The large amplitude motions of methylamine from the perspective of the highly correlated ab initio methods

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ABSTRACT

CCSD(T)-F12 theory in connection with extended basis sets is employed to determine the electronic ground state spectroscopic parameters of methylamine at low temperatures. The geometry, the rotational constants, all the fundamental frequencies, the dipole moment and its components, and the centrifugal distortion constants, are provided. The ground vibrational state rotational constants were found to be A_0 = 103067.15 MHz, B_0 = 22588.29 MHz, and C_0 = 21710.50 MHz and the dipole moment to be 1.4071D. Fermi displacements of the vibrational bands are predicted.

The low vibrational energy levels corresponding to the large amplitude motions are determine variationally using a flexible three-dimensional model depending on three variables: the HNH bending, the NH_2 wagging and the CH_3 torsional coordinates. The computed levels are compared with previous experimental and calculated energies. Methylamine parameters are very sensitive to the level of ab initio calculations.

1. Introduction

Methylamine (CH_3-NH_2), the simplest primary amine, plays important roles in gas phase chemistry. In air quality studies, it is considered a Volatile Organic Compound (VOC) precursor of Secondary Organic Aerosols (SOA) [1]. In 1974, it was detected in the interstellar medium, where it is considered a relatively abundant species [2,3].

Spectroscopic experimental and theoretical studies of methylamine are recurrent [4–27]. However, the motivation of many of these works concerns more to the peculiar molecular structure than to its applications [4–7], because it is contemplated as a prototype small non-rigid molecule where two interacting large amplitude motions, the torsion of the methyl group and the NH_2 wagging, govern its internal dynamics [4–5,7–10]. The electronic ground state potential energy surface displays six minima separated by relatively low potential energy barriers. Tunneling splittings are significant making challenging the interpretation and assignments of the spectra and attracting the attention of the scientific community dealing with theoretical spectroscopy. If non-rigidity is considered, the most abundant isotopologue can be classified in the G_{12} molecular symmetry group [7].

Methylamine microwave spectrum was first reported in 1947 [11]. From 1950, measurements of the high resolution infrared spectra and the rotational spectra are frequent [12–19]. Assignments of the rotational spectra have been performed for the ground and the two first excited torsional states [15–17,19]. Recent contributions evidence the incessant interest of methylamine [20–26]. Examples are the work of Illushin et al. [20], who have recorded 513 rotational transitions in the 49–326 GHz region, and the recent study of the first excited torsional state performed by Gulacyk et al. [21]. Recent efforts have been made to develop optimum effective Hamiltonians and fitting programs [22–23]. Examples are the works of Kleiner and Hougen [22], who have developed a new hybrid program for fitting rotationally resolved spectra of floppy molecules with one torsional and one inversion motions, and Gulaczyk and Kreglewski [23], who have adapted the Hamiltonian for the explicit treatment of the coupling between excited inversion-torsion states [23]. In new contributions, the high resolution infrared spectrum is studied in the regions of the CH_3 and CH stretching modes [24–26]

Few ab initio calculations devoted to the far infrared spectral region are available for methylamine. Some years ago, we performed a series of theoretical studies of the inversion-torsional spectrum using quantum chemical methods and by solving variationally two-dimensional Hamiltonians (2D) for obtaining the low vibrational energy levels [27–29]. In the second paper of the series [28], the interaction between the NH_2 wagging and bending modes was explicitly described in a 2D-model. In these works, performed using modest computational tools, the Hamiltonian param-
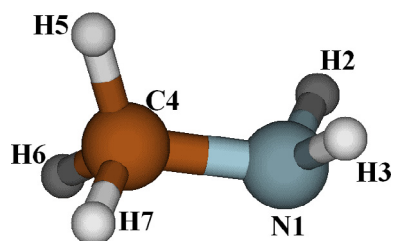
Fig. 1. The equilibrium geometry of methylamine.

eters were estimated at the second order Möller-Plesset level of theory. Later on, the results were improved adding the influence of the zero-point energy correction [29]. The resulting energy levels were accurate enough to be compared with those estimated by Kreglewsky using experimental data although they present important deviations [8,9].

Twenty years later, very sophisticated computational procedures are suitable for obtaining very accurate results. From the perspective of the highly correlated ab initio methods, methylamine can be considered a prototype target given the molecular size, the non-rigid properties and the attractiveness of the species. The size allows one to perform very accurate ab initio calculations to obtain reliable properties suitable as starting parameters for the fitting of effective Hamiltonian parameters. On the other hand, the attractiveness means the existence of numerous experimental data to evaluate the pure theoretical results. The species can be considered a benchmark to test our procedures.

The aim of this paper is the application of explicitly correlated coupled cluster methods (CCSD(T)-F12) to simulate the methylamine far infrared spectra. The present study strives to update results by improving the old procedures [28,29]. The improvements involve the employment of a three-dimensional Hamiltonian (3D) and the level of ab initio calculations. In the present paper, three coordinates, the HNH bending, the NH_2 wagging and the CH_3 torsion are considered explicitly because the separation of HNH bending and the NH_2 wagging seems to be not appropriate. In the old papers, two coordinates were considered to be indepen-

Table 1
Structural parameters (distances in Å; angles in degrees) and spectroscopic parameter of methylamine.

	CCSD(T)-F12 AVTZ		Calc.	Exp. [20]
E (a.u)	−95.732912	$\mu_B(D)$[b]	1.4071	
H2N1 = H3N1	1.0119	$\mu_A(D)$[b]	0.4270	
C4N1	1.4645	$\mu_C(D)$[b]	1.3408	
H5C4	1.0957	*Rotational constants (in MHz)*		
H6C4 = H7C4	1.0898	A_e	103855.40	
H3N1H2	106.6	B_e	22803.13	
H2N1C4 = H3N1C4	110.1	C_e	21926.39	
H5C4N1	114.8	A_0	103067.15	103155.887
H6C4N1 = H7C4N1	109.0	B_0	22588.29	22608.260
H5C4N1X[a]	270.0	C_0	21710.50	21730.562
H6C4N1H5 = −H7C4N1H5	121.5			

Fundamental frequencies (in cm^{-1})

Mode	Assign.[c]	ω CCSD(T)-F12 AVTZ)	v ($\omega + \Delta v$[b])	Exp. [Ref.] (gas phase)		
1	NH_2 st	3509	3357	3361	IR	[46]
				3360	Raman	
2	CH_3 st	3084	2953	2961	IR	[46]
				2960	Raman	[46]
3	CH_3 st	3002	2891	2820	IR	[46]
				2820	Raman	[46]
4	NH_2 b	1666	1610	1623		[46]
5	CH_3 b	1510	1470	1473	IR	[46]
6	CH_3 b	1463	1450	1430	IR	[46]
7	HCN b	1179	1134	1130	IR	[46]
8	NC st	1070	1043	1044	IR	[46]
9	NH_2 wag	850	762	780	IR	[46]
10	NH_2 st	3591	3423	3427	IR	[46]
11	CH_3 st	3121	2984	2985		[46]
12	CH_3 b	1528	1468	1485	Estimated	[46]
13	HNC b	1354	1310			
14	CH_3 b	975	963	1195	Estimated	[46]
15	CH_3 tor	296	274	268	IR	[46]
				264.58204	FIR	[16]
				264.58279	MW	[16]
				264.58314	MW	[19]
				264.58337		[21]

Centrifugal distortion constants[b]

	MP2/AVTZ	Exp. [20]		MP2/AVTZ	Exp [20]
Δ_J/MHz	0.03866	0.0394506(18)	Φ_J(Hz)	−0.16246	
Δ_K/MHz	0.65423	0.701049(24)	Φ_K(Hz)	21.98997	24.25(50)
Δ_{JK}/MHz	0.17073	0.170983(15)	Φ_{JK}(Hz)	−2.67886	
δ_J/MHz	0.00168	0.00175679(17)	Φ_{KJ}(Hz)	−12.33841	
δ_K/MHz	−0.25408	−0.33778(14)	ϕ_J(Hz)	−0.02334	
			ϕ_K(Hz)	−126.4114	
			ϕ_{JK}(Hz)	−5.27331	

[a] X represents a ghost atom lying in the HNC plane. The NX distance is perpendicular to the HNC angle bisector.
[b] Dipole moment and Centrifugal distortion constants calculated with MP2/AVTZ. Anharmonic displacements (Δv), were computed using MP2/VTZ.
[c] st = stretching; b = bending; w = wagging; tor = torsion.