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Submillimeterwave spectrum of CH_2PH and equilibrium structures of CH_2PH and CH_2NH

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Abstract

The rotational spectrum of phosphaethene (CH_2PH) was reinvestigated. One hundred and nineteen new lines were measured in the submillimeter range from 500 to 650 GHz. The determination of the centrifugal distortion constants is significantly improved. As the molecule is close to symmetric prolate top, both reduction *A* and *S* were compared. The equilibrium structure has been derived from experimental ground state rotational constants and ab initio rovibrational interaction parameters. This semi-experimental structure is in excellent agreement with the ab initio structure calculated at the CCSD(T) level of theory using a basis set of quintuple-zeta quality and a core correlation correction. The structure of CH_2PH was compared to that of CH_2NH which was also determined for this goal. It is found that the semi-experimental structure of CH_2NH is less accurate than the ab initio structure. It is also found that the methylene group is much more asymmetric in CH_2NH than in CH_2PH.

Keywords: Anharmonic force field; Ab initio; Equilibrium structure; Submillimeterwave; CH_2NH; CH_2PH

1. Introduction

Mainly due to its instability, there are not many experimental studies of phosphaethene (or methylidenephosphine), $H_2C{=}PH$. It was first synthesized in 1976 by pyrolysis of dimethylphosphine, $(CH_3)_2PH$ and identified by microwave spectroscopy [1]. Only the $J = 1 \leftarrow 0$ transition was measured. In 1981, Kroto et al. [2,3] extended the measurements up to 40 GHz for the parent species and for several isotopologues. They determined the dipole moment as well as an empirical structure. Brown et al. [4] improved the structure and the distortion constants with some measurements up to 125 GHz. The hyperfine structure due to the spin–rotation constants of ^{31}P was measured by Dyall et al. [5]. In all these studies, phosphaethene was obtained by pyrolysis. In 1988, Lacombe et al. [6] synthesized CH_2PH with a vacuum gas-solid reaction (VGSR) which enabled them to characterize its electronic structure.

This last approach makes the measurement of the rotational spectrum much easier. We used it to measure the submillimeter-wave spectrum in order to be able to get a better prediction of the spectrum which may be useful for the possible detection of this molecule in planetary atmospheres [7] or interstellar space.

As there is not yet an accurate equilibrium structure for this molecule, we investigated the possibility to determine such a structure by combining experimental ground state rotational constants and ab initio rovibrational interaction parameters (semi-experimental structure). We checked the accuracy of this structure by high level ab initio calculations. Finally, we also determined an accurate equilibrium structure for the structurally similar molecule, CH_2NH in order to compare it to that of CH_2PH and to better understand which parameters affect the accuracy of these structures. This comparison is particularly important because

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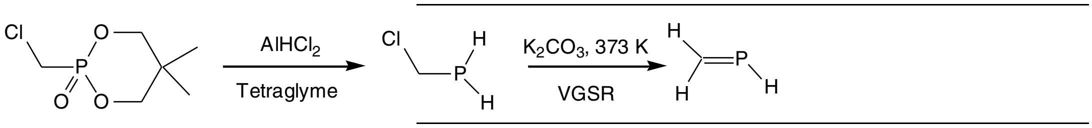
many experimental spectroscopic data have already been gathered for CH_2NH which will permit to check the accuracy of the computed anharmonic force field. A summary of the spectroscopic work may be found in Refs. [8,9]. The anharmonic potential of CH_2NH has already been calculated [10,11] but only with small basis sets.

2. Experimental details



The synthesis of CH_2PH has already been reported by Lacombe et al. [6]. The chloromethylphosphine precursor was prepared by reduction of 2-(chloromethyl)-5,5-dimethyl-, 2-oxide-1,3,2-dioxaphosphorinane by dichloroalane ($AlHCl_2$) in tetraglyme [12]. This phosphonate was used instead of chloromethylphosphonic acid, diethyl ester [6] to avoid the presence of small amounts of ethanol in the products. Chloromethylphosphine was then slowly vaporized on solid potassium carbonate heated at 373 K (previously dried by heating it at 573 K for 2 h under vacuum). Methylidenephosphine was characterized by direct analysis of the gaseous flow. The mesasurements were performed with a continuous flow. The pressure in the cell was 30 mTorr.

The source of the submillimeter spectrometer is a Russian backward-wave oscillator (Istok). It is phase locked on the harmonic of an active sextupler from Millitech (75–110 GHz). The harmonics are generated with an antiparallel pair Schottky diode from Virginia diode Inc. mounted in a parabolic structure. The detector is an InSb He-cooled bolometer. The uncertainty of the measurements is better than 100 kHz.

3. Analysis of the spectrum

The first prediction of the spectrum was made using the parameters determined from a fit of the microwave lines previously measured by Kroto et al. [3] and Brown et al. [4]. We first searched for μ_a-type lines because they are stronger ($\mu_a = 0.7233$ D to be compared to $\mu_b = 0.4657$ D [3]) and predicted more accurately. First, the lines corresponding to the rotational structure of the $J = 17 \leftarrow 16$ transitions were found close to their prediction. They were fitted together with the microwave lines in order to improve the prediction. This iterative procedure was repeated allowing us to assign 119 new lines (including 57 μ_b transitions) in the range from 525 to 650 GHz. The maximum value of J was equal to 50.

Finally these new submillimeter transitions were fitted together with the 34 ones from the previous studies [3,4]. In total 153 transitions were fitted. The weight of the frequencies used in the least squares was determined by the iteratively reweighted least-squares method [13,14]. At the end, we obtained quite similar weights for all transitions which are listed in Table S1 of the Supplementary material. This indicates that there is no misassignment. First, the standard Watsonian in its I^r representation and A reduction was used [15]. The standard deviation of the fit was 75 kHz. The derived molecular parameters are reported in Table 1. As the molecule is close to a prolate symmetric top, ($\kappa = -0.971$), we also tried the S reduction which should be more appropriate. However, the fit was not better, the standard deviation being even slightly larger

Table 1
Fitted spectroscopic constants of CH_2PH

A-reduction			*S*-reduction	
			Present	Previous[a]
A (MHz)	138 503.1218 (54)	A (MHz)	138 503.1367 (55)	138 503.2892 (394)
B (MHz)	16 418.1015 (94)	B (MHz)	16 417.78 882 (97)	16 417.7945 (41)
C (MHz)	14 649.08 234 (82)	C (MHz)	14 649.40 464 (79)	14 649.4073 (42)
Δ_J (kHz)	16.92 109 (89)	D_J (kHz)	16.36 509 (94)	16.419 (53)
Δ_{JK} (kHz)	212.306 (12)	D_{JK} (kHz)	215.710 (12)	216.07 (83)
Δ_K (MHz)	2.42 411 (26)	D_K (MHz)	2.42 214 (27)	2.4410 (124)
δ_j (kHz)	1.89 145 (12)	d_1 (kHz)	−1.88 819 (10)	−1.8876 (97)
δ_k (kHz)	158.055 (55)	d_2 (Hz)	−284.49 (10)	−284.04 (252)
Φ_{JK} (Hz)	1.0197 (61)	H_{JK} (mHz)	813.4 (62)	
Φ_{KJ} (Hz)	2.22 (33)	H_{KJ} (Hz)	2.999 (34)	
Φ_K (Hz)	−177.6 (33)	H_K (Hz)	−162.2 (34)	
ϕ_{jk} (Hz)	1.388 (27)	H_2 (mHz)	3.719 (51)	
σ[b] (kHz)	75		76	
No. of lines	153			
Max. K_a''	17			
Max. J''	20			

[a] From Ref. [4].

[b] Standard deviation of the fit.