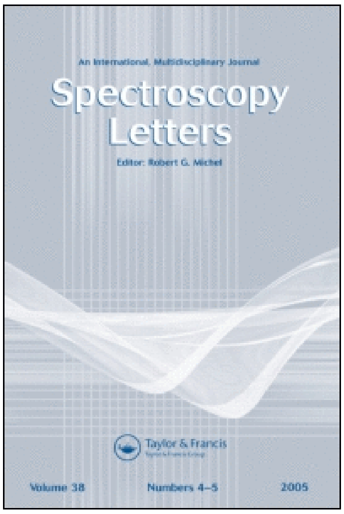

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# The Harmonic and Anharmonic Force Fields of Nitrosyl Halides

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# THE HARMONIC AND ANHARMONIC FORCE FIELDS OF NITROSYL HALIDES

Key Words: Force field calculations, stepwise coupling methods, nitrosyl halides.

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## ABSTRACT

Harmonic and anharmonic symmetry force constants matrices have been calculated using a stepwise coupling method for the twelve isotopic species of nitrosyl fluoride, chloride and bromide. The valence force fields derived from the above matrices were used to recalculate the normal frequencies and the potential energy distribution among force constants. The valence force fields are compared with others previously reported obtained by different methods.

## INTRODUCTION

In a previous paper (1) the way the different stepwise coupling methods handle the construction of the $F^S$ matrices have been discussed. We have shown that the Chacōn and Matzke's method (2) is particularly useful in determining the complete force field of a molecule if enough vibrational data is available. Thus for the formate anion (3) reliable harmonic and anharmonic force constants were derived.

The Chacōn and Matzke's method (hereafter denoted as CMM) yields a greater flexibility in the number of force constants to be calculated and reproduces EXACTLY the experimental frequencies. The method takes also into account the relationships between symmetry force constants belonging to different symmetry blocks.

In the present work we have tested further the ability of this method to convert the vibrational frequencies into physically well based force constants for the twelve isotopic species of nitrosyl halides (four isotopomers for each halide), namely nitrosyl fluoride, chloride and bromide. The results are compared with the harmonic force fields reported by Jones et al (4-7) for these species calculated with a standard normal coordinate analysis program and a least-squares refinement procedure.

## RESULTS AND DISCUSSION

The nitrosyl halides possess a $C_s$ molecular symmetry and the three normal modes belong to the A' irreducible representation.

$\nu_1$ corresponds to the N-O stretching mode, whereas $\nu_2$ and $\nu_3$ are the ONX bending and N-X stretching modes respectively.

Microwave or electron diffraction data give the following structural parameters: r(N-O) = 1.13 Å for the fluoride (8), 1.14 Å for the chloride (9,10) and 1.15 Å for the bromide (11). The N-X (X = F, Cl or Br) bond distances are 1.52, 1.97 and 2.14 Å, whereas the ONX bond angles are 110, 113 and 114° respectively.

The internal and symmetry coordinates were the changes in the N-O and N-X bond distances and the ONX bond angle. Since the internal coordinates are just the symmetry ones, the U and U* matrices are identical and correspond to the unitary matrix. Accordingly, the symmetry force constants are related to the valence force constants as follows: $F_{11} = \emptyset_{N=O}$; $F_{12} = \emptyset_{N=O/N-X}$; $F_{13} = \emptyset_{N=O/ONX}$; $F_{22} = \emptyset_{N-X}$; $F_{23} = \emptyset_{N-X/ONX}$ and $F_{33} = \emptyset_{ONX}$.

The calculations were carried out using the harmonic and anharmonic frequencies given by Jones et al. (4-7) for the twelve isotopic species. For each set of isotopomers average $F^S$ matrices (one harmonic and one anharmonic) were calculated from which the valence force constants were extracted. Table 1 gives the harmonic force constants sets calculated in the present work and those reported by Jones et al.

In order to compare our results with the previously reported calculations, all six force constants were inserted into a standard iterative computer program (12). In no case iteration was

Table 1

Valence force constants for Nitrosyl halides[a,b]

| Force | ONF |  |  | ONCl |  |  | ONBr |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  | $\phi$(I) | $\phi$(II) | $\phi$(III) | $\phi$(I) | $\phi$(II) | $\phi$(III) | $\phi$(I) | $\phi$(II) | $\phi$(III) |
| $\phi_{N=O}$ | 15.920 | 15.2566 | 15.7304 | 15.260 | 14.7159 | 14.1429 | 15.250 | 14.6960 | 14.1809 |
| $\phi_{N-X}$ | 2.260 | 1.9153 | 1.8955 | 1.380 | 1.1028 | 1.0740 | 1.130 | 0.9483 | 0.9321 |
| $\phi_{ONX}$ | 1.060 | 1.1273 | 1.1003 | 0.588 | 0.6284 | 0.6134 | 0.459 | 0.5021 | 0.4885 |
| $\phi_{N=O/N-X}$ | 2.360 | 0.1844 | 0.1842 | 2.020 | 0.1151 | 0.1121 | 1.470 | 0.1208 | 0.1148 |
| $\phi_{N=O/ONX}$ | 0.239 | 0.0655 | 0.0657 | -0.070 | 0.0381 | 0.0371 | 0.096 | 0.0403 | 0.0377 |
| $\phi_{N-X/ONX}$ | 0.138 | 0.2138 | 0.2147 | 0.041 | 0.1058 | 0.1029 | 0.047 | 0.0904 | 0.0868 |

a) All forces in mdynes/Å; b) $\phi$(I) Harmonic force constants Jones et al. (refs. 5,6,7); $\phi$(II) and $\phi$(III) harmonic and anharmonic force constants present work.

allowed and the frequencies were recalculated as well as the potential energy distribution percent (PED%) among the force constants.

From Table 1 it can be inferred that our main force constants are similar to those reported by Jones et al. for these species. The stretching/stretching and stretching/bending interaction force constants are very different, however from Table 2 one can see that for all these species the errors % in the calculated frequencies are comparable with the errors produced by Jones et al. force fields.

It is worthnoting that both force fields produce similar errors in the calculated frequencies despite the different values of three interaction force constants. This is particularly true for the ONF, being Jones' results better for the ONCl and ONBr.

Jones and Ryan (5) obtained a second refinement of the ONF force field by including centrifugal distortion data. All force constants are just slightly different of those derived from vibrational data only, but when inserted into the standard iterative program produce larger errors in the frequencies.

Since our and Jones' force fields produce comparable errors (at least for the fluoride and bromide), it can be concluded that in spite of the excess of vibrational data no unique solution can be found in keeping with the results previously reported for the six isotopic species of the formate anion (3).

Table 2

Calculated harmonic frequencies for all isotopic species of Nitrosyl halides[a]

| I | II | III | IV | V |
|---|---|---|---|---|
| $O^{18}N^{15}F^{19}$ | | | | |
| 1793.4 | 1791.0 | 0.13 | 1792.3 | 0.06 |
| 749.5 | 756.3 | 0.91 | 758.8 | 1.24 |
| 512.2 | 507.8 | 0.86 | 507.8 | 0.86 |
| $O^{18}N^{14}F^{19}$ | | | | |
| 1827.1 | 1824.8 | 0.13 | 1827.9 | 0.04 |
| 767.2 | 774.2 | 0.91 | 776.9 | 1.26 |
| 514.1 | 510.0 | 0.80 | 509.4 | 0.91 |
| $O^{16}N^{15}F^{19}$ | | | | |
| 1843.9 | 1841.5 | 0.13 | 1840.7 | 0.17 |
| 757.9 | 764.5 | 0.87 | 767.4 | 1.25 |
| 520.4 | 516.0 | 0.85 | 516.4 | 0.77 |
| $O^{16}N^{14}F^{19}$ | | | | |
| 1876.8 | 1874.4 | 0.13 | 1875.3 | 0.08 |
| 775.5 | 782.2 | 0.86 | 785.2 | 1.25 |
| 522.9 | 518.5 | 0.84 | 518.4 | 0.86 |
| $O^{16}N^{15}Cl^{35}$ | | | | |
| 1803.6 | 1805.0 | 0.08 | 1800.8 | 0.16 |
| 588.8 | 591.5 | 0.46 | 600.6 | 2.00 |
| 334.3 | 331.5 | 0.84 | 330.1 | 1.26 |
| $O^{16}N^{14}Cl^{35}$ | | | | |
| 1835.6 | 1837.2 | 0.09 | 1834.2 | 0.08 |
| 603.2 | 606.0 | 0.46 | 614.8 | 1.92 |
| 336.4 | 333.7 | 0.80 | 332.2 | 1.25 |

| | | | | |
|---|---|---|---|---|
| $O^{18}N^{14}Cl^{35}$ | | | | |
| 1786.4 | 1788.2 | 0.10 | 1786.8 | 0.02 |
| 595.5 | 598.4 | 0.49 | 606.6 | 1.86 |
| 329.3 | 326.5 | 0.85 | 325.0 | 1.31 |
| $O^{18}N^{15}Cl^{35}$ | | | | |
| 1753.4 | 1755.0 | 0.09 | 1752.5 | 0.05 |
| 580.7 | 583.6 | 0.50 | 591.7 | 1.89 |
| 327.3 | 324.6 | 0.82 | 323.2 | 1.25 |
| $O^{18}N^{15}Br^{80}$ | | | | |
| 1749.9 | 1744.1 | 0.33 | 1749.3 | 0.03 |
| 527.1 | 535.6 | 1.61 | 538.0 | 2.07 |
| 259.7 | 258.5 | 0.46 | 256.2 | 1.35 |
| $O^{18}N^{14}Br^{80}$ | | | | |
| 1783.0 | 1776.8 | 0.35 | 1783.4 | 0.02 |
| 541.0 | 549.9 | 1.65 | 551.8 | 2.00 |
| 261.7 | 260.7 | 0.38 | 258.4 | 1.26 |
| $O^{16}N^{15}Br^{80}$ | | | | |
| 1800.4 | 1794.5 | 0.33 | 1797.7 | 0.15 |
| 533.5 | 542.9 | 1.76 | 546.3 | 2.40 |
| 267.0 | 265.6 | 0.52 | 263.1 | 1.46 |
| $O^{16}N^{14}Br^{80}$ | | | | |
| 1832.8 | 1826.3 | 0.35 | 1830.9 | 0.10 |
| 548.0 | 556.9 | 1.62 | 559.9 | 2.17 |
| 269.2 | 268.1 | 0.41 | 265.6 | 1.34 |

a) I, observed harmonic frequencies (refs. 4-7); II, calculated harmonic frequencies (Jones et al. force field); III, percent deviation; IV, calculated harmonic frequencies (our force field) and V, percent deviation.

Table 3

Comparison of the errors % in calculated frequencies

| Species[a] | I | II | III |
|---|---|---|---|
| $O^{18}N^{15}F^{19}$ | 0.63 | 0.72 | 0.75 |
| $O^{18}N^{14}F^{19}$ | 0.61 | 0.74 | 0.77 |
| $O^{16}N^{15}F^{19}$ | 0.62 | 0.73 | 0.74 |
| $O^{16}N^{14}F^{19}$ | 0.61 | 0.73 | 0.74 |
| Total Error % | 0.618 | 0.730 | 0.750 |
| $O^{16}N^{15}Cl^{35}$ | 0.46 | 1.14 | 1.12 |
| $O^{16}N^{14}Cl^{35}$ | 0.45 | 1.08 | 1.09 |
| $O^{18}N^{14}Cl^{35}$ | 0.48 | 1.06 | 1.09 |
| $O^{18}N^{15}Cl^{35}$ | 0.47 | 1.06 | 1.10 |
| Total Error % | 0.465 | 1.085 | 1.100 |
| $O^{18}N^{15}Br^{80}$ | 0.80 | 1.15 | 1.10 |
| $O^{18}N^{14}Br^{80}$ | 0.79 | 1.09 | --- |
| $O^{16}N^{15}Br^{80}$ | 0.87 | 1.34 | 1.25 |
| $O^{16}N^{14}Br^{80}$ | 0.79 | 1.20 | 1.13 |
| Total Error % | 0.813 | 1.195 | 1.160 |

a) I, Jones et al. harmonic force field; II, our harmonic force field; III, our anharmonic force field.

Table 4

Potential energy distribution % in ONF, ONCl and ONBr

| | ONF | | | ONCl | | | ONBr | | |
|---|---|---|---|---|---|---|---|---|---|
| Force | 1792.3 | 758.8 | 507.8 | 1752.5 | 591.7 | 323.2 | 1749.3 | 538.0 | 256.2 |
| $\phi_{N=O}$ | 98.3 | 0.8 | 1.0 | 99.4 | 0.3 | 0.4 | 99.6 | 0.2 | 0.3 |
| $\phi_{N-X}$ | 0.4 | 35.4 | 66.5 | 0.3 | 25.4 | 76.0 | 0.4 | 21.9 | 79.5 |
| $\phi_{ONX}$ | 1.9 | 79.4 | 20.9 | 0.7 | 86.2 | 14.7 | 0.5 | 89.5 | 11.8 |
| $\phi_{NO/NX}$ | -0.4 | -0.4 | 0.6 | -0.3 | -0.2 | 0.3 | -0.4 | -0.1 | 0.3 |
| $\phi_{NO/ONX}$ | -0.4 | 0.2 | 0.1 | -0.2 | 0.1 | 0.1 | -0.2 | 0.1 | 0.1 |
| $\phi_{NX/ONX}$ | 0.3 | -15.4 | 10.9 | 0.1 | -11.9 | 8.5 | 0.1 | -11.6 | 8.0 |

The PED among the force constants in ONF, ONCl and ONBr molecules are given in Table 4, only for the $O^{18}N^{15}F^{19}$, $O^{18}N^{15}Cl^{35}$ and $O^{18}N^{15}Br^{80}$ isotopomers. The other isotopic species show minor changes only. From Table 4 it can be inferred that $\nu_1$ is clearly a N=O stretching mode, whereas $\nu_2$ and $\nu_3$ are strongly coupled. However, $\nu_2$ is mostly an ONX bending and $\nu_3$ is best described as N-X stretching. The PED% derived from the Jones' force fields shows that $\nu_2$ and $\nu_3$ are much more coupled. Thus, for the $O^{18}N^{15}F^{1}$ the $\phi_{NO}$, $\phi_{NX}$ and $\phi_{ONX}$ force constants make the following contribution to $\nu_2$ and $\nu_3$: 13.4, 37.9, 74.9 and 10.0, 86.5 and 24.5 respectively. In this sense our force field shows that these two modes have no contribution from $\phi_{NO}$ and the coupling is considerable smaller.

The present results along with other previously reported (1,3, 13) clearly show that the Chacõn and Matzke stepwise coupling method allows to calculate physically well based force fields and to predict isotopic shifts for small and large molecules (14).

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