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Thermodynamical stability of CH_3ONO and CH_3ONO^- : A coupled-cluster and Hartree–Fock-density-functional-theory study

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The structure and thermodynamic stability of methylnitrite and its anion are studied by the infinite-order coupled-cluster method with all singles and doubles and noniterative inclusion of triple excitations [CCSD(T)] and Hartree–Fock-density-functional theory (HFDFT). We have optimized the geometries and computed the harmonic vibrational frequencies of major fragments, H_2 , CH , NH , OH , CN , N_2 , CO , NO , O_2 , CH_2 , NH_2 , H_2O , HCN , HNC , HCO , HNO , O_2H , CO_2 , NO_2 , CH_3 , NH_3 , CNH_2 , HCO_2 , HNO_2 , CH_3N , CH_3O , CH_3NO , CH_3ON , CH_2NO_2 , and their anions, when the latter exist. Fragmentation energies obtained at both levels of theory are rather close to each other, except for channels involving CN as a product. The CH_3ONO^- and CH_3NO_2^- anions are shown to possess lower fragmentation energies than their neutral parents. This implies that the attachment of an extra electron to CH_3NO_2 or CH_3ONO may have a crucial role in initiating the decomposition of these compounds. Also, the attachment of an extra electron to CH_3NO_2 or CH_3ONO leads to the appearance of new exothermic decay channels of the anions. © 1999 American Institute of Physics. [S0021-9606(99)30801-1]

I. INTRODUCTION

Nitromethane is the simplest prototype of monopropellants and explosives and has been the subject of numerous experimental and theoretical investigations (see, e.g., Refs. 1 and 2 and references therein). Its isomer, methylnitrite, has been found³ to be responsible for a low-energy dissociation channel

However, reaction path (1) is competitive with the direct decomposition through the basic channel

due to a high barrier to isomerization in reaction (1). The barrier height appears to be close to the dissociation energy corresponding to reaction (2) according to experimental observations³ and results of *ab initio* studies.^{4,5}

Formation of negative ions is believed^{6,7} to be rate controlling in the detonation of liquid nitromethane. Gas-phase nitromethane was shown^{8,9} to form both dipole-bound and conventional (valence) anionic states upon attachment of an extra electron. A dipole-bound state of CH_3NO_2^- can be produced via attachment of a low-energy electron to the ground-state nitromethane and then this state may transform^{8,9} to the ground state of the nitromethane anion, which should possess lower decomposition energies. On the other hand, it might be anticipated that the nitromethane anion will have a lower

barrier to transformation to the methylnitrite anion, which would produce methylnitrite upon detachment of an extra electron.

The aim of the present work is to evaluate decomposition energies through different decay channels of methylnitrite and its anion with the infinite-order coupled-cluster method with all singles and doubles and noniterative inclusion of triple excitations [CCSD(T)] and the Hartree–Fock-density-functional-theory (HFDFT) approach using the 6-311++G(2d,2p) basis set, which has been applied in our previous calculations⁹ on nitromethane and nitromethane anion as well. Thus, one would know also the thermodynamic stability of nitromethane and its anion estimated at the same levels of theory.

II. COMPUTATIONAL DETAILS

The calculations have been performed with the ACES II suite of programs¹⁰ at the CCSD(T)^{11,12} and HFDFT^{13–16} levels of theory using the 6-311++G(2d,2p) basis set¹⁷ ([12s6p2d/5s4p2d] for C, N, O, and [6s2p/4s2p] for H). Harmonic vibrational frequencies of heavier species are computed at the MBPT(2)/6-311++G(2d,2p) level of theory. The optimizations were carried out until the root-mean-square (RMS) gradients fell below the threshold value of $0.1E-3$ a.u.

Generally, the HFDFT approach is computationally faster and its results are less dependent upon inclusion in the basis set of functions with higher angular momentum, which are required to recover the correlation energy in coupled-cluster methods. When performing the HFDFT calculations we have used the hybrid B3LYP exchange-correlation potential^{18,19} defined as

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FIG. 1. Equilibrium geometrical configurations of heavier fragments of CH_3ONO and CH_3ONO^- .

$$V_{\text{xc}} = (1-A)*E_x^{\text{Slater}} + A*E_x^{\text{HF}} + B*E_x^{\text{Becke}} + C*E_c^{\text{LYP}} + (1-C)*E_c^{\text{VWN}}, \quad (3)$$

where E_x^{Slater} is the classical Slater exchange,²⁰ E_x^{HF} is the HF exchange, E_x^{Becke} is a gradient correction to the exchange introduced by Becke,²¹ E_c^{LYP} is the Lee–Yang–Parr correlation potential,²² E_c^{VWN} is the Vosko–Wilk–Nusair correlation potential,²³ and A , B , and C are the constants obtained when fitting the theoretical results to the experimental heats of formation.¹⁸ Even within a Kohn–Sham approach, the partial inclusion of the HF exchange permits some self-interaction correction.

The adiabatic electron affinity (A_{ad}) of a molecular system is defined as the difference in the ground-state total energies of the system and its anion. Within the Born–Oppenheimer (BO) approximation, one may evaluate the A_{ad} as

$$A_{\text{ad}} = E_{\text{tot}}(N, R_e) + Z_N - E_{\text{tot}}(A, R_e^-) - Z_A = \Delta E_{\text{el}} + \Delta E_{\text{nuc}}, \quad (4)$$

where R_e and R_e^- denote the equilibrium geometrical configurations of the neutral molecule and the anion, respectively. The zero-point vibrational energies (Z) are estimated within the harmonic approximation.

Fragmentation energies are calculated as the differences in the total energies of fragments F_i formed in a particular decay channel and the total energy of an initial compound M corrected for the corresponding Z s

$$D_0(M) = \sum_i [E_{\text{tot}}(F_i) + Z_{F_i}] - E_{\text{tot}}(M) - Z_M = D_e(M) + \Delta Z_{\text{nuc}}. \quad (5)$$

TABLE I. Results of our calculations for diatomic species and their anions performed at the CCSD(T)/6-311++G(2d,2p) and HFDF/T/6-311++G(2d,2p) levels together with experimental data. Total energies are in hartrees, bond lengths are in Å, and vibrational frequencies are in cm^{-1} .^a

Species	CCSD(T)			HFDF/T		
	R_e	ω_e	E_{tot}	R_e	ω_e	E_{tot} (B3LYP)
H_2	0.7421	4413	-1.170 865	0.7452	4381	-1.172 545
Exp.	0.7414	4401	...	0.7414	4401	...
CH	1.1191	2839	-38.419 455	1.1267	2784	-38.465 475
Exp.	1.1199	2829	...	1.1199	2829	...
CH^-	1.1373	2593	-38.457 546	1.1356	2592	-38.509 264
NH	1.0368	3271	-55.145 915	1.0442	3232	-55.207 726
Exp.	1.0362	3282	...	1.0362	3282	...
NH^-	1.0397	3175	-55.144 545	1.0465	3122	-55.217 427
OH	0.9695	3748	-75.635 869	0.9806	3646	-75.724 429
Exp.	0.9697	3738	...	0.9697	3738	...
OH^-	0.9626	3763	-75.690 781	0.9710	3684	-75.783 862
CN	1.1729	2116	-92.577 623	1.1230	2804	-92.657 661
Exp.	1.1718	2068	...	1.1718	2068	...
CN^-	1.1831	2050	-92.716 317	1.1778	2077	-92.827 098
N_2	1.1029	2329	-109.380 021	1.0989	2365	-109.498 742
Exp.	1.0977	2359	...	1.0977	2359	...
CO	1.1340	2158	-113.160 786	1.1304	2181	-113.237 286
Exp.	1.1281	2170	...	1.1281	2170	...
NO	1.1541	2083	-129.714 851	1.1361	3072	-129.861 103
Exp.	1.1508	1904	...	1.1508	1904	...
NO^-	1.2759	1366	-129.709 253	1.2647	1427	-129.865 916
O_2	1.2168	1563	-150.120 937	1.2208	1559	-150.295 696
Exp.	1.2070	1580	...	1.2070	1580	...
O_2^-	1.3608	1107	-150.127 392	1.3612	1130	-150.310 979

^aExperimental data from Ref. 28.

III. RESULTS AND DISCUSSIONS

A. Geometrical configurations

In order to estimate fragmentation energies of CH_3ONO and CH_3ONO^- , we performed geometry optimizations and harmonic vibrational frequency calculations on the following species and their anions when the latter exist. Diatomics are H_2 , CH , NH , OH , CN , N_2 , CO , NO , and O_2 ; triatomics are CH_2 , NH_2 , H_2O , HCN , HNC , HCO , HNO , O_2H , CO_2 , and NO_2 ; tetra-atoms are CH_3 , NH_3 , CNH_2 , HCO_2 , and HNO_2 ; penta-atoms and hexa-atoms are CH_3N , CH_3O , CH_3NO , CH_3ON , and CH_2NO_2 . The neutral species have been the subject of an enormous amount of computations and we recalculated them in order to have the results at the same levels of theory which should be used in estimating fragmentation energies and adiabatic electron affinities. The equilibrium configurations of heavier species are presented in Fig. 1. Detailed discussions on the structures of “difficult” CH_3N (NHCH_2) and CH_2NO_2 can be found in Refs. 24 and 25 and Refs. 26 and 27, respectively.

Table I compares the results of our computations to experimental data²⁸ for the diatomics in order to get an insight into the accuracy to be expected at the CCSD(T)/6-311++G(2d,2p) and HFDF/T/6-311++G(2d,2p) levels. Generally, agreement is rather good, except for CN computed at the HFDF/T level. Tables II and III present our results for triatomics and tetra-atoms and their anions, and Table IV contains the total energies and Z s

TABLE II. Results of our calculations for triatomic species and their anions performed at the CCSD(T) and HFDFDFT levels with the $6-311++G(2d,2p)$ basis. Total energies are in hartrees, bond lengths are in Å, bond angles are in degree, and Zs are in kcal/mol.

Species	CCSD(T)			HFDFDFT		
	Geometry	Z	E_{tot}	Geometry	Z	E_{tot} (B3LYP)
CH_2 , 3B_2	$R(\text{C-H})=1.0763$ $\angle \text{HCH}^\circ=133.49$	10.88	-39.085 769	$R(\text{C-H})=1.0788$ $\angle \text{HCH}^\circ=136.30$	10.23	-39.132 985
CH_2^- , 2B_2	$R(\text{C-H})=1.1212$ $\angle \text{HCH}^\circ=102.31$	9.74	-39.099 081	$R(\text{C-H})=1.1244$ $\angle \text{HCH}^\circ=102.62$	9.61	-39.154 938
NH_2 , 2B_2	$R(\text{N-H})=1.0242$ $\angle \text{HNN}^\circ=102.90$	12.03	-55.796 160	$R(\text{N-H})=1.0321$ $\angle \text{HNN}^\circ=102.41$	11.73	-55.864 358
NH_2^- , 1A_1	$R(\text{N-H})=1.0271$ $\angle \text{HNN}^\circ=101.63$	11.72	-55.812 740	$R(\text{N-H})=1.0330$ $\angle \text{HNN}^\circ=102.41$	11.45	-55.884 828
H_2O , 1A_1	$R(\text{O-H})=0.9575$ $\angle \text{HOH}^\circ=104.33$	13.58	-76.329 639	$R(\text{O-H})=0.9673$ $\angle \text{HOH}^\circ=102.54$	13.12	-76.329 639
HCN , $^1\Sigma^+$	$R(\text{H-C})=1.0651$ $R(\text{C-N})=1.1588$	9.95	-93.285 048	$R(\text{H-C})=1.0682$ $R(\text{C-N})=1.1527$	10.14	-93.392 608
HNC , $^1\Sigma^+$	$R(\text{H-N})=0.9952$ $R(\text{C-N})=1.1743$	9.54	-93.260 990	$R(\text{H-N})=1.0008$ $R(\text{C-N})=1.1695$	9.47	-93.370 039
HCO , $^2A'$	$R(\text{C-H})=1.1186$ $R(\text{C-O})=1.1815$ $\angle \text{HCO}^\circ=124.32$	8.14	-113.687 752	$R(\text{C-H})=1.1295$ $R(\text{C-O})=1.1761$ $\angle \text{HCO}^\circ=123.07$	7.96	-113.822 240
HCO^- , $^1A'$	$R(\text{C-H})=1.2246$ $R(\text{C-O})=1.2420$ $\angle \text{HCO}^\circ=109.68$	6.29	-113.690 096	$R(\text{C-H})=1.2579$ $R(\text{C-O})=1.2289$ $\angle \text{HCO}^\circ=110.21$	5.97	-113.830 029
HNO , $^1A'$	$R(\text{N-H})=1.0512$ $R(\text{N-O})=1.2178$ $\angle \text{HNO}^\circ=108.05$	8.69	-130.295 482	$R(\text{N-H})=1.0646$ $R(\text{N-O})=1.2123$ $\angle \text{HNO}^\circ=108.37$	8.56	-130.443 193
HNO^- , $^2A''$	$R(\text{N-H})=1.0459$ $R(\text{N-O})=1.3449$ $\angle \text{HNO}^\circ=105.57$	7.78	-130.299 350	$R(\text{N-H})=1.0555$ $R(\text{N-O})=1.3413$ $\angle \text{HNO}^\circ=105.88$	7.77	-130.460 339
O_2H , $^2A''$	$R(\text{O-H})=0.9693$ $R(\text{O-O})=1.3418$ $\angle \text{OOH}^\circ=104.08$	8.93	-150.703 912	$R(\text{O-H})=0.9807$ $R(\text{O-O})=1.3238$ $\angle \text{HNO}^\circ=105.35$	8.75	-150.876 349
O_2H^- , $^1A'$	$R(\text{O-H})=0.9574$ $R(\text{O-O})=1.5402$ $\angle \text{OOH}^\circ=96.98$	8.13	-150.734 293	$R(\text{O-H})=0.9670$ $R(\text{O-O})=1.5191$ $\angle \text{OOH}^\circ=98.80$	8.20	-150.913 374
CO_2 , $^1\Sigma_g^+$	$R(\text{C-O})=1.1654$ $\angle \text{OCO}^\circ=180.0$	7.21	-188.324 975	$R(\text{C-O})=1.1655$ $\angle \text{OCO}^\circ=180.0$	7.20	-188.542 052
CO_2^- , 2A_1	$R(\text{C-O})=1.2364$ $\angle \text{OCO}^\circ=137.35$	5.15	-188.297 106	$R(\text{C-O})=1.2355$ $\angle \text{OCO}^\circ=137.29$	4.90	-188.520 668
NO_2 , 2A_1	$R(\text{N-O})=1.2025$ $\angle \text{ONO}^\circ=134.16$	5.57	-204.792 618	$R(\text{N-O})=1.2011$ $\angle \text{ONO}^\circ=133.44$	6.85	-205.027 644
NO_2^- , 1A_1	$R(\text{N-O})=1.2670$ $\angle \text{ONO}^\circ=116.55$	4.76	-204.868 845	$R(\text{N-O})=1.2665$ $\angle \text{ONO}^\circ=116.32$	4.90	-205.108 012

of heavier fragments required for calculations of fragmentation energies.

Table V displays the results of our computations for *cis* and *trans* conformations of CH_3ONO , which are compared to experimental geometries²⁹ and fundamentals,³⁰ as well as for two conformations of CH_3ONO^- . Both *cis* and *trans* conformations correspond to stationary states of CH_3ONO and CH_3ONO^- , whereas configurations obtained from them by π rotations around the C–N axis (see Fig. 2) are transition states and have one imaginary frequency each. The *trans* and *cis* conformations of both CH_3ONO and CH_3ONO^- differ in total energy by ≈ 1 kcal/mol only. The transition states are higher in total energy by several kcal/mol, in agreement with a theoretical result³¹ stating that the barrier height for the CH_3ONO isomerization equals 9.8 kcal/mol and experimental data (10 kcal/mol).²⁹ On the whole, the results of our computations for CH_3ONO are in rather good agreement

with both experimental data^{29,30} and previous theoretical results.^{4,5}

B. Adiabatic electron affinities

Since there are a lot of experimental data³² on the A_{ad} of fragments entering CH_3ONO , it is interesting to compare the ability of the CCSD(T) and HFDFDFT levels in reproducing the A_{ad} s when using the same moderate-sized basis, such as $6-311++G(2d,2p)$. Let us start with atomic electronic affinities presented in Table VI. Both CCSD(T) and HFDFDFT methods indicate the nonexistence of a stable nitrogen anion, in correspondence with the experiment.³³ However, while the HFDFDFT(B3LYP) approach reproduces all experimental values rather well, the CCSD(T) method underestimates the oxygen electron attachment (EA) by 0.4 eV. This can be attributed to the relative insensitivity of density functional

TABLE III. Results of calculations for tetra-atomic species and their anions performed at the CCSD(T)/6-311++G(2d,2p) and HFDFT/6-311++G(2d,2p) levels. Total energies are in hartrees, bond lengths are in Å, bond angles are in degree, and Zs are in kcal/mol.

Species	CCSD(T)			HFDFT		
	Geometry	Z	E_{tot}	Geometry	Z	E_{tot} (B3LYP)
CH ₃ , $^2A''$	$R(\text{C-H})=1.0768$ $\angle \text{ZCH}_{1,2,3}^\circ=90.0$	18.69	-39.766 397	$R(\text{C-H})=1.0809$ $\angle \text{ZCH}_{1,2,3}^\circ=90.0$	18.45	-39.819 105
CH ₃ ⁻ , 1A_1	$R(\text{C-H})=1.1016$ $\angle \text{ZCH}_{1,2,3}^\circ=110.44$	17.9	-39.760 117	$R(\text{C-H})=1.1024$ $\angle \text{ZCH}_{1,2,3}^\circ=109.04$	17.51	-39.816 672
NH ₃ , $^2A''$	$R(\text{N-H})=1.0108$ $\angle \text{ZNH}_{1,2,3}^\circ=112.02$	21.76	-56.474 293	$R(\text{N-H})=1.0183$ $\angle \text{ZNH}_{1,2,3}^\circ=111.74$	20.96	-56.542 955
CNH ₂ , 2A_1	$R(\text{C-N})=1.2996$ $R(\text{N-H})=1.0160$ $\angle \text{CNH}^\circ=122.64$	16.71	-93.784 491	$R(\text{C-N})=1.2921$ $R(\text{N-H})=1.0257$ $\angle \text{CNH}^\circ=122.90$	16.33	-93.899 648
NCH ₂ , 2A_1	$R(\text{C-N})=1.2517$ $R(\text{C-H})=1.0932$ $\angle \text{NCH}^\circ=121.07$	15.84	-93.831 964	$R(\text{C-N})=1.2124$ $R(\text{C-H})=1.1009$ $\angle \text{NCH}^\circ=121.47$	16.34	-93.939 187
NCH ₂ ⁻ , 1A_1	$R(\text{C-N})=1.2536$ $R(\text{C-H})=1.1417$ $\angle \text{NCH}^\circ=125.72$	14.25	-93.841 301	$R(\text{C-N})=1.2399$ $R(\text{C-H})=1.1554$ $\angle \text{NCH}^\circ=126.24$	13.79	-93.960 009
HCO ₂ , 2A_1	$R(\text{C-H})=1.1573$ $R(\text{C-O})=1.2292$ $\angle \text{HCO}^\circ=107.80$	9.62	-188.807 401	$R(\text{C-H})=1.1535$ $R(\text{C-O})=1.2282$ $\angle \text{HCO}^\circ=107.96$	190.66	-189.031 587
HCO ₂ ⁻ , 1A_1	$R(\text{C-H})=1.1285$ $R(\text{C-O})=1.2569$ $\angle \text{HCO}^\circ=114.87$	12.57	-188.934 947	$R(\text{C-H})=1.1389$ $R(\text{C-O})=1.2577$ $\angle \text{HCO}^\circ=114.78$	12.28	-189.159 845
HNO ₂ , 1A_1	$R(\text{N-H})=1.0313$ $R(\text{N-O})=1.2251$ $\angle \text{HNO}^\circ=115.90$ $\angle \text{ONHO}^\circ=180.0$	13.71	-205.412 175	$R(\text{N-H})=1.0436$ $R(\text{N-O})=1.2258$ $\angle \text{HNO}^\circ=115.98$ $\angle \text{ONHO}^\circ=180.0$	13.63	-205.648 745
HNO ₂ ⁻ , $^2A'$	$R(\text{N-H})=1.0235$ $R(\text{N-O})=1.3177$ $\angle \text{HNO}^\circ=112.71$ $\angle \text{ONHO}^\circ=145.75$	12.44	-205.413 001	$R(\text{N-H})=1.0353$ $R(\text{N-O})=1.3164$ $\angle \text{HNO}^\circ=112.23$ $\angle \text{ONHO}^\circ=143.16$	11.82	-205.659 770

theory (DFT)-based approaches to augmentations of *spd* basis sets by functions with higher angular momentum l ,³⁴ whereas the convergence of the correlation energy in coupled-cluster methods is proportional to $1/L^4$,^{35,36} where L is the maximum angular momentum of spherical harmonics in a given basis. In particular, harmonics up to $L=5$ are required in order to reach 0.03 eV accuracy in the computed atomic EA values.³⁷

Tables VII and VIII compare our A_{ad} s computed at both levels of theory to experimental data³². Note that all the A_{ad} s obtained at the different levels from HF to CCSD(T) are computed at the geometries optimized at the CCSD(T) level and the ΔZ corrections are obtained from harmonic vibrational frequency calculations performed also at the CCSD(T) level. The HFDFT A_{ad} s are obtained at the geometries optimized with the BLYP exchange-correlation functional. Generally, the HFDFT approach provides A_{ad} s which are somewhat closer to experimental data than the CCSD(T) method does, except for CN, where HFDFT fails seriously. This was also found previously³⁸ when using larger basis sets in conjunction with different exchange-correlation functionals.

The A_{ad} of CH₃ONO is somewhat higher than that of CH₃NO₂ computed at the same levels of theory. Since the HFDFT A_{ad} of CH₃NO₂ is very close⁹ to the experimental

value of 0.26 ± 0.08 eV,⁸ the HFDFT value of 0.60 eV could be recommended as the A_{ad} of CH₃ONO. Contrary to CH₃NO₂, CH₃ONO has a relatively small dipole moment of 2.2 D, which seems not to be sufficient to sustain a dipole-bound state of CH₃ONO⁻, because extensive investigations for organic compounds have shown^{39,40} that the critical value of the dipole moment required to sustain a dipole-bound state is 2.5–2.7 D.

TABLE IV. Results of our calculations for heavier species and their anions performed at the CCSD(T)/6-311++G(2d,2p) and HFDFT/6-311++G(2d,2p) levels. Total energies are in hartrees and Zs are in kcal/mol.

Species	CCSD(T)		HFDFT	
	E_{tot}	Z	E_{tot} (B3LYP)	Z
CH ₃ N (C_s , $^1A'$)	-94.479 902	25.32	-94.594 186	24.64
CH ₃ O (C_s , $^2A'$)	-114.876 179	23.22	-115.015 096	20.67
CH ₃ O ⁻ (C_{3v} , 1A_1)	-114.923 677	22.27	-115.066 624	21.52
CH ₃ NO (C_s , $^1A'$)	-169.545 047	29.35	-169.742 293	26.49
CH ₃ NO ⁻ (C_s , $^2A''$)	-169.544 190	27.68	-169.751 449	25.34
CH ₃ ON (C_s , $^1A'$)	-169.466 480	27.40	-169.662 577	26.13
CH ₂ NO ₂ (C_{2v} , 2B_2)	-243.990 115	22.87	-244.275 308	...
CH ₂ NO ₂ ⁻ (C_{2v} , 1A_1)	-244.074 974	22.74	-244.367 268	28.92

TABLE V. Results of calculations for CH_3ONO ($C_s, {}^1A'$) and CH_3ONO^- ($C_s, {}^2A''$) at the CCSD(T)/6-311++G(2d,2p) level. Frequencies are computed at the MBPT(2)/6-311++G(2d,2p) level. Raman intensities are in brackets. Total energies are in hartrees, bond lengths are in Å, angles are in degrees, vibrational frequencies are in cm^{-1} , Zs are in kcal/mol, and dipole moments (μ) are in Debye.

Property	CH_3ONO				CH_3ONO^-	
	<i>Cis</i>	Exp. ^a	<i>Trans</i>	Exp. ^a	<i>Trans</i>	<i>Cis</i>
$R(\text{C}-\text{O})$	1.4369	1.436	1.4379	1.436	1.3693	1.3765
$R(\text{C}-\text{H}_1)$	1.0800	1.089	1.0875	1.09	1.1135	1.1098
$R(\text{C}-\text{H}_{2,3})$	1.0848	1.094	1.0862	1.09	1.1104	1.1097
$\angle \text{OCH}_1^\circ$	104.44	102.6	109.62	109.5	111.43	111.55
$\angle \text{OCH}_{2,3}^\circ$	110.67	110.4	108.52	109.5	113.56	113.47
$R(\text{O}-\text{N})$	1.4011	1.418	1.4323	1.415	1.9549	1.9206
$\angle \text{CON}^\circ$	114.09	114.5	109.33	109.9	107.14	102.12
$R(\text{N}-\text{O})$	1.1933	1.181	1.1772	1.164	1.2096	1.2048
$\angle \text{ONO}^\circ$	114.41	114.5	111.05	111.8	109.52	110.25
$\angle \text{H}_1\text{COH}_{2,3}^\circ$	119.34	120.7	120.16	120.0	119.21	119.40
$\omega(a')$	359[1]	377	372[14]	340	297[0.3]	236[29]
$\omega(a')$	653[213]	623	562[160]	567	345[76]	285[35]
$\omega(a')$	852[91]	836	812[408]	812	551[16]	545[103]
$\omega(a')$	1024[133]	991	1071[61]	1048	1124[106]	1115[157]
$\omega(a')$	1197[1]	1171	1210[31]	1208	1188[2]	1178[5]
$\omega(a')$	1467[8]	1411	1485[5]	1423	1495[46]	1470[9]
$\omega(a')$	1519[6]	1460	1539[7]	1460	1511[23]	1511[7]
$\omega(a')$	1557[118]	1620	1620[162]	1678	1983[2379]	1852[266]
$\omega(a')$	3103[14]	2957	3101[37]	2943	2818[429]	2877[237]
$\omega(a')$	3241[4]	3040	3203[7]	3040	2876[116]	2892[366]
$\omega(a'')$	220[0.2]	186	100[1]	...	136[2]	77[3]
$\omega(a'')$	369[2]	249	227[1]	213	216[1]	138[1]
$\omega(a'')$	1177[1]	1140	1187[1]	1156	1177[0.1]	1175[0.1]
$\omega(a'')$	1507[10]	1446	1515[5]	1446	1493[3]	1490[3]
$\omega(a'')$	3190[14]	3000	3204[14]	3000	2870[285]	2876[272]
Z	30.65	30.73	29.03	29.22	28.71	28.19
μ	2.23	...	1.82	...	2.37	1.23
$\langle 2S+1 \rangle$	1.0	...	1.0	...	2.006	2.005
HF	-243.740 560	...	-243.739 119	...	-243.735 353	-243.736 517
MBPT(2)	-244.608 205	...	-244.606 224	...	-244.615 548	-244.612 814
CCSD	-244.618 050	...	-244.616 627	...	-244.624 544	-244.622 951
CCSD+T	-244.659 647	...	-244.658 071	...	-244.669 051	-244.666 721
CCSD(T)	-244.656 520	...	-244.654 913	...	-244.664 978	-244.662 703
B3LYP	-244.935 245	...	-244.934 505	...	-244.953 093	-244.952 290

^aExperimental geometries and frequencies are from Refs. 29 and 30, respectively.

As a matter of fact, we have computed the binding energy of a dipole-bound electron to be 0.05 meV (0.47 cm^{-1}) using the recently developed electron-attachment equation-of-motion coupled cluster (EA-EOMCC) method⁴¹ and the

6-311++G(2d,2p) basis augmented by seven diffuse *sp* shells in the same manner as was done before⁹ for CH_3NO_2 .

C. Fragmentation energies

Fragmentation energies of the ground-state CH_3ONO and CH_3ONO^- species, presented in Tables IX and X, re-

FIG. 2. Stationary configurations of CH_3ONO and CH_3ONO^- .

TABLE VI. Total energies (in hartrees) of the H, C, N, O atoms and their anions calculated with the 6-311++G(2d,2p) basis. Electron affinities are in eV.

Species	CCSD(T)	B3LYP	EA _{CCSD(T)}	EA _{B3LYP}	Exp. ^a
H	-0.499 818	-0.498 499	0.676	0.773	0.754
H ⁻	-0.519 726	-0.526 899	...	...	...
C	-37.792 982	-37.832 963	1.104	1.221	1.263
C ⁻	-37.833 535	-37.877 834	...	...	...
N	-54.523 227	-54.572 287	-0.607	-0.122	≤0
N ⁻	-54.500 887	-54.567 803	...	...	...
O	-74.973 873	-75.055 601	1.057	1.426	1.461
O ⁻	-75.012 704	-75.108 020	...	...	...

^aSee Ref. 33.

TABLE VII. Adiabatic electron affinities (in eV) calculated with the 6-311++G(2d,2p) basis. ΔZ s are calculated at the CCSD(T) level.

Level	CH	NH	OH	NO	O ₂	CN	HCO	HNO	CH ₂	NH ₂	O ₂ H	CO ₂	NO ₂	NCH ₂	HCO ₂	HNO ₂	CH ₃
HF	0.44	-1.51	-0.26	-0.28	-0.81	2.90	-0.78	-0.16	-0.97	-1.09	-0.53	-1.09	1.50	-1.30	3.07	0.14	-1.47
MBPT(2)	1.16	0.04	1.82	-0.11	0.17	4.76	0.06	0.13	0.34	0.68	1.12	-0.85	2.04	0.81	3.39	-0.17	-0.33
CCSD	1.00	-0.13	1.37	-0.09	0.15	3.76	0.09	0.17	0.32	0.34	0.76	-0.68	2.15	0.20	3.44	0.20	-0.24
CCSD+T	1.06	-0.02	1.52	-0.10	0.22	3.70	0.14	0.15	0.43	0.47	0.85	-0.66	2.10	0.32	3.44	0.08	-0.13
CCSD(T)	1.05	-0.02	1.50	-0.10	0.20	3.77	0.14	0.15	0.41	0.46	0.86	-0.67	2.11	0.32	3.34	0.08	-0.14
LDA	1.64	0.63	2.19	0.18	0.44	4.86	0.51	0.47	0.87	1.07	1.23	-0.53	2.23	1.14	3.34	0.08	-0.30
BLYP	1.20	0.38	1.73	0.10	0.46	4.64	0.29	0.44	0.72	0.65	1.14	-0.54	2.11	0.75	3.12	0.21	0.02
B3LYP	1.21	0.28	1.62	0.17	0.44	4.61	0.29	0.50	0.65	0.57	1.04	-0.49	2.22	0.64	3.36	0.36	-0.03
Exp.	1.24	0.38	1.83	0.02	0.44	3.82	0.30	0.34	0.65	0.78	1.08	-0.6	2.275	...	...	0.29	0.08

spectively, are calculated according to Eq. (5) with the ΔZ corrections obtained from CCSD(T) calculations. As is seen, there is rather good agreement between fragmentation energies obtained at the CCSD(T) and HFDFDFT levels, except for some channels involving CN as a product. This is apparently due to a poor description of the CN radical at the HFDFDFT level (see Tables I and VII). Therefore, the CCSD(T) results should be considered as more reliable in general. Our theoretical values compare well (within 5 kcal/mol accuracy) with experimental data,^{1,42-44} which are known for several decay channels of CH_3NO_2 and CH_3NO_2^- .

Table IX shows that the source of the high-energy density of CH_3ONO and CH_3NO_2 is due to their highly exothermic decomposition, into NH_3 and CO_2 . Note that ammonia and formic acid were found to be major products of the thermal decomposition of CH_3NO_2 .⁴⁵ Obviously, the direct decay $\text{CH}_3\text{NO}_2 \rightarrow \text{NH}_3 + \text{CO}_2$ requires three bonds to be ruptured, which energetically is highly unfavorable. Formic acid is a decay product through the next lowest bimolecular channel, $\text{NH}_2 + \text{HCO}_2$, which is twice as low in energy as the basic channel (1).

According to our results presented in Table X, the CH_3ONO^- anion has additional exothermic fragmentation channels with respect to those of its neutral parent. Especially interesting is the appearance of an exothermic channel $\text{CH}_3\text{ONO}^- \rightarrow \text{NH}_2 + \text{HCO}_2^-$, whose exothermicity is due to a rather large A_{ad} of HCO_2 (≈ 3.3 eV, see Table VII). Formally speaking, the HCO_2 radical belongs to the class of superhalogens⁴⁶⁻⁴⁸ of the general MX_2Y type. A relatively low electron affinity of HCO_2 with respect to MX_3 super-

halogens where X is a halogen atom⁴⁷ appears to be due to smaller electronegativities of H and O with respect to F or Cl.

Keeping in mind that formic acid was observed as a primary product of thermal decomposition of CH_3NO_2 , one might surmise that the formation of formic acid could be due to decomposition of CH_3NO_2^- through the channel $\text{NH}_2 + \text{HCO}_2^-$. Subsequent detachment of an extra electron from HCO_2^- and attachment of the electron to another CH_3NO_2 or CH_3ONO could initiate a chain reaction process.

The CH_3NO_2^- and CH_3ONO^- anions possess two other basic decay channels: to $\text{CH}_3\text{O}^- + \text{NO}$ and $\text{CH}_3 + \text{NO}_2^-$ which are lower in the energy than the corresponding decay channels of CH_3NO_2 and CH_3ONO to $\text{CH}_3\text{O} + \text{NO}$ and $\text{CH}_3 + \text{NO}_2$, respectively. On the whole, the fragmentation energy of a particular decay channel of CH_3NO_2^- and

TABLE IX. Fragmentation energies (in eV) of CH_3ONO computed at the CCSD(T)/6-311++G(2d,2p) and HFDFDFT/6-311++G(2d,2p) levels according to Eq. (5). Fragmentation energies of CH_3NO_2 are larger by 0.06 and smaller by 0.23 eV at the CCSD(T) and HFDFDFT levels, respectively. Experimental data are obtained for CH_3NO_2 .

Channel	CCSD(T)		B3LYP		Exp.
	D_e	D_0	D_e	D_0	
$\text{CH}_3\text{ONO} \rightarrow \text{NH}_3 + \text{CO}_2$	-3.97	-4.01	-4.12	-4.14	...
$\rightarrow \text{NH} + \text{CO}_2 + \text{H}_2$	0.32	-0.19	0.31	-0.15	...
$\rightarrow \text{CO} + \text{HNO} + \text{H}_2$	0.72	0.48	0.86	0.39	...
$\rightarrow \text{NH}_2 + \text{HCO}_2$	1.36	1.00	1.03	0.71	...
$\rightarrow \text{NHCH}_2 + \text{O}_2$	1.43	1.43	1.19	1.20	...
$\rightarrow \text{CH}_3\text{O} + \text{NO}$	1.70	1.54	1.57	1.46	1.68 ^a
$\rightarrow \text{HCN} + \text{H}_2\text{O} + \text{O}$	1.77	1.49	1.84	1.60	...
$\rightarrow \text{CH}_3 + \text{NO}_2$	2.57	2.33	2.37	2.22	2.5 ^b , 2.46 ^c
$\rightarrow \text{H}_2\text{O} + \text{OH} + \text{CN}$	3.00	2.54	3.22	3.06	...
$\rightarrow \text{HCO} + \text{H}_2\text{O} + \text{N}$	3.01	2.66	3.64	3.36	...
$\rightarrow \text{NCH}_2 + \text{O}_2\text{H}$	3.20	2.98	3.30	2.93	...
$\rightarrow \text{CH}_3\text{NO} + \text{O}$	3.66	3.64	3.71	3.60	...
$\rightarrow \text{CH}_2 + \text{HNO}_2$	4.23	4.00	4.14	3.92	...
$\rightarrow \text{CH}_3\text{NO}_2 + \text{H}$	4.45	4.15	4.35	4.05	...
$\rightarrow \text{HNO} + \text{HCO} + \text{H}$	4.64	4.07	4.62	4.09	3.89 ^c
$\rightarrow \text{H}_2\text{O} + \text{CH} + \text{NO}$	5.26	4.76	5.15	4.77	...
$\rightarrow \text{CH}_3\text{ON} + \text{O}$	5.80	5.69	5.87	5.81	...
$\rightarrow \text{CH}_2 + \text{OH} + \text{NO}$	5.91	5.44	5.86	5.41	...
$2\text{CH}_3\text{ONO} \rightarrow 2\text{CO} + \text{N}_2 + 2\text{H}_2\text{O} + \text{H}_2$	-6.08	-6.87	-5.71	-6.41	...
$2\text{NO} \rightarrow \text{N}_2 + \text{O}_2$	-1.98	-2.18	-1.99	-1.98	...

^aSee Ref. 42.

^bSee Ref. 43.

^cSee Ref. 1.

TABLE VIII. Electron affinities (in eV) calculated with the 6-311++G(2d,2p) basis. ΔZ s are calculated at the MBPT(2)/6-311++G(2d,2p) level.

Level	CH_3O	CH_3NO	CH_2NO_2	CH_3NO_2	CH_3ONO
HF	-0.32	-0.20	1.23	0.02	0.03
MBPT(2)	1.66	0.00	2.42	-0.25	0.27
CCSD	1.21	0.05	2.27	0.13	0.26
CCSD+T	1.35	0.05	2.31	0.05	0.33
CCSD(T)	1.33	0.03	2.32	0.03	0.30
LDA	2.03	0.28	2.86	0.01	0.59
BLYP	1.53	0.23	2.48	0.07	0.36
B3LYP	1.44	0.30	2.51	0.22	0.60
Exp.	1.57	...	2.48	0.27	...

TABLE X. Fragmentation energies (in eV) of CH_3ONO^- computed at the CCSD(T)/6-311++G(2d,2p) and HF/DFT/6-311++G(2d,2p) levels according to Eq. (5). Fragmentation energies of CH_3NO_2^- are smaller by 0.21 and larger by 0.02 eV at the CCSD(T) and HF/DFT levels, respectively.

Channel	CCSD(T)		B3LYP		
	D_e	D_0	D_e	D_0	
$\text{CH}_3\text{ONO}^- \rightarrow \text{NH}_3 + \text{CO}_2 + e$	-3.65	-3.64	-3.59	-3.64	...
$\rightarrow \text{NH}_3 + \text{CO}_2$	-2.90	-2.98	-3.01	-3.16	...
$\rightarrow \text{NH}_2 + \text{HCO}_2^-$	-1.80	-1.98	-1.94	-2.17	...
$\rightarrow \text{H}_2\text{O} + \text{OH}^- + \text{CN}^-$	-0.46	-0.76	-0.44	-0.79	...
$\rightarrow \text{CH}_3\text{O}^- + \text{NO}$	0.72	0.57	0.69	0.48	...
$\rightarrow \text{CH}_3 + \text{NO}_2^-$	0.81	0.58	0.71	0.41	0.56 ± 0.2^a
$\rightarrow \text{NH}_2^- + \text{HCO}_2$	1.22	0.91	1.00	0.64	...
$\rightarrow \text{H}_2\text{O} + \text{OH}^- + \text{CN}$	1.82	1.53	2.55	2.20	...
$\rightarrow \text{O}_2\text{H} + \text{H}_2 + \text{CN}^-$	2.01	1.55	2.10	1.61	...
$\rightarrow \text{CH}_2\text{NO}_2^- + \text{H}$	2.45	2.20	2.38	2.09	...
$\rightarrow \text{NCH}_2 + \text{O}_2\text{H}^-$	2.69	2.48	2.73	2.53	...
$\rightarrow \text{CH}_3\text{NO} + \text{O}^-$	2.92	2.95	2.79	2.67	...
$\rightarrow \text{NCH}_2^- + \text{O}_2\text{H}$	3.26	3.02	3.18	2.88	...
$\rightarrow \text{CH}_2^- + \text{HNO}_2$	4.18	3.95	4.07	3.80	...
$\rightarrow \text{CH}_2 + \text{HNO}_2^-$	4.52	4.29	4.36	4.05	...
$\rightarrow \text{CH}_2 + \text{OH}^- + \text{NO}$	4.72	4.18	4.77	4.30	...

^aSee Ref. 44.

CH_3ONO^- is lower than the fragmentation energy of the corresponding channel of their neutral parents by the A_{ad} of a decay fragment in the neutral channel, if the fragment possesses a positive A_{ad} . Since anions are generally more loosely bound than their neutral parents, the formation of CH_3NO_2^- or CH_3ONO^- would greatly facilitate initiating a decomposition reaction of nitromethane.

D. Geometrical transformations

Following McKee⁴ and Saxon and Yoshimine,⁵ who have considered transformations of nitromethane into methylnitrite, we can consider a transformation from CH_3NO_2^- to CH_3ONO^- . However, the anions have different ground-state symmetries $^2A'$ and $^2A''$, respectively. Therefore, such a transformation should be nonadiabatic and presumably proceed through a transition state of an appropriate symmetry. Optimized transition states of CH_3NO_2^- are displayed in Fig. 3. Optimizations as well as all other subsequent calculations are performed at the MBPT(2)/6-311++G(2d,2p) level. Note, that $^2A'$ transition configuration is similar to that of the ground state of CH_3NO_2^- and was obtained in optimizations starting with an initial configuration where the oxygens were

FIG. 3. Transition configurations of the CH_3NO_2^- anion.

FIG. 4. A transformation of CH_3ONO^- to a A'' transition configuration of CH_3NO_2^- .

tilted towards two hydrogens. This configuration is higher (than the ground-state) in total energy by 0.12 eV.

The barrier height to transformations of the ground-state CH_3ONO^- anion into the $^2A''$ transition configuration (see Fig. 3) was evaluated on the basis of calculations for intermediate configurations obtained via optimizing all geometrical parameters while keeping $R(\text{C}-\text{N})$ to be fixed and stepped by 0.2 Å. Fig. 4 shows that there is a rather high barrier for this transformation. The barrier height is approximately the same as that found previously for the transformation $\text{CH}_3\text{NO}_2 \rightarrow \text{CH}_3\text{ONO}$.^{4,5} Thus, this way of anion transformation appears not to be favorable.

We have considered another transformation path starting with the 2B_2 transition configuration and using the $R(\text{O}-\text{C})$ distance as a stepping parameter. Several steps of this transformation are shown in Fig. 5. The barrier height with respect to the CH_3ONO^- ground state decreases to about 2 eV and the barrier corresponds to equalizing the C-O and C-N bond lengths as in the preceding case. Thus, one cannot conclude from these two sets of calculations that the anion formation could greatly facilitate the transformation $\text{CH}_3\text{NO}_2 \rightarrow \text{CH}_3\text{ONO}$.

Because of controversial points of view^{3,49} on the existence of a barrier for the direct decomposition of ni-

FIG. 5. A transformation of a B_2 transition configuration of CH_3NO_2^- to CH_3ONO^- .

FIG. 6. Direct dissociation pathways $\text{CH}_3\text{NO}_2 \rightarrow \text{CH}_3 + \text{NO}_2$ and $\text{CH}_3\text{NO}_2^- \rightarrow \text{CH}_3 + \text{NO}_2^-$.

tromethane through channel (2), we performed a simulation of the decomposition of CH_3NO_2 and CH_3NO_2^- to $\text{CH}_3 + \text{NO}_2$ and $\text{CH}_3 + \text{NO}_2^-$, respectively. In both cases we started with the equilibrium configurations and kept stretching the C-N distance by 0.2 Å, while optimizing the rest of the geometrical parameters, to a C-N distance of 3.5 Å. The results of our simulation are presented in Fig. 6. Since a restricted Hartree-Fock (RHF)-based solution for CH_3NO_2 has the wrong dissociation limit, we have optimized also the triplet state of CH_3NO_2 (based on a unrestricted HF wave function) and found the total energies of the triplet and singlet states to cross at $R(\text{C-N}) \approx 2.5$ Å. At larger distances, one should use the total energy of the triplet state as corresponding to a proper dissociation to two doublet radicals.⁵⁰

We have not found any barrier for CH_3NO_2 when stretching the C-N bond length, in accord with experimental findings of Wodtke *et al.*³ The behavior of the anion is somewhat different. The anion preserves his NO_2 tilting shape up to $R(\text{C-N})=3.5$ Å, where the dissociation limit is practically achieved. However, the long-range Coulombic interaction still favors sharing an electron between a peripheral hydrogen and oxygens. Note that nitrogen has no positive electron affinity,³³ and the near-planar CH_3 itself cannot sustain an additional electron.⁵¹ We found a barrier of about 0.35 eV, which appears when the CH_3 group inverts through its planar configuration at $R(\text{C-N}) \approx 2.0$ Å. However, this barrier seems to be an artifact of the BO approximation, which has been found⁵² to be invalid for the cation dissociation $\text{CH}_3\text{NO}_2^+ \rightarrow \text{CH}_3\text{O}^+ + \text{NO}$, because the anion wave function at this separation has an appreciable spin contamination ($\langle 2S+1 \rangle = 2.16$) which is indicative of the appearance of some other close-lying states which, probably, correspond to decay channels $\text{CH}_2 + \text{HNO}_2^-$ or $\text{CH}_2^- + \text{HNO}_2$.

Nonadiabatic transformations in ions appear to be more common than in neutral systems. An example of such a nonadiabatic transformation is shown in Fig. 7, obtained when we simulated the dissociation of CH_3NO_2^- starting with a $^2A'$ transition state. Stretching the C-N bond, one reaches

FIG. 7. Decomposition of a A'' transition configuration of CH_3NO_2^- to $\text{CH}_3 + \text{NO}_2^-$.

$^2A''$ configurations corresponding to autodetachment of an extra electron, whereas the bonding configurations at similar geometries have $^2A'$ symmetry. Applications of a complicated diabatic approach (see, e.g., Ref. 53) to anion fragmentations are further complicated by the necessity of checking at each intermediate geometry whether there exists a supporting neutral parent state which can prevent autodetachment of the extra electron. Applications of electron-nuclear dynamics methods,⁵⁴ which avoid constructions of potential energy surfaces, could be a promising alternative for considering anion decay channels, especially if done purely quantum mechanically.

IV. CONCLUSIONS

Our coupled-cluster and Hartree-Fock-density-functional-theory studies of high-energy density compounds CH_3ONO and CH_3ONO^- as well as of their major fragments can be summarized briefly in several conclusions:

- The fragmentation energies obtained at both the CCSD(T) and HF-DFT levels of theory are in fair agreement with each other (and experimental data) except for channels containing CN as a product, where HF-DFT fails seriously.
- The adiabatic electron affinities of all the fragments computed at the HF-DFT(BLYP) and HF-DFT(B3LYP) levels are, generally, in somewhat better accord with experiment, except for CN, whose A_{ad} is overestimated by 0.8 eV.
- Attachment of an extra electron to CH_3ONO or CH_3NO_2 reduces substantially the fragmentation energies and leads to the appearance of new exothermic decay chan-

nels whose product anions correspond to the neutral parents with the high adiabatic electron affinity, such as CN or HCO_2^- .

(iv) One of possible mechanisms of aging processes in nitromethane and similar high-energy density materials could be related to attachment of low-energy electrons with subsequent transformations of diffuse dipole-bound anionic states to conventional (valence) anionic states, whose decomposition is much easier than the decomposition of neutral systems.

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