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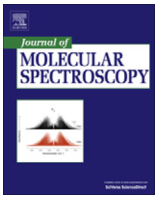

Rotational and vibrational energy levels of methyl fluoride calculated from a new potential energy surface

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ABSTRACT

A new potential energy surface of methyl fluoride is constructed using extended *ab initio* CCSD(T) calculations with the cc-pVQZ basis at 5100 nuclear configurations. Its analytical representation is determined through an expansion in symmetry adapted products of orthogonal coordinates involving 600 parameters up to 6th order. A good convergence for variational calculations of vibrational levels of the CH_3F molecule was obtained with a RMS(obs.-calc.) deviation of less than 4 cm^{-1} for fundamental band centers. The equilibrium geometry of the *ab initio* PES was empirically optimized using experimental $J = 1$ energy levels for four isotopologues $^{12}CH_3F$, $^{13}CH_3F$, $^{12}CD_3F$, and $^{13}CD_3F$. The resulting variational calculations with the full normal mode Hamiltonian in the irreducible tensor representation gave a RMS(obs.-calc) deviation of 0.00036 cm^{-1} for rotational energies up to $J = 5$ for the major isotopologue. This represents a considerable improvement with respect to available global predictions of vibration and rotational levels of methyl fluoride.

1. Introduction

Methyl fluoride is a molecule of interest both for experimental and theoretical spectroscopy [1–10] and for intramolecular dynamics [11–13] as well. Some recent papers [14,15] discuss problems related to theoretical description of the CH_3F vibrational energy levels. Accurate variational calculations of vibration–rotation energy levels of five-atomic molecules from a potential energy surface (PES) are known to be quite demanding. For example, in order to provide a precise description of lower energy levels, a PES expansion of at least 6th order has to be included. This results in a big number of PES parameters requiring much larger number of *ab initio* points for a robust PES fit. Another issue is a parameterization avoiding non-physical behavior of PES far from equilibrium geometry in the 9D space.

The complex structures of vibrational polyads, numerous resonance couplings and high dimensionality of the calculation models make an analysis of highly excited vibration–rotation energy levels of the CH_3F molecule a difficult task [1–7,12]. Predictions of “dark” vibrational states (that are not yet experimentally detected) and corresponding perturbations of observed bands are of particular interest for spectra analysis [16–21]. A better knowledge of PES would help resolving the problem of the characterization of these “dark” vibration states.

Atkinson and Law [6] have compared calculations from available cubic anharmonic potentials with observed energy levels for six isotopologues of: $^{12}CH_3F$, $^{13}CH_3F$, $^{12}CD_3F$, $^{13}CD_3F$, $^{12}CHD_2F$, and $^{12}CH_2DF$. Data fitting performed in their paper [6] resulted in an improved empirical PES. However, an accurate prediction of excited vibration–rotation states of CH_3F still remains an issue to be solved. Despite a progress in *ab initio* calculations [15] the errors in calculated band centers are yet too large for high-resolution spectroscopy application, even for fundamentals. This prevents a reliable description of accidental ro-vibrational resonances which are important for spectra analyses and modeling of various isotopic species [2,22–24,4]. The number of these resonances rapidly increases with vibrational excitation.

Some issues are common for global vibration–rotational predictions in polyatomic molecules. The precision of rotational predictions is known to be very sensitive to the equilibrium geometry [25], the required accuracy of the equilibrium nuclear configuration being hardly accessible by pure *ab initio* calculations. On the other hand a convergence of quantum variational calculations for the nuclear motion is very challenging for high energy levels.

This work is a part of an effort aimed at improving spectroscopic data analyses and calculations for isotopologues of the CH_3F molecule in the infrared range. The main goal of this study is a construction of a molecular PES in the electronic ground state combining extended *ab initio* calculations with empirical optimization of the equilibrium geometry.

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2. Electronic structure calculations and determination of *ab initio* PES

In order to obtain accurate calculations of vibrational and rotational energy levels from the theoretical PES useful for spectroscopic analysis, it is necessary to combine high level *ab initio* methods with sufficiently large basis sets in electronic structure calculations. The method employed in our study is the coupled cluster approach [26] including single and double excitations [27] with the perturbative treatment of triple excitations [28]: CCSD(T). We used well established Dunning's correlation consistent valence basis sets [29,30] cc-pVQZ. The relativistic effects are taken into account via the one-electrons Douglas–Kroll correction [31,32]. All the *ab initio* calculations were carried out using the MOLPRO program package [33] version 2009.1. As a first step for the PES construction 5100 ground state electronic energies were calculated with cc-pVQZ basis set on the grid of nuclear configurations described in Section 2.2 below. The distribution of the density of included geometrical configurations is given in Fig. 1 with a maximum number of configurations near 4000–7000 cm^{-1} but a significant number of points extends up to 11 000 cm^{-1}. Comparing with other molecules of the type XY_3Z, such as CH_3D, CH_3Cl [34] the stretching vibration fundamentals calculated from *ab initio* surface were less precise. The problems related to accurate *ab initio* calculations for CH_3F are discussed in [25,35,36].

2.1. The equilibrium geometry

One of the issues mentioned in the Introduction section concerns an accurate calculation of the equilibrium geometry [37]. In Ref. [25], the equilibrium structure determination of methyl fluoride has been based on *ab initio* geometry optimization at CCSD(T)/cc-pVQZ and CCSD(T)/cc-pCVQZ levels of the theory. The paper [25] treated the core correlation effect obtained using the CCSD(T) method with the cc-pCVQZ basis set as additive corrections to the CH_3F equilibrium geometry. The effect of the cc-pCV(5,Q)Z basis extension due to diffuse functions also has been calculated in Ref. [25] as additive correction resulting to three parameters of equilibrium geometry r_e(C–H) = 1.087 Å, r_e(C–F) = 1.383 Å, q_e(FCH) = 108.7°. In the present paper, these parameters are referred to as r_H, r_F, and q_e. As the rotational constants A_o and B_o depend on the CH_3F equilibrium geometry, these parameters are very important for accurate description of rotational spectra.

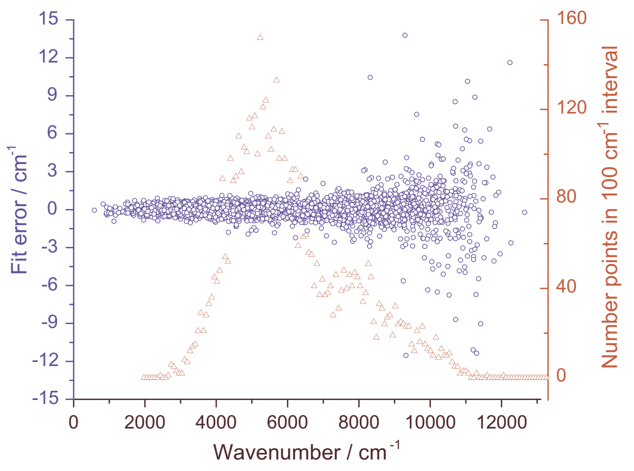

Fig. 1. Density distribution of calculated *ab initio* points (red triangles on the right-hand side scale) and errors of the PES fit to *ab initio* electronic energies (blue circles on the left-hand side scale). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Some results for the equilibrium geometry optimization obtained using different versions of calculations are summarized in Table 1. The convergence of equilibrium geometry with increasing basis set dimension was not as pronounced as in our previous study for the methane molecule [38]. Rotational energy levels of four isotopologues of CH_3F are experimentally known with high accuracy [39,40,23,41,42,4]. In order to improve the equilibrium geometry we applied an algorithm based on the optimization of the r_H, r_F, and q_e parameters using observed ground state $J = 1$ levels of four isotopologues of CH_3F. Computed rotation energies $E_{J=1}$ given in Table 1 suggest that the $r_F = 1.3824(8)$, $r_H = 1.08696(8)$, and $q_e = 108.76(3)$ values obtained from the fitting procedure described in Section 4 are the most suitable ones for calculations of CH_3F rotational levels using atomic masses (see Sections 4 and 5 for more discussion). The uncertainties shown in parentheses correspond to three standard deviations. Note that the r_H value was more accurately determined than that of r_F and q_e.

2.2. Sampling of ab initio points in the nuclear configuration space and analytical symmetry adapted PES representation

The PES of the CH_3F molecule can be described using nine coordinates corresponding to six elementary symmetry adapted *S*-tensors. To parameterize all possible nuclear geometries of the CH_3F molecule, it is convenient to use polar curvilinear valence coordinates because they are internally built in *ab initio* programs like MOLPRO. The internal polar coordinates are defined in a standard way *via* four vectors $\{\vec{r}_i\}$ (i = 1, 2, 3, 4) linking the *C* atom with the *F* atom and with three *H* atoms. The following coordinates were chosen as independent ones: four bond lengths $\{r_1, r_2, r_3, r_4\}$, three interbond angles $\{q_{12}, q_{13}, q_{14}\}$ and two torsion angles $\{t_{23}, t_{24}\}$. Two types of coordinates were used in this work. For sampling of *ab initio* points symmetrised internal coordinates were used. A convenient expression for the kinetic energy can be obtained in terms of mass-dependent orthogonal coordinates as discussed in Ref. [43]. Mass dependent coordinates (1) keep the same symmetry properties as the initial polar coordinates and are defined *via* four vectors $\{\vec{r}'_i\}$:

$$\vec{r}'_i = \sum_{j=1}^{4} d_{ij}\vec{r}_j, \tag{1}$$

where d_{ij} depend on atomic mass only. The mass dependent coordinates are used in Section 3. We follow the technique described in Refs. [44,38] to derive a symmetry adapted grid of points in the coordinate space suitable for a reliable determination of PES parameters. This approach based on the force field constants allows finding an optimal set of geometric nuclear configurations sufficient for a construction of the force field up to a certain order of expansion. The nine-dimensional PES was constructed in a four step process:

1. One dimensional curves corresponding to each of nine symmetrised coordinates were constructed first. These one-dimensional curves were interpolated using the sixth order power series expansions. Then the values of the symmetrised coordinates where the PES should take values 0, 1000, 2500, 4000, 7000, 12 000, 18 000 cm^{-1} were found.
2. Using the algorithm of our previous work [45], a full set of 967 totally symmetric irreducible tensors [46,47] up to the 6th order expansion was constructed. Every tensor was represented as the sum of symmetrised products

$$R_i^p = (((S_{RH,A_1}^{p_1} S_{RH,E}^{p_2})S_{RF,A_1}^{p_3})((S_{QH,A_1}^{p_4} S_{QH,E}^{p_5})S_{TH,E}^{p_6}))^{A_1} \tag{2}$$

of symmetry adapted coordinates S_i. Here S_R stands for radial, and S_Q, S_T for angular coordinates: (see [46,47] for more detail) and $p = p_1 + p_2 + p_3 + p_4 + p_5 + p_6$ is the total power of the term.