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Gutsev, G. L., Jena, P., Bartlett, R. J. Thermodynamical stability of CH<sub>3</sub>ONO and CH<sub>3</sub>ONO<sup>-</sup>: A coupled-cluster and Hartree-Fock-density-functional-theory study. *The Journal of Chemical Physics* 110, 403 (1999). Copyright © 1999 AIP Publishing LLC.

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# Thermodynamical stability of $\text{CH}_3\text{ONO}$ and $\text{CH}_3\text{ONO}^-$ : A coupled-cluster and Hartree–Fock-density-functional-theory study

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(Received 17 August 1998; accepted 29 September 1998)

The structure and thermodynamic stability of methyl nitrite 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,  $\text{H}_2$ ,  $\text{CH}$ ,  $\text{NH}$ ,  $\text{OH}$ ,  $\text{CN}$ ,  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{NO}$ ,  $\text{O}_2$ ,  $\text{CH}_2$ ,  $\text{NH}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{HCN}$ ,  $\text{HNC}$ ,  $\text{HCO}$ ,  $\text{HNO}$ ,  $\text{O}_2\text{H}$ ,  $\text{CO}_2$ ,  $\text{NO}_2$ ,  $\text{CH}_3$ ,  $\text{NH}_3$ ,  $\text{CNH}_2$ ,  $\text{HCO}_2$ ,  $\text{HNO}_2$ ,  $\text{CH}_3\text{N}$ ,  $\text{CH}_3\text{O}$ ,  $\text{CH}_3\text{NO}$ ,  $\text{CH}_3\text{ON}$ ,  $\text{CH}_2\text{NO}_2$ , 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  $\text{CN}$  as a product. The  $\text{CH}_3\text{ONO}^-$  and  $\text{CH}_3\text{NO}_2^-$  anions are shown to possess lower fragmentation energies than their neutral parents. This implies that the attachment of an extra electron to  $\text{CH}_3\text{NO}_2$  or  $\text{CH}_3\text{ONO}$  may have a crucial role in initiating the decomposition of these compounds. Also, the attachment of an extra electron to  $\text{CH}_3\text{NO}_2$  or  $\text{CH}_3\text{ONO}$  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, methyl nitrite, has been found<sup>3</sup> 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 observations<sup>3</sup> and results of *ab initio* studies.<sup>4,5</sup>

Formation of negative ions is believed<sup>6,7</sup> to be rate controlling in the detonation of liquid nitromethane. Gas-phase nitromethane was shown<sup>8,9</sup> to form both dipole-bound and conventional (valence) anionic states upon attachment of an extra electron. A dipole-bound state of  $\text{CH}_3\text{NO}_2^-$  can be produced via attachment of a low-energy electron to the ground-state nitromethane and then this state may transform<sup>8,9</sup> 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 methyl nitrite anion, which would produce methyl nitrite upon detachment of an extra electron.

The aim of the present work is to evaluate decomposition energies through different decay channels of methyl nitrite 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 calculations<sup>9</sup> 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 programs<sup>10</sup> at the CCSD(T)<sup>11,12</sup> and HFDFT<sup>13–16</sup> levels of theory using the 6-311++G(2d,2p) basis set<sup>17</sup> ([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<sup>18,19</sup> defined as

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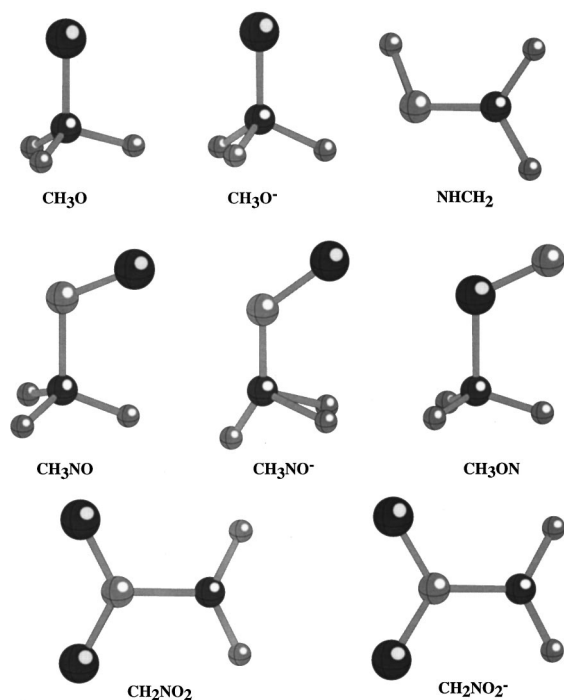


FIG. 1. Equilibrium geometrical configurations of heavier fragments of  $\text{CH}_3\text{ONO}$  and  $\text{CH}_3\text{ONO}^-$ .

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

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

The adiabatic electron affinity ( $A_{\text{ad}}$ ) 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  $A_{\text{ad}}$  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  $\text{cm}^{-1}$ .<sup>a</sup>

Species	CCSD(T)			HFDF/T		
	$R_e$	$\omega_e$	$E_{\text{tot}}$	$R_e$	$\omega_e$	$E_{\text{tot}}$ (B3LYP)
$\text{H}_2$	0.7421	4413	–1.170 865	0.7452	4381	–1.172 545
<b>Exp.</b>	0.7414	4401	...	0.7414	4401	...
$\text{CH}$	1.1191	2839	–38.419 455	1.1267	2784	–38.465 475
<b>Exp.</b>	1.1199	2829	...	1.1199	2829	...
$\text{CH}^-$	1.1373	2593	–38.457 546	1.1356	2592	–38.509 264
$\text{NH}$	1.0368	3271	–55.145 915	1.0442	3232	–55.207 726
<b>Exp.</b>	1.0362	3282	...	1.0362	3282	...
$\text{NH}^-$	1.0397	3175	–55.144 545	1.0465	3122	–55.217 427
$\text{OH}$	0.9695	3748	–75.635 869	0.9806	3646	–75.724 429
<b>Exp.</b>	0.9697	3738	...	0.9697	3738	...
$\text{OH}^-$	0.9626	3763	–75.690 781	0.9710	3684	–75.783 862
$\text{CN}$	1.1729	2116	–92.577 623	1.1230	2804	–92.657 661
<b>Exp.</b>	1.1718	2068	...	1.1718	2068	...
$\text{CN}^-$	1.1831	2050	–92.716 317	1.1778	2077	–92.827 098
$\text{N}_2$	1.1029	2329	–109.380 021	1.0989	2365	–109.498 742
<b>Exp.</b>	1.0977	2359	...	1.0977	2359	...
$\text{CO}$	1.1340	2158	–113.160 786	1.1304	2181	–113.237 286
<b>Exp.</b>	1.1281	2170	...	1.1281	2170	...
$\text{NO}$	1.1541	2083	–129.714 851	1.1361	3072	–129.861 103
<b>Exp.</b>	1.1508	1904	...	1.1508	1904	...
$\text{NO}^-$	1.2759	1366	–129.709 253	1.2647	1427	–129.865 916
$\text{O}_2$	1.2168	1563	–150.120 937	1.2208	1559	–150.295 696
<b>Exp.</b>	1.2070	1580	...	1.2070	1580	...
$\text{O}_2^-$	1.3608	1107	–150.127 392	1.3612	1130	–150.310 979

<sup>a</sup>Experimental data from Ref. 28.

### III. RESULTS AND DISCUSSIONS

#### A. Geometrical configurations

In order to estimate fragmentation energies of  $\text{CH}_3\text{ONO}$  and  $\text{CH}_3\text{ONO}^-$ , we performed geometry optimizations and harmonic vibrational frequency calculations on the following species and their anions when the latter exist. Diatomics are  $\text{H}_2$ ,  $\text{CH}$ ,  $\text{NH}$ ,  $\text{OH}$ ,  $\text{CN}$ ,  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{NO}$ , and  $\text{O}_2$ ; triatomics are  $\text{CH}_2$ ,  $\text{NH}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{HCN}$ ,  $\text{HNC}$ ,  $\text{HCO}$ ,  $\text{HNO}$ ,  $\text{O}_2\text{H}$ ,  $\text{CO}_2$ , and  $\text{NO}_2$ ; tetra-atomics are  $\text{CH}_3$ ,  $\text{NH}_3$ ,  $\text{CNH}_2$ ,  $\text{HCO}_2$ , and  $\text{HNO}_2$ ; penta-atomics and hexa-atomics are  $\text{CH}_3\text{N}$ ,  $\text{CH}_3\text{O}$ ,  $\text{CH}_3\text{NO}$ ,  $\text{CH}_3\text{ON}$ , and  $\text{CH}_2\text{NO}_2$ . 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”  $\text{CH}_3\text{N}$  ( $\text{NHCH}_2$ ) and  $\text{CH}_2\text{NO}_2$  can be found in Refs. 24 and 25 and Refs. 26 and 27, respectively.

Table I compares the results of our computations to experimental data<sup>28</sup> 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  $\text{CN}$  computed at the HFDF/T level. Tables II and III present our results for triatomics and tetra-atomics 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	$E_{\text{tot}}$	Geometry	Z	$E_{\text{tot}}$ (B3LYP)
$\text{CH}_2$ , $^3B_2$	$R(\text{C-H})=1.0763$ $\angle \text{HCH}^\circ=133.49$	10.88	-39.085 769	$R(\text{C-H})=1.0788$ $\angle \text{HCH}^\circ=136.30$	10.23	-39.132 985
$\text{CH}_2^-$ , $^2B_2$	$R(\text{C-H})=1.1212$ $\angle \text{HCH}^\circ=102.31$	9.74	-39.099 081	$R(\text{C-H})=1.1244$ $\angle \text{HCH}^\circ=102.62$	9.61	-39.154 938
$\text{NH}_2$ , $^2B_2$	$R(\text{N-H})=1.0242$ $\angle \text{HNH}^\circ=102.90$	12.03	-55.796 160	$R(\text{N-H})=1.0321$ $\angle \text{HNH}^\circ=102.41$	11.73	-55.864 358
$\text{NH}_2^-$ , $^1A_1$	$R(\text{N-H})=1.0271$ $\angle \text{HNH}^\circ=101.63$	11.72	-55.812 740	$R(\text{N-H})=1.0330$ $\angle \text{HNH}^\circ=102.41$	11.45	-55.884 828
$\text{H}_2\text{O}$ , $^1A_1$	$R(\text{O-H})=0.9575$ $\angle \text{HOH}^\circ=104.33$	13.58	-76.329 639	$R(\text{O-H})=0.9673$ $\angle \text{HOH}^\circ=102.54$	13.12	-76.329 639
$\text{HCN}$ , $^1\Sigma^+$	$R(\text{H-C})=1.0651$ $R(\text{C-N})=1.1588$	9.95	-93.285 048	$R(\text{H-C})=1.0682$ $R(\text{C-N})=1.1527$	10.14	-93.392 608
$\text{HNC}$ , $^1\Sigma^+$	$R(\text{H-N})=0.9952$ $R(\text{C-N})=1.1743$	9.54	-93.260 990	$R(\text{H-N})=1.0008$ $R(\text{C-N})=1.1695$	9.47	-93.370 039
$\text{HCO}$ , $^2A'$	$R(\text{C-H})=1.1186$ $R(\text{C-O})=1.1815$ $\angle \text{HCO}^\circ=124.32$	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
$\text{HCO}^-$ , $^1A'$	$R(\text{C-H})=1.2246$ $R(\text{C-O})=1.2420$ $\angle \text{HCO}^\circ=109.68$	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
$\text{HNO}$ , $^1A'$	$R(\text{N-H})=1.0512$ $R(\text{N-O})=1.2178$ $\angle \text{HNO}^\circ=108.05$	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
$\text{HNO}^-$ , $^2A''$	$R(\text{N-H})=1.0459$ $R(\text{N-O})=1.3449$ $\angle \text{HNO}^\circ=105.57$	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
$\text{O}_2\text{H}$ , $^2A''$	$R(\text{O-H})=0.9693$ $R(\text{O-O})=1.3418$ $\angle \text{OOH}^\circ=104.08$	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
$\text{O}_2\text{H}^-$ , $^1A'$	$R(\text{O-H})=0.9574$ $R(\text{O-O})=1.5402$ $\angle \text{OOH}^\circ=96.98$	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
$\text{CO}_2$ , $^1\Sigma_g^+$	$R(\text{C-O})=1.1654$ $\angle \text{OCO}^\circ=180.0$	7.21	-188.324 975	$R(\text{C-O})=1.1655$ $\angle \text{OCO}^\circ=180.0$	7.20	-188.542 052
$\text{CO}_2^-$ , $^2A_1$	$R(\text{C-O})=1.2364$ $\angle \text{OCO}^\circ=137.35$	5.15	-188.297 106	$R(\text{C-O})=1.2355$ $\angle \text{OCO}^\circ=137.29$	4.90	-188.520 668
$\text{NO}_2$ , $^2A_1$	$R(\text{N-O})=1.2025$ $\angle \text{ONO}^\circ=134.16$	5.57	-204.792 618	$R(\text{N-O})=1.2011$ $\angle \text{ONO}^\circ=133.44$	6.85	-205.027 644
$\text{NO}_2^-$ , $^1A_1$	$R(\text{N-O})=1.2670$ $\angle \text{ONO}^\circ=116.55$	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  $\text{CH}_3\text{ONO}$ , which are compared to experimental geometries<sup>29</sup> and fundamentals,<sup>30</sup> as well as for two conformations of  $\text{CH}_3\text{ONO}^-$ . Both *cis* and *trans* conformations correspond to stationary states of  $\text{CH}_3\text{ONO}$  and  $\text{CH}_3\text{ONO}^-$ , whereas configurations obtained from them by  $\pi$  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  $\text{CH}_3\text{ONO}$  and  $\text{CH}_3\text{ONO}^-$  differ in total energy by  $\approx 1$  kcal/mol only. The transition states are higher in total energy by several kcal/mol, in agreement with a theoretical result<sup>31</sup> stating that the barrier height for the  $\text{CH}_3\text{ONO}$  isomerization equals 9.8 kcal/mol and experimental data (10 kcal/mol).<sup>29</sup> On the whole, the results of our computations for  $\text{CH}_3\text{ONO}$  are in rather good agreement

with both experimental data<sup>29,30</sup> and previous theoretical results.<sup>4,5</sup>

## B. Adiabatic electron affinities

Since there are a lot of experimental data<sup>32</sup> on the  $A_{\text{ad}}$  of fragments entering  $\text{CH}_3\text{ONO}$ , it is interesting to compare the ability of the CCSD(T) and HFDFDFT levels in reproducing the  $A_{\text{ad}}$ 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.<sup>33</sup> 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 HFDF/T/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)			HFDF/T		
	Geometry	Z	$E_{\text{tot}}$	Geometry	Z	$E_{\text{tot}}$ (B3LYP)
CH <sub>3</sub> , <sup>2</sup> A''	R(C-H)=1.0768 ∠ZCH <sub>1,2,3</sub> <sup>o</sup> =90.0	18.69	-39.766 397	R(C-H)=1.0809 ∠ZCH <sub>1,2,3</sub> <sup>o</sup> =90.0	18.45	-39.819 105
CH <sub>3</sub> <sup>-</sup> , <sup>1</sup> A <sub>1</sub>	R(C-H)=1.1016 ∠ZCH <sub>1,2,3</sub> <sup>o</sup> =110.44	17.9	-39.760 117	R(C-H)=1.1024 ∠ZCH <sub>1,2,3</sub> <sup>o</sup> =109.04	17.51	-39.816 672
NH <sub>3</sub> , <sup>2</sup> A''	R(N-H)=1.0108 ∠ZNH <sub>1,2,3</sub> <sup>o</sup> =112.02	21.76	-56.474 293	R(N-H)=1.0183 ∠ZNH <sub>1,2,3</sub> <sup>o</sup> =111.74	20.96	-56.542 955
CNH <sub>2</sub> , <sup>2</sup> A <sub>1</sub>	R(C-N)=1.2996 R(N-H)=1.0160 ∠CNH <sup>o</sup> =122.64	16.71	-93.784 491	R(C-N)=1.2921 R(N-H)=1.0257 ∠CNH <sup>o</sup> =122.90	16.33	-93.899 648
NCH <sub>2</sub> , <sup>2</sup> A <sub>1</sub>	R(C-N)=1.2517 R(C-H)=1.0932 ∠NCH <sup>o</sup> =121.07	15.84	-93.831 964	R(C-N)=1.2124 R(C-H)=1.1009 ∠NCH <sup>o</sup> =121.47	16.34	-93.939 187
NCH <sub>2</sub> <sup>-</sup> , <sup>1</sup> A <sub>1</sub>	R(C-N)=1.2536 R(C-H)=1.1417 ∠NCH <sup>o</sup> =125.72	14.25	-93.841 301	R(C-N)=1.2399 R(C-H)=1.1554 ∠NCH <sup>o</sup> =126.24	13.79	-93.960 009
HCO <sub>2</sub> , <sup>2</sup> A <sub>1</sub>	R(C-H)=1.1573 R(C-O)=1.2292 ∠HCO <sup>o</sup> =107.80	9.62	-188.807 401	R(C-H)=1.1535 R(C-O)=1.2282 ∠HCO <sup>o</sup> =107.96	190.66	-189.031 587
HCO <sub>2</sub> <sup>-</sup> , <sup>1</sup> A <sub>1</sub>	R(C-H)=1.1285 R(C-O)=1.2569 ∠HCO <sup>o</sup> =114.87	12.57	-188.934 947	R(C-H)=1.1389 R(C-O)=1.2577 ∠HCO <sup>o</sup> =114.78	12.28	-189.159 845
HNO <sub>2</sub> , <sup>1</sup> A <sub>1</sub>	R(N-H)=1.0313 R(N-O)=1.2251 ∠HNO <sup>o</sup> =115.90 ∠ONHO <sup>o</sup> =180.0	13.71	-205.412 175	R(N-H)=1.0436 R(N-O)=1.2258 ∠HNO <sup>o</sup> =115.98 ∠ONHO <sup>o</sup> =180.0	13.63	-205.648 745
HNO <sub>2</sub> <sup>-</sup> , <sup>2</sup> A'	R(N-H)=1.0235 R(N-O)=1.3177 ∠HNO <sup>o</sup> =112.71 ∠ONHO <sup>o</sup> =145.75	12.44	-205.413 001	R(N-H)=1.0353 R(N-O)=1.3164 ∠HNO <sup>o</sup> =112.23 ∠ONHO <sup>o</sup> =143.16	11.82	-205.659 770

theory (DFT)-based approaches to augmentations of *spd* basis sets by functions with higher angular momentum  $l$ ,<sup>34</sup> whereas the convergence of the correlation energy in coupled-cluster methods is proportional to  $1/L^4$ ,<sup>35,36</sup> 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.<sup>37</sup>

Tables VII and VIII compare our  $A_{\text{ad}}$ s computed at both levels of theory to experimental data<sup>32</sup>. Note that all the  $A_{\text{ad}}$ s obtained at the different levels from HF to CCSD(T) are computed at the geometries optimized at the CCSD(T) level and the  $\Delta Z$  corrections are obtained from harmonic vibrational frequency calculations performed also at the CCSD(T) level. The HFDF/T  $A_{\text{ad}}$ s are obtained at the geometries optimized with the BLYP exchange-correlation functional. Generally, the HFDF/T approach provides  $A_{\text{ad}}$ s which are somewhat closer to experimental data than the CCSD(T) method does, except for CN, where HFDF/T fails seriously. This was also found previously<sup>38</sup> when using larger basis sets in conjunction with different exchange-correlation functionals.

The  $A_{\text{ad}}$  of CH<sub>3</sub>ONO is somewhat higher than that of CH<sub>3</sub>NO<sub>2</sub> computed at the same levels of theory. Since the HFDF/T  $A_{\text{ad}}$  of CH<sub>3</sub>NO<sub>2</sub> is very close<sup>9</sup> to the experimental

value of  $0.26 \pm 0.08$  eV,<sup>8</sup> the HFDF/T value of 0.60 eV could be recommended as the  $A_{\text{ad}}$  of CH<sub>3</sub>ONO. Contrary to CH<sub>3</sub>NO<sub>2</sub>, CH<sub>3</sub>ONO has a relatively small dipole moment of 2.2 D, which seems not to be sufficient to sustain a dipole-bound state of CH<sub>3</sub>ONO<sup>-</sup>, because extensive investigations for organic compounds have shown<sup>39,40</sup> 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 HFDF/T/6-311++G(2d,2p) levels. Total energies are in hartrees and Zs are in kcal/mol.

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

TABLE V. Results of calculations for  $\text{CH}_3\text{ONO}$  ( $C_s, ^1A'$ ) and  $\text{CH}_3\text{ONO}^-$  ( $C_s, ^2A''$ ) 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  $\text{cm}^{-1}$ , Zs are in kcal/mol, and dipole moments ( $\mu$ ) are in Debye.

Property	$\text{CH}_3\text{ONO}$				$\text{CH}_3\text{ONO}^-$	
	<i>Cis</i>	Exp. <sup>a</sup>	<i>Trans</i>	Exp. <sup>a</sup>	<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]	14903]
$\omega(a'')$	3190[14]	3000	3204[14]	3000	2870[285]	2876[272]
Z	30.65	30.73	29.03	29.22	28.71	28.19
$\mu$	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

<sup>a</sup>Experimental 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 ( $0.47 \text{ cm}^{-1}$ ) using the recently developed electron-attachment equation-of-motion coupled cluster (EA-EOMCC) method<sup>41</sup> and the

6-311++G(2d,2p) basis augmented by seven diffuse *sp* shells in the same manner as was done before<sup>9</sup> for  $\text{CH}_3\text{NO}_2$ .

### C. Fragmentation energies

Fragmentation energies of the ground-state  $\text{CH}_3\text{ONO}$  and  $\text{CH}_3\text{ONO}^-$  species, presented in Tables IX and X, re-

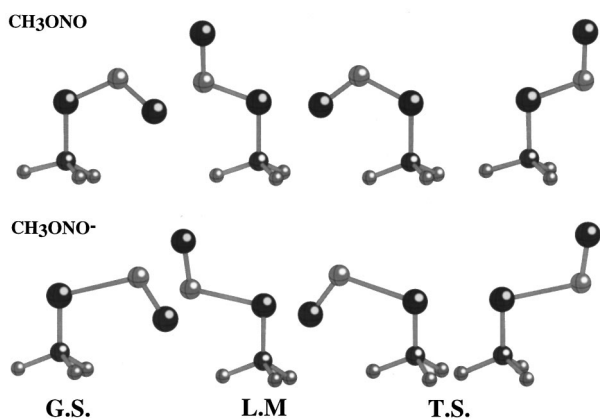


FIG. 2. Stationary configurations of  $\text{CH}_3\text{ONO}$  and  $\text{CH}_3\text{ONO}^-$ .

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

<sup>a</sup>See Ref. 33.

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

Level	CH	NH	OH	NO	O <sub>2</sub>	CN	HCO	HNO	CH <sub>2</sub>	NH <sub>2</sub>	O <sub>2</sub> H	CO <sub>2</sub>	NO <sub>2</sub>	NCH <sub>2</sub>	HCO <sub>2</sub>	HNO <sub>2</sub>	CH <sub>3</sub>
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  $\Delta Z$  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,<sup>1,42-44</sup> which are known for several decay channels of CH<sub>3</sub>NO<sub>2</sub> and CH<sub>3</sub>NO<sub>2</sub><sup>-</sup>.

Table IX shows that the source of the high-energy density of CH<sub>3</sub>ONO and CH<sub>3</sub>NO<sub>2</sub> is due to their highly exothermic decomposition, into NH<sub>3</sub> and CO<sub>2</sub>. Note that ammonia and formic acid were found to be major products of the thermal decomposition of CH<sub>3</sub>NO<sub>2</sub>.<sup>45</sup> Obviously, the direct decay CH<sub>3</sub>NO<sub>2</sub>→NH<sub>3</sub>+CO<sub>2</sub> requires three bonds to be ruptured, which energetically is highly unfavorable. Formic acid is a decay product through the next lowest bimolecular channel, NH<sub>2</sub>+HCO<sub>2</sub>, which is twice as low in energy as the basic channel (1).

According to our results presented in Table X, the CH<sub>3</sub>ONO<sup>-</sup> anion has additional exothermic fragmentation channels with respect to those of its neutral parent. Especially interesting is the appearance of an exothermic channel CH<sub>3</sub>ONO<sup>-</sup>→NH<sub>2</sub>+HCO<sub>2</sub><sup>-</sup>, whose exothermity is due to a rather large  $A_{ad}$  of HCO<sub>2</sub><sup>-</sup> ( $\approx 3.3$  eV, see Table VII). Formally speaking, the HCO<sub>2</sub><sup>-</sup> radical belongs to the class of superhalogens<sup>46-48</sup> of the general MX<sub>2</sub>Y type. A relatively low electron affinity of HCO<sub>2</sub><sup>-</sup> with respect to MX<sub>3</sub> super-

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

Level	CH <sub>3</sub> O	CH <sub>3</sub> NO	CH <sub>2</sub> NO <sub>2</sub>	CH <sub>3</sub> NO <sub>2</sub>	CH <sub>3</sub> ONO
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	...

halogens where X is a halogen atom<sup>47</sup> 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<sub>3</sub>NO<sub>2</sub>, one might surmise that the formation of formic acid could be due to decomposition of CH<sub>3</sub>NO<sub>2</sub><sup>-</sup> through the channel NH<sub>2</sub>+HCO<sub>2</sub><sup>-</sup>. Subsequent detachment of an extra electron from HCO<sub>2</sub><sup>-</sup> and attachment of the electron to another CH<sub>3</sub>NO<sub>2</sub> or CH<sub>3</sub>ONO could initiate a chain reaction process.

The CH<sub>3</sub>NO<sub>2</sub><sup>-</sup> and CH<sub>3</sub>ONO<sup>-</sup> anions possess two other basic decay channels: to CH<sub>3</sub>O<sup>-</sup>+NO and CH<sub>3</sub>+NO<sub>2</sub><sup>-</sup> which are lower in the energy than the corresponding decay channels of CH<sub>3</sub>NO<sub>2</sub> and CH<sub>3</sub>ONO to CH<sub>3</sub>O+NO and CH<sub>3</sub>+NO<sub>2</sub>, respectively. On the whole, the fragmentation energy of a particular decay channel of CH<sub>3</sub>NO<sub>2</sub><sup>-</sup> and

TABLE IX. Fragmentation energies (in eV) of CH<sub>3</sub>ONO 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<sub>3</sub>NO<sub>2</sub> 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<sub>3</sub>NO<sub>2</sub>.

Channel	CCSD(T)		B3LYP		Exp.
	$D_e$	$D_0$	$D_e$	$D_0$	
CH <sub>3</sub> ONO→NH <sub>3</sub> +CO <sub>2</sub>	-3.97	-4.01	-4.12	-4.14	...
→NH+CO <sub>2</sub> +H <sub>2</sub>	0.32	-0.19	0.31	-0.15	...
→CO+HNO+H <sub>2</sub>	0.72	0.48	0.86	0.39	...
→NH <sub>2</sub> +HCO <sub>2</sub>	1.36	1.00	1.03	0.71	...
→NHCH <sub>2</sub> +O <sub>2</sub>	1.43	1.43	1.19	1.20	...
→CH <sub>3</sub> O+NO	1.70	1.54	1.57	1.46	1.68 <sup>a</sup>
→HCN+H <sub>2</sub> O+O	1.77	1.49	1.84	1.60	...
→CH <sub>3</sub> +NO <sub>2</sub>	2.57	2.33	2.37	2.22	2.5 <sup>b</sup> , 2.46 <sup>c</sup>
→H <sub>2</sub> O+OH+CN	3.00	2.54	3.22	3.06	...
→HCO+H <sub>2</sub> O+N	3.01	2.66	3.64	3.36	...
→NCH <sub>2</sub> +O <sub>2</sub> H	3.20	2.98	3.30	2.93	...
→CH <sub>3</sub> NO+O	3.66	3.64	3.71	3.60	...
→CH <sub>2</sub> +HNO <sub>2</sub>	4.23	4.00	4.14	3.92	...
→CH <sub>2</sub> NO <sub>2</sub> +H	4.45	4.15	4.35	4.05	...
→HNO+HCO+H	4.64	4.07	4.62	4.09	3.89 <sup>c</sup>
→H <sub>2</sub> O+CH+NO	5.26	4.76	5.15	4.77	...
→CH <sub>3</sub> ON+O	5.80	5.69	5.87	5.81	...
→CH <sub>2</sub> +OH+NO	5.91	5.44	5.86	5.41	...
2CH <sub>3</sub> ONO→2CO+N <sub>2</sub> +2H <sub>2</sub> O+H <sub>2</sub>	-6.08	-6.87	-5.71	-6.41	...
2NO→N <sub>2</sub> +O <sub>2</sub>	-1.98	-2.18	-1.99	-1.98	...

<sup>a</sup>See Ref. 42.

<sup>b</sup>See Ref. 43.

<sup>c</sup>See Ref. 1.

TABLE X. Fragmentation energies (in eV) of  $\text{CH}_3\text{ONO}^-$  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  $\text{CH}_3\text{NO}_2^-$  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	$0.56 \pm 0.2^a$
$\rightarrow \text{NH}_2^- + \text{HCO}_2$	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	...

<sup>a</sup>See Ref. 44.

$\text{CH}_3\text{ONO}^-$  is lower than the fragmentation energy of the corresponding channel of their neutral parents by the  $A_{\text{ad}}$  of a decay fragment in the neutral channel, if the fragment possesses a positive  $A_{\text{ad}}$ . Since anions are generally more loosely bound than their neutral parents, the formation of  $\text{CH}_3\text{NO}_2^-$  or  $\text{CH}_3\text{ONO}^-$  would greatly facilitate initiating a decomposition reaction of nitromethane.

#### D. Geometrical transformations

Following McKee<sup>4</sup> and Saxon and Yoshimine,<sup>5</sup> who have considered transformations of nitromethane into methylnitrite, we can consider a transformation from  $\text{CH}_3\text{NO}_2^-$  to  $\text{CH}_3\text{ONO}^-$ . 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  $\text{CH}_3\text{NO}_2^-$  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  $\text{CH}_3\text{NO}_2^-$  and was obtained in optimizations starting with an initial configuration where the oxygens were

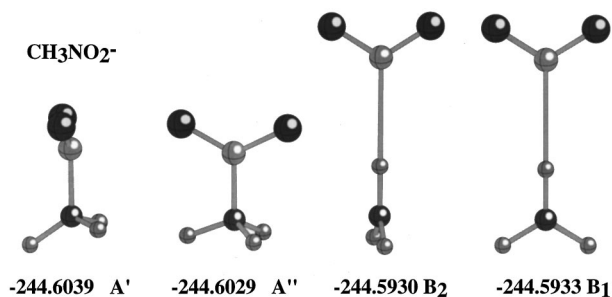


FIG. 3. Transition configurations of the  $\text{CH}_3\text{NO}_2^-$  anion.

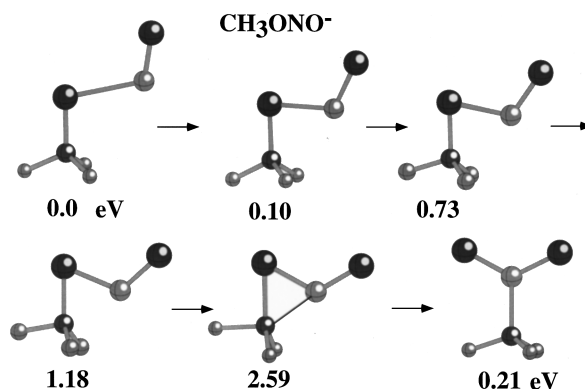


FIG. 4. A transformation of  $\text{CH}_3\text{ONO}^-$  to a  $A''$  transition configuration of  $\text{CH}_3\text{NO}_2^-$ .

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  $\text{CH}_3\text{ONO}^-$  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  $0.2 \text{ \AA}$ . 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  $\text{CH}_3\text{NO}_2 \rightarrow \text{CH}_3\text{ONO}$ .<sup>4,5</sup> 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  $\text{CH}_3\text{ONO}^-$  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<sup>3,49</sup> on the existence of a barrier for the direct decomposition of ni-

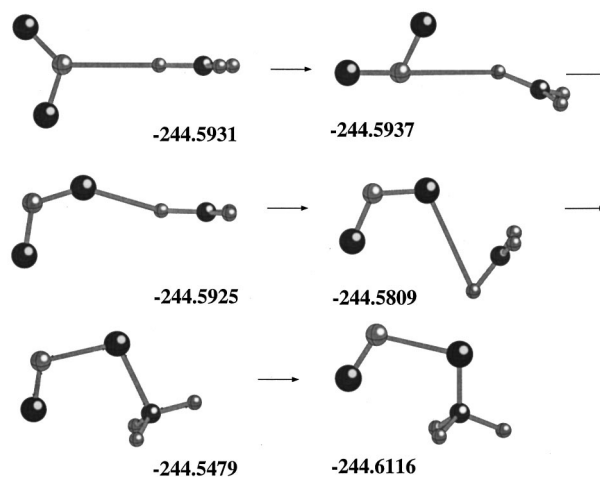


FIG. 5. A transformation of a  $B_2$  transition configuration of  $\text{CH}_3\text{NO}_2^-$  to  $\text{CH}_3\text{ONO}^-$ .



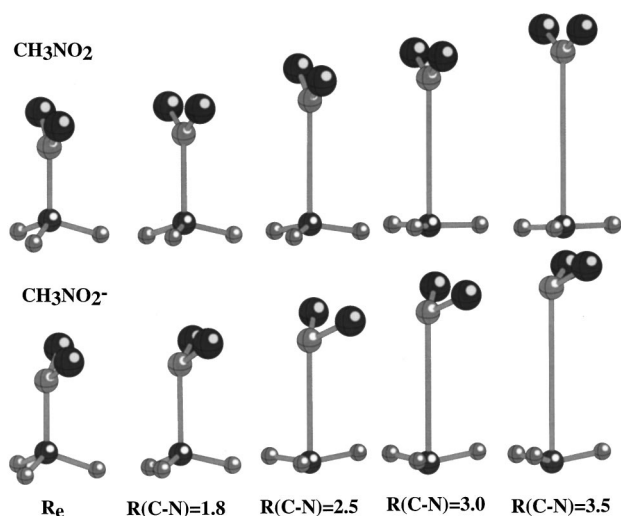


FIG. 6. Direct dissociation pathways  $\text{CH}_3\text{NO}_2 \rightarrow \text{CH}_3 + \text{NO}_2$  and  $\text{CH}_3\text{NO}_2^- \rightarrow \text{CH}_3 + \text{NO}_2^-$ .

tromethane through channel (2), we performed a simulation of the decomposition of  $\text{CH}_3\text{NO}_2$  and  $\text{CH}_3\text{NO}_2^-$  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  $\text{CH}_3\text{NO}_2$  has the wrong dissociation limit, we have optimized also the triplet state of  $\text{CH}_3\text{NO}_2$  (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.<sup>50</sup>

We have not found any barrier for  $\text{CH}_3\text{NO}_2$  when stretching the C–N bond length, in accord with experimental findings of Wodtke *et al.*<sup>3</sup> The behavior of the anion is somewhat different. The anion preserves his  $\text{NO}_2$  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,<sup>35</sup> and the near-planar  $\text{CH}_3$  itself cannot sustain an additional electron.<sup>51</sup> We found a barrier of about 0.35 eV, which appears when the  $\text{CH}_3$  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 found<sup>52</sup> 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  $\text{CH}_3\text{NO}_2^-$  starting with a  ${}^2A''$  transition state. Stretching the C–N bond, one reaches

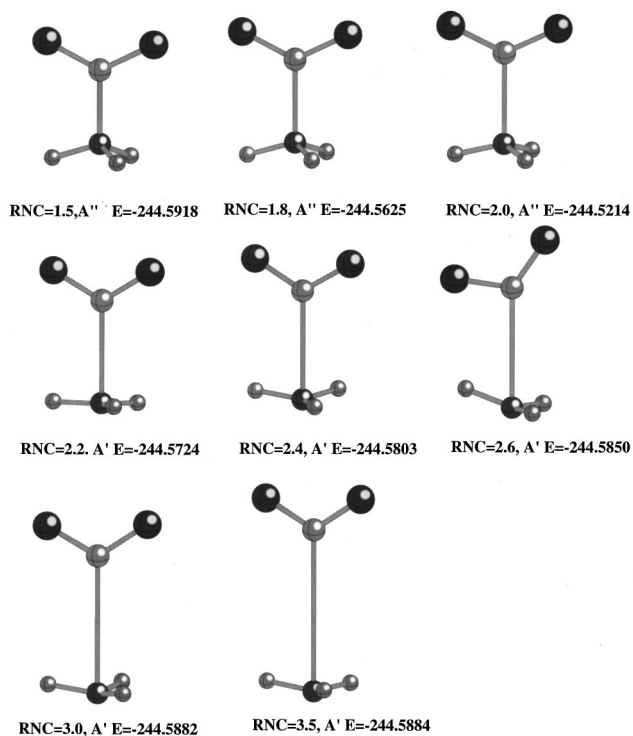


FIG. 7. Decomposition of a  ${}^2A''$  transition configuration of  $\text{CH}_3\text{NO}_2^-$  to  $\text{CH}_3 + \text{NO}_2^-$ .

${}^2A''$  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,<sup>54</sup> 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  $\text{CH}_3\text{ONO}$  and  $\text{CH}_3\text{ONO}^-$  as well as of their major fragments can be summarized briefly in several conclusions:

(i) 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.

(ii) 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  $A_{\text{ad}}$  is overestimated by 0.8 eV.

(iii) Attachment of an extra electron to  $\text{CH}_3\text{ONO}$  or  $\text{CH}_3\text{NO}_2$  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<sub>2</sub>.

(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.

## ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research Grant No. N00014-95-1-0614, Army Research Office Grant No. DAAL03-92-G-0106, and in part by a grant of HPC time from the DoD HPC Center. The authors appreciate the assistance of Dr. John Watts in performing some complicated frequency calculations.

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