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THEORETICAL PREDICTION OF VIBRATIONAL SPECTRA: THE HARMONIC FORCE FIELD AND THE VIBRATIONAL SPECTRUM OF 4-METHYLPYRIDINE

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ABSTRACT: The geometry, complete harmonic force field and dipole moment derivatives have been computed for 4-methylpyridine at the Hartree-Fock level using a 4-21 basis set of Gaussian orbitals. A set of eleven scale factors, six of which were previously derived from benzene and the other five for the vibrational motions of the methyl group from toluene by fitting their computed force fields to their observed vibrational spectra, was used to scale the computed harmonic force constants of 4-methylpyridine. The vibrational frequencies and the associated infrared absorption intensities of 4-methylpyridine were then predicted from this scaled force field without any fitting to the experimental data of 4-methylpyridine. Comparison with experimental spectra permitted a few corrections to be made in previous experimental or semiempirical assignments. The mean-deviations between experimental and predicted frequencies was only 5.6 cm^{-1} for the non-CH stretching frequencies or 8.3 cm^{-1} overall. Computed intensities are qualitatively in agreement with experiment. The optimization of scale factors for the five methyl vibrational motions produced a trivial improvement in the fit.

INTRODUCTION

The direct prediction of accurate vibrational force fields, which may be used to improve the completeness and reliability of vibrational spectral assignments for medium-sized organic molecules, poses an interesting challenge to current quantum chemical research[1]. It is known[2] that absolute calculations of molecular vibrational force fields with high accuracy would require an *ab initio* calculation using a basis set at least triple zeta in the valence shell with added polarization functions and a thorough treatment of electron correlation, a level of computation which cannot even be contemplated with existing computers for medium-sized molecules. Recently an effective computational procedure has been developed by combining theoretical with experimental information. The methodology, producing what is called a Scaled Quantum Mechanical (SQM) force field, is summarized in a recent paper on a variety of small molecules[3]. Briefly, it involves calculation of the complete harmonic force field at some appropriate quantum mechanical level (often, but not necessarily, double zeta Hartree-Fock) and deriving scale factors for different classes of molecular motions to fit the vibrational spectra calculated from that force field to the definitely assigned portions of the experimental spectra. The most interesting and significant part of this method is the assumed transferability of the scale factors, which represent systematic errors in the calculation of related quantities between similar molecules. If the transferability is good, this opens the way for the pure prediction of vibrational frequencies by calculating the force field of the molecule in question and scaling that force field by factors taken over from a known related molecule. The vibrational spectrum of the new molecule can then be calculated *a priori* without requiring any knowledge of the experimenal spectrum of the molecule under study.

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In a recent series of papers[4-9], we have been testing the transferability of sets of scale factors from known molecules to those whose spectra are entirely unknown, or in some test cases where they are assumed to be unknown until after complete predictions have been made. In the first example, the force field of benzene was calculated and fit with a few scale factors to the observed benzene spectrum[4]. After this, the complete harmonic force field of pyridine was calculated and scaled with the scale factors transferred from benzene, giving an SQM (pyridine 4-21/benzene)[3] force field. It is important in deriving such a Scaled Quantum Mechanical force field that calculations on the new molecule be carried out at the same level (in our cases with a split valence shell 4-21 basis) as used on the reference molecule from which the scale factors are transferred. For pyridine, the predicted spectrum showed an agreement with the known observed spectrum with an average deviation of 5.7 cm^{-1} in the non-CH frequencies of the in-plane motions, or 9.6 cm^{-1} for all in-plane frequencies[5], and 8.5 cm^{-1} for the out of plane frequencies[6]. Even the CH stretching frequencies, the ones most strongly perturbed, were well within the 1% accuracy that had been set as a conservative goal. Similar procedures have also been carried out for naphthalene, aniline and toluene. Three similar SQM force fields (naphthalene 4-21/benzene, aniline 4-21/benzene and toluene 4-21/benzene) were derived from calculations on naphthalene[7], aniline[8] and toluene[9] corrected by the scale factors derived from benzene. In these results, the computed vibrational spectra have shown that completely *a priori* predictions with an average deviation of less than 10 cm^{-1}, very similar to the results obtained for pyridine, could be made by using the transfer of scale factors from the known molecule to the related molecule under study.

It should be emphasized that this method does not assume that the force constants are similar in related molecules, but makes the much smaller assumption that the *error* in calculating the force field is similar for related types of vibrational motions in related molecules as determined by the identical computational procedure. The accuracy actually obtained has been found to be even better than the independent harmonic oscillator approximation should allow, suggesting that the transferred scale factors correct not only for correlation and basis set effects in the calculations but also for similarities in anharmonicity between similar motions in the related molecules.

As a further test, a similar study is presented here for 4-methylpyridine. Since the structure of 4-methylpyridine is in part similar to that of pyridine (the ring) and to that of toluene (the methyl group), the calculation of the vibrational spectrum of 4-methylpyridine is a helpful test of the transferability of the scale factors for the six-member ring from benzene and for the methyl group from toluene.

For 4-methylpyridine the infrared spectra of both the liquid and vapor states and the Raman spectrum of the liquid state were obtained by Long *et al*.[10] in 1957, followed by other workers[11]. Green and his co-workers[12] reported a rough assignment of the vibrational spectrum, the experimental values being mostly taken from the previous measurement of Long *et al*.[10]. In 1982, Draeger[13] calculated the vibrational spectrum of 4-methylpyridine by using the transfer of force constants among the methyl derivatives of pyridine and made an assignment for 4-methylpyridine. In spite of these several efforts, several uncertain experimental assignments, controversial in the previous reports, remain to be clarified.

METHODS AND RESULTS

Ab initio calculations have been performed by the Hartree-Fock gradient program TEXAS[14] using the standard 4-21 atomic basis set[15]. Both the computational techniques[15] and the methods used in obtaining the SQM force field[3] have been previously described and are the same as used in the previous studies[4-9].

Table 1. Reference (equilibrium) geometry of 4-methylpyridine[a]

R(1,2)	1.337	∠(1,2,3)	122.9
R(2,3)	1.392	∠(2,3,4)	119.3
R(3,4)	1.398	∠(3,4,5)	117.5
R(4,5)	1.398	∠(4,5,6)	119.3
R(5,6)	1.392	∠(5,6,1)	122.9
R(6,1)	1.337	∠(6,1,2)	118.1
R(7,2)	1.076	∠(7,2,1)	116.4
R(8,3)	1.076	∠(8,3,2)	120.1
R(9,4)	1.506	∠(9,4,3)	121.3
R(10,5)	1.076	∠(10,5,6)	120.1
R(11,6)	1.076	∠(11,6,1)	116.4
R(12,9)	1.090	∠(12,9,4)	110.2
R(13,9)	1.087	∠(13,9,4)	111.0
R(14,9)	1.087	∠(14,9,4)	111.0
		∠(12,9,13)	108.0
		∠(13,9,14)	108.5
		∠(14,9,12)	108.0

[a] See Fig. 1 for labeling of atoms. Geometry taken from the corrected theoretical one. Distances in Å, angles in degree.

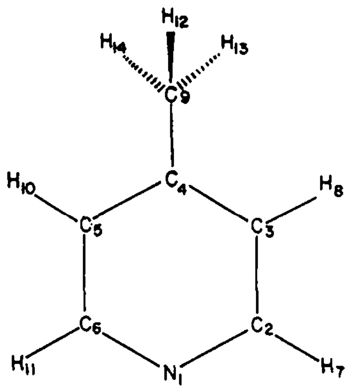

Figure 1. Labeling of the atoms in 4-methylpyridine. C_9 is in the ring plane.

The geometry, which we have used as the reference state, is listed in Table 1. This reference geometry at which the theoretical force field is evaluated[3] should be the true equilibrium geometry[15] and can be chosen using either of two possible methods: one can start from either the theoretical geometry or the experimental one. In order to facilitate comparison with the results for pyridine and toluene in which the experimentally corrected theoretical geometries have been used, this can best be approached in our case by using the computed minimum-energy geometry with suitable small corrections for consistent errors arising from neglect of electron correlation and use of a finite basis set. The geometry of 4-methylpyridine was optimized at two conformations. One, which we shall call the planar form, has one methyl C-H bond in the plane of the pyridine ring. The other, called the orthogonal form, is obtained by a 30° rotation of the methyl group and has one methyl C-H bond perpendicular to the ring plane. These two conformations must represent extrema in the potential function for the methyl group rotation. The computation gave results essentially the same as for toluene[16]. In both cases the orthogonal form is more stable, but only by a vanishingly small 3 cal/mole. Microwave spectroscopic studies[17,18] have also given a value of about 14 cal/mole for both rotation barriers. The entire carbon skeleton is constrained by symmetry to be coplanar in the planar conformation, and deviations from planarity in the orthogonal form are found to be vanishingly small. It is reasonable for us to obtain the true equilibrium geometry by using empirical correction from the orthogonal form, for which the deviations from planarity can be neglected, for comparison with toluene[9,16] since such small changes do not significantly affect force constants. We have used the scheme outlined in Ref. 15 to obtain corrections for the C-C and C-H bond lengths ($R(C_2\text{-}C_3) = R(C_5\text{-}C_6) = +0.011$Å, $R(C_4\text{-}C_3) = R(C_4\text{-}C_5) = +0.010$Å, $R(C_4\text{-}C_9) = -0.010$Å and $R(C\text{-}H) = +0.005$Å), and taken the correction of +0.004Å from pyridine[5] for the C-N bonds.

The harmonic vibrational force field of 4-methylpyridine has been computed as previously described[15] by numerical differentiation of the analytically determined energy gradient at displaced geometries using the program TEXAS. Internal coordinates were introduced according to the recommendations of our earlier paper[15] and are shown in Table 2. Finite displacements of 0.02Å or 2° in individual valence coordinates were used, with both positive and negative changes being made to minimize the effect of cubic anharmonicity. The resulting theoretical harmonic vibrational force field consisting of 780 independent elements is given in Table 3.

Table 2. Internal coordinate system[a]

No.	Internal Coordinate	Description
1,6	$q_1 = R(1,2)$; $q_6 = R(6,1)$	CN stretch
2-5	$q_2 = R(2,3)$; $q_3 = R(3,4)$; $q_4 = R(4,5)$; $q_5 = R(5,6)$	CC stretch
7,8,10,11	$q_7 = R(7,2)$; $q_8 = R(8,3)$; $q_{10} = R(10,5)$; $q_{11} = R(11,6)$	C-H stretch
9	$q_9 = R(9,4)$	Me-C stretch
12	$q_{12} = R(12,9) + R(13,9) + R(14,9)$	C-H stretch (Me)
13	$q_{13} = 2R(12,9) - R(13,9) - R(14,9)$	
14	$q_{14} = R(13,9) - R(14,9)$	
15	$q_{15} = \alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6$	Ring deformation
16	$q_{16} = 2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6$	
17	$q_{17} = \alpha_2 - \alpha_3 + \alpha_5 - \alpha_6$	
18,19	$q_{18} = \angle(7,2,1) - \angle(7,2,3)$; $q_{19} = \angle(8,3,2) - \angle(8,3,4)$	C-H deformation
21,22	$q_{21} = \angle(10,5,6) - \angle(10,5,4)$; $q_{22} = \angle(11,6,1) - \angle(11,6,5)$	
20	$q_{20} = \angle(9,4,3) - \angle(9,4,5)$	Me-C deformation
23	$q_{23} = \vartheta_1 + \vartheta_2 + \vartheta_3 - \beta_1 - \beta_2 - \beta_3$	C-H bend (Me)
24,25	$q_{24} = 2\vartheta_1 - \vartheta_2 - \vartheta_3$; $q_{25} = \vartheta_3 - \vartheta_2$	
26,27	$q_{26} = 2\beta_1 - \beta_2 - \beta_3$; $q_{27} = \beta_2 - \beta_3$	
28	$q_{28} =$ 7 out of (1,3,2) plane	C-H wagging
29	$q_{29} =$ 8 out of (2,4,3) plane	
31	$q_{31} =$ 10 out of (4,6,5) plane	
32	$q_{32} =$ 11 out of (5,1,6) plane	
30	$q_{30} =$ 9 out of (3,5,4) plane	Me-C wagging
33	$q_{33} = \tau_1 - \tau_2 + \tau_3 - \tau_4 + \tau_5 - \tau_6$	Ring torsion
34	$q_{34} = 2\tau_1 - \tau_2 - \tau_3 + 2\tau_4 - \tau_5 - \tau_6$	
35	$q_{35} = \tau_2 - \tau_3 + \tau_5 - \tau_6$	
36	$q_{36} = \tau_1' + \tau_2' + \tau_3' + \tau_4' + \tau_5' + \tau_6'$	Me-Ring torsion

[a] See Fig. 1 for labeling of atoms. $\alpha_1 = \angle(6,1,2)$; $\alpha_2 = \angle(1,2,3)$; $\alpha_3 = \angle(2,3,4)$; $\alpha_4 = \angle(3,4,5)$; $\alpha_5 = \angle(4,5,6)$; $\alpha_6 = \angle(5,6,1)$; $\vartheta_1 = \angle(13,9,14)$; $\vartheta_2 = \angle(12,9,14)$; $\vartheta_3 = \angle(12,9,13)$; $\beta_1 = \angle(12,9,4)$; $\beta_2 = \angle(13,9,4)$; $\beta_3 = \angle(14,9,4)$; $\tau_1 =$ dihedral $\angle(1,6,5,4)$; $\tau_2 = d\angle(2,1,6,5)$; $\tau_3 = d\angle(3,2,1,6)$; $\tau_4 = d\angle(4,3,2,1)$; $\tau_5 = d\angle(5,4,3,2)$; $\tau_6 = d\angle(6,5,4,3)$; $\tau_1' = d\angle(12,9,4,3)$; $\tau_2' = d\angle(12,9,4,5)$; $\tau_3' = d\angle(13,9,4,3)$; $\tau_4' = d\angle(13,9,4,5)$; $\tau_5' = d\angle(14,9,4,3)$; $\tau_6' = d\angle(14,9,4,5)$. $\tau = d\angle(a,b,c,d)$ is defined as the angle between the planes abc and bcd. τ is positive if a is in the direction of the vector product $\overrightarrow{cb} * \overrightarrow{cd}$.

Table 3. Theoretical and scaled quantum mechanical (SQM) force fields of 4-methylpyridine[a]

Potential energy term	Theor.	SQM(1)	SQM(2)
1 -1	7.79	7.09	7.09
-2	1.13	1.03	1.03
-3	-.67	-.61	-.61
-4	.82	.74	.74
-5	-.75	-.69	-.69
-6	1.05	.96	.96
-7	.22	.20	.20
-8	-.01	-.01	-.01
-9	-.07	-.06	-.06
-10	-.03	-.03	-.03
-11	-.02	-.02	-.02
-14	-.01	-.01	-.01
-15	.27	.23	.23
-16	.48	.41	.41
-17	.31	.27	.27
-18	.36	.31	.31
-19	.01	.01	.01
-20	.02	.02	.02
-21	-.03	-.03	-.03
-22	.03	.03	.03
-23	.01	.01	.01
-25	.01	.01	.01
-36	.01	.01	-.01
2 -2	7.20	6.56	6.56
-3	.90	.82	.82
-4	-.65	-.59	-.59
-5	.61	.55	.55
-6	-.75	-.69	-.69
-7	.09	.08	.08
-8	.07	.06	.06
-9	-.01	-.01	-.01
-10	-.02	-.02	-.02
-11	-.02	-.02	-.02
-14	.01	.01	.01
-15	-.01	-.01	-.01
-16	-.29	-.25	-.25
-17	-.08	-.07	-.07
-18	-.18	-.15	-.15
-19	.18	.15	.15
-20	-.02	-.02	-.02
-21	.03	.03	.03
-22	-.03	-.03	-.03
-24	.01	.00	.00
-25	-.01	-.01	-.01
-27	-.01	-.01	-.01
-36	-.01	-.01	-.01
3 -3	7.11	6.48	6.48
-4	.93	.84	.84
-5	-.65	-.59	-.59
-6	.82	.74	.74
-7	-.01	-.01	-.01
-8	.08	.07	.07
-9	.25	.22	.22
-10	-.01	-.01	-.01
-11	-.03	-.03	-.03
-15	.02	.02	.02
-16	.14	.12	.12
-17	-.31	-.27	-.27
-18	-.01	-.01	-.01
-19	-.21	-.18	-.18
-20	.26	.23	.24
-21	-.01	-.01	-.01
-23	-.02	-.02	-.02
-24	-.01	-.01	-.01
3 -25	.01	.01	.01
-26	-.01	-.00	-.00
-27	-.04	-.04	-.04
-30	.01	.01	.01
-36	.01	.01	.01
7 -7	6.01	5.18	5.18
-8	.02	.02	.02
-9	.01	.01	.01
-11	.01	.00	.00
-15	.10	.08	.08
-16	.04	.03	.03
-17	-.10	-.08	-.08
-18	-.02	-.02	-.02
-20	.01	.01	.01
-22	.01	.01	.01
8 -8	6.03	5.21	5.21
-9	.02	.01	.01
-12	.01	.01	.01
-14	.01	.01	.01
-15	-.13	-.11	-.11
-16	.06	.05	.05
-17	.11	.09	.09
-20	-.02	-.02	-.02
-21	-.01	-.01	-.01
-23	-.01	-.01	-.01
-27	.01	.01	.01
9 -9	5.11	4.46	4.61
-12	.12	.11	.11
-13	.05	.04	.05
-15	.21	.17	.18
-16	-.28	-.23	-.24
-18	-.01	-.01	-.01
-19	.02	.02	.02
-23	-.42	-.35	-.35
-24	.02	.02	.02
-26	-.04	-.03	-.03
-29	-.01	-.01	-.01
-30	.04	.04	.04
-33	.01	.01	.01
-35	.02	.01	.01
12 -12	5.73	4.94	4.98
-13	-.04	-.03	-.03
-15	.01	.01	.01
-16	-.01	-.01	-.01
-23	.15	.12	.12
-24	-.01	-.01	-.01
-26	.01	.01	.01
-30	-.01	-.00	-.00
13 -13	5.55	4.79	4.83
-16	-.01	-.00	-.01
-23	-.01	-.01	-.01
-24	-.19	-.15	-.15
-26	.15	.12	.12
-29	-.01	-.01	-.01
-30	.06	.04	.04
-33	.02	.01	.01
-35	.02	.02	.02
14 -14	5.61	4.84	4.88
-19	-.01	-.01	-.01
-20	-.09	-.07	-.08
-21	.01	.01	.01
-25	.18	.15	.15
-27	.14	.11	.11
-29	.01	.00	.00
14 -31	-.01	-.00	-.00
-36	.01	.01	.01
15 -15	1.62	1.31	1.31
-16	-.03	-.03	-.03
-18	.01	.01	.01
-23	-.03	-.02	-.02
-26	-.02	-.01	-.01
-30	.01	.01	.01
16 -16	1.57	1.27	1.27
-18	.09	.07	.07
-19	-.09	-.07	-.07
-23	.04	.03	.03
-26	.01	.01	.01
-30	-.01	-.01	-.01
17 -17	1.73	1.40	1.40
-19	.05	.04	.04
-20	-.10	-.08	-.09
-27	.03	.02	.02
18 -18	.69	.55	.55
-19	.01	.01	.01
-20	-.01	-.01	-.01
-22	.01	.01	.01
19 -19	.63	.50	.50
-21	.01	.01	.01
20 -20	.96	.81	.84
-22	.01	.01	.01
-25	.03	.02	.02
-27	-.12	-.10	-.10
-36	-.01	-.01	-.01
23 -23	.73	.56	.56
-26	.01	.01	.01
-30	-.01	-.01	-.01
24 -24	.70	.54	.54
-26	-.01	-.01	-.01
25 -25	.71	.54	.54
-27	.01	.01	.01
26 -26	.81	.62	.62
-29	-.02	-.01	-.01
-30	.13	.09	.10
-33	.04	.03	.03
-35	.04	.03	.03
27 -27	.86	.66	.66
-34	-.01	-.01	-.01
28 -28	.62	.46	.46
-29	-.08	-.06	-.06
-30	-.02	-.01	-.01
-31	-.03	-.03	-.03
-33	.17	.13	.13
-34	-.14	-.11	-.11
-35	-.09	-.07	-.07
29 -29	.58	.43	.43
-30	-.09	-.07	-.07
-33	-.19	-.14	-.14
-34	.15	.12	.12
-35	-.10	-.07	-.07
30 -30	.73	.54	.55
-33	.17	.13	.13
-35	.19	.14	.15
33 -33	.43	.33	.33
.35	.04	.03	.03
34 -34	.36	.28	.26
35 -35	.34	.26	.26
36 -36	.00	.00	.00

[a] Units are such that $F_{ij}\Delta q_i\Delta q_j$ is in mdyn Å, with distances in Å and angles in radians. Theor., SQM(1) and SQM(2) mean the directly computed, the *a priori* predicted and the optimized force fields respectively. The term i-j means the force constant F_{ij}. For internal coordinates, see Figure 1 and Table 2. To save space, force constants are not given here if they are less than 0.005 or they can be easily obtained from symmetry.

The directly calculated harmonic force constants were next scaled according to the procedure described in Ref. 3:

$$F_{ij}^{scaled} = F_{ij}^{Theor} (C_iC_j)^{1/2}$$

where C_i and C_j are scale factors of internal coordinate types q_i and q_j respectively. Six scale factors (Table 4), taken as those optimized for benzene, were used to scale the ring force constants of 4-methylpyridine, and the other five scale factors (Table 4) which correspond to five methyl group vibrational motions (C-H stretch, C-H bend, Me-C stretch, Me-C wagging and Me-C deformation), taken as those optimized for toluene, were used to scale the 4-methylpyridine methyl force constants. Moreover, the C-N stretch of 4-methylpyridine was scaled with the C-C stretch scale factor of benzene. For this transfer of scale factor, it was assumed that the difference between the N atom and a C-H group was insignificant to the extent that the systematic errors of the *ab initio* Hartree-Fock method should be very similar for benzene and pyridine or for toluene and 4-methylpyridine, since the N atom and C-H group are isoelectronic and nearly the same size. This assumption worked very well for pyridine. The result, an SQM (4-methylpyridine/benzene) force field, is given in Table 3 and was used to calculate the vibrational fundamentals shown in Table 5. Since the force and interaction constants (Table 3) of the methyl rotation motion are too small (i.e. nearly a free internal rotation of the methyl group) to obtain a significant fundamental frequency for this motion, it is obviously convenient for us to eliminate this internal coordinate while calculating the vibrational spectral frequencies.

Table 4. Scale factors

Description (coordinates)	Benzene	Toluene	4-methylpyridine
C-C, C-N stretch (1-6)	0.911	0.911	0.911
Me-C stretch (9)		0.873	0.903
C-H stretch (7,8,10,11)	0.863	0.863	0.863
C-H (Me) stretch (12-14)		0.863	0.870
Me-C deformation (20)		0.842	0.883
Ring deformation (15-17)	0.808	0.808	0.808
C-H deformation (18,19,21,22)	0.797	0.797	0.797
C-H (Me) bend (23-27)		0.765	0.765
C-H wagging (28,29,31,32)	0.739	0.739	0.739
Me-C wagging (30)		0.739	0.760
Ring torsion (33-35)	0.768	0.768	0.768

While it was not necessary for the main purpose of our study, the five independent scale factors for the methyl group motions were also fitted to the experimental methylpyridine frequencies while holding the six ring scale factors constant. The scale factors obtained in this way are listed in Table 4 and the resulting optimized SQM force field is given in Table 3.

Dipole moment derivatives have been calculated by numerical differentiation of the dipole moment components obtained at the displaced geometries and used to compute the infrared absorption intensities by methods reviewed in Ref. 15 and 19. The resulting values are given in Table 4 and also compared with experimental data provided by Long *et al.*[10]

DISCUSSION

The vibrational frequencies (35 fundamentals, omitting the methyl group torsion) of 4-methylpyridine, calculated from the force fields obtained (1) scaled with the scale factors for benzene in the ring and for toluene in the methyl group, and (2) scaled with the optimized scale factors (Table 4), are shown in Table 5 along with a variety of experimental measurements. The frequencies derived with transferred scale factors (1) are to be used in assessing the ability of our

Table 5. Computed and experimental vibrational spectrum and intensities of 4-methylpyridine[a]

			Computed data[b]			Experimental data[c]			Other work		
No.	Sym.	Approximate	(1)		(2)	Vapor	Liquid	Liquid	Green's	Draeger's	
		assignment	Freq.	Int.	Freq.	(I.R.)[d]	(I.R.)[e]	(R)[e]	Assign.	Assign.	Calc.
1	B_1	Methyl wagging	202	.70	203	203w[f]	210	211m	211	203	211
2	B_2	Methyl deformation	339	.09	345	(344)[g]	344	341w	341	344	350
3	A_2	Ring torsion	391	.00	391	(385)[g]	385	384vw	384	385	394
4	B_1	Ring torsion	479	23.02	482	482vs[f]	484	485w	485	482	464
5	A_1	Ring def.	512	6.33	513	512s[f]	515	514s	514	512	527
6	B_2	Ring def.	675	.49	675	(668)w[g]	668w	669s	669	668	657
7	B_1	Ring torsion	725	12.19	725	727[50]	727s	727vw	727	727	727
8	B_1	CH wagging	783	33.87	784	793(70)		793sh	793	800	795
9	A_1	Ring def.	793	14.49	797	800(47)	800vs	800vs	800	800	784
10	A_2	CH wagging	863	.04	863	(870)w[g]	870w	866vw	866	870	865
11	B_1	CH wagging	957	.13	957	959[23]	941sh			870	890
12	B_2	CH bend (methyl)	971	.00	971	971[28]	969m	969sh	866	969	977
13	A_2	CH wagging	985	.02	985	996[66]				969	979
14	A_1	CN stretch	985	6.63	985		993s	994vs	996	996	996
15	B_1	CH bend (methyl)	1048	6.45	1050	1046[47]	1039s		1042	1039	1033
16	B_2	CC stretch	1077	.83	1077	1066[31]	1070m	1068m		1112	1117
17	A_1	CC & CN stretch	1081	.21	1081	1080[25]	1087m			1066	1060
18	B_2	CN stretch	1115	.32	1116	1107[14]	1112w			1208	1225
19	A_1	CH def.	1221	4.18	1221	1216[69]	1208s	1212s	1216	1157	1167
20	A_1	Methyl-C stretch	1223	1.98	1231	1228[60]	1221vs	1220vs	1228	1228	1243
21	B_2	CH def.	1338	1.03	1339	1350[27]	1357m	1332w	1279	1279	1276
22	A_1	CH bend (methyl)	1384	1.69	1385	(1383)s[g]	1383s	1378m	1383	1383	1380
23	B_2	CH def.	1407	16.72	1408	1420(27)	1410s	1409w	1420	1420	1421
24	B_2	CH bend (methyl)	1446	18.69	1446	(1445)vs[g]	1442s	1449w	1445	1445	1448
25	B_1	CH bend (methyl)	1450	3.61	1450				1445	1445	1446
26	A_1	CH def.	1493	7.72	1493	1501(12)	1493s	1495m	1501	1501	1496
27	B_2	CC stretch	1581	18.04	1582	1575(22)	1559s	1561w	1575	1575	1576
28	A_1	CC stretch	1609	58.81	1610	1603(64)	1599vs	1603s	1603	1603	1588
29	A_1	CH stretch (methyl)	2922	17.26	2934	2937(44)	2921s	2920s	2937	2910	2915
30	B_1	CH stretch (methyl)	2978	28.85	2990	(2970)[g]	2963sh		2970	2937	2942
31	B_2	CH stretch (methyl)	2995	19.85	3007	3008(47)	2990s	2983m		2937	2943
32	B_2	CH stretch	3066	5.49	3066	3038(57)	3024s	3029sh	3008	3038	3034
33	A_1	CH stretch	3068	20.37	3068				3038	3038	3034
34	B_2	CH stretch	3087	35.06	3087	3070(58)	3067s	3050vs	3038	3070	3065
35	A_1	CH stretch	3092	2.68	3092				3070	3070	3068

[a] Frequencies in cm^{-1}, intensities in km/mol. [b] (1) Scaled with benzene and toluene scale factors, (2) Scaled with optimized scale factors. [c] Bands which we consider fundamentals based on our assignment. [d] Ref. 10. The intensity values in brackets and parentheses were measured at 4.2 mm and 1.3 mm sample pressure, respectively. [e] Ref. 11. [f] Values taken from the vapor spectrum of Ref. 11. [g] Values taken from the liquid IR spectra of Ref. 10 and 11.

procedure to predict *a priori* the spectrum of a molecule. They are also the ones to be considered in evaluating the reliability of empirical assignments of the vibrational spectra. The force field evaluated by fitting scale factors to the corrected vibrational assignments, giving frequencies labeled (2), is useful in that it provides the best vibrational force field for the molecule currently available by combined use of experimental and theoretical information.

For comparison, the assignments proposed by Draeger[13] and by Green[12] are also given in Table 5. Since the vibrational properties of a free molecule can best be characterized in the vapor-phase spectra, our analysis is based primarily on the vapor-phase results reported by Long *et al.*[10] Three of the six fundamentals below 700 cm^{-1} which were not in the region observed in the vapor-phase spectrum of Long *et al.* are taken from the vapor infrared data in Ref. 11, the others are taken from the liquid infrared data in Ref. 11. The results of infrared and Raman spectra in the liquid state also were of use in considering questions of doubtful assignments of fundamentals.

The symmetry of 4-methylpyridine can be assumed to be $C_{2\upsilon}$ since the molecule has a nearly free rotational methyl group. The vibrational modes are classified as $12\ A_1 + 3\ A_2 + 8\ B_1 + 12\ B_2$ as shown in Table 5. Our assignments based on the vapor data of Long *et al.*[10] are basically consistent with those reported by Green *et al.* and by Draeger[12,13]. However, the assignments of υ_8, υ_{12}, and υ_{19} differ between these two authors; we agree with Green for υ_8 and υ_{19}, and with Draeger for υ_{12}. Our new evidence requires us to make new assignments for an additional six bands, υ_{11}, υ_{13}, υ_{16}-υ_{18}, υ_{21}, and for the C-H stretching modes.

Our predicted frequencies for the υ_8 and υ_9 fundamentals are 783 and 793 cm^{-1} respectively, compared with 795 and 784 cm^{-1} calculated by Draeger in Ref. 13, although he assigned 800 cm^{-1} for both of those two fundamentals. In our opinion it is reasonable to consider that the difference of about 10 cm^{-1} could make the υ_8 (B_2 band) fall into the P branch of the υ_9 fundamental (A_1 band) at 793 cm^{-1}, since there are three branches 793(70), 800(47) and 807(46) cm^{-1} around the 800 cm^{-1} area in the vapor-phase spectrum[10] and the branch at 793 cm^{-1} is much stronger than the other two. Our assignments, 793 cm^{-1} for υ_8 and 800 cm^{-1} for υ_9, are also supported by the recent Raman spectrum[11] and by Green's assignments, shown in Table 5.

For the fundamental υ_{11} (B_1 band), our predicted value of 957 cm^{-1} is quite close to the observed band at 959 cm^{-1} in the vapor state, so we have assigned υ_{11} at 959 cm^{-1}, which seems to be confirmed by the shoulder at 941 cm^{-1} in the liquid infrared spectrum in Ref. 11. Draeger has assigned the υ_{11} mode at 870 cm^{-1} compared to the frequency of 890 cm^{-1} calculated from his empirical force field. All previous experience indicates that the 87 cm^{-1} difference between 870 cm^{-1} and our prediction of 957 cm^{-1} is impossibly large, so we are convinced that this reassignment must be correct.

Draeger suggested that the υ_{13} (A_2 band), forbidden by symmetry in infrared absorption, should be the same as the υ_{12} (A_1 band) of 969 cm^{-1} based on his calculations of 977 cm^{-1} for υ_{12} and 979 cm^{-1} for υ_{13}. Our predictions that υ_{14} and υ_{13} have the same frequency of 985 cm^{-1} and that υ_{14} is much stronger than υ_{13} show that υ_{13} should be hidden in the υ_{14} band observed at 996 cm^{-1} in the vapor spectrum.

In the 60 cm^{-1} region from 1060 to 1120 cm^{-1}, our predictions of three fundamentals, all of which belong to the ring stretching modes, are 1077 cm^{-1} for the υ_{16} (B_2 band), 1081 cm^{-1} for the υ_{17} (A_1 band) and 1115 cm^{-1} for the υ_{18} (B_2 band), and the liquid infrared spectra also have three peaks at 1070, 1087 and 1112 cm^{-1}.[10,11] We therefore believe that the five branches at 1061, 1071, 1080, 1110 and 1113 cm^{-1} observed in this region of the vapor infrared spectrum[10] can be assigned to the three fundamentals as 1066 cm^{-1} (center of 1061 and 1071 cm^{-1}) for υ_{16}, 1080 cm^{-1} for υ_{17} and 1107 cm^{-1} (center of 1100 and 1113 cm^{-1}) for υ_{18}.

For the υ_{19} (A_1 band), we support the assignment of Green *et al.* at 1216 cm^{-1} rather than that of Draeger at 1157 cm^{-1}, based on our prediction of 1221 cm^{-1}. This is a crowded and complex area of the spectrum where it is difficult to distinguish between the fundamentals on experimental evidence alone.

For the υ_{21} C-H deformation (B_2 band), our prediction of 1338 cm^{-1} offers an assignment of 1350 cm^{-1} (center of the branches 1344 and 1356 cm^{-1} in the vapor-phase spectrum[10]), compared with the 1279 cm^{-1} suggested by Green *et al.* and by Draeger[12,13]. Our assignment has been supported by other *ab initio* calculations and by experiments, in which the C-H deformation is at 1353 cm^{-1} for pyridine[5] and at 1338 cm^{-1} for toluene[9], and by the fact that only the peak at 1332 cm^{-1} and nothing else could be found in the region between 1250 and 1350 cm^{-1} in the recent liquid Raman spectrum[11].

The predicted values of 1446 and 1450 cm^{-1} for the C-H bend (methyl) modes υ_{24} and υ_{25}, respectively, confirmed the assignment of both fundamentals at 1445 cm^{-1}, taken from the liquid infrared spectrum rather than the vapor band at 1464 cm^{-1} reported by Long *et al.*[10], as assigned by both Green *et al.* and Draeger.

For the C-H stretching modes on the methyl group, υ_{29}, υ_{30} and υ_{31}, Green and Draeger reported quite different assignments as shown in Table 5. In Table 5 it also can be seen that our predicted values of 2922, 2978 and 2995 cm^{-1} for those three fundamentals basically support Green's assignments except for υ_{31}, which was assigned at the same frequency as υ_{30} by Green *et al.* The predicted frequencies also agree well with the measurements in the vapor and liquid states except for υ_{30} in the vapor spectrum of Long *et al.*[10] It is reasonable for us to assign υ_{29} at 2937 cm^{-1} and υ_{31} at 3008 cm^{-1} in the vapor spectrum, as well as υ_{30} at 2970 cm^{-1} taken from the liquid infrared spectrum[10] according to the suggestion by Green *et al.*

The C-H stretching vibrations exhibit a larger difference between experimental and computed values than is seen elsewhere in the spectrum. This situation is certainly due in part to experimental difficulties and strong perturbations by resonances, which are not fully considered in our calculations. In spite of these complications, the predicted values of even the C-H stretching frequencies fall within the 1% target set as an original goal. It should be noted that the consistent overestimation, average about 24 cm^{-1}, of the C-H stretching vibrations on the ring (Table 5) might be caused by too small a correction of C-H bond lengths. We used a geometrical correction of +0.005Å for obtaining the best estimate of the equilibrium C-H distances from that computed at the *ab initio* 4-21 levels. As pointed out in Ref. 15, the correction for C-H bonds originating at an sp^2-hybridized carbon atom is probably nearer to +0.007Å. As previously described in Ref. 5 and the rule of thumb[20] that a 0.001Å increase in a C-H bond length corresponds to a 10 cm^{-1} decrease in the associated frequency, the change of +0.002Å (from +0.005 to +0.007Å) in the C-H bond lengths would make our predictions of C-H stretching frequencies in perfect agreement with the observed ones. Our computation also provides added support for the suggestion in Ref. 15 that the offset value to be applied to sp^2-hybridized C-H bond lengths, calculated at the 4-21 level, should be +0.007Å rather than +0.005Å. Furthermore our predictions for the C-H stretching modes on the ring have obviously shown that the two weak bands υ_{32} and υ_{35} seem to hide in the two strong bands υ_{33} and υ_{34} respectively, which agrees with the experimental results and with Draeger's assignments shown in Table 4.

The prediction of the vibrational spectrum for 4-methylpyridine is a remarkably sucessful demonstration of the transferability of scale factors between related molecules. The average deviation between the predicted frequencies of 4-methylpyridine, obtained without reference to any experimental evidence on 4-methylpyridine, and the experimental data is 5.6 cm^{-1} in the non-CH stretching frequencies or 8.3 cm^{-1} overall.

The average deviation between the frequencies calculated by using five scale factors optimized for the methyl group in 4-methylpyridine and six benzene scale factors and the observed values is of 5.2 cm^{-1} in the non-CH stretching frequencies or 7.6 cm^{-1} overall. This result showing that separate optimization of scale factors for the five methyl vibrational motions to fit the observed spectrum produces only a trivial improvement in the fit offers promise that the scale factors in the methyl motions optimized for toluene should also be suitable for other aromatic molecules containing a methyl group.

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REFERENCES

1. The most recent review is given by G. Fogarasi and P. Pulay in Annual Rev. Phys. Chem., Vol. 35, Ed. B.S. Rabinovitch, Annual Reviews, Inc., Palo Alto, California, 1984, p. 191-243.
2. P. Pulay, J.G. Lee and J.E. Boggs: *J. Chem. Phys.*, **79**, 3382 (1983).
3. P. Pulay, G. Fogarasi, G. Pongor, J.E. Boggs and A. Vargha: *J. Am. Chem. Soc.*, **105**, 7037 (1983).
4. P. Pulay, G. Fogarasi and J.E. Boggs: *J. Chem. Phys.*, **74**, 3999 (1981).
5. G. Pongor, P. Pulay, G. Fogarasi and J.E. Boggs: *J. Am. Chem. Soc.*, **106**, 2765 (1984).
6. G. Pongor, G. Fogarasi, J.E. Boggs and P. Pulay: *J. Mol. Spectrosc.*, in press.
7. H. Sellers, P. Pulay and J.E. Boggs: *J. Am. Chem. Soc.*, in press.
8. Z. Niu, K.M. Dunn and J.E. Boggs: *Mol. Phys.*, **55**, 421 (1985).
9. Y. Xie and J.E. Boggs, J. Comput. Chem., in press.
10. D.A. Long, F.S. Murfin, J.L. Hales and W. Kynaston: *Trans. Fararday Soc.*, **53**, 1171 (1957).
11. American Petroleum Institute Research Project 44 at the Texas A&M University, *Catalog of Intrared Spectral Data*. Serial Nos 2593, 2651 and 2776; *Catalog of Raman Spectral Data*. Serial Nos 877.
12. J.H.S. Green, W. Kynaston and H.M. Paisley: *Spectrochim. Acta*, **19**, 549 (1963).
13. J.A. Draeger: *Spectrochim. Acta*, **39A**, 809 (1983).
14. P. Pulay: *Theor. Chem. Acta*, **50**, 299 (1979).
15. P. Pulay, G. Fogarasi, F. Pang and J.E. Boggs: *J. Am. Chem. Soc.*, **101**, 2550 (1979).
16. F. Pang, J.E. Boggs, P. Pulay and G. Fogarasi: *J. Mol. Struc.*, **66**, 281 (1980).
17. H.D. Rudolph, H. Dreizler, A. Jaeschke and P. Wendling: *Z. Naturforsch.*, **A22**, 940 (1967).
18. H.D. Rudolph, H. Dreizler and H. Seiler: *Z. Naturforsch. Teil A*, **22**, 1738 (1967).
19. R. Ditchfield, W.J. Hehre and J.A. Pople: *J. Chem. Phys.*, **54**, 724 (1971).
20. D.C. Mckean, J.L. Duncan and L. Batt: *Spectrochim. Acta. Part A*, **29A**, 1037 (1973).