Ab initio computation of force constants. IV. The theoretical anharmonic force fields and vibrational frequencies of methylamine, methanol, and methanethiol[a]

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The anharmonic force fields of methylamine, methanol, and methanethiol have been computed *ab initio*. The harmonic force constants agree fairly well with experiment. Better agreement is found between the experimental frequencies and the theoretical anharmonic frequencies. The stretching modes are predicted especially well. The calculated ν_{13} and ν_{14} for CH_3NH_2 agree with the solid phase but not the gas phase experimental results. Methylamine, methanol, and methanethiol exhibit Bohlmann bands, i.e., a lowering of the stretching frequency of a C–H bond antiperiplanar to a lone pair. The computations reveal that these bands are linked to a smaller force constant for the *anti* CH bond and to Fermi resonance between the symmetric C–H stretch and CH bending overtones.

I. INTRODUCTION

In Part I of this series,[1] a procedure for the computation of force constants *ab initio* was described. This procedure is based on the force method,[2] and it employs Cartesian Gaussian basis sets to calculate the harmonic and anharmonic force constants. The efficacy of the method was tested first by computations on second and third period hydrides, and it was found that a 4-31G basis set[3] yields force fields that agree particularly well with experiment.

The present paper is concerned with the vibrational spectra of methylamine, methanol, methanethiol, and their deuterated derivatives. These are of interest for a number of reasons. First, the extensive structural and spectroscopic data that are available permit a continued test of the reliability of the method. Secondly, we may begin to assess the utility of the information that is becoming available. Thirdly, methylamine, methanol, and methanethiol are prototypes of molecules that exhibit the Bohlmann bands,[4] and a physical interpretation of this phenomenon is one of our objectives.

A preliminary investigation into the origin of the Bohlmann bands was described in an earlier paper[5] using methylamine as the theoretical model compound. The two different C–H stretching force constants computed in this initial treatment of the problem agreed reasonably well with the experimentally determined C–H stretching force constants. However, it was recognized that the procedure employed in the preliminary investigation was somewhat arbitrary and that a more sophisticated approach to the problem was needed. In

the present work, the full harmonic force field has been calculated. The effects of cubic and quartic force constants on the harmonic vibrational frequencies are also considered. These anharmonicity corrections are particularly important for stretching vibrations. Two vibrational states, such as a doubly excited bending mode and a singly excited stretching mode, which would normally not interact through the harmonic force field, may interact via the cubic (and, in some cases, the quartic) force constants. When the vibrational states are nearly degenerate, this coupling, termed Fermi resonance,[6] can be very strong. The possible contribution of Fermi resonance to the existence of the Bohlmann bands has already been suggested by Ernstbrunner and Hudec.[7]

II. CALCULATIONS

The SCF wavefunctions were generated by the GAUSSIAN 70 program system,[3a] using the standard 4-31G basis set[3b] (convergence on the density matrix to 5×10^{-5}). The forces were computed analytically by a program discussed elsewhere.[1,8] The calculation of the forces is roughly as time consuming as the computation of the total energy. The energy $E(\mathbf{q})$ and the forces on the nuclei, $\mathbf{f}(\mathbf{q})$, were calculated at the geometry of interest, $\mathbf{q}_0$, and at small displacements $\Delta\mathbf{q}_i$, from this geometry. The force constants are then determined numerically from the energy and the forces.

The displacements can be chosen to lie along individual coordinates, e.g., let the kth component of the displacement, $(\Delta\mathbf{q}_j)_k = \Delta_j \delta_{jk}$, where Δ_j is an appropriate step size, and δ_{jk} has the usual meaning. The harmonic force constants can be determined from a two-point difference formula:

$$F'_{ij} = [f_i(\mathbf{q}_0 - \Delta\mathbf{q}_j) - f_i(\mathbf{q}_0 + \Delta\mathbf{q}_j)]/2\Delta_j, \tag{2.1a}$$

$$F_{ij} = (F'_{ij} + F'_{ji})/2, \tag{2.1b}$$

where f_i is the ith component of the force vector. Equa-

tion (2.1b) ensures that the harmonic force constant matrix is symmetric.

As in Paper I of this series and in the work of Pulay, step sizes of 0.05 Å for bond stretching and 2.5 Å (0.0437 rad) for bending were used. The finite step size used in Eq. (2.1) results in errors proportional to the quartic force constant. Additional error arises from the uncertainty in the computed forces caused by the finite convergence criterion used in the SCF procedure.[9] The uncertainty in the force, δf, is approximately equal to the convergence on the density matrix achieved in the SCF.[9]

Thus, the purely numerical error for Eq. (2.1) is

$$\delta F'_{ij} \cong (\delta f/2\Delta_j) + (F_{ijjj}\Delta_j^2/3). \qquad (2.2)$$

The optimum step size that minimizes this error is[9]

$$\Delta_{j_{opt}} \cong (3\,\delta f/4F_{ijjj})^{1/3} \ . \qquad (2.3)$$

While little experimental information is available concerning the magnitudes of quartic force constants F_{ijjj}, an estimate of 1 mdyn/Å^3 would not be unreasonable,[10a] except for the diagonal bond stretching (see below). With $\delta f \cong 5 \times 10^{-5}$ mdyn, the optimum choice of the step size, $\Delta_{j_{opt}}$, would then be 3.4×10^{-2}. Thus, the previously chosen[1,26] sizes are nearly optimal for the harmonic bending and interaction force constants. For unhindered rotation about a single bond, the quartic force constant is expected to be much less than unity, and a larger step size (5°) was chosen.

For the cubic force constants, a three point difference formula is used:

$$F_{ijj} = -[f_i(\mathbf{q}_0 + \Delta\mathbf{q}_j) - 2f_i(\mathbf{q}_0) + f_i(\mathbf{q}_0 - \Delta\mathbf{q}_j)]/\Delta_j^2, \qquad (2.4)$$

and the error is approximately[11]

$$\delta F_{ijj} \cong (\delta f/\Delta_j^2) + (F_{ijjjj}\Delta_j^2/12). \qquad (2.5)$$

The calculation of the diagonal bond stretching force constants must be performed in a different manner, because of the large anharmonicity. A fourth degree polynomial was fitted to the energy and the forces at three points:

$$F'_{ii} = 2[E(\mathbf{q}_0 + \Delta\mathbf{q}_i) - 2E(\mathbf{q}_0) + E(\mathbf{q}_0 - \Delta\mathbf{q}_i)]/|\Delta\mathbf{q}_i|^2$$
$$- [f_i(\mathbf{q}_0 - \Delta\mathbf{q}_i) - f_i(\mathbf{q}_0 + \Delta\mathbf{q}_i)]/2|\Delta\mathbf{q}_i| \ , \qquad (2.6)$$

$$F_{iiii} = 12\,\{[f_i(\mathbf{q}_0 + \Delta\mathbf{q}_i) - f_i(\mathbf{q}_0 + \Delta\mathbf{q}_i)]/2|\Delta\mathbf{q}_i|$$
$$- [E(\mathbf{q}_0 - \Delta\mathbf{q}_i) - 2E(\mathbf{q}_0)$$
$$+ E(\mathbf{q}_0 - \Delta\mathbf{q}_i)]/|\Delta\mathbf{q}_i|^2\}\,|\Delta\mathbf{q}_i|^{-2} \ . \qquad (2.7)$$

The corresponding expression for F_{iii} is the same as Eq. (2.4).

For Eq. (2.6) the numerical error is

$$\epsilon \cong \frac{2\delta E}{|\Delta\mathbf{q}_i|^2} + \frac{\delta F}{2|\Delta\mathbf{q}_i|} + \frac{F_{iiiii}|\Delta\mathbf{q}_i|^4}{360} , \qquad (2.8)$$

and for Eq. (2.7) the error is

$$\epsilon \cong \frac{12\delta E}{|\Delta\mathbf{q}_i|^4} + \frac{6\delta f}{|\Delta\mathbf{q}_i|^3} + \frac{F_{iiiii}|\Delta\mathbf{q}_i|^2}{15} \ . \qquad (2.9)$$

With a convergence on the density matrix to 5×10^{-5}, the

error in the energy can be expected to be $\sim 5 \times 10^{-7}$ mdyn-Å, after conversion to the appropriate units. From Eqs. (2.3), (2.5), (2.8), and (2.9), the estimated numerical errors in the harmonic, cubic, and quartic force constants are then $\sim 10^{-3}$ mdyn/Å, ~ 1 mdyn/Å^2, and ~ 10 mdyn/Å^3, respectively.

In addition to these purely numerical error bounds on the force constants, additional uncertainties enter because of the finite size of the basis set and the neglect of correlation effects (for a comparison of basis set effects, see Refs. 1 and 26). These latter uncertainties are difficult to assess quantitatively. The 4-31G basis set used in the present work reproduces diagonal harmonic force constants of second and third period hydrides with an average error of $\pm 6\%$ for stretching and 15% for bending. The relative error is expected to be less when force constants referring to similar bonds or angles in the same molecule are compared. The larger error in the bending force constants can be traced to the lack of angular polarization functions in the 4-31G basis set. The average error for interaction force constants is $\sim \pm 0.06$ mdyn/Å. Diagonal cubic and quartic stretching force constants deviate from the experimental values by an average of ± 2 mdyn/Å^2 and ± 60 mdyn/Å^3, respectively.

The harmonic frequencies and normal co-ordinates are calculated by the Wilson F–G method.[12] For second and third period hydrides, deviations from the experimental frequencies average $\pm 3\%$ for stretching and $\pm 8\%$ for bending, with the latter generally ~ 100 cm^{-1} too high. The error in the bending frequencies is linked to the basis set deficiencies noted above. Internal consistency for the frequencies is much better than the overall accuracy, e.g., $\sim 0.7\%$ error on stretching frequency differences.

In order to make the anharmonicity corrections, the force constants must be transformed from the (curvilinear) internal coordinate system to the (linear) normal coordinate system. The approach of Hoy, Mills, and Strey[10a] is used; however, the derivatives of the L matrix that are needed for this curvilinear transformation are computed numerically rather than analytically. In this procedure, the B matrix is recomputed for small linear displacements of the molecular geometry along a normal coordinate. Since the L matrix is related to the B matrix, it can be computed readily. The necessary derivatives of the L matrix can then be computed from the L matrix evaluated at several displacements along a normal coordinate.

The energies of the vibrational levels in a molecule can be expanded as a power series in the vibrational quantum numbers, v_r:

$$E(v) = \sum_r \omega_r(v_r + \tfrac{1}{2}) + \sum_{r>s} \chi_{rs}(v_r + \tfrac{1}{2})(v_s + \tfrac{1}{2}) + \cdots \ . \qquad (2.10)$$

Formulas relating the harmonic frequencies ω_r and the anharmonicity constants χ_{rs} to the quadratic, cubic, and quartic force fields are well known, although somewhat cumbersome. The second order perturbation formulas for asymmetric top molecules given by Mills[10c] are used

TABLE I. Geometry and internal coordinates of methylamine.[a]

Coor-dinate	Description	Initial value[b]	Relaxed value[c]	Experi-mental[d]
1	r_{CN}	1.474	1.452	1.471
2	r_{CH_3}	1.093	1.089	1.099
3	r_{CH_4} }	1.093	1.080	1.099
4	r_{CH_5}			
5	r_{NH_6} }	1.014	0.994	1.010
6	r_{NH_7}			
7	$< H_3CN$	109.50	114.56	113.81
8	$< H_4CN$ }	109.50	109.40	109.46
9	$< H_5CN$			
10	$< H_6NC$	112.20	115.20	110.27
11	$< H_7NC$	112.20	115.20	110.27
12	$< H_4CNH_3$ (dihedral) }	∓ 120.07	∓ 121.35	∓ 120.00
13	$< H_5CNH_3$ (dihedral)			
14	$< H_6NCH_3$ (dihedral) }	± 60.00	± 65.71	± 59.05
15	$< H_7NCH_3$ (dihedral)			
	Methyl tilt angle $(= \frac{1}{3}(2 \times \#7 - \#8 - \#9))$	0.0	3.4	2.9

[a]Bond lengths in Å; bond angles in degrees;
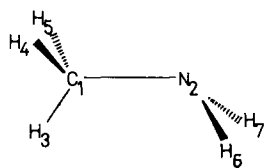
[b]Geometry at which the force field was calculated, Ref. 13(a).
[c]Using Eq. (2.11).
[d]Reference 14.

in the calculation of the anharmonicity constants χ.

The perturbation theory occasionally breaks down because of a near degeneracy of two interacting vibra-tional levels. When this occurs, the offending interaction can be removed from the perturbational treatment. Then, as a first approximation, the two unperturbed levels are allowed to interact directly via the appropriate anharmonic force constant, and the associated 2×2 eigenvalue problem is solved explicitly. The resulting level shifts are then added to the anharmonic frequencies calculated by perturbation theory. For XH_n and XD_n ($X = O$, S, N), the anharmonicity constants χ are reproduced with an average error of ± 10 cm^{-1} (± 2 cm^{-1} for H_2O/D_2O).

The forces $f(q_0)$, and the harmonic force constants, F, computed above, have been employed to relax the molecule[2] to the theoretical equilibrium geometry q_e, applying Eq. (2.11) once:

$$q_e = q_0 + F^{-1} f(q_0). \tag{2.11}$$

III. GEOMETRY AND INTERNAL COORDINATES

The internal coordinates of methylamine are shown in the first column, and the geometry employed for the calculation of the force field is shown in the second column of Table I. This geometry was chosen to be the same as the one used in the analysis of the experimental spectrum.[13a] The geometries employed for the calculation of the force constants of methanol and methanethiol are given in Columns 2 and 5 of Table II. These geometries are based upon a partial optimization with the 4-31G basis set, performed as part of another investigation.[13b]

The specification of the internal coordinates of the methyl group poses a problem, because the force method cannot be applied easily to coordinate systems which

TABLE II. Geometry and internal coordinates of methanol and methanethiol.[a]

Coor-dinate	Description	CH$_3$OH			CH$_3$SH		
		Initial	Relaxed	Exptl.[b]	Initial	Relaxed	Exptl.[c]
1	r_{CX}	1.433	1.429	1.427	1.883	1.885	1.819
2	r_{C-H_3}	1.096	1.075	1.093	1.096	1.076	1.091
3	r_{C-H_4} }	1.096	1.082	1.093	1.096	1.075	1.091
4	r_{C-H_5}						
5	r_{X-H}	0.960	0.951	0.945	1.333	1.354	1.336
6	$< H_3CX$	109.5	106.14	107.0	109.5	105.66	107.57
7	$< H_4CX$ }	109.5	110.43	111.9	109.5	110.17	110.84
8	$< H_5CX$						
9	$< HXC$	112.8	113.21	108.53	97.1	97.81	96.5
10	$< H_4CXH_3$ (dihedral) }	∓ 120.07[d]	∓ 118.71	∓ 120.0	∓ 120.07	∓ 118.65	∓ 120.0
11	$< H_5CXH_3$ (dihedral)						
12	$< H_6XCH_3$ (dihedral)	180.0	180.0	180.0	180.0	180.0	180.0
	Methyl tilt angle $[= \frac{1}{3}(\#7 + \#8 - 2\#6)]$	0.0	2.89	3.26	0.0	3.01	2.18

[a]Bond lengths in Å; bond angles in degrees.
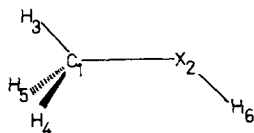
[b]Reference 15.
[c]Reference 16.
[d]Corresponds to a $H_4CH_3(H_5CH_3)$ valence angle of 109.5°.

TABLE III. Calculated force constants for methylamine.[a]

i	j =1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
F_{ij}															
1	5.410														
2	0.262	5.303													
3	0.117	0.066	5.439												
4	0.117	0.066	0.045	5.439											
5	−0.008	0.017	0.014	−0.026	7.141										
6	−0.008	0.017	−0.026	0.014	0.002	7.141									
7	0.554	−0.078	−0.077	−0.077	−0.023	−0.023	1.346								
8	0.458	−0.082	−0.044	−0.074	−0.000	0.056	0.166	1.224							
9	0.458	−0.082	−0.074	−0.044	0.056	−0.000	0.166	0.156	1.224						
10	0.414	−0.001	−0.005	0.032	0.048	−0.108	−0.018	−0.030	0.132	1.087					
11	0.414	−0.001	0.032	−0.005	−0.108	0.048	−0.018	0.132	−0.030	0.248	1.087				
12	−0.010	−0.172	−0.009	0.148	0.003	−0.000	0.249	0.010	−0.254	−0.005	0.002	0.917			
13	0.010	0.172	−0.148	0.009	0.000	−0.003	−0.249	0.254	−0.010	−0.002	0.005	−0.448	0.917		
14	0.036	−0.005	−0.012	−0.015	0.243	0.245	0.005	−0.014	−0.024	−0.323	−0.325	0.006	0.007	0.500	
15	−0.036	0.005	0.015	0.012	−0.245	−0.243	−0.005	0.024	0.014	0.325	0.323	0.007	0.006	−0.472	0.500
F_{iii}															
	−29.31	−32.06	−32.22	−32.22	−47.31	−47.31									

[a]Units: quadratic bending force constants, mdyn-Å; stretch–bend force constants, mdyn; stretch–stretch force constants, mdyn/Å; cubic stretching force constants, mdyn/Å².

contain redundancies. Cartesian displacement coordinates or symmetry adapted internal coordinates could be used[17] but we wish to examine force constants of individual bonds, as was done in Ref. 5. One might use only five of the six possible valence angles about the carbon.[18,19] The disadvantage of this procedure is that the internal coordinates are strongly coupled, and large off-diagonal force constants result. However, in the present work, cubic force constants of the type F_{ijk}, i, j, and k all different, and all quartic force constants other than diagonal stretching force constants, have been neglected. In a coordinate system which permits strong coupling, large values for the neglected force constants could result, and anharmonic frequencies would be affected.

The coordinate systems used in Tables I and II represent an alternative to the choices just discussed. Only three of the specified angles about the carbon are valence angles; the remaining two are dihedral angles about the C–X axis (a 109.5° valence angle between C–H bonds corresponds to a 120.07° dihedral angle). This choice of coordinate system avoids the problem of strong coupling of the internal coordinates. It should be noted that any coordinate system could have been used to calculate the harmonic frequencies, because all off-diagonal elements of the quadratic force constant matrix are calculated explicitly.

Once the forces and quadratic force constants had been obtained at the initial geometry, the molecule was allowed to "relax"[2] to its equilibrium geometry, by applying Eq. (2.11) once. In methylamine, as in the case of NH_3 (cf. Ref. 1), the calculated equilibrium geometry about nitrogen is poor. However, the methyl group is well described. In agreement with the preliminary study, the C–H bond antiperiplanar to the "lone pair" is slightly longer than the gauche C–H bonds. The tilt angle of the methyl group [in terms of the internal coordinates of Table I, the tilt angle is $\frac{1}{3}$ (2×# 7 − # 8 − # 9)] agrees well with experiment (calculated: 3.4°; observed[14]: 2.9°).

In methanol, the C–H bonds anti to the lone pairs are also slightly longer than the gauche C–H bonds; in methanethiol these two bond lengths are almost equal. However, in both compounds, the average C–H bond lengths are shorter than the experimental values. A 2.89° tilt angle for the methyl group is found in methanol and compares well with the experimental value[15] of 3.26 ± 0.18°. In methanethiol the tilt angle is 3.01°, somewhat larger than the observed[16] 2.18 ± 0.50°. The error in the C–S bond length (calculated: 1.885 Å; found: 1.819 Å) is considerably larger than the error in the C–O bond length (calculated: 1.429 Å; found: 1.427 Å). The difference can be traced to the lower quality of the 4-31G basis set for third period atoms.[1]

IV. FORCE CONSTANTS

A. Methylamine

The calculated force field of methylamine is shown in Table III (a tabulation of the complete set of calculated force constants is available in the supplementary material).[21] Bond length displacements of ± 0.05 Å and bond angle deflections of ± 2.5° were employed (except for #14 and #15, for which a ± 5.0° increment was used). Table IV shows the experimental quadratic force field. This was obtained by applying the necessary transformations to the symmetry adapted force field II of Ref. 13(a). Note that it differs slightly from the valence force field tabulated in this reference, because the latter was derived with certain restrictions upon the off-diagonal elements.

As observed previously,[1] the diagonal quadratic force constants appear, in general, to be overestimated. However, the HNC angle bends ($F_{10,10}$ and $F_{11,11}$) are curious exceptions, since they are lower than the experimental values (but see Sec. V). This result and the apparently large errors in $F_{14,14}$ and $F_{15,15}$ are possibly due to deficiencies in the nitrogen basis sets.

The difference in the anti and gauche C–H stretching force constants ($\Delta F = F_{3,3} − F_{2,2}$) is considerably larger

TABLE IV. Experimental quadratic force constants for methylamine.[a]

i	j=1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	5.126														
2	0.483	4.700													
3	0.483	-0.043	4.736												
4	0.483	-0.043	-0.079	4.736											
5	0.353	0.000	0.000	0.000	6.414										
6	0.353	0.000	0.000	0.000	0.030	6.414									
7	0.413	0.228	-0.046	-0.046	0.000	0.000	1.065								
8	0.413	-0.046	0.228	-0.046	0.000	0.000	0.113	1.090							
9	0.413	-0.046	-0.046	0.228	0.000	0.000	0.113	0.088	1.090						
10	0.333	0.000	0.000	0.000	0.125	-0.091	0.009	-0.044	0.091	1.159					
11	0.333	0.000	0.000	0.000	-0.091	0.125	0.009	0.091	-0.044	0.182	1.159				
12	0.000	-0.076	0.000	0.076	0.000	0.000	0.219	-0.024	-0.195	0.034	-0.034	0.730			
13	0.000	0.076	-0.076	0.000	0.000	0.000	-0.219	0.195	0.024	0.034	-0.034	-0.340	0.730		
14	0.067	0.000	0.000	0.000	0.130	0.130	-0.020	-0.010	-0.010	-0.221	-0.221	0.000	0.000	0.252	
15	-0.067	0.000	0.000	0.000	-0.130	-0.130	0.020	0.010	0.010	0.221	0.221	0.000	0.000	-0.228	0.252

[a]Units: see Table III; Ref. 13(a).

than in the experimental force field (calculated: ΔF =0.136; observed: 0.036). However, the difference is dominated by the nuclear component,[1] as was found in Ref. 5 ($\Delta F_{elec} = -0.007$, $\Delta F_{nucl} = 0.143$, $\Delta F_{total} = 0.136$), even though both the electronic and the nuclear contributions are significantly smaller in magnitude than was found in the preliminary investigation. The total difference is almost identical in the two studies (ΔF =0.136, 0.137).

In view of the dominance of the nuclear component in the differences in stretching force constants, one might anticipate a similar difference in the two HCN bending force constants ($\Delta F = F_{7,7} - F_{8,8}$) with the angle "gauche" to the lone pair easier to deform (because there are fewer nuclei in line with a *gauche* bending motion than with an *anti* bending motion). The *ab initio* calculations agree with this speculation ($\Delta F_{elec} = -0.044$, ΔF_{nucl} =0.167, $\Delta F_{total} = 0.122$ mdyn-Å) but the difference is not reproduced in the experimental force field. The source of this discrepancy is the tilt of the methyl group. The variation of the harmonic force constant with a change in geometry is directly proportional to the cubic force constant ($F_{ij}^{new} = F_{ij}^{old} + \sum_k F_{ijk}\Delta_k$, where Δ_k is the change in geometry of the kth coordinate and F^{old}, F^{new} are the force constants at the original and

the changed geometry, respectively). When the methyl tilt is taken into account in this way, the calculated difference is brought into closer agreement with the experimental difference (calculated: $\Delta F = -0.044$; observed: $\Delta F = -0.025$).

B. Methanol and methanethiol

The calculated and experimental[17-19] force fields of methanol and methanethiol are found in Tables V-VIII (see also the supplementary material).[21]

In agreement with the trends found earlier,[1] the theoretical harmonic force constants are generally higher than the experimental values. Of the two experimental force fields given in Table VI, the first, (A), was based originally upon a nonredundant internal coordinate system that uses five of the six available valence angles about carbon.[18] The methanethiol force field[19] is based upon a similar coordinate system. The problems associated with such a coordinate system have already been noted above. In the experimental methanol and methanethiol force fields, C–H bonds antiperiplanar to lone pairs are stronger than *gauche* C–H bonds. This is probably erroneous, because (i) the alternate methanol force field, (B)[17a]; (ii) the present calculations;

TABLE V. Calculated force constants of methanol.[a]

i	j=1	2	3	4	5	6	7	8	9	10	11	12
F_{ij}												
1	5.723											
2	0.110	5.371										
3	0.237	0.057	5.266									
4	0.237	0.057	0.073	5.266								
5	-0.093	-0.040	0.008	0.007	8.391							
6	0.498	-0.058	-0.066	-0.066	0.050	1.225						
7	0.570	-0.061	-0.064	-0.067	-0.025	0.167	1.325					
8	0.570	-0.061	-0.067	-0.064	-0.025	0.167	0.189	1.325				
9	0.454	0.017	-0.005	-0.005	0.195	0.124	-0.018	-0.020	0.844			
10	0.011	-0.153	0.010	0.169	-0.004	0.241	0.009	-0.243	0.009	0.943		
11	-0.011	0.153	-0.169	-0.010	0.004	-0.241	0.243	-0.009	-0.009	-0.466	0.943	
12	0.000	0.000	0.009	-0.009	0.000	0.000	0.020	-0.020	0.000	0.013	0.013	0.028
F_{iii}												
	-31.83	-31.66	-31.49	-31.49	-59.88							

[a]Units: see Table III.

TABLE VI. Experimental quadratic force constants of methanol.[a]

i	j=1	2	3	4	5	6	7	8	9	10	11	12
A. Ref. 15												
1	5.659											
2	−0.010	4.575										
3	−0.016	−0.023	4.726									
4	−0.016	−0.023	0.030	4.726								
5	0.005	−0.001	0.000	0.000	7.586							
6	0.157	0.012	0.011	0.011	0.002	1.185						
7	0.138	0.017	0.008	0.004	0.004	−0.038	1.072					
8	0.138	0.017	0.004	0.008	0.004	−0.038	0.076	1.072				
9	0.034	0.002	0.003	0.003	0.000	−0.024	0.027	0.027	0.834			
10	−0.006	0.005	0.002	0.002	−0.001	0.161	−0.083	0.124	−0.014	0.528		
11	0.006	−0.005	−0.002	−0.002	0.001	−0.161	−0.124	0.083	0.014	−0.172	0.528	
12	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.027
B. Ref. 14												
1	5.275											
2	0.000	4.838										
3	0.000	0.000	4.661									
4	0.000	0.000	0.000	4.661								
5	0.000	0.000	0.000	0.000	7.568							
6	0.454	0.000	0.000	0.000	0.000	1.097						
7	0.454	0.000	0.000	0.000	0.000	0.135	1.071					
8	0.454	0.000	0.000	0.000	0.000	0.135	0.135	1.071				
9	0.407	0.000	0.000	0.000	0.000	0.086	−0.010	−0.010	0.737			
10	0.000	0.000	0.000	0.000	0.000	0.190	0.000	−0.190	0.000	0.747		
11	0.000	0.000	0.000	0.000	0.000	−0.190	0.190	0.000	0.000	−0.369	0.747	
12	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.009	0.009	0.026

[a]Units: see Table III.

and (iii) two other theoretical studies[20] all indicate that the *anti* C–H bond should have the smaller stretching force constant. As in the case of methylamine, the difference between the *gauche* and *anti* HCX bending force constants is opposite to the experimental result (methanol: $F_{gauche} - F_{anti} = \Delta F = -0.100$ mdyne-Å, calc; ΔF =0.026, obs; methanethiol: $\Delta F = -0.058$, calc; ΔF =0.136, obs). This discrepancy is caused by the neglect of the methyl tilt in the theoretical calculations. If the cubic force constants are employed to estimate the change in the harmonic force constants caused by the

methyl tilt, the disagreement is less (methanol: ΔF = −0.041; methanethiol: ΔF =0.002).

For the off-diagonal force constants of methanol, agreement in both sign and magnitude between the theoretical force field and the experimental force field (B) is quite good, with the theoretical values slightly larger. However, some of the force constants which are constrained to be zero in the experimental force field are found to be relatively large in the theoretical computations. In particular, there are significant interactions

TABLE VII. Calculated force constants of methanethiol.[a]

i	j=1	2	3	4	5	6	7	8	9	10	11	12
F_{ij}												
1	3.036											
2	0.023	5.426										
3	0.043	0.038	5.358									
4	0.043	0.038	0.049	5.358								
5	−0.010	−0.022	0.012	0.011	4.368							
6	0.322	−0.071	−0.076	−0.076	0.021	1.021						
7	0.408	−0.075	−0.119	−0.075	0.001	0.165	1.079					
8	0.408	−0.075	−0.075	−0.119	0.001	0.165	0.178	1.079				
9	0.224	0.022	−0.007	−0.008	0.054	0.187	−0.050	−0.050	0.988			
10	0.020	−0.149	0.008	0.155	−0.002	0.256	0.000	−0.251	0.007	0.915		
11	−0.020	0.149	−0.155	−0.008	0.002	−0.256	0.251	0.000	−0.007	−0.449	0.915	
12	0.000	0.000	0.004	−0.004	0.000	0.000	−0.001	0.001	0.000	0.016	0.016	0.028
F_{jjj}	−12.20	−31.72	−31.78	−31.78	−23.29							

[a]Units: see Table III.

TABLE VIII. Experimental quadratic force constants of methanethiol. [a,b]

i	j = 1	2	3	4	5	6	7	8	9	10	11	12
1	3.093											
2	−0.060	4.682										
3	−0.035	−0.006	4.853									
4	−0.035	−0.006	0.044	4.853								
5	0.010	−0.010	0.000	0.000	3.904							
6	0.289	0.268	0.187	0.187	−0.015	1.259						
7	0.250	0.283	0.061	0.097	0.020	0.076	1.083					
8	0.250	0.283	0.097	0.061	0.020	0.076	0.138	1.083				
9	0.097	−0.014	0.009	0.009	0.000	−0.053	0.050	0.050	0.659			
10	0.017	0.132	0.077	0.051	−0.001	0.134	0.207	−0.049	−0.031	0.503		
11	−0.017	−0.132	−0.051	−0.077	0.001	−0.134	0.049	−0.207	0.031	−0.203	0.503	
12	0.000	0.000	−0.001	0.001	0.000	0.000	−0.003	0.003	0.000	0.002	0.002	0.038

[a]Units: see Table III.   [b]Reference 19.

between the C–H and C–O stretches ($F_{1,2}$, $F_{1,3}$, and $F_{1,4}$) and the HCH bends ($F_{2,10}$, $F_{2,11}$, $F_{3,11}$, and $F_{4,10}$) that are completely neglected in the experimental force field. The theoretical harmonic force field of methanethiol shows similar features.

V. VIBRATIONAL FREQUENCIES

A. Methylamine

The fundamental vibration frequencies of CH_3NH_2, CD_3NH_2, CH_3ND_2, and CD_3ND_2 are listed in Table IX, along with the experimentally observed frequencies (classified according to symmetry). Anharmonicity constants and harmonic frequencies are in the supplementary material.[21] The agreement between theory and experiment is satisfactory; stretching modes are predicted rather accurately, with an average deviation of only 35 cm^{-1} for 20 frequencies and, for bending modes, the average deviation is 77 cm^{-1} (31 frequencies).

Not all of the A'' bending frequencies have been observed in the gas phase, and there appears to be some ambiguity concerning the location of the NH_2 twist frequency.[13a,22] The calculated values for ν_{13} and ν_{14} of CH_3NH_2 and CH_3ND_2 agree well with the observed solid state vibrational bands.[23] Since the experimental quadratic force field shown in Table IV appears to have been based on an erroneous frequency assignment ($\nu_{14} = 1195$ cm^{-1}), some of the discrepancies between the ab initio and experimental force fields in this case may be due to errors in the experimental force field. This view is strengthened by the good agreement between the theoretical frequencies computed by Pulay[24] in a separate ab initio study of methylamine.

To assess the possible significance of Fermi resonance, it is desirable to examine more closely certain of the stretching vibrations.

TABLE IX. Fundamental vibration frequencies of methylamine.

	CH_3NH_2		CD_3NH_2		CH_3ND_2		CD_3ND_2	
	Calc	Exptl[a]	Calc	Exptl	Calc	Exptl	Calc	Exptl
A'								
ν_1	3340	3360	3339	3361	2966	2961	2460	2477
ν_2	2976	2962	2239(2328)[c]	2203	2897	2817	2229	2202
ν_3	2898	2820	2107	2077	2458	2479	2115	2073
ν_4	1713	1623	1796	1624	1604	1468	1314	1227
ν_5	1604	1474	1207	1142	1553	1430	1201	1123
ν_6	1551	1430	1161		1340	1234	1160	
ν_7	1238	1130	1009	973	1228	1117	989	942
ν_8	1056	1044	1001	913	1018	997	970	880
ν_9	862	780	818	740	694	625	669	601
A''								
ν_{10}	3426	3424	3425	3427	3002	2985	2560	2556
ν_{11}	3004	2985	2224	2236	2528	2556	2203(2108)[d]	2238
ν_{12}	1593	1476	1430		1603	1485	1136	1077
ν_{13}	1391	1337[b]	1148	1077	1275	1187	1103	
ν_{14}	992	995[b]	814		814	822[b]	919	910
ν_{15}	206	264	191		186	225	164	

[a]Reference 13(a), unless otherwise noted.
[b]From solid state measurements, Ref. 23.
[c]Before correction for resonance between ν_2 and $\nu_5 + \nu_7$.
[d]Before correction for resonance between ν_{11} and $\nu_5 + \nu_{13}$.

TABLE X. Fundamental vibration frequencies of methanol.[a]

	CH$_3$OH		CD$_3$OH		CH$_3$OD		CD$_3$OD	
	Calc	Obs[b]	Calc	Obs	Calc	Obs	Calc	Obs
A'								
ν_1	3730	3681.5	3727	3682.5	3004	3001.0	2746	2717.4
ν_2	3009	2999.0	2236	2242.0	2919	2840.8	2212	2250
ν_3	2919	2844.2	2117	2073.5	2748	2717.6	2114	2074.0
ν_4	1611	1478	1329	1295.8	1609	1479	1209	1134
ν_5	1571	1454.5	1198	1129	1570	1455	1174	1078
ν_6	1391	1334	1169	1068.2[c]	1285	1224.5	1089	1027.8
ν_7	1113	1074.5	1028	984.5	1062	1038	1012	980.0
ν_8	1046	1033.5	882	853	885	864	796	774.8
A''								
ν_9	2988	2970	2232	2212.4	2978	2970	2245	2212.6
ν_{10}	1583	1465	1162	1068.2[c]	1594	1463	1157	1069.3
ν_{11}	1234	1145	957	897.5[c]	1234	1142	952	895.0[c]
ν_{12}	262	271.5[c]	248	259.0[c]	212		195	

[a]Units: cm^{-1}.
[b]Reference 17.
[c]Ar matrix, Ref. 17.

1. CH_3NH_2

Of the five stretching vibrations, all are within 20 cm^{-1} of the observed values except for ν_3 which has an error of 78 cm^{-1}. A large cubic force constant, ϕ = − 175 cm^{-1} links the symmetrical C–H stretch ν_3 (with harmonic frequency ω_3 = 3073, cf. Table IV) with the first overtone of the symmetric HCN bending mode, $2\nu_6$ ($2\omega_6$ ≈ 3173). This leads to a lowering of ν_3 and a raising of $2\nu_6$. Because of the overestimation of the bending frequencies, the actual energy difference between the two interacting levels is overestimated. Since the interaction between the two levels is inversely proportional to the energy difference, the lowering of ν_3 must be underestimated. This rationalization is supported by the infrared and Raman spectra of the compound in the solid state.[23] A series of intense overtone and combination bands between 2840 and 2915 cm^{-1} appear to be in Fermi resonance with the symmetric C–H bands at 2794 and 2809 cm^{-1}. Additional confirmation can be obtained from the spectra of CD$_3$NH$_2$. Here the bending overtones and combination bands and the symmetric stretching fundamental are further apart and are not coupled as strongly. The agreement between computed and observed is much better in this case (calc: 2107 cm^{-1}; obs: 2077 cm^{-1}).

2. CD_3NH_2

In the calculated spectrum ν_2 (ω_2 = 2324.9 cm^{-1}) is abnormally high because of the presence of a combination band $\nu_5 + \nu_7$ ($\omega_5 + \omega_7$ = 2321.6 cm^{-1}). While the cubic force constant which couples the two levels is not very large, ϕ = 53 cm^{-1}, the very small energy difference ($\Delta\omega$ = 3.3 cm^{-1}) causes the second order perturbation expansion to break down. When this interaction is taken into account properly, by diagonalization of the associated 2×2 matrix, much better agreement with the observed frequency is obtained (calc: ν_2 = 2239 cm^{-1}; obs: 2203 cm^{-1}).

3. CH_3ND_2

As in the case of CH$_3$NH$_2$, the theoretical calculation appears not to produce a sufficiently strong interaction

between the symmetric stretch ν_2 (ω_2 = 3073 cm^{-1}) and the symmetric bend overtone $2\nu_5$ ($2\omega_5$ = 3172 cm^{-1}) (cubic force constant ϕ = − 175 cm^{-1}), because of the overestimation of the energy difference between the two levels. Consequently, ν_2 is not lowered by the correct amount.

4. CD_3ND_2

As with CD$_3$NH$_2$, an accidental near degeneracy leads to a breakdown of the second order perturbation expansion. When the interaction of ν_{11} with $\nu_5 + \nu_{13}$ is taken into account exactly (ϕ = 63 cm^{-1}, $\Delta\omega$ = 4.3 cm^{-1}), the value of ν_{11} becomes 2203 cm^{-1} (obs: 2238 cm^{-1}).

When the above corrections for resonance in CD$_3$NH$_2$ and CD$_3$ND$_2$ are taken into account, the average error in the stretching frequencies is reduced to 26 cm^{-1} (i.e., ~ 1%).

B. Methanol and methanethiol

The anharmonic frequencies of methanol, methanethiol, and some of their deuterated derivatives (CH$_3$OH, CD$_3$OH, CH$_3$OD, and CD$_3$OD; CH$_3$SH, CD$_3$SH, CH$_3$SD, and CD$_3$SD) are presented in Tables X and XI (see supplementary data for the harmonic frequencies and anharmonicity constants).[21]

The O–H, O–D and S–H, S–D stretching frequencies are predicted well, with an average deviation of 45 cm^{-1} or 1.6% (six frequencies). Even better agreement is obtained for the C–H, C–D stretching frequencies which have an average deviation of 24 cm^{-1} for 18 frequencies.

In CH$_3$OH and CH$_3$OD, the symmetric C–H stretching mode is too high by ~ 75 cm^{-1}. This may be due, in

TABLE XI. Fundamental vibration frequencies of methanethiol.[a]

	CH$_3$SH		CD$_3$SH	CH$_3$SD		CD$_2$SD
	Calc	Obs[b]	Calc	Calc	Obs	Calc
A'						
ν_1	3016	3015	2671	3014	3015	2338(2697)[d]
ν_2	2977	2948	2306(1301)[c]	2975	2949	2086
ν_3	2670	2605	2089	1935	1893	1935
ν_4	1589	1453	1158	1588	1453	1157
ν_5	1450	1332	1100	1451	1332	1101
ν_6	1155	1072	1051	1078	1007	882
ν_7	845	802	705	682	717	652
ν_8	677	710	640	660	623	603
A''						
ν_9	3014	3012	2226	3012	3011	2223
ν_{10}	1569	1444	1145	1569	1444	1145
ν_{11}	1025	956	776	1026	963	777
ν_{12}	202		182	168		145

[a]Units: cm^{-1}.
[b]Reference 25.
[c]Before correction for resonance between ν_2 and $2\nu_4$.
[d]Before correction for resonance between ν_1 and $2\nu_4$.

TABLE XII. Fundamental vibration frequencies of CH_2DOH and CHD_2OH. [a]

	CH₂DOH (C_s)		CH₂DOH (C_1)		CHD₂OH (C_s)		CHD₂OH (C_1)	
	Calc	Obs [b]	Calc	Obs	Calc	Obs	Calc	Obs
1	3729	3682	3729	3682	3727	3682	3728	3682
2	3000	2954	3022	2980	3018	2979	3008	2919
3	2983(3225)[c]	2886(2935)[d]	2978	(2908)[e]	2224	2204	2246	2239
4	2224	2193	2188	2156	2148	2108	2185(2246)[f]	2125
5	1603	1460	1580	1466	1432	1377	1467	1340
6	1497	1378	1457	1370	1415	1308	1438	1315
7	1411	1301	1425	1338	1328	1280	1307	1269
8	1296	1241	1344	1250	1180	1097	1172	1092
9	1181	(1110)[e]	1126	1063	1044	1011	1086	1039
10	1081	1050	1044	1025	976	923	999	942
11	905	892	975	914	960	899	890	863
12	257	265	256	(267)[e]	250	(262)[e]	252	262

[a]Units: cm^{-1}.
[b]Reference 17: where possible, gas phase measurements used.
[c]Before correction for resonance between #3 and #6.
[d]This reassignment of the fundamental frequency has been suggested in Ref. 20(b).
[e]Calculated in Ref. 17.
[f]Before correction for resonance between #4 and #9.

part, to Fermi resonance with the overtones of bending modes. A similar proposal has been made by Blom et al.[20b] The matrix isolation spectra of CH_3OH and CH_3OD[17] show several bands, assigned in each case to combination and overtone modes, at frequencies slightly higher than the symmetric C–H stretching fundamentals. The theoretical calculations indicate the existence of matrix elements which permit these states to interact. In particular, the overtone of the symmetric deformation can interact via a cubic force constant of -179 cm^{-1} in methanol, and -242 cm^{-1} in methanethiol. On the basis of the experimental spectra, it can be estimated that this effect should lower the symmetric C–H stretching mode of methanol by 15–45 cm^{-1}. However, since the bending frequencies are overestimated in the theoretical calculations, the energy difference between the levels is also overestimated, and the computed interaction is considerably weaker. In CD_3OH and CD_3OD there are fewer bands which can interact strongly, and agreement between theory and experiment is much better.

The possibility exists that the discrepancy in the symmetric C–H stretching frequency could also be a result of the neglect of certain anharmonic valence force constants of the type f_{ijk} (i, j, and k all different) and f_{ijkl} (i, j, k, and l not all equal). However, this explanation seems less likely than the resonance argument. The force constants that are omitted are expected to be small, and their neglect in computations on water[1] does not affect the quality of computed anharmonicity constants. The adequacy of the anharmonic force field is supported further by the good agreement obtained with methanethiol. In this case the symmetric C–H stretching mode is not perturbed strongly by resonances, because the methyl deformation frequencies are lower than in methanol.

For the bending modes of methanol, methanethiol, and their deuterated derivatives, an average deviation of 72 cm^{-1} is found (44 frequencies), arising mainly from

the overestimation of the CH_3 deformation frequencies (by an average of 125 cm^{-1}). Based on the results of computations on methane employing different sized basis sets, this error can be linked to the absence of angular polarization functions.[26]

The C–X stretching frequencies are predicted more accurately than the bending frequencies. In the methanol series, the theoretical frequencies are higher than the observed values, while in CH_3SH and CH_3SD the computed frequencies are lower. This latter result is attributed to the longer theoretical C–S bond length used in the present calculations.

In the theoretical spectra of CD_3SH and CD_3SD, the harmonic frequencies of the A' asymmetric C–D stretch and the first overtone of the A' asymmetric CD_3 deformation are accidentally degenerate. This causes a breakdown in the second order perturbation expansion for these two energy levels. When the interaction between the two levels is taken into account exactly (e.g., in a 2×2 matrix eigenvalue problem), a reasonable value for the stretching fundamental is obtained.

Table XII lists the experimental and observed frequencies of two unsymmetrically deuterated derivatives of methanol in each of two (internal) rotational conformations. The overall agreement with experiment is approximately as good as for the symmetrically deuterated species. With a few exceptions, the signs of the frequency differences between the C_s and C_1 symmetry species are predicted correctly. The approximate magnitudes of the differences are also reproduced fairly well. In one case (#3 of CH_2DOH), a spurious resonance is partly to blame. In the other cases (#5, a methyl deformation in both CH_2DOH and CHD_2OH), the error can be traced to the difference in the gauche and anti HCO bending force constants. It should be recalled that neglect of the methyl tilt angle causes the order of the theoretical force constants to be reversed, when these are compared to the experimental values.

TABLE XIII. Theoretical vibrational frequencies for CH_2DSH and CHD_2SH. [a]

| | CH$_2$DSH | | CHD$_2$SH | |
	C_s	C_1	C_s	C_1
1	3020	3029	3020	3006
2	2960	2976	2670	2671
3	2671	2670	2260	2290
4	2235	2181	2179(2221)[c]	2149
5	1557(1020)[b]	1550	1402	1418
6	1367	1376	1333	1342
7	1365	1350	1147	1135
8	1056	1126	1068	1044
9	999	894	780	867
10	765	781	770	721
11	643	668	662	642
12	193	193	187	187

[a]Units: cm^{-1}.

[b]Before correction for resonance between #5, #6, and #12.

[c]Before correction for resonance between #4, #5, and #9.

The data for methanethiol are shown in Table XIII. The trends are very similar to those of methanol. Again, a few frequencies are shifted by resonances peculiar to the theoretical calculations. The reversal of the frequency differences for vibration #5 is analogous to the one observed with methanol.

The frequent breakdown of the second order perturbation energy expansion, because of near degeneracies of the harmonic vibrational levels, is somewhat annoying. This problem can be expected to be more frequent as the size of the molecule increases. Ideally, it could be avoided by direct diagonalization of the appropriate Hamiltonian matrix. However, the size of this matrix quickly becomes prohibitively large, because it is approximately proportional to the cube of the number of

fundamental vibrations. An alternative method would be very desirable.

VI. THE BOHLMANN BANDS

As calculated in the preliminary investigation,[5] and reconfirmed in the present work, the stretching force constant of a C–H bond antiperiplanar to a lone pair is smaller than that of a C–H bond *gauche* to a lone pair. In addition, the more sophisticated calculations also show that this difference in the force constants parallels a difference in the nuclear component of the force constants. However, a calculation which deals only with the *harmonic* frequencies cannot reproduce the observed vibrational spectrum. As is readily evident from the frequency data just discussed, complicated anharmonic contributions and resonance corrections must be made to achieve satisfactory agreement with experimental spectra. Therefore, one should not expect that a quantitative description of the Bohlmann band phenomenon will be found within the framework of the harmonic force field. To test this hypothesis the theoretical anharmonic vibrational spectra must also be examined for features of the Bohlmann bands.

A. Methylamine

The harmonic and anharmonic frequencies of some deuterated methylamines not discussed previously are found in Table XIV.

(i) The CH and CD symmetric stretches of CH_3NH_2 and CD_3NH_2 are virtually unaffected by deuteration at nitrogen (CH_3ND_2 and CD_3ND_2; Table IX).

(ii) In CH_2DNH_2, the C–D stretch is effectively isolated from the C–H stretches so that the conformational dependence of stretching vibrations can be examined more closely. One would expect the C–D stretching frequency to be lower when the C–D bond is anti-peri-

TABLE XIV. Fundamental vibration frequencies of some unsymmetrically substituted methylamines. [a]

| | CH$_2$DNH$_2$ | | | | CH$_2$DND$_2$ | | | | CD$_2$HNH$_2$ | | | |
| | D gauche | | D anti | | D gauche | | D anti | | H gauche | | H anti | |
	Harmonic	Anharmonic	Harmonic	Anharmonic	Harmonic	Anharmonic	Harmonic	Anharmonic	Harmonic	Anharmonic	Harmonic	Anharmonic
1	3618	3425	3618	3426	3147	3007	3163	3015	3618	3426	3618	3424
2	3550	3340	3550	3340	3089	2952	3115	2957	3550	3339	3550	3339
3	3147	3011	3162	3016	2665	2560	2665	2564	3139	3002	3097	2992
4	3089	3009	3115	2957	2565	2454	2565	2455	2332	2210	2348	2505
5	2301	2248	2266	2179	2301	2230	2266	2192	2237	2106	2257	2179
6	1836	1942	1835	1839	1629	1586	1608	1578	1834	4234	1835	1839
7	1630	1585	1608	1577	1498	1455	1466	1436	1481	1454	1501	1472
8	1503	1458	1486	1459	1439	1412	1448	1416	1451	1420	1467	1416
9	1457	1415	1464	1433	1357	1327	1352	1321	1327	1294	1345	1303
10	1348	1310	1368	1318	1238	1193	1268	1220	1205	1179	1194	1171
11	1189	1145	1166	1110	1114	1087	1101	1077	1132	1106	1106	1054
12	1096	1061	1030	998	1026	1003	1008	981	1030	999	1072	1025
13	948	883	1008	969	785	760	827	804	917	872	891	839
14	876	842	896	842	737	688	722	677	858	822	845	820
15	278	199	281	199	225	176	227	176	271	194	269	194

[a]In cm^{-1}.

planar to the nitrogen lone pair and this effect is found. The *anti* C–D stretch is at 2179 cm^{-1} and the *gauche* stretch is at 2248 cm^{-1}. The difference is enhanced by resonance in the *gauche* form, since the difference in the harmonic frequencies is only 35 cm^{-1}. This effect is removed by replacing the amino hydrogens by deuteriums (2192 cm^{-1} *anti* vs 2230 cm^{-1} cm *gauche*), and the difference reduces to 38 cm^{-1} (35 cm^{-1} for harmonic frequencies).

Isolation of a C–H stretching vibration can be achieved by placing two deuterium atoms on carbon as in CD_2HNH_2. As expected, the *anti* C–H stretching frequency is lower: 2992 cm^{-1} *anti* vs 3002 cm^{-1} *gauche* for anharmonic frequencies (affected by a spurious resonance); 3097 cm^{-1} *anti* vs 3139 cm^{-1} *gauche* for harmonic frequencies; 2880 cm^{-1} *anti* vs 2955 cm^{-1} gauche for the observed frequencies.[27]

In the same way, a pair of C–H or C–D bonds adjacent to the nitrogen can be isolated, as in CH_2DND_2 and CD_2HNH_2. The conformation which places one C–H (C–D) gauche to the lone pair and one C–H (C–D) *anti* to the lone pair is expected to have the lower set of frequencies. This is found both in CH_2DND_2 (3147, 3089 cm^{-1} for one *gauche* and one *anti* C–H bond vs 3163, 3115 cm^{-1} for both C–H bonds *gauche*) and in CD_2HNH_2 (2332, 2237 cm^{-1} for one *gauche* and one *anti* C–D bond vs 2348, 2257 cm^{-1} for both C–D bonds *gauche*; only the harmonic frequencies are quoted because the anharmonic frequencies are complicated by a spurious resonance).

The above *gauche–anti* differences in the stretching vibrations of single and paired C–H (C–D) bonds can be compared to similar differences in isopropylamine (which has a single alpha C–H bond) and ethylamine (which has a pair of alpha C–H bonds).[28] In both cases, a single C–H or C–D bond anti to the lone pair has a lower stretching frequency. In addition, a pair of C–H or C–D bonds, one of which is *anti* to the lone pair, have lower stretching frequencies. Finally, the *gauche–anti* differences in the stretching frequencies are relatively small, and are generally less than 50 cm^{-1}, both in the experimental (isopropylamine and ethylamine) and theoretical (CH_2DND_2 and CD_2HNH_2) observations.

(iii) In methylamine (Table IX), the symmetric C–H stretching band (2820 cm^{-1}) is found to be 78 cm^{-1} lower than the computed theoretical frequency, because of resonance between bending overtone and combination bands and the symmetric stretching fundamental. This strong resonance does not exist in CD_3NH_2.

Several conclusions can now be reached concerning the Bohlmann bands. First, since the C–H stretching frequencies are not affected significantly by isotopic substitution at the nitrogen and the amino hydrogens, a *gauche* interaction[29] between vicinal N–H or N–C bonds and the C–H stretching mode can probably be ruled out as a contributor to the Bohlmann bands.

Secondly, although the stretching frequencies of isolated C–H or C–D bonds adjacent to nitrogen depend upon their orientation with respect to the nitrogen lone

pair, this shift in frequency amounts to less than 50 cm^{-1}. Similar, relatively small shifts are observed for pairs of C–H or C–D bonds in deuterated methylamines. Both of these findings are in agreement with the experimental data on larger aliphatic amines,[30] and it is clear that these shifts in themselves cannot account for the displacements of 100–250 cm^{-1} from the normal C–H stretching envelope that have occasionally been found in compounds displaying the Bohlmann bands.[5] Clearly, in larger cyclic amines conformational constraints, environmental differences and coupling to other antiperiplanar oriented C–H bonds could magnify the differences between *gauche* and *anti* C–H stretching frequencies. But it seems unlikely that this combination of factors can account completely for the spread, intensity and, often, complexity of the Bohlmann bands observed in the piperidine, quinolizidine, and sparteine alkaloids.

Finally, the probable existence of resonance interactions between the symmetric C–H stretching mode and the first overtone of the HCN bending modes in methylamine suggests that Fermi resonance should also contribute to the Bohlmann bands in larger cyclic amines. Together with the lower frequency C–H stretch *anti* to a lone pair, such an effect could account for the range, intensity, and structure of the Bohlmann bands. However, the essential feature of the explanation is still the presence of a low lying C–H stretching band which can interact with C–H bending, overtone, and combination bands in the 2600–2840 cm^{-1} region. In addition, since the C–H stretching and bending vibrations are affected in different ways by the substitution of deuterium for hydrogen, one should expect these Fermi resonance interactions to be altered by deuteration adjacent to nitrogen. The shapes of the Bohlmann band features in the C–D stretching region of α-deuterated amines should therefore differ from the shapes of these features in the C–H stretching region of the undeuterated compounds. These views on the origin of the Bohlmann bands are in harmony with those of Ernstbrunner and Hudec,[7] who based their conclusions on a Raman study of certain quinolizidines and piperidines.

B. Methanol and methanethiol

The existence of "Bohlmann bands"[4] in aliphatic alcohols and thiols has been demonstrated by Krueger.[4c] In Secs. IV and V of this paper, similar features have been reproduced theoretically for methanol and methanethiol and these resemble closely the effects found in methylamine.

Thus, the stretching force constant of a C–H bond anti-periplanar to a lone pair is smaller than that of a C–H bond *gauche* to a lone pair ($F_{anti} = 5.266$; $F_{gauche} = 5.371$ mdyn/Å for methanol and $F_{anti} = 5.358$; $F_{gauche} = 5.426$ mdyn/Å for methanethiol). This parallels the differences in the nuclear contributions to the force constants (methanol: $\Delta F_{nucl} = 0.145$; $\Delta F_{elec} = -0.040$; $\Delta F_{total} = 0.105$; methanethiol: $\Delta F_{nucl} = 0.149$; $\Delta F_{elec} = -0.083$; $\Delta F_{total} = 0.066$ mdyn/Å).

Secondly, in the case of methanol, evidence is found

TABLE XV. Differences in stretching frequencies for isolated CH and CD bonds *gauche* and *anti* to lone pairs on nitrogen, oxygen, and sulphur. [a]

| X | Calc | | | |
	Harmonic	Anharmonic	Obs [d]	Obs [e]
$\Delta\nu_{CD}$ in:		CH_2DX		$(CH_3)_2CDX$
NH_2	35	38 [b]		75
OH	30	36	37	73
SH	15	41 [c]		74
$\Delta\nu_{CH}$ in:		CHD_2X		$(CH_3)_2CDX$
NH_2	43	10	75	~50
OH	35	10	60	~89
SH	19	14		~100

[a] $\Delta\nu = \nu_{gauche} - \nu_{anti}$ in cm^{-1}.
[b] Value for CH_2DND_2 used because of resonance complications in CH_2DNH_2.
[c] Corrected for resonance.
[d] References 17 and 27.
[e] Reference 4(c).

for contributions of Fermi resonance to the lowering of the symmetric C–H stretch. In methanethiol, although the bending modes are lower in frequency and do not interact with the stretching modes in the same manner, the possibility remains that Fermi resonance may contribute to the Bohlmann bands in larger thiols and sulphides.

Data on the differences in the stretching frequencies of C–H and C–D bonds *gauche* and *anti* to lone pairs on nitrogen, oxygen, and sulphur are collected in Table XV. The calculated differences in the C–D stretching frequencies are approximately the same for the three heteroatoms, both in the calculated (anharmonic) values for CH_2DX and in the experimental values for $(CH_3)_2DCX$.

Examination of the calculated harmonic frequencies indicates that, if Fermi resonance is not present, the anharmonicity of the C–D bond contributes little to the *gauche–anti* difference, so that a harmonic force field alone would correctly predict the difference. However, because of the anharmonic force constants, interactions with nearby overtones are allowed and they can alter these differences. The differences can be increased in the theoretical calculations, as in the case of the C–D stretch in CH_2DSH, or decreased, as in the case of the C–H stretches in CHD_2NH_2 and CHD_2OH. The effect of resonance upon the experimental spectrum is necessarily somewhat different because of the different relative positions of the interacting bands.

VII. CONCLUSIONS

Ab initio computations of force constants and vibrational frequencies have been found to be feasible for methylamine, methanol, and methanethiol. When vibrational anharmonicity is taken into account, the calculated frequencies and, especially, the stretching modes, are in good agreement with experiment. Certain errors and inadequacies in the currently available experimental force fields have been revealed by the

present calculations and re-examination of these experimental force fields is suggested. Such an investigation could benefit from the use of the theoretical data. For example, some off-diagonal harmonic force constants might be selected from the theoretical calculations and the remainder varied to fit the experimental data. The cubic and quartic force constants or the anharmonicity constants might be employed to estimate which experimental harmonic frequencies are to be used to determine the experimental harmonic force field.

The theoretical calculations have permitted an investigation of the origin of the Bohlmann bands. For amines, alcohols, and thiols, a weakening of a C–H bond *anti* to a lone pair as well as Fermi resonance[7,20b] can be expected to contribute to the Bohlmann bands. Both effects have been found in methylamine and methanol; in methanethiol, the former factor predominates. This is in agreement with earlier theoretical and experimental work on amines.

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[21]See AIP document No. PAPS JCPSA-67-4181-13 for 13 pages of tables of calculated force constants, harmonic frequencies, and anharmonicity constants for methylamine, methanol, and methanethiol. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, NY 10017. The price is $1.50 for each microfiche, or $5 for photocopies. Airmail additional. Make checks payable to the American Institute of Physics. This material also appears in *Current Physics Microfilm*, the monthly microfilm edition of the complete set of journals published by AIP, on the frames immediately following this journal article.

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