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Subsequent work will investigate the ring transition state and the species resulting from its decomposition.

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Supplementary Material Available: Tables 8–29 containing complete geometries, total energies, and vibrational frequencies for all structures (including reactants) discussed in this paper (33 pages). Ordering information is given on any current masthead page.

Proton Affinity of Methyl Nitrate: Less than Proton Affinity of Nitric Acid

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Abstract: The equilibrium structures, dipole moments, harmonic vibrational frequencies, and infrared intensities of methyl nitrate, methanol, and ten structures of protonated methyl nitrate have been investigated using state-of-the-art ab initio quantum mechanical methods. The ab initio methods include self-consistent field (SCF), second-order Møller–Plesset (MP2) perturbation theory, single- and double-excitation coupled-cluster (CCSD) theory, and the CCSD(T) method, which incorporates a perturbational estimate of the effects of connected triple excitations. The MP2 equilibrium geometry and vibrational frequencies of methyl nitrate and methanol are in good agreement with experiment. The lowest energy gas-phase form of protonated methyl nitrate is a complex between methanol and NO_2^+, although the next lowest isomer is only 4.9 kcal/mol higher in energy. The $CH_3OH\cdots NO_2^+$ complex is bound by 19.6 ± 2 kcal/mol. The ab initio proton affinity (PA) of methyl nitrate is 176.9 ± 5 kcal/mol, in very good agreement with the experimental value of 176 kcal/mol. The results of this study are contrasted with an earlier study on protonated nitric acid, and it is shown that methyl nitrate possesses a *smaller* PA than nitric acid. An explanation for this phenomenon is presented.

1. Introduction

The proton affinity (PA) of nitric acid (HNO_3) has been the subject of two recent experimental papers[1,2] and a recent ab initio study.[3] The experimental data were interpreted to yield a PA for HNO_3 of 168 ± 3 kcal/mol, while the high-level ab initio study obtained a value of 182.5 ± 4.0 kcal/mol; clearly a discrepancy exists between theory and experiment. The experimental[4] PA of methyl nitrate, CH_3NO_3, would appear to support the experimental determination of the PA of nitric acid. That is, the experimental PA of methyl nitrate (176 kcal/mol[4]) is about 8 kcal/mol larger than the experimental PA of nitric acid, which is consistent with the general observation that the molecule HOA has an 8–15 kcal/mol smaller PA than the analogous CH_3OA molecule. For example, the PAs of H_2O and CH_3OH are 166 and 182 kcal/mol,[5] respectively. The larger PA of CH_3OA relative to HOA is due to the better σ electron donating ability of CH_3 relative to H.

As has been discussed in detail,[1–3,6] the most stable form of protonated nitric acid is a complex between H_2O and NO_2^+. By analogy it is expected that a complex between CH_3OH and NO_2^+ will, at the very least, be a low-lying isomer of protonated methyl nitrate. There is also experimental evidence for the existence of two distinct isomers of protonated methyl nitrate.[4,7] Hence it is certain that several structures of protonated methyl nitrate must be investigated in order to determine the most stable form. This task is further complicated by the various isomers that exist due to internal rotation of the methyl group and also those due to internal rotation of the NO_2 group. However, it is possible to restrict the number of important structures of CH_3NO_3 and $CH_3NO_3H^+$ to those with a planar NO_3 group. Smith and Marsden[8] have recently studied several forms of methyl nitrate and they found, consistent with nitric acid,[3,6] that the lowest energy forms of methyl nitrate always have a planar NO_3 moiety. Forms in which NO_3 is nonplanar are 6–9 kcal/mol higher in energy. Even with this restriction to molecules with planar NO_3 groups, we have identified ten different structures of protonated methyl nitrate.

Protonated methyl nitrate has been previously examined at the self-consistent field (SCF) level of theory using the STO-3G and 4-31G basis sets.[9] In that study only two isomers of $CH_3NO_3H^+$ were considered—one corresponding to a complex between CH_3OH and NO_2^+ and one corresponding to protonation of the nitro group. Using the 4-31G basis set, Bernardi et al.[9] found that the isomer arising from protonation of the nitro group was 6.7 kcal/mol more stable than the complex. However, given the

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Table I. Total Energies (E_H), Equilibrium Bond Lengths (Å), Bond Angles (deg), and Dipole Moments (D) for CH_3NO_3 (Ia), Obtained at Various Levels of Theory[a]

	SCF/DZP	MP2/DZP	CCSD/DZP	CCSD(T)/DZP	MP2/TZ2P	expt[b]
E[c]	0.553 670	0.482 352	0.418 093	0.452 147	0.739 378	
HI[d]	0	0				
T_1[e]			0.019	0.019		
μ	3.95	3.12	3.35	3.21	2.99	3.08
r_{CH_1}	1.079	1.088	1.090	1.091	1.081	1.088
r_{CH_2}	1.080	1.089	1.091	1.092	1.082	1.095
r_{CO_3}	1.430	1.439	1.445	1.448	1.436	1.437
r_{NO_1}	1.192	1.231	1.224	1.231	1.212	1.205
r_{NO_2}	1.182	1.225	1.215	1.222	1.206	1.208
r_{NO_3}	1.333	1.416	1.400	1.421	1.414	1.402
$\angle H_2CH_2$	110.5	110.3	110.5	110.5	110.2	109.8
$\angle H_1CH_2$	110.9	110.8	110.9	111.0	110.6	111.4
$\angle H_1CO_3$	103.2	102.7	102.6	102.5	103.2	103.4
$\angle CO_3N$	115.7	112.6	113.0	112.5	112.2	112.7
$\angle O_3NO_1$	118.0	117.4	117.8	117.6	117.2	118.1
$\angle O_3NO_2$	114.1	112.6	113.0	112.7	112.7	112.4

[a] See Figure 1 for labeling of atoms. [b] Reference 29. [c] The total energy for the SCF method is reported as $-(E + 318)$ and for the other methods as $-(E + 319)$. [d] Hessian index (i.e., the number of negative eigenvalues obtained from diagonalization of the force constant matrix). [e] The T_1 diagnostic, see text for details.

relatively low levels of theory used, it was not possible to make any definitive statements regarding the lowest energy gas-phase isomer of protonated methyl nitrate.

In an attempt to resolve the discrepancy between theory and experiment for the PA of nitric acid, we use the same theoretical methods as in our earlier investigation of nitric acid[3] to examine the molecular structure, vibrational spectrum, and PA of methyl nitrate. As will be shown, our calculated PA of methyl nitrate is in reasonable agreement with experiment, and this study provides an explanation for the fact that the PA of nitric acid is larger than the PA of methyl nitrate. Thus it is demonstrated that the PAs of nitric acid and methyl nitrate do not follow the usual trend. The ab initio methods used in this study are described in the next section, and a discussion of our results is presented in the following section. Conclusions are given in the final section.

2. Theoretical Approach

Geometry optimizations and vibrational frequencies have been determined using two one-particle basis sets. The smallest basis is designated DZP and consists of Dunning's[10] [4s2p]/[2s] contraction of Huzinaga's[11] (9s5p)/(4s) primitive basis sets for the heavy atoms and hydrogen, respectively, augmented with one set of polarization functions for each atom. The hydrogen s functions have been scaled by 1.2, as recommended by Dunning. The polarization orbital exponents are $\alpha_d = 0.85$, 0.80, and 0.75 for O, N, and C, respectively, and $\alpha_p = 1.0$ for H. The larger TZ2P basis set is constructed from Dunning's[12] [5s4p]/[3s] contraction of Huzinaga's[11] (10s6p)/(5s) primitive basis sets for the heavy atoms and hydrogen, respectively. This basis includes two sets of polarization functions per atom with orbital exponents of $\alpha_d = 1,5$ and 0.35 for the heavy atoms and $\alpha_p = 1.4$ and 0.25 for H.[13] For both the DZP and TZ2P basis sets, the full complement of six Cartesian d-functions has been included.

Equilibrium geometries of the forms of methyl nitrate and protonated methyl nitrate considered in this study were determined at the SCF and second-order Møller–Plesset (MP2) perturbation levels of theory in conjunction with the DZP basis set. Geometry optimizations of the energetically lowest-lying isomers were then performed with the DZP basis set using the single- and double-excitation coupled-cluster (CCSD) method[14-16] and also the CCSD(T) approach,[17] which incorporates a perturbational estimate of the effects of connected triple excitations. Finally, in order to obtain accurate equilibrium geometries of the most important isomers, geometry optimizations were performed using the MP2/TZ2P level of theory. Harmonic vibrational frequencies were determined for all structures at the SCF/DZP level of theory and, for the lowest energy isomers, also at the MP2/DZP level of theory. We note that the most important lowest energy isomers were confirmed to be genuine minima on the potential energy surface at both levels of theory. Infrared (IR) intensities (using the double harmonic approximation) were evaluated at the same levels of theory as the harmonic vibrational frequencies. Analytical gradient methods have been used for all of the electronic structure methods.[18-21] Analytical second-derivative methods have been used for the SCF and MP2 methods.[22-24]

In order to obtain a more accurate estimate of the relative energetics of the various structures and also a more accurate determination of the PA of methyl nitrate, single-point energies have been evaluated using the CCSD(T) method in conjunction with large atomic natural orbital (ANO) basis sets.[25] The ANO basis sets have been constructed from van Duijneveldt's[13] (13s8p)/(8s) primitive sets for the heavy atoms and hydrogen, respectively, augmented with a 6d4f/6p even-tempered set of polarization functions. The polarization function orbital exponents are defined by $\alpha = 2.5^n\alpha_0$ for $n = 0, ..., k$, with α_0 values of 0.13 and 0.39 for the d anf f functions of O, 0.10 and 0.30 for N, 0.07 and 0.22 for C, and 0.10 for the p functions of H. The smallest ANO basis set, which is designated ANO1, consists of [4s3p2d]/[4s2p] ANOs on the heavy atoms and hydrogen, respectively. The larger ANO basis set is designated ANO2 and consists of [4s3p2d1f]/[4s2p] ANOs on the heavy atoms and hydrogen, respectively. Only the pure spherical harmonic components of the d and f functions have been included in the ANO basis sets.

All electrons have been included in the correlation procedure for the MP2 calculations. In all CCSD and CCSD(T) calculations, the O, N, and C 1s-like molecular orbital is doubly occupied in all configurations. Additionally, for the DZP and TZ2P basis

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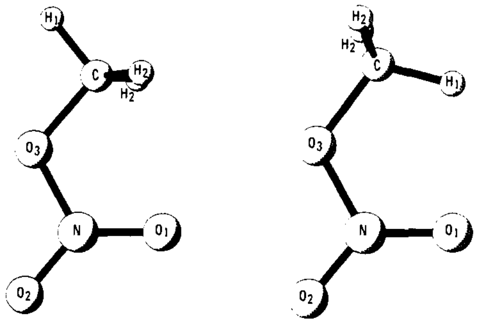
Table II. Total Energies (E_H), Equilibrium Bond Lengths (Å), Bond Angles (deg), and Dipole Moments (D) for CH_3NO_3 (Ib), Obtained at Various Levels of Theory[a]

	SCF/DZP	MP2/DZP
E^b	0.549 577	0.478 837
HI[c]	1	
μ	3.99	3.08
r_{CH_1}	1.075	1.086
r_{CH_2}	1.080	1.089
r_{CO_3}	1.435	1.442
r_{NO_1}	1.192	1.229
r_{NO_2}	1.182	1.225
r_{NO_3}	1.334	1.424
$\angle H_2CH_2$	110.7	110.9
$\angle H_1CH_2$	110.8	110.4
$\angle H_1CO_3$	111.3	110.8
$\angle CO_3N$	118.5	115.3
$\angle O_3NO_1$	119.0	118.7
$\angle O_3NO_2$	113.4	111.6

[a] See Figure 1 for labeling of atoms. [b] The total energy for the SCF method is reported as $-(E + 318)$ and for the MP2 method as $-(E + 319)$. [c] Hessian index.



Ia Ib

Figure 1. Graphical representation of two forms of methyl nitrate.

Table III. Harmonic Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for Two Forms of Methyl Nitrate, Obtained with the DZP Basis Set[a]

	approximate description	Ib	Ia		
		SCF	SCF	MP2	expt[b]
$\omega_1(a')$	CH_2 sym str	3407	3371 (12.4)	3282 (5.5)	3008
$\omega_2(a')$	CH_1 str	3259	3256 (25.8)	3139 (19.0)	2941
$\omega_3(a')$	NO_1,NO_2 antisym str	1879	1881 (820.2)	1863 (211.6)	1678
$\omega_4(a')$	methyl deformation	1631	1634 (71.1)	1542 (9.9)	1468
$\omega_5(a')$	methyl deformation	1620	1620 (82.5)	1498 (10.6)	1430
$\omega_6(a')$	NO_1,NO_2 sym str	1537	1547 (213.2)	1312 (235.5)	1287
$\omega_7(a')$	methyl rocking	1331	1324 (7.9)	1215 (5.8)	1176
$\omega_8(a')$	CO_3 str	1206	1216 (209.4)	1073 (128.3)	1017
$\omega_9(a')$	NO_3 str	1039	1053 (36.8)	868 (202.6)	854
$\omega_{10}(a')$	nitro deformation	774	784 (1.4)	677 (13.7)	657
$\omega_{11}(a')$	nitro planar rocking	663	663 (20.6)	581 (1.6)	578
$\omega_{12}(a')$	NO_3C bend	417	381 (5.5)	347 (2.5)	340
$\omega_{13}(a'')$	CH_2 antisym str	3349	3362 (22.1)	3263 (17.6)	3008
$\omega_{14}(a'')$	methyl deformation	1620	1609 (8.8)	1516 (7.9)	1455
$\omega_{15}(a'')$	methyl rocking	1274	1282 (2.3)	1188 (0.8)	1136
$\omega_{16}(a'')$	nitro nonplanar rocking	893	902 (30.8)	741 (10.5)	758
$\omega_{17}(a'')$	methyl–O_3–N torsion	125	241 (0.7)	218 (1.1)	
$\omega_{18}(a'')$	C–O_3–nitro torsion	205*i*	141 (2.5)	141 (2.8)	

[a] See Figure 1 for labeling of atoms. IR intensities are in parentheses. [b] Reference 30.

sets, the highest-lying unoccupied molecular orbital that is the core-counterpart has been deleted from the CCSD and CCSD(T) correlation procedures.

For all levels of theory, the dipole moment μ has been evaluated as an energy derivative, and for charged species μ has been determined with respect to the center of mass. All SCF and MP2 calculations were performed with the Cambridge Analytic Derivatives Package (CADPAC).[26] All coupled-cluster calculations were performed with the TITAN[27] set of electronic structure programs. The single-point coupled-cluster energies utilized the TITAN set of programs interfaced to the MOLECULE[28] integral program.

3. Results and Discussion

3a. Methyl Nitrate. The equilibrium structure of methyl nitrate (Ia) obtained at various levels of theory is presented in Table I together with the experimental vibrationally averaged structure.[29] The optimized structure of Ib obtained at the SCF/DZP and MP2/DZP levels of theory is given in Table II, and the harmonic vibrational frequencies of Ia and Ib are presented in Table III. The experimental fundamental vibrational frequencies[30] of Ia are also given in Table III. See Figure 1 for the labeling of the atoms in Ia and Ib.

Examining the DZP results given in Table I first, it is evident that electron correlation has a relatively small effect on the equilibrium geometry of methyl nitrate. Comparing the SCF and MP2 structures, the largest change in a bond length is 0.08 Å (r_{NO_3}) and the largest change in a bond angle is 3°. Moreover, comparison of the MP2, CCSD, and CCSD(T) equilibrium structures shows that electron correlation beyond the MP2 level has an even smaller effect on the structure of methyl nitrate. The T_1 diagnostic,[31] which is based on the t_1 amplitudes of the CCSD wave function, has been shown to be a reliable indicator of the importance of nondynamical electron correlation. A value for T_1 of 0.02 or larger suggests that nondynamical electron correlation is important and single-reference correlation methods that are limited to single and double excitations may not be adequate. The moderate value of the T_1 diagnostic (0.019) for the CCSD and CCSD(T) geometries of Ia indicates that low-level correlation methods should be adequate, consistent with the observations noted above. Thus it is important to include the effects of electron correlation, but unless very high accuracy is desired the MP2 level of theory provides a reasonably accurate equilibrium structure. A similar observation was noted regarding the equilibrium geometry of nitric acid,[3] although it was found that the MP2 level of theory did not perform very well for a few of the harmonic vibrational frequencies.

There are relatively small changes to the equilibrium geometry of methyl nitrate upon augmentation of the one-particle basis to the TZ2P basis set as found by comparing the MP2/DZP and MP2/TZ2P equilibrium structures. Not too surprisingly, the MP2/TZ2P geometry is in very good agreement with the experimental geometry—especially considering that the experimental geometry is a vibrationally averaged structure. The one qualitative difference between the experimental geometry and the theoretical equilibrium geometries is that r_{NO_1} is always greater than r_{NO_2} for the theoretical geometries but the opposite is true for the experimental geometry. It is possible that vibrational averaging is the cause of this phenomenon, though this seems unlikely. Since all of the ab initio equilibrium geometries consistently obtain $r_{NO_1} > r_{NO_2}$, and also because this type of structure (i.e., $r_{NO_1} > r_{NO_2}$) is consistent with that found for nitric acid,[3,32] it seems likely that the experimental geometry for methyl nitrate may be slightly in error for one or both of these NO bond lengths. This conclusion is still consistent with the experimental study,[29] however, since the stated uncertainty in the NO bond distances is ±0.005 Å.

The dipole moment μ obtained at the MP2/TZ2P level of theory (2.99 D) is in good agreement with the experimental value (3.08 D)—especially if the difference between the MP2/DZP and CCSD(T)/DZP dipole moment values is used to correct the MP2/TZ2P quantity. The second-derivative matrix determined

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Table IV. Total Energies (E_H), Equilibrium Bond Lengths (Å), Bond Angles (deg), and Dipole Moments (D) for $CH_3NO_3H^+$ (II), Obtained at Various Levels of Theory[a]

	SCF/DZP	MP2/DZP	CCSD/DZP	CCSD(T)/DZP	MP2/TZ2P
E^b	0.830463	0.789494	0.707227	0.744814	1.048844
HI[c]	0	0			
T_1[d]			0.018	0.018	
μ		2.18	2.24	2.15	2.02
r_{CH_1}	1.082	1.089	1.091	1.093	1.082
r_{CH_2}	1.083	1.090	1.092	1.093	1.082
$r_{O_3H_3}$	0.947	0.967	0.966	0.967	0.962
r_{CO_3}	1.430	1.448	1.450	1.453	1.449
r_{NO_1}	1.096	1.160	1.136	1.148	1.136
r_{NO_2}	1.095	1.160	1.136	1.148	1.136
r_{NO_3}	2.410	2.361	2.368	2.348	2.343
$\angle H_2CH_2$	110.2	110.5	110.5	110.6	110.6
$\angle H_1CH_2$	109.1	109.1	109.2	109.3	109.2
$\angle H_1CO_3$	107.5	106.7	106.8	106.7	106.9
$\angle CO_3H_3$	108.7	107.5	107.5	107.5	107.7
$\angle CO_3N$	128.7	125.8	126.8	126.4	126.4
$\angle O_3NO_1$	92.6	94.0	93.5	94.0	93.9
$\angle O_1NO_2$	175.3	174.0	174.3	173.5	174.1

[a] See Figure 2 for labeling of atoms. [b] The total energy for the SCF method is reported as $-(E + 318)$ and for the other methods as $-(E + 319)$. [c] Hessian index [d] The T_1 diagnostic, see text for details.

Table V. Total Energies (E_H), Equilibrium Bond Lengths (Å), Bond Angles (deg), and Dipole Moments (D) for $CH_3NO_3H^+$ (III), Obtained at Various Levels of Theory[a]

	SCF/DZP	MP2/DZP
E^b	0.829031	0.787953
HI[c]	1	
μ		2.11
r_{CH_1}	1.081	1.088
r_{CH_2}	1.083	1.090
$r_{O_3H_3}$	0.945	0.965
r_{CO_3}	1.436	1.452
r_{NO_1}	1.096	1.160
r_{NO_2}	1.096	1.160
r_{NO_3}	2.410	2.363
$\angle H_2CH_2$	110.1	110.5
$\angle H_1CH_2$	109.0	109.0
$\angle H_1CO_3$	110.5	110.4
$\angle CO_3H_3$	109.6	108.2
$\angle CO_3N$	126.6	123.6
$\angle O_3NO_1$	92.9	94.2
$\angle O_1NO_2$	175.3	174.2

[a] See Figure 2 for labeling of atoms. [b] The total energy for the SCF method is reported as $-(E + 318)$ and for the MP2 method as $-(E + 319)$. [c] Hessian index.

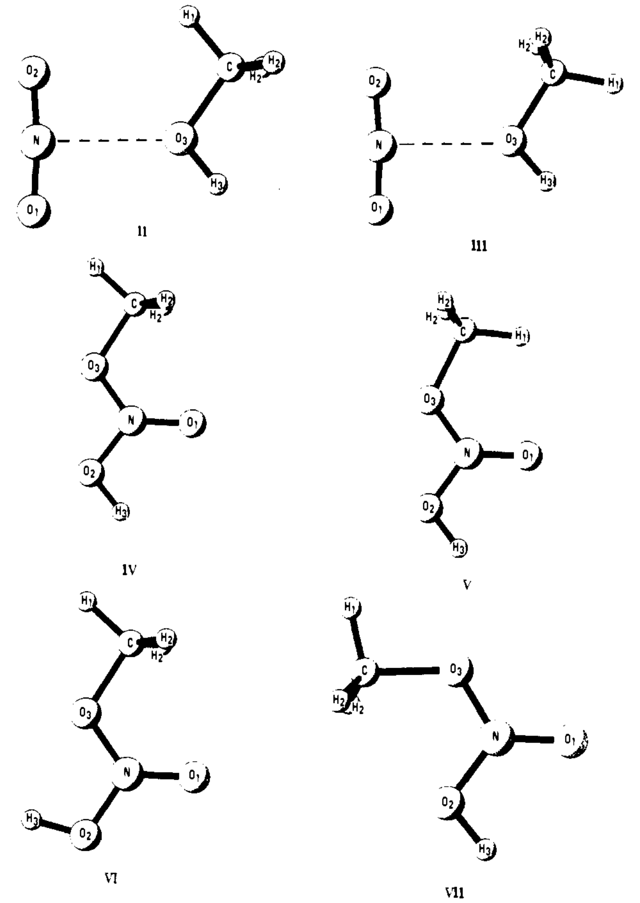

Figure 2. Graphical representation of six structures of protonated methyl nitrate.

at the SCF/DZP and MP2/DZP levels of theory explicitly demonstrates that structure Ia is a true minimum on the CH_3NO_3 potential energy surface (PES) as shown by the Hessian index values of 0. Conversely, the index for Ib, determined at the SCF/DZP level of theory and given in Table II, shows that this structure is a transition state connecting equivalent Ia structures. The effects of electron correlation on the optimum structure of Ib are similar to those noted for Ia.

The MP2 harmonic vibrational frequencies of Ia listed in Table III are in reasonable agreement with the experimental fundamental vibrational frequencies, especially considering the quality of the basis set (DZP). The C–H stretches exhibit the largest differences between theory and experiment, but these modes possess the largest anharmonic correction, and also, based on experience,[33,34] the MP2 harmonic frequency will be reduced by between 25 and 50 cm^{-1} when using a TZ2P quality basis set. For HNO_3 it was found that the N–O stretching modes were not as well described at the MP2 level of theory as the remaining vibrational degrees of freedom. This may also be the case for CH_3NO_3, but it is difficult to establish this hypothesis with the available data. Nonetheless, it is clear that the MP2/DZP harmonic frequencies are in reasonable agreement with the experimental fundamental vibrational frequencies. It is also interesting to note that the vibrational modes with large IR intensities (i.e., ω_3, ω_6, ω_8, and ω_9) correspond to those frequencies in the experimental study[30] that have either a strong or very strong IR gas-phase absorption.

The ab initio results presented in Tables I–III show that the MP2 level of theory performs reasonably well in describing the equilibrium structure and harmonic frequencies of methyl nitrate—similar to the situation found for HNO_3. The T_1 diagnostic indicates that methyl nitrate is a borderline case or, in other words, that CH_3NO_3 possesses some multireference character. However, a sophisticated single-reference based method such as

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Table VI. Total Energies (E_H), Equilibrium Bond Lengths (Å), Bond Angles (deg), and Dipole Moments (D) for $CH_3NO_3H^+$ (IV), Obtained at Various Levels of Theory[a]

	SCF/DZP	MP2/DZP	CCSD/DZP	CCSD(T)/DZP	MP2/TZ2P
E^b	0.847946	0.768093	0.711293	0.743791	1.022863
HI[c]	0	0			
T_1[d]			0.019	0.020	
μ		0.73	0.87	0.82	0.68
r_{CH_1}	1.075	1.085	1.087	1.088	1.078
r_{CH_2}	1.078	1.087	1.089	1.090	1.081
$r_{O_2H_3}$	0.962	0.986	0.982	0.984	0.982
r_{CO_3}	1.490	1.495	1.496	1.500	1.495
r_{NO_1}	1.154	1.213	1.191	1.200	1.191
r_{NO_2}	1.289	1.328	1.332	1.340	1.319
r_{NO_3}	1.264	1.298	1.307	1.315	1.285
$\angle H_2CH_2$	113.1	113.0	113.0	113.1	112.8
$\angle H_1CH_2$	112.7	112.9	112.6	112.8	112.8
$\angle H_1CO_3$	101.6	101.1	101.2	101.0	101.5
$\angle CO_3N$	116.5	113.6	113.7	113.3	113.2
$\angle O_3NO_1$	126.0	126.6	126.6	126.8	126.5
$\angle O_1NO_2$	123.6	124.7	124.7	124.9	124.6
$\angle NO_2H_3$	108.4	105.6	106.0	105.6	105.6

[a] See Figure 2 for labeling of atoms. [b] The total energy for the SCF method is reported as $-(E + 318)$ and for the other methods as $-(E + 319)$. [c] Hessian index. [d] The T_1 diagnostic, see text for details.

Table VII. Total Energies (E_H), Equilibrium Bond Lengths (Å), Bond Angles (deg), and Dipole Moments (D) for Structures of $CH_3NO_3H^+$, Obtained at the SCF/DZP and MP2/DZP Levels of Theory[a]

	V		VI		VII	
	SCF	MP2	SCF	MP2	SCF	MP2
E^b	0.845087	0.765547	0.846897	0.765194	0.842441	0.762116
HI[c]	1		0		0	
μ		0.73		3.01		2.91
r_{CH_1}	1.075	1.085	1.076	1.085	1.076	1.085
r_{CH_2}	1.077	1.086	1.078	1.087	1.077	1.086
$r_{O_2H_3}$	0.962	0.986	0.961	0.985	0.963	0.987
r_{CO_3}	1.501	1.501	1.494	1.497	1.496	1.500
r_{NO_1}	1.154	1.212	1.145	1.203	1.148	1.207
r_{NO_2}	1.291	1.330	1.290	1.325	1.298	1.341
r_{NO_3}	1.261	1.297	1.279	1.315	1.267	1.296
$\angle H_2CH_2$	112.9	112.8	113.2	113.1	113.5	113.5
$\angle H_1CH_2$	113.0	113.1	112.7	112.9	112.5	112.7
$\angle H_1CO_3$	109.5	109.7	101.6	101.2	100.8	100.5
$\angle CO_3N$	119.2	116.4	116.5	113.8	120.4	118.4
$\angle O_3NO_1$	126.9	127.7	125.8	126.3	122.1	122.4
$\angle O_1NO_2$	123.1	124.2	120.7	121.1	122.8	123.7
$\angle NO_2H_3$	108.3	105.4	109.3	107.3	108.3	105.3

[a] See Figure 2 for labeling of atoms. [b] The total energy for the SCF method is reported as $-(E + 318)$ and for the MP2 method as $-(E + 319)$. [c] Hessian index.

CCSD(T) should perform very well in describing the electronic structure.

3b. Protonated Methyl Nitrate. The equilibrium geometries of the two complex forms of protonated methyl nitrate are presented in Tables IV and V for II and III, respectively. Structures II and III, depicted in Figure 2, are complexes between methanol and NO_2^+—the only difference being due to rotation of the methyl group. The first point to note is that II is lower in energy than III at both the SCF/DZP and MP2/DZP levels of theory. Furthermore, the Hessian index values indicate that III is a transition state connecting equivalent isomers of II. Thus only the complex II has been studied at the CCSD/DZP, CCSD(T)/DZP, and MP2/TZ2P levels of theory.

Comparison of the DZP equilibrium geometries listed in Table IV shows that electron correlation has a significant effect on the molecular geometry. However, the MP2 level of theory performs reasonably well, as evidenced by the relatively small differences between the MP2/DZP and CCSD(T)/DZP equilibrium geometries. For example, the largest difference in a bond distance is only 0.013 Å, and the largest difference in a bond angle is 0.6°. In contrast, augmentation of the one-particle basis set from DZP to TZ2P has a larger effect on the equilibrium geometry, especially for the N–O distances, as demonstrated by comparison of the MP2/DZP and MP2/TZ2P structures. Based on the above observations and the results presented for methyl nitrate, it thus appears that the MP2/TZ2P equilibrium geometry of II should be reliable. Additional evidence in support of this assertion is provided by the T_1 diagnostic value of 0.018, which is similar to the value determined for methyl nitrate.

It is of interest to note that the MP2/TZ2P r_{NO_3} distance for II is less than the analogous quantity for protonated nitric acid.[3] This observation suggests that the complex between CH_3OH and NO_2^+ is more strongly bound than the complex between H_2O and NO_2^+. As will be shown later, this is indeed the case although the difference in the binding energies is small.

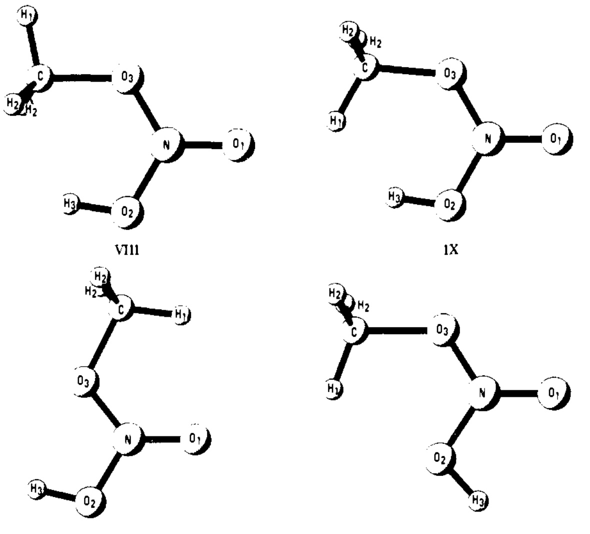
Tables VI–VIII contain the optimum geometries determined for structures IV–XI of protonated methyl nitrate. These structures, all of which correspond to protonation of the nitro group of methyl nitrate, are shown in Figures 2 and 3. IV was found to be the lowest energy isomer of this group at both the SCF/DZP and MP2/DZP levels of theory. Thus the equilibrium geometry of isomer IV was also obtained at the CCSD/DZP, CCSD(T)/DZP, and MP2/TZ2P levels of theory. Since the energy difference between IV and VI was computed to be very small, the equilibrium geometry of VI was also determined at the MP2/TZ2P level of theory. However, as will be demonstrated later, the total energy of IV was consistently 0.6–1.8 kcal/mol lower in energy than VI, and so the structure of VI was not determined with the coupled-cluster methods.

Examination of the equilibrium geometries of IV contained in Table VI shows that electron correlation has the usual effect of increasing bond distances somewhat and of affecting bond angles,

Table VIII. Total Energies (E_H), Equilibrium Bond Lengths (Å), Bond Angles (deg), and Dipole Moments (D) for Structures of $CH_3NO_3H^+$, Obtained at the SCF/DZP and MP2/DZP Levels of Theory[a]

	VIII		IX		X		XI	
	SCF	MP2	SCF	MP2	SCF	MP2	SCF	MP2
E^b	0.825019	0.744277	0.819624	0.739242	0.844039	0.762705	0.839410	0.759050
HI[c]	1		2		1		1	
μ		5.17		5.29		3.13		2.90
r_{CH_1}	1.076	1.086	1.079	1.087	1.076	1.085	1.074	1.082
r_{CH_2}	1.081	1.090	1.076	1.086	1.076	1.086	1.076	1.086
$r_{O_2H_3}$	0.955	0.980	0.953	0.978	0.961	0.985	0.963	0.986
r_{CO_3}	1.472	1.480	1.486	1.489	1.505	1.504	1.508	1.508
r_{NO_1}	1.139	1.198	1.141	1.199	1.145	1.202	1.149	1.208
r_{NO_2}	1.301	1.339	1.301	1.338	1.291	1.326	1.299	1.343
r_{NO_3}	1.290	1.321	1.284	1.317	1.278	1.314	1.263	1.293
$\angle H_2CH_2$	114.6	115.0	113.0	113.2	113.1	113.1	112.9	112.8
$\angle H_1CH_2$	110.6	110.5	111.2	110.9	112.9	112.9	113.1	113.1
$\angle H_1CO_3$	101.7	101.2	112.9	113.5	109.2	109.2	110.2	110.6
$\angle CO_3N$	121.7	119.6	126.5	124.4	119.1	116.4	123.4	121.4
$\angle O_3NO_1$	120.1	120.3	119.8	119.7	126.7	127.4	121.8	121.9
$\angle O_1NO_2$	118.8	119.0	118.4	118.6	120.3	120.6	122.3	123.2
$\angle NO_2H_3$	112.6	110.6	112.5	110.2	109.3	107.2	108.0	104.9

[a] See Figure 3 for labeling of atoms. [b] The total energy for the SCF method is reported as $-(E + 318)$ and for the MP2 method as $-(E + 319)$. [c] Hessian index.



VIII IX X XI

Figure 3. Graphical representation of four structures of protonated methyl nitrate.

Table IX. Harmonic Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for Two Forms of the Complex between CH_3OH and NO_2^+, Obtained with the DZP Basis Set[a]

	approximate description	III	II	
		SCF	SCF	MP2
$\omega_1(a')$	OH str	4196	4169 (115.8)	3894 (92.8)
$\omega_2(a')$	CH str	3334	3327 (37.2)	3263 (13.1)
$\omega_3(a')$	CH sym str	3229	3228 (31.5)	3137 (18.4)
$\omega_4(a')$	NO antisym str	2626	2626 (895.6)	2567 (80.5)
$\omega_5(a')$	HCH bend	1633	1636 (12.6)	1556 (10.1)
$\omega_6(a')$	HCH sym bend	1619	1615 (4.3)	1525 (4.6)
$\omega_7(a')$	COH bend	1477	1501 (57.8)	1403 (28.6)
$\omega_8(a')$	NO sym str	1667	1667 (2.5)	1304 (2.2)
$\omega_9(a')$	OCH bend	1210	1182 (37.1)	1108 (11.8)
$\omega_{10}(a')$	CO str	1107	1111 (124.8)	1045 (107.9)
$\omega_{11}(a')$	ONO ip-bend	674	675 (78.9)	449 (43.5)
$\omega_{12}(a')$	N···O str + CH_3OH ip-wag	253	255 (11.5)	250 (21.9)
$\omega_{13}(a')$	N···O str + CH_3OH ip-wag	197	196 (11.4)	189 (13.4)
$\omega_{14}(a')$	NO_2 ip-wag	114	124 (5.8)	116 (6.4)
$\omega_{15}(a'')$	CH antisym str	3321	3326 (28.0)	3263 (22.6)
$\omega_{16}(a'')$	HCH antisym bend	1619	1617 (5.7)	1530 (4.9)
$\omega_{17}(a'')$	HOCH torsion	1279	1276 (3.9)	1192 (1.6)
$\omega_{18}(a'')$	ONO op-bend	737	736 (25.1)	556 (0.4)
$\omega_{19}(a'')$	methyl rotation	181i	438 (183.7)	377 (171.4)
$\omega_{20}(a'')$	CH_3OH op-wag	250	102 (6.6)	95 (10.8)
$\omega_{21}(a'')$	CH_3OH···NO_2 twist	48	48 (0.03)	44 (0.001)

[a] See Figure 2 for labeling of atoms. IR intensities are in parentheses; ip = in-plane and op = out-of-plane.

except for $\angle CO_3N$ and $\angle NO_2H_3$, very little. Although $\angle CO_3N$ and $\angle NO_2H_3$ both decrease by about 3° due to electron correlation, the variation among the values from the different correlation methods is small. The MP2/DZP equilibrium geometry is in reasonable agreement with the CCSD(T)/DZP equilibrium geometry, and the SCF/DZP and MP2/DZP Hessian index values are both 0, indicating that IV is indeed a minimum on the $CH_3NO_3H^+$ potential energy surface. The MP2/TZ2P bond distances are shorter than the MP2/DZP quantities, as is expected when the one-particle basis set is improved from DZP to TZ2P. It is expected that the MP2/TZ2P equilibrium geometry of IV should have accuracy relative to experiment similar to that found for methyl nitrate.

The SCF and MP2 equilibrium geometries of structures V–XI all exhibit similar tendencies to those observed for IV. That is, electron correlation increases the bond distances and affects most of the bond angles very little. Moreover, for all of these structures the bond angles $\angle CO_3N$ and $\angle NO_2H_3$ are decreased by between 2 and 3°. It is noteworthy that of the forms V–XI, only VI and VII are predicted to be minima on the $CH_3NO_3H^+$ potential energy surface. Inspection of the normal mode corresponding to the imaginary frequency indicates that V is a transition state connecting equivalent forms of IV due to rotation of the methyl group. Similarly, it may be shown that X is a transition state connecting equivalent forms of VI, and XI is a transition state connecting equivalent forms of VII, both due to rotation of the methyl group. Isomer VIII, on the other hand, is a transition state connecting equivalent forms of VII, but due to rotation about the N–O_2 bond. The Hessian index for IX is 2.

The harmonic vibrational frequencies for the various structures of protonated methyl nitrate, including IR intensities for isomers that are minima, are presented in Tables IX–XI. Table IX contains the harmonic frequencies of II and III, i.e., those forms corresponding to a complex between CH_3OH and NO_2^+. Focusing on the MP2/DZP harmonic frequencies of II, it is evident that the harmonic frequencies of the individual monomers, i.e., CH_3OH and NO_2^+, are for the most part not greatly affected by complexation. For comparison, the ab initio harmonic frequencies of CH_3OH are presented in Table XII, and those for NO_2^+ are given in our earlier study.[3] For methanol the largest change due to complexation is only 77 cm^{-1} for the antisymetric combination of the C–H_2 stretches (see Figure 2). The other CH_3OH normal modes that are most affected by complexation are the other C–H stretches, the C–O stretch, and the methyl rotation. Because of

Table X. Harmonic Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for Several Structures of Protonated Methyl Nitrate, Obtained with the DZP Basis Set[a]

		V	VI	IV	
	approximate description	SCF	SCF	SCF	MP2
$\omega_1(a')$	OH str	3975	3988 (358.1)	3973 (369.1)	3664 (319.9)
$\omega_2(a')$	CH str	3436	3430 (1.8)	3431 (1.8)	3339 (4.7)
$\omega_3(a')$	CH sym str	3289	3277 (1.6)	3276 (1.9)	3163 (0.7)
$\omega_4(a')$	NO_1 str	1995	2079 (315.7)	2000 (407.0)	1729 (183.6)
$\omega_5(a')$	HCH bend	1672	1606 (146.9)	1673 (85.7)	1511 (22.2)
$\omega_6(a')$	HCH sym bend	1604	1590 (44.6)	1592 (22.2)	1500 (61.7)
$\omega_7(a')$	HON bend	1577	1547 (306.3)	1579 (8.9)	1468 (22.0)
$\omega_8(a')$	$NO_2 - NO_3$ str	1398	1444 (140.9)	1407 (447.2)	1283 (524.6)
$\omega_9(a')$	HCO bend	1323	1305 (39.0)	1304 (109.1)	1219 (94.4)
$\omega_{10}(a')$	$NO_2 + NO_3$ str	1119	1104 (64.3)	1123 (80.2)	1044 (6.8)
$\omega_{11}(a')$	CO str	941	940 (137.6)	959 (38.2)	903 (19.8)
$\omega_{12}(a')$	ONO bend	748	762 (8.7)	752 (1.2)	668 (0.5)
$\omega_{13}(a')$	ONO bend	556	555 (11.5)	563 (74.1)	532 (49.9)
$\omega_{14}(a')$	NOC bend	352	320 (16.9)	325 (9.6)	309 (7.0)
$\omega_{15}(a'')$	CH antisym str	3424	3410 (0.1)	3406 (0.2)	3313 (0.5)
$\omega_{16}(a'')$	HCH antisym bend	1588	1596 (22.7)	1598 (23.2)	1514 (22.7)
$\omega_{17}(a'')$	HCON tor	1252	1260 (4.2)	1262 (4.8)	1174 (3.4)
$\omega_{18}(a'')$	HCON + ONOC tor	850	844 (16.1)	857 (25.6)	729 (7.1)
$\omega_{19}(a'')$	HONO tor	554	500 (199.4)	551 (185.6)	544 (167.4)
$\omega_{20}(a'')$	methyl rot + HCON tor	157	200 (1.2)	201 (4.9)	195 (5.5)
$\omega_{21}(a'')$	methyl rot + HCON tor	171*i*	160 (7.0)	162 (6.4)	165 (1.6)

[a] See Figure 2 for labeling of atoms. IR intensities are in parentheses; rot = rotation and tor = torsion.

Table XI. Harmonic Vibrational Frequencies (cm^{-1}) for Several Structures of Protonated Methyl Nitrate, Obtained at the SCF/DZP Level of Theory[a]

	VII	VIII	IX	X	XI
$\omega_1(a')$	3953	4062	4095	3990	3959
$\omega_2(a')$	3432	3408	3399	3435	3453
$\omega_3(a')$	3283	3247	3277	3289	3296
$\omega_4(a')$	2049	2106	2094	2076	2041
$\omega_5(a')$	1659	1603	1637	1604	1670
$\omega_6(a')$	1592	1594	1603	1602	1606
$\omega_7(a')$	1569	1519	1509	1546	1565
$\omega_8(a')$	1360	1368	1363	1436	1373
$\omega_9(a')$	1290	1296	1277	1320	1277
$\omega_{10}(a')$	1163	1171	1184	1099	1172
$\omega_{11}(a')$	924	941	925	923	909
$\omega_{12}(a')$	689	684	666	758	685
$\omega_{13}(a')$	595	606	583	548	579
$\omega_{14}(a')$	337	337	365	349	365
$\omega_{15}(a'')$	3419	3367	3426	3426	3428
$\omega_{16}(a'')$	1601	1619	1562	1589	1586
$\omega_{17}(a'')$	1254	1253	1245	1248	1246
$\omega_{18}(a'')$	841	824	812	838	833
$\omega_{19}(a'')$	566	116*i*	265*i*	506	558
$\omega_{20}(a'')$	204	287	192	157	110
$\omega_{21}(a'')$	124	189	195*i*	172*i*	178*i*

[a] See Figures 2 and 3 for labeling of atoms. See Table X for approximate descriptions of the normal modes.

the obvious attractive interaction between H_1 and O_2 (see Figure 2), it is not too surprising that the methyl rotation harmonic frequency ω_{12} increases by 45 cm^{-1} due to complexation. In fact, it is partly due to this attractive interaction that $CH_3OH\cdots NO_2^+$ is more strongly bound than $H_2O\cdots NO_2^+$.[3] Most of the harmonic frequencies of NO_2^+ are not greatly affected by complexation, but the in-plane bending mode is decreased by 103 cm^{-1}, which is nearly twice the change observed for the $H_2O\cdots NO_2^+$ complex. Thus the harmonic frequencies of II are consistent with a $CH_3OH\cdots NO_2^+$ complex that is more strongly bound than the $H_2O\cdots NO_2^+$ complex.

The harmonic frequencies presented in Tables X and XI explicitly show that isomers IV, V, and VII are minima on the $CH_3NO_3H^+$ potential energy surface. With the exception of the frequencies corresponding to methyl rotation and rotation about the N–O_2 single bond (see Figures 2 and 3), the harmonic frequencies are similar for all of the structures IV–XI. The two normal modes with imaginary frequencies for some forms correspond to rotation of the methyl group and rotation about the N–O_2 bond (described in Table X as HONO torsion). It is expected that the MP2/DZP harmonic frequencies of IV should have an accuracy relative to experiment similar to that found for Ia. Thus, should it be possible to isolate IV, perhaps via a matrix isolation technique, the frequencies and IR intensities given in Table X will be useful in its identification.

In order to obtain a reliable binding energy for the complex II, it is necessary to investigate CH_3OH and NO_2^+ at the same levels of theory. Because NO_2^+ is produced in the protonation of nitric acid, it was included in our earlier study.[3] Table XII contains the dipole moment, equilibrium geometry, and harmonic vibrational frequencies of CH_3OH, obtained at the various levels of theory. The experimental dipole moment,[35] vibrationally averaged geometry,[36] and fundamental vibrational frequencies[37] are also given for comparison. The T_1 diagnostic for the CCSD/DZP and CCSD(T)/DZP equilibrium structures is found to be relatively small (only 0.009), and consequently it is not surprising that the MP2/DZP, CCSD/DZP, and CCSD(T)/DZP geometries agree very well. The harmonic frequencies at these three levels of theory also agree very well, with the exception of ω_2, ω_3, and ω_9. These normal modes all correspond to C–H stretching vibrations, and the MP2 values are between 40 and 60 cm^{-1} too high relative to the more reliable CCSD(T) quantities, with the CCSD values falling between MP2 and CCSD(T) frequencies. The MP2/TZ2P dipole moment, equilibrium geometry, and harmonic frequencies are in good agreement with the relevant experimental data—especially taking into consideration that the experimental geometry is a vibrationally averaged structure and that the experimental frequencies correspond to fundamental frequencies.

3c. Energetics. The energies of molecules Ib–XI relative to Ia are given in Table XIII. The last column in Table XIII refers to the amount that II is bound with respect to the separated monomers $CH_3OH + NO_2^+$. The relative energies do not contain effects due to zero-point vibrational energies (ZPVE) or basis set superposition errors. These effects will be discussed below. For convenience, the energy difference between Ib and Ia will be denoted ΔE_{Ib}, and similarly for the other structures. The binding energy of II relative to separated monomers will be designated ΔE_M.

Since ΔE_{Ib} is simply a barrier height with respect to rotation about a single bond, it is little affected by basis set augmentation

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Table XII. Total Energies (E_H), Equilibrium Bond Lengths (Å), Bond Angles (deg), Dipole Moments (D), Harmonic Frequencies (cm^{-1}), and IR Intensities (km/mol) for CH_3OH, Obtained at Various Levels of Theory[a]

	SCF/DZP	MP2/DZP	CCSD/DZP	CCSD(T)/DZP	MP2/TZ2P	expt[b]
E[c]	0.074 524	0.435 173	0.429 426	0.436 812	0.534 119	
T_1			0.009	0.009		
μ	1.90	1.87	1.86	1.84	1.75	1.66
r_{CH_1}	1.083	1.089	1.092	1.093	1.081	1.094
r_{CH_2}	1.089	1.095	1.098	1.099	1.086	1.094
r_{CO}	1.402	1.425	1.426	1.429	1.427	1.421
r_{OH_3}	0.943	0.964	0.963	0.964	0.958	0.963
$\angle H_1CH_2$	108.4	108.6	108.6	108.6	108.6	108.7
$\angle H_2CH_2$	108.7	108.9	108.9	108.9	109.2	108.5
$\angle H_1CO$	107.3	106.3	106.5	106.4	106.6	107.0
$\angle COH_3$	109.8	107.7	107.8	107.6	107.9	108.0
$\omega_1(a')$	4213 (47.8)	3932 (26.2)	3933 (18.1)	3911 (15.6)	3904 (43.1)	3681
$\omega_2(a')$	3299 (53.4)	3250 (30.0)	3207 (36.3)	3194 (36.6)	3226 (10.2)	3000
$\omega_3(a')$	3176 (76.3)	3096 (59.3)	3071 (60.6)	3054 (62.2)	3097 (38.8)	2844
$\omega_4(a')$	1634 (5.1)	1553 (4.3)	1548 (4.3)	1533 (5.6)	1560 (6.7)	1477
$\omega_5(a')$	1616 (9.6)	1525 (7.1)	1524 (8.0)	1512 (6.9)	1502 (1.6)	1455
$\omega_6(a')$	1480 (43.6)	1393 (25.6)	1405 (29.8)	1397 (28.4)	1395 (22.3)	1345
$\omega_7(a')$	1187 (102.8)	1104 (5.3)	1105 (14.2)	1093 (3.0)	1093 (9.8)	1060
$\omega_8(a')$	1154 (55.0)	1082 (118.7)	1086 (104.6)	1075 (112.6)	1045 (99.7)	1033
$\omega_9(a'')$	3234 (98.7)	3186 (63.9)	3144 (72.4)	3128 (72.8)	3172 (25.2)	2960
$\omega_{10}(a'')$	1623 (2.1)	1537 (2.1)	1531 (1.6)	1523 (1.6)	1548 (4.7)	1477
$\omega_{11}(a'')$	1278 (2.2)	1194 (0.5)	1193 (1.1)	1182 (1.0)	1191 (0.1)	1165
$\omega_{12}(a'')$	334 (148.0)	332 (134.1)	326 (131.5)	324 (129.7)	285 (108.9)	295

[a] Intensities are in parentheses. [b] Dipole moment from ref 35; vibrationally averaged geometry from ref 36; fundamental frequencies from ref 37. [c] The energy is reported as $-(E + 115)$.

Table XIII. Energetics (kcal/mol) of CH_3NO_3 and $CH_3NO_3H^+$, Relative to the Most Stable Form of CH_3NO_3 (Ia)[a]

method	Ib	II	III	IV	V	VI	VII	VIII	IX	X	XI	monomers[b]
SCF/DZP[c]	2.6	−173.7	−172.8	−184.7	−182.9	−184.0	−181.2	−170.3	−166.9	−182.2	−179.3	21.7
MP2/DZP[c]	2.2	−192.7	−191.8	−179.3	−177.7	−177.5	−175.6	−164.4	−161.2	−175.9	−173.6	22.2
MP2/TZ2P[c]		−194.2		−177.9		−176.4						21.7
CCSD/DZP[c]		−181.4		−184.0								22.4
CCSD(T)/DZP[c]		−183.6		−183.0								22.5
CCSD/ANO1[d]	2.4	−181.1	−180.3	−182.3	−180.5	−181.7	−179.1	−170.6	−167.1	−179.9	−176.9	21.5
CCSD(T)/ANO1[d]	2.3	−184.1	−183.3	−180.8	−179.1	−180.0	−177.7	−169.3	−165.8	−178.4	−175.5	21.5
CCSD/ANO1[e]		−183.8		−182.3								21.3
CCSD(T)/ANO1[e]		−186.0		−180.8								21.3
CCSD/ANO2[e]		−180.9		−181.1								21.8
CCSD(T)/ANO2[e]		−182.9		−179.5								21.8

[a] Zero-point vibrational energies not included. See text for energy differences that include zero-point effects. [b] Energy difference between II and the separated $CH_3OH + NO_2^+$ monomers. [c] Geometries optimized at the same level of theory. [d] Geometries optimized at the MP2/DZP level of theory. [e] Geometries optimized at the MP2/TZ2P level of theory.

and the treatment of electron correlation. The different ΔE_{Ib} values only span a range of 0.4 kcal/mol. The best computed ΔE_{Ib} value is 2.3 kcal/mol, which compares very well with the study of Smith and Marsden[8] (2.6 kcal/mol) and also with experiment[38] (2.8 kcal/mol).

The ΔE_{III} and ΔE_V–ΔE_{XI} energy differences are included in Table XIII for completeness. At each level of theory used, the magnitude of ΔE_{III} is always slightly smaller than the magnitude of ΔE_{II}, indicating that II is the lowest energy complex between CH_3OH and NO_2^+. Additionally, at each level of theory structures V–XI are higher in energy than IV, demonstrating that IV is the lowest energy form of protonated methyl nitrate in which the nitro group is protonated.

Of main interest here is to compare ΔE_{II} and ΔE_{IV} in order to determine the structure of the lowest energy isomer of protonated methyl nitrate. CCSD(T), our highest level of theory, consistently yields a larger magnitude for ΔE_{II} relative to ΔE_{IV}. At the CCSD(T)/ANO2 level of theory ΔE_{II} and ΔE_{IV} are −182.9 and −179.5 kcal/mol, respectively. While electron correlation favors II relative to IV, comparison of the ANO1 and ANO2 CCSD(T) ΔE_{II} and ΔE_{IV} values indicates that improvements in the one-particle basis set seem to favor IV relative to II. It is also clear from the energy differences in Table XIII that ΔE_{IV} is converging more rapidly than ΔE_{II} with respect to electron correlation treatment and improvements in the one-particle basis set. Since only a limited selection of ANO basis sets could be used in these calculations, it is somewhat difficult to assign reliably an estimated uncertainty for these energy differences. However, based upon the results in Table XIII and our earlier study of protonated nitric acid,[3] we may estimate that −182.9 kcal/mol for ΔE_{II} is accurate to ±5 kcal/mol and −179.5 kcal/mol for ΔE_{IV} is accurate to ±3 kcal/mol. Thus, without correction for ZPVE, it is not certain which isomer (II or IV) is the lowest energy form of protonated methyl nitrate.

Zero-point vibrational energy effects on ΔE_{II} and ΔE_{IV} may be estimated in two ways. Using the MP2/DZP harmonic frequencies for the relevant molecules, ZPVE reduces the magnitude of ΔE_{II} and ΔE_{IV} by 6.3 and 7.9 kcal/mol, respectively. Grev et al.[39] have suggested that accurate zero-point vibrational energies may be obtained by scaling SCF/DZP harmonic frequencies by 0.91. Note that this scale factor is different from that proposed by Pople and co-workers,[40] as the anharmonic correction to fundamental frequencies is different from that for the ZPVE. Using this approach we obtain ZPVE corrections to ΔE_{II} and ΔE_{IV} of 6.0 and 7.5 kcal/mol, which are slightly smaller than the values obtained from the MP2/DZP harmonic frequencies. Using the latter ZPVE corrections, our best estimates for ΔE_{II} and ΔE_{IV} are −176.9 ± 5 and −172.0 ± 3 kcal/mol. The computed PA of

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methyl nitrate is thus 176.9 ± 5 kcal/mol (the PA is $-\Delta E_{II}$), which is in excellent agreement with the experimental value of 176 kcal/mol.[4]

While there remains some overlap of the possible ΔE_{II} and ΔE_{IV} values, the results of this study suggest that isomer II is the lowest energy form of protonated methyl nitrate, although IV may be close in energy. A more appropriate approach to determining which is lower in energy is to compute directly the energy difference between II and IV. Performing this for the levels of theory defined in the last four rows of Table XIII, and including ZPVEs, we obtain 3.0, 6.7, 1.3, and 4.9 kcal/mol with the positive sign indicating that II is lower in energy than IV. Interestingly, the energy difference between II and IV is converging more rapidly with respect to basis set improvements than is ΔE_{II}. The best computed energy difference between II and IV is 4.9 kcal/mol, and a conservative estimate for the uncertainty is ±4 kcal/mol, which shows that at one extreme II and IV may be nearly isoenergetic or at the other extreme II may be 9 kcal/mol lower in energy than IV. Therefore, it is reasonable to take II as the lowest energy isomer of protonated methyl nitrate.

The binding energy of II relative to separated monomers, ΔE_M, is found to be insensitive with respect to improvements in the one-particle basis set and also with respect to the inclusion of electron correlation. In fact, the ΔE_M values in Table XIII only span a range of 1.2 kcal/mol. The best computed ΔE_M value is 21.8 kcal/mol with a conservative uncertainty of 2 kcal/mol. Incorporating the ZPVE effects, via the procedure outlined by Grev et al., reduces this value by 1.1 kcal/mol. In addition, estimating the BSSE by the counterpoise method[41] (performed at the CCSD(T)/ANO2 level of theory) results in a further reduction of 1.1 kcal/mol. Our best estimate for ΔE_M is thus 19.6 ± 2 kcal/mol.

It is of interest to compare the current ab initio results for methyl nitrate with our earlier study of nitric acid in which similar levels of theory were applied. In both cases the lowest energy form of the protonated species is a complex involving NO_2^+ with either H_2O or CH_3OH for nitric acid and methyl nitrate, respectively. The PAs of nitric acid and methyl nitrate are computed to be 182.5 ± 4 and 176.9 ± 5 kcal/mol, respectively. Although there is some overlap in the ranges of the PA values, as similar levels of theory were used in both studies it is likely that the error in the two results will also be similar (i.e., systematic). More importantly, however, the ab initio results *do not* support the expectation that the PA of methyl nitrate should be 8–15 kcal/mol larger than the PA of nitric acid. Conversely, if we focus on the PA values that would be derived from the *second* most stable isomers of protonated nitric acid and protonated methyl nitrate (that is, those isomers arising from protonation of the nitro group), then this simple expectation is born out. The second most stable isomer of protonated nitric acid has a PA of 161.2 ± 2 kcal/mol while the second most stable isomer of protonated methyl nitrate has a PA of 172.0 ± 3 kcal/mol. It is thus apparent that a different chemical intuition must be applied when examining the relative PA values derived from the complexes $H_2O\cdots NO_2^+$ and $CH_3OH\cdots NO_2^+$.

We start with the chemical equations for protonation of nitric acid and methyl nitrate (note that all of these computations are for 0 K)

$$HNO_3 + H^+ \rightarrow H_2O\cdots NO_2^+ + \Delta E_1 \qquad (1)$$

$$CH_3NO_3 + H^+ \rightarrow CH_3OH\cdots NO_2^+ + \Delta E_2 \qquad (2)$$

ΔE_1 is −PA of nitric acid, and ΔE_2 is −PA of methyl nitrate. Taking eqs 1 and 2 one step further to the dissociated monomers, we have

$$HNO_3 + H^+ \rightarrow H_2O + NO_2^+ + \Delta E_3 \qquad (3)$$

$$CH_3NO_3 + H^+ \rightarrow CH_3OH + NO_2^+ + \Delta E_4 \qquad (4)$$

In this case, ΔE_3 is given by −PA of nitric acid plus the binding energy of the complex $H_2O\cdots NO_2^+$ (17.3 kcal/mol), and, similarly, ΔE_4 is −PA of methyl nitrate plus the binding energy of the $CH_3OH\cdots NO_2^+$ complex (i.e., ΔE_M in this work). Using our best ab initio values for these quantities, we obtain −165.2 and −157.3 kcal/mol for ΔE_3 and ΔE_4, respectively. Subtracting eq 4 from eq 3 we obtain the reaction

$$HNO_3 + CH_3OH \rightarrow H_2O + CH_3NO_3 + \Delta E_5 \qquad (5)$$

ΔE_5 is thus given by $\Delta E_3 - \Delta E_4$, which is −7.9 kcal/mol, again using our best ab initio energy differences. Following the above analysis, it is clear that ΔE_5 represents the difference between the PAs of nitric acid and methyl nitrate plus the difference between the binding energies of the $H_2O\cdots NO_2^+$ and $CH_3OH\cdots NO_2^+$ complexes. Of the −7.9 kcal/mol value for ΔE_5, −5.6 kcal/mol arises due to the difference of the PA values and −2.3 kcal/mol is due to the difference in the complex binding energies. It has been shown that the uncertainty associated with our ab initio determination of the complex binding energies is small, and so the −2.3 kcal/mol component of ΔE_5 should be reliable. It is possible then to determine ΔE_5 via other means in order to establish the reliability of our ab initio PA values for nitric acid and methyl nitrate. The above analysis demonstrates that the relative PA values of nitric acid and methyl nitrate are dependent on the enthalpy of reaction 5 and not simply on the relative σ donating abilities of hydrogen and a methyl group.

Reaction 5 is known as an isodesmic reaction[40]—there are the same number of C–H, C–O, O–H, and N–O single bonds and the same number of N–O multiple bonds on each side of the reaction. It is well-established that the enthalpy of this type of reaction is predicted with reasonable accuracy even at low levels of ab initio theory. Thus it should be possible to predict very accurately the *difference* in the PAs of nitric acid and methyl nitrate even though evaluation of the individual PAs is more difficult. In other words, accepting that (1) the component of ΔE_5 due to the difference in the binding energies of the complexes is very accurately determined using ab initio methods and (2) that the total ΔE_5 can be accurately determined using ab initio methods, then the *difference* in the PAs of nitric acid and methyl nitrate may be accurately determined. We have performed additional calculations of the reactants and products in eq 5 using a [4s3p2d1f] ANO basis set for the heavy atoms and a [4s2p1d] ANO basis set for hydrogen. For consistency, MP2/TZ2P equilibrium geometries have been used, and the ZPVEs have been obtained using SCF/DZP harmonic frequencies and scaling as suggested by Grev et al. ΔE_5 is determined to be −7.5, −6.3, and −6.9 kcal/mol at the MP2, CCSD, and CCSD(T) levels of theory, respectively. The small variation of ΔE_5 among the different correlation treatments is evidence that ΔE_5 is rather insensitive to the particular treatment of electron correlation used. We may also evaluate ΔE_5 at the MP2, CCSD, and CCSD(T) levels using the DZP basis set and the respective DZP equilibrium geometries. Adopting this approach we obtain −7.4, −6.2, and −6.9 kcal/mol for ΔE_5 at the MP2, CCSD, and CCSD(T) levels of theory, respectively. Not surprisingly, ΔE_5 is also rather insensitive to augmentation of the one-particle basis set. Taking −6.9 kcal/mol as our best computed ΔE_5 value and subtracting −2.3 kcal/mol due to the difference in the complex binding energies, a value of −4.6 kcal/mol is obtained for the difference in the PAs of nitric acid and methyl nitrate—the negative quantity indicating that the PA of nitric acid is *larger* than the PA of methyl nitrate.

Gas-phase experimental heats of formation may also be used to determine ΔE_5. Obtaining ΔH_f^{298} for H_2O and HNO_3 from ref 42 and that for CH_3OH and CH_3NO_3 from ref 43, a value of −7.5 kcal/mol is obtained for ΔE_5^{298}. Correcting our computed ΔE_5 for thermal population of vibrational energy levels[44] at 298 K gives an ab initio ΔE_5^{298} value of −6.3 kcal/mol, which is in

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excellent agreement with the experimental quantity. Hence there is also strong experimental evidence that the PA of nitric acid is *larger* than the PA of methyl nitrate. Moreover, the excellent agreement between the ab initio and experimental ΔE_5^{298} values lends strong support to the reliability of our computed PAs for nitric acid and methyl nitrate. Since a gas-phase experimental estimate of ΔH_f^0 is not available for methyl nitrate, it is not possible to directly determine an experimental ΔE_5. Therefore, for later purposes we add the theoretical $\Delta E_5^{298} - \Delta E_5$ difference to estimate an experimental ΔE_5 value of −8.1 kcal/mol.

It is possible to understand the relative PA values of nitric acid and methyl nitrate by examining the HO–H, CH_3O–H, HO–NO_2, and CH_3O–NO_2 bond energies (hereafter referred to as $D_0(1)$, $D_0(2)$, etc. $D_0(1)$ and $D_0(2)$ are reasonably well-established,[43,45–48] and it is not surprising that the first bond energy is larger than the second due to the better σ donating ability of methyl relative to hydrogen. However, the difference between $D_0(1)$ and $D_0(2)$ is about 12 kcal/mol, which greatly favors a larger PA for nitric acid relative to methyl nitrate. We are not aware of any experimental or theoretical determinations of $D_0(3)$ or $D_0(4)$, although it is expected that $D_0(3)$ will be larger than $D_0(4)$ for the same reasons that $D_0(1)$ is larger than $D_0(2)$. $D_0(3)$ and $D_0(4)$ may be estimated using ΔH_f^{298} values,[42,43] for OH, NO_2, H, HNO_3, CH_3NO_3, and CH_3OH to obtain 49.3 and 42.7 kcal/mol, respectively. $D_0(3) > D_0(4)$ favors a larger PA for methyl nitrate relative to nitric acid, but the difference between $D_0(3)$ and $D_0(4)$ is not great enough to overcome the large difference between $D_0(1)$ and $D_0(2)$.

4. Conclusions

The equilibrium geometries, harmonic vibrational frequencies, IR intensities, and dipole moments of methyl nitrate, methanol, and several structures of protonated methyl nitrate have been determined at high levels of ab initio theory. The ab initio results for methyl nitrate and methanol are in good agreement with the available experimental data. The lowest energy form of protonated methyl nitrate is determined to be a complex between CH_3OH and NO_2^+, II. The binding energy of this complex, ΔE_M, is accurately determined to be 19.6 ± 2 kcal/mol. The second most stable isomer, IV, which arises due to protonation of the nitro group in methyl nitrate, is about 4.9 kcal/mol higher in energy. The uncertainty in this energy difference is conservatively estimated to be ±4 kcal/mol, and thus it is evident that II is the lowest energy isomer of protonated methyl nitrate.

The PA of methyl nitrate is determined to be 176.9 ± 5 kcal/mol, which is in excellent agreement with the experimental value 176 kcal/mol.[4] However, our computed PA for methyl nitrate is *smaller* than our previously[3] computed PA for nitric acid (182.5 kcal/mol), which is opposed to the usual observation that CH_3OA molecules have a larger PA than HOA species. This seeming discrepancy between the theoretical results has been explained in the following manner. Having established that II is the lowest energy form of protonated methyl nitrate, it is possible to set up a series of chemical reactions in order to determine the relative PAs of nitric acid and methyl nitrate. Since protonation of both nitric acid and methyl nitrate leads to the formation of a complex involving NO_2^+, it is possible to arrive at a simple isodesmic reaction, eq 5, whose enthalpy ΔE_5 is given by the difference between the PAs of nitric acid and methyl nitrate and the difference between the binding energies of the complexes. In other words, the relative PAs of nitric acid and methyl nitrate can be related to a chemical reaction that involves similar but *different* O–H and N–O single bonds.

In both this study and our earlier study,[3] it was shown that the ab initio determination of the $CH_3OH\cdots NO_2^+$ and $H_2O\cdots NO_2^+$ binding energies is very reliable. It is also well-known that the ab initio determination of the enthalpy of an isodesmic reaction is very straightforward, and we have shown explicitly for reaction 5 that ΔE_5 is sensitive neither to the particular treatment of electron correlation that is used nor to basis set improvements. ΔE_5 has been determined in three ways: (1) by using the best ab initio PA and ΔE_M values; (2) by directly computing the total energies of the reactants and products in eq 5 at a consistent level of theory; and (3) by using experimental heats of formation. These three approaches yield −7.9, −6.9, and −8.1 kcal/mol, respectively. Thus not only is there excellent agreement between theory and experiment but also the success of method 1 lends strong support to the reliability of our computed PAs of nitric acid and methyl nitrate.

The fact that ΔE_5 is negative and that its magnitude is larger than 2.3 kcal/mol (the difference in the binding energies of the $CH_3OH\cdots NO_2^+$ and $H_2O\cdots NO_2^+$ complexes) clearly shows that the PA of nitric acid *must be larger* than the PA of methyl nitrate. Hence the experimental estimate[2] (168 ± 3 kcal/mol) of the PA of nitric acid appears to be in error.

Finally, we note that our computed PA values for HNO_3 (182.5 kcal/mol) and CH_3NO_3 (176.9 kcal/mol) are for 0 K, while both experimental studies[2,4] were performed at 313 K. However, correcting our computed values for thermal population of vibrational energy levels, changes in the number of translational and rotational degrees of freedom, and the PV work term (assuming ideal gas behavior) at 313 K, the PA value of HNO_3 is changed by less than 0.1 kcal/mol and that of CH_3NO_3 is increased by 0.1 kcal/mol. Thus, temperature effects have a very small contribution.

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