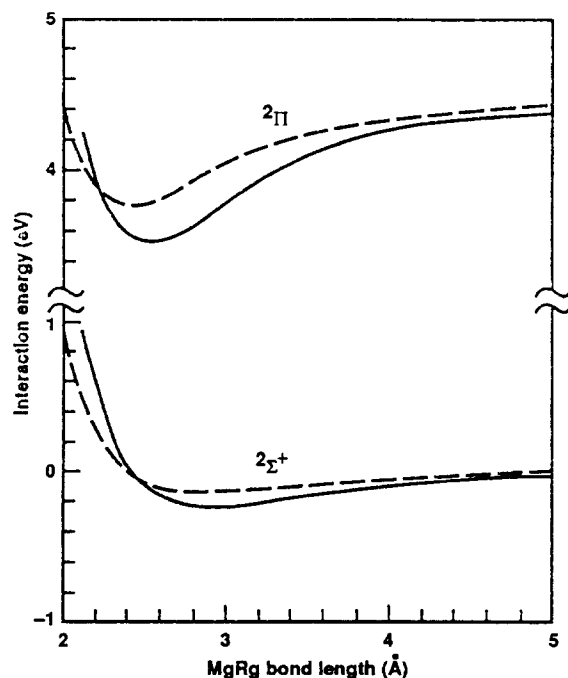


Fig. 1. The MgAr^+ (-----) and MgKr^+ (——) $^2\Sigma^+$ and $^2\Pi$ potentials.

For experiment we use the weighted average of the results for the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ components of the $^2\Pi$ state. Overall, the computed spectroscopic constants for MgAr^+ and MgKr^+ are in excellent agreement with experiment. We have found [12,24] that the computed D_0 converges more slowly with improvements in the calculations than the other spectroscopic constants, and based on other systems we expect to obtain only 80%–90% of the experimental D_0 for the metal–rare gas systems. Thus we believe that the true dissociation energy for MgKr^+ lies in the upper half of the experimental range. The computed MgKr^+ v_{00} value is 76 cm^{-1} smaller than that deduced from experiment, which is consistent with the computed $^2\text{P}-^2\text{S}$ separation, where theory is 104 cm^{-1} smaller than experiment. The r_0 value for the ground state of MgAr^+ is in very good agreement with experiment, while the r_5 value for the $^2\Pi$ state is 0.01 Å longer than experiment. With no Mg valence σ electrons, the bond length of the $^2\Pi$ state is probably determined by repulsion between the Ar atom and the Mg $2s2p$ orbitals. Such an intermolecular core–valence interaction is beyond what can be

expected from the CPP operator, and it is not surprising that the Mg core polarization and core–valence correlation are slightly underestimated, resulting in a bond length that is too long. Even if the CPP operator gives rise to a small error, it is much better to use the CPP operator than ignore Mg inner-shell effects. For example, if the Mg inner-shell effects are neglected the error in the $\text{Mg}^+ ^2\text{P}-^2\text{S}$ separation is 1260 cm^{-1} or more than ten times larger than that obtained using the CPP operation. The D_0 and $\Delta G_{1/2}$ values are also in much poorer agreement with experiment without the CPP operator.

The D_0 and v_{00} values for MgAr^+ show larger errors than those for MgKr^+ . For example, the computed D_0 values lie outside the experimental range, this is especially pronounced for the $^2\Pi$ state. As noted above this is consistent with our expected accuracy. The computed MgAr^+ v_{00} value is 138

Table 1

SDCI spectroscopic constants for the $^3\Sigma^+$ and $^2\Pi$ states; the experimental results^a are given in parentheses. The radiative lifetimes for the $^2\Pi$ state are also given

State	r_e (Å)	D_0 (cm^{-1})	$\Delta G_{1/2}$	v_{00}
MgAr⁺				
$^2\Sigma^+$	2.854 ^b	1041 (1210 ± 165)	90 (96)	
$^2\Pi$	2.406 ^c	5097 (5455 ± 165)	259 (265)	31585 (31447)
MgKr⁺				
$^2\Sigma^+$	2.886	1863 (1812 ± 591)	115 (112)	
$^2\Pi$	2.527	7020 (6914 ± 591)	251 (252)	30484 (30560)
v'	Radiative lifetime of the $^2\Pi$ state, in ns			
	MgAr⁺		MgKr⁺	
	bound ^d	total ^e	bound ^d	total ^e
0	10.33	6.42	7.82	7.66
1	12.46	6.33	8.74	7.56
2	11.44	6.23	10.75	7.45
3	11.98	6.14	10.98	7.35
4	11.51	6.05	10.70	7.25

^a The v_{00} values are from Ref. [9]. The $\Delta G_{1/2}$ values are computed using the ω_e and $\omega_e X_e$ values from the same source. The D_0 values are from Ref. [13].

^b The computed r_0 value is 2.884 Å compared with the experimental value [14] of $2.882(17)\text{ Å}$.

^c The computed r_5 value is 2.535 Å compared with the experimental value [14] of $2.524(14)\text{ Å}$.

^d Includes only the bound–bound contribution to the radiative lifetime.

^e Includes both the bound–bound and bound–free contributions.

Table 2

The computed transition energies, Franck–Condon factors, and oscillator strengths for the ${}^2\Pi \leftarrow {}^2\Sigma^+$ system in MgAr^+

v'	$v'' = 0$			$v'' = 1$			$v'' = 2$		
	ΔE	FC	f	ΔE	FC	f	ΔE	FC	f
0	31585	0.0007	0.0003	31495	0.0030	0.0015	31410	0.0075	0.0038
1	31844	0.0052	0.0027	31754	0.0188	0.0098	31669	0.0371	0.0192
2	32097	0.0207	0.0109	32006	0.0553	0.0290	31921	0.0796	0.0416
3	32343	0.0535	0.0284	32253	0.0980	0.0519	32168	0.0887	0.0468
4	32582	0.1013	0.0543	32492	0.1106	0.0591	32407	0.0445	0.0237
5	32815	0.1488	0.0805	32725	0.0743	0.0401	32640	0.0018	0.0010
6	33041	0.1758	0.0960	32951	0.0195	0.0106	32866	0.0201	0.0109
7	33261	0.1706	0.0940	33170	0.0012	0.0006	33086	0.0696	0.0381
8	33473	0.1377	0.0765	33383	0.0413	0.0228	33298	0.0736	0.0406
9	33679	0.0931	0.0522	33589	0.1068	0.0596	33504	0.0260	0.0144
10	33878	0.0529	0.0299	33788	0.1466	0.0825	33703	0.0004	0.0003
11	34070	0.0252	0.0143	33980	0.1385	0.0786	33895	0.0430	0.0243
12	34255	0.0100	0.0057	34165	0.0982	0.0562	34080	0.1140	0.0649
13	34433	0.0033	0.0019	34343	0.0541	0.0312	34258	0.1473	0.0846
14	34603	0.0009	0.0005	34513	0.0234	0.0136	34428	0.1243	0.0719

cm^{-1} larger than experiment. If the MgAr^+ v_{00} value is corrected for the error in the ${}^2\Pi-{}^2\Sigma$ separation, the MgAr^+ error is increased to 242 cm^{-1} , which is in contrast with MgKr^+ where the corrected value has an error of only 28 cm^{-1} . While these errors are both very small, it is surprising that the MgKr^+ results are in better agreement with experiment than those for MgAr^+ . This suggests we are benefiting from a favorable cancellation of errors in MgKr^+ .

The ${}^2\Pi-{}^2\Sigma^+$ transition moment corresponds to the strong ${}^2\Pi-{}^2\Sigma$ transition in Mg^+ . Since the transition is Mg centered, the transition moment is almost constant for all r values and is very similar for MgAr^+ and MgKr^+ . We compute the radiative lifetime for the bound–bound transitions using the computed SDCI potentials and transition moment – see Table 2. Given the similar transition energies and transition moment, it is somewhat surprising that the lifetimes for MgAr^+ and MgKr^+ differ significantly.

Table 3

The computed transition energies, Franck–Condon factors, and oscillator strengths for the ${}^2\Pi \leftarrow {}^2\Sigma^+$ system in MgKr^+

v'	$v'' = 0$			$v'' = 1$			$v'' = 2$		
	ΔE	FC	f	ΔE	FC	f	ΔE	FC	f
0	30484	0.0017	0.0008	30369	0.0078	0.0036	30258	0.0197	0.0091
1	30734	0.0116	0.0055	30619	0.0399	0.0188	30509	0.0728	0.0341
2	30981	0.0393	0.0188	30866	0.0927	0.0441	30755	0.1075	0.0509
3	31223	0.0866	0.0419	31108	0.1239	0.0596	30998	0.0687	0.0329
4	31461	0.1396	0.0682	31347	0.0967	0.0470	31236	0.0078	0.0038
5	31695	0.1747	0.0863	31580	0.0342	0.0168	31470	0.0135	0.0066
6	31925	0.1768	0.0883	31810	0.0001	0.0000	31699	0.0672	0.0332
7	32150	0.1482	0.0748	32035	0.0277	0.0139	31925	0.0795	0.0397
8	32371	0.1046	0.0533	32256	0.0896	0.0454	32146	0.0335	0.0169
9	32588	0.0627	0.0323	32473	0.1345	0.0688	32363	0.0001	0.0000
10	32801	0.0322	0.0167	32686	0.1359	0.0703	32576	0.0295	0.0152
11	33010	0.0142	0.0074	32895	0.1038	0.0542	32785	0.0923	0.0480
12	33215	0.0054	0.0028	33100	0.0631	0.0333	32989	0.1302	0.0683
13	33415	0.0017	0.0009	33300	0.0313	0.0167	33190	0.1209	0.0641
14	33611	0.0005	0.0003	33496	0.0129	0.0069	33385	0.0833	0.0446

This difference can be understood in terms of the difference in the potentials. The sum of the Franck–Condon factors for a given vibrational level of the $^2\Pi$ state to all levels of the $^2\Sigma^+$ state shows that the bound–bound transitions do not account for all of the radiative decay of the $^2\Pi$ state. This is a result of the large difference in r_e values for these two states and the shallow well for the ground state. Since the $^2\Sigma^+$ state of MgAr^+ has a shallower well than that of MgKr^+ the bound–bound contribution to the radiative lifetime of MgAr^+ is smaller than that for MgKr^+ . Once the bound–free contributions are added to the lifetimes, the radiative lifetimes for MgAr^+ and MgKr^+ are much more similar.

In Tables 2 and 3 we report the Franck–Condon factors and oscillator strengths for $v'' = 0-2$ for MgAr^+ and MgKr^+ , respectively. The very small values for the 0–0 transition for both systems makes it clear why it was difficult for Pilgrim et al. to identify the band origin for these systems. It is interesting to note that our computed Franck–Condon factor and oscillator strength for the 0–0 transition for MgKr^+ is larger than for MgAr^+ , however they were able to observe the 0–0 for MgAr^+ but not that for MgKr^+ . Given the very small size of our value, the difference between theory and experiment could either arise from experimental conditions that favor the observation of MgAr^+ or from small errors in the computed potentials that result in errors in these very small Franck–Condon factors. A comparison of our computed oscillator strengths and the experimental relative intensities would be an interesting check on theory and on the assigned numbering of the v' levels.

4. Conclusions

Overall the computed spectroscopic constants are in good agreement with experiment. The $\Delta G_{1/2}$ values are in excellent agreement with experiment for both states of MgAr^+ and MgKr^+ . The D_0 values for MgAr^+ are slightly smaller than experiment, as expected for this level of theory. The computed binding energy for MgKr^+ suggests that the true dissociation energies lie in the upper half of the experimental range. The computed v_{00} values are in good agreement with experiment. Radiative life-

times are reported for the $^2\Pi$ state and Franck–Condon factors and oscillator strengths are given for the $^2\Pi \leftarrow ^2\Sigma^+$ transitions.

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