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 (ν1) of the H64Zn35Cl, H66Zn35Cl, H68Zn35Cl, and H64Zn37Cl species, as well as the 2ν1–ν1 hot band of the most abundant isotopologue H64Zn35Cl, 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 I metal atoms K and Na react with HCl to give the ion pair M+HCl⁻, while Li reacts to give a metal atom adduct Li: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 (ν1), 449.6 cm⁻¹ for the bending mode (ν2), and ~420 cm⁻¹ for the Zn–Cl stretching mode (ν3), with assignments validated by the effects of isotopic substitution and by the results of density functional calculations.

The properties of HMCl (M = Zn, Cd, and Hg) have been compared with those of the corresponding metal dihydrides.7 HCl has a dissociation energy close to that of H2, and the polar metal–chlorine bonds have higher dissociation energies than the corresponding metal–hydrogen bonds. The ground-state reaction M(1S) + HCl(g) → HMCl(g) was predicted to be exoergic by 30, 17, and 1 kcal/mol for M = Zn, Cd, and Hg, respectively.7 The corresponding reactions with H2 are consistently endoergic.8 Therefore HCl offers a more energetically favorable opportunity for metal insertion than does H2, ZnH2, CdH2, and HgH2 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 (ν1) 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: H64Zn35Cl, H66Zn35Cl, H68Zn35Cl, and H64Zn37Cl.

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 cm x 120 cm) and heated to 470 °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 BaF2 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 1800–2200 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 ν1 mode of HZnCl, and Figure 2 is an expanded view. The spectrum contained lines from ZnH2 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 H64Zn35Cl 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 66Zn: 48.6%, 64Zn: 27.9%, 68Zn: 4.1%, 66Zn: 18.8%, 70Zn: 0.6%, and the natural chlorine abundances are 35Cl: 75.77%, 37Cl: 24.23%.14 Four of the five bands were assigned to the fundamental bands of the H–Zn stretching mode (ν1) of H64Zn35Cl, H66Zn35Cl, H68Zn35Cl, and H64Zn37Cl according to their relative intensities and B values, and one band was assigned to the 2ν1–ν1 (200–100) hot band of H64Zn35Cl.

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.
Vibration—Rotation Emission Spectrum of Gaseous HZnCl

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 ZnH₂ molecule.

Figure 2. An expanded view of the R branch of the fundamental band of the ν₁ (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 expression

\[ E = G(v₁, v₂, v₃) + B(J(J+1)) - D(J(J+1))^2 \]

where \( G(v₁, v₂, v₃) \) is the vibrational energy of the \((v₁, v₂, v₃)\) 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 \( \text{H}²\text{Zn}³\text{Cl} \) was finally obtained by fitting the fundamental band and the \( 2ν₁−ν₁ \) 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 \( \text{H}²\text{Zn}³\text{Cl} \). 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 \( \text{H}²\text{Zn}³\text{Cl} \) bands are correct.

### Table 1: Calculated Bond Lengths (in Å) and Vibrational Frequencies (in cm⁻¹) for HZnCl

<table>
<thead>
<tr>
<th>Species</th>
<th>HF</th>
<th>DFT(B3LYP)</th>
<th>MP2</th>
</tr>
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<tbody>
<tr>
<td>H—Zn bond (Å)</td>
<td>1.554</td>
<td>1.519</td>
<td>1.497</td>
</tr>
<tr>
<td>Zn—Cl bond (Å)</td>
<td>2.140</td>
<td>2.114</td>
<td>2.082</td>
</tr>
<tr>
<td>( \omega_1 (\sigma^+ )</td>
<td>1958.2866</td>
<td>1994.6726</td>
<td>2088.1332</td>
</tr>
<tr>
<td>( \omega_2 (\sigma^- )</td>
<td>1957.8139</td>
<td>1994.1839</td>
<td>2087.6188</td>
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<tr>
<td>( \omega_3 (\sigma^+ )</td>
<td>1957.3689</td>
<td>1993.7238</td>
<td>2087.1345</td>
</tr>
</tbody>
</table>

The MP4(SDQ) and QCISD methods were also used to calculate the bond lengths and the results are: \( r_{1,0} \) = 1.511 Å, \( r_{2,0} \) = 2.094 Å from the MP4(SDQ) calculation, and \( r_{1,0} \) = 1.519 Å, \( r_{2,0} \) = 2.102 Å from the QCISD calculation. 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. reported a value of 1952.3 cm⁻¹ for \( v₁ \) (H—Zn stretching) of \( \text{H}²\text{Zn}³\text{Cl} \) and four different values for \( v₁ \) (Zn—Cl stretching) for \( \text{H}²\text{Zn}³\text{Cl} \), \( \text{H}⁶\text{Zn}³\text{Cl} \), \( \text{H}⁸\text{Zn}³\text{Cl} \), and \( \text{H}²\text{Zn}³\text{Cl} \). We tried to predict \( v₁ \) for \( \text{H}⁶\text{Zn}³\text{Cl} \), \( \text{H}⁸\text{Zn}³\text{Cl} \), and \( \text{H}²\text{Zn}³\text{Cl} \) using the Teller—Redlich product rule:

\[
\frac{ν₁'}{ν₁} = \left( \frac{m₁m₃}{m₂m₃} \right)^{(1/2)} \left( \frac{M'}{M} \right)^{(1/2)}
\]

where the prime is an index for isotopologues \( \text{H}²\text{Zn}³\text{Cl} \), or \( \text{H}⁶\text{Zn}³\text{Cl} \), or \( \text{H}⁸\text{Zn}³\text{Cl} \); \( m₁, m₂ \) and \( m₃ \) are the masses of \( H \), \( Zn \), and \( Cl \) atoms; and \( M \) is the total mass of \( \text{HZnCl} \). It turned out that the \( ν₁ \) values observed in the argon matrix are not accurate enough to be useful because if \( ν₁ \) for \( \text{H}⁶\text{Zn}³\text{Cl} \) was changed from 426.6 cm⁻¹ to 426.7 cm⁻¹, the predicted \( ν₁ \) 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 \( \text{HZnCl} \) at several levels of theory using the Gaussian 03 program. 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 \( \text{HZnCl} \) 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 \( \text{H}²\text{Zn}³\text{Cl} \) were determined in this way. Table 2 gives the obtained spectroscopic constants for \( \text{H}²\text{Zn}³\text{Cl} \), \( \text{H}⁶\text{Zn}³\text{Cl} \), \( \text{H}⁸\text{Zn}³\text{Cl} \), and \( \text{H}²\text{Zn}³\text{Cl} \) from our least-squares fits.

The agreement between the observed and calculated (DFT) band origin shifts and \( ∆B \) value of the four isotopologues is quite good, except for the band origin shift of \( \text{H}⁶\text{Zn}³\text{Cl} \), 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 2: Spectroscopic Constants (in cm⁻¹) for the ν₁ (H–Zn Stretching) Vibrational Mode of HZnCl (all uncertainties are 1σ) Table 4S: Table 1S for H64Zn35Cl, Table 2S for H65Zn35Cl, Table 3S for H68Zn35Cl, and Table 4S for H64Zn37Cl. This material is available free of charge via the Internet at http://pubs.acs.org.

<table>
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<tr>
<th>molecule</th>
<th>Δν₁,obs.</th>
<th>Δν₁,calc.</th>
<th>ΔB₀0,obs.</th>
<th>ΔB₀0,calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H64Zn35Cl</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H65Zn35Cl</td>
<td>-0.4752</td>
<td>-0.4819</td>
<td>-0.0015286</td>
<td>-0.001554</td>
</tr>
<tr>
<td>H68Zn35Cl</td>
<td>-0.92282</td>
<td>-0.9356</td>
<td>-0.0029777</td>
<td>-0.003022</td>
</tr>
<tr>
<td>H64Zn37Cl</td>
<td>-0.06326</td>
<td>-0.0007</td>
<td>-0.0055416</td>
<td>-0.005571</td>
</tr>
</tbody>
</table>

* Δν₁ calculated at the DFT (B3LYP)/6-311++G(df,3d) level and ΔB₀₀ are calculated by B₀₀,obs./B₀₀,calc. of H64Zn35Cl.

The four observed B₀ values of the four isotopologues were used to calculate the r₁ values for the 000 level of HZnCl. Using the moment of inertia equation, we had six pairwise combinations to calculate the r₁–Zn and r₁–Cl bond lengths. The r₁–Zn values obtained from different combinations are quite different and range from 1.596 Å to 1.789 Å. The r₁–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 r₁–Zn bond distances.

We decided to use Kraitchman’s equation for linear molecules to calculate the r₁ bond length for the Zn–Cl bond. A value of 1.37175 Å was obtained for the distance of 35Cl from the center of the mass of H64Zn35Cl by using the observed B₀ values of H64Zn35Cl and H64Zn35Cl. An average value of 0.71171 Å was obtained for the distance of 64Zn from the center of the mass of H64Zn35Cl by using the observed B₀ values for the H64Zn35Cl/H65Zn35Cl and H64Zn35Cl/H84Zn35Cl pairs. Therefore, the r₁–Zn bond length is equal to 0.208346 Å, which agrees well with our ab initio calculations (≈2.08 Å) and with the r₁ values obtained from the moment of inertia equation. Because we did not observe DZnCl, we could not calculate the r₁–Zn bond length using Kraitchman’s equation. We derived the r₁–Zn bond length by substituting r₁–Zn = 0.208346 Å for H64Zn35Cl 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 r₁–Zn bond length at the theoretically calculated value of 1.52 Å and derived the r₂–Cl bond length using the moment of inertia equation, we obtained a value of 2.09218 Å, which is rather close to the r₂ value. Our experimental data are therefore not sufficient to provide information on the r₁–Zn bond length for HZnCl. The spectra of DZnCl need to be measured to obtain an accurate r₁–Zn bond length. For the time being, we prefer the partial r₁ 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 ν₁ vibrational modes of H64Zn35Cl, H65Zn35Cl, H68Zn35Cl, and H64Zn37Cl. The absolute J assignment of the most abundant isotopologue H64Zn35Cl 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). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(2) Davis, M. A.; Lindsay, D. M. Surf. Sci. 1985, 156, 335.