

FORCE FIELD FOR OUT-OF-PLANE VIBRATIONS OF PYRAZINE

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Received January 6th, 1986

A general quadratic force field has been calculated for the out-of-plane vibrations of pyrazine by the MINDO/3 method. The first derivatives of the energy were computed analytically and the second derivatives of energy numerically. The force constants so obtained have been refined to fit the observed frequencies of $-h_4$, $-d_4$ and *cis*-pyrazine- d_2 . The calculations proved our assignment suggested previously, though the disagreement between theory and experiment for the A_u vibrations of pyrazine needs additional experimental and theoretical data for clarification.

Prior to this work a revision of the vibrational assignments of the Raman and infrared active vibrations of pyrazine- h_4 and pyrazine- d_4 was done¹. In the present work we use these new assignments as the starting point for the computation of a harmonic force field involving the out-of-plane vibrations of both molecules as well as those of *cis*-pyrazine- d_2 for which there exist experimental data for the infrared active vibrations². Several attempts at computing an empirical force field for these vibrations have previously been published³⁻⁶. These, however, used the assignments of the fundamentals as they were previous to our revision¹.

When dealing with a polyatomic molecule, an essential point is that the initial guess of the force field must be sufficiently close to a physically acceptable potential energy function. The validity of force constants transferred between molecules, however, always retains a degree of uncertainty. Furthermore, transferring force constants may not be straightforward when they are given in symmetry coordinates or when redundancies are not removed.

We started with a semiempirical force field computed in cartesian coordinates, then transformed it to independent symmetry coordinates where cyclic and branching redundancies had been previously removed and subsequently refined it by fitting to vibrational frequencies of pyrazine- h_4 and pyrazine- d_4 . The obtained force field was checked by using it to compute frequencies and normal coordinates for *cis*-pyrazine- d_2 . Finally the force field was further refined to fit frequencies of pyrazine- h_4 , pyrazine- d_4 , and *cis*-pyrazine- d_2 simultaneously.

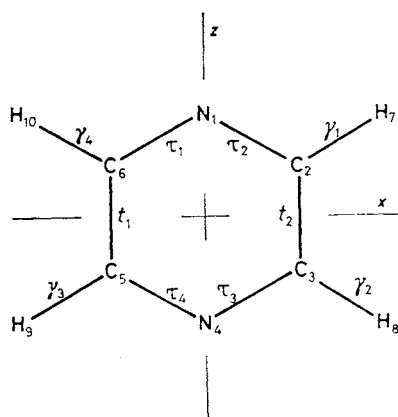
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SYMMETRY COORDINATES

Out-of-plane vibrations of pyrazine distribute as $2A_u + 1B_{1g} + 2B_{2u} + 2B_{3g}$, according to the D_{2h} symmetry. In *cis*-pyrazine- d_2 , they distribute as $4A_2 + 3B_2$ according to the C_{2v} symmetry and the branching rules:

C_{2v}	D_{2h}
A_2	$A_u + B_{3g}$
B_2	$B_{1g} + B_{2u}$

Coordinate axes have been orientated as in the literature referred to in ref.¹ and as shown in Scheme 1. That scheme also shows numbering of atoms and the out-of-



SCHEME 1

-plane internal coordinates of pyrazine that we defined. The wagging internal coordinates were defined according to ref.⁷ and the torsion coordinates according to Hildebrandt⁸. Because the internal coordinates span the representation $\Gamma_R = 3A_u + 2B_{1g} + 2B_{2u} + 3B_{3g}$ three redundancies of symmetries $A_u + B_{1g} + B_{3g}$ must be removed. Therefore we first constructed symmetry adapted linear combinations of internal coordinates as indicated by Γ_R . Table I shows these primitive symmetry coordinates which define the transformation $\mathbf{s} = \mathbf{UR} = \mathbf{Bx}$. The redundant symmetry coordinates as well as the independent symmetry coordinates were obtained by diagonalization of the product $\mathbf{B}\tilde{\mathbf{B}}$ (ref.⁹), the redundancies being the eigenvectors corresponding to zero eigenvalues, and independent symmetry coordinates being those corresponding to the non-zero ones. Table II shows these symmetry coordinates which allow us to define the transformation $\mathbf{S} = \mathbf{UR} = \mathbf{Bx}$. In the B_{2u} block there are no redundancy and s_9 and s_{10} are already independent symmetry coordinates.

RESULTS AND DISCUSSION

In order to obtain an initial guess set of harmonic force constants for pyrazine we used the semiempirical method MINDO/3 (ref.¹⁰). A semiempirical method was chosen because of machine limitations. Computations were carried out on a Perkin-Elmer 3220 minicomputer. Initially, an optimised MINDO/3 geometry was computed ignoring the experimental geometry in order to guarantee that the force constants were obtained at the MINDO/3 potential minimum. Table III shows this semiempirical geometry as well as that determined by electron diffraction¹¹; the agreement between the two sets of molecular parameters is fairly good. Cartesian force constants were computed with the MINDO/3 Hamiltonian by computing analytical first derivatives of the energy and numerical second derivatives¹²⁻¹⁴.

TABLE I

Symmetry adapted linear combinations of internal coordinates

A_u	B_{1g}
$s_1 = 1/2(\Delta\gamma_1 - \Delta\gamma_2 + \Delta\gamma_3 - \Delta\gamma_4)$	$s_7 = 1/2(\Delta\gamma_1 + \Delta\gamma_2 - \Delta\gamma_3 - \Delta\gamma_4)$
$s_2 = 1/2(\Delta\tau_1 + \Delta\tau_2 + \Delta\tau_3 + \Delta\tau_4)$	$s_8 = 1/2(\Delta\tau_1 + \Delta\tau_2 - \Delta\tau_3 - \Delta\tau_4)$
$s_3 = 1/2(\Delta t_1 + \Delta t_2)$	
B_{3g}	B_{2u}
$s_4 = 1/2(\Delta\gamma_1 - \Delta\gamma_2 - \Delta\gamma_3 + \Delta\gamma_4)$	$s_9 = 1/2(\Delta\gamma_1 + \Delta\gamma_2 + \Delta\gamma_3 + \Delta\gamma_4)$
$s_5 = 1/2(\Delta\tau_1 - \Delta\tau_2 - \Delta\tau_3 + \Delta\tau_4)$	$s_{10} = 1/2(\Delta\tau_1 - \Delta\tau_2 + \Delta\tau_3 - \Delta\tau_4)$
$s_6 = 1/2(\Delta t_1 - \Delta t_2)$	

TABLE II

Independent and redundant symmetry coordinates

A_u	B_{1g}
$S_1 = -0.9907s_1 - 0.0589s_2 + 0.1223s_3$	$S_5 = 0.8774s_7 + 0.4798s_8$
$S_2 = 0.1344s_1 - 0.5532s_2 + 0.8309s_3$	$S_{R3} = -0.4798s_7 + 0.8774s_8 = 0$
$S_{R1} = 0.0192s_1 + 0.8310s_2 + 0.5560s_3 = 0$	
B_{3g}	B_{2u}
$S_3 = 0.8383s_4 + 0.5436s_5 - 0.0410s_6$	$S_6 = 1.0s_9$
$S_4 = 0.4329s_4 - 0.6181s_5 + 0.6562s_6$	$S_7 = 1.0s_{10}$
$S_{R2} = -0.3314s_4 + 0.5678s_5 + 0.7535s_6 = 0$	

The transformation to our particular choice of symmetry coordinates is given by the relationship

$$F_{\text{sym}} = \tilde{\mathbf{B}}^{-1} F_{\text{cart}} \mathbf{B}^{-1} \quad (1)$$

which implies the inversion of the rectangular \mathbf{B} matrix. That problem has been treated in different ways^{15,16} and may be complicated when redundancies exist because $\mathbf{G} = \mathbf{B}\tilde{\mathbf{B}}$ becomes a singular matrix. We have avoided inverting \mathbf{G} directly in order to by pass that difficulty. The algorithm is as follows:

First we diagonalize \mathbf{G} and set up the similarity transformation:

$$\tilde{\mathbf{D}}\mathbf{G}\mathbf{D} = \mathbf{A}, \quad (2)$$

where \mathbf{A} is a diagonal matrix containing the eigenvalues and \mathbf{D} contains the respective eigenvectors in the same order. The inverse of \mathbf{G} is computed as

$$\mathbf{G}^{-1} = \mathbf{D} \mathbf{A}^{-1} \tilde{\mathbf{D}}, \quad (3)$$

where \mathbf{A}^{-1} is computed by setting $(\mathbf{A}^{-1})_{ii} = A_{ii}^{-1}$ for non-zero eigenvalues and $(\mathbf{A}^{-1})_{ii} = 0$ for the zero ones. Therefore,

$$\begin{aligned} \mathbf{B}^{-1} &= \tilde{\mathbf{B}}\mathbf{G}^{-1} \\ \tilde{\mathbf{B}}^{-1} &= \mathbf{G}^{-1} \mathbf{B}. \end{aligned} \quad (4)$$

The validity of this transformation was checked by comparison of the frequencies computed with F_{cart} and F_{sym} .

The MINDO/3 initial set of parameters, given in Table VII was refined by fitting to the experimental frequencies of the fundamentals of pyrazine- h_4 and pyrazine- d_4 as given in ref.¹. The refined set is referred to as set *a*) in Table VII. Table IV shows

TABLE III
Experimental and calculated parameters of pyrazine

Bond, Å	Exp. ^a	Calc.	Angle, deg	Exp. ^a	Calc.
(C—N)	1.339	1.334	(C—N—C)	115.60	119.31
(C—C)	1.403	1.405	(N—C—C)	122.20	120.36
(C—H)	1.115	1.115	(N—C—H)	113.90	116.98

^a Ref.¹¹; 1 Å = 10⁻¹⁰ m.

the results obtained with this set *a*). The same set was used to compute the frequencies for *cis*-pyrazine-*d*₂ which are shown in Table V. That the agreement with experimental values is quite satisfactory can be interpreted as a test of the validity of the force field. The final refinement was carried out by simultaneously fitting the frequencies of the *B*₂ vibrational species for all three of the isotopomers. This was done because no experimental data are available for the *A*₂ vibrations of *cis*-pyrazine-*d*₂.

As shown in Table VI, the calculated frequencies for the *B*₂ are now closer to the experimental ones. This final set of potential constants is given as set *b*) in Table VII. It is to be stressed that the differences between the two sets and the corresponding calculated frequencies are very small. The ratio between the number of experimental data and that of symmetry force constants under refinement has been as follows:

TABLE IV

Summary of observed and calculated frequencies (cm⁻¹) and potential energy distributions with set *a*) of refined force constants

Compound	ν_{obs}	ν_{calc}	$\Delta\nu$	P.E.D., %
Species <i>A</i> _u				
Py- <i>h</i> ₄	997.0	998.0	1.0	123(<i>F</i> ₁₁), 14(<i>F</i> ₂₂), -38(<i>F</i> ₁₂)
	422.0	432.7	10.7	2(<i>F</i> ₁₁), 109(<i>F</i> ₂₂), -11(<i>F</i> ₁₂)
Py- <i>d</i> ₄	—	875.3	—	114(<i>F</i> ₁₁), 4(<i>F</i> ₂₂), -18(<i>F</i> ₁₂)
	406.0	357.1	-48.9	10(<i>F</i> ₁₁), 120(<i>F</i> ₂₂), -30(<i>F</i> ₁₂)
Species <i>B</i> _{3g}				
Py- <i>h</i> ₄	983.0	983.7	0.7	39(<i>F</i> ₃₃), 30(<i>F</i> ₄₄), -10(<i>F</i> ₃₄)
	754.0	749.5	-4.5	61(<i>F</i> ₃₃), 31(<i>F</i> ₄₄), 8(<i>F</i> ₃₄)
Py- <i>d</i> ₄	834.0	830.2	-3.8	94(<i>F</i> ₃₃), 12(<i>F</i> ₄₄), -6(<i>F</i> ₃₄)
	647.0	653.2	6.2	6(<i>F</i> ₃₃), 89(<i>F</i> ₄₄), 5(<i>F</i> ₃₄)
Species <i>B</i> _{1g}				
Py- <i>h</i> ₄	918.6	920.2	1.6	100(<i>F</i> ₅₅)
Py- <i>d</i> ₄	721.1	718.0	-3.1	100(<i>F</i> ₅₅)
Species <i>B</i> _{2u}				
Py- <i>h</i> ₄	786.3	778.2	-8.1	95(<i>F</i> ₆₆), 5(<i>F</i> ₇₇)
	419.5	428.2	8.7	5(<i>F</i> ₆₆), 95(<i>F</i> ₇₇)
Py- <i>d</i> ₄	593.7	609.8	16.1	99(<i>F</i> ₆₆), 1(<i>F</i> ₇₇)
	402.9	396.2	-6.7	1(<i>F</i> ₆₆), 99(<i>F</i> ₇₇)

TABLE V
Observed and calculated frequencies (cm^{-1}) and potential energy distribution in *cis*-pyrazine- d_2 obtained with set *a*) of refined force constants

ν_{obs}	ν_{calc}	$\Delta\nu$	P.E.D., %
Species A_2			
—	992.6	—	79(F_{11}), 13(F_{33}), 24(F_{44})
—	846.4	—	33(F_{11}), 60(F_{33}), 15(F_{44})
—	714.7	—	27(F_{33}), 57(F_{44})
—	391.7	—	100(F_{22})
Species B_2			
873.0	869.8	-3.2	78(F_{55}), 20(F_{66})
638.0	642.5	4.5	21(F_{55}), 79(F_{66})
409.0	413.3	4.3	98(F_{77})

TABLE VI
Summary of observed and calculated frequencies (cm^{-1}) and potential energy distributions for the B_2 block, obtained with the set *b*) refined force constants

Compound	ν_{obs}	ν_{calc}	$\Delta\nu$	P.E.D., %
Species B_{1g}				
Py- h_4	918.6	920.8	2.2	100(F_{55})
Py- d_4	721.1	718.7	-2.4	100(F_{55})
Species B_{2u}				
Py- h_4	786.3	779.4	-6.9	95(F_{66}), 5(F_{77})
	419.5	429.4	9.9	5(F_{66}), 95(F_{77})
Py- d_4	593.7	601.4	7.7	100(F_{66})
	402.9	397.4	-5.5	100(F_{77})
Species B_2				
<i>cis</i> -Py- d_2	873.0	870.3	-2.7	78(F_{55}), 20(F_{66})
	638.0	641.1	3.1	20(F_{55}), 80(F_{66})
	409.0	411.8	2.8	98(F_{77})

to obtain set a) 4/2, 2/1, 4/3, and 3/3 for B_{2u} , B_{1g} , B_{3g} , and A_u blocks respectively, and to obtain set b) 9/3 in the B_2 block.

Tables IV, V, and VI show the potential energy distribution computed as $100F_{ii}L_{ik}^2/\lambda_k$ and $200F_{ij}L_{ik}L_{jk}/\lambda_k$ for diagonal and off-diagonal force constants, respectively. Finally, the atom displacement matrix was computed to verify the form and symmetry of each vibration. Scheme 2 shows the motion of nuclei for all modes calculated with the final set of force constant in pyrazine- h_4 (only y displacements are shown in this scheme). The frequency of each vibration is given inside the respective drawn. Decimal figures mean y displacements perpendicular to the ring plane; they are shown just for one carbon, nitrogen or hydrogen atom; those of the remaining ones in the respective series of equivalent nuclei have the same absolute value but the sign is as indicated inside the circles.

The results obtained confirm the assignments proposed for the infrared active fundamentals of *cis*-pyrazine- d_2 given by ref.² and allow us to predict with some

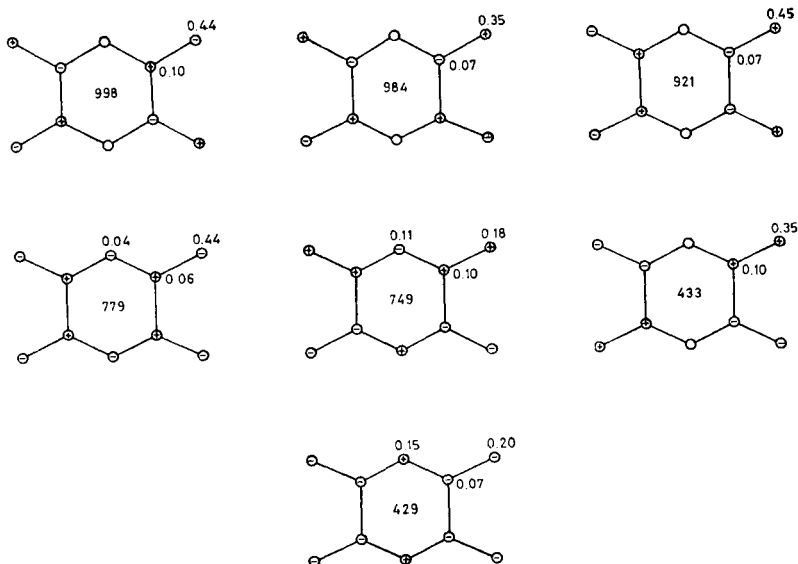
TABLE VII
MINDO/3 and refined sets of force constants^a for out-of-plane vibrations of pyrazine

set a)	set b)	MINDO/3
Species A_u		
$F_{11} = 0.392$	0.392	0.248
$F_{22} = 0.353$	0.353	0.163
$F_{12} = -0.165$	-0.165	-0.084
Species B_{3g}		
$F_{33} = 0.288$	0.288	0.194
$F_{44} = 0.326$	0.326	0.223
$F_{34} = -0.029$	-0.029	-0.027
Species B_{1g}		
$F_{55} = 0.376$	0.378	0.320
Species B_{2u}		
$F_{66} = 0.314$	0.313	0.270
$F_{77} = 0.235$	0.234	0.219
$F_{67} = 0.000^b$	0.000	0.002

^a All force constants are in $\text{mdyn } \text{Å rad}^{-2}$; $1 \text{ mdyn } \text{Å rad}^{-2} = 10^{-18} \text{ N m rad}^{-2}$.

^b As the MINDO/3 value is very small, we decided to keep this constants fixed.

confidence the frequencies of the Raman active modes which have not yet been observed. We think that some experimental work in this direction could be of interest. Concerning A_u vibrations, it is to be stressed that agreement between observed and



SCHEME 2

calculated frequencies is poorer than with the other species and consequently the force constants have been refined to values very different from the MINDO/3 ones. As there is some reasonable doubt on the assignment of these inactive vibrations¹, we suspect that the reported value for the frequency of vibration 16a probably corresponds to a vibration which also involves a lattice mode rather than a fundamental one. Similarly, some experimental work should be attempted to identify the A_2 fundamentals of *cis*-pyrazine- d_2 in the low frequency region.

On the basis of the results described here we are currently working on applying the method to the similar molecules dioxine and methylpyrazines whose vibrational spectra are being presently analysed.

The authors are grateful to Dr S. Ross for his help in the preparation of the manuscript. We are also indebted to CAYCIT for financial support of the work and to MEC for grants given to JTL-N and JCO.

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