in density of states with respect to vibrational energy. The additional torsional nonrigidity above the photoisomerization threshold may also relax symmetry restrictions on optical activity.

The difficulty of inferring temporal behavior from frequency domain data is evident from these spectra. The fwhm of  $S_1$  + 1246 cm<sup>-1</sup> (selected as it has no apparent overlapping transitions) is 1.6 cm<sup>-1</sup>. The  $S_1 + 987$  cm<sup>-1</sup> level (Figure 1) has a 1.1-cm<sup>-1</sup> fwhm contour in neon, and the contour shape is nearly identical with that of  $S_1 + 1246$  cm<sup>-1</sup>. From the frequency domain data, it is not possible to infer that  $S_1 + 987$  cm<sup>-1</sup> exhibits quantum beats, while  $S_1 + 1246$  cm<sup>-1</sup> decays biexponentially.

Spectral analysis of IVR is hampered in low-symmetry, nonrigid molecules by spectral congestion, which is severe even in supersonic jets (Figure 6). Torsional dynamics must be properly accounted for to fully understand rotational-vibrational coupling and IVR in these molecules.

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## Photochemical Synthesis of Magnesium Dihydride and Methyl Magnesium Hydride in **Cryogenic Matrices**

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Photolysis at the  $3p^1P \leftarrow 3s^1S$  resonance transition of magnesium atoms isolated in hydrogen-containing rare gas matrices is found to give rise to the first observed example of a group 2 metal atom dihydride, magnesium dihydride (MgH<sub>2</sub>), with no evidence for the fragmented products, MgH + H. Isotopic substitution studies in the infrared indicate that the molecule is linear as predicted by simple Walsh type MO diagrams and ab initio calculations. This is in contrast with gas-phase studies, where only fragments are observed. Possible reasons for the differing reaction behavior (i.e. in the matrix and gas phase) are discussed in terms of the matrix cage effect and differences between the vibrational relaxation rates in the condensed phase and those in the gas phase. Similar photochemical behavior is exhibited by magnesium atoms in neat methane matrices, where the linear inserted product, methyl magnesium hydride (CH<sub>3</sub>MgH), is formed as shown by infrared isotopic substitution experiments. No electronic absorptions were observed for either products in the range 230-800 nm. Emission is observed during magnesium atom photolysis in xenon and methane matrices. The bands present in the former matrix are assigned to singlet  $(3p^1P \rightarrow 3s^1S)$  and triplet  $(3p^3P \rightarrow 3s^1S)$  atomic magnesium emission, while the possible origins of the long-lived visible emission in the latter matrix are proposed. The presence of hydrogen in a xenon matrix  $(1:10 \text{ H}_2:\text{RG})$  causes a decrease in the emission intensity relative to a neat xenon matrix but adds no additional features. The observation of only linear inserted products (MgH<sub>2</sub> and CH<sub>3</sub>MgH) is interpreted in the context of a concerted insertion mechanism with no detectable contribution from an abstraction pathway.

#### Introduction

Excited-state reactions of gas-phase magnesium atoms with hydrogen and small hydrogen-containing molecules, yielding magnesium monohydride and a radical (reaction I), have received considerable experimental<sup>1,2</sup> and theoretical attention.<sup>3-6</sup> Analysis

$$Mg(^{1}P) + RH \rightarrow MgH(v,N) + R \cdot \qquad (R = H, D, CH_{3}, ...)$$
(I)

of the rotational distribution in the newly born MgH(v=0,N)product molecule by pump-probe methods<sup>2</sup> has shown a bimodal pattern which has been interpreted in terms of the two possibilities for the reaction coordinate; i.e. abstraction, end-on-attack (resulting in population of low J) or insertion, side-on-attack (giving population to high J). The intermediates involved in both mechanisms are, however, undetectable in the gas phase because of their transient nature. In this paper we report that photoexcitation of matrix-isolated magnesium atoms at the  $3p^{1}P \leftarrow 3s^{1}S$ resonance transition in 10% hydrogen/rare gas and neat methane matrices at 12 K results in the formation of magnesium dihydride (MgH<sub>2</sub>) (reaction II)

$$Mg(^{1}P) + H_{2} \rightarrow HMgH$$
 (II)

$$Mg(^{1}P) + CH_{4} \rightarrow HMgCH_{3}$$
 (III)

and methyl magnesium hydride (CH<sub>3</sub>MgH) (reaction III), respectively. This technique has previously been described for similar reactions of Mn,<sup>7</sup> Fe,<sup>8</sup> and Cu<sup>9</sup> in hydrogen-containing rare gas matrices, as well as metal atoms in neat methane matrices.<sup>10</sup>

#### **Experimental Section**

The apparatus used for matrix preparation has been described earlier.<sup>15,16</sup> The matrices were formed by cocondensing mag-

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Figure 1. UV-visible absorption spectra of magnesium atoms (A) in the gas phase, (B) in CH<sub>4</sub>, and in hydrogen-containing (C) Kr and (D) Xe matrices with the effects of magnesium atom photolysis shown by broken line.

nesium, vaporized from a resistively heated stainless steel Knudsen cell, with the rare gas/hydrogen mixture or methane gas on a NaCl, CsI, or sapphire window cooled to 12 K by an Air Products Displex closed-cycle helium refrigerator for UV-visible absorption/fluorescence, infrared, and EPR spectroscopic studies, respectively. Magnesium metal flow was monitored by a quartz crystal microbalance while the gas flow was set by a calibrated leak from a needle valve or controlled by a mass flow meter, Vacuum-General Model 80-4. Deposition conditions were chosen such that the magnesium atom  ${}^{1}P \leftarrow {}^{1}S$  resonance transition signal was optimized for each system with gas flows of typically 1 mmol/h. Magnesium metal was supplied by Dominion Magnesium Limited and research grade Ar, Kr, Xe, H<sub>2</sub>, and CH<sub>4</sub> and CP deuterium gas were supplied by Matheson of Canada. Merck Sharp and Dohme/Isotopes supplied HD (98%), CD<sub>4</sub> (99%), and  $^{13}CH_4$  (97%). The Knudsen cells were outgassed for periods of up to 30 min before deposition and all the gases were used from lecture bottles without further purification. All gas mixtures were made up at least 24 h prior to use to facilitate mixing. UV-visible near-IR absorption spectra were recorded on a Perkin-Elmer 330 spectrophotometer. Fluorescence spectra were recorded on a Perkin-Elmer MPF 44B fluorescence spectrometer, selecting both the excitation and emission wavelengths with scanning mono-

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Figure 2. Infrared transmittance spectra of magnesium atoms in 10% hydrogen-containing krypton matrices (A) on deposition and (B-D) after photolysis at 283 nm for 120 min showing the absorptions of (B) MgH<sub>2</sub>, (C) MgHD, and (D) MgD<sub>2</sub>. Insert shows the fine structure on the asymmetrical stretching mode of MgD<sub>2</sub> in absorbance, associated with the three naturally occurring isotopes of magnesium, exhibiting the expected relative absorption intensities, in accordance with their abundances

chromators. The fluorescence spectrometer was used in both chopped ac and unchopped dc excitation modes. Excitation and emission spectra were not corrected for instrumental factors arising from the spectral output intensity of the 150-W Xe arc lamp or the spectral response characteristics of the Hamamatsu R 928 photomultiplier tube. Infrared spectra in the range 4000-250 cm<sup>-1</sup> were recorded on a Perkin-Elmer 180 and X-band EPR spectra (0-6000 G) on a Varian Model E4. The photolysis source was a 450-W Xe arc lamp with an Oriel Model 7240 grating monochromator and a 10-cm water cell.

#### **Results and Discussion**

UV-visible absorption spectra of magnesium (vaporized from a stainless steel Knudsen cell) cocondensed with 1:10 H<sub>2</sub>:RG mixtures at 10-12 K (RG = Kr and Xe) are essentially unchanged from those of the neat rare gas. The presence of hydrogen in argon matrices at 12 K gave substantially more magnesium dimer and higher clusters than in neat argon. The absorptions centered at 2815, 2836, and 2914 Å in argon, krypton, and xenon, respectively, have been ascribed<sup>11,12</sup> to the  $3p^1P \leftarrow 3s^1S$  atomic transition which occurs at 2852.1 Å in the gas phase.<sup>13</sup> The threefold structure on the absorption bands of matrix-isolated magnesium atoms has been explained in terms of site-induced crystal field effects<sup>14</sup> and the Jahn-Teller effect.<sup>12</sup> The latter explanation seems the more likely as MCD studies<sup>12</sup> have shown the triplet splitting arising from a single substitutional site with nonsymmetric modes contributing to the bandwidth, this being a necessary requirement for the Jahn-Teller effect.

Narrow-band  $3p^1P \leftarrow 3s^1S$  magnesium atom photolysis (10 nm fwhm) at 283 and 292 nm in  $H_2/Kr$  and  $H_2/Xe$  matrices for a 20-min period caused complete bleaching of this absorption (Figure 1), with no indication of growth of any new peaks in the 230-850-nm region. This decrease in the intensity of the atomic resonance absorption was found to exhibit a simple Beer's law

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TABLE I: Infrared Absorptions (cm<sup>-1</sup>) and Assignments of Magnesium Dihydride in Solid Krypton and Solid Xenon Matrices Resulting from Mg Atom Photolysis at 283 and 292 nm, respectively

krypton			xenon			
MgH <sub>2</sub>	MgHD	MgD <sub>2</sub>	MgH <sub>2</sub>	MgHD	MgD <sub>2</sub>	mode assignmt <sup>a</sup>
			1569			ν(MgH), A
1558			1544			$\nu(MgH), B$
				1564		$\nu(MgH), A$
	1548			1536		$\nu(MgH), B$
430					1160	$\nu(MgD), A$
		1153			1144	$\nu(MgD), B$
				1156		$\nu(MgD), A$
	1127			1116		$\nu(MgD), B$
			417			$\delta(MgH_2) A, B$
	380			366		$\delta(MgHD) A,B$
		309			300	$\delta(MgD_2) A, B$

<sup>a</sup>Site A was unstable to annealing at 25 K for 20 min in xenon matrices. Only site B was resolved in krypton matrices.

type dependence on photon flux. Green emission was observed during photolysis at this wavelength in both neat and hydrogencontaining xenon matrices but not in the corresponding argon or krypton systems.

Infrared spectra of samples formed under similar conditions as the above UV-visible experiment (shown in Figure 2) showed growth of a magnesium-hydrogen asymmetric stretching  $\nu_3$  and a bending mode  $\nu_2$  at 1558 and 430 cm<sup>-1</sup>, respectively, in a 10% H<sub>2</sub>/krypton matrix upon excitation at 283 nm. An unresolved feature on the high-frequency side of the main band at 1558 cm<sup>-1</sup> was found to be thermally unstable upon annealing to 25 K for 20 min and is ascribed to a secondary trapping site. Similar studies on the hydrogen/xenon system gave frequencies shifted to lower energies by approximately 14 cm<sup>-1</sup>, again with a thermally unstable high-frequency band but with a larger separation (Table I). No evidence was obtained for the formation of matrix-isolated magnesium monohydride<sup>17,18</sup> in any of the matrices in optical, EPR, and infrared experiments.

The frequency shifts obtained upon isotopic substitution of  $H_2$ by D<sub>2</sub> in krypton and xenon matrices are those expected for a linear  $XY_2$  molecule, where the symmetric stretching mode  $\nu_1$  is not observed in the infrared.<sup>19</sup> In the case of the asymmetric stretch<sup>20</sup> it was possible, in well-annealled matrices, to resolve the frequencies associated with the three naturally occurring isotopes of magnesium, with absorption intensities corresponding to their natural abundancies, i.e. <sup>24</sup>Mg, <sup>25</sup>Mg, and <sup>26</sup>Mg at 78.7, 10.1, and 11.2%, respectively (Figure 2). This is indicative of a molecule containing a single magnesium atom. In matrices containing HD, bands associated with mostly MgH and mostly MgD stretches were observed (see Table I), with frequencies shifted slightly from the parent MgH<sub>2</sub> and MgD<sub>2</sub> positions. No absorptions associated with a scrambling process were observed in HD/rare gas matrices. Similarly no mixed product HMgD was observed in Kr or Xe matrices containing equal amounts of hydrogen and deuterium, 1:1:20  $H_2:D_2:RG$ . These observations suggest that the mechanism for the formation of this molecule under matrix-isolation conditions is a one-step concerted reaction, involving a bent transition state leading directly to a linear ground-state product.

Magnesium atoms isolated in methane matrices  $(1:10^4 \text{ Mg:} CH_4)$  at 12 K exhibit a UV-visible absorption spectrum similar

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TABLE II: Infrared Absorption Frequencies  $(cm^{-1})$  and Tentative Assignments for Methyl Magnesium Hydride Formed by Photolysis of Magnesium Atoms in  $CH_4$ ,  $CD_4$ , and  ${}^{13}CH_4$  Matrices

Mg/CH <sub>4</sub>	Mg/CD <sub>4</sub>	Mg/ <sup>13</sup> CH <sub>4</sub>	mode assignmt <sup>a</sup>	
2932	2190	2924	$\nu_{a}(CH_{3})$	
2896	2036	2896	$\nu_{\rm s}({\rm CH_3})$	
1524	1115	1524	$\nu(MgH)$	
1122	872		$\delta_{s}(CH_{3})$	
550	441	546	$\rho_r(MgCH_3)$	
539	424	528	$\nu(MgC)$	
353	300	350)	(CMall)	
340	288	340 <b>š</b>	o(CmgH)	

<sup>*a*</sup> Referring to  $CH_4$ .



Figure 3. Infrared spectra of magnesium atoms isolated in neat methane (A) on deposition and (B) after 120-min photolysis at 285 nm, showing peaks associated with the product  $CH_3MgH$ .

to those of magnesium atoms in rare gas matrices (Figure 1). Narrow-band (10-nm fwhm) photolysis at the  $3p^{1}P \leftarrow 3s^{1}S$  Mg atom resonance absorption (283 nm) resulted in rapid and complete loss of magnesium atoms with no evidence of dimer or cluster formation. As in the case of Mg/xenon matrices, green emission was observed during photolysis while magnesium atoms were present. No absorbances corresponding to products were observed in the region 230-850 nm. Photolysis at 283 nm gave rise to infrared absorbances (Table II) corresponding to a linear insertion product, CH<sub>3</sub>MgH, which was found to be photochemically stable at this wavelength (cf. CH<sub>3</sub>CuH<sup>10a</sup>). Studies done in CD<sub>4</sub> and <sup>13</sup>CH<sub>4</sub> matrices resulted in isotopic shifts which are consistent with this formulation (see Figure 3, Table II). EPR spectra of freshly deposited methane matrices containing magnesium atoms exhibited no absorptions before and after 283-nm photolysis, indicating the absence of paramagnetic species both on deposition and as a result of photolysis. As with the dihydride system these observations are consistent with a mechanism involving a one-step insertion pathway, leading directly to the formation of a linear product.

As mentioned above, excitation at the  $3p^{1}P$  magnesium atom resonance transition in xenon and methane matrices resulted in visible green emissions. Spectral analysis (in the region 200–900 nm) of these, as well as the argon and krypton systems, using a Perkin-Elmer MPF-44B spectrofluorimeter, revealed the presence of other emissions. Figure 4 shows the emission intensity for Xe and CH<sub>4</sub> matrices as a function of wavelength, while exciting at the  $3p^{1}P$  resonance of magnesium atom centered at 294 and 285 nm, respectively.

The emission of magnesium in freshly deposited xenon matrices is seen to consist of a set of ultraviolet bands at 364 and 377 nm and a visible set at 480 and 540 nm. Excitation profiles obtained by using narrow slits (<2 nm) of the emission features labeled A and B are clearly different. The excitation profile of A shows closest similarity to the intense threefold feature on the absorption spectrum shown in Figure 1, while that of B corresponds to the lower intensity, higher and lower frequency side bands straddling the main threefold feature. This demonstrates that the emissions

<sup>(19)</sup> The absence of  $\nu_1$  for MgH<sub>2</sub>, although strongly supportive of the linear form, does not unequivocally eliminate a bent form since (a) a slight deviation from linearity could result in a very low absorbance intensity for  $\nu_1$  and (b) an accidental overlap (within 1 cm<sup>-1</sup>) of  $\nu_1$  and  $\nu_3$  could occur. The latter possibility is unlikely as the  $\nu_1$  and  $\nu_3$  bands of all three isotopic molecules MgH<sub>2</sub>, MgHD, and MgD<sub>2</sub> would have to be degenerate.





Figure 4. (A) Uncorrected emission and excitation spectra of magnesium atoms in solid xenon matrices showing the presence of sites A and B. The broken line corresponds to the emission obtained from a freshly deposited matrix while exciting with narrow-band radiation (<2 nm fwhm) centered at 289 or 303 nm. The solid line is the emission resulting from excitation at 294 nm under the same spectral conditions as above or using broad band (10-nm fwhm) radiation after annealing to 55 K for a 30-min period. (B) Uncorrected emission and excitation spectra for magnesium atoms in solid methane. The solid trace corresponds to the emission in a freshly deposited matrix resulting from excitation at 285 nm while the broken trace is the emission obtained by exciting at 299 nm. The excitation profiles of both emissions (i.e. 520 and 560 nm) are shown on the left. The shoulder to the red of the main band present in the excitation profile of the 560-nm emission is found to be thermally unstable, see text.

are dependent upon population of the 3p<sup>1</sup>P level. Annealing to 55 K for a 30-min period caused total removal of feature B. Accordingly emission bands A and B are assigned as emissions from thermally stable and thermally unstable sites, respectively. The emissions at 480 and 540 nm in unannealed matrices show different behavior upon changing from direct mode excitation (dc) to chopped excitation mode (ac), in that the signal of the 540-nm band is annihilated while that of the 480-nm band remains unchanged, as do the ultraviolet emissions. This differing behavior is explained in terms of the 540-nm emission having a longer lifetime than that of the 480-nm emission. No lifetime measurements have been performed on these emissions as yet but qualitative estimates can be made since the modulation frequency is known to be 56 Hz. This means the lower limit on the 540-nm emission lifetime is  $\sim 20$  ms while the lifetimes of the other emissions are shorter than this value. The Stokes' shift for the two emission bands (377 and 480 nm) from the thermally stable site is 7130 and 13000 cm<sup>-1</sup>, respectively, relative to excitation at 294 nm. Because of the existence of only the 3p<sup>3</sup>P state for atomic magnesium<sup>13</sup> between the 3p<sup>1</sup>P and the 3s<sup>1</sup>S ground state and the absence of all internal degrees of freedom except delocalized low-frequency (<40 cm<sup>-1</sup>) phonon modes in solid xenon, one is forced to conclude that the emission at 377 nm arises from the spin and parity allowed  $3p^1P_1 \rightarrow 3s^1S_0$  transition with a 7130-cm<sup>-1</sup> Stokes shift, while the emission at 480 nm arises from the  $3p^3P_1 \rightarrow 3s^1S_0$  intercombination band which is spin forbidden. With this assignment the Stoke's shift relative to the gas-phase triplet absorption  $(3p^3P_1)$  at 457.1 nm<sup>13</sup> (which is not observed in the absorption spectra or excitation profiles) is 1010 cm<sup>-1</sup>. The larger Stoke's shift in the 3p<sup>1</sup>P emission compared with that of

the 3p<sup>3</sup>P emission is in agreement with calculations of the spatial extent of the 2p wave functions of similar terms (i.e.  $2p^{1}P$  and 2p<sup>3</sup>P) of Be atoms<sup>21a</sup> where the size of the former is almost double that of the latter (<sup>1</sup>P, 5.0254 au and <sup>3</sup>P, 2.8831 au). This size difference arises as a result of the effect of exchange interaction<sup>21b</sup> between the 2s and 2p electrons. It is likely that the lifetime of this 480-nm emission resulting from the thermally stable site is quite long (milliseconds) as hinted by the value for its thermally unstable partner at 540 nm, whose lifetime is longer than  $\sim 20$ ms. These values are in approximate agreement with the measured radiative lifetime of the  $(3p^3P_1)$  triplet state in the gas phase of  $4.5 \pm 0.5 \text{ ms}^{22}$  observed at 457.2 nm and the theoretically predicted value of 4.40 ns.<sup>23</sup> It also correlates with the much longer triplet emission lifetimes ( $\sim 1$  s) previously observed for matrix-isolated beryllium atoms<sup>24</sup> which has smaller spin-orbit coupling than magnesium. The emission spectra of xenon matrices containing 10% hydrogen consist of bands at the same frequencies as neat xenon matrices but with decreased intensities. No additional emission bands were observed for these H2-containing matrices. The decrease in the emission intensity with the addition of hydrogen presumably reflects the presence of the chemical quenching channel which will compete with the radiative and nonradiative processes for the depletion of the 3p<sup>1</sup>P state population.

Studies of the atomic magnesium emission in neat and hydrogen-containing argon and krypton matrices in progress and the subject of future publication corroborate the previous emission studies of matrix-isolated magnesium atoms,<sup>25</sup> where only ultraviolet emissions were observed. Thus it would appear that the extra triplet-state emission (phosphorescence) observed only in xenon matrices arises because of xenon's larger spin-orbit coupling, a phenomenon which has been called the "external heavy atom effect".26

Magnesium atom emission in neat methane matrices is only observed at 520 and 560 nm (Figure 4B). Excitation profiles of these emissions again show their origin to be the 3p<sup>1</sup>P Mg atom excited state. Annealing and photochemical "hole-burning" experiments indicate that the two bands arise from Mg atom occupation of different sites, analogous to the xenon system. In contrast to Xe, however, both emissions in neat CH<sub>4</sub> matrices are dependent upon the excitation mode, vis ac or dc, thereby reflecting their long lifetimes and presumably their spin-forbidden nature. As a result all the bands have been assigned to atomic or molecular triplet emissions. The absence of relaxed singlet  $(3p^1P \rightarrow 3s^1S)$ atomic magnesium emission in CH4 is anomalous, but a similar effect has been observed for matrix-isolated beryllium atoms in rare gases.<sup>24</sup> Similarly the observation of the tentatively assigned atomic triplet-state emission in a solid methane cage is anomalous since chemical quenching is expected to be dominent because of the large chemical quenching cross section measured for the  $Mg(3p^{1}P) + CH_{4}$  gas-phase system.<sup>2b</sup> The presence of the atomic triplet emission presumably reflects (i) a competitive physical quenching channel, where the nonradiative intersystem crossing is facilitated by the presence of the extra vibrational and rotational degrees of freedom in methane (the accompanying increase in the density of states in CH<sub>4</sub> are absent in a solid krypton matrix which shows no such emission and has greater spin-orbit coupling but similar polarizability) or (ii) a chemical quenching channel which yields triplet atomic magnesium (3p3P) via a correlating triplet molecular state.

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An alternative explanation for the long-lived emission at 520 and 560 nm in the methane system is that of product chemiluminescence. As in the case of the magnesium dihydride  $(MgH_2)$ the formation of methyl magnesium hydride (CH<sub>3</sub>MgH) from (3p<sup>1</sup>P) Mg is expected to be highly exothermic (linear inserted MgH<sub>2</sub> product is predicted to be  $\sim 5$  kcal/mol above Mg(<sup>1</sup>S) +  $H_2$  or ~95 kcal/mol exothermic relative to Mg(3p<sup>1</sup>P) +  $H_2^{2a}$ ) so it is conceivable that some of this excess energy could be dissipated in the form of a radiative transition between an intermediate state and the ground-state product. Considering the long lifetime observed for these emissions, it is probable that they are spin forbidden transitions involving triplet and singlet product surfaces. This assignment would explain the absence of the relaxed  $3p^{1}P \rightarrow 3s^{1}S$  atomic emission and the presence of the apparently extremely large intersystem crossing rate constant.

The absence of such emissions in the case of magnesium dihydride (MgH<sub>2</sub>) can be rationalized in terms of the allowed surface crossings, in  $C_{2p}$  symmetry, of the attractive <sup>1</sup>B<sub>2</sub> state with the strongly bound  ${}^{I}A_{1}$  state. The resulting radiationless transitions, induced by vibronic coupling with asymmetric vibrations  $b_{2}$ ,<sup>27</sup> allow the  ${}^{1}A_{1}$  state to evolve directly from the  ${}^{1}B_{2}$  state to the  ${}^{1}\Sigma_{g}^{+}$  state of the linear inserted product without the intervention of the lower, slightly repulsive  ${}^{3}B_{2}$  state.<sup>2a,5,6</sup> Energy migration from this newly born highly vibrationally excited (in the  $\nu_2$  bending mode) molecule could then easily occur by collision with the cage having librational degrees of freedom or the phonon continuum as the accepting modes.<sup>28</sup> However, in the case of  $Mg(^{1}P) + CH_{4}$  insertion, the intermediate symmetry is  $C_s$ , giving rise to avoided crossing of the two <sup>1</sup>A' states (which in  $C_{2v}$  symmetry (Mg + H<sub>2</sub>) crossed) and the participation of the lower <sup>3</sup>A' state in the production of the  ${}^{1}A'$  ground state. From the relative energy separations of the <sup>1</sup>A' surface (correlating with Mg(<sup>1</sup>P) + CH<sub>4</sub>) from the <sup>3</sup>A' surface  $(Mg(^{3}P) + CH_{4})$  and the  $^{3}A'$  state from the ground-state  $^{1}A'$  $(Mg(^{1}S) + H_{2})^{29}$  it would seem reasonable to propose that the first transition be radiationless with the second being radiative (because of the "energy gap law" in radiationless transitions), the latter being radiative coupling of the spin disallowed  ${}^{3}A' \rightarrow {}^{1}A'$ process. The increase in the density of states on going from H<sub>2</sub> to RH (where  $R = CH_3, C_2H_5, ...$ ) is also expected to contribute to the greater involvement of the triplet surface in the production of the ground state R-Mg-H as postulated for the  $O(^{3}P)$  + RH system.<sup>30</sup> Further theoretical studies need to be completed on the Mg(<sup>1</sup>P) + CH<sub>4</sub> potential energy surfaces<sup>30</sup> in order to substantiate this speculation.

The observation of linear insertion products resulting from the photochemical reaction of magnesium atoms with hydrogen and methane under matrix isolation conditions is in contrast with those of gas-phase studies in which only the fragmented products are observed.<sup>21</sup> These fragments can result from two possible mechanisms, vis. end-on abstraction and side-on insertion followed by fragmentation, the latter being dominant in the gas phase. The results of the present study are most consistent with the side-on insertion pathway, since no fragments such as MgH, H, or CH<sub>3</sub> are observed. However, one cannot rule out a two-step mechanism involving the fragmentation of a bent inserted intermediate leading to a low translational energy H atom or CH<sub>3</sub> methyl radical and a rotationally excited MgH molecule with subsequent recombination to form the linear inserted product. This is possible due to the matrix "cage effect" which will tend to retard the escape of such low kinetic energy fragments from the reaction sphere,<sup>31</sup> thereby facilitating recombination. Such an effect will not be present in low-pressure gas-phase studies. The same type of matrix effect would be expected to operate in a pathway involving the

abstraction mechanism, where the linear inserted product could be formed by rotation of the MgH molecule<sup>32</sup> followed by recombination with H atoms or CH3 methyl radicals. Despite these matrix effects, hydrogen and methyl fragmentation products have been observed in matrices for the  $Cu/H_2/Kr^9$  and  $Cu/CH_4^{10a}$ systems where EPR spectroscopy has proven to be particularly sensitive to hydrogen atoms and methyl radicals. In light of these studies it seems likely that processes involving a fragmentation step do not contribute significantly to the overall mechanism.<sup>33</sup> Thus we can conclude that the dominant pathway is that involving a side-on, concerted insertion leading to a linear insertion product. The observation of the linear form of magnesium dihydride (MgH<sub>2</sub>) suggests that the electronic state of MgH<sub>2</sub> in the matrix phase is the  ${}^{1}A_{1}$  (strictly speaking  ${}^{1}\Sigma_{g}^{+}$  in  $D_{\infty h}$  symmetry) ground state predicted by ab-initio CI calculations<sup>3,5</sup> and simple Walsh type MO diagrams.<sup>34</sup> This implies that a vibronically induced surface transition<sup>27</sup> must have occurred between the predicted slightly bound  ${}^{1}B_{2}$  surface<sup>5,6</sup> (which correlates with Mg( ${}^{1}P$ ) and H<sub>2</sub>) and the more strongly bound (at large H-H nuclear separation) <sup>1</sup>A<sub>1</sub> surfaces, leading to molecules in a highly excited bending mode in this  ${}^{1}A_{1}$  ground electronic state. It is expected that the presence of the matrix cage surrounding this highly vibrationally excited molecule will provide an efficient channel for vibrational relaxation via a relatively low order multiphonon process<sup>28,32</sup> because of the exponential energy gap law for relaxation rates since the spacings are small between the bending vibrational levels (fundamental frequencies of MgD<sub>2</sub> and MgH<sub>2</sub> bending modes are 309 and 430 cm<sup>-1</sup>, respectively, in a krypton matrix, cf Table I). An alternate mechanism, in which relaxation in the matrix is facilitated by rotational motion, has been found prevelant especially in asymmetrical diatomic hydrides, with high vibrational frequencies and large rotational constants  $B^{32}$ . The latter mechanism has been found dominant especially in hydrogen-containing molecules and hydrides, the former dominant for molecules with small vibrational spacings as in heavy diatomic molecules or vibrational levels of light molecules near the dissociation limit.  $^{\mbox{\tiny 28}}$  Thus it would seem reasonable to suggest that one or both processes to be operative in the vibrational relaxation of MgH<sub>2</sub> in the  ${}^{1}A_{1}$  ground state, depending on whether it is formed at moderately or very high vibrational levels.<sup>28</sup> The extent of energy migration arising from intramolecular vibrational relaxation between the other normal modes will again depend critically on the density of vibrational levels on the  ${}^{1}A_{1}$  surface in the region where the molecule is created and on the extent of Fermi resonances in this region. From the experimental values obtained for such vibrational relaxation rate constants in matrices it is likely that the newly born molecule spends few vibrational periods in its vibrationally excited state before deactivation to the ground vibrational level.<sup>28,32</sup> The existence of this efficient vibrational relaxation channel in the matrix and its absence in the gas phase may explain the observation of the linear inserted product  $(MgH_2)$  in the former and the observation of the fragment products (MgH + H) in the latter.

Furthermore, one may infer a decreased contribution from a reaction coordinate along the asymmetrical stretching mode of  $MgH_2$  as this would give rise to an avoided crossing in  $C_s$  symmetry<sup>11</sup> and the adiabatic production of the MgH molecule and H atom, which is a postulated mechanism for the gas-phase reaction. It is also likely there is an increased contribution from the triplet surface in the condensed phase to the formation of CH<sub>1</sub>MgH, an effect predicted to be present in other saturated

<sup>(27)</sup> In a nonlinear triatomic molecule the only vibration allowing interaction of A<sub>1</sub> and B<sub>2</sub> electronic states is the asymmetric stretching mode b<sub>2</sub>. See G. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules", Van Nostrand, New York, 1966, pp 65–68. (28) V. E. Bondybey, Annu. Rev. Phys. Chem., **35**, 591 (1984), and ref-

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<sup>(32)</sup> It is also known that small hydride molecules (mostly diatomics) exhibit rotation in solid rare gas matrices and as such the reorientation step is also feasible. See H. Dubost in "Inert Gases—Potentials, Dynamics and Energy Transfer in Doped Crystals", M. L. Klein, Ed., Springer-Verlag, West Berlin, 1984, and references cited therein

<sup>(33)</sup> For heavy diatomics like ClI and I2 the quantum yield for fragmentation is decreased substantially in the matrix compared with the gas phase because of the matrix cage effect.<sup>31</sup> Such an effect is not expected to be dominant for light molecules and especially for hydrides where one of the fragments is a hydrogen atom. As a result of the lack of observation of fragments in the Mg +  $H_2$  reaction it would seem that the dissociative mechanism is absent or a minor contribution is present.

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hydrocarbon molecules.

Note Added in Proof. Recently, theoretically predicted vibrational frequencies for  $MgH_2(X^{1}\Sigma_{g}^{+})$  have appeared in the literature,<sup>35</sup> with  $v_1$ ,  $v_2$ , and  $v_3$  at 1641, 475, and 1667 cm<sup>-1</sup>,

respectively, which are in good agreement with the infrared data reported here.

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Registry No. MgH<sub>2</sub>, 7693-27-8; CH<sub>3</sub>MgH, 63533-51-7; CH<sub>4</sub>, 74-82-8; H<sub>2</sub>, 1333-74-0; Mg, 7439-95-4; Xe, 7440-63-3.

# Porphyrin Thin Film Cells in Ultrahigh Vacuum: The Requirement of Water and Oxygen for Photovoltaic Response

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Porphyrin sandwich cells [substrate/Al/MgTPP/Ag] (MgTPP = magnesium tetraphenylporphyrin) were prepared and studied in ultrahigh vacuum. It was found that an oxide layer is needed on the Al for a functioning Ag electrode to be formed, and without the oxide layer the Ag is islanded. With an oxide layer present, two devices with  $\tilde{C} \approx 20$  nF were prepared and carefully studied. Resistance is low until shunts are burned out by pulse biasing the device.  $R_1$  (defined as V/I at 1 V) varied from 1 k $\Omega$  to 1 M $\Omega$  depending on the history. I-V curves are nonlinear and symmetric, curving upward at higher voltages, until the devices are exposed to both oxygen and water vapor at pressures comparable to that of ambient air. Neither rectification nor a photovoltaic response is observed prior to exposure to both oxygen and water vapor; in one case a photovoltaic response was observed in the absence of a rectifying I-V curve. Capacitance/voltage measurements are consistent with its characterization as a MIS (metal-insulator-semiconductor) device. These observations are explained by a photoelectrochemical process involving water-catalyzed Al oxidation by O<sub>2</sub> and photogenerated porphyrin cation charge carriers.

#### Introduction

In a previous paper,<sup>1</sup> Kampas and Gouterman (KG) reported on the photovoltaic properties of porphyrin thin film devices. These devices were prepared at high vacuum ( $\approx 10^{-6}$  torr) by vapor deposition on a glass substrate. The devices can be represented as

[substrate/Al(
$$\approx 200 \text{ Å}$$
)/porphyrin( $\approx 2000 \text{ Å}$ )/Ag( $\approx 150 \text{ Å}$ )] (1)

The KG paper reported photovoltaic action spectra. Peak quantum yields (electrons/photon absorbed) were 0.9% for tetraphenylporphyrin and 3.4% for octaethylporphyrin. In the model that described these devices the Al/porphyrin interface was taken as a blocking contact where a Schottky barrier forms while the porphyrin/Ag interface was taken as ohmic. This type of device has been used by various other authors. $^{2-7}$ 

Subsequent to the KG paper, Kampas, Yamashita, and Fajer (KYF) tested some 30 different porphyrins.<sup>8</sup> In their most studied configuration the devices consisted of porphyrin vapor deposted on an Al electrode. However, for an ohmic contact a Pt electrode in a solution of ferri-ferrocyanide was used, i.e., a Wang cell.<sup>9</sup> KYF reported a wide variation in quantum yield  $(0.2-10^{-4})$  depending on the porphyrin. "The best results were obtained with magnesium tetraphenylporphyrin (MgTPP) and cadmium porphin which yielded open circuit voltages of  $\approx 1$  V, quantum yield of  $\approx$ 0.2, and  $\approx$ 1% power conversion efficiency." Since the gram price of tetraphenylporphyrin is comparable to the milligram price of porphine, MgTPP was chosen by us for the studies reported here,

in which device structures 1 were prepared and studied in ultrahigh vacuum (UHV).

The UHV studies to be described here had two motivations. (i) Surface effect: At 10<sup>-6</sup> torr a monolayer can cover a surface in  $\approx 2$  s, if the sticking coefficient (i.e., the probability of an incident molecule remaining on the surface)<sup>10</sup> is unity. Since any residual oxygen should rather effectively stick to Al, there is every reason to believe that the Al electrode has a thin oxide coat when the devices are not made in UHV. (ii) Ambient atmosphere effect: KG devices exhibited rectifying I-V curves in which the Al donates electrons to the porphyrin. It was thought that  $O_2$  in the porphyrin film might provide the sites where electrons are trapped, since earlier work on phthalocyanines,<sup>11</sup> porphyrins,<sup>12</sup> and xanthine dyes<sup>13</sup> showed that photocurrent depended on  $O_2$  pressure. As will be described below, there is indeed a surface effect (i) and

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