

Note

The mm-wave rotational spectrum of dichlorodimethylgermane

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Dedicated to Professor Vincenzo Balzani.

Abstract

The rotational spectra of three isotopologues of dichlorodimethylgermane were measured by free jet absorption millimeterwave spectroscopy. A partial r_0 structure was obtained. The barrier to internal rotation of the methyl groups is too high to cause splittings observable within our spectral resolution. Corresponding to the resolving power of the experiment, the lower limit to the V_3 barrier is about 5.8 kJ/mol.

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1. Introduction

During the latest years investigations of organometallic molecules containing methyl groups gained the attention of rotational spectroscopists for various reasons: (i) an analysis of the internal large amplitude motions in these molecules is particularly interesting in order to understand the concurring and competing mechanisms leading to barriers of internal rotation; (ii) rotational spectra resolve nuclear quadrupole coupling hyperfine structures and thus provide information on the bonding characters in these organometallic molecules; (iii) rotational spectroscopy determines the structure of isolated molecules with the highest precision available to date. Furthermore, it can be used to benchmark the equilibrium geometries calculated using *ab initio* calculations.

So far, a considerable number of relatively small molecules containing two methyl groups was investigated by rotational spectroscopy. Among these, dimethylether can be considered as a prototype molecule and its rotational

spectrum was analyzed in great detail [1]. The rotational spectra of this class of molecules are complicated by the nine structurally equivalent energy minima accessible by an internal rotation of the two methyl groups, which split the vibrational ground state in one non-degenerate, two doubly degenerate and one fourfold degenerate torsional sub-levels. The rotational–torsional energy levels of difluorodimethylsilane when internal rotation tunneling is allowed for, relate to the molecular symmetry (MS) group G_{36} introduced for dimethylacetylene [2] and later given for acetone [3]. The torsional wavefunctions $|k_1 k_2\rangle = |00\rangle$, $|\pm 1 \pm 1\rangle$, $|\pm 1 \mp 1\rangle$ and $|\pm 1 0\rangle$ or $|0 \pm 1\rangle$ can be symmetry classified as A_1 , E_1 , E_3 and G , respectively.

For low barriers to the large amplitude motions between the structurally equivalent configurations, the rotational spectra of this class of molecules are very congested and have been assigned only for a few relatively simple species. The internal rotation of two methyl groups has been investigated in molecules such as propane [4], dimethylsulfide [5], dimethylamine [6], and the organometallic molecules dimethylsilane [7], chlorodimethylsilane [8], difluorodimethylsilane [9] and dimethylgermane [10]. The V_3 barrier of $(\text{CH}_3)_2\text{GeH}_2$ is $4.950 \text{ kJ mol}^{-1}$ [10], significantly lower than for $(\text{CH}_3)_2\text{SiH}_2$ ($6.887 \text{ kJ mol}^{-1}$, [7]) mainly due to

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the different covalence radii of Ge and Si (1.22 and 1.17 Å, respectively). Substituting a hydrogen by a chlorine atom under formation of $(\text{CH}_3)_2\text{SiHCl}$ leads to a slight increase in the V_3 barrier (7.16 kJ mol^{-1} [8]), which might be explained with increased steric repulsion due to the significantly larger chlorine atom. The covalence radius of chlorine is 0.99 Å versus 0.3 Å for hydrogen. On the other hand, for $(\text{CH}_3)_2\text{SiF}_2$, where two hydrogen atoms have been substituted by two fluorine atoms (covalence radius of fluorine is 0.58 Å and thus about twice the size as for hydrogen), the V_3 barrier is significantly reduced to $5.256(3) \text{ kJ mol}^{-1}$ [9] although steric issues should become more severe here than for $(\text{CH}_3)_2\text{SiH}_2$. Consequently, the decrease of the V_3 barrier might be attributed to electronic contributions/interactions originating from the large electronegativity that gives rise to an increased ionic bond character.

The data on the V_3 barrier of $(\text{CH}_3)_2\text{SiCl}_2$ and $(\text{CH}_3)_2\text{GeCl}_2$, which can provide insights into these mechanisms, are not available yet. In the present work, we will focus on the millimeterwave spectrum of the latter species, $(\text{CH}_3)_2\text{GeCl}_2$, the first di-chloro compound in this class of molecules to provide experimental data for a better understanding of the internal dynamics of organometallic molecules containing two methyl groups.

In the case of dichlorodimethylgermane (DCDMG), see Fig. 1, the spectrum is considerably complicated due to the high number of isotopes of Ge (^{76}Ge , ^{74}Ge , ^{72}Ge , ^{70}Ge) and the two Cl sites (^{35}Cl , ^{37}Cl). The nuclear spin ($I = 3/2$ for both ^{35}Cl and ^{37}Cl nuclei) further splits each rotational level in 16 sublevels; the even more complicated ^{73}Ge isotopologue ($I = 9/2$) was not observed. Jet-cooled rotational spectra of supersonic expansions are considerably simplified due to the population transfer to low- J energy levels, but the high resolving power of velocity-equilibrated Fourier transform spectra can reveal a very large number of line components caused by various overlapping internal rotation species, quadrupole pattern and isotopologues. To facilitate a preliminary assignment of the spectrum, we chose to use a free jet absorption millimeter wave spec-

trometer, that provides a moderate resolving power, and to observe relatively high J transitions, for which the magnitude of quadrupole and internal rotation splittings is reduced.

2. Experiment

A sample of DCDMG, commercially supplied by ABCR GmbH & Co. KG (Germany), was used without further purification.

The Stark- and pulse-modulated free jet absorption millimeter-wave spectrometer used in this study has already been described elsewhere [11]. The spectrum was observed by expanding a mixture of about 5% of DCDMG in Ar at room temperature from approx. $3 \times 10^4 \text{ Pa}$ to about 0.2 Pa through a nozzle orifice with a diameter of 0.35 mm , reaching an estimated “rotational” temperature of about 10–20 K.

3. Quantum chemical calculations and rotational spectrum

DFT/B3LYP calculations (6-311++G(d, p) basis sets) [12] were employed to predict the rotational spectrum. Fig. 1 shows the geometry of the optimized molecular structure. The molecule belongs to the C_{2v} point symmetry group, with the twofold symmetry axis coinciding with the bisectors of both Cl–Ge–Cl and C–Ge–C valence angles. The rotational constants of this structure are $A = 2230.3 \text{ MHz}$, $B = 1626.1 \text{ MHz}$, and $C = 1431.3 \text{ MHz}$ for the most abundant isotopic species ($^{74}\text{Ge}^{35}\text{Cl}^{35}\text{Cl}$). The permanent molecular dipole moment is directed along the b -axis ($\mu_b = 3.5 \text{ D}$) and thus only a μ_b -type spectrum is expected.

The germanium atom, which possesses three main isotopes ^{74}Ge ($\approx 36\%$), ^{72}Ge ($\approx 28\%$) and ^{70}Ge ($\approx 21\%$), is located quite close to the center of mass of the molecule. Consequently, the rotational transitions of the homo-substituted species with either two ^{35}Cl or two ^{37}Cl atoms appear as triplets, with the components corresponding to each one of the three Ge isotopic species. The same is true for the hetero-substituted species containing one ^{35}Cl and one ^{37}Cl atom. The isotopic substitution of one ^{35}Cl atom with one ^{37}Cl atom produces a large frequency shift, since the chlorine atoms are significantly away from the centre of mass of the molecule. Statistically, the mixed species $^{35}\text{Cl}^{37}\text{Cl}$ should have transitions with an intensity about $2/3$ of those of the $^{35}\text{Cl}^{35}\text{Cl}$ species. However, the former appear more intense using our Stark-modulated free-jet absorption spectrometer, because the asymmetric substitution generates a small μ_a -dipole moment component which allows for a complete Stark-modulation of the transitions we observed. Still, the overall intensity of the spectrum is very weak. For the reason described, the largest number of transitions (26) has been measured for the $^{74}\text{Ge}^{35}\text{Cl}^{37}\text{Cl}$ species; 14 and 16 lines were measured for the $^{74}\text{Ge}^{35}\text{Cl}^{35}\text{Cl}$ and $^{72}\text{Ge}^{35}\text{Cl}^{37}\text{Cl}$ species, respectively. All transitions are reported in Table 1. All of them, except for one weak dou-

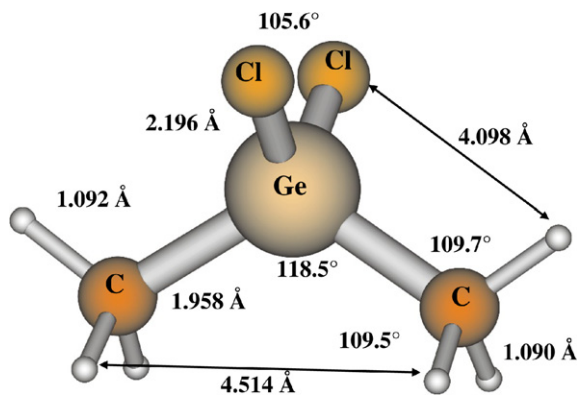


Fig. 1. Optimized equilibrium structure of DCDMG (B3LYP/6-311++G(d, p)).

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