

Potential energy surface of CH₃Cl

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The tentative potential energy surface is constructed for the CH₃Cl molecule. The possibility of making quite accurate analytical calculations of the isotopic shifts has been demonstrated.

Introduction

In recent years, rather accurate *ab initio* potential energy surfaces have been constructed for many triatomic and some tetratomic molecules. The aim of this work was to consider the specific features of constructing *ab initio* surfaces for pentatomic molecules with the CH₃Cl molecule taken as an example. We have made an attempt to construct the potential energy surface (PES) for CH₃Cl near the minimum with the accuracy close to that of the PES calculated by the CCSD(T) method with the cc-VQZ basis. The increasing number of atoms in a molecule, makes the *ab initio* calculations increasingly cumbersome for each of the geometric configurations of a molecule possible, and the number of geometric configurations, in which the calculations are to be performed, increase sharply as well.

The molecular symmetry allows a considerable decrease in the number of geometric configurations to be achieved, in which the *ab initio* calculations of the energy are to be carried out. Methane is the simplest and the most studied pentatomic molecule from the viewpoint of *ab initio* calculations.^{1,2}

Despite the high symmetry of the methane molecule, it is difficult to calculate accurately the energy levels above 6000 cm⁻¹ because of a strong effect of the high-energy part of the potential energy surface. Similar problems with the description of the high-energy part of the potential energy surface appear in CH₃Cl as well, and the accuracy of calculations rapidly drops down with the increasing vibrational energy.

Comparison of *ab initio* calculation methods

The *ab initio* calculations of the CH₃Cl molecule have already been carried out, for example, in Refs. 3–5. In Ref. 3, the fourth-order force field was calculated by the MP4 method. The comparison of the potential energies calculated by the CCSD(T) method and by MP4 in the cc-VQZ basis (hereinafter VQZ) indicates that near the minimum both of the methods give close results (Figs. 1 and 2). At the same time, the calculation by the CCSD(T) method in the cc-VTZ basis (hereinafter VTZ) even near the

minimum differs strongly from the calculation by this method in the cc-VQZ basis. The calculations by the MP2 method in the cc-VQZ basis are also inaccurate and quite slow. Table 1 presents the equilibrium geometries calculated by different methods in cc-VTZ and cc-VQZ bases.

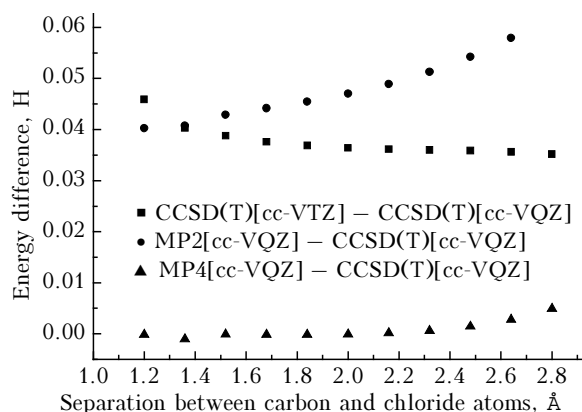


Fig. 1. Difference between energies calculated by different methods as a function of the separation between the C and Cl atoms, other coordinates being in the equilibrium state.

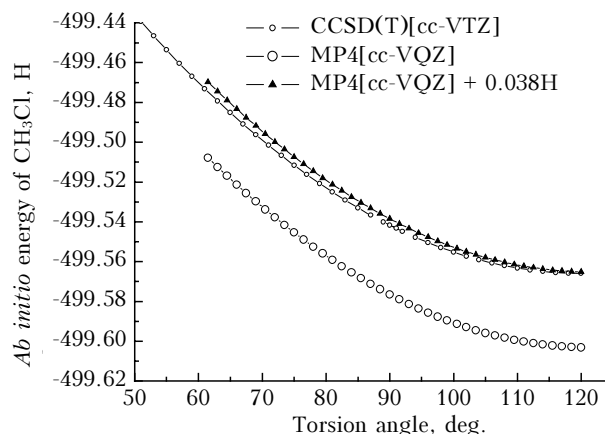


Fig. 2. Comparison of different methods of PES calculation in the form of the function of the torsion angle, other coordinates being in the equilibrium state.

As in Ref. 3, the calculations were mostly performed by the MP4 method in the cc-VQZ basis, but some calculations also used the MP4 method in the cc-VTZ basis.

Table 1. Energy minimum and equilibrium geometry of the CH₃Cl molecule in different methods and bases

Method and basis	Energy minimum, N	r_{Cl} , Å	r_{H} , Å	q , deg	Mean computational time*
MP2[cc-VQZ]	-499.5580669	1.77417389	1.08240282	108.5204987	20 min
CCSD(T)[cc-VTZ]	-499.5659487	1.79009850	1.08589341	108.4485916	15 min
MP4[cc-VQZ]	-499.6032040	1.78525502	1.08522046	108.3803364	2 h
CCSD(T)[cc-VQZ]	-499.6030255	1.78537299	1.08495702	108.3588049	2 h 15 min

* The mean time for computation of one geometric configuration on the Athlon 1466 MHz computer. As in Ref. 3, the computations were mostly carried out by the MP4 method in the cc-VQZ basis, and some computations were performed by the MP4 method in the cc-VTZ basis.

Calculation of potential energy surfaces

We did not try to describe the PES correctly in the whole possible space of geometries, but constructed the surface, realistically describing energy levels near the minimum. Initially, the trial surface was constructed by the CCSD(T) method in the cc-VTZ basis. All geometric configurations (points), needed for the calculation of the force field, up to the fourth order, as well as all one-dimensional surfaces for r_{Cl} , r_{H} , q , and t were calculated.

The tentative trial surface was constructed of the points calculated. Then 1000 random points were generated in the limited range of the parameters r_{Cl} , r_{H} , q , and t values and energies. Every point was spaced by at least 0.1 Å from all the previous ones. For new points, the quantum-chemical potential energy was calculated and the tentative analytical surface was refined. Then new random points were generated in a wide range of the parameters r_{Cl} , r_{H} , q , and t values and energies. After several iterations, 6652 points were calculated by the CCSD(T) method in the cc-VTZ basis and the analytical form of the surface was found. For accuracy control, 100 more points were taken, and energy at this points was well predicted by the analytical surface.

The cause, for which the geometric configurations were not calculated for the force constants up to a certain order to be determined from them, was that different degrees of freedom correspond to different energies. Thus, the vibrational frequency ν_3 , corresponding to r_{Cl} , was fourfold as low as the frequencies ν_1 and ν_4 , corresponding to r_{H} . Therefore, for r_{Cl} the density of points should be four times higher than for r_{H} . In addition, the algorithm based on random points is more universal. For example, this algorithm can be used in the case of complex molecules, when vibrational frequencies are not known *a priori*. A disadvantage of this method is that the

fraction of random points satisfying the selection condition is small, and the generation of points takes certain time.

To refine the tentative surface near the minimum, 3559 points were calculated by the MP4 method in the cc-VQZ basis. All one-dimensional and two-dimensional surfaces, as well as random points with the energy lower than 20000 cm⁻¹, were calculated. For accuracy control, 50 points were also calculated by the CCSD(T) method in the cc-VQZ basis. The simultaneous use of different quantum-chemical calculation methods requires a reduction of the number of points calculated by the CCSD(T) method in the cc-VTZ basis. Upon the reduction, the equilibrium geometry of CCSD(T) in the cc-VTZ basis should transit into equilibrium geometry of MP4 in the cc-VQZ basis. Since the equilibrium torsion angles in both cases are equal to 120°, only the coordinates r_{Cl} , r_{H} , and q are subject to reduction for all points of CCSD(T) in the cc-VTZ basis. Different reduction methods yielded quite close results. We employ one of the simplest methods: multiplication by the ratio of the equilibrium coordinates calculated by the MP4 method in the cc-VQZ to the equilibrium coordinates calculated by the VTZ method. In addition, the quantum-chemical energy of all points of the VTZ reduction was increased by the energy difference at the minimum $E(\text{VQZ}) - E(\text{VTZ})$. The standard deviations of fitting of different PESs with and without reduction are summarized in Table 2.

The least-squares fitting of all *ab initio* points yielded 4.7 cm⁻¹ rms deviation. The weighting function W was taken equal to 1 if $E \leq 20000$ cm⁻¹; $W(E) = \exp\{-(E - 20000)/2000 + 5[(E - 20000)/20000]^2\}$ if $20000 < E \leq 40000$ cm⁻¹, and 0 if $E > 40000$ cm⁻¹. The points *ab initio* calculated by the CCSD(T) method in the cc-VTZ basis were taken with the weight $0.05 \cdot W(E)$, and their values were reduced. In addition, only 5805 of 6652 VTZ points were included in fitting. The VTZ points close to VQZ points with the energy below 10 000 cm⁻¹ were rejected.

Table 2. Standard deviation of PES fitting, cm⁻¹

PES order	Number of parameters	Fitting of 6652 points of CCSD(T) in cc-VTZ basis. Equilibrium configuration		Fitting of all points. Equilibrium configuration of MP4 in cc-VQZ basis	
		CCSD(T) in cc-VTZ basis	MP4 in cc-VQZ basis	with reduction of points of CCSD(T) in cc-VTZ basis	without reduction
4	153	20	35	33.4	34.2
5	402	7.3	21	12.4	14.3
6	967	2.2	16	4.7	8.5

The calculations in the less accurate cc-VTZ basis were needed to increase the number of points with the energy above $10\,000\text{ cm}^{-1}$ and to better describe PES far from the minimum.

The analytical form of the potential energy surface is presented as a sum of balanced binary trees from symmetrized powers of elementary radial and angular functions.^{6,7} The elementary radial functions were taken in the form

$$f^n(r) = (1 - e^{-0.5(r-r_0)})^n,$$

and the elementary functions of bending angles were

$$f^n(q) = [\cos(q) - \cos(q_0)]^n.$$

For better convergence, the torsion functions are taken as follows

$$f^n(t) = (\cos(t) - \cos(t_0) + \alpha[\cos(t) - \cos(t_0)]^2)^n,$$

where $\alpha=0.3$ for $n < 3$ and 0 for $n \geq 3$. Without the use of square terms $f^n(t)$, the standard deviation of the fitting with the reduction was 6.2 cm^{-1} , whereas with square terms it was 4.7 cm^{-1} . Analogous improvement of the convergence with the use of square terms is also observed for methane.

Calculation of energy levels

In spite of our efforts, we failed to fully get rid of nonphysical minima in PES. The PES constructed can be used only with highly localized wave functions. In addition, since we had to construct two-dimensional symmetrized torsion wave functions, for calculating matrix elements additional localization of two-dimensional torsion functions was carried out through the introduction of the additional torsion potential. The dependence of the vibrational energy levels on this additional potential was less than 10^{-3} cm^{-1} . To find the vibrational energy levels, the localized symmetrized wave functions (WFs) were used:

$$F^{G\sigma}(n_1n_2n_3, n_t, n, n_4n_5n_6) =$$

$$= \{Q_{n_1}(q_1)Q_{n_2}(q_2)Q_{n_3}(q_3)\} \times$$

$$\times T_{n_t}^{G_t\sigma_t}(t_{12}, t_{13})R'_n(r_{Cl})\{R_{n_4}(r_1)R_{n_5}(r_2)R_{n_6}(r_3)\},$$

where G and σ are the WF representation and series; $n_1 - n_6$ are the numbers of one-dimensional localized WFs; $Q(q)$ is the one-dimensional localized WF of the angle between \mathbf{r}_{Cl} and \mathbf{r}_H . $T^{n_t G_t \sigma_t}(t_{12}, t_{13})$ is the symmetrized and localized two-dimensional WF of two torsion angles; $R'(r)$ and $R(r)$ is the one-dimensional localized WF of the radial coordinates. The use of symmetry allowed the problem on eigenvalues to be solved separately for each of the blocks A_1 , A_2 , E_a , and E_b . The dimensions of the blocks E_a and E_b amounted to $1/3$ of the dimension of the initial non-symmetrized block. The vibrational Hamiltonian was used in the form presented in Ref. 8. Table 3 gives the experimental⁹ and calculated energy levels for two isotopic modifications of CH_3Cl . The comparison shows quite a satisfactory agreement of all energy levels, except for ν_6 . The poor description of ν_6 is attributed to the fact that the sixth-order PES is insufficient for the description of the torsion part of the potential. The last column presents the difference between calculation errors for two isotopic species. The relatively small difference confirms the possibility of using *ab initio* calculations for determination of isotopic shifts.

Conclusions

A logical continuation of this work should be the improvement in description of the torsion part of the potential, as well as the correction of the potential, taking into account the experimental energy levels.

Table 3. Vibrational energy levels of $\text{CH}_3^{35}\text{Cl}$ and $\text{CH}_3^{37}\text{Cl}$

Level	35		37		Exp ₃₅ - Calc ₃₅ - Exp ₃₇ + Calc ₃₇
	Exp	Calc	Exp	Calc	
ν_3	732.84216	730.717	727.02947	724.918	0.014
ν_6	1018.07090	1195.740	1017.68240	1195.335	-0.017
ν_2	1354.88112	1358.966	1354.69081	1358.779	0.004
ν_5	1452.17844	1469.912	1452.15524	1469.876	-0.013
$2\nu_3$	1456.76266	1453.064	1445.35088	1441.666	0.014
$\nu_3 + \nu_6$	1745.37113	1919.507	1739.23566	1913.372	0.001
$2\nu_6(A_1)$	2029.37523	2379.943	2028.59289	2379.142	-0.018
$2\nu_6(E)$	2038.32636	2392.352	2037.55525	2391.544	-0.037
$\nu_2 + \nu_3$	2080.53577	2082.950	2074.45262	2076.871	0.004
$3\nu_3$	2171.88765	2167.180	2155.11791	2150.415	0.005
$\nu_3 + \nu_5$	2182.57173	2197.479	2176.75039	2191.666	0.008
$\nu_2 + \nu_6$	2367.72216	2549.443	2367.13939	2548.846	-0.014
$\nu_5 + \nu_6(A_1)$	2464.90270	2663.141	2464.46907	2662.697	-0.010
$\nu_5 + \nu_6(A_2)$	2467.66902	2666.675	2467.24701	2666.229	-0.024
$\nu_5 + \nu_6(E)$	2461.64821	2655.283	2461.48491	2654.834	-0.286
$2\nu_3 + \nu_6(E)$	2463.81796	2634.756	2451.90461	2623.114	0.271
$2\nu_5(A_1)$	2879.360	2909.420	2879.057	2909.346	0.229
ν_1	2967.777	2974.323	-	2974.352	-
ν_4	3039.286	3044.292	3039.176	3044.268	0.085

For the latter, the dimensionality of the basis should be increased for a more accurate description of the high-excited vibrations and for the possibility of calculating rotational-vibrational energy levels.

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