The vibration-rotation emission spectra of gaseous CdH_2 and CdD_2

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The vibration-rotation emission spectra of CdH_2 and CdD_2 molecules have been recorded at high resolution using a Fourier-transform spectrometer. The molecules were generated in a furnace-discharge emission source by reaction of cadmium vapor with molecular hydrogen or deuterium. The fundamental bands for the antisymmetric stretching mode (v_3) of CdH_2 and CdD_2 were detected at about 1771.5 and 1278.3 cm^{-1}, respectively. In addition, the $002(\Sigma_g^+)-001(\Sigma_u^+)$ and $011(\Pi_g)-010(\Pi_u)$ hot bands were observed for CdH_2. Spectroscopic constants were determined for each of the 12 observed isotopologs: $^{110}CdH_2$, $^{111}CdH_2$, $^{112}CdH_2$, $^{113}CdH_2$, $^{114}CdH_2$, $^{116}CdH_2$, $^{110}CdD_2$, $^{111}CdD_2$, $^{112}CdD_2$, $^{113}CdD_2$, $^{114}CdD_2$, and $^{116}CdD_2$. The average Cd-H and Cd-D bond distances (r_0) were determined to be 1.683028(10) and 1.679161(16) Å, respectively. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1895888]

I. INTRODUCTION

Many metal dihydrides have been identified at low temperatures by matrix-isolation spectroscopy,[1] but only FeH_2, BeH_2, MgH_2, and ZnH_2 have been observed in the gas phase.[2–5] Recently, we reported briefly on the observation of gaseous CdH_2 and HgH_2 molecules.[6] The complete analysis of the vibration-rotation emission spectra of CdH_2 and CdD_2 is reported in this paper.

Barbaras *et al.*[7] synthesized solid CdH_2 in 1951 from the reaction of dimethylcadmium with lithium aluminum hydride in diethyl ether solution, and it was noticed that solid CdH_2 is unstable and rapidly decomposes into Cd atoms and molecular hydrogen above $-20\ °C$. It was reported recently that the reduction of aqueous Cd(II) with sodium tetrahydroborate ($NaBH_4$) leads to formation of both atomic and molecular cadmium species.[8–10] The molecule formed in the reduction reaction could be CdH_2, but this has not been confirmed yet. The interaction of Cd atoms in ^1P or ^3P excited states with H_2 or D_2 in the gas phase was investigated experimentally[11,12] and theoretically,[12–15] and it was speculated that bent CdH_2 and CdD_2 molecules in excited electronic states are reaction intermediates in the formation of CdH and CdD or linear CdH_2 and CdD_2.

The only spectroscopic studies on cadmium dihydride are the infrared spectra of CdH_2, CdHD, and CdD_2 in argon, neon, and hydrogen matrices.[16,17] Recently, CdH_2 was also observed as a by-product in a few matrix-isolation experiments studying the reactions of Cd with SiH_4, HCl, and H_2O in a solid argon matrix.[18–20] The equilibrium geometry of CdH_2 has been the subject of several theoretical investigations[1,14,16,21–23] and values ranging from 1.67 to 1.74 Å have been obtained for the Cd-H bond distance. A high-level *ab initio* calculation [coupled-cluster with single and double and perturbative triple excitations CCSD(T)] showed that the overall reaction to form gaseous CdH_2 from ground-state Cd and H_2 is endoergic by 17.0 kcal/mol.[16]

In our experiment, we observed the fundamental bands for the antisymmetric stretching mode (v_3) of CdH_2 and CdD_2, as well as the $002(\Sigma_g^+)-001(\Sigma_u^+)$ and $011(\Pi_g)-010(\Pi_u)$ hot bands of CdH_2. Lines from different isotopologs of CdH_2 and CdD_2 were fitted separately and spectroscopic constants were determined for each of the 12 observed isotopologs: $^{110}CdH_2$, $^{111}CdH_2$, $^{112}CdH_2$, $^{113}CdH_2$, $^{114}CdH_2$, $^{116}CdH_2$, $^{110}CdD_2$, $^{111}CdD_2$, $^{112}CdD_2$, $^{113}CdD_2$, and $^{114}CdD_2$, $^{116}CdD_2$. The obtained B_{000} values were used to calculate the average Cd-H and Cd-D r_0 bond distances and the average r_s structure.

II. EXPERIMENT

In our experiment, CdH_2 and CdD_2 molecules were generated in an emission source with an electrical discharge inside a high-temperature furnace, which was the same as in our previous studies of metal dihydrides.[3–5] A tantalum boat containing cadmium granules was placed inside an alumina tube (5 cm × 120 cm) and heated to 350 °C. About 0.8 Torr of hydrogen or deuterium gas flowed slowly through the tube and a dc discharge was used at a current of about 220 mA. The resulting radiation was focused by a BaF_2 lens into the entrance aperture of a Bruker IFS 120 high-resolution (HR) Fourier-transform spectrometer.

The infrared emission spectrum of CdH_2 was measured at a resolution of 0.01 cm^{-1} in the 1200–2200-cm^{-1} region with a KBr beam splitter and a liquid-nitrogen-cooled HgCdTe (MCT) detector, and the recording time was about 5 h (about 300 scans). The spectrum also contained strong emission lines from impurity CO, which was used for calibration. The accuracy of the measured wave numbers is approximately 0.001 cm^{-1} for the CdH_2 lines.

The spectrum of CdD_2 was measured at a resolution of 0.01 cm^{-1} in the 800–1600-cm^{-1} region with the same beam splitter and detector, and the recording time was about 9 h (about 500 scans). The calibration of this spectrum was
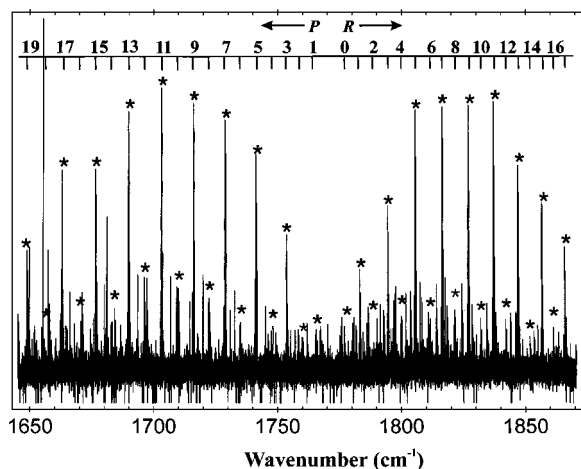
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FIG. 1. An overview of the infrared emission spectrum of CdH$_2$ recorded at a resolution of 0.01 cm^{-1}. The base line was corrected with the Bruker OPUS software and the absorption lines are due to atmospheric H$_2$O vapor. The marked lines with a 3:1 intensity alternation are from the 001-000 band and the unmarked lines are from the 002–001 and 011-010 hot bands.

based on 13 lines that were common with the CdH$_2$ spectrum. The accuracy of the measured CdD$_2$ lines is of the same order, 0.001 cm^{-1}, as the CdH$_2$ lines.

III. RESULTS AND DISCUSSION

Figure 1 shows the overview spectrum of CdH$_2$ that we obtained, which confirmed the predicted linear structure of CdH$_2$.[16] Cadmium has eight naturally occurring isotopes, ^{106}Cd (1.25%), ^{108}Cd (0.89%), ^{110}Cd (12.49%), ^{111}Cd (12.80%), ^{112}Cd (24.13%), ^{113}Cd (12.22%), ^{114}Cd (28.73%), and ^{116}Cd (7.49%).[24] The observed series were assigned to $001(\Sigma_u^+)-000(\Sigma_g^+)$, $002(\Sigma_g^+)-001(\Sigma_u^+)$, and $011(\Pi_g)-010(\Pi_u)$ bands for six of the eight possible isotopologs of CdH$_2$. Figure 2 shows an expanded view of the CdH$_2$ spectrum. Lines from the $002(\Sigma_g^+)-001(\Sigma_u^+)$ hot band have smaller isotopic shifts as compared to lines of the $001(\Sigma_u^+)-000(\Sigma_g^+)$ and $011(\Pi_g)-010(\Pi_u)$ bands because of

the interaction of the $002(\Sigma_g^+)$ state with the nearby $200(\Sigma_g^+)$ state (see below). The CdD$_2$ spectrum was much weaker than the CdH$_2$ spectrum, and we only observed the $001(\Sigma_u^+)-000(\Sigma_g^+)$ fundamental band for six out of the eight isotopologs of CdD$_2$.

In the spectra of CdH$_2$ and CdD$_2$, we also observed the vibration-rotation spectra of CdH and CdD. Cd atoms in both ^1P and ^3P excited states can react with H$_2$ to produce CdH and CdH$_2$.[11–15] In our experiment, Cd atoms are excited to several electronic states such as ^1P and ^3P by the dc discharge and then react with H$_2$ to generate CdH$_2$ molecules. However, because the ^3P state is metastable, the reaction of Cd atoms in the ^3P state with H$_2$ is assumed to contribute more to the generation of CdH$_2$ in our experiment than the reaction of Cd atoms in other electronic states. The dissociation energies of H$_2$ and CdH are 103.3 and 15.6 kcal/mol,[25] respectively, which indicates that the CdH+H asymptote lies at 87.7 kcal/mol above the ground-state Cd+H$_2$. The ground-state reaction $Cd(^1S)+H_2(g)\rightarrow CdH_2(g)$ was predicted to be endoergic by 17.0 kcal/mol.[16] The first dissociation energy of CdH$_2$ to make CdH+H is 70.7 kcal/mol, much larger than the second dissociation energy of 15.6 kcal/mol to make Cd+H.

We had no problem in the rotational assignment of the $001(\Sigma_u^+)-000(\Sigma_g^+)$ fundamental band of CdH$_2$ because we observed the first lines for both the P and R branches. The assignments were confirmed by small perturbations at $J'=12-17$, which are due to the interaction between the $001(\Sigma_u^+)$ and $030(\Pi_u$ or $\Phi_u)$ levels. The ν_3 and ν_2 fundamental bands are observed in an argon matrix at 1753.8 and 601.7 cm^{-1}, and were calculated to be 1790 and 574 cm^{-1} using the CCSD(T) method,[16] respectively. Three times the matrix value for ν_2 is 1805 cm^{-1}, which is close to our ν_3 value of 1772 cm^{-1}. The 3:1 intensity alternation from nuclear-spin statistics also helped to confirm our assignment for the fundamental band. Combination differences were used to determine the absolute J assignment of the $002(\Sigma_g^+)-001(\Sigma_u^+)$ hot band of CdH$_2$. For the $011(\Pi_g)-010(\Pi_u)$ hot band, the assignment was based on perturbations at $J'=9-13$ of the e component, which is caused by the interaction between the $011(\Pi_g)$ and $040(\Sigma_g^+,\Delta_g,$ or $\Gamma_g)$ levels, and was confirmed by fitting together the P and R branches of both the e and f components of the $011(\Pi_g)-010(\Pi_u)$ transition.

We did not observe any perturbations in the CdD$_2$ spectrum. The rotational assignment of the $001(\Sigma_u^+)-000(\Sigma_g^+)$ fundamental band of CdD$_2$ was based on the mass relationship between the B_{000}'s of CdH$_2$ and CdD$_2$, and was aided by the 2:1 intensity alternation of CdD$_2$ lines.

Lines from different isotopologs were fitted separately. The customary energy-level expression for linear triatomic molecules

$$E(J) = G(\nu_1,\nu_2,\nu_3) + BJ(J+1) - D[J(J+1)]^2 \tag{1}$$

was used for the vibration-rotation levels of the $000(\Sigma_g^+)$ and $001(\Sigma_u^+)$ states of CdD$_2$. In Eq. (1), $G(\nu_1,\nu_2,\nu_3)$ is the vibrational energy of the (ν_1,ν_2,ν_3) state relative to the zero-point energy (ZPE), $G(0,0,0)$. The constants obtained for CdD$_2$ are provided in Table I. The observed line positions
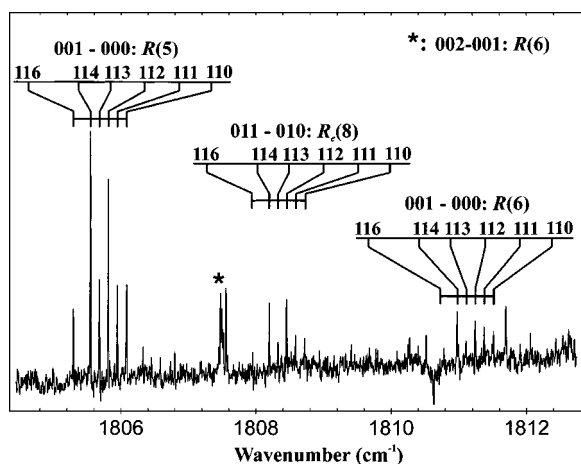

FIG. 2. An expanded view of the infrared spectrum of CdH$_2$ near 1808 cm^{-1}. Six out of the eight isotopologs of CdH$_2$ were observed and the numbers on the top of the lines refer to the mass numbers of the cadmium atom. The interaction between the 002 and the 200 vibrational levels makes the isotopic splitting of lines from the 002-001 band very small (see the text).

TABLE I. Spectroscopic constants (in cm^{-1}) for CdD$_2$ (all uncertainties are 1σ).

	Level	G_v-ZPE	$B_{v_1 v_2 v_3}$	$D_{v_1 v_2 v_3}/10^{-6}$
^{110}CdD$_2$	000	0.0	1.484 200(16)	7.917(20)
	001	1279.082 37(58)	1.4722 67(15)	7.944(19)
^{111}CdD$_2$	000	0.0	1.484 197(18)	7.910(23)
	001	1278.884 76(51)	1.472 264(19)	7.921(26)
^{112}CdD$_2$	000	0.0	1.484 240 3(98)	7.973(11)
	001	1278.690 03(29)	1.472 317(10)	7.992(12)
^{113}CdD$_2$	000	0.0	1.484 246(14)	7.974(24)
	001	1278.498 47(39)	1.472 329(13)	7.990(21)
^{114}CdD$_2$	000	0.0	1.484 208 4(96)	7.935(10)
	001	1278.311 67(28)	1.472 294 6(98)	7.955(11)
^{116}CdD$_2$	000	0.0	1.484 243(18)	7.988(19)
	001	1277.943 01(66)	1.472 355(19)	8.029(19)

and the output files of the least-squares fits are provided in the supplementary tables S1–S6, which have been placed in the Electronic Physics Auxiliary Publication Service (EPAPS).[26]

For each of the six isotopologs of CdH$_2$, we observed the $001(\Sigma_u^+)$–$000(\Sigma_g^+)$ fundamental band, and two hot bands, $002(\Sigma_g^+)$–$001(\Sigma_u^+)$ and $011(\Pi_g)$–$010(\Pi_u)$. Since there is no connection between the $011(\Pi_g)$–$010(\Pi_u)$ band and the other two bands, we fitted the $011(\Pi_g)$–$010(\Pi_u)$ band separately. We observed perturbations in the $001(\Sigma_u^+)$, $002(\Sigma_g^+)$, and $011(\Pi_g)$ vibrational states of CdH$_2$. We tried to consider these three perturbations in our fits, and we succeeded in the deperturbation of the $001(\Sigma_u^+)$ state, but not in the deperturbation of the $002(\Sigma_g^+)$ and $011(\Pi_g)$ states because the hot band lines involving these two excited states are very weak, and the most perturbed lines are missing. We used the energy-level expression, Eq. (1), for the $002(\Sigma_g^+)$ state and the usual energy-level expression for Π states:

$$E(J) = G(v_1, v_2, v_3) + B[J(J+1) - l^2] - D[J(J+1) - l^2]^2$$
$$\pm \tfrac{1}{2}[qJ(J+1) + q_D J^2 (J+1)^2], \qquad (2)$$

for the $011(\Pi_g)$ and $010(\Pi_u)$ states. In Eq. (2), l is the vibrational angular momentum quantum number ($l=1$ for Π states); q and q_D are l-type doubling parameters; the upper (lower) sign refers to $e(f)$ parity. The observed line positions and the output files of the fits for the $011(\Pi_g)$–$010(\Pi_u)$ band of the five CdH$_2$ isotopologs are provided in the supplementary tables S7–S11. Since this band is relatively weak and suffers from perturbations, a weight of 0.002 cm^{-1} was used for most lines and the perturbed excited-state levels were fitted as term values. The constants obtained are given in Table II. The l-type doubling parameter q is negative in the $011(\Pi_g)$ and $010(\Pi_u)$ vibrational states of CdH$_2$, so that the f parity level lies above the e parity level for a given J. The energy of the bending mode (v_2) cannot be determined directly from the fit and therefore the value of $G(0,1,0)-G(0,0,0)$ was fixed at 0.0 in separate fits of the $011(\Pi_g)$–$010(\Pi_u)$ band of each isotopolog of CdH$_2$. However, v_2 has been observed at 601.7 cm^{-1} in an argon matrix for CdH$_2$ and was calculated to be 574 cm^{-1} at the CCSD(T) level of theory.[16] Values for v_2 can also be estimated by the

deperturbation of the $001(\Sigma_u^+)$ state and from the relationship involving q_{010}, B_e, ω_2, and ω_3 (see below).[27–29]

The perturbations in the $001(\Sigma_u^+)$ state are small, and using the ordinary energy expression in Eq. (1), a reasonable fit of the $001(\Sigma_u^+)$–$000(\Sigma_g^+)$ band could be obtained for each CdH$_2$ isotopolog by deweighting the perturbed lines. The perturbation in the $001(\Sigma_u^+)$ state could be caused by either the $03^10(\Pi_u)$ or the $03^30(\Phi_u)$ levels. The $001(\Sigma_u^+)$ rotational levels have e parity and only interact with the $03^10(\Pi_u)$ or $03^30(\Phi_u)$ state e parity levels. The $03^10(\Pi_u)$ and $03^30(\Phi_u)$ levels also interact with each other and the detailed theory of their interaction was derived by Maki, Jr. and Lide, Jr.[27] This interaction depends on the separation between the $03^10(\Pi_u)$ and $03^30(\Phi_u)$ levels. Because we do not have information on this separation, we ignore this interaction. To find which state, $03^10(\Pi_u)$ or $03^30(\Phi_u)$, causes the perturbation in the $001(\Sigma_u^+)$ state, we performed two different fits for the $001(\Sigma_u^+)$–$000(\Sigma_g^+)$ band. If the $03^30(\Phi_u)$ state is assumed to cause the perturbation then we cannot fit the $001(\Sigma_u^+)$–$000(\Sigma_g^+)$ band, but we can easily fit this band if the $03^10(\Pi_u)$ state is assumed to cause the perturbation. In addition, it can be clearly seen from the spectra of the $001(\Sigma_u^+)$–$000(\Sigma_g^+)$ band that the perturbation pushes the $001(\Sigma_u^+)$ state $J=12$–14 levels to lower energy, and pushes the $J=15$–17 levels to higher energy, which means the perturbation in the $001(\Sigma_u^+)$ state is caused by a state with a smaller B_{eff} value. Using B_{000} obtained from the fit of the $001(\Sigma_u^+)$–$000(\Sigma_g^+)$ band with perturbed lines deweighted, and B_{010} and q_{010} values obtained from the fits of the $011(\Pi_g)$–$010(\Pi_u)$ band, we can estimate the effective B values (B_{eff}) for the e levels of the $03^10(\Pi_u)$ and $03^30(\Phi_u)$ states.[28,29] Compared with the B value of the $001(\Sigma_u^+)$ state, the estimated B_{eff} value of the $03^10(\Pi_u)$ state e levels is smaller while the estimated B_{eff} value of the $03^30(\Phi_u)$ state e levels is larger. Therefore, the $03^10(\Pi_u)$ state is believed to be responsible for the perturbations in the $001(\Sigma_u^+)$ state.

The following Hamiltonian matrix was used for the interacting $001(\Sigma_u^+)$ and $03^10(\Pi_u)$ e levels:

$$\mathbf{H} = \begin{pmatrix} E_\Sigma^0 & W_{01} \\ W_{01} & E_\Pi^0 + W_{11} \end{pmatrix}, \qquad (3)$$

where

$$E_\Sigma^0 = G(0,0,1) + B_{001}J(J+1) - D_{001}J^2(J+1)^2, \qquad (4)$$

$$E_\Pi^0 = G(0,3^1,0) + B_{03^10}[J(J+1) - 1]$$
$$- D_{03^10}[J(J+1) - 1]^2, \qquad (5)$$

$$W_{11} = +\tfrac{1}{2}[q_{03^10}J(J+1) + q_{D03^10}J^2(J+1)^2], \qquad (6)$$

$$W_{01} = -k_{01}[J(J+1)]^{1/2}. \qquad (7)$$

E_Σ^0 is the usual energy expression for a Σ^+ state and ($E_\Pi^0 + W_{11}$) is the ordinary energy expression for Π ($l_2=1$) state e levels. W_{01} is the term connecting the $001(\Sigma_u^+)$ state with the $03^10(\Pi_u)$ state and k_{01} is the perturbation constant. We did not observe transitions from the $03^10(\Pi_u)$ state, so the only constants for this state that we can obtain from

TABLE II. Spectroscopic constants (in cm^{-1}) for CdH_2 (all uncertainties are 1σ).

	Level	Gv-ZPE[a]	$B_{v_1v_2v_3}$	$D_{v_1v_2v_3}/10^{-5}$	$q/10^{-2}$	$q_D/10^{-6}$	$(k_{01}/10^{-3})$[b]
$^{110}CdH_2$	000	0.0	2.952 567(12)	3.187 1(21)			
	001	1772.067 42(32)	2.919 633(12)	3.199 0(21)			4.75(14)
	03^10[c]	1782.479 0(63)					
	002	3541.106 56(57)	2.877 639(12)	3.004 6(19)			
	010	c	2.945 723(43)	3.256(10)	$-4.358\ 4(83)$	0.84(19)	
	011	$c+1759.085\ 11(91)$	2.912 967(40)	3.237 1(89)	$-4.302\ 6(81)$	1.37(18)	
$^{111}CdH_2$	000	0.0	2.952 560 1(88)	3.185 1(14)			
	001	1771.929 91(24)	2.919 632 6(81)	3.198 4(12)			4.97(11)
	03^10[c]	1782.325 2(53)					
	002	3540.960 15(42)	2.877 565 3(86)	2.999 4(13)			
	010	c	2.945 762(27)	3.266 5(54)	$-4.346\ 2(56)$	0.59(12)	
	011	$c+1758.949\ 09(65)$	2.913 011(30)	3.243 9(72)	$-4.294\ 1(62)$	1.27(15)	
$^{112}CdH_2$	000	0.0	2.952 573 1(78)	3.186 82(96)			
	001	1771.794 17(24)	2.919 648 7(79)	3.197 5(10)			4.96(12)
	03^10[c]	1782.191 4(55)					
	002	3540.812 22(42)	2.877 543 6(85)	2.999 0(12)			
	010	c	2.945 667(27)	3.226 7(47)	$-4.371\ 7(53)$	1.489(93)	
	011	$c+1758.818\ 55(51)$	2.912 964(27)	3.226 5(50)	$-4.309\ 7(54)$	1.70(10)	
$^{113}CdH_2$	000	0.0	2.952 536 9(95)	3.177 1(13)			
	001	1771.660 28(28)	2.919 633 0(95)	3.191 3(13)			5.03(12)
	03^10[c]	1782.073 5(53)					
	002	3540.670 32(70)	2.877 475(11)	2.994 1(16)			
	010	c	2.945 816(31)	3.268 1(60)	$-4.389\ 9(60)$	1.86(12)	
	011	$c+1758.689\ 32(64)$	2.913 088(30)	3.258 5(60)	$-4.334\ 2(62)$	2.33(12)	
$^{114}CdH_2$	000	0.0	2.952 538 5(77)	3.179 21(99)			
	001	1771.529 58(22)	2.919 644 3(79)	3.194 2(11)			4.97(11)
	03^10[c]	1781.919 6(54)					
	002	3540.529 53(36)	2.877 447 8(84)	2.996 2(12)			
	010	c	2.945 659(22)	3.222 2(38)	$-4.379\ 9(45)$	1.689(76)	
	011	$c+1758.561\ 58(50)$	2.912 946(23)	3.214 2(43)	$-4.322\ 0(46)$	2.035(84)	
$^{116}CdH_2$	000	0.0	2.952 542(16)	3.183 9(40)			
	001	1771.273 82(34)	2.919 674(15)	3.2027(32)			5.38(13)
	03^10[c]	1781.649 3(77)					
	002	3540.259 33(56)	2.877 355(16)	2.991 5(40)			

[a]The 011-010 hot band was fitted separately from the 001-000 and 002-001 bands, and the value of c was not determined from our experiment and was fixed at 0.0. The v_2 value was estimated to be 594 cm^{-1} from our work (see the text). Also v_2 has been observed as 601.7 cm^{-1} in an argon matrix and was calculated to be 574 cm^{-1} at the CCSD(T) level of theory (Ref. 16).
[b]Perturbation constant connecting the $001(\Sigma_u^+)$ state with the $03^10(\Pi_u)$ state.
[c]The vibrational energy of the $03^10(\Pi_u)$ state was obtained by the observed perturbation between the $03^10(\Pi_u)$ state and the $001(\Sigma_u^+)$ state with B fixed at 2.931 915 cm^{-1}, D at 3.3128×10^{-5} cm^{-1}, $q=-0.087\ 598$ cm^{-1}, and $q_D=3.378\times10^{-6}$ cm^{-1} for the $03^10(\Pi_u)$ state (see the text).

fitting the perturbed $001(\Sigma_u^+)-000(\Sigma_g^+)$ band are the vibrational energy and the perturbation constant, k_{01}. For all six isotopologs of CdH_2, the B_{03^10} constant was fixed at 2.931 915 cm^{-1} calculated by $B_{03^10}=B_{000}-3\alpha_2$ with $\alpha_2=B_{000}-B_{010}$; the D_{03^10} constant was set to 3.3128×10^{-5} cm^{-1} calculated by $D_{03^10}=D_{000}+3\beta_2$ with $\beta_2=D_{010}-D_{000}$; the q_{03^10} constant was $2q_{010}=-0.087\ 598$ cm^{-1} and q_{D03^10} was $2q_{D010}=3.378\times10^{-6}$ cm^{-1}.[27] B_{000}, B_{010}, D_{000}, D_{010}, q_{010}, and q_{D010} from the main isotopolog $^{114}CdH_2$ were used in all of the above calculations for the different isotopologs of CdH_2. The observed line positions and the output files of the fits are provided in the supplementary tables S12–S17. The fits are quite good and most lines for these two bands can be fitted with residuals (observed-calculated values) of the order of 0.001 cm^{-1}.

Although the usual energy-level expression [Eq. (1)] was used for the perturbed $002(\Sigma_g^+)$ state, the perturbed lines do not need to be deweighted because the perturbation of the $002(\Sigma_g^+)$ state by the $200(\Sigma_g^+)$ state is a global interaction.[28,29] The levels of the $002(\Sigma_g^+)$ and $200(\Sigma_g^+)$ states do not cross and lines of the $002(\Sigma_g^+)-001(\Sigma_u^+)$ transition can still be fitted with the ordinary energy-level expression for the $002(\Sigma_g^+)$ state to produce effective molecular constants.

The constants obtained for CdH_2 are provided in Table II. The band origins obtained for the $001(\Sigma_u^+)-000(\Sigma_g^+)$ transition are 1771.529 58(22) cm^{-1} for $^{114}CdH_2$ and 1278.311 67(28) cm^{-1} for $^{114}CdD_2$, which agree well with the observed argon matrix values of 1753.8 and 1264.9 cm^{-1}, and the *ab initio* values of 1790 and 1278 cm^{-1} at the CCSD(T) level.[16] The difference between the band origins of the $001(\Sigma_u^+)-000(\Sigma_g^+)$ transitions of $^{112}CdH_2$ and $^{114}CdH_2$,

which is the isotopic frequency shift between ^{112}CdH$_2$ and ^{114}CdH$_2$, is 0.264 59(32) cm^{-1} and matches the observed isotopic splitting of 0.25 cm^{-1} in the matrix-isolation experiment and the *ab initio* value of 0.27 cm^{-1}.[17] However, the difference between the band origins of the $002(\Sigma_g^+)$ $-001(\Sigma_u^+)$ transitions of ^{112}CdH$_2$ and ^{114}CdH$_2$ is only 0.018 10(64) cm^{-1}, which is much smaller than the isotopic splitting in the $001(\Sigma_u^+)-000(\Sigma_g^+)$ transition (Fig. 2). The change in the isotopic splitting in the $002(\Sigma_g^+)-001(\Sigma_u^+)$ band is caused by the mixing of $002(\Sigma_g^+)$ and $200(\Sigma_g^+)$ vibrational levels [ν_3 and ν_1 were calculated to be 1790 and 1794 cm^{-1} at the CCSD(T) level[16]].

The $03^10(\Pi_u)$ state vibrational energies [$G(0,3^1,0)$ $-G(0,0,0)=3\omega_2+15x_{22}+\frac{3}{2}x_{12}+\frac{3}{2}x_{23}+g_{22}$ (Ref. 29)] of the six CdH$_2$ isotopologs were used to estimate ν_2 [$G(0,1^1,0)$ $-G(0,0,0)=\omega_2+3x_{22}+\frac{1}{2}x_{12}+\frac{1}{2}x_{23}+g_{22}$ (Ref. 29)] for CdH$_2$. Because we do not have information on g_{22}, x_{22}, x_{12}, and x_{23}, we estimated ν_2 by using $\nu_2 \approx [G(0,3^1,0)-G(0,0,0)]/3$, and an average value of 594 cm^{-1} was obtained for ν_2. The value of ν_2 can also be estimated[27–29] using the *l*-type doubling constants q_{010} using

$$q_{010} = -\frac{2B_e^2}{\omega_2}\left(1+\frac{4\omega_2^2}{\omega_3^2-\omega_2^2}\right). \tag{8}$$

In Eq. (8), equilibrium constants are required but are not available so B_{000}, ν_2, and ν_3 were used instead. The q_{010}, B_{000}, and $G(0,0,1)-G(0,0,0)$ constants from different isotopologs of CdH$_2$ were used to calculate ν_2 for each isotopolog, and values ranging from 614 to 640 cm^{-1} were obtained. The average value for ν_2, estimated from Eq. (8), is 632 cm^{-1}, which differs by about 38 cm^{-1} from the estimated value of 594 cm^{-1} from $[G(0,3^1,0)-G(0,0,0)]/3$. The ν_2 value is very sensitive to the value of q_{010} and, for example, the ^{114}CdH$_2$ q_{010} value is $-0.043\,799(45)$ cm^{-1} (Table II). A value of 622 cm^{-1} was obtained for ν_2 if a value of $-0.043\,799$ cm^{-1} was used for q_{010}, and values of 625 and 618 cm^{-1} were obtained if $-0.043\,754$ and $-0.043\,844$ cm^{-1} ($-0.043\,799$ cm^{-1} minus or plus its 1σ uncertainty) were used for q_{010}, respectively. We therefore prefer the value of 594 cm^{-1} from $[G(0,3^1,0)-G(0,0,0)]/3$, which is closer to the argon matrix value of 601.7 cm^{-1} and the *ab initio* value of 574 cm^{-1} at the CCSD(T) level of theory.[16]

The B_{000} value obtained for each isotopolog was used to calculate the corresponding Cd–H or Cd–D r_0 bond distance. The average Cd–H and Cd–D r_0 bond distances were calculated to be 1.683 028(10) and 1.679 161(16) Å, respectively, with two standard deviation statistical errors enclosed in parentheses. These errors are obtained from the six values obtained from each isotopolog of CdH$_2$ or CdD$_2$. Since we observed both dihydride and dideuteride for each of the six isotopes of cadmium, we also calculated the r_s structure for CdH$_2$ by using Kraitchman's procedure for multiple isotopic substitutions.[30] The formula we used for CdH$_2$ is

$$r_s = \left[\frac{1}{2(m_D-m_H)}(I_z'-I_z)\right]^{1/2}, \tag{9}$$

where m_D and m_H are the masses of H and D atoms, respectively; I_z' and I_z are the moments of inertia of the H/D iso-

TABLE III. Spectroscopic constants (in cm^{-1}) for ^{114}CdH$_2$ and ^{114}CdD$_2$.

	^{114}CdH$_2$	^{114}CdD$_2$
B_0	2.952 538 5(77)	1.484 208 4(96)
r_0/Å	1.683 034 0(22)	1.679 171 7(54)
α_2	0.006 880(23)	⋯
α_3	0.032 894(11)	0.011 914(14)
q_{010}	$-0.043\,799(45)$	⋯
$\nu_2(\pi_u)$	594[a]	⋯
$\nu_3(\sigma_u)$	1771.529 58(22)	1278.311 67(28)
x_{23}	$-12.968\,00(65)$	⋯
x_{33}	$-1.264\,82(65)$[b]	⋯

[a]Estimated from $\nu_2 \approx [G(0,3^1,0)-G(0,0,0)]/3$ (see the text).
[b]Not reliable because the vibrational origin of the $002(\Sigma_g^+)$ state is perturbed by the $200(\Sigma_g^+)$ state (see the text).

topologs with the same Cd atom. The average r_s bond distance is determined to be 1.675 279(37) Å, with two standard deviation errors enclosed in parentheses. Again, the error was computed from the six possible CdH$_2$ and CdD$_2$ pairs. Both r_0 and r_s bond distances are reasonably close to the theoretical r_e values, which range from 1.67 to 1.74 Å.[1,14,16,21–23] For convenience, Table III lists the equilibrium constants obtained for the main isotopologs, ^{114}CdH$_2$ and ^{114}CdD$_2$. Since the $002(\Sigma_g^+)$ vibrational energy level obtained from our fit is perturbed by the nearby $200(\Sigma_g^+)$ state, the value of $-1.264\,82(65)$ cm^{-1} obtained for the CdH$_2$ x_{33} equilibrium constant is not reliable.

In conclusion, the vibration-rotation emission spectra of gaseous CdH$_2$ and CdD$_2$ were recorded. The antisymmetric stretching mode (ν_3) of CdH$_2$ and CdD$_2$, as well as two hot bands of CdH$_2$, was rotationally analyzed and their spectroscopic constants were determined. The predicted linear structure of CdH$_2$ was confirmed and the average Cd–H and Cd–D bond distances (r_0) were determined to be 1.683 028(10) and 1.679 161(16) Å, respectively.

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[26] See EPAPS Document No. E-JCPSA6-122-001520 for the observed line positions and the output files of the least-squares fits for all the bands. A direct link to this document may be found in the online article's HTML reference section. The document may also be reached via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory/epaps/. See the EPAPS homepage for more information.

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