

# Theoretical Prediction of Vibrational Spectra. 1. The In-Plane Force Field and Vibrational Spectra of Pyridine

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**Abstract:** The complete harmonic vibrational force field and the diagonal and semidiagonal cubic force field elements have been computed for pyridine at the 4-21 Hartree-Fock level. The harmonic constants were scaled by using scale factors previously derived by fitting the computed force field of benzene to the observed benzene vibrational spectrum. The scaled force field was then used to predict the vibrational spectrum of pyridine. Comparison with experimental spectra, after a few corrections in the experimental assignments, shows a mean deviation of 5.7 cm<sup>-1</sup> for the non-CH frequencies. Computed intensities are qualitatively in agreement with experiment. This successful a priori accurate prediction of the vibrational spectrum of a moderately complex molecule offers hope that completely unknown spectra of such molecules can be computed to harmonic oscillator accuracy if the spectrum of a related substance is known.

A great deal of research is currently being directed toward the goal of accurate prediction of the vibrational spectra of molecules. Ideally, such predictions should require no experimental measurements on the compound of interest, and the predicted frequencies should have an accuracy limited, at least as an interim target, only by the difference between the independent harmonic oscillator model and the real anharmonic molecule. As a rough rule, this objective demands evaluation of harmonic vibrational force constants to about 2% accuracy, corresponding to about 1% in the frequencies.

In principle, the stated goal can be reached by known theoretical methods. We have recently shown, however, that even for molecules the size of HF, HCN, and NH<sub>3</sub>, strictly ab initio evaluation of the diagonal force constants is just approaching the required level of accuracy.<sup>2</sup> These calculations were made at the level of a triple  $\zeta$  basis set augmented by two sets of polarization functions with single and double substitutions in the CI treatment plus a correction for unlinked clusters. As indicated also by previous studies, an encouraging result from that work was that the off-diagonal vibrational coupling constants and the cubic and quartic constants appear to be calculated with an accuracy exceeding that which can be tested by comparison with the best experimental values. Nevertheless, it is clear that the desired goal of accuracy cannot be met at present by purely computational methods, especially for chemically interesting molecules ranging in size from 5 to 50 atoms.

Force fields or vibrational spectra for medium-sized molecules computed by either ab initio Hartree-Fock or especially by semiempirical techniques are of too low accuracy to meet our goal. It is, however, known that the errors are largely systematic so that a computed force field can be scaled by only a few multiplicative factors to fit the observed vibrational frequencies.<sup>3</sup> The first systematic application of this approach to ab initio force fields is due to Blom and Altona.<sup>4</sup> Their work, however, deals with saturated compounds where transferability is expected to be good. We have extended the procedure, and the most accurate existing force field for benzene has been obtained by the scaling approach.<sup>5</sup> The best present hope for accurate prediction of unknown spectra appears to lie in transferring the scale factors from experimentally well-studied model compounds to analogous but experimentally less-well-known molecules.

It would obviously be desirable if the quantum chemical calculations could be done by semiempirical or low-level ab initio

techniques. In fact, molecules in the larger end of the interesting range can be treated only by such methods at present. As the level of computational precision is reduced, however, the numerical values of the scale factors deviate more strongly from unity so that errors in their transfer between related molecules would be expected to be more serious.

It is not yet fully clear if transfer of scale factors between related molecules can yield harmonic vibrational force fields of the desired few percent accuracy. Even if this can be done, it is not known how similar the "related molecules" must be or to what extent one can relax the level of the quantum mechanical calculation. This paper is directed toward exploring such questions for the specific case of pyridine. We calculate the harmonic force field of pyridine ab initio, at the same level used in our previous study of benzene,<sup>5</sup> and then use the benzene scale factors to correct the computed pyridine force field. We then calculate the expected vibrational spectra of pyridine and its deuterated forms. Only then do we make reference to the observed spectra of pyridine to determine how accurate the prediction has been. *It should be made very clear that our predicted spectra of pyridine make no use of the experiments on pyridine.*

Aside from attacking methodological questions, a study of the pyridine force field and the related vibrational spectra can be expected to resolve a number of remaining spectroscopic questions about this molecule. Early investigations of the pyridine spectrum were reviewed by Innes et al. in 1967.<sup>6</sup> Two subsequent publications dealt with the vibrational spectrum of crystalline<sup>7</sup> and matrix-isolated<sup>8</sup> pyridine. Kakiuti et al.<sup>9</sup> reassigned the nonplanar vibrations of several deuterium-substituted pyridines. More recently, Stidham and DiLella have published an impressive series<sup>10-13</sup> of experiments on the vibrational spectra of pyridine and its deuterated derivatives of C<sub>2v</sub> symmetry.

The in-plane harmonic force field of pyridine has been dealt with by several authors.<sup>14-19</sup> The first calculations of this type

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(16) Berezin, V. I. *Opt. Spektrosk.* **1963**, *15*, 310-314; *Opt. Spectrosc. (Engl. Transl.)* **1963**, *15*, 167.

(1) (a) Eötvös Loránd University. (b) University of Arkansas. (c) University of Texas.

(2) Pulay, P.; Lee, J.-G.; Boggs, J. E. *J. Chem. Phys.* **1983**, *79*, 3382-3391.

(3) See, for example, the forthcoming review paper by Fogarasi and Pulay: Fogarasi, G.; Pulay, P. In "Vibrational Spectra and Structure"; Durig, J. R., Ed.; Elsevier: Amsterdam, Vol. 14.

(4) Blom, C. E.; Altona, C. *Mol. Phys.* **1976**, *31*, 1377.

(5) Pulay, P.; Fogarasi, G.; Boggs, J. E. *J. Chem. Phys.* **1981**, *74*, 3999-4014.

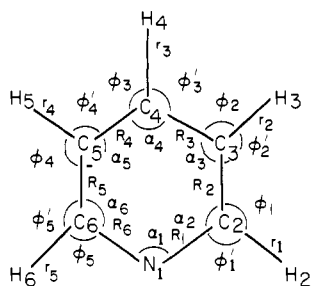


Figure 1. Labeling of geometric parameters in pyridine.

were carried out by Long et al.,<sup>14</sup> who attempted to generate the force constants of pyridine by transferring them from Whiffen's benzene force field.<sup>20</sup> Their method tested the direct transferability of the force constants; for example, the stretching constant for the C-N bond was assumed to be the same as that for the C-C bond in benzene. Unfortunately, such an assumption is rather poor, as can be seen from our calculated values which show the C-N diagonal stretching constant to be larger than the mean value of the C-C diagonal stretching constants by about 8%.

Among the experiment-based force fields for pyridine, we believe Berezin's simplified general valence force field<sup>16</sup> to be generally good, although his difference between the values for the C-N and C-C diagonal stretching constants is only about 3%. Cummings and Wood<sup>17</sup> elaborated a force field for the in-plane vibrations of pyridine in which no distinction was made between parameters involving the C or the N atoms. Suzuki and Orville-Thomas<sup>18,19</sup> have determined a modified Urey-Bradley force field with 16 force constants which appears slightly superior to that of Zerbi et al.<sup>15</sup>

A paper which is entirely in the spirit of the present work was published by Harsányi and Kilár.<sup>21</sup> These workers calculated the in-plane vibrational force field of pyridine at the semiempirical CNDO/2 level. They first attempted to scale their computed force field with the CNDO/2 scale factors derived earlier for benzene.<sup>22</sup> This effort was not particularly successful, yielding errors up to 150 cm<sup>-1</sup> in the frequencies. It is not clear whether the cause of the failure was the nontransferability of scale factors derived at the CNDO/2 level or whether the fact that only 3 distinct scale factors were used gave too little flexibility in the fitting. Harsányi and Kilár did, however, use the experimental spectra for pyridine to derive a new set of scale factors for pyridine. It is of interest to compare the scaled force field obtained at the CNDO/2 level with that resulting from a medium-sized ab initio calculation. We have also evaluated the diagonal cubic force constants for the in-plane vibrations of pyridine plus the semidiagonal cubic constants of the form  $F_{ijj}$ . This is the first determination of these quantities.

### Quantum Chemical Calculations

Molecular geometries and force constants were evaluated according to the force (gradient) method<sup>23,24</sup> using TEXAS, an ab initio Hartree-Fock gradient program.<sup>25</sup> All calculations were carried out with the standard 4-21 atomic basis set<sup>26</sup> which is a somewhat simplified thus significantly less time-consuming version of the 4-31G Gaussian basis set of Ditchfield et al.<sup>27</sup> and gives results of equal quality. The dipole moment derivatives were

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 (19) Suzuki, S. *J. Mol. Struct.* **1982**, *86*, 387-391.  
 (20) Whiffen, D. H. *Philos. Trans. R. Soc. London, Ser. A* **1955**, *248*, 131.  
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 (22) Fogarasi, G.; Pulay, P. *J. Mol. Struct.* **1977**, *39*, 275-280.  
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 (25) Pulay, P. *Theor. Chim. Acta* **1979**, *50*, 299-312.  
 (26) Pulay, P.; Fogarasi, G.; Pang, F.; Boggs, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 2550-2560.  
 (27) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724-728.

Table I. Theoretical and Experimental Structures for Pyridine<sup>a</sup>

	theoretical <sup>b</sup>	ref <sup>c</sup>	exptl <sup>d</sup>
Distances			
N, C <sub>2</sub>	1.333	1.337	1.338
C <sub>2</sub> , C <sub>3</sub>	1.382	1.393	1.394
C <sub>3</sub> , C <sub>4</sub>	1.384	1.394	1.392
C <sub>2</sub> , H <sub>2</sub>	1.071	1.076	1.087
C <sub>3</sub> , H <sub>3</sub>	1.070	1.075	1.083
C <sub>4</sub> , H <sub>4</sub>	1.072	1.077	1.082
Angles			
C <sub>6</sub> , N, C <sub>2</sub>	118.4	118.7	116.9
N, C <sub>2</sub> , C <sub>3</sub>	122.8	122.7	123.8
C <sub>2</sub> , C <sub>3</sub> , C <sub>4</sub>	118.5	118.5	118.5
C <sub>3</sub> , C <sub>4</sub> , C <sub>5</sub>	119.0	118.9	118.4
N, C <sub>2</sub> , H <sub>2</sub>	116.4	116.5	116.0
C <sub>2</sub> , C <sub>3</sub> , H <sub>3</sub>	120.4	120.4	120.1
C <sub>3</sub> , C <sub>4</sub> , H <sub>4</sub>	120.5	120.6	120.8

<sup>a</sup> Distances in Å = 10<sup>-10</sup> m, angles in deg. Numbering of the atoms in Figure 1. <sup>b</sup> 4-21 ab initio Hartree-Fock equilibrium geometry from ref 28. <sup>c</sup> Experimentally corrected theoretical geometry, see text. <sup>d</sup> Microwave substitution structure from ref 29.

Table II. In-Plane Internal Coordinates for Pyridine<sup>a</sup>

no.	coordinate	description
1-5	$r_1, \dots, r_5$	CH stretching
6-11	$R_1, \dots, R_6$	CN and CC stretchings
12-16	$\beta_1 = 2^{-1/2}(\phi_1 - \phi_1'), \dots, \beta_5$	CH in-plane deformations
17	$q_{17} = 6^{-1/2}(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6)$	
18	$q_{18} = 12^{-1/2}(2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6)$	A <sub>1</sub> ring deformation
19	$q_{19} = 1/2(\alpha_2 - \alpha_3 + \alpha_5 - \alpha_6)$	B <sub>2</sub> ring deformation

<sup>a</sup> See Figure 1.

obtained by numerical differentiation from the dipole moments at the distorted geometries.

Results of our earlier geometry calculations for pyridine<sup>28</sup> are summarized in Table I; the numbering of the atoms is shown in Figure 1. For comparison, data of Mata et al.<sup>29</sup> obtained by microwave spectroscopy are also included in the table. In order to account for systematic errors in the ab initio Hartree-Fock method, following Blom and Altona,<sup>4</sup> we have used an empirically corrected theoretical geometry as the reference point around which the potential is expanded to obtain the force constants.

For the 4-21 basis set, geometrical corrections were established in ref 26. These involve corrections for bond lengths whereas theoretical bond angles are usually unchanged. With ring systems such as pyridine, however, corrections applied to ring bond lengths necessarily entail small changes in bond angles. The latter were negligible in this case ( $\leq 0.15^\circ$ ) as shown in Table I. Such small changes in valence angles do not significantly affect force constants.

We have used the scheme outlined in ref 26 to obtain corrections for the CC and CH bond lengths (C<sub>2</sub>-C<sub>3</sub> = +0.0108 Å, C<sub>3</sub>-C<sub>4</sub> = +0.0106 Å, and C-H = +0.005 Å). For the C-N bond there is insufficient data available to determine an accurate value. We have therefore estimated this correction from experimental<sup>30</sup> and 4-21 theoretical<sup>26</sup> data on HCN and CH<sub>3</sub>NH<sub>2</sub>, arriving at N-C<sub>2</sub> = +0.004 Å. The corrected theoretical geometry at which the theoretical force constants have been evaluated is given in Table I.

The in-plane internal coordinates are listed in Table II. These were introduced according to the recommendations of our previous

(28) Pang, F.; Pulay, P.; Boggs, J. E. *J. Mol. Struct. (THEOCHEM)* **1982**, *88*, 79-89.

(29) Mata, F.; Quintana, M. J.; Sorensen, G. O. *J. Mol. Struct.* **1977**, *42*, 1-5.

(30) (a) For HCN: Douglas, A. E.; Sharma, D. *J. Chem. Phys.* **1953**, *21*, 448-458. Tyler, J. K.; Sheridan, J. *Trans. Faraday Soc.* **1963**, *59*, 2661-2670. (b) For CH<sub>3</sub>NH<sub>2</sub>: Lide, D. R. *J. Chem. Phys.* **1957**, *27*, 343-352. Nishikawa, T.; Itoh, T.; Shimoda, K. *Ibid.* **1955**, *23*, 1735-1736.

Table III. Ab Initio 4-21 Theoretical and SQM (Pyridine 4-21/Benzene) Force Fields for Pyridine<sup>a</sup>

potential energy term	4-21		potential energy term	4-21		SQM	
	4-21	SQM		4-21	SQM	4-21	SQM
$r_1^2/2$	6.023	5.198	$r_2\beta_1$	-0.0029	-0.0024		
$r_1r_2$	0.0174	0.0150	$r_2\beta_2$	-0.0050	-0.0041		
$r_1r_3$	0.0033	0.0028	$r_2\beta_3$	0.0062	0.0051		
$r_1r_4$	0.0020	0.0017	$r_2\beta_4$	-0.0078	-0.0065		
$r_1r_5$	0.0049	0.0042	$r_2\beta_5$	0.0007	0.0006		
$r_1R_1$	0.2233	0.1980	$r_2q_{17}$	-0.1223	-0.1021		
$r_1R_2$	0.0858	0.0761	$r_2q_{18}$	0.0505	0.0422		
$r_1R_3$	-0.0051	-0.0045	$r_2q_{19}$	0.1040	0.0868		
$r_1R_4$	-0.0324	-0.0287	$r_3^2/2$	6.005	5.183		
$r_1R_5$	-0.0198	-0.0176	$r_3R_1$	-0.0212	-0.0188		
$r_1R_6$	-0.0221	-0.0196	$r_3R_2$	-0.0090	-0.0080		
$r_1\beta_1$	0.0187	0.0155	$r_3R_3$	0.0865	0.0767		
$r_1\beta_2$	-0.0006	-0.0005	$r_3\beta_1$	0.0083	0.0069		
$r_1\beta_3$	-0.0082	-0.0068	$r_3\beta_2$	-0.0069	-0.0057		
$r_1\beta_4$	0.0013	0.0011	$r_3q_{17}$	0.1148	0.0959		
$r_1\beta_5$	0.0060	0.0050	$r_3q_{18}$	-0.1091	-0.0911		
$r_1q_{17}$	0.0973	0.0813	$R_1^2/2$	7.804	7.110		
$r_1q_{18}$	0.0335	0.0280	$R_1R_2$	1.1108	0.8598		
$r_1q_{19}$	-0.0977	-0.0816	$R_1R_3$	-0.6492	-0.4187		
$r_2^2/2$	6.058	5.228	$R_1R_4$	0.8270	0.5334		
$r_2r_3$	0.0151	0.0130	$R_1R_5$	-0.7361	-0.4748		
$r_2r_4$	0.0022	0.0019	$R_1R_6$	1.0202	0.7897		
$r_2R_1$	-0.0125	-0.0111	$R_1\beta_1$	-0.3666	-0.3124		
$r_2R_2$	0.0688	0.0610	$R_1\beta_2$	-0.0063	-0.0054		
$r_2R_3$	0.0834	0.0739	$R_1\beta_3$	0.0212	0.0181		
$r_2R_4$	-0.0064	-0.0057	$R_1\beta_4$	-0.0324	-0.0276		
$r_2R_5$	-0.0225	-0.0200	$R_1\beta_5$	0.0284	0.0242		
$r_2R_6$	-0.0324	-0.0287	$R_1q_{17}$	0.2711	0.2326		
$R_3^2/2$	7.167	6.529	$R_1q_{18}$	0.4552	0.3277		
$R_3R_3$	0.9078	0.7027	$R_1q_{19}$	0.3101	0.2232		
$R_3R_4$	-0.6553	-0.4227	$\beta_1^2/2$	0.6951	0.5540		
$R_3R_5$	0.6220	0.4012	$\beta_1\beta_2$	0.0091	0.0073		
$R_3\beta_1$	0.1799	0.1533	$\beta_1\beta_3$	-0.0131	-0.0104		
$R_3\beta_2$	-0.1759	-0.1499	$\beta_1\beta_4$	-0.0024	-0.0019		
$R_3\beta_3$	-0.0107	-0.0091	$\beta_1\beta_5$	-0.0105	-0.0084		
$R_3\beta_4$	0.0299	0.0255	$\beta_1q_{17}$	-0.0134	-0.0108		
$R_3\beta_5$	-0.0301	-0.0256	$\beta_1q_{18}$	-0.0875	-0.0702		
$R_2q_{17}$	0.0015	0.0013	$\beta_1q_{19}$	-0.0046	-0.0037		
$R_2q_{18}$	-0.2998	-0.2159	$\beta_2^2/2$	0.6223	0.4960		
$R_2q_{19}$	-0.0910	-0.0655	$\beta_2\beta_3$	0.0105	0.0084		
$R_3^2/2$	7.255	6.610	$\beta_2\beta_4$	-0.0129	-0.0103		
$R_3R_4$	0.9172	0.7099	$\beta_2q_{17}$	-0.0015	-0.0012		
$R_3\beta_1$	0.0142	0.0121	$\beta_2q_{18}$	0.0897	0.0720		
$R_3\beta_2$	0.1977	0.1685	$\beta_2q_{19}$	-0.0546	-0.0438		
$R_3\beta_3$	-0.1894	-0.1614	$\beta_3^2/2$	0.6334	0.5048		
$R_3\beta_4$	-0.0047	-0.0040	$\beta_3q_{19}$	0.1031	0.0827		
$R_3\beta_5$	-0.0023	-0.0020	$q_{17}^2/2$	1.595	1.288		
$R_3q_{17}$	0.0055	0.0047	$q_{17}q_{18}$	-0.0094	-0.0076		
$R_3q_{18}$	0.1574	0.1133	$q_{18}^2/2$	1.512	1.222		
$R_3q_{19}$	-0.3228	-0.2324	$q_{19}^2/2$	1.738	1.404		

<sup>a</sup> Units: energy in aJ, coordinates in Å = 10<sup>-10</sup> m and radian, respectively. Ab initio 4-21 force constants are evaluated at the reference geometry (see text). SQM means Scaled Quantum Mechanical force field, see text for details. For the internal coordinates, see Table II and Figure 1.

paper.<sup>26</sup> For the generation of distorted molecular geometries, each of the coordinates was changed so as to give a displacement of 0.015 Å or 2° in individual valence coordinates. Both positive and negative displacements were made, permitting a partial examination of cubic anharmonicity and canceling the effect of cubic anharmonicities on the quadratic force constants. The economy of the force (gradient) method is shown by the fact that ab initio Hartree-Fock calculations at 23 geometries (including the reference geometry) were sufficient to determine the 100 independent elements of the complete in-plane quadratic force field of pyridine plus the 10 diagonal ( $F_{ii}$ ) and the 180 semidiagonal ( $F_{ij}$ ) non-zero and nonequivalent cubic constants.

The required scale factors could have been determined by a least-squares fitting of the calculated vibrational frequencies to the experimental ones. The resulting force field, which we have called a Scaled Quantum Mechanical (SQM) force field,<sup>31</sup> would

Table IV. Ab Initio 4-21 Cubic Force Constants for Pyridine<sup>a</sup>

potential energy term	4-21		potential energy term	4-21		potential energy term	SQM	
	4-21	SQM		4-21	SQM		4-21	SQM
$r_1^3/6$	-36.0		$R_3^2r_2/2$	-0.25		$\beta_2^2r_2/2$	-0.24	
$r_1^2r_2/6$	-35.8		$R_2^2R_1/2$	-0.32		$\beta_2^2R_2/2$	-0.42	
$r_1^2r_3/6$	-35.4		$R_2^2R_3/2$	-0.33		$\beta_2^2R_3/2$	-0.43	
$R_1^3/6$	-50.8		$R_2^2R_4/2$	-0.34		$\beta_2^2R_6/2$	0.10	
$R_2^3/6$	-42.6		$R_2^2R_6/2$	-0.51		$\beta_2^2q_{17}/2$	0.21	
$R_3^3/6$	-42.4		$R_2^2\beta_1/2$	-0.45		$\beta_2^2q_{18}/2$	-0.14	
$q_{17}^3/6$	-0.19		$R_2^2\beta_2/2$	0.45		$\beta_2^2q_{19}/2$	-0.24	
$q_{18}^3/6$	-0.67		$R_2^2q_{18}/2$	0.21		$\beta_3^2r_3/2$	-0.23	
$r_1^2R_1/2$	0.30		$R_3^2r_2/2$	-0.31		$\beta_3^2R_3/2$	-0.43	
$r_1^2R_2/2$	0.10		$R_3^2r_3/2$	-0.30				
$r_1^2R_6/2$	-0.14		$R_3^2R_1/2$	-0.55		$\beta_3^2q_{17}/2$	-0.21	
$r_2^2R_2/2$	0.12		$R_3^2R_2/2$	-0.24		$\beta_3^2q_{18}/2$	0.28	
$r_2^2R_3/2$	0.16		$R_3^2R_4/2$	-0.24		$q_{17}^2r_1/2$	-0.10	
$r_3^2R_3/2$	0.16		$R_3^2R_5/2$	-0.57		$q_{17}^2R_1/2$	-0.49	
$R_1^2r_1/2$	-1.25		$R_3^2\beta_2/2$	-0.44		$q_{17}^2R_2/2$	-0.42	
$R_1^2R_2/2$	-1.89		$R_3^2\beta_3/2$	0.48		$q_{17}^2R_3/2$	-0.49	
$R_1^2R_3/2$	0.32		$R_3^2q_{19}/2$	0.19		$q_{17}^2q_{18}/2$	-0.17	
$R_1^2R_4/2$	-1.01		$\beta_1^2r_1/2$	-0.27		$q_{18}^2R_1/2$	-0.32	
$R_1^2R_5/2$	0.49		$\beta_1^2R_1/2$	-0.64		$q_{18}^2R_2/2$	-0.47	
$R_1^2R_6/2$	-1.71		$\beta_1^2R_2/2$	-0.44		$q_{18}^2R_3/2$	-0.59	
$R_1^2\beta_1/2$	0.97		$\beta_1^2R_3/2$	0.10		$q_{18}^2q_{17}/2$	-0.24	
$R_1^2q_{17}/2$	-0.35		$\beta_1^2R_5/2$	0.10		$q_{19}^2R_1/2$	-0.76	
$R_1^2q_{18}/2$	-0.38		$\beta_1^2q_{17}/2$	-0.22		$q_{19}^2R_2/2$	-0.49	
$R_1^2q_{19}/2$	-0.15		$\beta_1^2q_{18}/2$	-0.13		$q_{19}^2R_3/2$	-0.47	
$R_2^2r_1/2$	-0.44		$\beta_1^2q_{19}/2$	0.27		$q_{19}^2q_{18}/2$	0.35	

<sup>a</sup> Direct calculated values obtained around the reference geometry (see text). Only the dominant independent cubic diagonal and semidiagonal constants are shown whose absolute value is  $\geq 0.10$ . See Table III for units.

be a reasonable combination of ab initio quantum chemical and experimental information. For the purpose of the present work, however, we do not wish to make use of the experimental data on pyridine but to treat it as though its spectrum were completely unknown. We therefore simply transfer scale constants derived for the SQM force field of benzene<sup>5</sup> and use them to scale the computed harmonic force field of pyridine.

Considering the fact that the N atom and the C-H group are isoelectronic and nearly the same size, it can be expected that the systematic errors of the ab initio Hartree-Fock method should be very similar for benzene and pyridine. It must be emphasized that this transfer of information is much less drastic than that applied by other workers who have either considered the C-N and C-C bonds to be identical or have assumed that the force constants of pyridine were identical with those of benzene. Our strategy is based on the similarity and transferability of systematic errors in the force constant calculations, and it does not depend on the direct transferability or similarity of the force constants themselves.

The 7 scale factors used as set II to fit the in-plane force field of benzene<sup>5</sup> computed at the same quantum mechanical level as in the present work were adopted here for pyridine. In addition to the CH stretching, CC stretching, and in-plane deformations, this set contains three extra scale factors for in-plane interactions in order to compensate for apparent overestimations in the theoretical values of some couplings. This is a slight departure from the standard procedure. We shall use an obvious terminology, denoting the results as an SQM (pyridine 4-21/benzene) force field; it is shown in Table III. Table IV gives the diagonal cubic constants and the more important ( $\geq 0.1$ ) semidiagonal cubic constants.

#### Assignment of Vibrational Spectra

As a test of the accuracy of our pyridine force field we have calculated the fundamental frequencies of pyridine and some of its isotopomers. The original assignment of the vibrational spectrum of pyridine was made by Kline and Turkevich<sup>32</sup> and by Corrsin et al.,<sup>33</sup> followed by many other works.<sup>6-19,34</sup> The most

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Table V. Calculated and Experimental In-Plane Frequencies of Isotopic Pyridines<sup>a</sup>

	$d_0$			$4-d_1$			$2,6-d_2$			$3,5-d_2$		
	exptl	calcd	int	exptl	calcd	int	exptl	calcd	int	exptl	calcd	int
A <sub>1</sub>	603	604	572	596	597	536	595	596	629	595	597	476
	991	980	802	989	980	898	891	881	650	827	824	596
	1030	1025	771	1010	1005	686	985	980	410	965	955	409
	1069	1073	39	1067	1073	39	1019	1016	281	1033	1032	633
	1217	1214	197	1214	1214	197	1089	1087	100	1174	1171	239
	1483	1475	1084	1475	1470	1220	1414	1411	181	1434	1422	1302
	1581	1585	2457	1574	1578	2176	1577	1573	2949	1573	1569	1741
	3042 <sup>b</sup>	3065	0	2286	2276	826	2257	2285	1403	2294	2286	94
	3065 <sup>b</sup>	3078	2643	3050	3073	1548	3063	3067	409	3044	3075	1358
	3077 <sup>b</sup>	3102	27	3050	3098	136	3063	3097	756	3044	3082	1110
B <sub>2</sub>	654	654	55	648	649	63	641	644	55	641	642	58
	1052 <sup>c</sup>	1053	67	861	861	40	906	900	3	866	870	22
	1146	1156	272	1085	1090	333	1131	1134	0	1086	1076	3
	1227	1240	29	1223 <sup>d</sup>	1231	45	1184	1183	661	1224	1233	175
	1355	1353	32	1330	1333	36	1245	1240	11	1323	1318	312
	1437	1436	3567	1412	1403	2475	1418	1419	2836	1408	1405	3209
	1574	1582	1101	1559	1570	1847	1567	1574	1021	1558	1568	1242
	3034	3071	855	3035	3071	856	2249	2274	2524	2272	2286	684
	3079	3093	3310	3072	3093	3303	3063	3088	1356	3035	3076	2880
	A <sub>1</sub>	$2,4,6-d_3$			$3,4,5-d_3$			$2,3,5,6-d_4$			$d_5$	
exptl		calcd	int	exptl	calcd	int	exptl	calcd	int	exptl	calcd	int
590		591	591	588	590	445	587	589	528	581	583	494
884		876	711	826	823	620	824	821	729	824	819	782
982		979	358	964	955	372	896	889	252	888	885	245
1012		1006	324	1017	1015	667	963	954	388	963	954	380
1083		1084	73	1169	1170	215	1019	1016	250	1009	1005	237
1408		1407	223	1426	1415	1389	1347	1338	177	1339	1330	207
1560		1564	2753	1569	1564	1544	1558	1552	2381	1550	1544	2220
2257		2276	959	2273	2265	291	2254	2272	1077	2252	2262	0
2276	2285	1262	2296	2297	621	2288	2299	351	2271	2280	2236	
3059	3089	182	3038	3082	1462	3042	3075	998	2294	2305	0	
B <sub>2</sub>	637	639	63	633	636	67	631	632	58	624	627	66
	840	835	42	839	841	51	824	823	0	824 <sup>e</sup>	822	1
	946	941	23	887	885	0	988	982	38	835	840	55
	1181	1180	673	1223	1230	9	1131	1133	48	1041	1036	7
	1229	1232	8	1243	1241	816	1236	1234	198	1228	1231	51
	1370	1367	1749	1395	1386	1854	1364	1366	3011	1298	1290	2221
	1551	1560	1745	1546	1555	1953	1552	1560	1153	1537	1546	1832
	2257	2274	2524	2281	2285	665	2250	2267	910	2248	2267	904
	3059	3088	1351	3035	3076	2878	2283	2292	2347	2281	2292	2334

<sup>a</sup> exptl and calcd means the experimental (ref 10-13) and calculated fundamental frequencies (in  $\text{cm}^{-1}$  units), respectively. int means the calculated absolute intensities of IR absorption, in  $\text{cm}^2/\text{mmol}$  units. The mean deviation between the experimental and calculated frequencies =  $9.6 \text{ cm}^{-1}$ ; for the non-CH frequencies alone, the mean deviation is  $5.7 \text{ cm}^{-1}$ . <sup>b</sup> From ref 8. DiLella and Stidham<sup>11</sup> give  $3057 \text{ cm}^{-1}$  for all three of these bands. <sup>c</sup> Recommended assignment in this work. The original assignment (ref 11) was  $1069 \text{ cm}^{-1}$ . <sup>d</sup> Recommended assignment in this work. The original assignment (ref 11) was  $1214 \text{ cm}^{-1}$ . <sup>e</sup> Recommended assignment in this work. The original assignment (ref 13) was  $867 \text{ cm}^{-1}$ .

extensive information currently available comes from the papers by Stidham and DiLella<sup>10-13</sup> on the parent molecule and the seven deuterated species having  $C_{2v}$  symmetry. We have therefore calculated these frequencies and the corresponding absolute infrared absorption intensities; the comparison is shown in Table V.

We consider the prediction of frequencies shown in Table V to be a remarkably successful demonstration of the transferability of scale factors between related molecules. The calculated frequencies of pyridine, obtained without reference to any experimental evidence on pyridine, agree with the experimental data even more closely than might be expected on the basis of the independent harmonic oscillator assumption used in the calculation. The reason for this is that the scale factors derived from benzene presumably incorporate some measure of the anharmonicity of benzene, which partially compensates for the anharmonicity in pyridine. In any case, it appears that the SQM (pyridine 4-21/benzene) calculation has been able to furnish a predicted

spectrum of pyridine, treated as a completely unknown molecule, in excellent agreement with experiment. The mean deviation of the non-CH frequencies is only  $5.7 \text{ cm}^{-1}$ .

The contrast with earlier efforts by Harsányi and Kilár<sup>21</sup> to transfer CNDO/2 scale constants from benzene to pyridine is striking. In that case, the predicted frequencies were in error by as much as  $146 \text{ cm}^{-1}$ , although it is possible that transfer of a larger number of scale factors would have improved the result. It should be noted, however, that the second force field of Harsányi and Kilár<sup>21</sup> scaled by five scale factors obtained from the observed spectrum of pyridine, i.e., an SQM (pyridine CNDO/pyridine) force field, is in fair agreement with our results. However, even this force field of theirs shows some systematic discrepancies from our scaled ab initio force field. Some of their smaller couplings differ in sign from ours; this is systematic for the  $(R_i, r_j)$  couplings of type 1,3, e.g.,  $(R_1, r_2)$ ,  $(R_2, r_3)$ , and so on. Perhaps the most significant deviation between the two force fields is in the value of the important  $R, \beta$  and  $R, \alpha$  couplings which are too low after scaling in the CNDO result.

The overall agreement between prediction and experiment shown in Table V suggests that variations exceeding 10 or  $15 \text{ cm}^{-1}$  ought to be inspected for possible experimental misassignment. The C-H vibrations present a special problem, and these will be

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discussed below. Otherwise, we see no need to modify any of the assignments of Stidham and DiLella<sup>10-13</sup> for the  $A_1$  species in any of the eight isotopic forms they investigated except for the three C-H stretchings of the parent molecule whose region is strongly perturbed by Fermi resonance and for which Stidham and DiLella made no attempt to determine the unperturbed frequencies.

Turning next to the  $B_2$  species, our calculations support the assignment of Suzuki and Orville-Thomas<sup>18,19</sup> for the  $\nu_{18b}$  fundamental of pyridine- $d_0$  at 1052  $\text{cm}^{-1}$  (for Wilson's notation of the fundamental frequencies of pyridine, see, e.g., ref 12 and 13). DiLella and Stidham<sup>11</sup> originally assigned this band at 1069  $\text{cm}^{-1}$ , considering the weak shoulder at 1052  $\text{cm}^{-1}$  to be a combination band of  $A_2$  symmetry. Our computed frequency of 1053  $\text{cm}^{-1}$  with a weak intensity favors the revised assignment.

In the case of pyridine- $4-d$ , the calculated value for the  $\nu_3$  frequency is 1231  $\text{cm}^{-1}$  while the experimental value<sup>11</sup> is 1214  $\text{cm}^{-1}$ . Although this difference is marginal to support a reassignment, there seems to be no strong evidence in favor of the experimental assignment. It may be better to consider the band at 1224  $\text{cm}^{-1}$  in the vapor IR spectrum as the  $\nu_3$  fundamental of pyridine- $4-d$ . Again, our predicted intensity is quite low.

Our predicted frequencies for the  $\nu_{18b}$  and  $\nu_{15}$  fundamentals of pyridine- $d_5$  are 822 and 840  $\text{cm}^{-1}$ , respectively, compared with the 835 and 867  $\text{cm}^{-1}$  suggested in ref 11. In our opinion it is reasonable to consider the band at 835  $\text{cm}^{-1}$  as a  $B_2$  fundamental, but not the weak shoulder at 867  $\text{cm}^{-1}$ . Stidham and DiLella, for example, were not able to assign any combination bands based on the assignment of 867  $\text{cm}^{-1}$  as a fundamental. We believe the polarized band of weak medium intensity observed at 824  $\text{cm}^{-1}$  is a superposition of the very weak  $B_2$  band ( $\nu_{18b}$ ) we have predicted at 822  $\text{cm}^{-1}$  and a more intense  $A_1$  fundamental ( $\nu_{18a}$ ) rather than being the  $A_1$  plus  $B_1$  superposition suggested in ref 11. This alteration of assignment was also concluded from the normal coordinate analysis of Suzuki and Orville-Thomas.<sup>18,19</sup> It must be emphasized that the minor corrections suggested here in a few of the vibrational assignments do not affect seriously the product and sum rules.

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; for example, the identification of the two extremely weak bands  $\nu_{13}$  and especially  $\nu_{20a}$  of the parent species in the wings of very intense bands is problematical. Even more importantly, the C-H vibrations are surely perturbed strongly by resonances which are not considered in our calculations except to the extent to which correction may be inadvertently made in the scale factors transferred from benzene. 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.

One computational factor hindering the achievement of still higher accuracy is the stringent requirement for having the true equilibrium geometry for the power series expansion of the vibrational energy. The sensitivity can be illustrated well by considering the C-H stretching frequencies. We used a geometrical correction of +0.005 Å 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 the footnote to Table IV of ref 26, the correction for C-H bonds originating at an  $sp^2$ -hybridized

carbon atom is probably nearer to +0.007 Å. The cubic constants we have calculated make it possible to see how much difference this geometrical error produces.

Using only diagonal and semidiagonal cubic force constants, we can calculate the approximate values of the quadratic force constants with the C-H bonds lengthened by 0.002 Å. Let us consider only the diagonal quadratic C-H force constants, for example,  $F_{11}$ . The theoretical unscaled value of this element at the original reference geometry is 6.0231  $\text{aJ}/\text{Å}^2$ . Correction from the diagonal and semidiagonal cubic constants (for which we consider only the CH stretch-CH stretch-CH stretch terms) is  $-0.072 \text{ aJ}/\text{Å}^2$  for a bond lengthening of 0.002 Å. This lowers  $F_{11}$  to 5.951  $\text{aJ}/\text{Å}^2$ , i.e., by 1.2%, corresponding to a reduction of about 0.6% or 20  $\text{cm}^{-1}$  in the C-H stretching fundamental. This change is in perfect agreement with the rule of thumb<sup>35</sup> that a 0.001-Å increase in a CH bond length corresponds to a 10- $\text{cm}^{-1}$  decrease in the associated frequency. With this correction, the overestimation of the CH frequencies is greatly reduced while the CD frequencies are slightly too low. This is a natural consequence of the different anharmonicity of the CH and CD bonds.

The consistent overestimation of the hydrogen vibrations in Table V provides added support for the suggestion in ref 26 that the offset value to be applied to  $sp^2$ -hybridized CH bond lengths, calculated at the 4-21 level, should be +0.007 Å rather than +0.005 Å.

## Conclusions

It has been demonstrated that the fundamental vibrational frequencies of a moderately complex molecule can be computed a priori to an accuracy approximating the harmonic oscillator limitations by transfer of SQM scale factors from a related molecule. In the test case of pyridine, the computed spectrum permits the resolution of a number of problems of assignment as well as lending confidence in the accuracy of the scaled force field from which other molecular vibrational properties can be computed. More generally, however, the results suggest that the method will permit the accurate evaluation of truly unknown vibrational spectra. The approach should be applicable to molecules containing up to about 20 atoms, depending on molecular symmetry and given the present level of widely available computer power. This limit will certainly rise in the near future. The technique does require the availability of a related reference substance for which the vibrational spectrum is at least partially understood, although it is not yet known how closely related the reference substance must be. It is quite possible, at least for organic molecules, that a general set of standard scale factors can be derived, applicable to most ground-state systems.

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