

VIBRATIONAL ANALYSIS OF AB INITIO POTENTIAL ENERGY SURFACES FOR NITRYL FLUORIDE*

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A series of self-consistent molecular orbital (SCF-MO) calculations using the method of linear combination of Gaussian type functions (GTF), were performed on nitril fluoride, using variable geometry, in order to obtain an *ab initio* potential hypersurface. This hypersurface was used to obtain harmonic force constants for an FG matrix calculation, from which the fundamental frequencies associated with the normal modes were calculated. The calculations reported here found hypersurfaces for two different basis sets, containing 24 and 44 GTF, respectively. It was found that using the larger basis set, the values of the fundamental frequencies agreed very well with experimental values, even if the interaction force constants were scaled from the smaller calculations using 24 GTF.

Introduction

To perform a single near-Hartree—Fock calculation on the 32 electron molecule nitril fluoride (NO_2F) requires a basis set of 112 uncontracted GTF [1]. On the other hand a single calculation using the most recent technique, in which a basis set of 136 primitive GTF is contracted to 40 basis functions [2], requires about 18 hours on the present generation of computing machinery. It follows that to study the general properties of *ab initio* surfaces, where many such calculations would be required, it is necessary to use a much smaller basis set so that enough points may be calculated. Then, if accurate results are needed, it may be possible to make generalizations that permit the calculation of more accurate surfaces with larger basis sets, without having to calculate a prohibitively large number of individual points.

In this work, uncontracted basis sets [3] of 24 GTF were used for the preliminary calculation of a complete hypersurface. This basis set consisted of 3s-type and 1p-type Gaussians on each atom [abbreviated as: ($3^s, 1^p$)]. For the more accurate calculations, cross-sections were taken using 44 GTF ($5^s, 2^p$).

All energy values are given in Hartree atomic units. The computations were carried out using a modified POLYATOM system [4] on an IBM-7094-II computer.

* Dedicated to Prof. P. GOMBÁS on his 60th birthday.

The FG matrix calculation

(i) *Fitting analytical function to ab initio surfaces*

It was found that the nature of the surfaces made least squares fitting of a general quadratic potential impossible, even in regions very near the minima. The cross-sections of the surfaces contained an inherent and consistent asymmetry in the vicinity of the minima, and a "weighted" parabola

$$E(X) = E_0 + a(X - X_0)^2 e^{-b(X-X_0)} \quad (1)$$

provided an excellent fit to points on such cross-sections. This curve could have been used to provide anharmonic corrections to the fundamental frequencies, but within the accuracy of the present calculations, no attempt was made to include such corrections. Changing the coordinate system in such a way that $x = X - X_0$ then (1) may be written as (1a)

$$E(x) = E_0 + ax^2 e^{-bx}. \quad (1a)$$

Diagonal force constants can then be obtained directly from (1a).

$$\begin{aligned} F_{xx} &= \left(\frac{d^2 E(x)}{dx^2} \right)_{x=0} \\ &= (2ae^{-bx} - 4abxe^{-bx} + ab^2x^2e^{-bx})_{x=0} \\ &= 2a, \end{aligned} \quad (2)$$

$$\text{i. e.} \quad a = 1/2 F_{xx}. \quad (2a)$$

If a two-dimensional surface is now considered, a study of interaction force constants is possible. An analogous relative coordinate system is chosen for which $x = y = 0$ at E_{00} , the absolute minimum of the surface.

$$E(x, y) = E_{00} + 1/2 F_{xx} x^2 e^{-bx} + 1/2 F_{xy} xy + 1/2 F_{yy} y^2 e^{-cy}. \quad (3)$$

If the behaviour of (3) is studied near the minima, for fixed values of y , the exponential terms become approximately equal to 1. Then, if successive cross-sections of (3) are taken at $y = 0$ and $y = \delta y$, (3) becomes (4) and (5) respectively.

$$E(x, 0) = E_{00} + 1/2 F_{xx} x^2, \quad (4)$$

$$E(x, \delta y) = (E_{00} + 1/2 F_{yy} \delta y^2) + 1/2 F_{xx} x^2 + 1/2 F_{xy} x \delta y. \quad (5)$$

Of these, it can be seen that (5) is a parabola with respect to x with a minimum not exactly at $x = 0$, but rather at some non-zero value of x , say $x = \delta x_0$, which can be obtained graphically, or from a least squares curve fit.

From geometrical consideration, the equation of such a parabola with minimum at δx_0 is

$$E(x, \delta y) = E_0 + 1/2 F_{xx} x^2 - F_{xx} x \delta x_0. \quad (6)$$

Comparing terms in (5) and (6), and taking the limit as $\delta y \rightarrow 0$,

$$1/2 F_{xy} x \delta y = - F_{xx} x \delta x_0, \quad (7)$$

$$F_{xy} = -2 F_{xx} \left(\frac{dx_0}{dy} \right)_{y=0}. \quad (7a)$$

Thus, at least in principle, the way is open for a rigorous theoretical study of the normal modes of vibration of a polyatomic molecule like NO_2F . This method can be extended to include anharmonic interaction force constants if the functional variation of the minima is considered, rather than just the slope at $y = 0$.

(iii) Calculation of F -matrix elements (Small Basis Set)

It was found that unnormalized symmetry coordinates could be used, so that simple bond stretching and bending could be represented by them, since the constant introduced by the degree of unnormalization was inversely accounted for in the calculation of G -matrix elements. The symmetry coordinates used are shown in Fig. 1.

Calculations with a small basis set provided results which were only qualitatively useful, as was expected from a basis set of this size. Four surfaces were studied — the three pairwise combinations of the three A_1 symmetry coordinates (S_1 , S_2 and S_3), and the pair of B_1 symmetry coordinates (S_4 and S_4).

It should be noted that for bending modes in which the asymmetry was small, parabola fits were used, rather than the anharmonic potential previously chosen in Equ. (1). The subscripts of the F -matrix elements refer to the symmetry coordinates defined in Fig. 1.

(iii) Scaling of interaction force constants (Medium Basis Set)

Though the force constants obtained by calculations using small (24 GTF) basis sets were quantitatively very poor, it is seen that qualitatively they fall in the right sequence. (A trial FG -matrix calculation using the force con-

stants from Table VII would give frequencies uniformly too high by a factor of 3, so the force constants are too high by an order of magnitude.) As the basis set sizes for the MO calculations were increased to 44 GTF the improvements in the diagonal force constants were very encouraging, and these new force constants were found to remain proportional to those determined using the smaller basis set. It was also found in the calculation with the small basis set that even

TYPE	SYMMETRY	COORDINATE	FORM
A_1	$S_1 = \frac{1}{2}(\Delta d_1 + \Delta d_2)$	NO_2 symmetric stretch	
A_1	$S_2 = \Delta D$	F-N stretch	
A_1	$S_3 = -(\Delta\beta_1 + \Delta\beta_2) = \Delta\alpha$	O-N-O deformation	
B_1	$S_4 = \frac{1}{2}(\Delta d_1 - \Delta d_2)$	NO_2 asymmetric stretch	
B_1	$S_5 = \frac{1}{2}(\Delta\beta_1 - \Delta\beta_2)$	fluorine wag	
B_2	$S_6 = \zeta$	out-of plane deformation	

Fig. 1. Symmetry coordinates for NO_2F (unnormalized)

fairly large changes in the interaction force constants did not greatly affect predicted frequencies. Thus it might be assumed that the inaccuracy introduced using interaction force constants scaled from those found with the smallest basis set should be much less than the inaccuracy arising from the use of a single determinant wave function considerably above the Hartree-Fock limit. Since using a very large basis set, calculation of many points on a potential surface becomes economically infeasible, it was decided that scaled interaction force constants should be studied in some detail. The formula adopted for this purpose was

$$F'_{xy} = F_{xy} \left(\frac{F'_{xx} F'_{yy}}{F_{xx} F_{yy}} \right)^{1/2}, \quad (8)$$

Table I
Elements of the G -matrix*

	$G_{11} = \frac{1}{2} (\mu_1 (1 + \cos \alpha) + \mu_3)$	$G_{12} = \mu_1 \cos \beta$	$G_{13} = -\mu_1 \frac{\sin \alpha}{d}$
A_1 type		$G_{22} = \mu_1 + \mu_2$	$G_{23} = 2\mu_1 \frac{\sin \beta}{d}$
			$G_{33} = \frac{2}{d^2} (\mu_1 (1 - \cos \alpha) + \mu_3)$
	$G_{44} = \frac{1}{2} (\mu_1 (1 - \cos \alpha) + \mu_3)$	$G_{45} = \mu_1 \frac{\sin \beta (D \cos \beta - d)}{Dd}$	
B_1 type		$G_{55} = \mu_1 \left(\frac{D \cos \beta - d}{Dd} \right)^2 + \frac{\mu_2}{D^2} + \frac{\mu_3}{2d^2}$	
	$G_{66} = \frac{\mu_1}{2d^2 \cos \alpha/2} + \frac{\mu_2}{D^2} + \mu_3 \cdot \frac{(D + d \cos \alpha)^2}{D^2 d^2 \cos^2 \alpha/2}$		
B_2 type			

* The numbering for the reciprocal masses, μ_i , is as follows: 1 : N, 2 : F, 3 : O. All other symbols are defined in Fig. 1.

where the prime represents the new set of force constants associated with the larger basis set. If only the diagonal elements of the F matrix (i.e. F'_{xx} , F'_{yy} , etc. were computed in an *a priori* manner with the large basis set (44 GTF) then the interaction force constant for the basis set, F'_{xy} , is to be scaled. Since the coordinates x and y used in this description are merely one of the symmetry coordinates S_i ($i = 1, \dots, 6$), the force constants are henceforth specified using the subscripts of the relevant symmetry coordinates. (8) can conveniently be written as (8a).

$$F'_{ij} = F_{ij} \left(\frac{F'_{ii} F'_{jj}}{F_{ii} F_{jj}} \right)^{1/2}. \quad (8a)$$

A comparison of results using scaled and computed interaction force constants for the larger basis set is included in the reported frequencies and force constants.

(iv) The FG matrix formalism

Once the numerical values for the elements of the F -matrix are known the elements of the G -matrix have to be calculated. These are given in Table I, using the labels from 1 to 6 of the unnormalized symmetry coordinates (S_1, \dots, S_6) from Fig. 1. Due to symmetry, the 6×6 matrix was blocked to a 3×3

(A_1), a 2×2 (B_1) and a 1×1 (B_2), block. The fundamental frequencies, ν_i , can be obtained using WILSON's method [5], by solving the secular equation

$$|FG - \lambda| = 0, \quad (9)$$

which is normally done by diagonalization of the FG matrix product. The solutions, λ_i , of (9) are related to the ν_i by the equation

$$\lambda_i = 4\pi^2 c^2 \nu_i^2, \quad (10)$$

i.e.
$$\nu_i = \frac{(\lambda_i)^{1/2}}{2\pi c}. \quad (11)$$

Equ. (11), however, obtains λ_i from an FG matrix in c.g.s. units. If λ_i is obtained using the usual units for such calculations, viz., masses in a.m.u., lengths in angstroms, angles in radians, stretching force constants in mdyne/Å, bending force constants in mdyne Å/rad.² and stretch-bend interactions in mdyne/rad., then (11) becomes

$$\nu_i = 1,302 \cdot 9 \sqrt{\lambda_i}. \quad (11a)$$

Results and discussion

The calculations which used only 24 GTF gave energies of the order of -284 hartrees, or only about 90% of the Hartree-Fock limit. Previous calculations [6] have also indicated that the force constants found with the minimal basis sets have been rather inconsistent with those computed with more functions. The calculations using 44 GTF gave considerably better energies, about 99% of the Hartree-Fock limit, and the force constants were expected to be much better. The energies for the various cross-sections calculated using 44 GTF, are given in Tables II to VI. The set of A_1 cross-sections at the experimental conformation was used together with interaction force constants scaled from the minimum basis set using (8a), while the second set of A_1 cross-sections was taken at the absolute minimum of the hypersurface, and was used to calculate interaction force constants. The B_1 cross-sections were used with a scaled interaction constant only.

The diagonal force constants given in Table VII are in good general agreement with experimental values, except that the value of the FN stretching constant (F_{22}) is considerably higher. This result could arise from the way in which fluorine is represented in the present molecular orbital calculations or from the method by which experimental force constants are found. Since the determination of experimental force constants is made by reconstructing the

Table II
Energies for N—O symmetric bond stretching (S_1)

r_{NO} (Å)	experimental configuration*	$r_{NF} = 1.413 \text{ \AA}$, $\sphericalangle \text{ONO} = 132^\circ$
1.13	-300.16445	—
1.18	-300.23121	—
1.23	-300.27335	-300.28293
1.28	-300.29566	-300.30310
1.21	-300.30113	—
1.33	-300.30211	-300.30784
1.36	-300.29953	-300.30467
1.39	—	-300.29780

* Taken to be [7]: $r_{NF} = 1.35 \text{ \AA}$, $\text{ONO} = 125^\circ$, apart from r_{NO} which is varied here but which at equilibrium is 1.23 \AA .

Table III
Energies for N—F bond stretching (S_2)

r_{NF} (Å)	experimental conformation	$r_{NO} = 1.33 \text{ \AA}$, $\sphericalangle \text{ONO} = 132^\circ$ *
1.25	-300.24245	—
1.30	-300.26201	—
1.333	—	-300.29926
1.35	-300.27335	—
1.373	—	-300.30448
1.40	-300.27793	—
1.413	—	-300.30586
1.443	—	-300.30484
1.45	-300.27725	—
1.473	—	-300.30230

* First s exponent on nitrogen taken as 0.42 instead of 0.425 results in slight energy discrepancy.

Table IV
Energies for ONO bending (S_3)

$\sphericalangle \text{ONO}$	experimental configuration	$r_{NO} = 1.33 \text{ \AA}$, $r_{NF} = 1.413 \text{ \AA}$
120°	-300.26667	—
125°	-300.27335	—
127°	—	-300.30727
130°	-300.27526	—
132°	—	-300.30784
135°	-300.27459	—
137°	—	-300.30566

Table V
Cross-sections of B_1 surface*

S_1/S_2	0	$\pm 0.05 \text{ \AA}$	$\pm 0.10 \text{ \AA}$
0°	-300.30701	-300.30180	-300.28893
$\pm 5^\circ$	-300.30472	—	—
$\pm 10^\circ$	-300.29815	—	—

* $\angle \text{ONO} = 132^\circ$, $r_{\text{NF}} = 1.418 \text{ \AA}$, $\frac{r_{\text{NO}_1} + r_{\text{NO}_2}}{2} = 1.329 \text{ \AA}$

FG matrix from the observed frequencies (and hence the known eigenvalues), some suitable way of estimating the signs and magnitudes of the off-diagonal force constants must be determined. Although it is possible then to reconstruct the observed frequencies, if these off-diagonal force constants are substantially inaccurate, the numerical value of the resulting diagonal force constants will also be greatly changed.

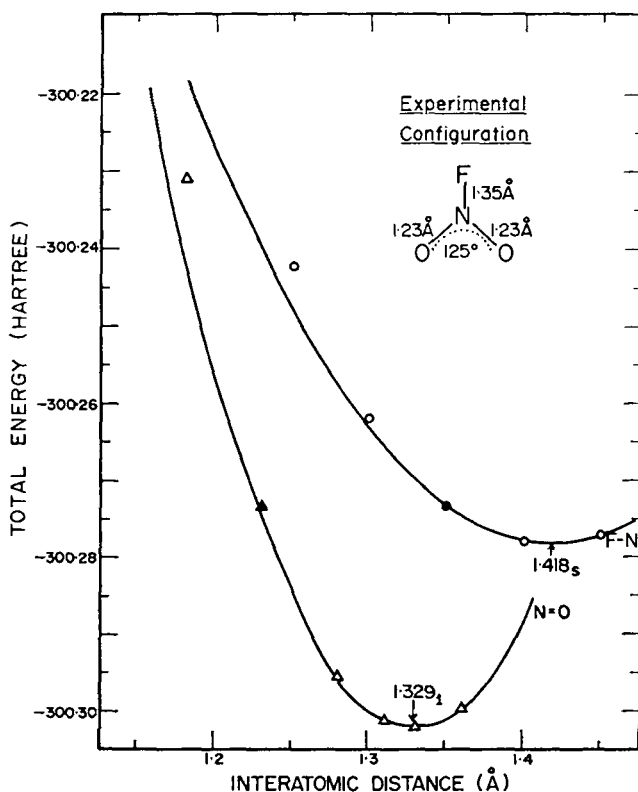


Fig. 2. Parabola fit to S_1 and S_2 potential curves

Table VI
Total energy for out-of-plane bending (S_6)

S_6	total energy
0°	-300.27289
$\pm 5^\circ$	-300.27213
$\pm 10^\circ$	-300.27059
$\pm 20^\circ$	-300.26488
$\pm 30^\circ$	-300.25491

For example, the off-diagonal force constant for the interaction between the asymmetric stretch (S_4) and the asymmetric bend (S_5), was taken [8] to be $+1.24$ mdyne/rad., giving as the diagonal stretching and bending constants 21.9 mdyne/Å and 2.81 mdyne Å/rad.², respectively. This result is rather unusual in the sense that normally, a lower force constant is expected for an asymmetric stretching mode than for the corresponding symmetric one. The

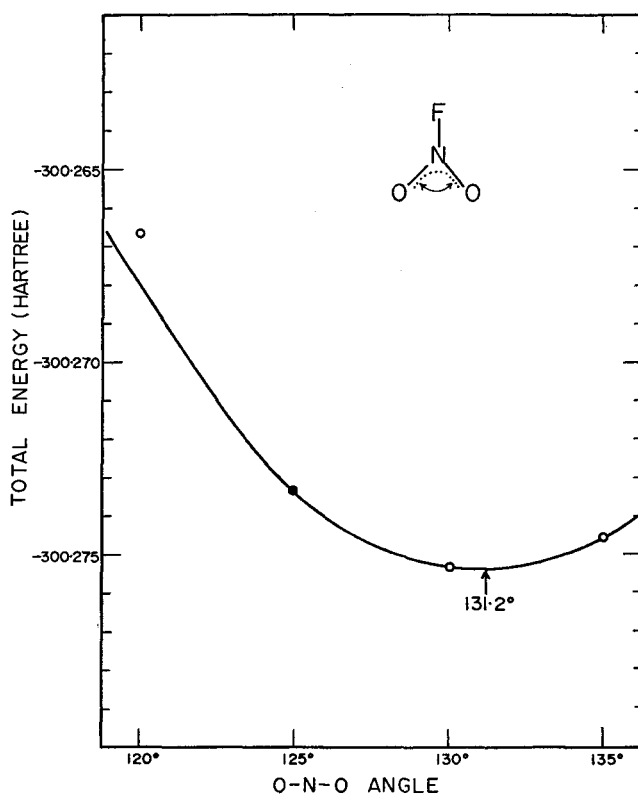


Fig. 3. Potential curve for variation of S_3

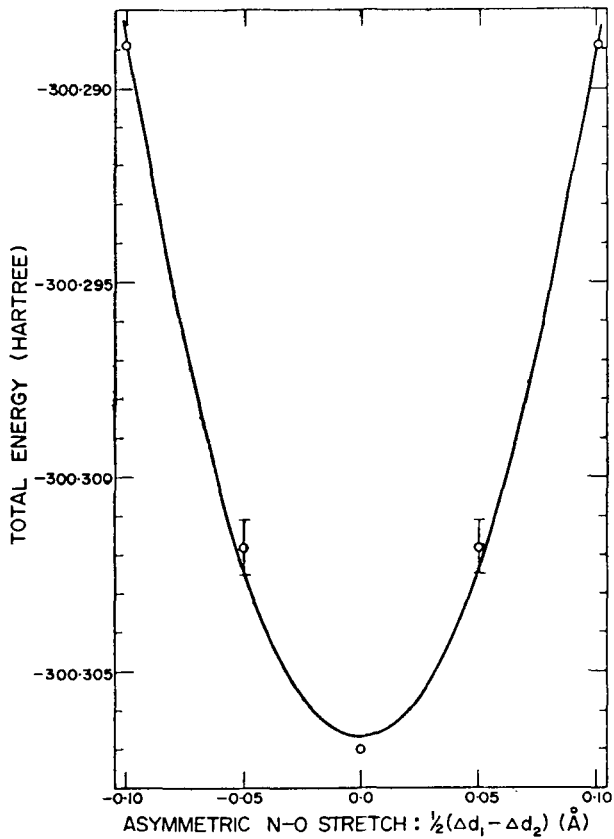


Fig. 4. Potential curve for asymmetric NO stretch (S_4)

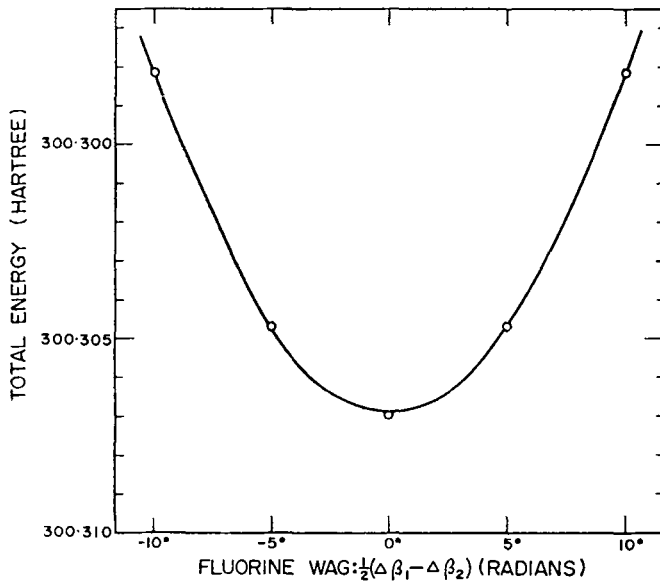


Fig. 5. Potential curve for variations of S_5

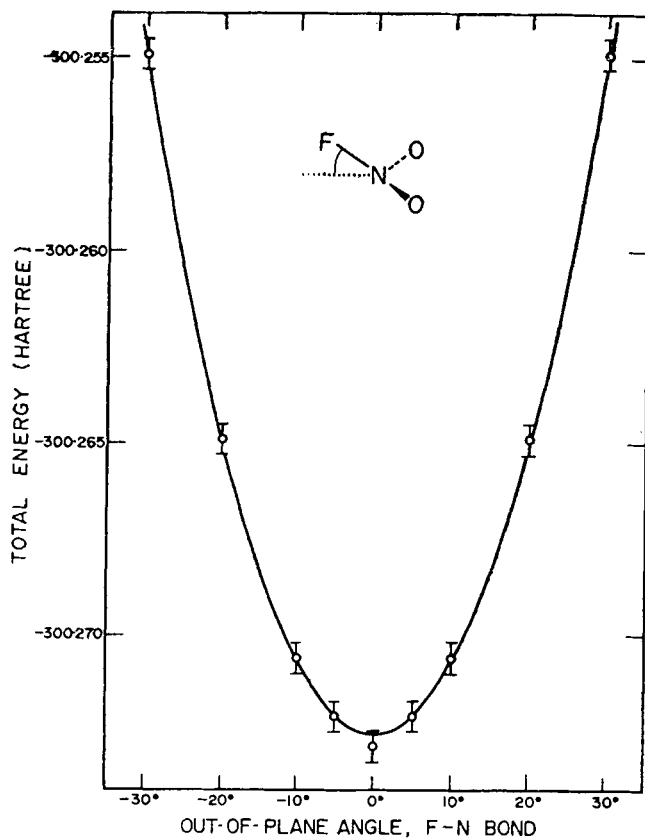


Fig. 6. Potential curve for out-of-plane deformation (S_6)

Table VII
Force constants for nitril fluoride*

F_{ij}	24 GTF calculated	44 GTF scaled	44 GTF calculated	reported [8]**	reported [9]**
F_{11}	81.69	22.26	22.26	18.8	25.5
F_{12}	3.61	1.05	1.6	1.49	0.0
F_{13}	1.94	0.572	1.0	-1.57	1.82
F_{22}	27.25	8.478	8.478	4.57	2.66
F_{23}	-2.38	-0.75	-0.73	-0.583	-0.808
F_{33}	3.60	1.149	1.149	1.36	2.235
F_{44}	78.12	15.432	—	21.9	19.36
F_{45}	-5.41	-1.649	—	+1.24	0.0
F_{55}	5.366	2.524	—	2.82	2.63
F_{66}	—	(0.859)	—	—	0.501

* Units are mdyne/Å for stretch, mdyne Å/rad.² for bend and mdyne/rad for stretch-bend interaction. Subscripts refer to the symmetry coordinates given in Fig. 1.

** Values converted from valence force constants with appropriate charges of normalization for the symmetry coordinates used (Fig. 1).

Table VIII
Calculated fundamental frequencies (cm^{-1}) for nitril fluoride

	scaled	calculated	reported [10]	reported [9]
$\nu_1 (A_1)$	1480	1415	1312	1310
$\nu_2 (A_1)$	1030	1060	822	822
$\nu_3 (A_1)$	510	510	460	568
$\nu_4 (B_1)$	1740	—	1793	1792
$\nu_5 (B_1)$	465	—	570	560
$\nu_6 (B_2)$	(880)	—	742	742

Table IX
Summary of normal coordinate analysis*

	Q_1	Q_2	Q_3	Q_4	Q_5
λ_k	1.2889	0.6300	0.1549	1.7869	0.1271
ν_k	1480	1030	510	1740	465
N	Δx_1	0.0	0.0	-0.2293	-0.0569
	Δy_1	-0.2097	-0.0514	0.0972	0.0
	Δz_1	0.0	0.0	0.0	0.0
F	Δx_2	0.0	0.0	0.0238	0.1392
	Δy_2	0.0847	0.1420	0.0995	0.0
	Δz_2	0.0	0.0	0.0	0.0
O_1	Δx_3	0.0777	-0.1195	0.1045	-0.0578
	Δy_3	0.0415	-0.0619	-0.1016	0.0220
	Δz_3	0.0	0.0	0.0	0.0
O_2	Δx_4	-0.0777	0.1195	-0.1045	-0.0578
	Δy_4	0.0415	-0.0619	-0.1016	-0.0220
	Δz_4	0.0	0.0	0.0	0.0

* In this notation, the relative values of the cartesian displacement coordinates are given in such a way that the molecule is lying in the xy plane, with N at the origin and F on the positive x -axis.

calculated surface suggests that this interaction force constant is actually negative, and if the calculations are repeated assuming -1.24 mdyne/rad. for this constant, it is found that greatly changed values of the diagonal force constants (see Table VII), are obtained; viz. $F_{44} = 16.5$ mdyne \AA and $F_{55} = 3.58$ mdyne $\text{\AA}/\text{rad}^2$. It might be assumed that similar changes would occur if the symmetric stretch-bend interaction constant (F_{13}) had been taken [8] as positive instead of negative.

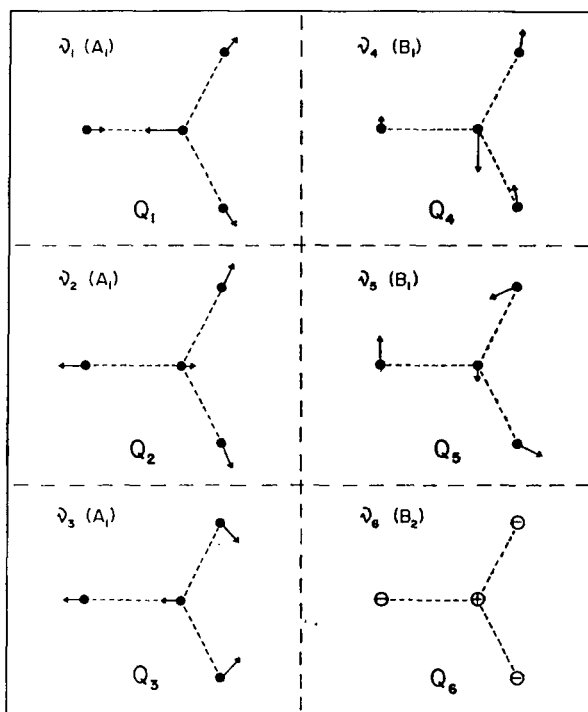


Fig. 7. Normal coordinates for NO_2F

A computer program was used to calculate numeric values of G -matrix elements and the FG matrix. The FG matrix was diagonalized, yielding the eigenvalues and eigenvectors. The results of this calculation are given in Tables VIII and IX and shown in Fig 7.

Conclusion

It can be seen that although theoretical surfaces using the smallest basis sets give force constants which are too high by an order of magnitude, surfaces found even with the next larger basis set provide a very reasonable quantitative estimate of force constants and fundamental frequencies. In particular, the calculated interaction force constants could be used together with experimental frequencies and FG calculations to give a more unique set of experimental force constants, while the theoretically predicted frequencies might occasionally be helpful in clarifying assignments of the fundamental frequencies. It is hoped that further calculations using larger basis sets would give even more accurate predictions.

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ВИБРАЦИОННЫЙ АНАЛИЗ ПОВЕРХНОСТЕЙ AB INITIO ПОТЕНЦИАЛЬНОЙ ЭНЕРГИИ ДЛЯ НИТРИЛОФЛУОРИДА

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Резюме

Проведена серия вычислений самосогласованных молекулярных орбит (SCF—MO) для нитрилофлуорида, применяя метод линейной комбинации функций типа Гаусса (GTF). Для получения гиперповерхности ab initio потенциала применяется варьируемая геометрия. Данная гиперповерхность использована для получения гармонических силовых констант для FG матричного вычисления, из которого определяются основные частоты, связанные с нормальными частотами. Представленные в данной работе вычисления resultируют гиперповерхности для двух различных базисных сетей, содержащих 24 и 44 GTF соответственно. Найдено, что применяя широкую базисную сеть, значения основных частот очень хорошо согласуются с экспериментальными данными, даже в том случае, если силовые константы взаимодействия определены приемом, использующим 24 GTF.