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A global *ab initio* dipole moment surface for methyl chloride

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ABSTRACT

A new dipole moment surface (DMS) for methyl chloride has been generated at the CCSD(T)/aug-cc-pVQZ(+d for Cl) level of theory. To represent the DMS, a symmetry-adapted analytic representation in terms of nine vibrational coordinates has been developed and implemented. Variational calculations of the infrared spectrum of CH_3Cl show good agreement with a range of experimental results. This includes vibrational transition moments, absolute line intensities of the ν_1, ν_4, ν_5 and $3\nu_6$ bands, and a rotation–vibration line list for both $CH_3{}^{35}Cl$ and $CH_3{}^{37}Cl$ including states up to $J=85$ and vibrational band origins up to 4400 cm^{-1}. Across the spectrum band shape and structure are well reproduced and computed absolute line intensities are comparable with highly accurate experimental measurements for certain fundamental bands. We thus recommend the DMS for future use.

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1. Introduction

The proposal of methyl chloride as a potential bio-signature gas [1–3] in the search for life outside of the Solar System has ignited interest in its infrared spectrum. There is now considerable motivation for a comprehensive rotation–vibration line list of CH_3Cl. Since methyl chloride is known to contribute to ozone depletion, any such line list would undoubtedly be useful in terrestrial studies. Its importance as an atmospheric molecule is confirmed by the huge number of recent spectroscopic studies [4–31].

The HITRAN database [32] has the most detailed coverage with over 212 000 lines for the two main isotopologues, $^{12}CH_3{}^{35}Cl$ and $^{12}CH_3{}^{37}Cl$ (henceforth labelled as $CH_3{}^{35}Cl$ and $CH_3{}^{37}Cl$). This includes rovibrational transitions up to $J=82$ and covers the 0–3200 cm^{-1} region. However, there are deficiencies and we will see in Section 4.3 that HITRAN is missing a band around 2880 cm^{-1}. Some line positions and intensities are also from theoretical predictions using a fairly old, empirically refined anharmonic force field [33]. Given the numerous high-resolution studies since then, notably in the 3.4 μm region [4] (included in HITRAN2012) and in the 6.9 μm region [14], improvements can be expected in the coverage of CH_3Cl. Another valuable resource is the PNNL spectral library [34] which covers the 600–6500 cm^{-1} region at a resolution of around 0.06 cm^{-1} for temperatures of 5, 25 and 50 °C. Other databases such as GEISA [35] include CH_3Cl but the datasets are not as extensive, whilst the JPL [36] catalogue has been incorporated into HITRAN.

Intensity information is vital for practical applications such as atmospheric modelling or remote sensing. The six fundamental bands of CH_3Cl have all been considered at some stage [4,14,37–50]. Notably, absolute line intensities have been measured for the ν_1, ν_4 and $3\nu_6$ bands in the 2920–3100 cm^{-1} range [4], and for over 900 rovibrational transitions in the ν_5 band [14]. These two studies are the most reliable and complete line intensity measurements for both $CH_3{}^{35}Cl$ and $CH_3{}^{37}Cl$ to date. From a theoretical perspective, calculations of dipole moment derivatives and

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infrared intensities have been reported [27,33,51–57]. However, we are unaware of any global DMS which could be used for intensity simulations of the rotation–vibration spectrum of CH_3Cl.

Previously we reported [58] two state-of-the-art *ab initio* potential energy surfaces for the two main isotopologues of methyl chloride. Variational calculations of the vibrational $J=0$ energies and equilibrium geometry showed excellent agreement with experimental results. Building on this work, we present a new nine-dimensional *ab initio* DMS which has been computed using high-level electronic structure theory. A symmetrized molecular bond (SMB) representation for XY_3Z-type molecules has been implemented into the nuclear motion code TROVE [59] to represent the DMS analytically. Comprehensive calculations of the rotation–vibration spectrum are then carried out to evaluate the quality of the DMS. The work presented here represents the next step towards generating a complete rovibrational line list applicable for elevated temperatures.

The paper is structured as follows: In Section 2 the electronic structure calculations and analytic representation of the DMS are described. Details of the variational calculations are given in Section 3. In Section 4 the DMS is evaluated against a range of experimental measurements as well as the HITRAN and PNNL spectroscopic databases. Results include vibrational transition moments, absolute line intensities of the ν_1, ν_4, ν_5 and $3\nu_6$ bands, and an overview of the rotation–vibration spectrum for states up to $J=85$ in the 0–6500 cm^{-1} frequency range. Concluding remarks are offered in Section 5.

2. Dipole moment surface

2.1. Electronic structure calculations

The first derivative of the electronic energy with respect to external electric field strength defines the electric dipole moment of a molecule. Working in a Cartesian laboratory-fixed *XYZ* coordinate system with origin at the C nucleus, an external electric field with components ± 0.005 a.u. was applied along each axis and the respective dipole moment component μ_A for $A = X, Y, Z$ determined using finite differences. Calculations were carried out at the CCSD(T) [coupled cluster with all single and double excitations and a perturbational estimate of connected triple excitations] level of theory with the augmented correlation consistent quadruple zeta basis set, aug-cc-pVQZ(+d for Cl) [60–63], in the frozen core approximation. MOLPRO2012 [64] was used for all calculations.

The DMS was evaluated on a nine-dimensional global grid of 44,820 points with energies up to $hc \cdot 50\,000\ cm^{-1}$ (h is the Planck constant and c is the speed of light). The grid included geometries in the range $1.3 \le r_0 \le 2.95$ Å, $0.7 \le r_i \le 2.45$ Å, $65 \le \beta_i \le 165^\circ$ for $i = 1,2,3$ and $55 \le \tau_{jk} \le 185^\circ$ with $jk = 12,13$. Here, the nine internal coordinates are the C–Cl bond length r_0; three C–H bond lengths r_1, r_2 and r_3; three $\angle(H_iCCl)$ interbond angles β_1, β_2 and β_3; and two dihedral angles τ_{12} and τ_{13} between adjacent planes containing H_iCCl and H_jCCl. The grid utilized for the DMS is the same as that used for the PESs previously reported [58].

2.2. Analytic representation

Before fitting an analytic expression to the *ab initio* data it is necessary to establish a suitable molecule-fixed *xyz* coordinate system. Methyl chloride is a prolate symmetric top molecule of the $\mathbf{C}_{3v}(M)$ symmetry group [65]. There are six symmetry operations $\{E, (123), (132), (12)^*, (23)^*, (13)^*\}$ which make up $\mathbf{C}_{3v}(M)$. The cyclic permutation operation (123) replaces nucleus 1 with nucleus 2, nucleus 2 with nucleus 3, and nucleus 3 with nucleus 1; the permutation-inversion operation $(12)^*$ interchanges nuclei 1 and 2 and inverts all particles (including electrons) in the molecular centre of mass; the identity operation E leaves the molecule unchanged. The symmetrized molecular bond (SMB) representation has been successfully applied to molecules of $\mathbf{C}_{3v}(M)$ symmetry [66,67] and this approach is employed for the present study.

We first define unit vectors along each of the four bonds of CH_3Cl,

$$\mathbf{e}_i = \frac{\mathbf{r}_i - \mathbf{r}_C}{|\mathbf{r}_i - \mathbf{r}_C|}; \quad i = 0, 1, 2, 3, \tag{1}$$

where $\mathbf{r}_C$ is the position vector of the C nucleus, $\mathbf{r}_0$ the Cl nucleus, and $\mathbf{r}_1$, $\mathbf{r}_2$ and $\mathbf{r}_3$ the respective H atoms. The *ab initio* dipole moment vector $\boldsymbol{\mu}$ is projected onto the molecular bonds and can be described by molecule-fixed *xyz* dipole moment components,

$$\mu_x = \frac{1}{\sqrt{6}}(2(\boldsymbol{\mu} \cdot \mathbf{e}_1) - (\boldsymbol{\mu} \cdot \mathbf{e}_2) - (\boldsymbol{\mu} \cdot \mathbf{e}_3)), \tag{2}$$

$$\mu_y = \frac{1}{\sqrt{2}}((\boldsymbol{\mu} \cdot \mathbf{e}_2) - (\boldsymbol{\mu} \cdot \mathbf{e}_3)), \tag{3}$$

$$\mu_z = \boldsymbol{\mu} \cdot \mathbf{e}_0. \tag{4}$$

Symmetry-adapted combinations have been formed for μ_x and μ_y and these transform according to E symmetry, while the μ_z component is of A_1 symmetry. The advantage of the SMB representation is that the unit vectors $\mathbf{e}_i$ used to define $\boldsymbol{\mu}$ for any instantaneous positions of the nuclei are related to the internal coordinates only.

To construct the three dipole surfaces corresponding to the components given in Eqs. (2)–(4), a numerical, on-the-fly symmetrization procedure has been implemented. This is similar to the approach employed for the PES [58] but because $\boldsymbol{\mu}$ is a vector quantity we have to consider the transformation properties of the dipole moment components themselves. For μ_z, which points along the C–Cl bond, the process is trivial owing to its A_1 symmetry and invariance to the $\mathbf{C}_{3v}(M)$ symmetry operations. Building an analytic expression follows the same steps as the PES. For the two E symmetry components, μ_x and μ_y, the construction is more subtle and they must be treated together.

We consider an initial (reference) term in the dipole expansion belonging to μ_x,

$$\begin{pmatrix} \mu_x \\ \mu_y \end{pmatrix} = \begin{pmatrix} \mu_{x,ijk\ldots}^{\text{initial}} \\ 0 \end{pmatrix}, \tag{5}$$

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