Indian Journal of Pure & Applied Physics
Vol. 55, August 2017, pp. 604-615

Theoretical insight into the structure and stability of TNT and RDX in external electric field

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Received 25 July 2016; accepted 16 May 2017

A comparison of the effect of external electric field on the C–NO_2 or N–NO_2 bonds with the C–H and N–O bonds in 2,4, 6-trinitrotoluene (TNT) or hexahydro-1,3,5-trinitro-*s*-triazine (RDX) has been carried out using the M06-2x method with the 6-311++G** and aug-cc-pVTZ basis sets. The result shows that for TNT the fields have a minor effect on the C–NO_2 and C–H bonds but a major effect on the N–O bonds, while in RDX the fields greatly affect the N–NO_2 bond but the N–O and C–H bonds are slightly affected. Thus, in TNT the N–O bond can be the trigger bond, and in RDX the N–NO_2 bond is always the trigger bond in electric fields. The explosive sensitivities may be reduced and the stabilities may be increased under the external electric fields in the negative direction along the C–NO_2 bond axis for TNT and in the positive direction along the N–NO_2 or N–O bond axis for RDX. The opposite trends can be suggested in the fields of the opposite directions along above bond axes. The introduction of external electric field into energetic material may be an available way to adjust explosive sensitivity. The analyses of AIM (atoms in molecules) and frequencies support the above viewpoints. The linear correlations between the field strengths and the changes of N−O/N−N bond lengths, $\rho_{(N-O/N-N)}$ values, or stretching frequencies of the N−O/N−N bonds have been found.

Keywords: Trigger linkage, External electric field, Stability, M06-2x, AIM

1 Introduction

Energetic material is a kind of compounds or complexes composed of high energetic density molecules, which show high density, high detonation velocity and high detonation pressure. It has been anticipated that the introduction of external electric field into energetic material can increase the energy content of the conduction gases in the vicinity of detonation front, and consequently accelerate the detonation velocity and lead to an increase of detonation pressure[1–3]. However, it is well known that the performance and stability of explosive could not be possessed simultaneously, and in general the high performance may result in the high explosive sensitivity. Thus, the energy molecules, which can show high energy, high density, high detonation velocity and high detonation pressure, etc., may be more unstable in the presence of external electric fields. Therefore, it is extremely urgent to investigate the stability (sensitivity) of explosive in external electric fields.

It has been found that the explosive sensitivity of nitro explosive has a close relation to the bond strength of the C–NO_2 or N–NO_2 "trigger linkages", the breaking of which is a key factor in detonation initiation[4–10]. Recently it has been shown from some theoretical studies that the external electric fields had a significant effect on the bond length and stretching frequency of the C–NO_2 and N–NO_2 trigger bonds[11–13], suggesting that one could use the changes of a trigger linkage to infer whether it was made stronger or weaker by the imposition of a field[12,14]. Thus, the changes of the strengths of trigger linkages could be used to judge whether the sensitivities are reduced or increased in the presence of external electric fields.

In fact, for the C- or N-nitro explosives, breaking of the C–NO_2 or N–NO_2 bond is not the only mechanism for initiating detonation, and there are many others, such as nitro-nitrite isomerization, formation of nitrosoaromatic intermediates, reactions of the –NO_2 group with an *ortho* substituent, etc[15,16]. Thus, the C–NO_2 or N–NO_2 bond is not the only trigger linkage, and proton dissociation and oxygen transfer from the nitro may also play an important role in the decomposition

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process of nitro explosive. 2,4,6-trinitrotoluene (TNT) is a kind of explosives with the C–NO_2 trigger linkage (Fig. 1). The density, detonation velocity and detonation pressure are 1.630 g/cm^3, 6713.0 m/s and 18.5 Gpa, respectively. TNT is easy to be decomposed[17]. Revital *et al.*[18] found that at relatively low temperatures, reaction of the methyl substituent on the ring (C–H α attack) of TNT, leading to the formation of 2,4-dinitro-anthranil, was both kinetically and thermodynamically the most favorable pathway. At ~1250–1500 K, the C–NO_2 homolysis pathway dominated TNT decomposition. Rearrangement of the NO_2 moiety to ONO followed by O–NO homolysis was a thermodynamically more favorable pathway than the C–NO_2 homolysis pathway at room temperature[18]. Hexahydro-1,3,5-trinitro-*s*-triazine (RDX) is also one kind of explosives with good comprehensive performance (Fig. 1). The density is 1.816 g/cm^3 and the detonation velocity is 8350 m/s. RDX is easy to explode[9]. For the most stable RDX isomer, which is a chair conformation with one nitro group in the equatorial position and two nitro groups in the axial position[19], the possible two initial channels of the thermal decomposition, N–NO_2 bond dissociation and HONO elimination were calculated. The N–NO_2 bond dissociation was the main initial channel in gas-phase RDX decomposition. The competing reactions of C–N bonds of ring and N–NO_2 bonds splitting, which occurred in the initial stage of RDX decomposition, were affected by the experimental conditions and sample phase state[20]. 1,3,5-Trinitro-hexahydro-1,3,5-triazin-2(1*H*)-one (Keto-RDX) belongs to orthorhombic system with space group *Pnma*. The density is 1.933 g/cm^3, and there is a single sharp exothermic decomposition with peak maximum at 211.4 °C (DSC)[21]. Golovina *et al.*[22] found that the thermal decomposition of keto-RDX occurred through the homolysis of the N–NO_2 bond and this bond was longer (1.438 Å) than the analogous bond in the RDX molecule (1.382 Å). The rearrangement into unstable diazoxy esters, a process typical of linear nitramides, did not occur in keto-RDX because of steric hindrances[22]. These results suggest that the proton dissociation or oxygen transfer from the nitro may also relate to the initiation of energetic material. In other words, except for the C–NO_2 and N–NO_2 bonds, the C–H bond of the –CH_2 moiety and the N–O bond of nitro group may also become the trigger linkages. Therefore, in order to reveal the nature of explosive sensitivity, it is very necessary to predict the changes of the N–O and C–H bonds in the presence of external electric field. Recently, by using the DFT-B3LYP and MP2 methods with the 6-311++G(2d,p) and aug-cc-pVTZ basis sets, we have found that the external electric fields have a minor effect on the C–N or C–H bond but a major effect on the N–O bond in CH_3NO_2, while in NH_2NO_2 the fields greatly affect the N–NO_2 bond but the N–O or N–H bond is slightly affected. Thus, in CH_3NO_2 oxygen transfer or unimolecular isomerization to methyl nitrite might be prior to the breaking of the C–N bond in the initial stage of decomposition, and the N–O bond can be the trigger bond in electric fields. In NH_2NO_2, however, the N–NO_2 bond rupture may be preferential in electric field and consequently the N–NO_2 bond might be always the real trigger bond[23]. To our knowledge, few theoretical investigations into the effects of the external electric fields on the C–NO_2, N–NO_2, C–H and N–O bonds were presented for nitro explosives.

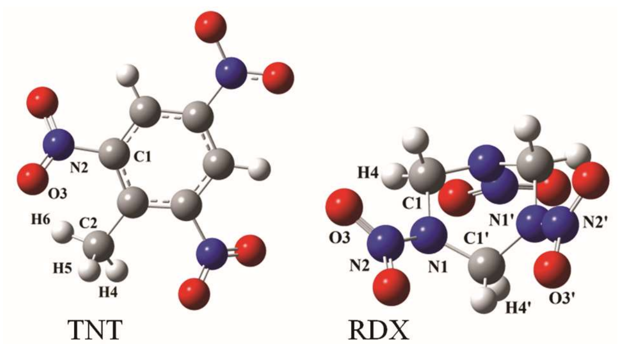


Fig. 1 — Molecular structures of TNT and RDX.

The technique of electro-hydraulic discharge, integrating multiple effects such as high temperature pyrogenation, photochemistry oxidation, cavitation degradation, super-critical water oxidation, has the advantages of normal temperature and press, high efficiency, no-selectivity, no secondary pollution, low energy, and thus is efficient in disposing disdegradable wastewater[24,25]. Recently the electro-hydraulic pulse plasma waste-water treatment apparatus has been used to investigate the influence factors and degradation mechanism of the degradation of explosive waste-water. The experiment results have shown that increasing discharge voltage can enhance degradation rate, while increasing conductance of waste-water will reduce degradation rate[26]. Although there have been many investigations on the influence factors, degradation mechanism, joins techniques, product analyse of explosive waste-water treatment by electro-hydraulic discharge, it is not clear how external electric field influences the structures and reactivities of explosives in waste-water. Only the changes of the structure and reactivity (or stability) of explosive in external electric field are clarified which is the nature of the electro-hydraulic discharge revealed completely and is the degradation rate of explosive waste-water by using the technique of electro-hydraulic discharge increased further.

In this paper, we present a detailed and extensive comparison of the effects of external electric fields on the C–NO_2 or N–NO_2 bond with the C–H or N–O bond in TNT and RDX (the chair conformation with one nitro group in the equatorial position and two nitro groups in the axial position) by using the M06-2x method. Our goal is to predict theoretically which chemical bond is affected more notable and even ruptured more easily in detonation initiation in the presence of external electric field. This investigation can help us understand the initiation mechanism of energetic materials in the presence of external electric fields. It must be very useful for safe using of explosives, avoiding the catastrophic explosion in external electric fields and enhancing the degradation rate of explosive waste-water by using the technique of electro-hydraulic discharge.

2 Computational Details

All calculations were performed with Gaussian 03 programs[27]. Each molecular geometry was fully optimized and the AIM (Atoms in Molecules)[28,29] results were computed using the M06-2x method with the 6-311++G** and aug-cc-pVTZ basis sets in the presence of external electric fields (as well as no fields). Energy minima were confirmed by the absence of imaginary frequencies.

Three kinds of field directions, parallel to the C–NO_2/N–NO_2 (in TNT or RDX) and N–O bond axes as well as perpendicular to the −NO_2 plane, were considered with the field strengths of ±0.002, ±0.004, ±0.006, ±0.008, ±0.010 a.u. The sign of electric field is taken to be positive in the direction from the electron-donating to the electron-attracting group. Thus, for the fields along the C–NO_2 or N–NO_2 bond axes, the positive direction means from the C or N atom to the NO_2 group, and for those parallel to the N–O bonds the positive direction denotes from the N to O atom. It is worth mentioning that the strong external fields imposed are likely to exceed the dielectric strengths of materials in application, and cause their breakdown.

3 Results and Discussion

The fields parallel to the C–NO_2, N–NO_2 and N–O bond axes affect the structures and properties considerably more than the fields perpendicular to the –NO_2 plane. Thus, in this paper emphasis will be placed on the geometric and property changes accompanying fields parallel to the C–NO_2, N–NO_2 and N–O bond axes. The calculated geometrical parameters and properties as well as their change trends at two levels of theory are almost in agreement with each other.

3.1 Structure and AIM analysis

Table 1 summarizes the selected geometric parameters and AIM results of TNT calculated using the M06-2x method with the 6-311++G** and aug-cc-pVTZ basis sets. There are two kinds of N–NO_2 groups in RDX: one is in the equatorial position and the other is in the axial position of the RDX ring. The geometrical parameters and AIM results of RDX in the field orientations involving the N–NO_2 groups in the equatorial and axial positions are shown in Tables 2 and 3, respectively.

At two levels of theory, the fields in the positive direction along the C–NO_2 and N–NO_2 bond axis shorten the N−N and C−H bonds and lengthen the N−O bonds, while those in the negative direction do the opposite. The fields in the positive direction parallel to the N–O bond axis shorten the N−N bonds and lengthen the C−N bonds, and lengthen one of the N−O bonds while shorten the other N−O bonds. The C–NO_2 distances are elongated in the fields of the negative direction along the C–NO_2 bond axes but they do not show unambiguous trends with the changes of field strengths in the positive direction, which is in accordance with the previous investigations[11] for CH_3NO_2.

For TNT, the changes of the C−NO_2 and C−H bond lengths compared with those in no field are less than those of the N−O bond, and in RDX the changes of the N−N bond lengths are larger than those of the N−O and N−H distances. The C−NO_2 bond length in TNT is little affected by even the strong electric fields, as evidenced by the fact that the change is only 0.0011 Å in the field of +0.010 a.u. parallel to the N–O bond axis at the M06-2x/aug-cc-pVTZ level, while the corresponding change of the N−O bond length is up to 0.0076 Å. The change of the N−O bond length is about seven times larger than that of the C−NO_2 bond length, as can also be seen from in the fields parallel to the C–NO_2 bond axes in the positive direction. For RDX,

Table 1 — Optimized geometrical parameters and AIM results of TNT in the different field orientations at the M06-2x/6-311++G** (in blank) and M06-2x/aug-cc-pVTZ (in bold) levels

Field [a]	$R_{C1–N2}$ (Å)	$R_{N2–O3}$ (Å)	$R_{C2–H6}$ (Å)	$\rho_{C1–N2}$ (a.u.)	$\rho_{N2–O3}$ (a.u.)	$\rho_{C2–H6}$ (a.u.)
No field	1.4827	1.2228	1.0882	0.2528	0.4910	0.2839
	1.4829	1.2202	1.0863	0.2555	0.5063	0.2955
-0.0100 (C–N)	1.4840	1.2196	1.0891	0.2519	0.4942	0.2829
	1.4855	1.2160	1.0876	0.2542	0.5103	0.2943
-0.0080 (C–N)	1.4838	1.2202	1.0889	0.2521	0.4936	0.2832
	1.4847	1.2178	1.0873	0.2547	0.5096	0.2946
-0.0060 (C–N)	1.4835	1.2210	1.0888	0.2525	0.4931	0.2833
	1.4840	1.2185	1.0872	0.2550	0.5086	0.2947
-0.0040 (C–N)	1.4830	1.2216	1.0887	0.2527	0.4924	0.2834
	1.4838	1.2190	1.0871	0.2550	0.5078	0.2950
-0.0020 (C–N)	1.4828	1.2222	1.0886	0.2527	0.4916	0.2835
	1.4833	1.2196	1.0869	0.2551	0.5072	0.2951
+0.0020 (C–N)	1.4829	1.2235	1.0882	0.2528	0.4904	0.2839
	1.4835	1.2209	1.0864	0.2552	0.5055	0.2952
+0.0040 (C–N)	1.4832	1.2243	1.0881	0.2529	0.4894	0.2838
	1.4838	1.2215	1.0862	0.2550	0.5048	0.2951
+0.0060 (C–N)	1.4836	1.2249	1.0881	0.2529	0.4883	0.2837
	1.4842	1.2222	1.0862	0.2548	0.5040	0.2951
+0.0080 (C–N)	1.4835	1.2255	1.0880	0.2528	0.4872	0.2837
	1.4838	1.2226	1.0861	0.2545	0.5032	0.2950
+0.0100 (C–N)	1.4832	1.2262	1.0879	0.2527	0.4862	0.2837
	1.4836	1.2233	1.0860	0.2542	0.5020	0.2951
+0.0100 (N–O)	1.4836	1.2126	1.0878	0.2523	0.5041	0.2805
	1.4840	1.2278	1.0896	0.2547	0.5167	0.2973
+0.0080 (N–O)	1.4833	1.2142	1.0876	0.2525	0.5020	0.2812
	1.4837	1.2256	1.0891	0.2549	0.5159	0.2967
+0.0060 (N–O)	1.4830	1.2166	1.0877	0.2526	0.4990	0.2815
	1.4835	1.2243	1.0887	0.2551	0.5135	0.2969
+0.0040 (N–O)	1.4828	1.2182	1.0879	0.2527	0.4960	0.2836
	1.4832	1.2236	1.0868	0.2556	0.5107	0.2972
+0.0020 (N–O)	1.4827	1.2210	1.0880	0.2528	0.4940	0.2837
	1.4831	1.2217	1.0865	0.2555	0.5091	0.2950
-0.0020 (N–O)	1.4826	1.2242	1.0882	0.2529	0.4893	0.2839
	1.4828	1.2225	1.0861	0.2552	0.5032	0.2955
-0.0040 (N–O)	1.4821	1.2263	1.0883	0.2530	0.4861	0.2818
	1.4826	1.2246	1.0860	0.2552	0.5002	0.2947
-0.0060 (N–O)	1.4815	1.2293	1.0888	0.2531	0.4843	0.2792
	1.4820	1.2267	1.0858	0.2556	0.4963	0.2928
-0.0080 (N–O)	1.4813	1.2325	1.0893	0.2532	0.4800	0.2789
	1.4815	1.2291	1.0856	0.2557	0.4922	0.2916
-0.0100 (N–O)	1.4810	1.2458	1.0896	0.2528	0.4785	0.2772
	1.4809	1.2315	1.0854	0.2556	0.4867	0.2910

[a] C–N and N–O mean the field directions parallel to the C–N and N–O bond axes, respectively.

the field of +0.010 a.u. along the N–NO_2 bond axis of the equatorial position causes the N–NO_2 to be shortened by 0.0343 Å; while N−O or C−H is only changed by 0.0094 or 0.0025 Å at the M06-2x/aug-cc-pVTZ level. These results show that the fields oriented parallel to the C–NO_2 and N–O bond axes have a minor effect on the C–NO_2 or C–H bond length but a major effect on the N–O bond length in TNT, while in RDX the external fields greatly affect the N–NO_2 bond length but the N–O or N–H bond is slightly affected.

There are six linear correlations between the changes of the N−O bond length ($\Delta R_{N–O}$) and field strengths (E) with the linear correlation coefficients equal to the range of 0.9879 – 0.9993 along the different field orientations at two levels of theory. Two good linear correlations between the changes of the N−N bond length ($\Delta R_{N–N}$) and field strengths (E) are also observed with the linear correlation coefficient of 0.9975 and 0.9974, respectively (Fig. 2). These results show that the external electric field has an important

Table 2 — The optimized geometrical parameters and AIM results of RDX in the field orientations parallel to the N–N and N–O bond axes of the N–NO$_2$ group in the equatorial position at the M06-2x/6-311++G** (in blank) and M06-2x/aug-cc-pVTZ (in bold) levels

Field [a]	R_{N1-N2} (Å)	R_{N2-O3} (Å)	R_{C1-H4} (Å)	ρ_{N1-N2} (a.u.)	ρ_{N2-O3} (a.u.)	ρ_{C1-H4} (a.u.)
No field	1.3762	1.2278	1.0936	0.3668	0.4528	0.2956
	1.3745	1.2251	1.0911	0.3759	0.4755	0.3152
-0.0100 (N–N)	1.4105	1.2202	1.0969	0.3408	0.4611	0.2962
	1.4102	1.2181	1.0932	0.3512	0.4832	0.3153
-0.0080 (N–N)	1.4034	1.2219	1.0963	0.3459	0.4594	0.2959
	1.4061	1.2200	1.0925	0.3587	0.4807	0.3154
-0.0060 (N–N)	1.3957	1.2236	1.0957	0.3513	0.4573	0.2958
	1.3953	1.2213	1.0920	0.3602	0.4799	0.3153
-0.0040 (N–N)	1.3899	1.2247	1.0943	0.3569	0.4558	0.2956
	1.3885	1.2223	1.0916	0.3668	0.4789	0.3153
-0.0020 (N–N)	1.3822	1.2262	1.0941	0.3613	0.4545	0.2955
	1.3812	1.2236	1.0915	0.3706	0.4777	0.3152
+0.0020 (N–N)	1.3703	1.2278	1.0935	0.3713	0.4511	0.2954
	1.3672	1.2268	1.0906	0.3803	0.4738	0.3151
+0.0040 (N–N)	1.3682	1.2279	1.0932	0.3751	0.4490	0.2953
	1.3590	1.2285	1.0901	0.3862	0.4711	0.3150
+0.0060 (N–N)	1.3593	1.2282	1.0928	0.3802	0.4468	0.2952
	1.3501	1.2301	1.0896	0.3903	0.4702	0.3149
+0.0080 (N–N)	1.3500	1.2283	1.0923	0.3873	0.4453	0.2950
	1.3451	1.2325	1.0892	0.3978	0.4672	0.3147
+0.0100 (N–N)	1.3998	1.2292	1.0919	0.3902	0.4440	0.2948
	1.3392	1.2345	1.0886	0.4011	0.4650	0.3143
-0.0100 (N–O)	1.3917	1.2156	1.0927	0.3534	0.4710	0.2966
	1.3989	1.2295	1.0907	0.3621	0.4899	0.3166
-0.0080 (N–O)	1.3892	1.2175	1.0930	0.3573	0.4643	0.2965
	1.3920	1.2287	1.0908	0.3653	0.4872	0.3162
-0.0060 (N–O)	1.3857	1.2202	1.0932	0.3593	0.4613	0.2963
	1.3875	1.2272	1.0908	0.3683	0.4832	0.3159
-0.0040 (N–O)	1.3822	1.2229	1.0934	0.3621	0.4587	0.2962
	1.3800	1.2268	1.0910	0.3731	0.4792	0.3157
-0.0020 (N–O)	1.3781	1.2261	1.0935	0.3635	0.4559	0.2958
	1.3762	1.2264	1.0911	0.3744	0.4787	0.3154
+0.0020 (N–O)	1.3739	1.2302	1.0940	0.3685	0.4500	0.2952
	1.3721	1.2238	1.0913	0.3782	0.4718	0.3147
+0.0040 (N–O)	1.3693	1.2325	1.0943	0.3703	0.4456	0.2950
	1.3683	1.2227	1.0915	0.3805	0.4689	0.3145
+0.0060 (N–O)	1.3640	1.2358	1.0947	0.3725	0.4420	0.2948
	1.3623	1.2220	1.0919	0.3828	0.4657	0.3140
+0.0080 (N–O)	1.3593	1.2375	1.0951	0.3743	0.4362	0.2940
	1.3602	1.2209	1.0920	0.3857	0.4612	0.3137
+0.0100 (N–O)	1.3532	1.2387	1.0955	0.3766	0.4303	0.2938
	1.3583	1.2193	1.0923	0.3886	0.4589	0.3133

[a] N–N and N–O mean the field directions parallel to the N–N and N–O bond axes, respectively.

effect on the strength of the N−O bond in TNT and the N−N bond of RDX.

The AIM results show that, at two levels of theory, as the external electric field becomes stronger in the positive direction along the C–NO$_2$ or N–NO$_2$ bond, there is an increase in the values of $\rho_{(N–N)}$, while decrease in $\rho_{(N–O)}$ (Tables 1−3). Fields in the negative direction correspondingly show the opposite trends. The values of $\rho_{(C–N)}$ decrease in the negative C–NO$_2$ bond axis direction while they do not show unambiguous trends with the changes of the field strengths in the positive direction.

The changes of the $\rho_{(C–N)}$ values in comparison with those in the absence of field are very small in TNT, even if the external field is up to ±0.010 a.u. along the C–NO$_2$ or N–O bond axis. However, the changes of $\rho_{(N–O)}$ are marked, especially in the external fields parallel to the N–O bond axis. According to the AIM theory of Bader, the larger the change of electron density ρ at bond critical point, the more notable the

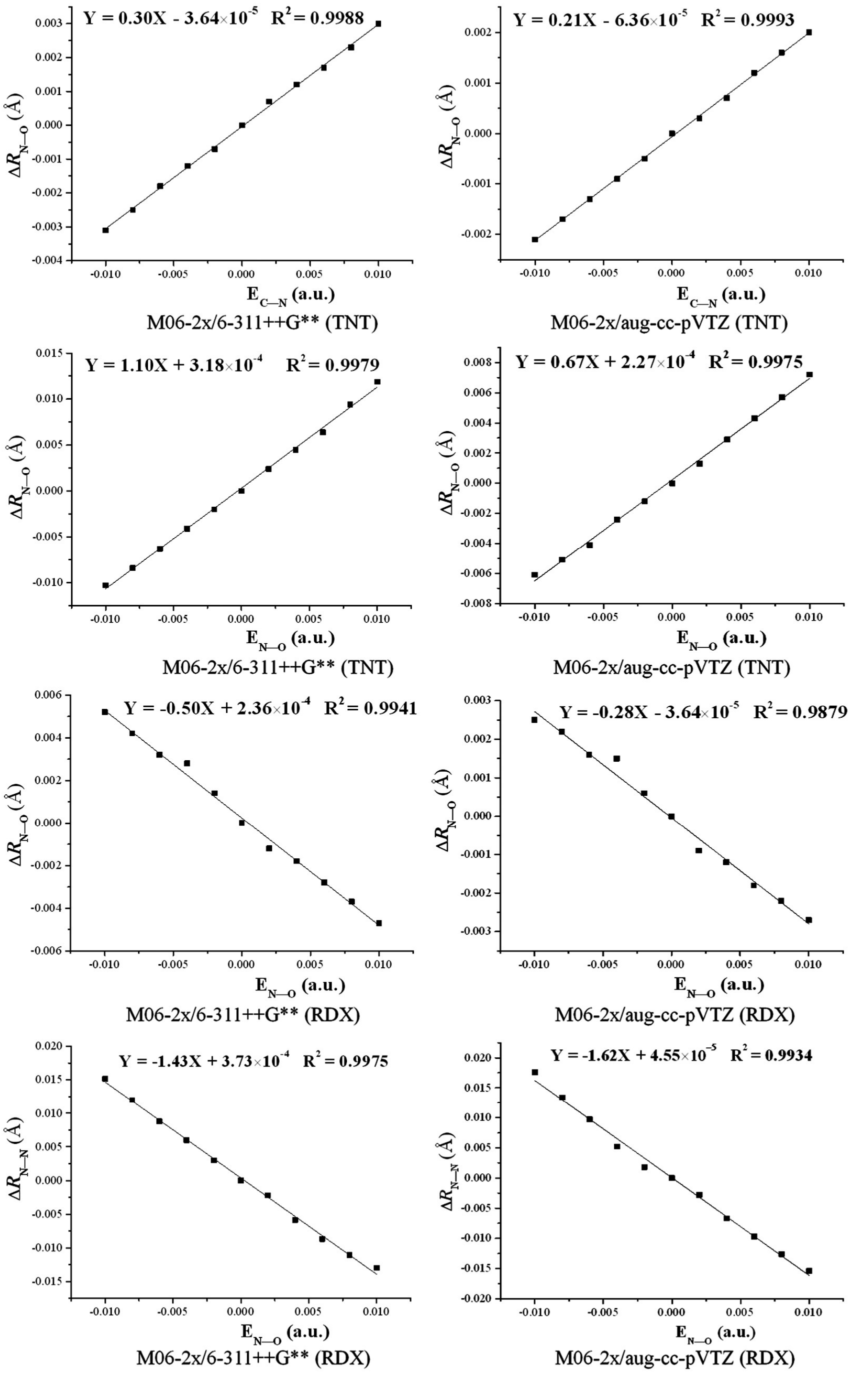


Fig. 2 — The changes of the N−O or N−N bond lengths ($\Delta R_{\text{N-O}}$ or $\Delta R_{\text{N-N}}$) versus field strengths in the different field orientations ($E_{\text{C-N}}$ and $E_{\text{N-O}}$) at the different levels of theory for TNT and RDX ($E_{\text{C-N}}$ or $E_{\text{N-O}}$ means the field direction parallel to the C–N or N–O bond axis).

change of bond strength becomes[30]. This explains the fact that the changes of the C−N bond length are far lower than those of the N–O bond length in the presence of external electric fields. The reverse occurs for RDX; the change of $\rho_{(\text{N-N})}$ is far larger than that of $\rho_{(\text{N-O})}$. For example, the change of $\rho_{(\text{N-N})}$ reaches 0.0234 a.u. in the field of +0.010 a.u. along the N–NO_2 bond axis in the equatorial position at the M06-2x/6-311++G** level, while that of $\rho_{(\text{O-N})}$ is only 0.0088 a.u. Thus, the change of the N−N bond length is greater than that of the N–O bond length. Except for the $\rho_{(\text{C-H})}$ values at the M06-2x/aug-cc-pVTZ level, the changes of the $\rho_{(\text{C/N-H})}$ values are all slight.

Table 3 — The optimized geometrical parameters and AIM results of RDX in the field orientations parallel to the N–N and N–O bond axes of the N–NO_2 group in the axial position at the M06-2x/6-311++G** (in blank) and M06-2x/aug-cc-pVTZ (in bold) levels

Field [a]	$R_{N1'–N2'}$ (Å)	$R_{N2'–O3'}$ (Å)	$R_{C1'–H4'}$ (Å)	$\rho_{N1'–N2'}$ (a.u.)	$\rho_{N2'–O3'}$ (a.u.)	$\rho_{C1'–H4'}$ (a.u.)
No field	1.3774	1.2283	1.0939	0.3672	0.4531	0.2960
	1.3756	1.2254	1.0912	0.3773	0.4762	0.3153
-0.0100 (N–N)	1.4118	1.2207	1.0971	0.3420	0.4618	0.2963
	1.4115	1.2186	1.0931	0.3526	0.4834	0.3158
-0.0080 (N–N)	1.4046	1.2222	1.0962	0.3477	0.4598	0.2940
	1.4075	1.2204	1.0923	0.3601	0.4811	0.3157
-0.0060 (N–N)	1.3968	1.2239	1.0956	0.3527	0.4575	0.2956
	1.3913	1.2217	1.0922	0.3618	0.4796	0.3155
-0.0040 (N–N)	1.3909	1.2253	1.0945	0.3573	0.4559	0.2959
	1.3894	1.2229	1.0917	0.3682	0.4793	0.3157
-0.0020 (N–N)	1.3835	1.2268	1.0942	0.3629	0.4548	0.2962
	1.3820	1.2242	1.0916	0.3722	0.4779	0.3156
+0.0020 (N–N)	1.3715	1.2283	1.0933	0.3727	0.4517	0.2960
	1.3684	1.2273	1.0907	0.3819	0.4740	0.3153
+0.0040 (N–N)	1.3693	1.2284	1.0934	0.3766	0.4493	0.2961
	1.3603	1.2289	1.0905	0.3876	0.4718	0.3147
+0.0060 (N–N)	1.3605	1.2286	1.0927	0.3818	0.4477	0.2956
	1.3513	1.2307	1.0895	0.3919	0.4710	0.3152
+0.0080 (N–N)	1.3515	1.2288	1.0924	0.3888	0.4457	0.2953
	1.3463	1.2332	1.0893	0.3994	0.4679	0.3148
+0.0100 (N–N)	1.4007	1.2291	1.0922	0.3916	0.4536	0.2951
	1.3403	1.2351	1.0886	0.4027	0.4658	0.3140
-0.0100 (N–O)	1.3928	1.2162	1.0928	0.3548	0.4725	0.2968
	1.3999	1.2302	1.0908	0.3636	0.4887	0.3167
-0.0080 (N–O)	1.3905	1.2181	1.0932	0.3589	0.4642	0.2963
	1.3933	1.2293	1.0907	0.3668	0.4876	0.3166
-0.0060 (N–O)	1.3868	1.2208	1.0934	0.3607	0.4618	0.2966
	1.3888	1.2279	1.0911	0.3699	0.4835	0.3157
-0.0040 (N–O)	1.3835	1.2233	1.0933	0.3637	0.4590	0.2967
	1.3813	1.2272	1.0912	0.3746	0.4786	0.3155
-0.0020 (N–O)	1.3793	1.2266	1.0932	0.3651	0.4551	0.2953
	1.3775	1.2268	1.0913	0.3750	0.4788	0.3152
+0.0020 (N–O)	1.3753	1.2308	1.0942	0.3698	0.4512	0.2951
	1.3735	1.2243	1.0916	0.3797	0.4716	0.3150
+0.0040 (N–O)	1.3706	1.2331	1.0942	0.3719	0.4457	0.2952
	1.3696	1.2233	1.0917	0.3822	0.4692	0.3140
+0.0060 (N–O)	1.3653	1.2362	1.0943	0.3738	0.4426	0.2951
	1.3636	1.2225	1.0922	0.3842	0.4669	0.3139
+0.0080 (N–O)	1.3606	1.2381	1.0955	0.3757	0.4368	0.2953
	1.3615	1.2213	1.0923	0.3880	0.4621	0.3138
+0.0100 (N–O)	1.3545	1.2392	1.0952	0.3782	0.4315	0.2936
	1.3593	1.2199	1.0926	0.3903	0.4613	0.3127

[a] N–N and N–O mean the field directions parallel to the N–N and N–O bond axes, respectively.

There are six linear correlations between the changes of the $\rho_{(N–O)}$ values ($\Delta\rho_{(N–O)}$) and field strengths (E) with the linear correlation coefficients equal to the range of 0.9956 – 0.9989 along the different field orientations at two levels of theory. Two linear correlations between the changes of $\rho_{(N–N)}$ ($\Delta\rho_{(N–N)}$) and field strengths (E) are also found with the good linear correlation coefficients (R^2 = 0.9947 and 0.9981) (Fig. 3).

In general, the notable changes in bond length and electron density might lead to the remarkable changes of bond strength, even companied by the breaking of chemical bond. For TNT, the more notable elongate of the N–O bond than that of the C–NO_2 bond implies that, in the presence of certain external electric field of the positive direction along the C–NO_2 or N–O bond axis, oxygen may transfer from the nitro to the methyl group or rearrangement of the NO_2 moiety to ONO followed by O–NO homolysis will be a thermodynamically more favorable pathway than the C–NO_2 homolysis pathway in the initial stage of decomposition. As mentioned above, it has been shown

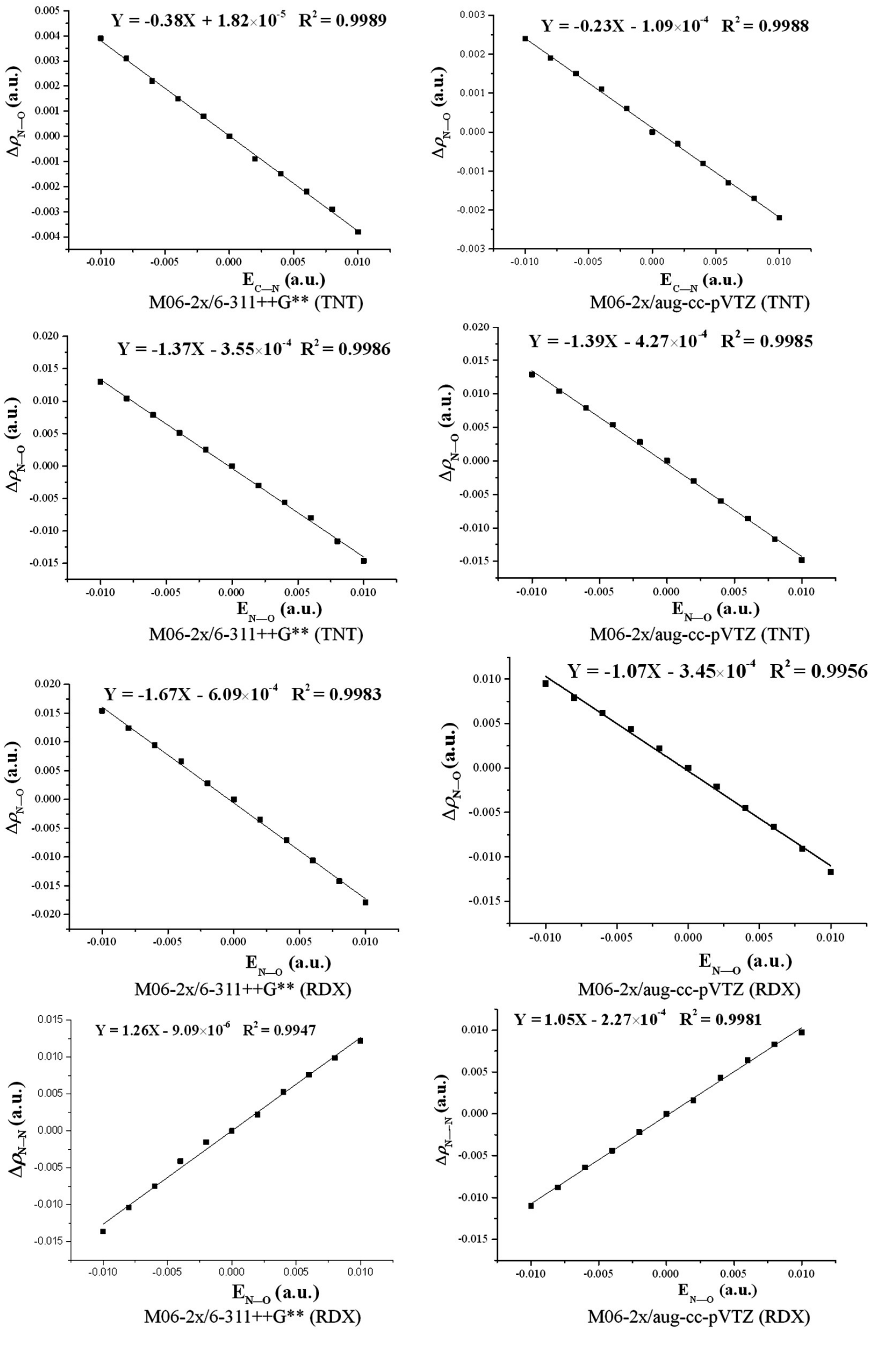


Fig. 3 — The changes of the $\rho_{(N\text{–}O)}$ or $\rho_{(N\text{–}N)}$ values ($\Delta\rho_{(N\text{–}O)}$ or $\Delta\rho_{(N\text{–}N)}$) versus field strengths in the different field orientations ($E_{C\text{–}N}$ or $E_{N\text{–}O}$) at the different levels of theory for TNT and RDX.

from the literature[17], rearrangement of the NO_2 moiety to ONO occurred more easily than the breaking of the C–NO_2 bond at high temperatures. In this case, the N–O bond might be the trigger bond in the presence of electric field. However for RDX, on one hand, the bond dissociation energy of the N−O bond in nitro group is far larger than that of the N−N bond[31], and the N–NO_2 bond is more easily ruptured than the N–O bond in the absence of a field; on the other hand, the changes of the bond length and electron density of the N–NO_2 bond are larger than those of the N–H or N–O bond in the presence of electric fields. Thus, the N–NO_2 bond might be always the real trigger bond. As mentioned above, the strong external fields imposed are likely to exceed the dielectric strengths of materials, and cause their breakdown. In this case, oxygen transfer from the nitro to the methyl group or rearrangement of the NO_2 moiety to ONO for TNT and breaking of the N–NO_2 bond of RDX may not be the mechanism for initiating detonations, and consequently the N–O and N–NO_2 bonds are not the trigger linkages.

As mentioned above, for TNT, as the external electric field becomes stronger in the negative direction along the C–NO_2 bond axis, there will be an increase of the N−O bond strength; for RDX, with the increasing external electric field strengths in the positive direction along the N–NO_2 or N–O bond axis, the N−N bond strength will also be strengthened. In these cases, the bond dissociation energies of the trigger linkages N–O or N–N bonds are enhanced, and the breaking of them becomes difficult in detonation initiation in comparison with those in no external electric field. Thus, the explosive sensitivities are reduced and the stabilities are increased in the presence of external electric fields in the negative direction along the C–NO_2 bond axis for TNT and in the positive direction along the N–NO_2 or N–O bond axis for RDX. The opposite trends, the explosive sensitivities being increased and the stabilities being reduced, can be suggested in the fields of the positive direction along the C–NO_2 bond axis for TNT and those in the negative direction along the N–NO_2 or N–O bond axis of RDX. In these cases, the energy molecules may be more unstable in the presence of external electric fields. Therefore, a conclusion can be drawn that the change of the directions and strengths of external electric fields can change the explosive sensitivities, and the introduction of external electric field into energetic material will be an available way to adjust explosive sensitivity. Furthermore, the introduction of external electric field into energetic material can reduce the stabilities of explosives, and thus enhance the degradation rate of explosive waste-water by using the technique of electro-hydraulic discharge. This is the origin of the treatment for explosive-waste-water by using the technique of electro-hydraulic discharge.

It is worth mentioning that the bond distances of the C–NO_2, N–NO_2, N–O, and C–H bonds of –CH_2 and –CH_3 moieties are in the ranges of 1.4809~1.4855 Å, 1.3392~1.4115 Å, 1.2160~1.2351 Å, and 1.0854~1.0932 Å in the considered external electric fields at the M06-2x/aug-cc-pVTZ level, respectively, which fall into the common accepted values for the corresponding bond lengths. In other words, these bonds do not happen rupture. Consequently, the bond dissociation energies of the C–NO_2, N–NO_2, N–O, and C–H bonds are in the ranges of 275.28~288.69 kJ/mol, 180.10~213.67 kJ/mol, 301.37~338.55 kJ/mol, and 402.28~46266 kJ/mol at the M06-2x/aug-cc-pVTZ level, respectively, which fall into the accepted values of the corresponding bond dissociation energies. The large bond dissociation energies suggest that it is still difficult to be broken in the given external electric fields. These results confirm stability of various structures in external electric field.

3.2 Frequency analysis

According to Politzer *et al.*[13], the changes in the trigger linkage frequency might enhance or inhibit the vibrational excitation that is thought to precede its rupture in detonation initiation. In order to further clarify the stability of TNT and RDX in external electric field, the harmonic frequency analysis was carried out. It should be noted that, for the harmonic approximation, there is often a significant difference between the experimental and calculated frequencies, and the calculated results are more qualitative than quantitative. In external electric fields, except for the C–NO_2, N–NO_2, N–O, and C–H bonds, the vibrational modes of other bonds are also affected. However, as mentioned above, these four bonds are “trigger linkages”, the breaking of which is a key factor in detonation initiation. Therefore, only the vibrational modes of these four bonds are considered in this work.

From Table 4, at two levels of theory, for TNT, the external electric fields in the negative direction along the C–NO_2 and N−O bond axes increase greatly the asymmetrical/symmetrical stretching vibration frequencies υ of the N−O bond, while those in the positive direction do the opposite. The significant changes of υ suggest a notable enhancive or inhibitive vibrational excitation. Thus, the oxygen transfer from the nitro to the methyl group or rearrangement of the NO_2 moiety to ONO will occur easily in detonation initiation under the influence of the external electric fields. However, the influence of the fields on the vibration frequency of the C−N bond can be negligible. For example, the change of υ is no more than 4.0 cm^{-1} by even the strongest fields (for example, +0.010 a.u. along the C–NO_2 bond axes) at the M06-2x/aug-cc-pVTZ level. The frequency shifts of the N−O bond are much greater than those of the C−N bond, leading to the possible more significant change of the vibrational excitation in the N−O bond than that in the C−N bond. Thereby, the rupture of the C−N bond might not be influenced by the external electric fields, and the oxygen transfer from the nitro to the methyl group or rearrangement of the NO_2 moiety to ONO might play

Table 4 — Vibration frequencies in TNT and RDX in the different field orientations at the M06-2x/6-311++G(2d,p) (in blank) and M06-2x/aug-cc-pVTZ (in bold) levels

Field [a]	$\upsilon_{\text{C–N}}$ (cm^{-1})	$\upsilon_{\text{N–O}}$ (TNT) (cm^{-1})	$\upsilon^{b}_{\text{C–H}}$ (cm^{-1})	$\upsilon^{c}_{\text{C–H}}$ (cm^{-1})	$\upsilon^{d}_{\text{C–H}}$ (cm^{-1})	$\upsilon_{\text{N–N}}$ (cm^{-1})	$\upsilon_{\text{N–O}}$ (RDX) (cm^{-1})	$\upsilon^{e}_{\text{C–H}}$ (cm^{-1})	$\upsilon^{f}_{\text{C–H}}$ (cm^{-1})
No field	907.5	1587.2	3127.4	3150.6	3197.6	1314.2	1591.5	3053.3	31173
	909.2	1590.5	3131.6	3153.8	3203.5	1313.5	1594.2	3055.3	3119.8
-0.0100	903.6	1604.2	3117.8	3136.2	3182.9	1295.1	1627.6	3033.8	3090.6
(C/N–N)	903.5	1612.2	3124.2	3146.5	3193.6	1313.0	1305.2	3035.5	3100.3
-0.0080	904.8	1601.2	3119.9	3143.3	3185.3	1300.0	1618.8	3039.6	3096.9
(C/N–N)	905.3	1607.3	3125.0	3147.1	3195.8	1314.1	1626.8	3041.3	3103.2
-0.0060	905.3	1599.2	3123.2	3147.7	3192.8	1312.3	1611.7	3044.2	3100.2
(C/N–N)	906.4	1602.8	3127.4	3148.0	3196.9	1313.9	1617.5	3047.7	3108.6
-0.0040	906.1	1594.2	3124.0	3148.0	3194.5	1314.8	1607.5	3049.5	3106.7
(C/N–N)	907.8	1598.6	3129.3	3149.4	3198.6	1313.8	1610.3	3051.8	3111.7
-0.0020	907.0	1590.5	3125.5	3149.5	3195.7	1313.7	1598.1	3050.2	3110.8
(C/N–N)	908.5	1595.1	3130.8	3150.9	3199.3	1313.6	1602.6	3053.6	3114.7
+0.0020	907.2	1583.0	3127.1	3150.6	3198.1	1317.6	1586.0	3055.0	3122.1
(C/N–N)	909.1	1586.4	3130.3	3153.6	3203.4	1314.0	1584.1	3058.5	3123.3
+0.0040	907.2	1580.1	3127.5	3150.8	3200.2	1321.8	1580.4	3058.7	3128.6
(C/N–N)	910.0	1582.0	3130.7	3152.2	3204.1	1315.4	1578.8	3061.3	3128.8
+0.0060	906.8	1575.3	3127.5	3151.0	3202.8	1325.2	1576.8	3060.5	3133.9
(C/N–N)	909.0	1578.9	3129.2	3151.5	3205.8	1316.0	1566.7	3063.2	3137.1
+0.0080	906.1	1571.7	3127.6	3151.7	3204.3	1331.5	1572.6	3063.2	3139.5
(C/N–N)	908.2	1575.1	3130.3	3150.0	3206.6	1318.3	1556.5	3068.3	3142.3
+0.0100	907.3	1566.5	3127.9	3152.1	3206.9	1334.0	1563.3	3067.6	3143.4
(C/N–N)	908.6	1570.3	3130.5	3148.3	3203.2	1320.8	1542.0	3071.5	3159.9
-0.0100 (N–O)	906.5	1599.0	3120.8	3146.0	3191.5	1302.3	1610.2	3039.8	3102.2
	902.7	1609.7	3130.0	3147.1	3194.7	1306.2	1618.4	3039.2	3102.2
-0.0080 (N–O)	906.2	1596.1	3122.2	3147.6	3193.8	1305.5	1604.0	3042.0	3107.6
	904.0	1604.2	3130.2	3149.9	3197.3	1308.6	1615.5	3045.6	3106.8
-0.0060 (N–O)	906.8	1593.8	3125.1	3148.5	3194.6	1307.4	1598.4	3048.5	3109.1
	906.3	1600.8	3130.8	3150.6	3198.2	1310.3	1607.6	3049.3	3110.5
-0.0040 (N–O)	907.0	1590.9	3125.5	3149.2	3195.4	1310.6	1595.2	3050.6	3110.7
	907.6	1595.0	3131.3	3151.2	3198.6	1312.2	1601.3	3053.2	3114.6
-0.0020 (N–O)	907.4	1588.7	3126.3	3149.8	3195.5	1312.8	1592.3	3052.3	3113.6
	908.5	1593.9	3131.5	3152.3	3199.3	1313.0	1595.8	3055.7	3118.9
+0.0020 (N–O)	907.5	1585.3	3127.0	3150.2	3196.0	1314.5	1587.9	3053.8	3117.5
	909.3	1589.7	3131.2	3153.7	3203.4	1313.7	1591.7	3055.7	3120.0
+0.0040 (N–O)	907.8	1583.6	3126.2	3149.1	3197.7	1315.3	1585.7	3054.0	3118.7
	910.8	1588.3	3131.7	3150.5	3203.6	1313.9	1586.1	3056.3	3123.6
+0.0060 (N–O)	908.6	1581.5	3126.5	3149.5	3197.5	1316.6	1582.2	3053.7	3120.5
	911.5	1585.2	3132.1	3148.2	3203.9	1314.6	1582.3	3054.5	3126.2
+0.0080 (N–O)	909.1	1580.2	3125.6	3148.1	3198.8	1318.0	1578.6	3054.9	3123.4
	912.0	1584.6	3132.6	3145.6	3204.2	1315.3	1580.5	3054.6	3128.3
+0.0100 (N–O)	908.0	1578.3	3123.1	3147.0	3199.2	1319.9	1573.6	3055.2	3127.0
	913.3	1583.0	3133.0	3141.0	3205.0	1317.5	1578.6	3053.1	3131.5

[a] C/N–N and N–O mean the field directions parallel to the C/N–N and N–O bond axes, respectively. For RDX, the field orientations are parallel to the N–N and N–O bond axes of the N–NO_2 group in the equatorial position.

[b] Symmetrical stretching vibration frequencies of three C–H (TNT).

[c] Asymmetrical stretching vibration frequencies of three C–H (TNT).

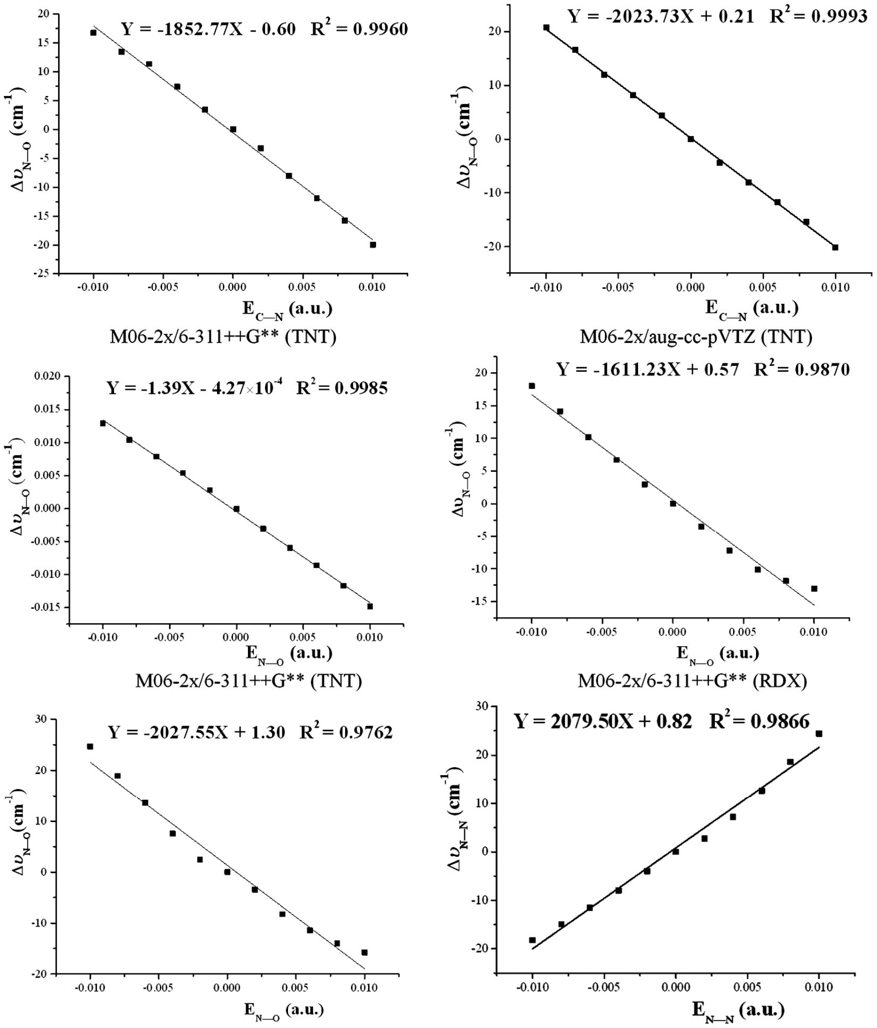
[d] Asymmetrical stretching vibration frequencies of two C–H bond (TNT).

[e] Symmetrical stretching vibration frequencies of two C–H bonds (RDX).

[f] Asymmetrical stretching vibration frequencies of two C–H bonds (RDX).

an important role in the decomposition process when an electric field is imposed. Thus, the N−O bond might become the trigger linkage of TNT in the external electric fields, as is in accordance with the result from the structure.

For RDX, at two levels of theory, the changes of the stretching vibration frequencies υ of the N−N bond are near to those of the N−O bond in the external electric fields. However, as mentioned above, the bond dissociation energy of the N−O bond in nitro group is



M06-2x/6-311++G** (TNT) M06-2x/aug-cc-pVTZ (TNT)

M06-2x/6-311++G** (TNT) M06-2x/6-311++G** (RDX)

M06-2x/aug-cc-pVTZ (RDX) M06-2x/6-311++G** (RDX)

Fig. 4 — The changes of the stretching vibration frequencies of the N−O or N−N bonds ($\Delta\upsilon_{\text{N-O}}$ or $\Delta\upsilon_{\text{N-N}}$) versus field strengths in the different field orientations ($E_{\text{C-N}}$, $E_{\text{N-O}}$ or $E_{\text{N-N}}$) at the different levels of theory for TNT and RDX ($E_{\text{N-N}}$ means the field direction parallel to the N–NO_2 bond axis).

far larger than that of the N−N bond[31]. Thus, the N−N bond will rupture more easily than the N−O bond in detonation initiation in external electric fields.

Five good (R^2 = 0.9762−0.9993) linear correlations between the changes of the stretching vibration frequencies of the N−O bond ($\Delta\upsilon_{\text{N-O}}$) and field strengths ($E$) are observed along the different field orientations at the different levels of theory (Fig. 4). One strong (R^2 = 0.9866) linear correlations between the changes of the stretching vibration frequencies of the N−N bond ($\Delta\upsilon_{\text{N-N}}$) and field strengths ($E$) are also shown in Fig. 4. These results show again that the external electric field has an important effect on the N−O bond of TNT and N−N bond in RDX.

For RDX, the frequency shifts of two C−H bonds are smaller than those of the N−N bond at the M06-2x/aug-cc-pVTZ level level. For TNT, the frequency shifts of three C−H bonds are small with no more than 11.0 cm^{-1}. These results also suggest that the frequency shifts of the C−H bonds are little affected by the external electric fields.

4 Conclusions

A comparison of the effect of external electric field on the C–NO_2 or N–NO_2 bonds with the C–H and N–O bonds in TNT or RDX was carried out using the M06-2x method. The result shows that for TNT the fields have a minor effect on the C–NO_2 and C–H bonds but a major effect on the N–O bonds, while in RDX the fields greatly affect the N–NO_2 bond but the N–O and C–H bonds are slightly affected. Thus, in TNT oxygen transfer from the nitro to the methyl group or rearrangement of the NO_2 moiety to ONO might be prior to the breaking of the C–NO_2 bond in the initial stage of decomposition, and the N–O bond can be the trigger bond in electric fields. In RDX, however, the N–NO_2 bond rupture may be preferential in electric field and consequently the N–NO_2 bond might be always the trigger bond. The explosive sensitivities may be reduced and the stabilities may be increased in the presence of external electric fields in the negative direction along the C–NO_2 bond axis for TNT and in the positive direction along the N–NO_2 or N–O bond axis for RDX. The opposite trends can be suggested in the fields of the opposite directions along above bond axes. The change of the directions and strengths of external electric fields can change the explosive sensitivities, and the introduction of external electric field into energetic material will be an available way to adjust explosive sensitivity. Twenty-two good linear correlations were found along the different field orientations, including those between the field strengths and the changes of N−O/N−N bond lengths, $\rho_{(N-O/N-N)}$ values, or stretching frequencies of the N−O/N−N bonds. This investigation can help us to understand the initiation mechanism of energetic materials in the presence of external electric fields. It must be very useful for safe using of explosives, avoiding the catastrophic explosion in external electric fields and enhance the degradation rate of explosive waste-water by using the technique of electro-hydraulic discharge.

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