# LETTERS

## Anharmonic Force Field of $N_2O$

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The anharmonic force field of $N_2O$ has been determined from high-quality ab initio calculations. The results suggest that among the available experimental sextic force fields the field obtained by algebraic contact transformation is the most reliable, although even in this experimental field most higher-order terms (especially at fifth and sixth order) appear to be phenomenological in nature, *i.e.*, do not directly correspond to the associated derivatives of the potential energy surface. The accuracy of computed force fields has further been demonstrated by anharmonic force field calculations on the diatomics $\tilde{X}$ $^1\Sigma_g^+$ $N_2$ and $\tilde{X}$ $^2\Pi$ NO.

Ab initio studies of anharmonic force fields of small polyatomic molecules, including linear molecules,[1-4] symmetric tops,[5,6,7a] and asymmetric tops,[7-10] proved unambiguously that (a) most calculated cubic and quartic force constants show reasonably small variation with respect to basis set extension and treatment of electron correlation; (b) particularly accurate ab initio force fields can be obtained if methods incorporating a large portion of the electron correlation energy with extended basis sets are used; (c) a substantial part of the discrepancy between force constants calculated at theoretical stationary points and force constants obtained from experiments comes from the differences in the underlying reference geometries;[1b] thus, shifting the theoretical reference geometry close to the true equilibrium geometry results in force constants which are in dramatically better agreement with their experimental counterparts; (d) some of the higher-order experimental constants (especially the quintic and sextic ones) are phenomenological in nature,[2] *i.e.*, not directly correspondent with the associated derivatives of the potential energy surface; and (e) while there is a delicate balance between the approximate electronic energy and exact nuclear–nuclear repulsion energy ($V_N$) derivative terms of opposite sign, for higher-order force constants the contributions of the derivatives of $V_N$ become increasingly dominant, resulting in more accurately calculated values.

To the author's knowledge $N_2O$ is the only polyatomic molecule besides $CO_2$ for which experimental attempts have been made to determine the complete anharmonic force field through sixth order. These attempts include various approaches: (a) numerical, algebraic contact transformation;[11] (b) second-order perturbation theory;[12] and (c) direct numerical diagonalization.[13,14] While the early studies[11a,12] relied upon vibrational data only, the more recent investigations[11b,13,14] employed both vibrational band centers and rotational band constants during the fit of the anharmonic force field. A recent ab initio study[2] on the sextic force field of $CO_2$ suggested that, even for this molecule, where the complete sextic force field in internal coordinates contains only 28 independent terms, most quintic and sextic constants determined experimentally seem to be completely phenomenological in nature. It seemed to be of interest to compare the anharmonic force fields of $N_2O$ determined experimentally to accurate ab initio fields in order to check whether for this molecule, where the complete internal coordinate sextic force field contains considerably more, altogether 47, independent constants,[15] problems in the experimental force fields similar to those in $CO_2$ existed. Therefore, the present communication describes, for the first time, the ab initio determination of the complete sextic force field of $N_2O$ and, for purposes of comparison, those of $\tilde{X}$ $^1\Sigma_g^+$ $N_2$ and $\tilde{X}$ $^2\Pi$ NO. Note that the complete quartic force field of $N_2O$ has been determined previously at several theoretical

**TABLE 1: Theoretical and Experimental Sextic Force Fields and Molecular Constants for X̃ $^1\Sigma_g^+$ N₂, Calculated at $r_e$ = 1.097 685 Å**[a]

| param | cc-pVTZ | | | cc-pVQZ | | | exptl[b] | |
|---|---|---|---|---|---|---|---|---|
| | SCF | CCSD | CCSD(T) | SCF | CCSD | CCSD(T) | RKR | SP |
| $f_1$ | 0.8501(0.8892) | 0.0236(0.1803) | −0.1409(0.0093) | 0.8868(0.8878) | 0.1099(0.1716) | −0.0602(−0.0038) | 0.0 | |
| $f_{11}$ | 25.00(24.72) | 24.07(23.40) | 23.73(23.04) | 24.70(24.69) | 23.68(23.49) | 23.34(23.14) | 22.94 | 22.95 |
| $f_{111}$ | −172.7(−171.3) | −172.2(−169.6) | −172.5(−169.8) | −171.2(−171.2) | −170.0(−169.2) | −170.3(−169.4) | −169.6 | −169.7 |
| $f_{1111}$ | 1003.9(993.5) | 1013.0(999.4) | 1014.7(1001.2) | 997.2(995.4) | 1001.7(997.1) | 1003.3(998.8) | 997.6 | 998.5 |
| $f_{11111}$ | −6057.2(−5963.8) | −6041.0(−5926.7) | −6039.0(−5923.9) | −5896.7(−5845.3) | −5882.0(−5823.6) | −5877.4(−5820.0) | −5860.7 | |
| $f_{111111}$ | 40 685(41 340) | 39 949(40 245) | 39 927(40 096) | 37 589.8(36 753) | 37 284(36 334) | 37 114.9(36 316) | 37 975.1 | |
| $r_e^c$ | 1.0671(1.0655) | 1.0967(1.0902) | 1.1038(1.0973) | 1.0656(1.0655) | 1.0931(1.0906) | 1.1003(1.0978) | 1.0977 | 1.0977 |
| $\omega_e^d$ | 2461.6(2447.5) | 2415.1(2381.2) | 2398.2(2363.2) | 2446.4(2446.4) | 2395.8(2385.9) | 2378.4(2368.0) | 2357.8 | 2358.6 |
| $\alpha_e^e$ | 0.0149(0.0150) | 0.0160(0.0166) | 0.0166(0.0172) | 0.0150(0.0150) | 0.0163(0.0164) | 0.0168(0.0170) | 0.0173 | 0.0173 |
| $\omega_e\chi_e^f$ | 11.86(12.00) | 13.00(13.49) | 13.62(14.17) | 11.95(11.97) | 13.11(13.24) | 13.75(13.90) | 14.33 | 14.33 |

[a] The force constants, $f$, are given in units of aJ Å$^{-n}$, where $n$ is the order of the constant. The numbers reported in parentheses were obtained with completely uncontracted basis sets polarized into the core region with two tight (d,f) manifolds (for details see text) and no orbitals frozen. [b] The potential function whose derivatives are reported as RKR values here was obtained by Allen and Császár[1b] by a fit to the RKR data of ref 25. The spectroscopic (SP) values are taken from ref 23. [c] The optimized bond length, $r_e$, given in Å, was determined by a fit of a force field through fourth order to five energy points. [d] The harmonic vibrational frequency, $\omega_e$, given in cm$^{-1}$, was determined using the formula $1302.7913(f_{11}/\mu)^{1/2}$, where $\mu$ is the reduced mass in amu. [e] The vibrational–rotational constant, $\alpha_e$, given in cm$^{-1}$, was determined using the formula $(-6B_e^2/\omega_e)[1 + 1.05052 \times 10^{-3}\omega_e f_{111}/(B_e f_{11}^3)^{1/2}]$, where $B_e$ (in cm$^{-1}$) is the equilibrium rotational constant. [f] The anharmonicity constant, $\omega_e\chi_e$, given in cm$^{-1}$, was determined using the formula $(0.702418/\mu)(5f_{111}^2/f_{11}^2 - 3f_{1111}/f_1)$.

**TABLE 2: Theoretical Sextic Force Fields and Molecular Constants for X̃ $^2\Pi$ NO, Calculated at $r_e$ = 1.150 70 Å**[a]

| param | cc-pVTZ | | | cc-pVQZ | | | exptl[b] |
|---|---|---|---|---|---|---|---|
| | SCF | CCSD | CCSD(T) | SCF | CCSD | CCSD(T) | |
| $f_1$ | 0.7189(0.7395) | 0.0618(0.1627) | −0.0950(−0.0005) | 0.7425 | 0.1283 | −0.0342 | |
| $f_{11}$ | 17.12(16.86) | 16.90(16.35) | 16.63(16.06) | 16.85 | 16.60 | 16.32 | 15.95 |
| $f_{111}$ | −127.7(−126.1) | −124.7(−121.9) | −124.1(−121.3) | −126.0 | −122.8 | −122.2 | −121.1 |
| $f_{1111}$ | 730.5(733.3) | 745.7(744.7) | 758.2(756.8) | 726.0 | 737.5 | 744.5 | 737.6 |
| $f_{11111}$ | −4221.8(−4309.5) | −4340.0(−4460.3) | c(−4439.3) | −4197.4 | −4306.6 | c | |
| $f_{111111}$ | 31 278(29 296) | 28 180(26 944) | c(24 102)[c] | 30 661 | 27 583 | c | |
| $r_e$ | 1.1141(1.1127) | 1.1471(1.1411) | 1.1565(1.1507) | 1.1125 | 1.1432 | 1.1528 | 1.1507 |
| $\omega_e$ | 1972.5(1957.6) | 1960.0(1927.8) | 1943.9(1910.5) | 1957.2 | 1942.3 | 1925.9 | 1904.4 |
| $\alpha_e$ | 0.0161(0.0162) | 0.0159(0.0164) | 0.0163(0.0169) | 0.0163 | 0.0161 | 0.0165 | 0.0171 |
| $\omega_e\chi_e$ | 14.14(14.02) | 13.16(13.30) | 13.34(13.55) | 14.15 | 13.18 | 13.49 | 14.19 |

[a] See footnotes in Table 1. [b] Reference 24. [c] Not reported due to problems with numerical accuracy.

levels.[1,3,4] The corresponding optimized geometries have been used as reference geometries at the levels DZP SCF,[1b] TZ2P SCF,[1a] TZ2P CISD,[1a] and cc-pVTZ CCSD(T).[3] The experimental geometry[11b] ($r_e$(NN) = 1.1273 Å and $R_e$(NO) = 1.1851 Å) has been used as reference at the DZP SCF, and TZ(2d1f) SCF, CCSD, and CCSD(T) levels.[1b] These ab initio quartic force field studies confirmed the general trends noted above.

Two basis sets have been selected for this study, the correlation-consistent cc-pVTZ and cc-pVQZ basis sets of Dunning and co-workers.[16] All 1s core orbitals have been kept frozen in correlated level calculations except where noted otherwise. To estimate the effect of 1s correlation for N₂ and NO, the cc-pVTZ and cc-pVQZ basis sets have been uncontracted and polarized into the core region with two tight (d,f) manifolds in an even-tempered manner (multiplying the largest d and f exponents by 3 and 9). The resulting basis sets are denoted as CV(TZ) and CV(QZ). Only the pure spherical components of the basis functions have been used; thus, for each atom the cc-pVTZ, cc-pVQZ, CV(TZ), and CV(QZ) basis sets contain 30, 55, 66, and 92 contracted Gaussian functions (CGFs), respectively. Electronic wave functions and analytic geometric first derivatives have been determined in this study at the SCF,[17] CCSD,[17–19] and CCSD(T)[20] levels. The complete sextic force fields have been obtained from energy points for the diatomics and from analytic first derivatives for N₂O by application of appropriate, carefully selected, symmetric finite-difference formulas.[2] No orbitals have been kept frozen, due to program limitations, during the cc-pVTZ CCSD(T) gradient calculations. The program systems PSI[21] and ACES II[22] have been used for the ab initio calculations. The open-shell CCSD(T) energy calculations for X̃ ²Π NO employed the ROHF-CCSD(T) methodology of Scuseria.[20c]

To demonstrate the accuracy of ab initio force fields at the levels used in this study, the anharmonic fields of X̃ $^1\Sigma_g^+$ N₂ and

X̃ ²Π NO have been determined at the cc-pVTZ, cc-pVQZ, CV(TZ), and CV(QZ) SCF, CCSD, and CCSD(T) levels. The results obtained are presented in Tables 1 and 2 for N₂ and NO, respectively. These calculations have been performed, similarly to those for N₂O, at the corresponding experimental equilibrium geometries ($r_e$ = 1.097 685 Å[23] and $r_e$ = 1.150 70 Å[24] for N₂ and NO, respectively), so that the effect of geometric shift on the force constants[1b] is separated. In the case of N₂ the ab initio results are compared to RKR values defined as the appropriate derivatives of a functional form obtained by Allen and Császár[1b] through a well-designed fit to RKR points.[25] The cc-pVTZ CCSD(T) equilibrium bond lengths ($r_e$) are about 0.006 Å too long (0.0061 Å for N₂ and 0.0058 Å for NO). These errors decrease to about 0.0025 Å by extending the basis to cc-pVQZ. Thus, for both diatomics the concentration is about 0.0035 Å upon going from a cc-pVTZ to a cc-pVQZ basis set, in agreement with the trend reported in ref 3. Furthermore, it is quite interesting to note that the combined effect of 1s correlation and basis set contraction on $r_e$ is almost the same as the residual error of CCSD(T) calculations employing uncontracted basis sets; to wit, for N₂(NO) the CV(TZ) CCSD(T) $r_e$ distances differ from experiment by only −0.0004(0.000 07) Å, respectively (see Table 1). As far as the force constants are concerned, the results obtained for N₂ and NO (a) show the steady convergence of theoretical force constant values toward their experimental counterparts as the basis is extended and the level of electron correlation increased and (b) suggest that agreement between theoretical and experimental force constants can be substantially improved if the effect of 1s correlation[26] is included in the theoretical treatment. In these two diatomics, 1s correlation engenders the following ($r_e$, $\omega_e$, $\omega_e\chi_e$) shifts (in Å, cm$^{-1}$, cm$^{-1}$): N₂ (−0.002, −8, +0.1) and NO (−0.002, −6, +0.1).[27] Furthermore, the results support two important assertions about cc-pVTZ CCSD(T) force constants

**TABLE 3: Theoretical and Experimental Internal Coordinate Anharmonic Force Fields for $N_2O^a$**

| const | theory | | | exptl | | |
|---|---|---|---|---|---|---|
| | cc-pVTZ SCF//exptl | cc-pVTZ CCSD(T)//exptl | cc-pVTZ CCSD(T)$^b$ | ref 11b | ref 14$^c$ | ref 13 |
| $r$(NN) | 1.0607 | −0.0313 | 0.0 | | | |
| $R$(NO) | 0.2864 | 0.0006 | 0.0 | | | |
| rr | 19.166 | 18.755 | 18.126 | 18.251 | 18.236 | 18.588 |
| rR | 2.241 | 0.965 | 0.960 | 1.028 | 1.029 | 1.134 |
| RR | 10.291 | 12.334 | 12.021 | 11.960 | 11.966 | 11.802 |
| αα | 0.797 | 0.728 | 0.683 | 0.666 | 0.666 | 0.666 |
| rrr | −149.0 | −142.6 | −138.0 | −133.6 | −132.4 | −150.5 |
| rrR | 1.027 | −2.476 | −2.532 | −6.872 | −9.842 | −4.54 |
| rRR | −3.690 | −0.387 | −0.295 | 1.498 | 2.451 | −5.90 |
| RRR | −106.9 | −100.7 | −98.00 | −98.83 | −96.33 | −94.74 |
| rαα | −1.812 | −1.716 | −1.691 | −1.580 | −2.567 | −2.918 |
| Rαα | −1.821 | −1.483 | −1.449 | −1.537 | −1.101 | −0.784 |
| rrrr | 800.6 | 839.8 | 811.4 | 691.4 | 674.7 | 52.6 |
| rrrR | 12.2 | 10.1 | 10.1 | 46.5 | 65.6 | −51.6 |
| rrRR | 8.5 | 0.85 | 0.080 | −3.485 | 8.77 | 172.0 |
| rRRR | 3.8 | 18.5 | 17.8 | −8.67 | −20.8 | 9.84 |
| RRRR | 596.8 | 605.0 | 587.2 | 634.9 | 590.3 | 623.3 |
| rrαα | −1.5 | 1.1 | 1.11 | 1.81 | 12.67 | −0.96 |
| rRαα | 4.9 | 4.0 | 4.04 | 5.11 | 7.22 | 0.10 |
| RRαα | 1.7 | 2.1 | 2.39 | 1.49 | −6.16 | 2.60 |
| αααα | 1.46 | 1.24 | 1.98 | 1.90 | 2.28 | 2.65 |
| rrrrr | −4937 | −4812 | | −3693 | [−3880] | −5857 |
| rrrrR | 58 | 5 | | 781 | | 7268 |
| rrrRR | −38 | −76 | | 357 | | −3453 |
| rrRRR | 17 | 5 | | 588 | | 1671 |
| rRRRR | −224 | −120 | | −428 | | 1245 |
| RRRRR | −2752 | −3367 | | −5923 | [−3468] | 1416 |
| rrrαα | −5 | 7 | | 84 | | 233 |
| rrRαα | −2 | −6 | | 43 | | −163 |
| rRRαα | −6 | −3 | | −33 | 0.5 | −41 |
| RRRαα | −1 | −2 | | | 15 | 50 |
| rαααα | −3 | −1 | | −5 | 0.9 | 32 |
| Rαααα | −5 | −6 | | −2 | 1.6 | −16 |
| rrrrrr | 32 382 | 26 961 | | 135 824 | [19 411] | 1 232 568 |
| rrrrrR | −758 | d | | | | −54 514 |
| rrrrRR | 341 | d | | | | −87 080 |
| rrrRRR | 178 | d | | −4472 | | −99 145 |
| rrRRRR | −169 | d | | −14 600 | | −48 985 |
| rRRRRR | −370 | d | | | | 139 259 |
| RRRRRR | 25 679 | 19 214 | | 87 165 | [19 230] | −110 081 |
| rrrrαα | −35 | −48 | | −2236 | | 2920 |
| rrrRαα | −18 | d | | −870 | | −2637 |
| rrRRαα | 31 | d | | 531 | | −2405 |
| rRRRαα | 3 | d | | −350 | | 862 |
| RRRRαα | 22 | 185 | | 840 | | 1044 |
| rrαααα | −30 | −7 | | 33 | 104 | −161 |
| rRαααα | 21 | −15 | | | 27 | 60 |
| RRαααα | 7 | 37 | | 13 | −15 | 134 |
| αααααα | −5 | 58 | | 6 | −32 | −58 |

$^a$ Units for the force constants are consistent with energy measured in attojoules, stretching coordinates ($r$ and $R$) in angstroms, and bending coordinates ($\alpha$) in radians. The designation // means "at the geometry of". The abbrevation "exptl" means that the force field was calculated at the experimental geometry of $r_e$(NN) = 1.1273 Å and $r_e$(NO) = 1.1851 Å. $^b$ Reference 3. $^c$ Set (iii). $^d$ Not reported due to problems with numerical accuracy.

if evaluated at the experimental geometry: (a) they are accurate to within about 2% and (b) due to incompleteness in the cc-pVTZ basis set, the stretching force constants are overestimated, which results in too large harmonic frequencies $\omega_e$ and too small $\omega_e x_e$ values.[28]

The anharmonic force fields of $N_2O$, determined at the cc-pVTZ SCF and CCSD(T) levels, are reported in Table 3 along with the available experimental anharmonic fields. The experimental quadratic and cubic force constants agree quite well with each other and with the calculated values. Among these constants correlation has a large, even qualitatively important effect on the stretch–stretch interaction constants $f_{rR}$, $f_{rrR}$, and $f_{rRR}$. For $f_{rR}$ the large basis set SCF values overestimate the experimental value by more than 100%. The sign of $f_{rrR}$ is predicted with the wrong sign at the SCF level (with all basis sets $f_{rrR}$ is calculated to be a small positive constant),[1,4] while correlated level calculations yield small negative values (though still a factor of 2–3

smaller than experiment). Only methods which incorporate a substantial part of electron correlation (CCSD and CCSD(T)) yield quantitatively correct results, especially if large spdfg basis sets are employed. Variances among correlated level force fields seem to be acceptable. These findings are identical to those observed for $CO_2$,[2] another molecule with cumulenic multiple bonds. In the field of Lacy and Whiffen (LW),[13] obtained by direct numerical diagonalization, $f_{rr}$ and $f_{rrr}$ appear to be too large and too small, respectively. Furthermore, the values of $f_{rrrr}$ (52.6 aJ Å$^{-4}$) and $f_{rrrrrr}$ (1 232 568 aJ Å$^{-6}$) are too small and too large, respectively, by orders of magnitude. These inaccuracies in the LW diagonal force field could be reflected in the fitted off-diagonal values. Indeed, the great majority of the LW quintic and sextic coupling constants are orders of magnitude different from the ab initio constants. Most ab initio higher-order stretch–stretch coupling constants are small, usually orders of magnitude smaller than the diagonal ones. Thus, they should safely be

neglected in an empirical fit, as was done by Kobayashi and Suzuki.[14] Furthermore, it is interesting to note that the signs of the stretch–stretch coupling constants in higher orders do not seem to follow any simple rule, while the signs of the quadratic and cubic constants can be rationalized using simple arguments.[1] The bending modes of $N_2O$, similarly to those of $CO_2$,[2] appear to be quite harmonic. The diagonal bending constants in fourth and sixth order are rather small, as are the stretch–bend interaction constants. Overall, among the experimental fields the Teffo–Chédin force field appears to be the most reliable.

The conclusions obtained above are basically the same as those obtained for $CO_2$;[2] most importantly, for both $CO_2$ and $N_2O$ the force fields obtained by Chédin using algebraic contact transformation appear to be the most reliable and those obtained by Lacy using direct numerical diagonalization the least reliable, although even in the best experimental field most higher-order terms (especially at fifth and sixth order) appear to be phenomenological in nature, *i.e.*, do not directly correspond to the associated derivatives of the potential energy surface.

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(26) Two sets of calculations have been performed to obtain an estimate of the 1s effect. In the first set no orbitals have been kept frozen (the results of these calculations are reported in Tables 1 and 2 for $N_2$ and NO, respectively), while in the second set the 1s core orbitals and all virtual orbitals above 200 au have been kept frozen.

(27) The numbers for $N_2$ are somewhat different from the estimates reported recently by Bauschlicher and Partridge (BP) (Bauschlicher, C. W., Jr.; Partridge, H. *J. Chem. Phys.* **1994**, *100*, 4329), as BP's values are –0.002 Å and +9 cm$^{-1}$ for $r_e$ and $\omega_e$, respectively. The reason for the discrepancy in $\omega_e$ is that BP advocate a different strategy to measure the 1s effect: they do not separate the important effect caused by geometry change from those of changes in the treatment of the electronic problem.

(28) The tendency of the CCSD(T) level of theory to result in too large $r_e$ and quadratic force constant values at the same time can be used advantageously to calculate force fields and related molecular constants, such as frequencies, at the corresponding optimized theoretical geometry, as was demonstrated a number of times (see, for example, ref 3 and Lee, T. J.; Rice, J. E. *J. Chem. Phys.* **1991**, *94*, 1220).