# Gaseous $HgH_2$, $CdH_2$, and $ZnH_2$

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**Abstract:** Gaseous $HgH_2$, $CdH_2$, and $ZnH_2$ molecules were synthesized by the direct gas-phase reaction of excited mercury, cadmium, and zinc atoms with molecular hydrogen. The molecules were identified by their high-resolution infrared emission spectra, and the metal–hydrogen bond lengths were determined from the rotational analysis of the antisymmetric stretching fundamental bands.

**Keywords:** gas-phase reactions · group 12 elements · hydrides · IR spectroscopy · mercury

## Introduction

Mercury and its compounds are hazardous air pollutants, being released to the atmosphere from both anthropogenic and natural sources.[1,2] Emission of gaseous elemental mercury ($Hg^0$) from the surface of oceans plays an important role in the global mercury cycle. In this process, aqueous $Hg^{II}$ in natural waters is reduced by microorganisms to $Hg^0$, which is released into the atmosphere as vapor-phase elemental mercury.[3] In fact, reducing aqueous $Hg^{II}$ to $Hg^0$ and its subsequent detection in the gas phase is the most commonly used method for determining trace amounts of mercury in liquid and solid samples. Developed in the late 1960s, this method is called "cold vapor generation", in which aqueous $Hg^{II}$ is reduced to $Hg^0$ by using $NaBH_4$ or $SnCl_2$ solutions.[4] Because the resultant $Hg^0$ is only sparingly soluble in water and has a high vapor pressure at room temperature, it can be easily purged into the gas phase for detection by atomic absorption spectroscopy.[4] In a very similar technique called "hydride generation", $NaBH_4$ is added to acidified solutions of group 13, 14, 15, and 16 metals to form volatile metal hydrides, which can be detected in the gas phase after atomization.[4] The use of this technique for all group 12 metals revealed that Hg-, Cd-, and Zn-containing molecules are formed in the reduction process, and are released into the gas phase.[5–7] Although these molecules are probably metal dihydrides ($HgH_2$, $CdH_2$, and $ZnH_2$), their identities have not yet been determined with certainty.

The existence of solid $HgH_2$, $CdH_2$, and $ZnH_2$ has been known for about fifty years, and several methods have been reported for their synthesis.[8–11] Very recently obtained infrared spectra of these solids suggest that $HgH_2$ is a covalent molecular solid,[12,13] whereas $CdH_2$ and $ZnH_2$ solids probably have hydrogen-bridge bonding.[14] Nonetheless, these solids are rather unstable, and it is probably not possible to vaporize them without their decomposition into their constituent elements. In fact, the decomposition of solid $HgH_2$, $CdH_2$, and $ZnH_2$ to metal atoms and molecular hydrogen has been observed at approximately −125 °C, −20 °C, and +90 °C, respectively.[8,9]

High level theoretical calculations performed for the $HgH_2$, $CdH_2$, and $ZnH_2$ molecules have predicted the ground electronic states to be closed-shell $\tilde{X}^1\Sigma_g^+$ states.[15–17] Equilibrium bond lengths, dissociation energies, and vibrational frequencies were also estimated, and matrix isolation techniques were employed to study these molecules at very low temperatures (5–12 K). Excited metal atoms reacted with molecular hydrogen in solid argon, neon, or hydrogen matrices, and metal dihydrides were formed.[12–14,17,18] Infrared spectra of these molecules in solid matrices were recorded and vibrational frequencies were obtained.

The direct gas-phase reactions of Hg, Cd, and Zn with $H_2$ have been studied extensively by using both theoretical calculations[19–21] and various experimental methods.[22,23] It is generally accepted that mercury, cadmium, and zinc in their $^1S$ ground states do not react with molecular hydrogen, because large energy barriers exist and the overall reactions (with the production of gaseous MH or $MH_2$) are endoergic. However, if these atoms are excited to either $^3P$ or $^1P$ electronic states, they can react efficiently with molecular hydrogen to produce gaseous HgH, CdH, or ZnH.[19–23] These studies were focused mainly on the production of metal monohydrides, that is, $M(g)+H_2(g)\rightarrow MH(g)+H(g)$, perhaps

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DOI: 10.1002/chem.200500332

because gaseous HgH, CdH, and ZnH molecules have been recognized since the 1920s, and their electronic spectra in the visible/near-ultraviolet region have been analyzed.[24] Although all experimental and theoretical work on these reactions[19–23] has supported the idea that an unstable H–M–H* excited species is formed as a reaction intermediate in the production of gaseous MH molecules, little attention has been given to the possibility of forming stable linear H–M–H molecules (M = Hg, Cd, Zn) in the gas phase.[19,20]

Gaseous $ZnH_2$ and $ZnD_2$ have been synthesized recently in our laboratory,[25] and identified by their high-resolution infrared spectra. Here, we report the first observation of gaseous $HgH_2$, $HgD_2$, $CdH_2$, and $CdD_2$ from the direct reaction of mercury or cadmium vapor with molecular hydrogen/deuterium in the presence of an electrical discharge. High-resolution infrared emission spectra of these molecules confirm their identities and the linear H–M–H structure.

## Experimental Section

An emission source that combines an electrical discharge with a high temperature furnace was used to generate $HgH_2$, $CdH_2$, and $ZnH_2$ molecules in the gas phase. A small zirconia or tantalum boat containing about 100 g of mercury, cadmium, or zinc was placed inside the central part of an alumina tube (120 cm long, 5 cm inside diameter). Two stainless-steel electrodes were located inside the alumina tube, one at each end, and were connected to a 3 kV/333 mA dc power supply. The tube was sealed with barium fluoride windows and evacuated by using a rotary pump. Pure hydrogen or deuterium was allowed to flow slowly through the tube at pressures ranging from 0.5 to 2.5 Torr. Both ends of the alumina tube were cooled by a constant flow of water on the outside surface, and a dc discharge was created between the two stainless-steel electrodes. Mercury has a vapor pressure of 2 mTorr at room temperature, and heating was not necessary; however, in the presence of an electrical discharge, the temperature increased slowly to around 50–100 °C. For the cadmium and zinc experiments, the central part of the alumina tube was heated to 350 and 470 °C, respectively, by using a tube furnace, to produce about 0.5 Torr of metal vapor. The ground state Hg, Cd, or Zn atoms are excited (particularly to the metastable $^3P$ state) in the presence of the electrical discharge, and then react with molecular hydrogen or deuterium to produce gaseous $HgH_2$, $CdH_2$, or $ZnH_2$. A fraction of the metal dihydride molecules generated in this source are in excited vibrational and rotational states, and they relax to the ground state by collisions or by emission of infrared light. A barium fluoride lens was used to focus this emission onto the entrance aperture of a Bruker IFS 120 HR Fourier transform spectrometer. The spectrometer was operated under vacuum with a KBr beamsplitter and appropriate infrared filters. Infrared emission spectra were recorded in the 800–2200 $cm^{-1}$ spectral range by using InSb or HgCdTe (MCT) detectors cooled by liquid nitrogen, and the instrumental resolution was set to 0.01 $cm^{-1}$. To improve the signal-to-noise ratio, several hundred spectra were co-added during a few hours of recording.

## Results

The spectra contained molecular emission lines due to vibration–rotation transitions of gaseous metal dihydrides, as well as atomic emission lines. In the zinc and cadmium experiments, emission lines from vibration–rotation transitions of ZnH, ZnD, CdH, and CdD were also observed, but HgH and HgD were not seen in the mercury experiment. Carbon monoxide, which appeared as an impurity in the spectra, was used for wavenumber calibration. The absolute accuracy of line positions measured in our spectra is about 0.001 $cm^{-1}$. The molecular emission lines were assigned to the antisymmetric stretching fundamental bands, $001(\Sigma_u^+)\rightarrow 000(\Sigma_g^+)$, of $HgH_2$, $HgD_2$, $CdH_2$, $CdD_2$, $ZnH_2$, and $ZnD_2$ for the following reasons: a) the band origins observed in our spectra match the peaks observed in matrix isolation experiments[12–14,17,18] if matrix shifts are taken into account, and the general appearance of the spectra (single $P$ and $R$ branches only) is consistent with a closed-shell $^1\Sigma_g^+$ electronic state; b) the line spacings in our spectra match the $2B$ values that can be estimated from the theoretical bond lengths of these molecules,[15–17] and are consistent with a linear H–M–H structure; c) the adjacent rotational lines for $MH_2$ and $MD_2$ have alternating 3:1 and 1:2 intensity ratios, respectively, due to the *ortho–para* nuclear-spin statistical weights associated with hydrogen and deuterium nuclei. A portion of the $HgH_2$ spectrum in Figure 1 shows the intensity alternation in $P$-branch lines. Lines from different isotopes of Hg, Cd, and Zn were resolved in all spectra, and their intensity ratios match the terrestrial abundances of those isotopes, confirming the identity of the metals. Figure 2 shows the isotope splitting in an expanded view of one rotational line in the $HgH_2$ spectrum.

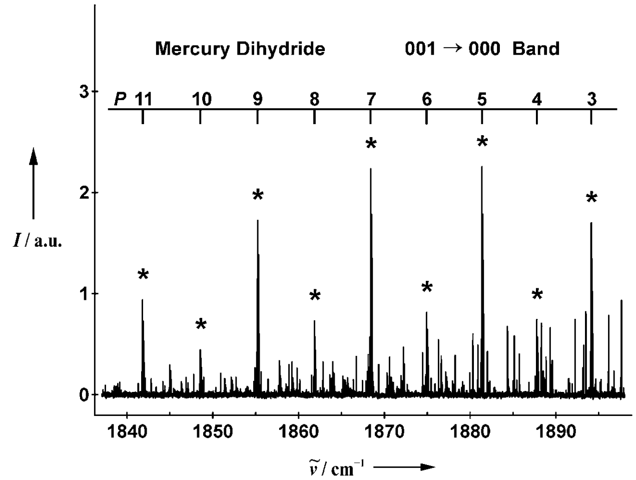

Figure 1. A portion of the infrared emission spectrum of gaseous $HgH_2$ showing the 3:1 intensity alternation in $P$-branch lines of the antisymmetric stretching fundamental band. The weaker lines are due to hot bands of $HgH_2$ and carbon monoxide impurity.

Lines from the antisymmetric stretching fundamental band, 001 $(\Sigma_u^+)\rightarrow$000 $(\Sigma_g^+)$, were fitted by using the customary energy level expression for linear triatomic molecules, represented by Equation (1):

$$E(v_1,v_2,v_3,J) = G(v_1,v_2,v_3)+BJ(J+1)-DJ^2(J+1)^2 \tag{1}$$

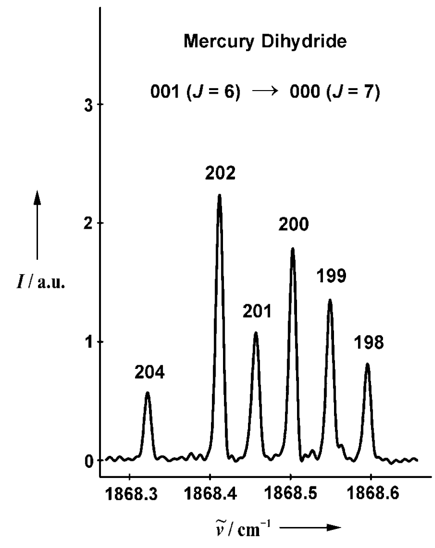

Figure 2. An expanded view of the $P(7)$ rotational line of the $HgH_2$ fundamental band. Lines have been marked by mass numbers of mercury isotopes (see text).

In this equation, $v_1$, $v_2$, and $v_3$ are the vibrational quantum numbers for the symmetric stretching ($\sigma_g$), bending ($\pi_u$), and antisymmetric stretching ($\sigma_u$) modes, respectively, and $J$ is the rotational quantum number. The vibrational band origin $\nu_3$ [$\equiv G(0,0,1)-G(0,0,0)$], the inertial rotational constants ($B_{000}$, $B_{001}$), and the centrifugal distortion constants ($D_{000}$, $D_{001}$) were determined for all metal dihydride species by employing least-squares fitting, and the ground-state vibrational energy $G(0,0,0)$ was set to zero. The $r_0$ bond lengths were then calculated from $B_{000}$ by using the moment of inertia equation. The 000 ground state for $MD_2$ molecules always lies lower than that of the corresponding $MH_2$ molecules on any potential energy surface, and therefore, the $r_0$ bond lengths of $MD_2$ species are slightly shorter than those of the corresponding $MH_2$ molecules. The vibrational band origins ($\nu_3$) and the $r_0$ metal–hydrogen bond lengths for the most abundant isotopologues of $HgH_2$, $HgD_2$, $CdH_2$, $CdD_2$, $ZnH_2$, and $ZnD_2$ are presented in Table 1. $HgH_2$ has a shorter bond length than $CdH_2$, as predicted by theoretical calculations[15–17] and attributed to relativistic effects. A few hot bands were also found and analyzed for several isotopologues of these molecules, and a comprehensive analysis of all the data will be published elsewhere.

Table 1. Bond lengths and vibrational frequencies of gaseous metal dihydrides. The numbers in parentheses are three standard deviation statistical uncertainties in the last quoted digit.

| Molecule | $r_0$ [Å] | $\nu_3$ [cm$^{-1}$] | Ref. |
|---|---|---|---|
| $^{202}HgH_2$ | 1.646543(2) | 1912.8143(2) | |
| $^{202}HgD_2$ | 1.642534(6) | 1375.7885(4) | |
| $^{114}CdH_2$ | 1.68303(2) | 1771.530(1) | |
| $^{114}CdD_2$ | 1.67917(2) | 1278.312(1) | |
| $^{64}ZnH_2$ | 1.535271(4) | 1889.4326(3) | [25] |
| $^{64}ZnD_2$ | 1.53184(3) | 1371.631(1) | [25] |
| $^{24}MgH_2$ | 1.70333(1) | 1588.6716(7) | [28] |
| $^{24}MgD_2$ | 1.70087(3) | 1176.503(2) | [29] |
| $^{9}BeH_2$ | 1.333761(6) | 2178.8656(7) | [26] |
| $^{9}BeD_2$ | 1.33136(1) | 1689.679(1) | [27] |

## Discussion

The bond lengths and vibrational frequencies for group 2 metal dihydrides[26–29] are also reported in Table 1 for comparison. The $HgH_2$, $CdH_2$, and $ZnH_2$ molecules have shorter bond lengths and higher vibrational frequencies than those for magnesium dihydride. Electronegativities of Hg, Cd, and Zn are also considerably larger than those of group 2 metals.[30] The relatively short bond lengths and high vibrational frequencies of $HgH_2$, $CdH_2$, and $ZnH_2$, as well as the large electronegativities of group 12 metals, indicate that these gas-phase molecules have strong covalent bonds. In fact, average bond strengths should not be considered in discussions of bonding in $HgH_2$, $CdH_2$, and $ZnH_2$ molecules; it appears that breaking the first metal–hydrogen bond (in $MH_2$) requires a significant amount of energy, but the second bond (MH) can be broken by only a small fraction of that energy. For example, experimental values for the dissociation energies of $H_2$ and HgH are 103.3 and 8.6 kcal mol$^{-1}$, respectively,[31] whereas the predicted heat of formation of gaseous $HgH_2$ from mercury vapor and molecular hydrogen[17] is 1.048 eV $\approx$ 24.2 kcal mol$^{-1}$. Therefore, it can be readily calculated that breaking the first mercury–hydrogen bond in $HgH_2$, that is, $HgH_2(g) \rightarrow HgH(g) + H(g)$, requires about 70 kcal mol$^{-1}$ of energy, whereas only 8.6 kcal mol$^{-1}$ is needed to break the second bond (HgH). Thus, the divalent molecules $HgH_2$, $CdH_2$, and $ZnH_2$ are much more stable than the corresponding metal monohydrides HgH, CdH, and ZnH. On the other hand, although the decomposition of ground-state linear H–M–H molecules to M atoms and molecular $H_2$ is predicted to be slightly exoergic for Hg, Cd, and Zn,[17] large energy barriers significantly reduce the rate of these reactions. Although the existence of HgH, CdH, and ZnH free radicals has been known since the 1920s, the more stable metal dihydrides have been overlooked for decades.

The relative stability of gaseous $HgH_2$, $CdH_2$, and $ZnH_2$ molecules supports the hypothesis that these species are formed during the reduction of aqueous Hg, Cd, and Zn ions in the "hydride generation" technique.[4] Volatile hydrides of a few elements from groups 14, 15, and 16 (e.g., $SnH_4$, $PH_3$, $AsH_3$, and $H_2S$) are detectable in the environment, and anaerobic bacteria produce these hydrides by the reduction of aqueous ions.[32] Considering the fact that aqueous $Hg^{II}$ in natural waters is reduced to volatile $Hg^0$ by microorganisms,[3] $HgH_2$, $CdH_2$, and $ZnH_2$ may be produced similarly in the environment under certain conditions.

In summary, gaseous $HgH_2$, $HgD_2$, $CdH_2$, and $CdD_2$ were observed for the first time from the direct reaction of metal vapor with molecular hydrogen/deuterium in the presence of an electrical discharge. High-resolution infrared emission spectra of these molecules were recorded, and the antisymmetric stretching fundamental bands were rotationally analyzed to obtain $r_0$ bond lengths. Gaseous $HgH_2$, $CdH_2$, and $ZnH_2$ molecules have a linear H–M–H structure, and are considerably more stable than the corresponding HgH, CdH, and ZnH free radicals.

## Acknowledgements

Financial support for this work was provided by the Natural Sciences and Engineering Research Council (NSERC) of Canada.

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[1] E. Stokstad, *Science* **2004**, *303*, 34.
[2] W. H. Schroeder, J. Munthe, *Atmos. Environ.* **1998**, *32*, 809–822.
[3] R. P. Mason, F. M. M. Morel, H. F. Hemond, *Water Air Soil Pollut.* **1995**, *80*, 775–787.
[4] R. E. Sturgeon, Z. Mester, *Appl. Spectrosc.* **2002**, *56*, 202A–213A.
[5] A. Sanz-Medel, M. C. Valdés-Hevia y Temprano, N. Bordel García, M. R. Fernández de la Campa, *Anal. Chem.* **1995**, *67*, 2216–2223.
[6] A. S. Luna, R. E. Sturgeon, R. C. de Campos, *Anal. Chem.* **2000**, *72*, 3523–3531.
[7] Y.-L. Feng, R. E. Sturgeon, J. W. Lam, *Anal. Chem.* **2003**, *75*, 635–640.
[8] E. Wiberg, W. Henle, R. Bauer, *Z. Naturforsch.* **1951**, *6b*, 393.
[9] E. Wiberg, W. Henle, *Z. Naturforsch.* **1951**, *6b*, 461–462.
[10] G. D. Barbaras, C. Dillard, A. E. Finholt, T. Wartik, K. E. Wilzbach, H. I. Schlesinger, *J. Am. Chem. Soc.* **1951**, *73*, 4585–4590.
[11] J. J. Watkins, E. C. Ashby, *Inorg. Chem.* **1974**, *13*, 2350–2354.
[12] X. Wang, L. Andrews, *Inorg. Chem.* **2004**, *43*, 7146–7150.
[13] X. Wang, L. Andrews, *Phys. Chem. Chem. Phys.* **2005**, *7*, 750–759.
[14] X. Wang, L. Andrews, *J. Phys. Chem. A* **2004**, *108*, 11006–11013.
[15] P. Pyykkö, *J. Chem. Soc. Faraday Trans. 2* **1979**, *75*, 1256–1276.
[16] P. Schwerdtfeger, G. A. Heath, M. Dolg, M. A. Bennet, *J. Am. Chem. Soc.* **1992**, *114*, 7518–7527.
[17] T. M. Greene, W. Brown, L. Andrews, A. J. Downs, G. V. Chertihin, N. Runeberg, P. Pyykkö, *J. Phys. Chem.* **1995**, *99*, 7925–7934.
[18] N. Legay-Sommaire, F. Legay, *Chem. Phys. Lett.* **1993**, *207*, 123–128.
[19] A. Bernier, P. Millie, *J. Chem. Phys.* **1988**, *88*, 4843–4854.
[20] J. A. Boatz, M. Gutowski, J. Simons, *J. Chem. Phys.* **1992**, *96*, 6555–6564.
[21] P. E. M. Siegbahn, M. Svensson, R. H. Crabtree, *J. Am. Chem. Soc.* **1995**, *117*, 6758–6765.
[22] W. H. Breckenridge, C. Jouvet, B. Soep, *J. Chem. Phys.* **1986**, *84*, 1443–1450.
[23] W. H. Breckenridge, J.-H. Wang, *J. Chem. Phys.* **1987**, *87*, 2630–2637.
[24] R. S. Mulliken, *Phys. Rev.* **1928**, *32*, 388–416.
[25] A. Shayesteh, D. R. T. Appadoo, I. E. Gordon, P. F. Bernath, *J. Am. Chem. Soc.* **2004**, *126*, 14356–14357.
[26] P. F. Bernath, A. Shayesteh, K. Tereszchuk, R. Colin, *Science* **2002**, *297*, 1323–1324.
[27] A. Shayesteh, K. Tereszchuk, P. F. Bernath, R. Colin, *J. Chem. Phys.* **2003**, *118*, 3622–3627.
[28] A. Shayesteh, D. R. T. Appadoo, I. Gordon, P. F. Bernath, *J. Chem. Phys.* **2003**, *119*, 7785–7788.
[29] A. Shayesteh, D. R. T. Appadoo, I. Gordon, P. F. Bernath, *Can. J. Chem.* **2004**, *82*, 947–950.
[30] D. R. Lide, *CRC Handbook of Chemistry and Physics*, 85th ed., CRC Press, Boca Raton, FL, (USA), **2005**.
[31] K. P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure IV: Constants of Diatomic Molecules*, Van Nostrand, New York, **1979**.
[32] J. S. Thayer, *Environmental Chemistry of the Heavy Elements: Hydrido and Organo Compounds*, VCH, New York, **1995**.

Received: March 24, 2005