

On the characteristic vibrations of the NH₂ group

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The group frequency factorization procedure developed by King and Crawford (1) for the reduction in size of a vibrational secular determinant, by factorizing from it those frequencies that are characteristic of a constituent group, and subsequently extended by us (2), has now been successfully applied to NH₂ group vibrations.

The method is exemplified by the skeletal vibrations of methylamine, for which satisfactory results are obtained on factorization from the secular determinant of frequencies that are characteristic of both NH₂ and CH₃ groups.

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The NH₂ group in both primary amines and amides is associated with three characteristic infrared (i.r.) absorption bands. Two, with frequencies around 3500 and 3300 cm⁻¹, are identified respectively with the antisymmetric and symmetric NH stretching vibrations. In the third, in the range 1590–1650 cm⁻¹, the HNH bending mode is considered to predominate (3). The NH₂ group can also engage in inter- and intramolecular hydrogen bonds, but no attempt is made to account for these effects in our considerations.

Analysis of the NH₂ group vibrations involves the consideration of a "standard molecule", NH₂—R, with the geometry of Fig. 1, and in

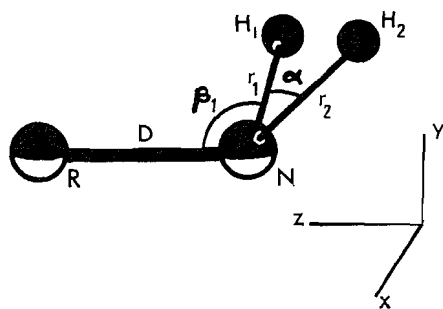


FIG. 1. The "standard molecule" RNH₂: $r = 1.014$ Å, $D = 1.474$ Å, $\alpha = 106^\circ$, $\beta = 112^\circ$.

which R is assigned infinite mass (actually 10⁶ a.m.u.). This "standard molecule" belongs to the symmetry point group C_s; and the symmetry coordinates chosen for the A' and A'' vibrational species are given in Table I.

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TABLE I
Symmetry coordinates in C_s for the "standard molecule"

Species	Coordinate
A'	$S_1 = (r_1 + r_2)/\sqrt{2}$ $S_2 = \alpha$ $S_3 = D$ $S_4 = (\beta_1 + \beta_2)/\sqrt{2}$ } Group coordinates
A''	$S_5 = (r_1 - r_2)/\sqrt{2}$ $S_6 = (\beta_1 - \beta_2)/\sqrt{2}$ } Group coordinate

The calculations of the frequencies in NH₂R reported here constitute an extension and improvement of those first reported by King (4) and use the same values for the force constants (Table III), and the valence force field of Table II. In Table III, the constant K_D is representative

TABLE II
Valence force field for NH₂R*

2V	r ₁	r ₂	D	α	β ₁	β ₂
r ₁	K _r	F _r	0	0	0	0
r ₂		K _r	0	0	0	0
D			K _D	0	rF _{DB}	rF _{DB}
α				r ² H _α	0	0
β ₁					r ² H _β	r ² F _β
β ₂						r ² H _β

*r = r(N—H)_{eq}.

TABLE III
Force constants for "standard molecule"
NH₂R (mdyn Å⁻¹)

Force constant	Value	Force constant	Value
K _r	6.40	F _r	0.00
K _D	4.80	F _{DB}	0.14
H _α	0.65	F _β	-0.03
H _β	0.47		

of an N—C bond, with the intention to extend the calculation to organic molecules.

The calculations were performed on an English-Electric KDF-9 computer. The calculated frequencies are listed in Table IV, and the normal

TABLE IV
Calculated frequencies of "standard molecule"
NH₂R (cm⁻¹)

Species	Mode	Frequency	Species	Mode	Frequency
A'	v ₁	3371	A''	v ₅	3432
	v ₂	1630		v ₆	967
	v ₃	688			
	v ₄	786			

coordinate matrices, taken with experimental evidence, indicate that v₁ and v₂ in A', and v₅ in A'' are group vibrations. The orthogonal transformation matrices A relating new displacement coordinates D to symmetry coordinates S through $D = A^*S$, and which are required in the group factorization procedure (1), are given in Table V. Since the leading elements in the A matrices greatly exceed the off-diagonal entries, the success of the NH₂ group frequency factorization procedure was assured, and the submatrix \bar{H}_{gf} was null as required by the method.

The corrections, Φ_{ff} , which are to be made to the force field of a framework to which the NH₂ group is attached are given in Table VI; those in the A'' species are so small as to be negligible.

The effective-mass tensor, $(M^{-1})^+_{NN}$, of the NH₂ group whose elements are the effective inverse masses in (a.m.u.)⁻¹ of the nitrogen atom required in the construction of a reduced kinetic matrix G^+_{ff} , is given in Table VII.

TABLE VI
The corrections, Φ_{ff} , to the force constants for framework vibrations (mixed units)

$\Phi_{ff}(A')$	S ₃	S ₄
S ₃	0.0278	-0.0382
S ₄	-0.0382	0.0641
$\Phi_{ff}(A'')$	S ₆	
S ₆	0.0004	

TABLE VII
Effective mass tensor $(M^{-1})^+_{NN}$ for the nitrogen atom in the NH₂ group

$(M^{-1})^+_{NN}$ (a.m.u. ⁻¹)	X _N	Y _N	Z _N
X _N	0.06529	0	0
Y _N	(symmetrical)	0.06758	0
Z _N			0.06561

The coordinates S₄ and S₆ which describe respectively the symmetric and antisymmetric HNR angular deformation frequencies, and which are coupled to the vibrations of the framework to which the NH₂ group is attached, involve the displacements of both N and H atoms. The complete effective mass matrix $(M^{-1})^+$ which is required for the factorization of the NH₂ group frequencies will hence contain cross-terms involving these atoms. The diagonal elements $(G^+)_{ii}$ (i = 4, 6), of the reduced kinetic matrix G^+_{ff} require effective inverse hydrogen masses for their calculation. Following the methods described in (1) with the molecular geometry of Fig. 1, and the assumption that the expressions for μ^+_H are relatively insensitive to

TABLE V
The orthogonal transformation matrix, A, for NH₂ group frequency factorization

A (A')	D ₁	D ₂	D ₃	D ₄
S ₁	-0.9995	-0.0168	-0.0260	0.0013
S ₂	0.0124	-0.9403	0.1464	0.3071
S ₃	0.0284	-0.1755	-0.9815	-0.0706
S ₄	-0.0005	0.2912	-0.1203	0.9490
A (A'')	D ₅	D ₆		
S ₅	0.9999	-0.0083		
S ₆	-0.0083	-0.9999		

changes in geometry, the following results were obtained

$$G^+_{44} = \mu^+_{H(2)}/r^2(2m^2/\sin^2 \beta)(1/D - \cos \beta/r)^2 \mu_{Ny} + [2(1 + n \cos \beta)^2/r^2 \sin^2 \beta] \mu_{Nx} + (2m^2/D^2 \sin^2 \beta) \mu_R$$

where

$$\mu^+_{H(2)} = 0.4973 + 0.0450a$$

$$G^+_{66} = \mu^+_{H(1)}/r^2 + (2l^2/\sin^2 \beta)(\cos \beta/r - 1/D)^2 \mu_{Nx} + (2l^2/D^2 \sin^2 \beta) \mu_R$$

where $\mu^+_{H(1)} = 0.9917 - 0.0015a$, $a = r/D$, and l, m, n are the direction cosines of the N—R bond.

For the off-diagonal elements of G^+ involving the interactions of S_i ($i = 4, 6$), with any framework coordinate S_j , and for which $(G^+)_{ij} = B_i(M^{-1})^+ B^*_j$, the required row vectors $B_i(M^{-1})^+$ are given in Table VIII. It is therefore to be noted that when the terms $(1/D - \cos \beta/r)$ and $(1 + n \cos \beta)$ arise in the elements of the G matrix of the A' vibrational species of molecules with NH₂ groups, then on taking account in the G^+_{ff} matrix for vibrational interaction between v_4 and the group vibrations in such molecules, these terms are to be modified respectively to

$$(1/D - \cos \beta/r + 0.6453/r)$$

and

$$(1 + n \cos \beta - 0.4026 + 0.0319a)$$

Similarly, in considering the vibrations of species A'' , when the term $(1/D - \cos \beta/r)$ arises in G , it must be replaced in G^+_{ff} by $(1/D - \cos \beta/r - 0.0076/r)$ to account for the interaction of v_6 and the NH₂ group vibrations.

Application of first-order perturbation theory (1) leads to the following approximation equations for the NH₂ group frequencies.

Species A'

$$\lambda_1 = 6.6948 + 1.0434\Delta F_{11} + 0.0147\Delta F_{22} + 0.0016\Delta F_{33} + 0.0006\Delta F_{44} - 0.0020\Delta F_{34}$$

$$[1] \lambda_2 = 1.5648 + 0.0004\Delta F_{11} + 2.0120\Delta F_{22} + 0.0042\Delta F_{33} + 0.4623\Delta F_{44} + 0.0881\Delta F_{34}$$

$$[2] \lambda_5 = 6.9376 + 1.0831\Delta F_{11} + 0.0115\Delta F_{22}$$

$\Delta F_{ij} = F_{ij} - F^0_{ij}$, wherein F^0_{ij} refers to the "standard molecule", and F_{ij} is the corresponding force constant in the molecule bearing the NH₂ group. $\lambda_i = 4\pi^2 c^2 v_i^2 / N_0$, where N_0 = Avogadro's number.

When applied to the methylamine molecule (with the notational changes of Tables I and X and with the force constants of Table XII), eqs. [1] and [2] give the encouraging results of Table IX.

It was then decided to attempt the factorization from the vibrational secular equations for methylamine of both the methyl and amino group frequencies. The methylamine molecule has 15 modes of vibration, and in C_s point symmetry, these may be subdivided as in:

$$\begin{array}{ll} \text{characteristic group modes: } & 6A' + 3A'' \\ \text{framework modes} & : 3A' + 3A'' \end{array}$$

One of the A'' framework modes involves the relative internal rotation of the NH₂ and CH₃

TABLE VIII

Row vectors, $B_i(M^{-1})^+$, for the calculation of G^+ involving the interaction of group and framework coordinates*

Vector	N			R		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
$B_4(M^{-1})^+$	0	<i>b</i>	0	0	$(-\sqrt{2}m/D \sin \beta) \mu_R$	0
$B_6(M^{-1})^+$	<i>e</i>	0	0	$(\sqrt{2}l/D \sin \beta) \mu_R$	0	0

*Wherein $b = (\sqrt{2}m/\sin \beta)(1/D - \cos \beta/r + 0.6453/r) \mu_{Ny}$

$c = (\sqrt{2}l/\sin \beta)(1 + n \cos \beta - 0.4026 + 0.0319a) \mu_{Nx}$

$e = (-\sqrt{2}l/\sin \beta)(1/D - \cos \beta/r - 0.0764/r) \mu_{Nx}$

l, m, n are direction cosines of the N—R bond, and are respectively $\sin \alpha/2, -\cos \beta, (\cos^2 \alpha/2 - \cos^2 \beta)^{1/2}$.

TABLE IX
Application of NH₂ group frequency eqs. [1] and [2]
to methylamine

Vibrational species in C _s	Approximate description	NH ₂ frequencies (cm ⁻¹)	
		Complete solution	Approximate solution
A'	v ₁	3366	3366
	v ₄	1641	1635
A''	v ₁₀	3464	3464

TABLE X
Symmetry coordinates for methylamine

Species	Coordinate	Approximate description of mode	
A'	$S_1 = (r_1 + r_2)/\sqrt{2}$	Group coordinates N—H sym. stretch C—H antisym. stretch C—H sym. stretch HNH deformation CH ₃ antisym. deformation CH ₃ sym. deformation Redundant coordinate	
	$S_2 = (2d_3 - d_4 - d_5)/\sqrt{6}$		
	$S_3 = (d_3 + d_4 + d_5)/\sqrt{3}$		
	$S_4 = \alpha$		
	$S_5 = (2\phi_3 - \phi_4 - \phi_5)/\sqrt{6}$		
	$S_6 = (\theta_3 - \phi_3 + \theta_4 - \phi_4 + \theta_5 - \phi_5)/\sqrt{6}$		
	$S_7 = (\theta_3 + \phi_3 + \theta_4 + \phi_4 + \theta_5 + \phi_5)/\sqrt{6}$		
	$S_8 = D$		Framework coordinates Methyl rock C—N stretch Sym. HNC deformation
	$S_9 = (\beta_1 + \beta_2)/\sqrt{2}$		
A''	$S_{10} = (r_1 - r_2)/\sqrt{2}$	Group coordinates N—H antisym. stretch CH antisym. stretch CH ₂ antisym. deformation Methyl rock Antisym. HNC deformation	
	$S_{11} = (d_4 - d_5)/\sqrt{2}$		
	$S_{12} = (\phi_4 - \phi_5)/\sqrt{2}$		
	$S_{13} = (\theta_4 - \theta_5)/\sqrt{2}$		
	$S_{14} = (\beta_1 - \beta_2)/\sqrt{2}$		

TABLE XI
Valence force field* for methylamine

2V	r ₁	r ₂	D	d ₃	d ₄	d ₅	α	β ₁	β ₂	θ ₃	θ ₄	θ ₅	φ ₃	φ ₄	φ ₅
r ₁	K _r														
r ₂		F _r													
D		K _r													
d ₃			K _D												
d ₄				K _d	F _d										
d ₅					K _d	F _d									
α							F _α								
β ₁								r ² H _α							
β ₂									r ² H _β						
θ ₃										r ² F _β					
θ ₄											r ² H _β				
θ ₅										d ² H _θ					
φ ₃											d ² F _θ				
φ ₄												d ² F _θ			
φ ₅													d ² H _φ		
														d ² H _φ	
															d ² H _φ

*r = r(N—H)_{eq}; d = r(C—H)_{eq}.

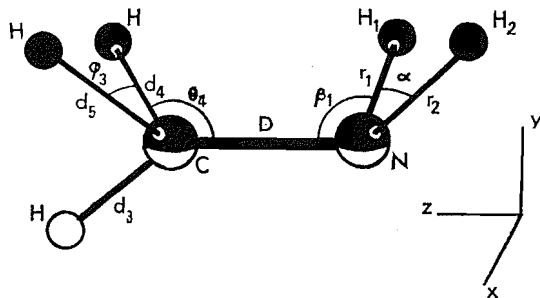


FIG. 2. The methylamine molecule: $r = 1.014 \text{ \AA}$, $d = 1.093 \text{ \AA}$, $D = 1.474 \text{ \AA}$, $\alpha = 106^\circ$, $\beta = 112^\circ$, $\theta = \phi = 109^\circ 27'$.

TABLE XII
Valence force constants for methylamine (mdyn \AA^{-1})

Force constant	Value	Force constant	Value	Force constant	Value
K_r	6.45	H_α	0.64	F_r	-0.07
K_D	4.70	H_β	0.40	F_d	0.08
K_d	4.71	H_ϕ	0.67	F_β	0.07
		H_ϕ	0.44	F_α	-0.04
				$F_{D\phi}$	0.31

TABLE XIII
Reduced kinetic matrices, G^+_{ff} , for framework vibrations of methylamine

$G^+_{ff}(A')$	S_7	S_8	S_9
S_7	$[\mu^+_{H(3)/d^2} + (3/2d^2)(a+1/3)^2\mu_{Cy} + (3a^2/2d^2)\mu_{Ny}]$	0	$[-(\sqrt{3}ma/d \sin \beta)(1/D - \cos \beta/r + 0.6453/r)\mu_{Ny} - (\sqrt{3}m/dD \sin \beta)(a+1/3+g)\mu_{Cy}]$
S_8	(symmetrical)	$[\mu_{Nz} + \mu_{Cz}]$	$[-(\sqrt{2}/r \sin \beta)(1+n \cos \beta - 0.4026 + 0.0319a)\mu_{Nz}]$
S_9			$[\mu^+_{H(2)/r^2} + (2m^2/\sin^2 \beta)(1/D - \cos \beta/r)^2\mu_{Ny} + [2(1+n \cos \beta)^2/r^2 \sin^2 \beta]\mu_{Nz} + (2m^2/D^2 \sin^2 \beta)\mu_{Cy}]$
$G^+_{ff}(A'')$	S_{13}	S_{14}	
S_{13}	$[\mu^+_{H(3)/d^2} + (3/2d^2)(a+1/3)^2\mu_{Cx} + (3a^2/2d^2)\mu_{Nx}]$	$[-(\sqrt{3}al/d \sin \beta)(1/D - \cos \beta/r - 0.0076/r) - (\sqrt{3}/D \sin \beta)(a + 1/3 + g)\mu_{Cx}]$	
S_{14}	(symmetrical)	$[\mu^+_{H(1)/r^2} + (2l^2/\sin^2 \beta)(\cos \beta/r - 1/D)^2\mu_{Nx} + (2l^2/D^2 \sin^2 \beta)\mu_{Cx}]$	

NOTES: $g = 0.2523$; $\mu^+_{H(3)}$, $\mu^+_{H(1)}$, and $\mu^+_{H(2)}$ refer to the reduced hydrogen masses in CH_3 and NH_2 , respectively.

TABLE XIV
The reduced symmetry force fields, F^+_{ff} , for framework vibrations of methylamine (mixed units)

$F^+_{ff}(A')$	S_7	S_8	S_9
S_7	$d^2(H_\phi - F_\phi + 0.0781)$	0	0
S_8	(symmetrical)	$K_D - 0.0158^*$	-0.0382
S_9			$r^2(H_\beta + F_\beta) + 0.0641$
$FF^+_{ff}(A'')$	S_{13}	S_{14}	
S_{13}	$d^2(H_\phi - F_\phi + 0.0781)$	0	
S_{14}	(symmetrical)	$r^2(H_\beta - F_\beta) + 0.0004$	

*Average of corrections for NH_2 and CH_3 .

groups; this has been assumed to be free, and is omitted from the discussion. The remaining 14 modes were treated in terms of the symmetry coordinates of Table X, the molecular geometry of Fig. 2, and the force field and force constants of Tables XI and XII.

The reduced kinetic matrices G^+_{ff} for the framework vibrations and corrected for interactions with both CH_3 and NH_2 groups, are presented in Table XIII, whilst Table XIV gives the reduced force constant matrices F^+_{ff} including the corrections Φ_{ff} for the NH_2 group from Table VI and for the CH_3 group from refs. (1) and (2a).

Solution of the reduced secular equation,

$$|G^+_{ff}F^+_{ff} - \lambda E_{ff}| = 0$$

gave the vibrational frequencies which are compared in Table XV with those obtained from a complete solution by us, and based on the assignment and force constants reported by King (4). A more recent, and somewhat different

TABLE XV
Framework vibration frequencies in methylamine (cm^{-1})

Species	Mode	Frequencies		
		Complete solution	Approximate solution	Observed (ref. 4)
A'	ν_7	1142	1147	1145
	ν_8	1036	1048	1041
	ν_9	754	748	779
A''	ν_{13}	1142	1145	1145
	ν_{14}	784	782	779

vibrational assignment for methylamine has been reported by Gray and Lord (5), but clearly since our aim was simply to provide an approximation method, having used King's force field, then comparison must be made with the frequencies on which it is based.

Acknowledgments

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