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Recently, the XNO (X=H, F, Cl) molecules have been investigated using the singles and doubles coupled-cluster method that includes a perturbational estimate of the effect of connected triple excitations, denoted CCSD(T).[1–3] In one of these studies, the transition state structure for the HNO→HON isomerization was reported to have been located,[2] but we have determined that the structure reported therein appears to be the transition state for the HON→H +ON reaction and not the isomerization reaction (note that the other two transition states reported in Ref. 2 for the FNO→FON and ClNO→ClON isomerization reactions are correct). In another previous study,[3] the experimental fundamental vibrational frequencies[4] of HNO are very well reproduced by the CCSD(T) method, which attest to the reliability of the CCSD(T) method for this system.

In this letter, we present the structural, energetic, and vibrational properties of the HNO→HON transition structure (HON(TS)) using density functional theory (DFT) and the CCSD(T) approach. The particular DFT method used here is the Becke3-LYP hybrid method[5] (denoted B3LYP), as implemented within the Gaussian94/DFT quantum chemical package.[6] The 6-311+G(2d) basis set of Pople *et al.*[7] has been used in the DFT calculations. For the CCSD(T) calculations, Dunning's[8] cc-pVTZ and cc-pVQZ basis sets were used, with the quadratic force constants and vibrational frequencies having been determined with the cc-pVTZ basis set. The nitrogen and oxygen core $1s$-like molecular orbitals have been required to remain doubly occupied in the CCSD(T) calculations (i.e., the frozen core approximation), and only spherical harmonic components of the d, f, and g functions have been included in the basis.

The DFT calculations have been performed using the Gaussian94/DFT quantum chemical package,[6] while the CCSD(T) calculations have been performed using the TITAN[9] self-consistent field, transformation, and coupled-cluster programs interfaced to the SEWARD[10] integral program.

In Table I, the structural and vibrational properties of HON(TS) are reported. It is important to note that the isomerization reaction is spin forbidden if it is to connect the ground states of HON ($^3A''$) and HNO ($^1A'$).[11] Here we have considered HON, HNO, and HON(TS) in their $^1A'$ electronic state (closed-shell systems with $<S^2>=0$). Com-

parison of the CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ geometries shows that the CCSD(T) one-particle basis set limit has nearly been achieved. Indeed, the difference between the CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ HON(TS) geometries is very small. In addition, the $\mathcal{T}_1$ diagnostic[12] for the CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ calculations (0.036 and 0.034, respectively) indicates that CCSD(T) level of theory should perform well for HNO(TS).

A further inspection of the geometrical parameters shows that the DFT results agree well with the CCSD(T) ones, and are in best agreement with the CCSD(T)/cc-pVQZ quantities although the [DFT−CCSD(T)/cc-PVQZ] difference is quite a bit larger than the [CCSD(T)/cc-pVTZ −CCSD(T)/cc-PVQZ] difference. We note that ∠HON ≈62° is between those for HNO ∠HON(HNO)≈33° and HON ∠HON(HON)≈112°, as it should be in order to connect the HNO and HON minima. The N–O bond distance varies as NO<HNO<HON<HON(TS), which correlates with the N–O bond force constant variation, i.e., NO>HNO >HON>HON(TS). As shown in Table I, one imaginary frequency has been found, corresponding to the HNO bending mode, which indicates a first-order transition state.

A comparison of the [HON(TS)−HNO] energy differences (i.e., the barrier height from the HNO minimum), shows that there is qualitative agreement among the three levels of theory, with the DFT quantity being 4.4 kcal mol^{-1} larger than the CCSD(T)/cc-pVQZ value. Again, the difference between the CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ barrier heights (0.5 kcal mol^{-1}) shows that the CCSD(T)/cc-pVQZ value is very close to the CCSD(T) one-particle basis set limit.

The HON/HNO isomerization energy computed at the DFT level of theory (41.2 kcal mol^{-1}) is in good agreement with an accurate value determined previously[2] at the CCSD(T)/$spdfg$ level of theory (42.5 kcal mol^{-1}). Since the heat of formation of HNO is now well known,[13] it is easily seen that HON is only weakly bound relative to the H+ON dissociated products, and therefore that HON(TS) is well above this dissociation channel. Thus the large

TABLE I. Structural and vibrational properties of HON(TS).

Parameters	DFT	CCSD(T)/ cc-pVTZ	CCSD(T)/ cc-pVQZ
r_{N-O} (Å)	1.322	1.341	1.335
r_{H-O}	1.114	1.101	1.103
$\angle$HON (deg.)	62.3	62.0	62.1
E (au)[a]	$-130.394\,130$	$-130.182\,330$	$-130.221\,227$
ΔE (kcal mol^{-1})[b]	77.8	72.9	73.4
Harmonic frequencies			
ω_1 (cm^{-1})	2759.9	2820.2	
ω_2	2287.9i	2201.0i	
ω_3	1257.6	1174.3	
f_{NO} (aJ/Å^2)[c,d]	6.90	5.63	

[a]The electronic energy of HNO is $-130.518\,123$, $-130.298\,456$, and $-130.338\,133$ a.u. by DFT, CCSD(T)/cc-pVTZ, and CCSD(T)/cc-pVQZ, respectively.

[b]The barrier height without ZPE corrections.

[c]The DFT value of f_{NO} is 16.79, 12.56, and 8.37 aJ/Å^2, for NO, HNO, and HON, respectively.

[d]For completeness, the CCSD(T)/cc-pVTZ unique quadratic force constants are: $f_{11} = 2.521\,25$, $f_{21} = 1.846\,36$, $f_{22} = 5.630\,39$, $f_{31} = 3.528\,43$, $f_{32} = -0.653\,12$, and $f_{33} = -0.721\,36$, given in units consistent with energy in aJ, bond lengths in Å, and bond angle in radians. Here 1 and 2 label the OH and NO stretches and 3 refers to the HON angle.

HNO→HON barrier height obtained in the present work implies that the isomerization to HON should not occur to any appreciable degree even in rather severe combustion environments.

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