Matrix-isolation Studies by Electronic Spectroscopy of Group IIIA Metal–Water Photochemistry

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This paper reports an investigation of the electronic structures of the Group IIIA metal atom hydration reaction intermediates ($M \cdots OH_2$ adducts) and their subsequent photolysis products (HMOH, MOH and MO) where M = AI, Ga and In. The metal-water interaction in the adduct is sufficiently strong to perturb the electronic structure of the metal atom; consequently, one observes a unique band structure for the adduct that is red shifted from the metal's atomic resonance transition. Molecular orbital and electronic state-to-state correlations are presented.

Margrave and co-workers¹ have performed infrared matrix-isolation studies of the interactions of Group IIIA metal atoms with water, demonstrating that Al atoms spontaneously undergo oxidative insertion to form the divalent HMOH species, whereas Ga, In and Tl atoms form the $M \cdots OH_2$ adduct or complex as evidenced by a decrease in the v_2 bending mode frequency of water. Upon photolysis, each of these adducts, except for Tl $\cdots OH_2$, forms the divalent hydroxy metal hydride, HMOH; extended photolysis of the HMOH molecules generates the monovalent metal monohydroxides, MOH.

Theoretical calculations²⁻⁴ have been performed on the $M \cdots OH_2$ and the HMOH molecules to evaluate their stabilities, geometries and reaction pathway potentialenergy barriers. Preliminary results of Kurtz and Jordan² indicate that the HAIOH molecule is non-linear, experiences no potential-energy barrier to formation from $Al + H_2O$ and is stable by at least 38 kcal mol⁻¹ relative to $Al + H_2O$. These theoretical predictions are corroborated by experimental results. Margrave and co-workers¹ observed spontaneous insertion of the Al atom into the OH bond of H_2O to form the HAIOH species having C_s symmetry. Oblath and Gole⁵ proposed that the excited HAIOH molecule is one of several plausible candidates that may be responsible for the white-blue chemiluminescent emission continuum emanating from the oxidative interaction of aluminium and water vapours under single and multiple collision conditions.

Upper atmospheric (90–220 km) studies of wind currents, diffusion, temperature and other atmospheric properties are conducted by either releasing trimethyl aluminium (TMA) or exploding aluminium grenades in the upper atmosphere, both of which generate a chemiluminescent glow characterized by an unresolvable emission continuum. This chemiluminescent continuum has been reproduced in a number of laboratories, and various suggestions regarding the nature of the continuum emitter have been made. Oblath and Gole⁵ have directly investigated the oxidative gas-phase hydration of aluminium vapours and find that the interaction, under single and multiple collision conditions, generates a weak chemiluminescent flame having a spectrum very reminiscent of the upper atmospheric glows. Other oxidisers (O₂, SO₂,

 CO_2 and H_2O_2) interacting with aluminium vapours yielded no observable chemiluminescence. In contrast, previous studies⁶ investigating the reaction of aluminium vapours with N₂O, O₂ and CO₂ gases reported chemiluminescence similar to the upper atmospheric glows. Oblath and Gole⁵ noted that most of the water vapour present in the upper atmosphere was deposited by the payload rockets dispersing the TMA and aluminium grenades and suggested that the continuum emitter was a complex involving aluminium and several water molecules or a 1:1 aluminium–water adduct which rearranged to form aluminium hydroxyhydride in an excited state, HAIOH^{*}.

In view of the matrix-isolation infrared studies, the theoretical calculations and the studies of aluminium-beam-water reactions, it is of considerable interest to probe the electronic structures of the Group IIIA metal atom hydration reaction intermediates and products when isolated in rare-gas matrices. This study also reports electronic spectra for MOH molecules, which are photolytic products of the HMOH species. Quantum-chemical calculations predict that the first electronically excited states of AlOH are at least 30000 cm⁻¹ above the ${}^{1}\Sigma^{+}$ ground state.⁷

EXPERIMENTAL

The matrix-isolation apparatus employed in this study has been described elsewhere.⁸ Briefly, cryogenic temperatures (15 K) were achieved using an Air Products Displex closed cycle helium refrigerator, model CS-202. Matrices were formed on aluminium-coated, second surface sapphire mirrors in good thermal contact with an aluminium block which, in turn, was thermally bound to the cold station of the refrigerator. U.v.-vis. absorption spectra were recorded using a $\frac{1}{4}$ m Perkin-Elmer model 210 grating monochromator (calibrated with mercury emission lines), a Hamamatsu R-928 PMT and a pair of PAR phase sensitive amplifiers (models 128A and 186). The assignments for the electronic transitions were generally accurate to ± 15 cm⁻¹. The optical design had provisions for referencing of the host matrix to circumvent the severe light-scattering problems that normally plague the u.v. matrix spectra. Specifically, during cocondensation of the guest and host species, shadowing techniques were employed. A copper shuttered slit, interposed between the guest source crucible and the sapphire substrate, selectively occluded the high-temperature guest vapour from depositing on the top half of the sapphire substrate. In this manner, the rare-gas host matrix solid, which was homogeneously deposited over the whole of the sapphire substrate, was referenced by the custom optical array of the dual-beam spectrometer. A quartz crystal microbalance mounted on the aluminium cold block enabled one to measure the deposition rates for the residual background gases and the host and guest species. These measurements were indispensible for establishing accurate M/Rratios in the matrices. The matrices were photolysed subsequent to trapping with a 100 W short-arc mercury lamp that was focused down to a 1 in. diameter spot.

Aluminium, gallium and indium metals were of better than 99.9% purity. H_2O and D_2O were vacuum distilled, going through at least 5 freeze-thaw cycles. High-purity Kr was used (Matheson research grade, 99.995%) and passed through a liquid-nitrogen cold trap. Aluminium was vaporised from a molybdenum cell with carbon spacers to support the cell in a resistively heated, 1 mm Ta foil furnace. The gallium and indium metals were vaporised from alumina cylindrical crucibles. The furnace-crucible assembly was out-gassed for 2 h prior to deposition at the temperatures employed during deposition. The pressure in the vacuum chamber after cool down and oven outgassing was ca. 10^{-8} Torr. Host-to-guest ratios in the matrices were measured with the quartz crystal microbalance and are reported for each experiment. Each matrix sample required 15 min to prepare.

RESULTS

ALUMINIUM AND WATER

Cocondensation of aluminium atoms with water molecules at 15 K in an excess of krypton generated a transparent, colourless solid matrix.

Fig. 1 shows electronic absorption spectra corresponding to four experiments: (a) Al/Kr, (b) $Al/H_2O/Kr$, (c) $Al/H_2O/Kr + hv$ and (d) $Al/D_2O/Kr$. Presentation of multiple-trace figures precludes using precise, quantitative absorption axes. However, unless stated otherwise, the largest metal band represents an absorbance of ca. 0.5.



Fig. 1. U.v.-vis. absorption spectra for aluminium and water isolated in a krypton matrix; (a) Al:Kr = 1:500, (b) Al:H₂O:Kr = 1:10:675, (c) same as (b) but photolysed for 5 min with light of $\lambda > 3000$ Å and (d) Al:D₂O:Kr = 1:3.5:350.

The microbalance makes it possible to establish and consistently maintain certain levels of absorbance for any particular species. Table 1 lists the assignments corresponding to band maxima for each of these spectra. Fig. 1(a) shows the strongly allowed electronic resonance transitions of the Al atom. Comparison with gas-phase transition energies^{9,10} allowed assignment of the peaks denoted by 'A' to the $4s(^2S) \leftarrow 3p(^2P)$ resonance transition and those denoted by 'B' to the $3d(^2D) \leftarrow 3p(^2P)$ atomic transition. The major 'A' and 'B' peaks were blue shifted by 1900 and 500 cm^{-1} , respectively, relative to their respective gas-phase transitions. These matrix blue shifts can be attributed to a strongly repulsive matrix interaction in the atom's excited state.¹² Subordinate 'A' and 'B' bands may be attributed to the Al atom residing in multiple and/or low symmetry trapping sites since a series of dilution and contaminant dopant (O₂, CO, H₂O) studies showed no relative changes in these peak intensities. E.s.r. results^{13, 14} indicated that the Al atom can be isolated in three different sites in a solid Kr matrix. These assignments basically concur with those made by Ammeter and Schlosnagle¹³ for atomic aluminium. However, at higher dilutions (Kr:Al > 1000), the 'C' bands disappeared yet the 'D' bands persisted at the same

peak	λ/Å	$\bar{v}^c/\mathrm{cm}^{-1}$	species	assignment ^f	gas phase ^b /cm ⁻¹
Α	3902	25 627	Al	$4s(^2S) \leftarrow 3p(^2P)$	25 348
Α	2695	27 062	Al	$4s(^2S) \leftarrow 3p(^2P)$	25 348
Α	2651	27 389	Al	$4s(^2S) \leftarrow 3p(^2P)$	25 348
В	3292	30 375	Al	$3d(^{2}D) \leftarrow 3p(^{2}P)$	32 435
В	3122	32 127	Al	$3d(^{2}D) \leftarrow 3p(^{2}P)$	32 435
В	3040	32 891	Al	$3d(^{2}D) \leftarrow 3p(^{2}P)$	32 435
В	3002	33 314	Al	$3d(^{2}D) \leftarrow 3p(^{2}P)$	32 435
С	4083	24 493	Al_2	$B({}^{1}\Sigma_{u}^{+}) \xleftarrow{(m, 0)^{a}} X({}^{1}\Sigma_{g}^{+})$?
С	4039	24 756	Al_2	$B({}^{1}\Sigma_{u}^{+}) \stackrel{(n+1,0)}{\longleftarrow} X({}^{1}\Sigma_{g}^{+})$?
С	4001	24 996	Al_2	$B({}^{1}\Sigma_{u}^{+}) \xleftarrow{(n+2,0)}{\longleftarrow} X({}^{1}\Sigma_{g}^{+})$?
C	3964	25 227	A1	$R^{(1\Sigma^+)} \longleftarrow Y^{(1\Sigma^+)}$	2
D	2624	29 115	A 1	$D(\underline{u}_u) \longleftarrow R(\underline{u}_g)$	27 690
ע ת	2024	36 113		$SS(-S) \leftarrow Sp(-P)$	3/089
D E	2401	26 444		$4a(-D) \leftarrow Sp(-F)$	30 929
E E	2/44	27 095		$A(000) \leftarrow X(000)^{*}$: 2
E	2090	37 063		$A(110) \leftarrow A(000)$ $A(200) \leftarrow V(000)$: 9
E	20//	37 332	Al ₂ O	$A(200) \leftarrow A(000)$	4
г G	4524	22 103	HAIOH	$A(^{2}A'') \leftarrow X(^{2}A')$	ca. 20 000
Н	4576	21 851	AlO	$B(^{2}\Sigma^{+}) \stackrel{(0, 0)}{\leftarrow} X(^{2}\Sigma^{+})$	20 635 ^e
н	4400	22 723	AlO	$\overset{(1, 0)}{B} \leftarrow X$	
I	2486	40 227	AlOH	$A(^{1}\Pi) \leftarrow X(^{1}\Sigma^{+})$?
Ĵ	6993	14 300	Al,	$A({}^{1}\Pi_{u}) \leftarrow X({}^{1}\Sigma_{a}^{+})$?

Table 1. Assignments for the optical absorption spectra of the Al/Kr, Al/H₂O/Kr, Al/H₂O/Kr + $h\nu$ and Al/D₂O/Kr systems

^a (v', v''). ^b From ref. (9)-(11). ^c ±15 cm⁻¹. ^d (v_1, v_2, v_3) . ^e v_{00} .

^f Energies of transition are taken from band maxima unless noted otherwise.

intensity relative to the other atomic bands. Also, upon annealing, the 3902 Å 'A' band disappeared, revealing a previously buried, weak, third 'C' band at 3968 Å which forms a Franck–Condon envelope with the other two bands, having an average $\Delta G'_{\nu+\frac{1}{2}}$ of 245 cm⁻¹. This band system has been assigned to Al₂ from other studies in our laboratory.¹⁵

In view of their triplet structure, similar to the other Al resonance transitions, and their concentration dependence, the 'D' bands have been tentatively assigned to the $5s(^2S) \leftarrow 3p(^2P)$ and $4d(^2D) \leftarrow 3p(^2P)$ atomic resonance transitions. The large line-width is probably partially due to the overlapping of the two transitions. The 'E' bands correspond to vibronic transitions for the Al₂O molecule⁸ which was generated by molten aluminium metal reducing the aluminium sesquioxide impurity in the metal sample. Extended operation of the furnace discriminated against these bands. From dilution and contaminant dopant experiments, the 'F' band could not be associated with any of the other bands; however, it did decrease in intensity when the oven was operated at slightly lower temperatures. This band was also observed in other metal atom matrix-isolation experiments in this laboratory where alumina spacers were used at high temperatures. This band is presently left unexplained.

In fig. 1(b), the band denoted by 'G' has been assigned to the reaction product of aluminium and water which, from previous infrared studies,¹ may be identified with the HAIOH molecule. This very broad absorption has a short wavelength onset at ca. 4000 Å, maximizes at ca. 4500 Å and tails out to ca. 6300 Å. This absorption correlates well with the densely structured chemiluminescent continuous emission spectra observed in beam-gas experiments involving the hydration of aluminium which typically ranged from 3500 to 8000 Å, peaking at ca. 4500 Å. Due to the enhanced sensitivity to weak spectroscopic features intrinsic to fluorescence detection, it is easy to understand a discrepancy in the red cut-off when compared with the absorption technique. The Kr:H₂O ratio was varied from 300:1 to 65:1 while maintaining the Kr:Al ratio at 650:1. Over this concentration range, only the 'G' band was observed and its intensity was maximised at a ratio of 110:1. At higher concentrations, the band diminished in intensity, which was perhaps indicative of a higher-order water-metal interaction. Neither varying the water concentration nor annealing noticeably affected the structure of the 'G' band.

Photolysis of the 'G' band with light having a 4500 Å short-wavelength cut-off (Corning 3-72+water-Pyrex filters) for 10 min caused no change in the band structure. Fig. 1(c) shows that a 5 min photolysis with light having a 3000 Å short-wavelength cut-off (water-Pyrex filter) destroyed the 'G' band totally and generated the 'H' and 'I' bands. The 'H' bands have been assigned to the AlO molecular species since the peak positions correlate very well with previous matrixisolation studies of the $B^{2}\Sigma^{+} \leftarrow X^{2}\Sigma^{+}$ system for AlO.¹⁴ The 'I' band was assigned to a transition of the AlOH molecule, which was the major photolysis product noted in the infrared matrix studies.¹ The presence of the 'I' band unfortunately is obscured by the broad 'D' band seen in fig. 1(b). However, in fig. 1(c) it is apparent that absorption increased in this region while it decreased elsewhere. Fortunately, MOH formation was mostly unobscured and more dramatic in the gallium- and indiumwater studies described below. The 'I' band position is similar in energy to the analogous gas-phase AlF diatomic $A^{1}\Pi \leftarrow X^{1}\Sigma^{+}$ system $(T_{e} = 43949 \text{ cm}^{-1})^{11}$ and quantum-chemical calculations indicated that the lowest-lying excited states of AlOH lie at energies in excess of 30000 cm⁻¹ above the ground ${}^{1}\Sigma^{+}$ state.^{5, 7} The A excited state of AlOH is predictably a 1II state by analogy with the 1II first excited singlet state of AIF. The 'G' band in fig. 1(d) was assigned to the DAIOD molecule, which is identical in structure to the HAlOH molecule, except for superimposed AlO ($B^{2}\Sigma \rightarrow X^{2}\Sigma$) 'H' bands. Evidently DAIOD formation was accompanied by AIO formation whereas HAIOH was not.

GALLIUM AND WATER

Cocondensation of Ga atoms with H_2O molecules at 15 K in an excess of Kr generated a transparent, colourless matrix.

Fig. 2 shows electronic absorption spectra corresponding to three experiments: (a) Ga/Kr, (b) Ga/H₂O/Kr and (c) Ga/H₂O/Kr + hv. Table 2 lists the assignments corresponding to band maxima for each of these spectra. Fig. 2(a) shows the strongly allowed electronic resonance transitions for the Ga atom. According to reasoning previously developed when discussing the aluminium system, bands 'A' and 'B' are assigned to the $5s(^2S) \leftarrow 4p(^2P)$ and the $4d(^2D) \leftarrow 4p(^2P)$ gallium atomic resonance transitions, respectively. For the major 'A' and 'B' bands, blue shifts of 2391 and 1983 cm⁻¹ were observed from their respective gas-phase transitions. The 'A' and 'B' bands were triplets, undoubtedly due to multiple sites and/or crystal-field removal



Fig. 2. U.v.-vis. absorption spectra for gallium and water isolated in a krypton matrix; (a) Ga:Kr = 1:1150 (Ga₂ assignment made from other spectra), (b) Ga:H₂O:Kr = 1:5:1280 and (c) same as (b) by photolysed for 5 min with light of $\lambda > 300$ nm (GaOH assignment made from other spectra).

peak	λ/Å	$\bar{v}^a/\mathrm{cm}^{-1}$	species	assignment ^c	gas phase ^b /cm ⁻¹
Α	3990	25 065	Ga	$5s(^2S) \leftarrow 4p(^2P)$	24 788
Α	3761	26 592	Ga	$5s(^2S) \leftarrow 4p(^2P)$	24 788
Α	3679	27 179	Ga	$5s(^2S) \leftarrow 4p(^2P)$	24 788
В	3341	29 934	$Ga;Ga_2$	$4d(^{2}D) \leftarrow 4p(^{2}P);$ $B(^{1}\Sigma^{+}) \leftarrow X(^{1}\Sigma^{+})$	34 782;?
В	3141	31 835	Ga	$4d(^{2}D) \leftarrow 4p(^{2}P);$	34 782;
В	3111	32 142	Ga	$4d(^{2}D) \leftarrow 4p(^{2}P);$	34 782;
В	2720	36 771	Ga	$4d(^{2}D) \leftarrow 4p(^{2}P);$	34 782;
С	6413	15 592	Ga,	$A({}^{1}\Pi_{u}) \leftarrow \hat{X}({}^{1}\Sigma_{a}^{+})$?
D	4922	20316	Ga···OH。	$A(^{2}A_{1}) \leftarrow X(^{2}B_{2})$?
D	4547	21 994	Ga…OH.	$A(^{2}A_{1}) \leftarrow X(^{2}B_{2})$?
E	2555	39 133	GaOH	$A({}^{1}\Pi) \leftarrow X({}^{1}\Sigma^{+})$?

Table 2. Assignments for the optical absorption spectra of the Ga/Kr, Ga/H₂O/Kr and Ga/H₂O/Kr+hv systems

 $a^{\pm} \pm 15 \text{ cm}^{-1}$. ^b From ref. (9)-(11). ^c Energies of transition are taken from band maxima unless noted otherwise.

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of orbital degeneracy. E.s.r. results indicate that Ga atoms can reside in two different sites in a Kr solid. The long-wavelength 'A' band was discriminated against by annealing. These assignments agreed with those made by Ammeter and Schlosnagle¹³ for Ga atoms isolated in a Kr matrix. However, note that their spectra for Al and Ga were plagued by light scattering in the deep u.v. which, in the case of Al, made it impossible to see the $5s(^2S) \leftarrow 3p(^2P)$ and the $4d(^2D) \leftarrow 3p(^2P)$ transitions. By referencing the host matrix with the spectrometer, these as well as other absorptions in the deep ultraviolet were distinct in these studies.

Our energy assignments for the ${}^{2}S \leftarrow {}^{2}P$ transitions of Ga and Al almost perfectly concurred with those made by Ammeter and Schlosnagle when compensation was made for the blue shift that occurs when lowering the temperature of the rare-gas solid from 15 to 4 K. However, the agreement was not as good for the assignments of the ${}^{2}D \leftarrow {}^{2}P$ transitions of Al and Ga, especially for the subordinate 'B' peaks, indicating that these peaks could be quite temperature sensitive. The 3341 Å 'B' band had a peculiar concentration dependence since at higher concentrations it grew in much more rapidly than the other monomeric 'B' bands; however, at very high dilutions where no metal clusters were expected to have formed, this 'B' band still persisted with relatively good intensity. The concentration dependence of this band was a little less than the second power of the metal deposition rate. Therefore, it was quite possible that a Ga dimer electronic transition overlapped the 3341 Å Ga atomic transition. Band 'C' was assigned to the Ga, molecule since concentration studies showed it was the first peak to grow in after the atomic bands, and its growth was a precise quadratic function of the metal deposition rate. In the gas phase, emission bands in the region from 18000 to 21700 cm⁻¹ were observed for Ga₂.¹¹ If the gas-phase and matrix transitions were identical, this would indicate the dimer spectrum was red shifted in the matrix by ca. 4500 cm^{-1} . Since this is an unacceptably large shift, the transition observed in absorption in the matrix probably cannot be identified with the transition observed in emission in the gas phase. Thus, the lower state observed in emission probably was not the ground state of Ga₂, as discussed in more detail elsewhere.¹⁵

In fig. 2(b), the bands denoted by 'D' were assigned to the reaction product of gallium and water which, on the basis of previous infrared studies,¹ was identified with the Ga···OH₂ adduct. The nature of the long-wavelength 'D' shoulder will be discussed in more detail in the next section in view of more extensive photolysis work. The band was symmetric and quite broad having a 1500 cm⁻¹ f.w.h.m. Water concentration studies showed no change in the spectrum over the Kr:H₂O range of 300:1 to 50:1. A 2 s photolysis with light of $\lambda > 4000$ Å (Corning 3–75 filter) reduced the intensity of the adduct absorption band by 50%. A 10 s photolysis with the same colour light completely eliminated the adduct band. No new bands were generated as a consequence of this photolysis; however, a 5 min photolysis with the same light ($\lambda > 4000$ Å) generated a blue shoulder on the major 'B' band. No change in the intensity of the Ga atomic absorptions was observed except for a slight decrease in the 3390 Å 'A' band which was observed to be heat sensitive.

Fig. 2(c) shows the blue shoulder on the 2720 Å 'B' band generated by a 5 min photolysis with light of $\lambda > 3600$ Å (Corning 3–94). The atomic absorptions decreased in intensity. This new 'E' band has been assigned to GaOH, the final photolysis product observed in the infrared study of metal–water chemistry. The analogous GaF diatomic has its first allowed electronic transition at 47366 cm⁻¹ in the gas phase.¹¹ With the consideration that infrared studies show that the adduct is initially formed upon cocondensation and that the 'D' bands show very similar photosensitivity as the adduct bands did in the infrared work, the assignment of the 'D' band to the adduct seems quite plausible. A few experiments were conducted in argon with the

same qualitative results described above. Photolysing the adduct bands to total depletion generated no new bands; however, continued photolysis in this same region $(\lambda > 4000 \text{ Å})$ generated GaOH without decreasing the intensity of the atomic bands. Photolysing with light of $\lambda > 3600$ Å overlaps an atomic band which undoubtedly induced annealing, allowing the Ga atomic species to migrate from its site and react with H₂O molecules residing in neighbouring sites.

In view of these findings, the HGaOH intermediate insertion species probably had an extremely broad absorption band that was difficult to discern by absorption techniques, similar to that of HAIOH, or an energy of absorption beyond the range of the spectrometer.

INDIUM AND WATER

Cocondensation of In atoms with H₂O molecules at 15 K in an excess of Kr generated a transparent, colourless matrix.

Fig. 3 shows the electronic absorption spectra corresponding to three experiments: (a) In/Kr, (b) In/H₂O/Kr and (c) In/H₂O/Kr+hv. Table 3 lists assignments corresponding to the band maxima for each of these spectra. Fig. 3(a) shows the strongly allowed electronic resonance transitions for the In atom. Bands 'A' and 'B' are assigned to the $6s(^2S) \leftarrow 5p(^2P)$ and the $5d(^2D) \leftarrow 5p(^2P)$ indium resonance transitions, respectively. For the major 'A' and 'B' bands, blue shifts of 1440 and 2070 cm^{-1} from their respective gas-phase transitions were observed. The major ${}^{2}S \leftarrow {}^{2}P$ transition was not split as it was for Al and Ga and was observed as a doublet. The ${}^{2}D \leftarrow {}^{2}P$ transition was observed as a triplet with the major band having a very large linewidth of 6400 cm⁻¹ f.w.h.m. These results do not agree very well with those of Duley and Garton,¹⁶ who reported that 'there is little evidence for any absorption bands which might correspond to resonance transitions of In'; however, they noted several strong autoionising transitions. The longest-wavelength transition they observed was at 2845 Å and they assigned it to the $5s5p^2(^4P) \leftarrow 5s^25p(^2P)$ autoionising transition. That corresponds fairly well to the 2860 Å $5d(^2D) \leftarrow 5p(^2P)$ resonance transition observed in this study. Duley and Garton stated that thicker films would be needed to observe the resonance transitions. Since metal atom resonance transitions in the gas phase and in the matrix have very strong oscillator strengths, it is not readily apparent why these authors did not observe them along with the autoionising transitions. The 'C' bands may be attributed to the In₂ molecule in view of their concentration dependence. In the gas phase, emission bands were observed between 16800 and 20000 cm⁻¹, and absorption bands were observed between 26000 and 28000 cm^{-1} .¹¹ The matrix-phase $B \leftarrow X$ absorption centred at 27691 cm⁻¹ was in good agreement with the absorption system observed in the gas phase ranging from 26000 to 28000 cm^{-1} , which leads one to believe that the transitions are identical. However, identification of the broad matrix $A \leftarrow X$ absorption which was centred around 13000 cm^{-1} with the 16800 to 20000 cm⁻¹ gas-phase emission system is dubious since the red shift required would be too large to make the correlation reasonable. Therefore, as was noted for the gas-phase Al₂ and Ga₂ emission systems, the lower state observed in emission probably did not involve the ground state of In₂.¹⁵

In fig. 3(b), the bands denoted by 'D' have been identified with an electronic transition of the In \cdots OH₂ adduct for the same reasons developed above for the Ga-H₂O system. Photolysis of the red 'D' shoulder with light of $\lambda > 5000$ Å (Corning 3-70 + Pyrex-water filters) for 50 min totally eliminated the red 'D' band; however, the blue 'D' band was left totally intact. Subsequent photolysis with $4500 < \lambda/\text{Å} < 4700$ light (Corning 3–72 and 7–59 + Pyrex-water filters) for 35 min reduced the intensity of the blue 'D' band by ca. 50% without regenerating the red

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Fig. 3. U.v.-vis. absorption spectra for indium and water isolated in a krypton matrix: (a) In: Kr = 1:500, (b) In: $H_2O: Kr = 1:10:1560$ and (c) same as (b) but photolysed for 5 min with light of $\lambda > 3000$ Å.

Table 3. Assignmen	its for the optic	al absorption	spectra of t	the In/Kr,
In/H	2O/Kr and In/	$H_2O/Kr + hv$	systems	

peak	λ/Å	$\bar{v}^a/\mathrm{cm}^{-1}$	species	assignment ^c	gas phase ^b /cm ⁻¹
A	4083	24 494	In	$6s(^2S) \leftarrow 5p(^2P)$	24 373
Α	3874	25 811	In	$6s(^2S) \leftarrow 5p(^2P)$	24 373
В	3309	30 222	In	$5d(^{2}D) \leftarrow 5p(^{2}P)$	32 892
В	2963	33 755	In	$5d(^2D) \leftarrow 5p(^2P)$	32 892
В	2860	34 965	In	$5d(^{2}D) \leftarrow 5p(^{2}P)$	32 892
С	7692	13 000	In,	$A({}^{1}\Pi_{u}) \leftarrow X({}^{1}\Sigma_{a}^{+})$?
С	3611	27 691	In,	$B(1\Sigma_{u}^{+}) \leftarrow X(1\Sigma_{u}^{+})$	ca. 27000
D	4932	20 274	In ··· OH,	$A(^{2}A_{1}) \leftarrow X(^{2}B_{2})$?
D	4614	21 675	In…OH,	$A(^{2}A_{1}) \leftarrow X(^{2}B_{2})$?
Ε	2707	36 943	InOH	$A(^{1}\Pi) \leftarrow X(^{1}\Sigma^{+})$?

 $a \pm 15 \text{ cm}^{-1}$. ^b From ref. (9)-(11). ^c Energies of transition are taken from band maxima unless noted otherwise.

shoulder; however, a blue 'E' shoulder grew in on the 2960 Å 'B' band. Further photolysis with light of $\lambda > 3300$ Å (Pyrex-water filter) totally eliminated the 'D' bands generating an increased intensity in the 'E' band, as seen in fig. 3(c). In view of these experiments, it was concluded that the red 'D' shoulder was not associated with the blue 'D' band.

Bonds attributable to HInOH were not observed. Possible reasoning for this will be developed shortly. The 'E' band was associated with the InOH molecule. The first allowed electronic transition of the analogous InF diatomic is observed at 42809 cm⁻¹ in the gas phase.¹¹

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DISCUSSION

ALUMINIUM AND WATER

NATURE OF ELECTRONIC TRANSITIONS FOR HAIOH

In view of the close similarity of the electronic transition of the matrix-isolated HAIOH molecule with the chemiluminescence features observed in the gas-phase oxidation of aluminium vapours in the upper atmosphere^{17, 18} and in the laboratory,⁵ it is possible to identify the continuum emitter with the divalent oxidative insertion product of a 1:1 aluminium hydration reaction, HAIOH.



Fig. 4. Walsh molecular orbital correlation diagram for linear and bent HAB molecules.

The nature of the electronic transition for the HAIOH molecule may be derived from an examination of a simple Walsh molecular orbital correlation diagram for a linear and bent HAB molecule¹⁹ (see fig. 4) which identifies the OH fragment with the B atom. The electronic structure of the HAIOH molecule should be analogous with other 11 electron HAB species such as the HCO radical, which has been extensively studied. The predicted ground-state electron configuration for a bent

HAIOH molecule

$$...(la'')^2(6a')^2(7a')$$

corresponds to a ${}^{2}A'$ electronic ground state. The highest occupied molecular orbital (HOMO) is the 2π -7a' orbital, which is singly occupied. Since the 7a' orbital is lower in energy relative to the 2π degenerate orbitals, the equilibrium geometric configuration for HAIOH is expected to be bent and the HAIO angle is consistent with experimental¹ and theoretical^{2, 3} results. Jordan and Kurtz² calculated a bond angle of 117°. The electronic configuration for the first excited state of HAIOH would be

$$\dots (la'')^2 (6a')^2 (2a'').$$

This is in accord with the lowest-lying excited electronic configuration for the HCO radical.²⁰ This configuration corresponds to a ${}^{2}A''$ electronic state. Therefore, the $A \leftarrow X$ transition observed in the matrix for HAlOH is predicted to be a symmetry allowed ${}^{2}A'' \leftarrow {}^{2}A'$ electronic transition. Since the electronic transition involves vacating the 2π -7a' orbital, which primarily accounts for the bent configuration of the HAB species,¹⁹ and subsequent occupation of the $2\pi - 2a''$ orbital, which is a non-bonding p orbital, the excited state equilibrium geometric configuration is, in all probability, linear, which is the case for the first excited state of the HCO radical.²¹ In fact, it seems highly probable that the ground and the first excited states for the HAlOH molecule are derived from a Renner-Teller distortion of a doubly degenerate linear ²Π state, so the ${}^{2}A'$ and ${}^{2}A''$ states are ${}^{2}\Sigma^{+}$ and ${}^{2}\Sigma^{-}$ states in the linear conformation. Since the equilibrium bond angle changes dramatically in going from the ground state to the first excited state, the off-diagonal Franck-Condon factors should be of sufficient magnitude to create a long progression in the bending mode that would generate a very broad band for this electronic transition if the vibrational structure can not be resolved. In all probability, this explains the origin of the broad continuum observed experimentally in the matrix absorption and the chemiluminescent emission studies of the HAlOH molecule.

ORBITAL AND STATE CORRELATIONS

Initially, it is appropriate to examine the molecular orbital correlation diagram for Group IIIA metal-water interactions as shown in fig. 5. This MO correlation diagram analyses two different reaction coordinates: (1) the metal atom approaching the water molecule along the line defined by the bisector of the H-O-H angle in water so that the system remains in the C_{2v} point group and (2) the metal atom approaching the water molecule along the perpendicular bisector of an O-H bond so the system remains in the C_s point group (even with in-plane deviations from the perpendicular bisector). This diagram depicts the formation of the metal-water adduct of C_{2v} symmetry and the HMOH molecule of C_s symmetry. In both approaches, the unfilled $4a_1$ antibonding valence orbital of water correlates into the 7a' orbital for HMOH. The degenerate, singly occupied p orbital is split by the interaction into three orbitals, one of which is of a" symmetry (out-of-plane p orbital) that correlates into the low-lying 2a" MO of the insertion product. According to this orbital occupancy, a 2A" potentialenergy surface is generated which correlates the $H_2O(^1A_1)$ and the M (2P_u) reactants in their ground states into the ... $(6a')^2 (2a'')$ configuration for the insertion product that corresponds to the ${}^{2}A''$ excited state observed in absorption and emission (see fig. 6). Because the ground state of the insertion product is more stable by ca. 63 kcal mol⁻¹ (see table 4) relative to the reactants in their respective ground states, the ${}^{2}A''$ potential surface that correlates into the ${}^{2}A''$ excited state of the insertion product is still exothermic overall by ca. 30 kcal mol⁻¹ and encounters no potentialenergy barrier to reaction since the state correlation follows directly from the orbital



Fig. 5. Molecular orbital correlation diagram for Group IIIA metal-water interactions.

correlation. (Since the red cut-off in the aluminium chemiluminescent flame was ca. 8000 Å, the difference in the potential-energy well minima for the ${}^{2}A'$ and ${}^{2}A''$ states is equal to or less than 35 kcal mol^{-1} .) The reactant orbital occupancy that would be required to generate a ${}^{2}A'$ surface which would correlate diabatically into the ${}^{2}A'$ ground state of the insertion product corresponds to a singly occupied $4a_1$ orbital of water and a vacant 3p orbital of the metal, which creates a Coulombic or charge-transfer potential surface derived from the Al⁺ (${}^{1}S_{q}$) and H₂O⁻ (${}^{2}A_{1}$) reactants. The chargetransfer ${}^{2}A'$ surface generated by the metal cation and water anion correlates diabatically into the $^{2}A'$ ground state of HAlOH; however, there is an avoided surface intersection between this ${}^{2}A'$ surface and the ${}^{2}A'$ surface derived from water's ${}^{1}A_{1}$ state and the metal's ${}^{2}P_{u}$ state where the unpaired electron is in the in-plane p orbital not directed toward the water (b_2 orbital in the C_{2v} point group). (The latter ${}^2A'$ surface diabatically correlates into the first excited ${}^{2}A'$ state of HAIOH which, although it has been undocumented, is expected to be quite high in energy above the ${}^{2}A'$ ground state because of the highly excited electron configuration that it requires. For example, the first excited ${}^{2}A'$ state of HBF has been calculated to be ca. 4.6 eV above the ground state.²⁵) The net result is that the ground-state reactants are expected to encounter a potential-energy barrier to reaction along the ground-state ${}^{2}A'$ potential-energy surface.

These correlations predict two fundamental aspects regarding the reaction dynamics of the Al-H₂O interaction that are corroborated by experimental results. First, since



Fig. 6. Electronic state correlation diagram for the aluminium-water interaction; ..., repulsive states; ---, unobserved states; O, avoided surface intersection.

	$\Delta H/\text{kcal mol}^{-1}$
$Al + H_2O \rightarrow HAlOH$ $Al + H_2O \rightarrow AlO + H_2$ $Al + H_2O \rightarrow AlOH + H$ $Cr + H_2O \rightarrow AlOH + H$	-64 ± 10 -5 ± 2 -12 ± 5 34 ± 10
$Ga + H_2O \rightarrow HGaOH$ $Ga + H_2O \rightarrow GaO + H_2$ $Ga + H_2O \rightarrow GaOH + H$ $In + H O \rightarrow HInOH$	-34 ± 10 +26 ± 2 +16 ± 5 -17 + 10
$In + H_2O \rightarrow InO + H_2$ $In + H_2O \rightarrow InOH + H$	$+42\pm2$ +32±5

Table 4. Estimated heats of reaction^a

^a Heats of reaction were estimated using bond-energy data from ref. (11) and (22)–(24). Promotional energies were estimated by taking the difference in bond energies for M—OH and M—(OH)₂.

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the ${}^{2}A''$ surface, derived from the reactant ${}^{2}A''$ state of Al (${}^{2}P_{u}$) and (${}^{1}A_{1}$), correlates without any avoided surface crossings into the ${}^{2}A''$ state of HAIOH in an exothermic manner, the Al metal atom should spontaneously insert into the O—H bond as observed experimentally in the matrix¹ as well as in the gas phase.⁵ Secondly, since the ${}^{2}A''$ potential surface is the only unhindered pathway to the insertion product, spontaneous chemical reaction should populate the ${}^{2}A''$ excited state causing chemiluminescence from that state, as observed experimentally in the gas-phase interaction of aluminium and water vapours in the laboratory and upper atmosphere.^{5, 17, 18}



Fig. 7. Molecular orbital correlation diagram describing the predissociation of HMOH to $MO+H_2$ and MOH+H.

PHOTODISSOCIATION OF HAIOH

Upon irradiation, the HAlOH molecule photodissociates into two pairs of products: (1) AlOH + H and (2) AlO + H₂. Fig. 7 shows molecular orbital correlations for the HAlOH molecule evolving into both pairs of products along the symmetry elements of the C_s point group. Fig. 8 shows the state correlation diagram for HAlOH evolving into AlO + H₂ that includes only the important avoided surface crossings. The ²A' state of HAlOH correlates adiabatically into the ²\Sigma⁺ state of AlO and the ¹\Sigma⁺_g state of H₂. The ²A'' state of HAlOH correlates diabatically into the C²II state of AlO and the ¹\Sigma⁺_g state of H₂; however, an avoided surface crossing causes the ²A'' state to correlate adiabatically into the A²II state of AlO and the ¹\Sigma⁺_g state of H₂ with the formation of a potential barrier to recombination from this product state.

Predissociation of the excited ${}^{2}A''$ state of HAIOH will take place into the ${}^{2}\Sigma^{+} + {}^{1}\Sigma_{g}^{+}$ or the $A {}^{2}\Pi + {}^{1}\Sigma_{g}^{+}$ states of the AIO + H₂ products since the energy of the second ${}^{2}A''$ excited state of the products is much too high. Potentially, HAIOH can heterogeneously or homogeneously predissociate into the AIO + H₂ products. The ${}^{2}A''$ state (${}^{2}\Sigma^{-}$ in the linear case) of HAIOH may heterogeneously predissociate into the ${}^{2}A''$ (${}^{2}\Sigma^{+}$ in the linear conformation) potential-energy surface that correlates with the AIO (${}^{2}\Sigma^{+}$) + H₂ (${}^{1}\Sigma^{+}$) products by interaction with the out-of-plane torsional mode of A'' symmetry. Rotational interaction is not expected to play an important role in this heterogeneous



Fig. 8. Electronic state correlation diagram describing the predissociation of HAlOH to $AlO + H_2$; \bigcirc , avoided surface intersection.

predissociation since rotation for HAIOH is probably forbidden in the matrix cage. If sufficiently energetic photons are available, the ${}^{2}A''$ state may also homogeneously predissociate $({}^{2}A'' \rightarrow {}^{2}A'')$ for the bent and ${}^{2}\Sigma^{-} \rightarrow {}^{2}\Sigma^{-}$ for the linear confirmation) into the low-lying $A {}^{2}\Pi$ state of AIO and the ${}^{1}\Sigma_{g}^{+}$ ground state of H₂ by following the ${}^{2}A''$ potential surface which has a potential-energy barrier to recombination generated by the avoided surface crossing. The $A {}^{2}\Pi$ state of AIO would then decay to its ${}^{2}\Sigma^{+}$ ground state. From this study, it was not possible to determine the relative importance of the two channels in predissociation.

Fig. 9 shows the state correlation diagram for HAlOH evolving into AlOH+H along ${}^{2}A''$ and ${}^{2}A'$ potential surfaces where only the important surface crossings are depicted. The ${}^{2}A'({}^{2}\Sigma^{+})$ ground state of HAlOH diabatically correlates into AlOH

in its highly excited ${}^{3}\Sigma^{+}$ state and H in its ${}^{2}S_{g}$ ground state along a ${}^{2}A'$ surface. However, this surface is intersected by another ${}^{2}A'$ surface derived from the ${}^{1}\Sigma^{+} + {}^{2}S_{g}$ ground states of the products in an avoided crossing; therefore, the ${}^{2}A'$ ground state of HAIOH adiabatically correlates in the ${}^{1}\Sigma^{+} + {}^{2}S_{g}$ ground states for AIOH + H by virtue of an avoided crossing that creates a potential-energy barrier to recombination. The ${}^{2}A''$ (${}^{2}\Sigma^{-}$) excited state of HAIOH adiabatically correlates into AIOH in its ${}^{3}\Pi$ excited state and H in its ${}^{2}S_{g}$ ground state. Predissociation of the excited ${}^{2}A''$ state



Fig. 9. Electronic state correlation diagram describing the predissociation of HAlOH to AlOH+H; \bigcirc , avoided surface intersection.

of HAIOH must take place into the ${}^{1}\Sigma^{+} + {}^{2}S_{g}$ state of AIOH + H since the energy of the first excited state $({}^{2}A'')$ of the products is much too high. Therefore the predissociation is heterogeneous $({}^{2}A'' \rightarrow {}^{2}A'$ for the bent and ${}^{2}\Sigma^{-} \rightarrow {}^{2}\Sigma^{+}$ for the linear conformation) and can arise from interaction of the ${}^{2}A''$ electronic state with the HAIOH out-of-plane torsional mode of A'' symmetry. There is no apparent homogeneous predissociative pathway to form AIOH + H from HAIOH.

As previously noted, HAIOH did not predissociate when vigorously irradiated with light having a short-wavelength cut-off at 4500 Å (2.75 eV); however, light of $\lambda > 3000$ Å (4.1 eV) was readily successful in generating both AlO and AlOH products. Fig. 8 and 9 show that at least 2.2 eV of energy must be supplied to HAlOH to generate AlOH (${}^{1}\Sigma^{+}$)+H (${}^{2}S_{g}$), and at least 2.5 eV is required to generate AlO (${}^{2}\Sigma^{+}$)+H₂ (${}^{1}\Sigma_{g}^{+}$). Therefore, the 4500 Å photolysis was unable to access the heterogeneous predissociative pathways to form AlO and AlOH, not because of overall reaction thermodynamics but possibly because this photon energy was insufficient to access the higher vibrational levels of the ${}^{2}A''$ excited state that are in the proximity of that portion of the ${}^{2}A''$ potential-energy surface that intersects the surface where the Franck-Condon factors are of sufficient magnitude to allow heterogeneous predissociation. Certainly, this wavelength of light was energetically insufficient to access the homogeneous predissociative pathway to form AlO+H₂. The more energetic light having a 3000 Å (4.1 eV) short-wavelength cut-off was sufficient to access those high vibronic states that strongly couple into the ${}^{2}A'$ surface, allowing a heterogeneous predissociation to form both AlO and AlOH. The light was also sufficiently energetic to activate the homogeneous predissociative channel to form AlO.

Electronic transitions from the minimum of the ${}^{2}A'$ ground-state potential well to the potential minimum of the ${}^{2}A''$ excited state require < 1.5 eV of energy; therefore, to supply the energy required for the endothermic photoreactions to form AlO (2.5 and 3.2 eV) and AlOH (2.2 eV), the electronic transition from the ${}^{2}A'$ ground state of HAlOH must access very high vibrational levels of the ${}^{2}A''$ first excited state. As previously discussed, the ${}^{2}A''$ and ${}^{2}A'$ electronic states are probably derived from a Renner–Teller distortion of a linear ${}^{2}\Pi$ state, which implies a large change in conformation between the ${}^{2}A'$ and ${}^{2}A''$ states if the interaction is sufficiently strong.²² A dramatic geometric difference between the two states generates large off-diagonal Franck–Condon factors for the ${}^{2}A'' \leftarrow {}^{2}A'$ transition. Therefore, the electronic transition should be able to access those high vibronic states on the ${}^{2}A''$ surface that are necessary for the endothermic predissociative photochemistry.

It is striking to note that the infrared investigation of the aluminium-water chemistry did not confirm the formation of AlO upon irradiation of HAlOH with 3000 Å photons, yet this work reported a very good yield of AlO for the identical photolysis study. One distinguishing feature between these two studies was that the i.r. studies used argon as the matrix medium whereas the u.v.-vis. work employed krypton as the host. In the gas phase, Oblath and Gole⁵ studied the oxidative interaction of aluminium and water vapours by observing emission from the $B^{2}\Sigma^{+}$ state of AlO during the multiple collision studies; however, no emission for AlO was displayed during the single collision studies, which indicated that AlO was probably formed in its ground or $A^{2}\Pi$ state by reaction of aluminium with water. They suggested that the HAlOH* (${}^{2}A''$) species collisionally activated the $B^{2}\Sigma^{+}$ state of AlO was not investigated.

Examination of fig. 8 and 9 indicates that there is no potential-energy barrier to the formation of HAIOH (${}^{2}A'$) from a recombination of AIO (${}^{2}\Sigma^{+}$) and H₂ (${}^{1}\Sigma_{g}^{+}$); however, there is a barrier to recombination of AIOH (${}^{1}\Sigma^{+}$) and H(${}^{2}S_{g}$) to reform HAIOH (${}^{2}A'$). So rapid separation of the AIO + H₂ products as they dissociate may be necessary to stabilise them with respect to recombination. This rapid separation can readily be achieved in the gas phase, but the rare-gas solid matrix enclosure probably hinders product separation. Therefore, photodissociative AIO formation may be inhibited in an argon matrix because of smaller cage dimensions and/or more efficient nuclear kinetic energy quenching of the products.

GALLIUM, INDIUM AND WATER

NATURE OF THE ELECTRONIC TRANSITION OF THE METAL-WATER COMPLEX

Unlike aluminium, the gallium and indium metal atoms did not spontaneously insert into the O—H bond; rather, they formed a complex with water with the metal coordinated to the $3a_1$ lone-pair electrons on the oxygen atom in the plane of the water

molecule. Hydrate or adduct formation perturbed the electronic structure of Ga and In such that the ${}^{2}S \leftarrow {}^{2}P$ atomic transition for the metal when complexed with water was significantly broadened and red shifted from the uncomplexed atomic resonance transition. Insight into the nature of the perturbation that led to red-shifted spectra may be gleaned from an examination of fig. 10, which shows the metal in its ground and excited states approaching the water molecule from infinite separation. At suitable metal-water separations, the metal atom is unperturbed by the water molecule and a normal atomic resonance transition is observed of energy E_{2} . As the metal approaches the water molecule, an attractive interaction is encountered resulting in



Fig. 10. Schematic diagram of the potential-energy surfaces of the metal-water interaction with the metal in its ground and excited states.

a metal-water complex bound in a potential-energy well. For reasons that will be developed shortly, the water is more highly attracted to the metal in its excited state than its ground state, with the result that the potential-energy well depth in the excited state, ε^* , is greater than that of the ground state, ε . Consequently, the energy of the $A \leftarrow X$ metal-water complex transition, E_1 , is less than that of the atomic resonance transition, E_2 , thereby generating red-shifted spectra for the adduct relative to the atomic resonance lines. The energy difference between E_1 and E_2 corresponds to the stabilisation enhancement in going from the ground to the excited state of the complex.

The energy values for stabilisation enhancement for the gallium- and indium-water complexes are 19 and 17.5 kcal mol⁻¹, respectively. These are in qualitative agreement with a number of quantum-chemical calculations that have yielded dissociation energies for metal-water complexes in their ground and excited states for a variety of metal atoms. For example, the difference in dissociation energies between the ${}^{2}A_{1}$ adduct ground state and the ${}^{2}B_{2}$ excited state is *ca*. 10 kcal mol⁻¹ for the lithium-water complex.⁴ In the case of the beryllium-water complex, the energy difference is *ca*. 18 kcal mol^{-1.4} Since these *ab initio* studies dealt with metals from different chemical groups than studied in this work, the qualitative agreement is interesting; however, the nature of the bonding interaction is probably not the same.

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The gallium-water and indium-water complexes have three low-lying electronic states corresponding to the water molecule splitting the p orbital degeneracy in the C_{2n} point group. The three electronic states generated are ${}^{2}B_{2}$, ${}^{2}B_{1}$ and ${}^{2}A_{1}$, corresponding to the unpaired electron residing in the $b_2 - p_y$, the $b_1 - p_x$ or the $a_1 - p_z$ orbital, respectively. If the unpaired electron occupies the $a_1 - p_z$ orbital, it will directly confront the electron density in the $3a_1$ lone pair on water so the 2A_1 state is probably not stable due to electron-electron repulsion. Both the ${}^{2}B_{2}$ and ${}^{2}B_{1}$ states are expected to be attractive since these states correspond to an orbital occupancy that disperses the unpaired electron density away from the nucleus so the $3a_1$ lone pair on water may encounter enhanced electrostatic attraction. Ab initio results⁴ for (Li...OH₂)* indicate that the ${}^{2}B_{2}$ and the ${}^{2}B_{1}$ states are attractive and that the ${}^{2}B_{2}$ state is more stable than the ${}^{2}B_{1}$ state because the occupation of the $b_{2}-p_{y}$ orbital makes possible a favourable quadrupole-quadrupole interaction between the water quadrupole along the y axis in the yz plane and the $b_2 - p_y$ orbital quadrupole of the metal. Thus, the electronic ground state of the gallium-water complex is most likely ${}^{2}B_{2}$ due to a favourable Coulombic interaction that is unfavourable in the ${}^{2}B_{1}$ state.

The $A \leftarrow X$ transition for the complex involves promotion of the unpaired electron to the a_1 -5s orbital of the metal, which generates an unequivocal 2A_1 electronic state since the a_1 -5s orbital is not degenerate. Thus, the observed $A \leftarrow X$ transition for the gallium-water and indium-water complexes may be identified with a ${}^2A_1 \leftarrow {}^2B_2$, symmetry allowed, electronic transition that corresponds to an electron configuration rearrangement of $\ldots (3a_1)^2 (2b_2) \rightarrow \ldots (3a_1)^2 (5a_1)$ for the Ga-H₂O complex. Bentley⁴ has stated that the principal non-covalent attractive force between the metal and the water is electrostatic in origin with minor polarisation and charge-transfer components. This result is consistent with the interpretation that the metal-water bonding arises from an electrostatic attraction between the metal nucleus and the $3a_1$ lone pair of water.

ORBITAL AND STATE CORRELATIONS

The electronic state-to-state correlation diagrams that describe the gallium-water and indium-water chemical interactions are very similar to the aluminium-water state diagram. Hence, reference to fig. 6 will be of assistance during the course of the following discussion.

Table 4 indicates that gallium-atom insertion into the O—H bond of water is exothermic by ca. 34 kcal mol⁻¹, which is almost one-half of the amount of energy released in the aluminium insertion reaction. The indium insertion is only exothermic by ca. 17 kcal mol⁻¹. Although the ²A" first excited state of HMOH (M = Ga or In) was not observed spectroscopically in the matrix, the energy of transition may be roughly estimated by assuming the value is close to that observed for HAIOH. These facts lead to the conclusion that the ²A" states of HGaOH and HInOH are higher in energy relative to the reactant ²A" state derived from ²P_u + ¹A₁. Consequently, the spontaneous reaction of gallium or indium inserting into the O—H bond of water, although suitably exothermic, is not expected to occur for two reasons: (1) direct reaction along the ²A' ground-state surface is hindered by a potential-energy barrier generated by an avoided surface crossing, also encountered in the aluminium–water insertion reaction, and (2) reaction along the ²A" excited potential surface is also hindered by a potential-energy barrier generated by the endothermicity of the reaction to form HGaOH or HInOH in the ²A" state.

On the other hand, the gallium and indium metal atom insertion reactions have been induced by irradiation of the metal-water complex in the C_{2v} point group which has a ${}^{2}B_{2}$ ground state. The first observed excited state of this complex is the ${}^{2}A_{1}$ state

 $({}^{2}A' \text{ in } C_{s} \text{ symmetry})$ derived from M (${}^{2}S$) and H₂O (${}^{1}A_{1}$). The charge-transfer state that diabatically correlates into the ${}^{2}A'$ ground state of the HMOH molecule is also of ${}^{2}A'$ symmetry, so it intersects the ${}^{2}A'$ state of the complex in an avoided surface crossing, thereby permitting it to evolve adiabatically into a lower ${}^{2}A'$ state of the HMOH molecule. Since the ionisation potential of M (${}^{2}S$) is only 3.0 eV and the electron affinity of water (${}^{1}A_{1}$) is *ca*. 0, the surface intersection is expected to occur very early in the rearrangement of the complex to form HMOH, so a significant potential barrier is not expected. Also, favourable Franck-Condon factors would probably allow more energetic photons to access sufficiently high vibrational levels in the ${}^{2}A_{1}$ state to overcome any barrier to reaction that may exist. Therefore, photolysing the metal-water complex with the appropriate wavelength of light populates the ${}^{2}A_{1}$ excited state of the adduct, which is unstable with respect to rearrangement, to form the HMOH molecule in its second excited ${}^{2}A'$ state. The excited HMOH molecule may then decay into its ${}^{2}A'$ ground state.

Table 5. Estimated heats of reacting

	$\Delta H/\text{kcal mol}^{-1}$
HAIOH $({}^{2}A') \rightarrow \text{AIOH} ({}^{1}\Sigma^{+}) + \text{H} ({}^{2}S)$ HAIOH $({}^{2}A') \rightarrow \text{AIO} ({}^{2}\Sigma^{+}) + \text{H}_{2} ({}^{1}\Sigma^{+}_{a})$	+ 52 + 59
HGaOH (² A') → GaOH (¹ Σ ⁺) + H (² S) HGaOH (² A') → GaO (² Σ ⁺) + H ₂ (¹ Σ ⁺ _g)	+50 +60
HINOH $({}^{2}A') \rightarrow$ INOH $({}^{1}\Sigma^{+}) +$ H $({}^{2}S)$ HINOH $({}^{2}A') \rightarrow$ INO $({}^{2}\Sigma^{+}) +$ H ₂ $({}^{1}\Sigma^{+}_{g})$	+49 +59

^a Heats of reaction were estimated using bond-energy data from ref. (11) and (22)–(24). Promotional energies were estimated by taking the difference in bond energies for M—OH and M—(OH)₂.

PHOTODISSOCIATION OF HGaOH AND HINOH

Bands attributable to HMOH (M = Ga and In) were not observed. This may be understood in the context of a qualitative molecular orbital argument involving orbital correlations for the linear and bent conformations of HAB (see fig. 4). The HAB molecule models the insertion product where the OH fragment is identified with the B atom and the metal atom is identified with the A atom. In accord with perturbation theory, the greater the difference in electronegativity between the A and **B** atoms, the greater the disparity of p orbital contribution to the $5a'-1\pi_x$ MO and the $7a'-2\pi_x$ MO from A and B, such that for a very large difference in electronegativity $(X_{\rm B} \gg X_{\rm A})$, the 7a' MO is primarily the p_x orbital of A and the 5a' MO is primarily the p_x orbital of B. A larger p AO contribution from A to 7a' favours a smaller HAB bond angle since there is an improved AO overlap.¹⁹ Since gallium and indium have greater electronegativities than aluminium, the electronegativity differences are smaller for the HGaOH and HInOH molecules compared with HAlOH, thereby generating a smaller bond angle change upon exciting the ${}^{2}A''$ state of the HMOH* species. This favours the absorption of lower-energy light and a smaller bending mode progression since the diagonal Franck-Condon factors are larger in magnitude. Therefore, the ${}^{2}A'' \leftarrow {}^{2}A'$ transition for HGaOH and HInOH may be beyond the

long-wavelength limit of the u.v.-vis. spectrophotometer since the ${}^{2}A''(v_{2} = 0) \leftarrow {}^{2}A'(v_{2} = 0)$ electronic transition for HAIOH is < 12500 cm⁻¹.

Irradiation of the HGaOH and HInOH molecules generated only the metal hydroxide product. The correlations for these predissociations are expected to be very similar to those constructed for the HAIOH molecule predissociating to form AlOH + H and AlO + H₂ (see fig. 8 and 9). Table 5 shows that the heats of reaction for the HAIOH, HGaOH and HInON reactions to form the metal hydroxide and metal monoxide are all very similar, with the MOH $({}^{1}\Sigma^{+}) + H_{2}({}^{1}\Sigma_{g}^{+}) {}^{2}A'$ product ground state being *ca*. 21000 cm⁻¹ above the HMOH ${}^{2}A'$ ground state. The ${}^{2}A''$ state of HMOH can heterogeneously predissociate into the ${}^{2}A'$ ground state of the MOH product by interaction with the out-of-plane torsional mode of HMOH. There is a potential-energy barrier to recombination generated by an avoided surface intersection which stabilises the metal hydroxide product; however, as before, there is not a potential barrier to recombination of the MO + H₂ products.

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