

The Vibration–Rotation Emission Spectrum of Gaseous HZnCl

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Gaseous HZnCl has been synthesized for the first time in a high-temperature tube furnace with a dc discharge in a flowing mixture of pure HCl and Zn vapor. The vibration–rotation emission spectrum of HZnCl was recorded at high resolution using a Fourier transform spectrometer. The H–Zn stretching modes (ν_1) of the $\text{H}^{64}\text{Zn}^{35}\text{Cl}$, $\text{H}^{66}\text{Zn}^{35}\text{Cl}$, $\text{H}^{68}\text{Zn}^{35}\text{Cl}$, and $\text{H}^{64}\text{Zn}^{37}\text{Cl}$ species, as well as the $2\nu_1-\nu_1$ hot band of the most abundant isotopologue $\text{H}^{64}\text{Zn}^{35}\text{Cl}$, were observed near 1966 cm^{-1} . A least-squares fit was performed for each of the four observed isotopologues, and their spectroscopic constants were determined.

1. Introduction

In the past twenty years, matrix-isolation techniques have been applied in the investigation of the reactions between HCl and metal atoms. The group 1 metal atoms K and Na react with HCl to give the ion pair M^+HCl^- , while Li reacts to give a metal atom adduct $\text{Li}:\text{HCl}$.^{1–3} Fe and Hg can insert into the H–Cl bond to form the linear metal hydrochloride HMCl, and Al inserts into the H–Cl bond to form the bent HAICl molecule.^{4–6} Recently, the reactions between HCl and the group 12 metal atoms Zn, Cd and Hg were studied in solid argon matrices.⁷ Zn and Cd can also insert into the H–Cl bond to form the linear metal hydrochloride HMCl. Macrae et al. reported a value of 1952.3 cm^{-1} for the H–Zn stretching mode (ν_1), 449.6 cm^{-1} for the bending mode (ν_2), and $\sim 420\text{ cm}^{-1}$ for the Zn–Cl stretching mode (ν_3), with assignments validated by the effects of isotopic substitution and by the results of density functional calculations.

The properties of HMCl ($\text{M} = \text{Zn}, \text{Cd}, \text{and Hg}$) have been compared with those of the corresponding metal dihydrides.⁷ HCl has a dissociation energy close to that of H_2 , and the polar metal–chlorine bonds have higher dissociation energies than the corresponding metal–hydrogen bonds. The ground-state reaction $\text{M}(\text{S}) + \text{HCl}(\text{g}) \rightarrow \text{HMCl}(\text{g})$ was predicted to be exoergic by 30, 17, and 1 kcal/mol for $\text{M} = \text{Zn}, \text{Cd}, \text{and Hg}$, respectively.⁷ The corresponding reactions with H_2 are consistently endoergic.⁸ Therefore HCl offers a more energetically favorable opportunity for metal insertion than does H_2 . ZnH_2 , CdH_2 , and HgH_2 have just been observed in the gas phase.^{9–11} Surprisingly, no gaseous metal hydrochloride has ever been observed.

The present paper reports on the first observation of gaseous zinc hydrochloride. The high-resolution vibration–rotation emission spectrum of HZnCl was recorded using a Fourier transform spectrometer and the H–Zn stretching mode (ν_1) has been detected near 1966 cm^{-1} . The spectra were analyzed with the guidance of ab initio calculations, and spectroscopic constants were obtained for four isotopologues of HZnCl: $\text{H}^{64}\text{Zn}^{35}\text{Cl}$, $\text{H}^{66}\text{Zn}^{35}\text{Cl}$, $\text{H}^{68}\text{Zn}^{35}\text{Cl}$, and $\text{H}^{64}\text{Zn}^{37}\text{Cl}$.

2. Experimental Section

The emission source used to generate HZnCl was the same as in our previous studies of metal hydrides.^{12,13} A Zn rod was placed inside an alumina tube ($5\text{ cm} \times 120\text{ cm}$) and heated to $470\text{ }^\circ\text{C}$. About 0.6 Torr of pure HCl gas flowed slowly through the tube and a dc discharge was used at a current of about 250 mA. The resulting radiation was focused by a BaF_2 lens into the entrance aperture of a Bruker IFS 120 HR Fourier transform spectrometer. Eleven hundred scans were recorded at a resolution of 0.01 cm^{-1} with a KBr beam splitter using a liquid nitrogen cooled InSb detector. The recording time was about 19 h. The spectral region was limited to $1800\text{--}2200\text{ cm}^{-1}$ by the detector response and a 2200 cm^{-1} long-wave pass filter.

3. Results and Discussion

Figure 1 shows an overview of the spectrum of the ν_1 mode of HZnCl, and Figure 2 is an expanded view. The spectrum contained lines from ZnH_2 ⁹ and strong emission lines from impurity CO, which were used for calibration. The accuracy of measured wavenumbers is approximately 0.001 cm^{-1} for lines from the fundamental band of the most abundant isotopologue $\text{H}^{64}\text{Zn}^{35}\text{Cl}$ and 0.002 cm^{-1} for the other bands. The band origin of the strongest band in our spectrum is 1966.87 cm^{-1} , which matches the matrix-isolation value of 1952.3 cm^{-1} if a matrix shift is taken into account.⁷ The line spacing is about 0.3 cm^{-1} , which is close to the calculated value of $2B$ for the HZnCl molecule. We found five series of lines with the help of a Loomis–Wood program.

The natural zinc isotope abundances are ^{64}Zn : 48.6%, ^{66}Zn : 27.9%, ^{67}Zn : 4.1%, ^{68}Zn : 18.8%, ^{70}Zn : 0.6%, and the natural chlorine abundances are ^{35}Cl : 75.77%, ^{37}Cl : 24.23%.¹⁴ Four of the five bands were assigned to the fundamental bands of the H–Zn stretching mode (ν_1) of $\text{H}^{64}\text{Zn}^{35}\text{Cl}$, $\text{H}^{66}\text{Zn}^{35}\text{Cl}$, $\text{H}^{68}\text{Zn}^{35}\text{Cl}$, and $\text{H}^{64}\text{Zn}^{37}\text{Cl}$ according to their relative intensities and B values, and one band was assigned to the $2\nu_1-\nu_1$ ($200\text{--}100$) hot band of $\text{H}^{64}\text{Zn}^{35}\text{Cl}$.

The spectrum is very dense and the lines near the band origin overlap severely. It was not possible to assign the first P and R branch lines for the bands by looking at the spectrum or with even the help of the Loomis–Wood program. A least-squares fit was performed separately for each of the five observed bands

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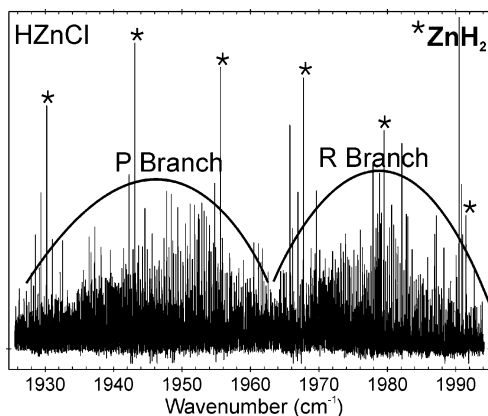


Figure 1. An overview of the vibration–rotation emission spectrum of HZnCl recorded at resolution of 0.01 cm^{-1} . This spectrum was the result of 1100 coadditions and the recording time was about 19 h. The baseline was corrected with the Bruker OPUS software and the strong lines are due to atomic zinc or the ZnH_2 molecule.

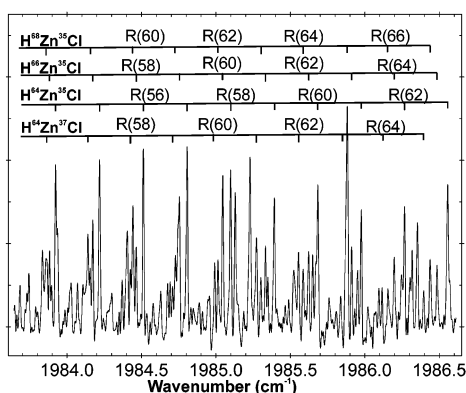


Figure 2. An expanded view of the R branch of the fundamental band of the ν_1 (H–Zn stretching) mode of HZnCl near 1984 cm^{-1} . The assignments were based on the relative intensities, band origin ratios, and B value ratios of these four isotopologues of HZnCl.

and the lines were fitted using the simple energy level expression¹⁵

$$E = G(\nu_1, \nu_2, \nu_3) + B_v J(J+1) - D_v [J(J+1)]^2 \quad (1)$$

where $G(\nu_1, \nu_2, \nu_3)$ is the vibrational energy of the (ν_1, ν_2, ν_3) state relative to the zero point energy (ZPE), $G(0, 0, 0)$. It turned out that we could shift the J assignment for each band and still obtain almost the same standard deviations for the fits (i.e., if J was changed by $+1, +2$, etc. in the P branch and $-1, -2$, etc. in the R branch, then the standard deviation of the fit was unchanged).

The absolute J assignment of the main isotopologue $\text{H}^{64}\text{Zn}^{35}\text{Cl}$ was finally obtained by fitting the fundamental band and the $2\nu_1 - \nu_1$ hot band together. Combination differences were used to determine the relative J assignment of the 100–000 fundamental band and the 200–100 band of $\text{H}^{64}\text{Zn}^{35}\text{Cl}$. Although the standard deviations for the separate fits of these two bands did not change with the shifts of the J assignment, the standard deviation did change when these two bands were fitted together, and a minimum of 0.79 was found for the reduced standard deviation. The standard deviation increased by about 5% when the J assignment was changed by -1 in the P branch and $+1$ in the R branch, or by $+1$ in the P branch and -1 in the R branch. The standard deviation of the fits increased steadily for larger shifts in the J assignment. Although the minimum in the standard deviation is not very sharp, we believe that our assignments for the $\text{H}^{64}\text{Zn}^{35}\text{Cl}$ bands are correct.

TABLE 1: Calculated Bond Lengths (in Å) and Vibrational Frequencies (in cm^{-1}) for HZnCl

	HF	DFT(B3LYP)	MP2
H–Zn bond (Å)	1.554	1.519	1.497
Zn–Cl bond (Å)	2.140	2.114	2.082
ω_1 (σ^+)			
$\text{H}^{64}\text{Zn}^{35}\text{Cl}$	1958.2866	1994.6726	2088.1332
$\text{H}^{66}\text{Zn}^{35}\text{Cl}$	1957.8139	1994.1839	2087.6188
$\text{H}^{68}\text{Zn}^{35}\text{Cl}$	1957.3689	1993.7238	2087.1345
$\text{H}^{64}\text{Zn}^{37}\text{Cl}$	1958.2863	1994.6719	2088.1323
ω_2 (π)			
$\text{H}^{64}\text{Zn}^{35}\text{Cl}$	413.0094	439.3647	452.9212
$\text{H}^{66}\text{Zn}^{35}\text{Cl}$	412.7326	439.0724	452.6201
$\text{H}^{68}\text{Zn}^{35}\text{Cl}$	412.4717	438.7968	452.3362
$\text{H}^{64}\text{Zn}^{37}\text{Cl}$	412.8496	439.1978	452.7495
ω_3 (σ^+)			
$\text{H}^{64}\text{Zn}^{35}\text{Cl}$	418.4033	417.4151	440.8885
$\text{H}^{66}\text{Zn}^{35}\text{Cl}$	416.2157	415.2341	438.5854
$\text{H}^{68}\text{Zn}^{35}\text{Cl}$	414.1421	413.1668	436.4024
$\text{H}^{64}\text{Zn}^{37}\text{Cl}$	410.9917	410.0210	433.0787

^a The MP4(SDQ) and QCISD methods were also used to calculate the bond lengths and the results are: $r_{\text{H-Zn}} = 1.511 \text{ Å}$, $r_{\text{Zn-Cl}} = 2.094 \text{ Å}$ from the MP4(SDQ) calculation, and $r_{\text{H-Zn}} = 1.519 \text{ Å}$, $r_{\text{Zn-Cl}} = 2.102 \text{ Å}$ from the QCISD calculation. ^b Three decimal places were kept for bond lengths and four for the vibrational frequencies because we were interested in the ratios of B values and band origins for different isotopologues.

To obtain the corresponding absolute J assignments for the other three isotopologues, we needed some additional information such as the isotopic shifts for the band origins or for the B values. Macrae et al.⁷ reported a value of 1952.3 cm^{-1} for ν_1 (H–Zn stretching) of $\text{H}^{64}\text{Zn}^{35}\text{Cl}$ and four different values for ν_3 (Zn–Cl stretching) for $\text{H}^{64}\text{Zn}^{35}\text{Cl}$, $\text{H}^{66}\text{Zn}^{35}\text{Cl}$, $\text{H}^{68}\text{Zn}^{35}\text{Cl}$, and $\text{H}^{64}\text{Zn}^{37}\text{Cl}$. We tried to predict ν_1 for $\text{H}^{66}\text{Zn}^{35}\text{Cl}$, $\text{H}^{68}\text{Zn}^{35}\text{Cl}$, and $\text{H}^{64}\text{Zn}^{37}\text{Cl}$ using the Teller–Redlich product rule:

$$\frac{\nu_1' \times \nu_3'}{\nu_1 \times \nu_3} = \left(\frac{m_1 m_2 m_3}{m_1' m_2' m_3'} \right)^{(1/2)} \left(\frac{M'}{M} \right)^{(1/2)} \quad (2)$$

where the prime is an index for isotopologues $\text{H}^{66}\text{Zn}^{35}\text{Cl}$, or $\text{H}^{68}\text{Zn}^{35}\text{Cl}$, or $\text{H}^{64}\text{Zn}^{37}\text{Cl}$; m_1, m_2 and m_3 are the masses of H, Zn, and Cl atoms; and M is the total mass of HZnCl.¹⁶ It turned out that the ν_3 values observed in the argon matrix are not accurate enough to be useful because if ν_3 for $\text{H}^{64}\text{Zn}^{35}\text{Cl}$ was changed from 426.6 cm^{-1} to 426.7 cm^{-1} , the predicted ν_1 values for other isotopologues changed by 0.5 cm^{-1} .

To guide our assignments, we carried out ab initio calculations for the vibrational frequencies and the bond lengths of HZnCl at several levels of theory using the Gaussian 03 program.¹⁷ The 6-311++G(3df, 3pd) basis set was used in all these calculations and the results are given in Table 1. We chose the DFT(B3LYP) method to obtain vibrational frequency ratios and B value ratios for the four HZnCl isotopologues. We then shifted the J assignments for the three minor isotopologues and compared the observed band origin ratios and B value ratios with those obtained from the ab initio calculations. The observed band origin ratios and B value ratios are very sensitive to the shifts in the J assignments, and the assignments of the three minor isotopologues relative to the main isotopologue $\text{H}^{64}\text{Zn}^{35}\text{Cl}$ were determined in this way. Table 2 gives the obtained spectroscopic constants for $\text{H}^{64}\text{Zn}^{35}\text{Cl}$, $\text{H}^{66}\text{Zn}^{35}\text{Cl}$, $\text{H}^{68}\text{Zn}^{35}\text{Cl}$, and $\text{H}^{64}\text{Zn}^{37}\text{Cl}$ from our least-squares fits.

The agreement between the observed and calculated (DFT) band origin shifts and ΔB value of the four isotopologues is quite good, except for the band origin shift of $\text{H}^{64}\text{Zn}^{37}\text{Cl}$, and this comparison is given in Table 3. The observed line positions and the output files of the fits are provided as Supporting Information in Tables 1S–4S: Table 1S for $\text{H}^{64}\text{Zn}^{35}\text{Cl}$, Table 2S for $\text{H}^{66}\text{Zn}^{35}\text{Cl}$, Table 3S for $\text{H}^{68}\text{Zn}^{35}\text{Cl}$, Table 4S for $\text{H}^{64}\text{Zn}^{37}\text{Cl}$.

TABLE 2: Spectroscopic Constants (in cm^{-1}) for the ν_1 (H–Zn Stretching) Vibrational Mode of HZnCl (all uncertainties are 1σ)

	level	$G_v - \text{ZPE}$	$B_{\nu_1\nu_2\nu_3}$	$D_{\nu_1\nu_2\nu_3}/10^{-8}$
$\text{H}^{64}\text{Zn}^{35}\text{Cl}$	000	0.0	0.16203125(96)	8.8287(61)
	100	1966.86928(12)	0.16179977(96)	8.8061(62)
	200	3923.72224(28)	0.16157547(98)	8.7827(65)
$\text{H}^{66}\text{Zn}^{35}\text{Cl}$	000	0.0	0.1605027(21)	8.685(13)
	100	1966.39405(20)	0.1602766(21)	8.660(13)
$\text{H}^{68}\text{Zn}^{35}\text{Cl}$	000	0.0	0.1590536(29)	8.523(24)
	100	1965.94646(26)	0.1588326(29)	8.497(24)
$\text{H}^{64}\text{Zn}^{37}\text{Cl}$	000	0.0	0.1564897(33)	8.272(32)
	100	1966.80602(26)	0.1562691(32)	8.251(30)

TABLE 3: Comparison of the Observed and Calculated (DFT) Band Origin Shifts and ΔB Values (in cm^{-1}) for Different Isotopologues of HZnCl

molecule	$\Delta\nu_{1,\text{obs.}}$	$\Delta\omega_{1,\text{calc.}}^a$	$\Delta B_{000,\text{obs.}}$	$\Delta B_{e,\text{calc.}}^b$
$\text{H}^{64}\text{Zn}^{35}\text{Cl}$	0	0	0	0
$\text{H}^{66}\text{Zn}^{35}\text{Cl}$	-0.47523	-0.4819	-0.0015286	-0.001554
$\text{H}^{68}\text{Zn}^{35}\text{Cl}$	-0.92282	-0.9356	-0.0029777	-0.003022
$\text{H}^{64}\text{Zn}^{37}\text{Cl}$	-0.06326	-0.0007	-0.0055416	-0.005571

^a ω_1 calculated at the DFT (B3LYP)/6-311++G(3df, 3pd) level and $\Delta\omega_1$ are scaled by $\nu_{1,\text{obs.}}/\omega_{1,\text{calc.}}$ of $\text{H}^{64}\text{Zn}^{35}\text{Cl}$. ^b B_e calculated at the DFT (B3LYP)/6-311++G(3df, 3pd) level and ΔB_e are scaled by $B_{000,\text{obs.}}/B_{e,\text{calc.}}$ of $\text{H}^{64}\text{Zn}^{35}\text{Cl}$.

The four observed B_0 values of the four isotopologues were used to calculate the r_0 bond lengths for the 000 level of HZnCl. Using the moment of inertia equation, we had six pairwise combinations to calculate the $r_{\text{H-Zn}}$ and $r_{\text{Zn-Cl}}$ bond lengths. The $r_{\text{H-Zn}}$ values obtained from different combinations are quite different and range from 1.596 Å to 1.789 Å. The $r_{\text{Zn-Cl}}$ values obtained are more consistent and range from 2.079 Å to 2.088 Å. We were not very satisfied with these results, especially with the $r_{\text{H-Zn}}$ bond distances.

We decided to use Kraitchman's equation for linear molecules¹⁸ to calculate the r_s bond length for the Zn–Cl bond. A value of 1.37175 Å was obtained for the distance of ^{35}Cl from the center of the mass of $\text{H}^{64}\text{Zn}^{35}\text{Cl}$ by using the observed B_0 values of $\text{H}^{64}\text{Zn}^{35}\text{Cl}$ and $\text{H}^{64}\text{Zn}^{37}\text{Cl}$. An average value of 0.71171 Å was obtained for the distance of ^{64}Zn from the center of the mass of $\text{H}^{64}\text{Zn}^{35}\text{Cl}$ by using the observed B_0 values for the $\text{H}^{64}\text{Zn}^{35}\text{Cl}/\text{H}^{66}\text{Zn}^{35}\text{Cl}$ and $\text{H}^{64}\text{Zn}^{35}\text{Cl}/\text{H}^{68}\text{Zn}^{35}\text{Cl}$ pairs. Therefore, the $r_{\text{Zn-Cl}}$ bond length is equal to 2.08346 Å, which agrees well with our ab initio calculations (~ 2.08 Å) and with the r_0 values obtained from the moment of inertia equation. Because we did not observe DZnCl, we could not calculate the $r_{\text{H-Zn}}$ bond length using Kraitchman's equation. We derived the $r_{\text{H-Zn}}$ bond length by substituting $r_{\text{Zn-Cl}} = 2.08346$ Å for $\text{H}^{64}\text{Zn}^{35}\text{Cl}$ into the moment of inertia equation and into the center of mass equation and obtained the values of 1.70480 Å and 1.75796 Å, respectively. These two values are quite different from our ab initio calculations (~ 1.52 Å). Furthermore, when we fixed the $r_{\text{H-Zn}}$ bond length at the theoretically calculated value of 1.52 Å and derived the $r_{\text{Zn-Cl}}$ bond length using the moment of inertia equation, we obtained a value of 2.09218 Å, which is rather close to the r_s value. Our experimental data are therefore not sufficient to provide information on the $r_{\text{H-Zn}}$ bond length for HZnCl. The spectra of DZnCl need to be measured to obtain an accurate $r_{\text{H-Zn}}$ bond length. For the time being, we prefer the partial r_s value of 2.08346 Å for the Zn–Cl bond length and the ab initio value of 1.52 Å for the H–Zn bond length.

In conclusion, we made the first observation of gaseous HZnCl by infrared emission spectroscopy of the ν_1 vibrational modes of $\text{H}^{64}\text{Zn}^{35}\text{Cl}$, $\text{H}^{66}\text{Zn}^{35}\text{Cl}$, $\text{H}^{68}\text{Zn}^{35}\text{Cl}$, and $\text{H}^{64}\text{Zn}^{37}\text{Cl}$. The absolute J assignment of the most abundant isotopologue $\text{H}^{64}\text{Zn}^{35}\text{Cl}$ was obtained by fitting the fundamental band and the 200 – 100 hot band together. The relative assignment of the four isotopologues was established by using band origin ratios and B value ratios obtained from ab initio calculations. We are still not completely certain of our J assignments, and microwave spectra of HZnCl are desirable.

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Supporting Information Available: Observed line positions and output files of the fits (Tables 1S – 4S: Table 1S for $\text{H}^{64}\text{Zn}^{35}\text{Cl}$, Table 2S for $\text{H}^{66}\text{Zn}^{35}\text{Cl}$, Table 3S for $\text{H}^{68}\text{Zn}^{35}\text{Cl}$, Table 4S for $\text{H}^{64}\text{Zn}^{37}\text{Cl}$). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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