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Rotational Spectroscopy of ClZnCH_3 (X^1A_1): Gas-phase Synthesis and Characterization of a Monomeric Grignard-Type Reagent

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Abstract

The pure rotational spectrum of the organozinc halide, ClZnCH_3 (X^1A_1), has been measured using Fourier-transform microwave (FTMW) and millimeter-wave direct-absorption methods in the frequency range 10 – 296 GHz. This work is the first study of ClZnCH_3 by gas-phase spectroscopy. The molecule was created in a DC discharge from the reaction of zinc vapor, produced either by a Broida-type oven or by laser ablation, with chloromethane in what appears to be a metal insertion process. Rotational and chlorine quadrupole constants were determined for three zinc isotopologues. The Zn-Cl bond was found to be partly ionic and significantly shorter than in EtZnCl .

1. Introduction

Interest in organozinc halides ($RZnX$) has existed for well over a century, beginning with the synthesis of $EtZnI$ in 1864 [1]. Such compounds have many versatile applications, particularly in organic synthesis but also in polymer chemistry [e.g. 2, 3]. Their high chemoselectivity and functional group tolerance makes them excellent synthetic reagents. For example, in the Barbier reaction, the nucleophilic addition of the alkyl group across a carbonyl bond occurs through the intermediate $XZnR$ [4]. The Reformatsky process converts an α -haloester and ketone or aldehyde into a β -hydroxyester with an organozinc reagent, the “Reformatsky enolate” [5]. Organozinc halides have also been found to react with aryl isocyanates to yield the corresponding *N*-substituted carbamates [6], and have been successfully employed in the total synthesis of natural products such as indoles [7] and polycyclic ethers [8]. Because the organozinc species easily undergo transmetalation, they are ideal reagents for cross-coupling reactions, as well. One of the most versatile schemes of this type in contemporary organic synthesis is the Negishi coupling, which forms carbon-carbon bonds from an organic halide and an organozinc halide in the presence of a nickel or palladium catalyst. The exact mechanism of the Negishi coupling has not yet been determined, however.

Because of their widespread chemical use, there have been various structural studies of alkyl zinc halides. Crystal structures have been determined for several ethyl compounds of this type, including $EtZnCl$, $EtZnI$, and the monomeric adduct $EtZnCl, TMEDA$ [9,10,11]. Such species have shown to exhibit sheet and “wavy-sheet”-like geometries or a distorted tetrahedron, as for the adduct compound. Theoretical studies [12, 13] have focused on CH_3ZnX as a model system to probe, for example, the transmetalation step and its cis-trans isomerization in the Negishi reaction [14]. Theoretical calculations suggest these compounds have linear $X-Zn-C$

backbones, and thus are “symmetric tops”. Gas-phase spectroscopy has also been carried out for one alkyl zinc species, IZnCH_3 . The pure rotational spectrum of this molecule, including various isotopically-substituted species, has been measured by the Ziurys group, who established the first experimental structure of a monomeric alkyl zinc halide compound [15]. Previous to this work, the rotational spectrum of the zinc insertion product, HZnCH_3 , was also recorded [16]. Measurement of various isotopologues of this species also resulted in the determination of its structure. Surprisingly, IZnCH_3 and HZnCH_3 have remarkably similar, C_{3v} geometries, despite the large size difference between the hydrogen and iodine atoms.

Here we present the first gas-phase observation and spectroscopic characterization of monomeric ClZnCH_3 . Pure rotational spectra of this molecule in the main zinc isotope, $\text{Cl}^{64}\text{ZnCH}_3$, and two other Zn isotopologues ($\text{Cl}^{66}\text{ZnCH}_3$, $\text{Cl}^{68}\text{ZnCH}_3$), were measured in their natural abundances using both millimeter-wave direct absorption and Fourier transform microwave (FTMW) techniques. The obvious K-ladder structure found in spectra indicates this species exhibits C_{3v} symmetry, as predicted by theory. Quadrupole hyperfine splittings arising from the ^{35}Cl nucleus were also resolved in the FTMW data, providing insight into the Zn-Cl bond. In this paper we present our measurements, spectroscopic analysis, and preliminary structure of ClZnCH_3 in monomeric form.

2. Experimental

Two complimentary instruments of the Ziurys group were used to record the gas-phase rotational spectrum of ClZnCH_3 : a millimeter/sub-mm direct absorption spectrometer and a FTMW system. The direct absorption spectrometer consists of a three basic parts: a tunable, coherent source of mm/sub-mm radiation, a stainless steel reaction cell containing a Broida-type oven, and a detector. The radiation source is a suite of phase-locked Gunn oscillator/varacter

multiplier combinations, covering the range 65-850 GHz. The double-pass reaction cell is coupled with a Roots-type blower pumping system, while the detector is a helium-cooled InSb hot-electron bolometer. Radiation from the source is quasi-optically propagated through the cell and into the detector through a series of optical elements. Phase-sensitive detection is carried out by frequency modulation of the radiation source. Signals from the InSb detector are processed by a lock-in amplifier at twice the frequency modulation rate, resulting in second derivative line profiles. Transition frequencies were measured from scans 5 MHz in width, fit with Gaussian profiles. The measurement uncertainty is estimated to be ± 50 kHz. For more details, see ref. [17].

The FTMW spectrometer is a Balle-Flygare-type instrument consisting of a vacuum chamber that houses a Fabry-Pérot cavity with two spherical aluminum mirrors in a near-confocal arrangement [18]. For 4 – 40 GHz operation, the frequency source is a synthesizer (Agilent), and the detector is a low noise amplifier (Miteq or Spacek). Molecules are introduced into the chamber by a pulsed supersonic nozzle (General Valve), oriented 40° relative to the optical axis and operating at 10 Hz. Radiation at a given frequency is pulsed into the cavity, which has an instantaneous bandwidth of about 600 kHz, from an antenna imbedded in one mirror. If there is a resonant transition, molecules created in the jet absorb the radiation and their subsequent emission is detected by a low-noise amplifier as a function of time, the Free Induction Decay (FID). Frequency domain spectra are then generated with 2 kHz resolution by a Fast Fourier transform (FFT). More details can be found in [18].

ClZnCH₃ was created in both systems in the gas phase in a DC discharge from the reaction of zinc vapor and CH₃Cl in the presence of argon gas. For the mm-wave spectrometer, zinc vapor was generated by heating metal pieces in a Broida-type oven. About 20 – 30 mTorr of

CH₃Cl vapor was introduced to the cell directly above the oven. In addition, about 15 mTorr of argon was added from underneath it and also flowed over the back lens of the spectrometer to prevent metal coating. The discharge was sustained directly over the oven.

In the FTMW system, the molecule was created using the Discharge Assisted Laser Ablation Source (DALAS) of the Ziurys group; see ref. [19]. A mixture of 0.2 – 0.5 % CH₃Cl in argon gas was pulsed through a supersonic nozzle into the cell with a backing pressure of 40 psi. Zinc vapor was generated by laser ablation of a translating, rotating metal rod using the second harmonic of Nd:YAG laser (Surelite II), and added to the mixture in the supersonic expansion. A relatively low DC discharge of 600 V was then applied to the expanding gas. ClZnCH₃ was not observed when the discharge was higher than 800 V. The pulse valve was opened for 750 μs and the discharge applied for 990 μs thereafter. Typically 1000 – 5000 shots were averaged to achieve a satisfactory signal-to-noise ratio. All spectra are recorded as Doppler doublets; the average of these doublets is the measured transition frequency.

2. Results and Analysis

The search for ClZnCH₃ was initially conducted with the millimeter wave spectrometer. Based on the previous studies of IZnCH₃ and HZnCH₃, it was assumed that the molecule would have C_{3v} symmetry, and a rotational constant of $B = 2429$ MHz was estimated, scaled from those of the iodine and hydrogen analogs. A frequency range of 260-292 GHz was continuously scanned, resulting in the identification of two very similar spectral patterns, each exhibiting the classic symmetric top signature with a B constant near the predicted value. The two patterns had a relative intensity ratio of 1: 0.56, close to that of the two most abundant zinc isotopes ⁶⁴Zn and ⁶⁶Zn. Removal of the zinc vapor caused the signals to disappear, indicating that they were indeed arising from Zn-bearing species. These two sets of transitions were then identified as Cl⁶⁴ZnCH₃

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4 and $\text{Cl}^{66}\text{ZnCH}_3$. By searching nearby frequency ranges, symmetric top patterns arising from
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6 $\text{Cl}^{68}\text{ZnCH}_3$ were also found. Contamination from CH_3Cl was a common problem.
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9 Once spectral constants were established from the mm-wave data, searches for
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11 $\text{Cl}^{64}\text{ZnCH}_3$, $\text{Cl}^{66}\text{ZnCH}_3$ and $\text{Cl}^{68}\text{ZnCH}_3$ were conducted using the FTMW system in the
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13 frequency range 10-31 GHz. Lines for the three species were readily found, all exhibiting
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15 quadrupole hyperfine structure attributable to the ^{35}Cl nucleus of $I = 3/2$. These measurements
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17 confirmed that the molecule contained chlorine, lending further credence to the identification.
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19 Only the stronger hyperfine transitions were measured.
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23 Figure 1 displays spectra of the $K = 0$ through $K = 6$ components of the $J = 58 \leftarrow 57$
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25 rotational transition of $\text{Cl}^{64}\text{ZnCH}_3$, recorded with the mm-wave spectrometer near 296 GHz.
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27 Although there are strong lines arising from methyl chloride in the spectrum, the distinctive K -
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29 component progression of a symmetric top is clearly visible in the data, with the lines having a
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31 relative frequency spacing of 1:3:5:7.... The $K = 3$ and 6 components also appear roughly a
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33 factor of 2 greater in intensity relative to adjacent K components, resulting from nuclear spin
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35 statistics due to exchange of the three identical protons ($I = 1/2$) upon rotation of the methyl
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37 group about the C_3 axis [20]. There is no evidence of chlorine quadrupole structure in these data,
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39 as expected at higher J transitions of a closed-shell molecule. The species clearly has C_{3v}
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41 symmetry with a $^1\text{A}_1$ ground electronic state.
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48 Representative FTMW spectra of $\text{Cl}^{64}\text{ZnCH}_3$ are shown in Figure 2. Here chlorine
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50 hyperfine components, labeled by quantum number F , are displayed, arising from the $K = 0$ and
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52 1 components of the $J = 3 \rightarrow 2$ transition near 15 GHz. There is a frequency break in the figure
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54 to show multiple lines. Each feature consists of Doppler doublets, as indicated by brackets on the
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56 spectrum. The $F = 9/2 \rightarrow 7/2$ and $F = 7/2 \rightarrow 5/2$ components for $K = 0$ are within 4 kHz of each
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other, and are almost totally collapsed. There may be a hint of a shoulder to higher frequency on the measured line. For $K = 1$, these two components are separated by about 1.7 MHz, as expected. The weaker $F = 5/2 \rightarrow 3/2$ transition is also visible in both K ladders. The hyperfine patterns will vary according to the value of K , as the quadrupole energies scale by the factor $I-3K^2/J(J+1)$ [20,21].

As shown in Table 1, a total of 7 to 10 rotational transitions $J + I \leftrightarrow J$ were recorded for $\text{Cl}^{64}\text{ZnCH}_3$, $\text{Cl}^{66}\text{ZnCH}_3$, and $\text{Cl}^{68}\text{ZnCH}_3$, respectively, each consisting of several K components. For the mm-wave data, typically $K = 0$ through 6 components were recorded, but severe contamination by CH_3Cl often limited the frequency coverage. For the FTMW data, only the $K = 0$ and 1 lines were measured, each consisting of multiple hyperfine components whose pattern varies with K , as mentioned. Note that for all three zinc isotopologues, hyperfine splittings arising from the chlorine nucleus produce a similar pattern. A total of 119 individual frequencies were recorded, 33 from the FTMW spectrometer and the remainder with the mm-wave instrument.

The transitions frequencies for $\text{Cl}^{64}\text{ZnCH}_3$, $\text{Cl}^{66}\text{ZnCH}_3$ and $\text{Cl}^{68}\text{ZnCH}_3$ were analyzed individually with a symmetric top Hamiltonian using the non-linear least square routine SPFIT [22]. The data were weighted according to the instrumental uncertainty: ± 50 kHz for the mm-wave data and ± 2 kHz for the FTMW frequencies, respectively. From this analysis, rotational, centrifugal distortion and electric quadrupole hyperfine terms were determined, and are presented in Table 2. Because transitions were measured only within K ladders, the parameters B , D_J , D_{JK} , and the sixth order centrifugal distortion term H_{JK} ($\text{Cl}^{64}\text{ZnCH}_3$ and $\text{Cl}^{66}\text{ZnCH}_3$ only) could be determined for each isotopologue, but not A or D_K , as defined below in the energy level expression [20,21]

$$F(J,K) = BJ(J + 1) - D_J J^2(J + 1)^2 + (A-B)K^2 - D_{JK}J(J + 1)K^2 - D_K K^4 + H_{JK}J^2(J+1)^2 K^2 \quad (1)$$

To fit the data, A was fixed to the value measured for HZnCH_3 [16]. Also, the quadrupole constant eqQ was determined for each zinc species. The rms of the individual fits is in the range of 66 - 81 kHz, which is within the experimental uncertainty.

4. Discussion

This study suggests that ClZnCH_3 can be formed in the gas phase through the oxidative addition of zinc to chloromethane. The fact that fragment species such as ZnCH_3 and ZnCl were not observed in the mm-wave data, where large frequency regions were scanned, is strong evidence for such facile zinc insertion. The spectra are sufficiently well-known for these two molecules to make their appearance obvious [23, 24]. Furthermore, use of a higher discharge voltage with DALAS resulted in the destruction of ClZnCH_3 ; if the species was created from radical fragments, the higher discharge voltage should enhance the signals. It should be noted that production of ClZnCH_3 did require the discharge, which is likely needed to activate the zinc, i.e. promote it into an excited electronic state such as ^3P or ^1P [25]. This result is consistent with theoretical modeling, which predicts that the insertion of zinc into the C-Cl bond of CH_3Cl is exothermic by 29.6 kcal/mol [12]. However, there is a 44.3 kcal/mol activation barrier that first must be overcome; hence the need for the discharge. According to theory, the C-Cl bond is elongated as the zinc approaches, resulting in a transition state with C_s symmetry.

Our past studies have suggested that zinc insertion leads to HZnCH_3 and IZnCH_3 [15, 16]. The iodine analog was produced in the mm-wave instrument under very similar conditions to ClZnCH_3 ; however, the signals for IZnCH_3 were substantially stronger. This finding likely reflects the relative C-Cl and I-C bond enthalpies, which are 328 kJ/mol and 220 kJ/mol, respectively [26,27].

The symmetry of ClZnCH_3 is clearly C_{3v} . The observed rotational spectrum is unambiguously that of a symmetric top, as found for HZnCH_3 and IZnCH_3 [15,16]. The Cl-Zn-C backbone is linear, as predicted by theory [12]. In contrast, calculations predict that calcium and palladium form insertion products that have a bent backbone [12]. This bent geometry in ClZnCH_3 would produce additional splittings generated by asymmetry doubling, which were simply not observed.

Because only the zinc atom was isotopically substituted for ClZnCH_3 , a full structure cannot be derived. Nevertheless, if the Zn-C and C-H bond lengths and the H-C-H angle are fixed to the values found for IZnCH_3 , where isotopic substitutions were carried out for the carbon and hydrogen atoms, the Zn-Cl bond distance can be estimated. The bond length was found to be $r_{\text{Zn-Cl}} = 2.23(7) \text{ \AA}$. This value is a $\sim 0.1 \text{ \AA}$ increase from that in the ZnCl radical, which has $r_{\text{Zn-Cl}} = 2.133(2) \text{ \AA}$. It is also somewhat shorter than those found in the crystal structure of $\text{ClZnCH}_2\text{CH}_3$ ($r_{\text{Zn-Cl}} = 2.3486(6) \text{ \AA}$ and $2.5408(7) \text{ \AA}$ [9]), and that measured for EtZnCl, TMEDA [11] of $2.269(3) \text{ \AA}$. In these two structures, however, zinc is bonded to four instead of two ligands. In crystalline $\text{ClZnCH}_2\text{CH}_3$, the zinc atom is tetrahedrally linked to one ethyl and three chloride ligands in an infinite sheet, with two different Zn-Cl bonds. In the other complex, the bidentate TMEDA ligand forms the two additional bonds to the central zinc atom. Therefore, it is not surprising that the zinc-chlorine bond lengths vary within these three structures. Note that the sum of the covalent radii of zinc and chlorine yields $2.33 \text{ \AA}$. Diatomic ZnCl is likely to be quite ionic. Because its Zn-Cl bond length is longer, ClZnCH_3 likely has more covalent character relative to the chloride. Ethyl zinc chloride and the TMEDA adduct have longer bond lengths because of steric hindrance.

For ClZnCH_3 , eqQ was found to be $-27.443(41) \text{ MHz}$, significantly smaller than that of

the ^{35}Cl nucleus, which has a value of -80 MHz [28]. This difference suggests that the molecule also has significant ionic character. Using the Townes and Dailey approximation [21], the fraction of ionic character χ in the Zn-Cl bond can be estimated from the following equation:

$$\chi = \left(1 - \frac{eqQ(\text{ClZnCH}_3)}{eqQ(\text{Cl})}\right) \times 100\% \quad (2)$$

For ClZnCH_3 , the fraction is calculated to be $\chi = 65.7\%$. A comparison with the quadrupole coupling constant for CH_3Cl , $eqQ = -74.7631(35)$ MHz [28], can also give insight into the relative bonding properties. This value is - 2.7 times greater in magnitude than that of ClZnCH_3 , and indicates 6.5% ionic character in the Cl-C bond. Clearly, the insertion of zinc substantially increases the ionic properties of the molecule, although not to the degree of ZnCl . The charge distribution in methyl zinc chloride is $\text{Cl}^{\delta-}\text{Zn}^{\delta+}\text{-CH}_3$, as predicted for Grignard-type species, e.g. [4,5].

Oxidative addition of a metal to the C-Cl bond of CH_3Cl has been examined using DFT methods in the context of an Activation Strain model by de Jong et al. [12]. These calculations predict that other metals such as Pd, Be, and Mg are easier to insert into C-Cl bond than Zn. Our experiment thus opens the door to other potential metal insertion products including the gas-phase Grignard reagent itself.

5. Conclusion

The first study of a Grignard-type reagent in monomeric form, methyl zinc chloride, has been conducted. The pure rotational spectrum demonstrates that the molecule has C_{3v} symmetry with a linear Cl-Zn-C backbone. Based on zinc isotopic substitution, an estimate of the Zn-Cl bond length has been derived, which was found to be over 0.1 Å shorter than those found in the ethyl zinc chloride, based on crystal structures. The Cl-Zn bond appears to be a mixture of covalent and ionic character. This study demonstrates that gas-phase spectroscopic studies of

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4 monomeric organic reagents can provide insight into their basic chemical properties. It also
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7 suggests that activated zinc can readily insert into the C-Cl bond.
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References:

- [1] E. Frankland, B.F. Duppa, J. Chem. Soc. 17 (1864) 29.
- [2] H.L. Hsieh, J. Polym. Sci., J.Polym.Sci.A. Polym. Chem. 14 (1976) 379.
- [3] J.R. Zhou, G.C Fu, J. Am. Chem. Soc. 125 (2003) 14726.
- [4] R. Lasch, M.R. Heinrich, J. Org. Chem. 80 (2015) 10412.
- [5] A. Conan, S. Sibille, J. Périchon, J. Org. Chem. 56 (1991) 2018.
- [6] H. Yang, D. Huang, K. Wang, C. Xu, T. Niu, Y. Hu, Tetrahedron 69 (2013) 2588.
- [7] B.A. Haag, Z. Zhang, J. Li, P. Knochel, Angew. Chem. Int. Ed. 49 (2010) 9513.
- [8] I. Kadota, H. Takamura, K. Sato, Y. Yamamoto, J. Org. Chem. 67 (2002) 3494.
- [9] A. Guerrero, D.L. Hughes, M. Bochmann, Organometallics 25 (2006) 1525.
- [10] P.T. Moseley, H.M.M. Shearer, Chem. Commun. 23 (1966) 876.
- [11] P.C. Andrews, C.L. Raston, B.W. Skelton, A.H White, Organometallics 17 (1998) 779.
- [12] G.T. de Jong, R. Visser, F.M. Bickelhaupt, J. Organomet. Chem. 691 (2006) 4341.
- [13] X. Lin, D.L. Phillips, J. Org. Chem. 73 (2008) 3680.
- [14] J.A. Casares, P. Espinet, B. Fuentes, G. Salas, J. Am. Chem. Soc. 129 (2007) 3508.
- [15] M.P. Bucchino, J.P. Young, P.M. Sheridan, L.M. Ziurys, J. Phys. Chem. A 118 (2014) 11204.
- [16] M.A. Flory, A.J. Apponi, L.N. Zack, L.M. Ziurys, J. Am. Chem. Soc. 132 (2010) 17186.
- [17] L.M. Ziurys, W.L. Barclay Jr., M.A. Anderson, D.A. Fletcher, J.W. Lamb, Rev. Sci. Instrum. 65 (1994) 1517.
- [18] M. Sun, A.J. Apponi, L.M. Ziurys, J. Chem. Phys. 130 (2009) 034309.
- [19] M. Sun, D.T. Halfen, J. Min, B. Harris, D.J. Clouthier, L.M. Ziurys, J. Chem. Phys. 133 (2010) 174301.

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2
3
4 [20] W. Gordy, R.L. Cook, Microwave Molecular Spectra, Wiley, New York, 1984.
5
6 [21] C.H. Townes, A.L. Schawlow, Microwave Spectroscopy, Dover, New York, 1975.
7
8
9 [22] H.M. Pickett, J. Mol. Spectrosc. 148 (1991) 371.
10
11 [23] T.M. Cerny, X.Q. Tan, J.M. Williamson, E.S.J. Robles, A.M. Ellis, T.A. Miller, J. Chem.
12 Phys. 99 (1993) 9376.
13
14
15 [24] E.D. Tenenbaum, M.A. Flory, R.L. Pulliam, L.M. Ziurys, J. Mol. Spectrosc. 244 (2007)
16 153.
17
18 [25] S. Castillo, S. Ramírez-Solís, D. Díaz, E. Poulain, O. Novaro, Mol. Phys. 81 (1994) 825.
19
20 [26] B.D. Darwent, Nat. Stand. Ref. Data. Ser., Nat. Bur. Stand. 31 (1970) 1.
21
22 [27] C.A. McDowell, B.G. Cox, J. Chem. Phys. 20 (1952) 1496.
23
24 [28] L. Stříteská, M. Šimečková, P. Kania, P. Musil, L. Kolesníková, J. Koubek, Š. Urban, J.
25 Mol. Struct. 919 (2009) 89.
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Table 1. Rotational Transition Frequencies for ClZnCH₃ (X¹A₁)^a

J' → J''	K	F' → F''	Cl ⁶⁴ ZnCH ₃		Cl ⁶⁶ ZnCH ₃		Cl ⁶⁸ ZnCH ₃	
			v	v _{obs} - v _{cal}	v	v _{obs} - v _{cal}	v	v _{obs} - v _{cal}
2 → 1	0	5/2 → 5/2	10227.269	-0.006				
		5/2 → 3/2	10234.136	0.001				
		7/2 → 5/2	10234.136	0.000				
		3/2 → 3/2	10239.037	-0.002				
	1	5/2 → 3/2	10228.196	0.003				
		7/2 → 5/2	10235.050	-0.001				
3 → 2	0	5/2 → 3/2	15348.920	-0.001				
		7/2 → 5/2	15350.619	-0.002	15328.876	0.002		
		9/2 → 7/2	15350.623	0.001	15328.876	0.001		
	1	5/2 → 3/2	15349.024	0.004				
		7/2 → 5/2	15349.069	0.000	15327.302	0.000		
		9/2 → 7/2	15350.781	-0.004				
4 → 3	0	5/2 → 3/2	20466.429	0.006	20437.408	-0.002	20409.434	-0.001
		7/2 → 5/2	20466.429	0.006	20437.408	-0.001	20409.434	-0.000
		9/2 → 7/2	20467.217	-0.002	20438.223	0.004	20410.259	0.008
		11/2 → 9/2	20467.217	-0.002	20438.223	0.004	20410.259	0.008
	1	5/2 → 3/2	20466.732	-0.001				
		9/2 → 7/2	20466.402	-0.001				
		11/2 → 9/2	20467.089	-0.001	20438.095	-0.001	20410.126	-0.005
5 → 4	0	11/2 → 9/2			25547.581	0.003	25512.620	0.003
		13/2 → 11/2			25547.581	0.003	25512.620	0.003
	1	11/2 → 9/2	25583.189	0.000	25546.936	-0.000	25511.971	-0.004
		13/2 → 11/2	25583.533	0.001	25547.276	-0.009	25512.323	-0.004
6 → 5	0	13/2 → 11/2					30614.960	0.002
		15/2 → 13/2					30614.960	0.002
51 ← 50	0				260356.620	0.186		
	1				260352.188	-0.136		
	3				260319.594	0.148		
53 ← 52	0		270931.171	-0.016	270547.289	-0.122		
	1		270927.235	0.321	270543.310	0.168	270173.012	-0.057
	2		270914.111	0.015	270530.248	-0.087	270160.254	0.028
	3		270892.705	-0.027	270509.033	0.043	270138.912	0.092
	4		270862.851	0.028	270479.152	0.044	270108.736	-0.116
	5		270824.285	-0.084	270440.542	-0.145	270070.447	0.125
	6		270777.387	0.019	270393.728	-0.001		
54 ← 53	0		276033.020	-0.056	275642.086	0.007	275264.936	-0.121
	1		276028.747	0.022	275637.746	0.015	275260.640	-0.056

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5	2	276015.664	-0.007	275624.760	0.075		
6	3	275993.889	-0.025	275602.929	-0.014	275225.947	0.147
7	4	275963.408	-0.047	275572.481	-0.023		
8	5	275924.482	0.188				
9	6	275876.424	-0.005			275107.966	-0.062
10							
11							
12	55 ← 54	0	281134.281	-0.123	280736.164	-0.023	
13		1	281129.979	0.005	280731.726	-0.033	
14		2	281116.744	0.060			
15		3	281094.357	-0.179	280696.393	0.057	280312.356
16		4	281063.381	-0.146	280665.443	0.102	
17		5	281023.703	0.043	280625.473	-0.017	280241.074
18		6	280974.966	0.034	280576.813	0.029	280192.238
19							-0.030
20							
21	56 ← 55	0	286235.131	-0.028	285829.658	-0.065	285438.655
22		1	286230.685	0.035	285825.244	0.028	
23		2					285420.799
24		3	286194.570	-0.016			0.110
25		4	286162.978	-0.051			
26		5	286122.425	-0.031			
27		6	286072.842	-0.025			
28							
29							
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31	57 ← 56	0	291335.351	0.020			
32		1	291330.714	-0.031	290918.166	0.075	
33		2	291316.952	-0.034	290904.283	-0.049	
34		3	291294.072	0.018	290881.280	-0.119	
35		4			290849.316	0.023	
36		6			290757.607	0.044	
37							
38							
39							
40	58 ← 57	0	296434.922	0.012	296015.039	-0.002	
41		1	296430.286	0.040	296010.344	-0.031	
42		2	296416.238	-0.015	295996.430	0.052	
43		3	296392.990	0.059	295973.025	-0.024	
44		4	296360.319	0.039	295940.171	-0.217	
45		5	296318.294	-0.006	295898.472	0.076	
46		6	296267.002	0.010			
47							

^a In MHz

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Table 2. Spectroscopic Constants for ClZnCH₃ (*X*¹A₁)^a

	Cl ⁶⁴ ZnCH ₃	Cl ⁶⁶ ZnCH ₃	Cl ⁶⁸ ZnCH ₃
A	148000 ^b	148000 ^b	148000 ^b
B	2558.39022(56)	2554.76481(66)	2551.26855(61)
D _J	0.00043354(10)	0.00043267(12)	0.00043176(14)
D _{JK}	0.04081(20)	0.04053(24)	0.040388(29)
H _{JK}	0.000000089(33)	0.000000046(39)	--
eqQ	-27.443(41)	-27.89(31)	-28.14(52)
rms	0.066	0.079	0.081

^a. In MHz; uncertainties are 3σ

^b. Held fixed (see text).

Table 3. Structures of HZnCH₃, XZnCH₃, and Related Compounds

	$r_{\text{X-Zn}} (\text{\AA})$	$r_{\text{Zn-C}} (\text{\AA})$	$r_{\text{C-H}} (\text{\AA})$	$\angle\text{MCH (deg)}$	$\angle\text{HCH (deg)}$	method	ref
HZnCH ₃	1.5209(1)	1.9281(2)	1.140(9)	110.2(3)	108.7(3)	r_0	[16]
	1.533	1.954	1.098	110.7		theory, r_e	[12]
IZnCH ₃	2.4076(2)	1.9201(2)	1.105(9)	110.2(5)	108.7(5)	r_0	[15]
							This
ClZnCH ₃	2.23(7)	1.9201 ^a	1.105 ^a	110.2 ^a	108.7 ^a	r_0	work
	2.129	1.937	1.096	109.6		theory, r_e	[12]
ClZnCH ₂ CH ₃ ^b	2.5408(7)						[9]
	2.3486(6)						
ClZnEtTMEDA ^b	2.269(3)						[11]
ZnCl	2.133(2)					r_0	[24]

a. Fixed.

b. X-ray crystal structure.

Figure 1: Millimeter-wave spectrum of $\text{Cl}^{64}\text{ZnCH}_3$ (X^1A_1), showing the K components of the $J = 58 \leftarrow 57$ transition near 296 GHz. Contaminating lines arise from CH_3Cl . The relative frequency spacing of the components ($K = 0 - 6$), as well as their relative intensities, indicates that the molecule is clearly a prolate symmetric top with C_{3v} symmetry. This spectrum is created from two 110 MHz wide scans, each acquired in ~ 70 s.

Figure 2: FTMW spectrum of the $J = 3 \rightarrow 2$ rotational transition of $\text{Cl}^{64}\text{ZnCH}_3$, showing the ^{35}Cl hyperfine lines arising from quadrupole coupling in the $K = 0$ and 1 components, labeled by the quantum number F . Doppler doublets are indicated on the figure by brackets. There is one frequency break in the spectrum in order to show multiple lines. The $F = 9/2 \rightarrow 7/2$, $F = 7/2 \rightarrow 5/2$, and $F = 5/2 \rightarrow 3/2$ hyperfine components are present for both $K = 0$ and 1, although in some case they are blended. Each spectral feature was acquired in one, 600 kHz-wide scan, averaged over 2500 shots, and cropped to show the given frequency range.

Figure 1

Figure 2