Vibration−Rotation Emission Spectra of Gaseous ZnH$_2$ and ZnD$_2$

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Gaseous ZnH$_2$ and ZnD$_2$ have been discovered in an emission source that combines an electrical discharge with a high-temperature furnace. High-resolution infrared emission spectra of ZnH$_2$ and ZnD$_2$ have been recorded with a Fourier transform spectrometer. The antisymmetric stretching fundamental bands were rotationally analyzed, and the r_0 bond distances for linear ^{64}ZnH$_2$ and ^{64}ZnD$_2$ were determined.

Metal hydrides are among the simplest inorganic molecules. They are favorite target molecules for ab initio quantum chemists because of the simplicity of metal−hydrogen bonding. Theoretical calculations can predict reliable molecular properties for metal hydrides because they have a relatively small number of electrons. Experimental data on these molecules serve as a test for the accuracy of ab initio methods.

The reaction of excited zinc atoms with molecular hydrogen in the gas phase was studied by Breckenridge et al.[1] using laser-pump−probe techniques. Zinc atoms in ^{3}P or ^{1}P excited states can activate the H−H bond, and it was assumed that gaseous ZnH$_2$ is a reaction intermediate in the formation of ZnH and H products.[2] Solid ZnH$_2$ was synthesized by Barbaras et al.[3] from the reaction of dimethylzinc with a diethyl ether solution of lithium aluminum hydride. Watkins and Ashby[4] found an alternative and convenient method for the preparation of solid zinc dihydride, using the reaction of alkali metal hydrides with zinc halides in tetrahydrofuran. The only spectroscopic studies on the zinc dihydride molecule are the infrared spectra of ZnH$_2$, ZnHD, and ZnD$_2$ trapped in argon and krypton matrices[5,6] at 10−12 K. ZnH$_2$ has been the subject of a few ab initio calculations, predicting the equilibrium geometry and the Zn−H bond energy.[7−9] The average Zn−H bond energy was recently calculated[9] to be 51.24 kcal/mol, while the H−H bond energy is 103.3 kcal/mol.[10] Therefore, the overall reaction is nearly ergoneutral.

$$\text{Zn(g)} + \text{H}_2\text{(g)} \rightarrow \text{ZnH}_2\text{(g)}$$
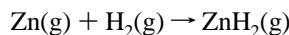
However, there was no observation of gaseous ZnH$_2$ prior to this work. The only other metal dihydrides known in the gas phase are FeH$_2$,[11] BeH$_2$,[12,13] and MgH$_2$.[14,15]

The discharge furnace source used for the production of ZnH$_2$ is described in detail in our earlier papers on BeH$_2$[13] and MgH$_2$.[14] About 100 g of zinc was placed in an alumina tube and heated to 470 °C using a CM Rapid Temp furnace. Pure hydrogen or deuterium (0.5−2.5 Torr) flowed slowly through the tube, and a dc discharge (3 kV, 333 mA) was applied between two stainless steel electrodes located inside the water-cooled ends of the alumina tube. The tube was sealed with BaF$_2$ windows, and a BaF$_2$ lens was used to focus the emitted light onto the entrance aperture of a Bruker IFS HR 120 Fourier transform spectrometer. The infrared spectra of ZnH$_2$ and ZnD$_2$ were recorded in the 800−2200 cm^{-1} region using a KBr beam splitter and a HgCdTe (MCT) detector. The instrumental resolution was 0.01 cm^{-1}, and several hundred scans were co-added to improve the signal-to-noise ratio. An
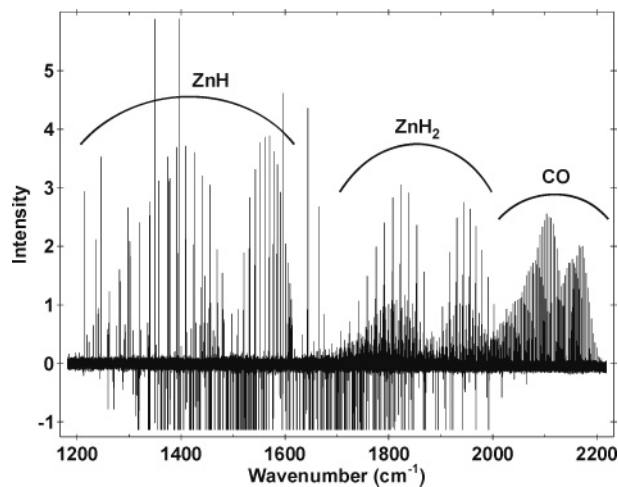
Figure 1. The infrared emission spectrum of ZnH$_2$ contained several atomic lines as well as ZnH and CO lines. The baseline of this spectrum was corrected using the Bruker OPUS program, and the absorption lines are from atmospheric water vapor.
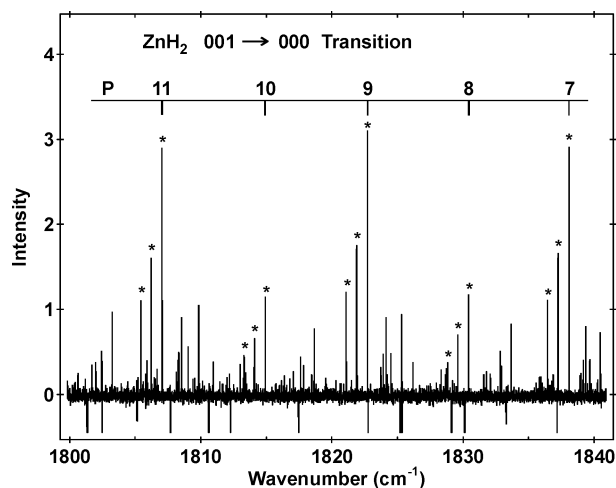
Figure 2. This expanded view of the ZnH$_2$ spectrum shows a 3:1 intensity ratio alternation of adjacent rotational lines. The three marked lines corresponding to each rotational transition are from ^{64}ZnH$_2$, ^{66}ZnH$_2$, and ^{68}ZnH$_2$ (see Table 1).

overview of the ZnH$_2$ spectrum, which also contains strong ZnH and CO lines, is shown in Figure 1. The WSPECTRA program was used to determine the line positions. The spectra were calibrated using the impurity CO lines, and the absolute accuracy of the line positions is better than 0.001 cm^{-1}.

The lines of Table 1 are assigned to the antisymmetric stretching fundamental band, 001 (Σ_u^+) → 000 (Σ_g^+), of ZnH$_2$ and ZnD$_2$ for the following reasons:

(1) The observed band origins of 1889.4 and 1371.6 cm^{-1} for gaseous ^{64}ZnH$_2$ and ^{64}ZnD$_2$, respectively, match the values observed

Table 1. Line Positions (cm^{-1}) of the Antisymmetric Stretching Fundamental Band, 001 (Σ_u^+) → 000 (Σ_g^+), of ZnH$_2$ and ZnD$_2$[a]

J' [b]	J'' [b]	^{64}ZnH$_2$	^{66}ZnH$_2$	^{64}ZnD$_2$
12	13	1791.1174(2)	1790.2893(0)	1322.9638(−1)
11	12	1799.1204(−2)	1798.2912(0)	1326.8777(0)
10	11	1807.0547(−1)	1806.2243(2)	1330.7645(3)
9	10	1814.9187(0)	1814.0870(2)	1334.6233(1)
8	9	1822.7112(1)	1821.8782(1)	1338.4546(2)
7	8	1830.4308(−1)	1829.5968(−1)	1342.2576(2)
6	7	1838.0768(0)	1837.2421(1)	1346.0313(−6)
5	6	1845.6480(3)	1844.8123(0)	1349.7778(2)
4	5	1853.1426(0)	1852.3064(0)	1353.4936(−6)
3	4	1860.5598(−2)	1859.7231(−2)	1357.1814(−2)
2	3	1867.8985(−3)	1867.0621(2)	1360.8387(−5)
1	2	1875.1581(0)	1874.3212(4)	1364.4676(8)
0	1	1882.3362(−1)	1881.4988(−2)	1368.0615(−28)
1	0	1896.4452(−4)	1895.6075(−9)	1375.1678(7)
2	1	1903.3744(2)	1902.5378(5)	1378.6723(3)
3	2	1910.2174(2)	1909.3813(6)	1382.1457(4)
4	3	1916.9735(0)	1916.1374(0)	1385.5863(−7)
5	4	1923.6419(2)	1922.8062(−1)	1388.9965(−2)
6	5	1930.2209(1)	1929.3865(4)	1392.3725(−14)
7	6	1936.7095(−1)	1935.8758(−1)	1395.7189(4)
8	7	1943.1068(−1)	1942.2739(−1)	1399.0305(2)
9	8	1949.4111(−4)	1948.5796(−2)	1402.3095(6)
10	9	1955.6220(−1)	1954.7918(1)	1405.5540(1)
11	10	1961.7379(1)	1960.9085(0)	1408.7654(2)
12	11	1967.7571(0)	1966.9295(2)	1411.9402(−23)

[a] Numbers in parentheses are the observed − calculated values (in units of 1 × 10^{-4} cm^{-1}) computed with the constants of Table 2. [b] J' and J'' are the rotational angular momentum quantum numbers of the 001 and 000 levels, respectively.

in the argon (1870 and 1357 cm^{-1}) and krypton (1861 and 1351 cm^{-1}) matrices[5,6] if the matrix shifts are taken into account.

(2) The adjacent rotational lines for ZnH$_2$ and ZnD$_2$ have alternating 3:1 and 1:2 intensity ratios, respectively, because of the ortho-para nuclear spin statistical weights associated with hydrogen and deuterium nuclei.

(3) The r_0 Zn−H bond distance of 1.535 Å determined in this study is close to the calculated r_e value[9] of 1.542 Å.

Lines corresponding to the three naturally abundant isotopes of zinc (^{64}Zn, ^{66}Zn, and ^{68}Zn) were found in both ZnH$_2$ and ZnD$_2$ spectra, but the signal-to-noise ratio of the ZnD$_2$ spectrum was less than that of ZnH$_2$. The customary energy expression for a linear triatomic molecule, $E(v_1,v_2,v_3, J) = G(v_1,v_2,v_3) + B_v J(J + 1) - D_v[J(J + 1)]^2$, was used in our least-squares fitting program, and the spectroscopic constants in Table 2 were determined for the 000 ground state and the 001 excited state of ^{64}ZnH$_2$, ^{66}ZnH$_2$, and ^{64}-ZnD$_2$. The r_0 bond distances were calculated for these isotopologues using the ground-state rotational constant (B_{000}). The r_0 bond distance of ^{64}ZnD$_2$ is considerably smaller than that of ^{64}ZnH$_2$ because the zero-point level of ^{64}ZnD$_2$ lies lower than that of ^{64}-ZnH$_2$ in the anharmonic potential-energy surface.

The wavenumber of the antisymmetric stretching mode is close to three times the wavenumber of the bending mode (i.e., $\nu_3 \approx 3\nu_2$, for both ZnH$_2$ and ZnD$_2$).[6] We observed perturbations in the 001 (Σ_u^+) level at high J values, which are caused by the nearby

Table 2. Spectroscopic Constants of ZnH$_2$ and ZnD$_2$ (cm^{-1})[a]

constant	^{64}ZnH$_2$	^{66}ZnH$_2$	^{64}ZnD$_2$
B_{000}	3.548227(6)	3.548233(11)	1.783449(21)
$10^5 \times D_{000}$	4.914(3)	4.915(5)	1.235(10)
B_{001}	3.506608(7)	3.506676(11)	1.768021(23)
$10^5 \times D_{001}$	4.917(3)	4.919(6)	1.232(13)
$\tilde{\nu}_3$	1889.4326(1)	1888.5953(1)	1371.6311(3)
r_0 (Å)	1.535271(1)	1.535269(2)	1.531836(9)

[a] Numbers in parentheses are one standard deviation uncertainties.

030 level. The largest perturbation was at $J' = 18$ for ZnH$_2$ and at $J' = 22$ for ZnD$_2$. Therefore, only rotational lines corresponding to $J' = 0-12$ were used in our analysis for the determination of r_0.

Several hot bands of ZnH$_2$ and ZnD$_2$ involving all three vibrational modes were also identified in the spectra (i.e., 002 → 001, 003 → 002, 101 → 100, 011 → 010, 021 → 020, and so forth). Small local perturbations were observed in almost all of the hot bands, and in all cases, the perturbation effects in ZnD$_2$ were smaller than those in ZnH$_2$. A complete analysis of all of the bands, including the perturbation effects, is deferred to a later paper. Using the rotational constants of the 000, 100, 010, and 001 levels, the equilibrium rotational constant (B_e) and the equilibrium bond distance (r_e) will be determined for both ZnH$_2$ and ZnD$_2$.

In summary, gaseous ZnH$_2$ and ZnD$_2$ were discovered, and their vibration−rotation emission spectra were recorded with a Fourier transform spectrometer. Rotational analysis of the antisymmetric stretching fundamental bands confirmed the linear structure and yielded r_0 bond distances of 1.535 271(1) and 1.531 836(9) Å for ^{64}ZnH$_2$ and ^{64}ZnD$_2$, respectively.

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