Laser Photoluminescence of Matrix-Isolated CaMg, SrMg, and SrCa in Solid Argon at 12 K

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Abstract: The CaMg, SrMg, and SrCa van der Waals molecules have been synthesized by codepositing the atoms from separate sources with argon or krypton at 12 K. The van der Waals ground state was studied by laser-induced fluorescence resulting in ω_e'' values of 97 and 60 cm^{-1} for CaMg and SrCa, respectively. Dye laser excitation spectra of CaMg and SrMg are compared with their absorption spectra. The molecular constants are discussed in terms of those of the parent homonuclear molecules.

I. Introduction

The heteronuclear alkaline earth dimers were first identified in absorption studies of Ca_2 and Sr_2 isolated in rare gas matrices at 10 K.[1] Banded absorption spectra were assigned to the CaMg and SrMg molecules produced by reaction of magnesium impurity in the calcium and strontium metal samples. Confirmation came from experiments using two separate metal sources, and in further experiments, absorptions due to BaMg and SrCa were also observed.[1] Heteronuclear group 2B molecules and group 2A–2B dimers were synthesized in a subsequent study.[2] The electronic transition energy and the excited state vibrational spacings were found to be intermediate to those of the corresponding homonuclear species as might be expected. Similar observations have been made for heteronuclear diatomics within other groups of the periodic table,[3,4] in particular for the alkali metal dimers.

However, owing to the excimer nature of the alkaline earth dimers, the properties of the van der Waals ground state are of great interest.[5] These ground-state constants must be extracted from emission studies for matrix-isolated species as no hot bands can be observed in absorption. Because of the recent interest in alkaline earth species and in excimer species in general, laser excited fluorescence studies were initiated. Results for CaMg, SrMg, and SrCa are reported here and compared to those obtained for the matrix-isolated parent homonuclear diatomics Mg_2,[6] Ca_2,[7-10] and Sr_2.[11] Only Mg_2[12-14] and Ca_2[15,16] have been studied in the gas phase. Strictly speaking the heteronuclear diatomics should be referred to as mixed excimers, heteroexcimers, or exciplexes; however, rare gas–halogen lasers are commonly called "excimer" lasers and this term will be used here.

II. Experimental Section

The experimental apparatus and metal effusion techniques have been described previously.[1,6-9] Magnesium-24 (99.99%, Dow Chemical), magnesium-26 (>95%, Oak Ridge National Laboratory), calcium (Alfa Inorganics), or strontium (Alfa Inorganics) samples were cut or filed in a glovebag under argon to remove surface oxidation products, loaded into a Knudsen cell, and outgassed under vacuum at elevated temperatures. Typical Knudsen cell temperatures for deposition of metal atoms were 300–350 °C for Mg, 360–450 °C for Ca, and 440–500 °C for Sr. The matrix gases, argon (Air Products, 99.99%) and krypton (Airco, 99.95%), were used without further purification.

Single metal matrices were prepared by codepositing the effusing metal atoms with matrix gas (2–3 mM/h) onto a polished copper block maintained at 12 K. Double metal samples were prepared in several ways. Initial Ca/Mg and Sr/Mg experiments took advantage of the magnesium impurity in the calcium or strontium metals as described previously.[1] Alternately, in some experiments, the magnesium level was enhanced by putting calcium and magnesium chunks in the same Knudsen cell and heating to form an alloy. This method was successful for Ca/Mg, but inconvenient and inconsistent. Ulti-

mately, the majority of the experiments were performed by codepositing different metal atoms from separately controlled Knudsen cells mounted so that their beams crossed at the substrate. This allowed maximum control over deposition concentrations of metals with widely separated vapor pressures. In addition, this method allows confirmation that all band systems assigned to heteronuclear molecules do indeed require two different metal atoms. Matrix deposition was monitored by following the growth of the emission bands of interest.

Excitation was provided by the fixed visible lines of argon and krypton ion lasers (Coherent Radiation) or by a tunable dye laser pumped with 4–6 W of total argon ion laser output. Rhodamine 6G or 110 were used as received (Exciton or Matheson Coleman and Bell). Ion laser plasma emission or dye laser background fluorescence was removed with either a dielectric spike filter or a prism and slit arrangement. Luminescence was focused on the entrance slit of a Spex 1401 double monochromator and detected with a cooled RCA C31034 phototube and Keithley 414S picoammeter. Spectra were not corrected for phototube or spectrometer response. Excitation spectra were scanned by attaching a motor drive to the birefringent tuning element of the dye laser. Calibration of the excitation and emission was obtained by superimposing low-pressure mercury arc lines or the fixed ion laser lines on the spectrum.

III. Results

A. CaMg. After calcium and magnesium were codeposited with argon, the spectrum shown in Figure 1 was obtained. The observed spectrum is independent of the three methods of matrix preparation discussed in the previous section, and of excitation energy. The spectrum shown in Figure 1a resulted from 568.2-nm Kr$^+$ laser excitation. Figure 1b shows extra bands that appeared following higher energy dye laser excitation in the 4 ← 0 absorption[1] band. The band energies and spacings, calibrated from the 568.2-nm Kr$^+$ line, are listed in Table I. The emission, centered about 16 700 cm^{-1}, is richly structured, with a strong, sharp (10 cm^{-1} FWHM) progression of about 95 cm^{-1} in the most intense part of the band and an intermediate broader (~15 cm^{-1}) series of the same frequency. In the higher energy portion of the spectrum, progressions of 155 and 95 cm^{-1} were observed.

When a sharp, well-resolved band in the emission spectrum was monitored and the excitation frequency scanned by tuning the dye laser, the excitation spectrum shown in Figure 2 was obtained. A progression of sharp zero-phonon lines was observed with a relatively intense broad multiphonon wing to the high-energy side. The energies of the sharp progression whose spacings range from 150 to 158 cm^{-1} are listed in Table II. Exciting into the zero phonon line or into the adjacent phonon wing produced identical emission spectra. Pumping the lowest energy excitation band at 17 275 cm^{-1} (later shown to be the 0–0 band) resulted in a spectrum showing several members of the strong, sharp progression; the intermediate series was either not present or not resolved. Excitation in the next threshold at 17 433 cm^{-1} (1 ← 0) clearly showed both series and was
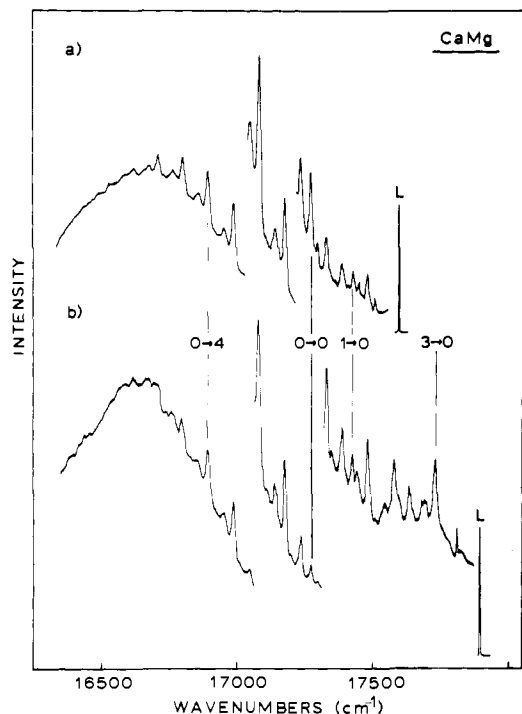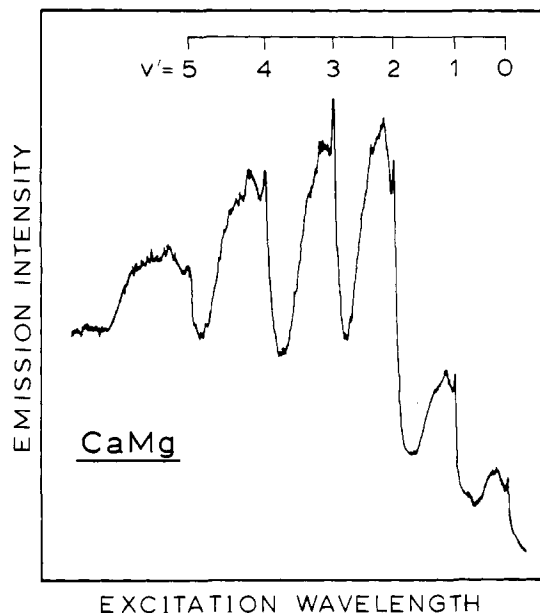
Figure 1. Fluorescence spectrum of CaMg in solid argon at 12 K following (a) 568.2-nm Kr^+ laser excitation and (b) 558.8-nm dye laser excitation into the 4 ← 0 excitation threshold. The laser excitation is labeled L and several vibronic bands are identified. The inset scans represent different amplifications. Spectral slit width is 2 cm^{-1}.

Figure 2. Excitation spectrum of CaMg in argon obtained by monitoring the change in intensity of 0 → 2 emission line and continuously tuning the dye laser. The horizontal axis is in arbitrary wavelength units. The v' numbering is given for each peak, and peak energies are listed in Table II.

Table II. Excitation Thresholds for CaMg in Solid Argon at 10 K

$v'-v''$	$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, cm^{-1}
0-0	17 275	
1-0	17 433	158
2-0	17 583	150
3-0	17 738	155
4-0	17 895	157

similar to the spectrum of Figure 1a. Excitation in each of the successive thresholds gave identical spectra with each excitation revealing more high-energy fine structure. Figure 1b shows the detailed high-energy fine structure following 17 895-cm excitation (4 ← 0). Excitation below the first threshold gave a weaker, structureless band centered about 13 700 cm^{-1}.

Several experiments were run with ^{26}Mg in order to confirm the magnesium-containing nature of the emission system. The very small isotope shifts expected (2.4 cm^{-1} for ground-state

Table I. Emission Band Energies, Spacings, and Assignments for CaMg in Solid Argon at 12 K

$v' \rightarrow v''$	cm^{-1}	$v' \rightarrow 0$		$3 \rightarrow v''$
3-0	17 734	152		97
3-1	17 637		$2 \rightarrow v''$	
2-0	17 582			95
3-2	17 542		98	
2-1	17 484	153		96
3-3	17 446		95	
1-0	17 429		$1 \rightarrow v''$	
2-2	17 389	155		
1-1	17 332		97	93
2-3	17 296	0-v''		
0-0	17 274		96	
1-2	17 236	96		
0-1	17 178		94	
1-3	17 142	95		
0-2	17 083		93	
1-4	17 049	95		
0-3	16 988		95	
1-5	16 954	94		
0-4	16 894		95	
1-6	16 859	94		
0-5	16 800		95	
1-7	16 764	91		
0-6	16 709		88	
1-8	16 676	87		
0-7	16 622			

progressions) and the absolute measurement accuracy (±5 cm^{-1}) do not allow line by line comparisons of isotope shifts. However, relative energy spacings on a given spectrum can be measured more accurately (±2 cm^{-1}) and the accumulation of isotope shifts over several members of a progression allows some meaningful conclusions to be drawn. For instance, the isotope shift over four members of the 95-cm^{-1} progression is 10 ± 4 cm^{-1} and the shift over two members of the 155-cm^{-1} progression is 5 ± 4 cm^{-1}. These should be compared to values of 9.6 and 7.6 cm^{-1}, respectively, calculated for a harmonic Ca–Mg vibration. Unfortunately, isotopic calcium used in previous experiments,[6-8] which would give a larger shift, was not available.

Upon codepositing calcium and magnesium with krypton at 12 K and exciting with the Kr^+ laser or dye laser in the vicinity of the CaMg/Kr absorption band,[1] only a broad, featureless emission peaking around 15 975 cm^{-1} was observed. Monitoring this band and scanning the dye laser excitation produced a spectrum very similar to that of Figure 2 except that no zero phonon lines were observed. A six-member progression of broad peaks, with average spacing of 150 cm^{-1}, and bands at 17 945, 17 785, 17 635, 17 509, and 17 344 cm^{-1}, was observed. Allowing for the bandwidth and calibration differences, agreement with the absorption spectrum of ref 1 is considered satisfactory. Finally, in connection with a study of Ca_2 in neon matrices at 3–5 K,[9] bands attributed to CaMg were observed in the absorption spectra. This band system consisted of a seven-member progression with average spacing of 144 cm^{-1}, which is listed in Table III. Following 568.2-nm excitation, only a broad band emission peaking at 16 400 cm^{-1}

**Table III.** Absorption Band Energies and Vibrational Spacings for CaMg in Solid Ne at 3 K

λ, nm	$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, cm^{-1}
552.5	18 100	
548.0	18 248	148
543.6	18 396	148
539.6	18 532	146
535.5	18 674	142
531.5	18 815	141
527.6	18 954	139
		av 144

was observed which is appropriate for CaMg by comparison to the other matrices.

B. SrMg. Emission from SrMg in solid argon was again first observed in single-oven experiments with strontium containing magnesium impurity, as in the absorption studies.[1] Unfortunately, only a broad, unstructured emission centered around 15 200 cm^{-1} was observed following dye laser excitation with rhodamine 6G. The dye laser excitation spectrum, shown in Figure 3, is characterized by an 11-member progression of relatively broad peaks with spacings ranging from 110 to 129 cm^{-1} and averaging 117 cm^{-1}. The excitation spectrum is very similar in appearance to the absorption spectrum,[1] but is better resolved and somewhat more extensive. The band energies and spacings are listed in Table IV.

C. SrCa. Because the absorptions of Ca$_2$ and Sr$_2$ at 650 and 710 nm are so close in energy, the intermediate SrCa absorption at 685 nm overlaps both homonuclear absorptions.[1] It is very difficult to excite SrCa without simultaneous excitation of Ca$_2$ or Sr$_2$. For example, when calcium and strontium were codeposited with argon and excited with 647.1- or 676.4-nm Kr$^+$ laser light, only the very strong Ca$_2$ emission was observed. Fortunately, the weak 687.0-nm Kr$^+$ line falls just below the Ca$_2$ origin[1] band at 678.0 nm and only excites Sr$_2$ very weakly yet falls within the SrCa absorption. This excitation produced the spectrum shown in Figure 4, which consists of a seven-member progression of very sharp (7–10 cm^{-1}) bands with an average spacing of 56 cm^{-1} and merges into a continuum centered about 13 300 cm^{-1}. The band energies and spacings are listed in Table V.
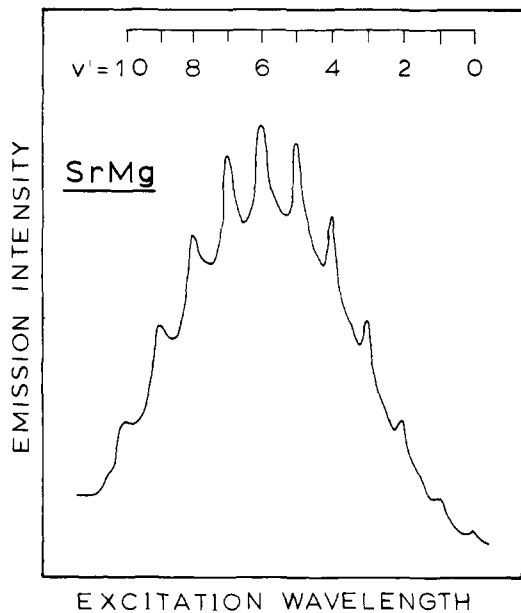
Table IV. Excitation Band Energies and Assignments[a] for SrMg in Solid Argon

v'	$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, cm^{-1}
0	16 139	
1	16 268	129
2	16 388	120
3	16 510	122
4	16 633	123
5	16 750	117
6	16 866	116
7	16 980	114
8	17 090	110
9	17 206	116
10	17 316	110
		av 117

[a] First observed band assigned to the origin.

IV. Discussion

A. Assignment. For each of the combinations Ca/Mg, Sr/Mg, and Sr/Ca a single emission was observed which was either not present or only very weakly present in the single-oven experiments. In the latter cases, Ca/Mg and Sr/Mg, the two-oven technique enhanced the emission intensity. These results confirm that two different metal species are required for the emission. Furthermore, the emissions were observed following excitation into absorption bands previously assigned to the heteronuclear dimers.[1] For Ca/Mg and Sr/Mg, the excitation spectra are sufficiently similar to the absorptions in their energy and spacing to link the emission systems to the absorptions.[1] The emissions are therefore assigned to the CaMg, SrMg, and SrCa dimers, and originate from the excited states previously observed in the absorption studies. For CaMg additional support comes from the isotope shifts which demand a magnesium-containing species; the magnitudes of the shifts are appropriate for the mixed dimer. As the electronic transition is the same, the assignment is likewise given in general as $^1\Sigma^+$ (^{1}P (heavier) + ^{1}S (lighter) → $^1\Sigma^+$ (^{1}S + ^{1}S)). For example, for the CaMg molecule, the observed transition is $^1\Sigma^+$ (^{1}P(Ca) + (^{1}S(Mg)) → $^1\Sigma^+$ (^{1}S(Ca) + (^{1}S(Mg)). A transition to the other upper state with the same symmetry, $^1\Sigma^+$ (^{1}S (heavier) + ^{1}P (lighter))', which is expected at higher energy has not been observed. Interaction between these two $^1\Sigma^+$ states will displace the observed $^1\Sigma^+$ (^{1}P (heavier) + ^{1}S (lighter)) to lower energy than might be expected from comparison of the homonuclear molecules.

B. Vibrational Analysis. CaMg. Similar to the Mg$_2$[5] and Ca$_2$[6–9] emissions, CaMg shows progressions in the excited-state

v' = 1 0   8   6   4   2   0

SrMg

EMISSION INTENSITY

EXCITATION WAVELENGTH

Figure 3. Excitation spectrum of SrMg in solid argon obtained by monitoring the broad continuous emission and tuning the excitation.

SrCa

INTENSITY

0–5

0–0

L

13000   13500   14000   14500
WAVE NUMBERS (cm^{-1})
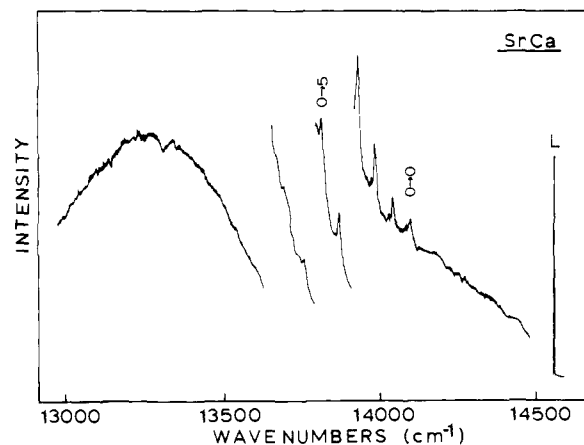
Figure 4. Fluorescence spectrum of SrCa following 687.0-nm excitation. The laser excitation is marked L and several vibronic peaks are identified. Inset scans represent different amplification ranges.

Table V. Emission Band Energies and Vibrational Spacings for SrCa in Solid Argon at 10 K

v''	$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, cm^{-1}
0	14 098	
1	14 046	52
2	13 986	60
3	13 928	58
4	13 871	57
5	13 815	56
6	13 759	56
		av 56

Table VI. Summary of Ground-State Data (cm^{-1}) for Alkaline Earth Dimers in Argon

		0–0	ω_e''	$\omega_e X_e''$
Mg$_2$	Ar[a]	26 226	90.8	0.60
	gas[b]	26 139	51.1	1.64
CaMg	Ar	17 274	96.6	0.3
Ca$_2$	Ar[c]	14 750	81.7	0.52
	gas[d]		65.0	1.07
SrMg	Ar	16 139		
SrCa	Ar	14 098	60	
Sr$_2$	Ar[e]	13 424	44	

[a] Reference 6. [b] Reference 12. [c] Reference 9. [d] Reference 15. [e] Reference 11.

frequency,[1] ~155 cm^{-1}, in the high-energy portion of the spectrum, indicating vibrationally unrelaxed emission. Thus, the electronic origin cannot be simply assigned to the highest energy band nor are the isotope shifts for Ca^{26}Mg sufficiently accurate to establish the 0–0 bands. However, the origin can be assigned as 17 274 cm^{-1} by the following argument. First, inspection of the spectrum of Figure 1 and the band energies tabulated in Table I shows that the lowest energy member of the 155-cm^{-1} progression and the highest energy member of the sharp 95-cm^{-1} series coincide at the 17 274-cm^{-1} band. In addition, the broader 95-cm^{-1} series terminates at 17 429 cm^{-1}, one excited state quantum higher than the 17 274-cm^{-1} band, consistent with a $1 \rightarrow v''$ assignment. Second, the lowest excitation band also falls at 17 275 cm^{-1}. Although excitation to lower energy still gives a weak, unstructured emission, no vibrational fine structure has been seen with excitation less than 17 274 cm^{-1}. Finally, consideration of other numbering schemes leads to unassigned bands or contradictory assignments. With this assignment, the ground-state constants ω_e'' = 96.6 $\pm$ 0.3 cm^{-1} and $\omega_e x_e''$ = 0.3 $\pm$ 0.1 cm^{-1} were calculated from the usual plot of vibrational energy vs. quantum number. An upper limit to the dissociation energy of ground-state CaMg calculated from the standard expression D_e'' = $(\omega_e'')^2/4\omega_e x_e''$ is 7800 $\pm$ 2500 cm^{-1}, which appears unreasonably high. A lower limit is given by the highest observed vibronic band at 652 cm^{-1}. The corresponding upper state constants were not calculated as only three vibrational spacings were observed in the emission spectrum and the four spacings observed in the excitation are not known very precisely. An ω_e' value near 156 cm^{-1} is reasonable.

Comparison of the emission and excitation spectra with the absorption spectrum[1] allows several interesting observations. The absorption spectrum is characterized by a progression of triplets with each of the three series having about the same spacings, averaging 140, 141, and 144 cm^{-1}. These series presumably reflect three different matrix sites. The emission shows only one site with sharp structure. A second matrix site can be inferred from the observation of a broad, unstructured emission following excitation below 17 274 cm^{-1}. It was not possible to characterize more than one site, even with tunable excitation. In contrast, the Ca$_2$ experiments gave three discrete sites, which could be separately excited.[8] The emission data apparently correspond to the high-energy site seen in absorption based on the near coincidence of the $4 \leftarrow 0$ and $3 \leftarrow 0$ excitations with the first two absorptions.[1] This correspondence requires renumbering Table IV of ref 1 where the observed peaks should be assigned to $3 \leftarrow 0$ to $12 \leftarrow 0$. The appearance of fewer sites in the emission studies reported here relative to the absorption is attributed to the much less concentrated samples used in the more sensitive laser fluorescence method. The lower and middle energy sites in the absorption studies are probably due to dimers perturbed by nearby magnesium and calcium atoms. In the more dilute studies reported here, these sites are less important.

For CaMg in a krypton matrix, no sharp bands were ob-

served. The absorption[1] and excitation spectra are characteristic of strong guest–host interaction leading only to broad multiphonon bands. These bands may merge and overlap to give a continuous emission. Alternately, stronger ground-state matrix interaction could lead to displacement of this potential curve relative to that of the excited state leading to only bound-free emission.

SrMg. The SrMg dimer in solid argon exhibited similar spectroscopic properties to CaMg in krypton. Only a broad, unstructured emission was observed while the absorption and excitation spectra consisted of broad multiphonon bands, indicative of strong matrix interaction, and no zero phonon lines were observed. Again, the lack of structured emission may also indicate bound-free emission due to displaced potential curves.

SrCa. Owing to the overlap in the absorption spectra with Ca$_2$ and Sr$_2$ only one excitation gave emissions attributable to SrCa. As the 56-cm^{-1} spacing is appropriate for the mixed dimer, and no excited-state intervals were observed, the emission is assumed to be vibrationally relaxed, and the first observed band can reasonably be assigned to the band origin. Table V is numbered accordingly. The absorption bands observed earlier[1] should now be numbered $4 \leftarrow 0$ to $11 \leftarrow 0$.

C. Comparison with Homonuclear Dimers. The available data on the van der Waals ground state of the alkaline earth dimers are collected in Table VI. Gas-phase[12-16] and argon matrix[6-11] data from other studies are included.

When discussing heteronuclear molecules composed of atoms within the same group, various empirical combining rules are often used to estimate molecular parameters of the mixed dimer from those known for the homonuclear molecules. For chemically bound molecules, these rules have been recognized for some time.[3,4,17] For the bound $^1\Sigma_u^+$ state of the mixed alkaline earth dimers the ω_e' values for CaMg, SrMg, and SrCa were found to be within a few wavenumbers of the arithmetic mean of those of the parent homonuclear dimers.[1]

Similar combining rules have been investigated for diatomic van der Waals states,[5] particularly for the rare gas dimers. Apparently, these combining rules do not work well, particularly in potential well depth predictions, which appear to reflect the properties of the less polarizable atom.[18] Also the more dissimilar the atoms involved, the more likely the failure of the combining rules.[5] Although extended analysis is not warranted, several observations are relevant. The three mixed dimers studied here span the range from very similar (SrCa) to very dissimilar (SrMg) component atoms. Strontium and calcium atoms are very similar in their size, polarizability, and electronegativity and the Ca$_2$ and Sr$_2$ dimers are quite similar in their electronic properties. It is therefore not surprising that the 0–0 band of SrCa (14 098 cm^{-1}) and the vibrational frequency (60 cm^{-1}) are very close to the arithmetic mean of the corresponding values for Ca$_2$ and Sr$_2$ (14 087 and 63 cm^{-1}).

In contrast, however, the magnesium atom is considerably smaller than calcium or strontium and hence less polarizable. For CaMg the electronic transition energy is red shifted from the mean of Ca_2 and Mg_2 and the ω_e'' is greater than for either Mg_2 or Ca_2! Likewise, the SrMg transition is red shifted but no ground-state constants could be determined. Unfortunately, the most interesting property of these van der Waals molecules, the potential well depth, cannot be compared as only relatively crude estimates can be made from the matrix data.

The two homonuclear molecules Ca_2 and Mg_2 exhibited large gas to matrix shifts in ω_e'' of 17 and 40 cm^{-1}, respectively. The large shift for Mg_2 is probably matched by CaMg; if this suggestion is correct, gaseous CaMg is predicted to have $\omega_e'' \approx 55 \pm 5$ cm^{-1}.

Finally, the observation of vibrationally unrelaxed emission for CaMg is of interest, particularly in light of the large guest–host interaction evidenced by the intense multiphonon bands in the excitation spectrum. Similar, more extensive hot bands were seen for Mg_2[6] and Ca_2,[7,10] where the lifetime is known to be short[10] and less phonon interaction was observed.

V. Conclusions

Emission from the heteronuclear group 2A dimers CaMg, SrMg, and SrCa has been observed and assigned to the same $^1\Sigma^+ \rightarrow {}^1\Sigma^+$ transition previously observed in absorption studies. For CaMg and SrCa vibronically discrete spectra provided constants describing the van der Waals ground state. Excitation spectra were similar to the absorption spectra. Several comparisons with the corresponding homonuclear dimers were made and matrix effects were discussed. Unrelaxed emission was observed from CaMg which indicates an extremely short fluorescence lifetime for this molecule.

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Excited State Proton Transfer of Ruthenium(II) Complexes of 4,7-Dihydroxy-1,10-phenanthroline. Increased Acidity in the Excited State

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Abstract: Studies are reported for acid–base equilibria for aqueous solutions of ground and lowest excited states of complexes of the general formula $[L_2Ru(4,7\text{-dihydroxy-1,10-phenanthroline})]^{2+}$ (L = 2,2'-bipyridine, 1,10-phenanthroline, 4,4'-dimethyl-2,2'-bipyridine, and 3,4,7,8-tetramethyl-1,10-phenanthroline). Optical emission from both the fully protonated and fully deprotonated forms of the complexes allows the direct determination of the excited state equilibrium constant for the deprotonation–protonation associated with the two hydroxy groups on one of the ligands. The complexes are stronger acids in the excited state compared to the ground state. Data for L = 2,2'-bipyridine are representative: $pK_a = 10.1$ and $|pK_a^*| = 5.1$ for the two-proton ground and excited state equilibria, respectively. Optical spectral features are consistent with a more acidic excited state; absorption maxima and emission maxima red shift upon deprotonation of the complex from ~450 to ~500 nm and from ~650 to 735 nm, respectively. The data suggest that the deprotonated 4,7-dihydroxy-1,10-phenanthroline is a strong π donor and in the excited state the π-donor capability is more fully exploited and serves to stabilize the Ru → L charge transfer. Resonance structures associated with the aromatic heterocyclic hydroxy compound allow rationalization of the π-donor properties. Emission quantum yield and lifetime data for all of the complexes are reported at 298 and 77 K.

We recently added[1] excited state proton transfer to the growing list of bimolecular processes of electronic excited inorganic and organometallic complexes.[2-12] The study of acid–base chemistry *in the excited state* has proven to be valuable in the understanding of charge redistribution upon electronic excitation of organic molecules[13] and such should be useful in the study of inorganic and organometallic substances as well. In particular, we have set out to study such chemistry in complexes having lowest lying metal to ligand charge transfer (MLCT) states. In our first study[1] we found that the lowest excited state of Ru(2,2'-bipyridine)$_2$(4,4'- dicarboxylate-2,2'-bipyridine) is a stronger base than the ground state, consistent with the direction of the CT.

In this paper we wish to report on the ground and excited state acid–base chemistry of the four complexes [(4,7-dihydroxy-1,10-phenanthroline)RuL$_2$]$^{2+}$ (L = 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine, 1,10-phenanthroline, and 3,4,7,8-tetramethyl-1,10-phenanthroline). We have found that both the protonated and deprotonated forms are emissive in aqueous solutions and have carried out spectroscopic studies which allow the evaluation of the ground and excited state acid dissociation constants, pK_a and pK_a^*, respectively.