

Harmonic force field for nitro compounds

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Abstract Molecular simulations leading to sensors for the detection of explosive compounds require force field parameters that can reproduce the mechanical and vibrational properties of energetic materials. We developed precise harmonic force fields for alanine polypeptides and glycine oligopeptides using the FUERZA procedure that uses the Hessian tensor (obtained from ab initio calculations) to calculate precise parameters. In this work, we used the same procedure to calculate generalized force field parameters of several nitro compounds. We found a linear relationship between force constant and bond distance. The average angle in the nitro compounds was 116° , excluding the 90° angle of the carbon atoms in the octanitrocubane. The calculated parameters permitted the accurate molecular modeling of nitro compounds containing many functional groups. Results were acceptable when compared with others obtained using methods that are specific for one type of molecule, and much better than others obtained using methods that are too general (these ignore the chemical effects of surrounding atoms on the bonding and therefore the bond strength, which affects the mechanical and vibrational properties of the whole molecule).

Keywords Nitro compounds · Energetic materials · Harmonic force fields · DFT

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Introduction

Some attempts have been made to calculate force field parameters for specific explosive compounds in order to perform molecular mechanics and molecular dynamics simulations and to study several properties and molecular interactions [1–6]. For instance, Davande et al. developed a quantum chemistry based force field for dinitro compounds [2]; Boyd et al. calculated a nonreactive force field to simulate the formation, diffusion, and agglomeration of point defects in the crystal lattice of the alpha modification of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) [3]; Klauda et al. developed parameters for nitroalkenes and nitroarenes to fit densities, hydration energies, and conformational energies [5]; and Wallis et al. calculated harmonic parameters in order to study conformational changes of RDX in isolation and in dense Xe [6]. In a series of papers, Thompson, Rice, and Sorescu developed an intermolecular potential that can accurately describe the structures of several nitramines; their potential energy is composed of pairwise atom–atom (6-exp) Buckingham and Coulombic interactions. They showed that their potential accurately reproduces the crystallographic structures and lattice energies [7–10].

In the work described in this paper, we calculated generalized parameters for a harmonic force field using the parameters of several related explosive molecules. These parameters can be used in simulations of nitro compounds interacting with other molecules, molecular systems, and surfaces, including sensors for the detection of explosive compounds [11–14].

The parameters were obtained according to the FUERZA [15–18] procedure, which uses results from ab initio calculations and extracts the parameter values without fitting procedures that compute parameters in an iterative way until reproducing the vibrational frequencies or conformational energies [1–4]. Using the FUERZA procedure, precise

harmonic force constants for alanine polypeptides [19] and glycine oligopeptides [16] were calculated, tested, and used to transfer information through the vibrational spectrum [20]. The parameters obtained from the FUERZA procedure allowed us to perform accurate molecular modeling that accounted for the chemical effects of surrounding atoms on the bonding and the effect of bond strength on the mechanical and vibrational properties of the whole molecule.

Methodology

We optimized the molecular structure and calculated the vibrational frequencies of all of the studied explosives using the program Gaussian 03. We used the B3PW91 hybrid functional [21, 22] and the 6-31G(*d*) basis set [23], with convergence thresholds for the density matrix of 10^{-6} and 10^{-8} for the root mean square and maximum density matrix error between iterations, respectively. This and related methodologies have produced excellent results in the past

[24–34]. The optimizations were followed by a second derivative calculation that was done to determine the existence of a local minimum and to obtain the Hessian matrix that allowed us to calculate the force field parameters.

To calculate the force constant from the *ab initio* calculations, we used the program FUERZA [15]. This program considers that, for a molecular system of N atoms, the atomic interaction can be expressed as $\delta F = -[\kappa]\delta x$, where $[\kappa]$ is the Hessian matrix. For any two atoms A and B, the problem can then be defined by

$$\begin{bmatrix} \delta F_{x_A} \\ \delta F_{y_A} \\ \delta F_{z_A} \end{bmatrix} = - \begin{bmatrix} \frac{\partial^2 E}{\partial x_A \partial x_B} & \frac{\partial^2 E}{\partial x_A \partial y_B} & \frac{\partial^2 E}{\partial x_A \partial z_B} \\ \frac{\partial^2 E}{\partial y_A \partial x_B} & \frac{\partial^2 E}{\partial y_A \partial y_B} & \frac{\partial^2 E}{\partial y_A \partial z_B} \\ \frac{\partial^2 E}{\partial z_A \partial x_B} & \frac{\partial^2 E}{\partial z_A \partial y_B} & \frac{\partial^2 E}{\partial z_A \partial z_B} \end{bmatrix} \times \begin{bmatrix} \delta x_B \\ \delta y_B \\ \delta z_B \end{bmatrix}. \quad (1)$$

The force constant that describes the harmonic interaction between two atoms (κ_{AB}) can be calculated as the sum of the

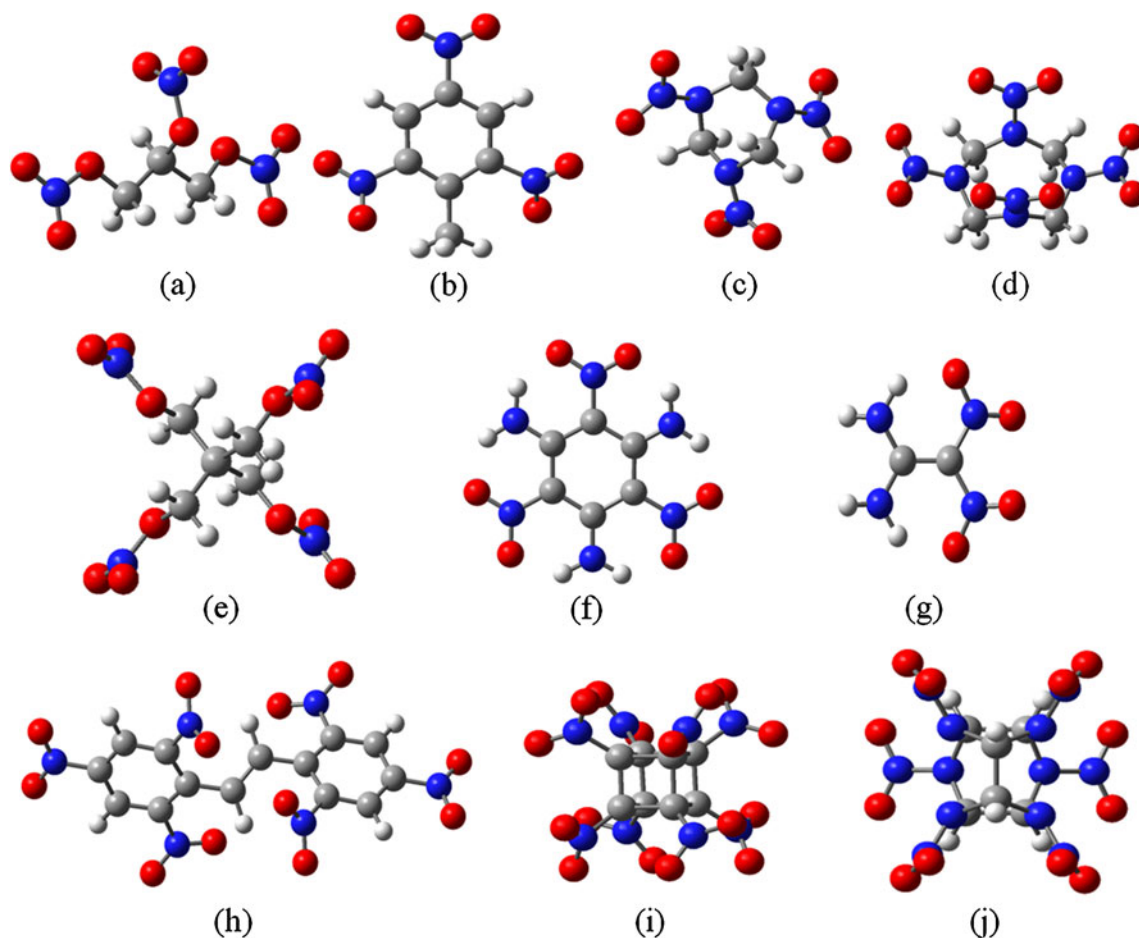


Fig. 1 Ball and stick representations of nitroglycerin (a), trinitrotoluene (b), cyclotrimethylene-trinitramine (c), cyclotetramethylene-tetranitramine (d), pentaerythritol-tetranitrate (e), triamino-trinitrobenzene (f), diamino-dinitroethene (g), hexanitrostilbene (h),

octanitrocubane (i) and hexanitrohexaazaisowurtzitane (j). The atoms are color-coded: nitrogen in blue, oxygen in red, carbon in gray, and hydrogen in white

contributions of the matrix eigenvalues (λ_i^{AB}) weighted by the projection of its corresponding eigenvectors onto the direction of the bond (\hat{v}_i^{AB}) along the direction of the bond (\hat{u}_i^{AB}) [15]:

$$\kappa_{AB} = \sum_{i=1}^3 \lambda_i^{AB} |\hat{u}_i^{AB} \cdot \hat{v}_i^{AB}|. \quad (2)$$

Consider bonds AB and BC with the calculated eigenvalues (λ_i^{AB}) and (λ_i^{BC}), and the eigenvectors (\hat{v}_i^{AB}) and (\hat{v}_i^{BC}), respectively. (\hat{u}_i^{PA}) and (\hat{u}_i^{PC}) are two unit vectors that are perpendicular to the unit vectors along the bonds AB and BC, respectively. If R_{AB} and R_{BC} are the corresponding bond lengths, then the angle force constant (κ_θ) can be defined as follows [15]:

$$\frac{1}{\kappa_\theta} = \frac{1}{R_{AB}^2 \sum_{i=1}^3 \lambda_i^{AB} |\hat{u}_i^{PA} \cdot \hat{v}_i^{AB}|} + \frac{1}{R_{BC}^2 \sum_{i=1}^3 \lambda_i^{BC} |\hat{u}_i^{PC} \cdot \hat{v}_i^{BC}|} \quad (3)$$

To model TNT molecules, we performed molecular dynamics (MD) simulations using LAMMPS [35]. For the nonbonded interactions, we considered the Lennard–Jones potential and Coulombic interactions. The Lennard–Jones parameters employed were generic parameters used in CHARMM [36], and the partial charges were obtained from the ab initio simulations. The MD simulations were carried out with a time step of 0.5 fs and inner and outer cutoffs of 8 Å and 10 Å, respectively, with an NVT

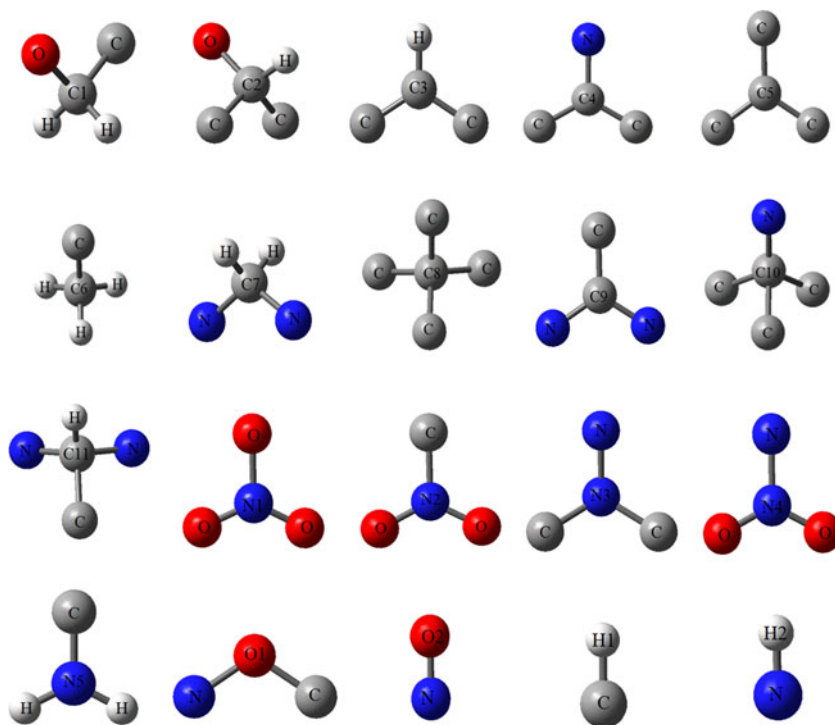
ensemble. The simulations started with an energy minimization, and then the temperature was ramped with a Nose–Hoover thermostat [37] from 10 K to 300 K in 25 ps. A damping time of 100 fs was used. Then the system was kept at 300 K for 2.5 ns, during which time it reached equilibrium. Once the system was in equilibrium, the vibrational spectrum was obtained at intervals of 25 ps.

Results

We calculated parameters for trinitroxypropane [commonly known as nitroglycerin (NG)], trinitrotoluene (TNT), cyclotrimethylene-trinitramine (RDX), cyclotetramethylene-tetranitramine (HMX), pentaerythritol-tetranitrate (PETN), triamino-trinitrobenzene (TATB), diamino-dinitroethene (FOX-7), hexanitrostilbene (HNS), octanitrocubane (OC), and hexanitrohexaazaisowurtzitane (HNIW), as shown in Fig. 1. Using the dependence of each parameter on the bond type and angle type, we calculated generic parameters that could be applied to any nitro compound. To define these parameters, we first defined the atom types for all of the compounds, based on the geometry adopted by the atom and its neighbors, as seen in Fig. 2. In this way, we were able to consider the effects of atom chemistry on the force field parameters.

The FUERZA procedure [15] calculates the parameters for each bond and angle in a molecule; therefore we grouped them according to bond and angle types. We used

Fig. 2 Ball and stick representations of the types of atoms used to define the bond and angle types that were used to calculate the force field parameters. The atoms are color-coded: nitrogen in *blue*, oxygen in *red*, carbon in *gray*, and hydrogen in *white*



the average bond force constant and bond length in each case. Table 1 shows the calculated parameter values for each type of bond. For the angles, the average angle force constant and the average angle were calculated for all of the studied molecules. Table 2 shows the calculated angle parameters as well as their standard deviations. The standard deviation of the bond force constant was on average smaller than 5% in most cases, and the standard deviation of the bond distance was smaller than 1%; the values of the standard deviation of the angle force constant were smaller than 5%, and those for the standard deviation of the angle were smaller than 1%. These small standard deviation values demonstrate the high precision of the method and therefore of the obtained results.

Table 1 Calculated bond force constants (κ_{AB}) and their standard deviations (σ_{κ}) as well as bond lengths and their standard deviations (σ_{bond}) for the nitrocompounds

Bond type	κ_{AB} (kcal/mol/Å ²)	σ_{κ}	Bond length (Å)	σ_{bond}
C2–H1	361	–	1.09	–
C1–H1	367	3	1.09	0.00
C1–C2	234	0	1.52	0.00
C2–O1	224	–	1.43	–
O1–C1	227	5	1.43	0.00
N1–O1	138	15	1.42	0.01
N1–O2	710	24	1.20	0.00
C3–C4	401	11	1.39	0.00
C4–C5	341	11	1.41	0.00
C5–C6	241	–	1.50	–
H1–C3	399	4	1.08	0.00
H1–C6	368	7	1.09	0.00
N2–C4	158	11	1.46	0.02
N2–O2	687	18	1.22	0.00
H1–C7	365	14	1.09	0.00
C7–N3	241	12	1.45	0.01
N3–N4	129	24	1.41	0.01
N4–O2	652	11	1.22	0.00
C1–C8	193	0	1.54	0.00
C4–C4	276	2	1.44	0.00
N5–C4	502	0	1.32	0.00
H2–N5	481	21	1.01	0.00
C9–C9	303	–	1.42	–
N5–C9	474	0	1.34	0.00
N2–C9	186	0	1.43	0.00
C3–C5	272	8	1.47	0.00
C3–C3	581	–	1.34	–
C10–C10	182	5	1.56	0.00
C10–N2	139	1	1.48	0.00
C11–H1	378	2	1.09	0.00
C11–C11	142	3	1.58	0.00
N3–C11	225	19	1.45	0.01

Table 2 Calculated angle force constants (κ_{θ}) and their standard deviations (σ_{κ}), as well as angles and their standard deviations (σ_{Angle}) for the nitrocompounds

Angle type	κ_{θ} (kcal/mol/rad ²)	σ_{κ}	Angle (deg)	σ_{Angle}
H1–C2–C1	34	1	110	0
H1–C2–O1	37	–	109	–
H1–C1–O1	43	1	110	0
C2–C1–H1	30	0	111	0
C1–C2–C1	75	–	111	–
C1–C2–O1	74	3	108	0
C2–C1–O1	85	1	105	0
H1–C1–H1	22	2	109	0
C2–O1–N1	84	–	116	–
C1–O1–N1	70	0	114	0
O1–N1–O2	70	2	115	3
O2–N1–O2	57	0	131	0
C4–C3–C4	103	0	118	0
C4–C5–C4	97	6	114	0
C3–C4–C5	83	3	124	0
C4–C5–C6	75	0	123	0
C3–C4–C3	78	0	122	0
C4–C3–H1	33	1	121	0
C5–C6–H1	34	8	111	0
C3–C4–N2	77	8	117	2
C5–C4–N2	85	5	121	0
H1–C6–H1	18	1	108	1
C4–N2–O2	68	5	118	2
O2–N2–O2	62	3	126	4
H1–C7–N3	36	3	109	2
H1–C7–H1	21	3	109	0
C7–N3–C7	89	5	120	4
C7–N3–N4	86	8	117	1
N3–C7–N3	67	8	112	3
N3–N4–O2	72	6	116	0
O2–N4–O2	60	2	128	1
C8–C1–H1	31	0	111	0
C1–C8–C1	76	7	110	2
C8–C1–O1	69	0	106	0
C4–C4–C4	77	2	120	1
C4–C4–N5	77	0	121	0
C4–C4–N2	75	1	120	0
C4–N5–H2	37	0	117	0
H2–N5–H2	24	1	124	3
C9–C9–N5	79	0	121	0
C9–C9–N2	73	0	122	0
C9–N5–H2	37	2	118	2
N5–C9–N5	89	–	117	–
N2–C9–N2	71	–	117	–
C9–N2–O2	71	1	119	1
C4–C5–C3	80	1	123	0
C5–C3–C3	75	0	123	0

Table 2 (continued)

Angle type	κ_{θ} (kcal/mol/rad ²)	σ_{κ}	Angle (deg)	σ_{Angle}
C5–C3–H1	34	0	116	0
C3–C3–H1	34	0	120	0
C10–C10–C10	52	4	90	0
C10–C10–N2	55	5	125	1
C10–N2–O2	45	0	116	1
H1–C11–C11	32	3	113	1
H1–C11–N3	35	3	110	1
C11–C11–N3	72	4	107	3
C11–N3–C11	96	2	110	5
N3–C11–N3	58	2	109	4
C11–N3–N4	92	4	117	0

Comparing our results with other results from the literature, we find an agreement for some of the molecules listed in Table 3; for example, for HMX, the values for the C7–H1, N3–C7 and O2–N4 bonds calculated by Smith et al. [1] agree fairly well with those obtained in this work. Good agreement with literature values [1] was also seen for the angles in HMX. Comparing our results for RDX with those obtained by Boyd et al. [3], the angle parameter values are in good accord, as shown in Table 3. This comparison of the parameter values for individual molecules confirms that the calculated parameter values obtained using our approach can be used to accurately model several types of nitro compounds.

Upon analyzing the data further, it became apparent that there was a relationship between bond length and bond force constant and another between angle and angular force constant. We found that there was a linear relation between bond length and bond force constant, as shown in Fig. 3a, where $\text{bondlength} = -4.86 \times 10^{-4} \kappa_{\text{AB}} + 1.57$ if the bonds that include hydrogen atoms (represented by blue diamonds

in Fig. 3a) are not included. While there was no clear relation between angle and angular force constant, the angles were around 116°, except for the angle between the carbon atoms of OC (90°), as shown in Fig. 3b.

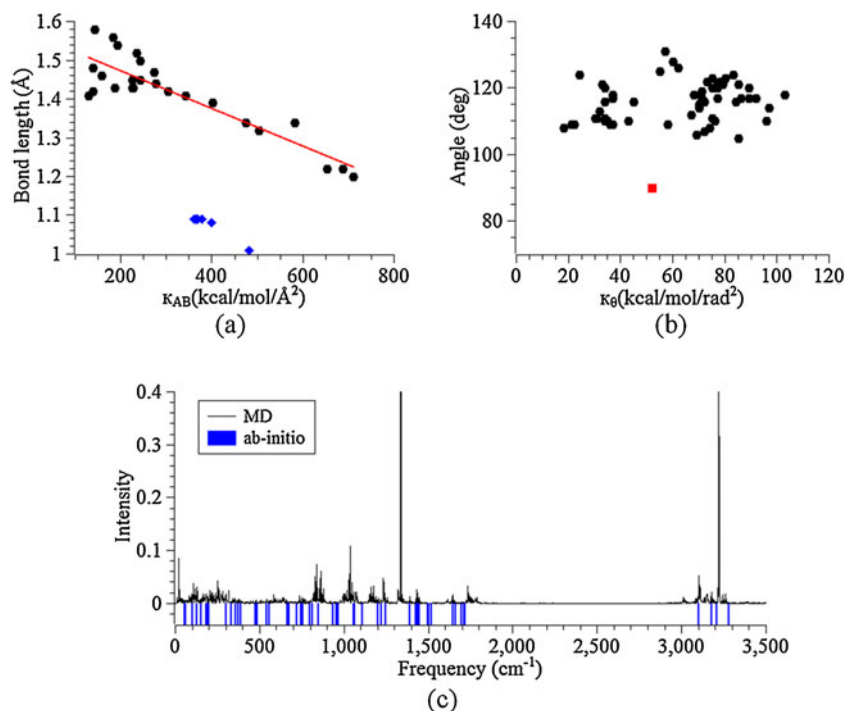
To test the obtained parameters, we ran MD simulations of TNT molecules and obtained its vibrational spectrum. Four cases were modeled: a single molecule, where partial charge on each atom and Coulombic interactions were included (case 1); a single molecule without partial charges (case 2); a box containing 100 molecules, with van der Waals and Coulombic interactions as well as the partial charge on each atom included (case 3); and a box containing 100 molecules, with van der Waals interactions included but not partial charges (case 4). In each case, we calculated the vibrational spectrum for each bond, and obtained very similar results in all the cases, showing the main influences on the vibrational spectrum are the bond and angle components of the force field, while the charge and nonbonding interactions do not strongly affect the molecular vibrational modes

Table 4 shows the peak frequencies for several vibrational modes for the four MD cases described above, as well as the results from the DFT ab initio calculations. Two main peaks were obtained for the N–O bond: one at around 1400 cm⁻¹ and the other at around 1740 cm⁻¹. We can attribute these values to symmetric and asymmetric stretching. Several peaks were found for C(ring)–C(CH₃) bond stretching, which were components of vibrational modes. The two peaks with the greatest intensities were seen at 1420 and 1230 cm⁻¹. Similarly, for C–C bonds in the ring, several peaks corresponding to several vibrational modes of the ring were noted, with a high-intensity peak appearing close to 1620 cm⁻¹ and another at around 990 cm⁻¹. A large peak corresponding to the stretching mode of C–H bonds occurred at 3250 cm⁻¹. All of these results are in good agreement with the vibrational spectrum obtained by ab initio calculations, as shown in Fig. 3c, where the

Table 3 Comparison of the calculated values for bond force constants (κ_r), bond lengths, angle force constants (κ_{θ}), and angles with their corresponding literature values [1, 3]

Bond / angle type	$\kappa_r / \kappa_{\theta}$ (FUERZA)	$\kappa_{\text{AB}} / \kappa_{\theta}$ (literature)	Bond length / angle (FUERZA)	Bond length / angle (literature)
C7–H1	365 kcal/mol/Å ²	320 kcal/mol/Å ² [1]	1.09 Å	1.09 Å
N3–C7	241 kcal/mol/Å ²	336 kcal/mol/Å ² [1]	1.45 Å	1.44 Å
N3–N4	129 kcal/mol/Å ²	496 kcal/mol/Å ² [1]	1.41 Å	1.36 Å
O2–N4	652 kcal/mol/Å ²	995 kcal/mol/Å ² [1]	1.22 Å	1.23 Å
O2–N4–O2	60 kcal/mol/rad ²	62 kcal/mol/rad ² [1]	128°	120°
H1–C7–N3	36 kcal/mol/rad ²	43 kcal/mol/rad ² [1]	109°	107°
O2–N4–N3	72 kcal/mol/rad ²	62 kcal/mol/rad ² [1]	116°	107°
N4–N3–C7	86 kcal/mol/rad ²	65 kcal/mol/rad ² [3]	117°	116°
C7–N3–C7	89 kcal/mol/rad ²	72.5 kcal/mol/rad ² [3]	120°	115°
N3–N4–O2	72 kcal/mol/rad ²	62.5 kcal/mol/rad ² [3]	116°	117°
N3–C7–N3	67 kcal/mol/rad ²	72.7 kcal/mol/rad ² [3]	112°	109°

Fig. 3 **a** Bond length vs. bond force constant; *blue diamonds* are bonds with hydrogen atoms. **b** Angle vs. angular force constant; the *red square* represents the angle between carbon atoms in OC. **c** Vibrational spectrum of a TNT molecule obtained with the calculated parameters



vibrational spectrum obtained by MD simulations of one TNT molecule without partial charges (case 2) is compared with the frequencies obtained by ab initio DFT. Based on this analysis, we can confirm that the parameters obtained using the FUERZA procedure can accurately reproduce the vibrational properties of nitro compounds.

Conclusions

We developed a set of precise harmonic force field parameters for nitro compounds using the FUERZA procedure. The parameters calculated in this manner show small standard deviations and incorporate the effects of neighboring atoms on

the bond and angle strengths. We found a linear relationship between bond force constant and bond length, excluding the bonds formed by hydrogen atoms. The parameters obtained using FUERZA accurately model the vibrational modes of nitro compounds, as shown by comparing the spectrum obtained for TNT with the corresponding one yielded by ab initio calculations. This is important when the simulation requires precise reproduction of vibrational modes, which is the case for vibronic signal transmission [20] and sensors based on vibrational measurements [13]. Furthermore, the FUERZA parameters can be coupled with other parameters that have been optimized for nonbonded interactions to achieve a very realistic model which can be utilized in multiple applications, including the sensing of explosive compounds.

Table 4 Comparison of the DFT vibrational frequencies (all frequencies are in cm^{-1}) with those from MD for the single molecule including Coulombic interactions (case 1), single molecule without Coulombic

interactions (case 2), 100 molecules box with van der Waals and Coulombic interactions (case 3) and 100 molecules box with van der Waals interactions without Coulombic interactions (case 4)

Mode	DFT 1 molec.	MD 1 molec. +Coulomb	MD 1 molec.	MD 100 molec. +vdW+Coulomb	MD 100 molec. +vdW
N–O symmetric	1420	1400	1390	1410	1380
N–O asymmetric	1710	1780	1730	1740	1750
C _{ring} –CH ₃ stretching	1240	1220	1230	1240	1240
C–C asymmetric	1640	1600	1650	1600	1620
C–H	3270	3240	3220	3270	3260
CH ₃ stretching	1430	1400	1430	1410	1440
C–C symmetric	960	970	1020	970	1010

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