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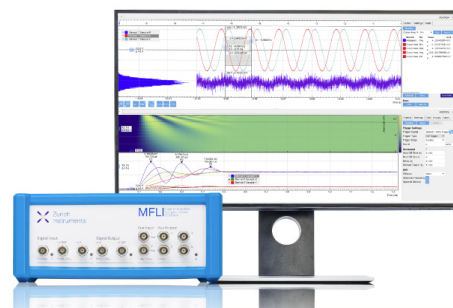
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The weakly bound dinitrogen tetroxide molecule: High level single reference wavefunctions are good enough

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Ab initio studies of dinitrogen tetroxide (N_2O_4) have been performed to predict the equilibrium geometry, harmonic vibrational frequencies, and fragmentation energy ($N_2O_4 \rightarrow 2 NO_2$). The structure was optimized at the self-consistent field, configuration interaction, and coupled-cluster levels of theory with large basis sets. At the highest level of theory, the N–N bond distance was 1.752 Å, in excellent agreement with the experimental value of 1.756 ± 0.01 Å. In addition, the harmonic vibrational frequencies were predicted with an average absolute error of 51 cm^{-1} relative to experimental fundamental values with differences largely attributed to anharmonic effects. The fragmentation energy corrected for zero point vibrational energy and basis set superposition error was 7.2 kcal/mol, in fair agreement with the experimental value of 12.7 kcal/mol. Despite the suggestion that a multireference wavefunction may be necessary to accurately describe the biradical nature of N_2O_4 , single reference treatments with large basis sets and high levels of electron correlation yield molecular parameters remarkably close to experimental values. © 1997 American Institute of Physics. [S0021-9606(97)01517-1]

I. INTRODUCTION

The properties of nitrogen oxides and their reactions with ozone have been of considerable interest in atmospheric and environmental chemistry. Many NO_x species, including nitrogen dioxide radicals, are believed to play important roles in ozone depletion cycles in the stratosphere and also in the formation of acid rain and smog in the troposphere. Because of the tendency of nitrogen dioxide radicals to form weakly bound dimers, the resulting species, dinitrogen tetroxide (N_2O_4), has been the subject of a number of experimental and theoretical investigations.^{1–4}

Dinitrogen tetroxide has no permanent dipole moment and, consequently, has no pure rotational spectrum from which the molecular structure might be deduced. However, experimental studies including gas phase electron diffraction,⁵ rotationally resolved infrared spectroscopy,⁶ and solid state neutron diffraction⁷ have revealed that the most stable conformation is planar (D_{2h}) with a nitrogen-nitrogen linkage between the NO_2 monomers as shown in Fig. 1. The N–N bond distance is exceptionally long (1.75–1.78 Å) while the N–O bond distances and angles remain virtually unchanged from free NO_2 . The long N–N bond is also rather weak, as evidenced by the experimentally determined fragmentation enthalpy. Hisatsune's estimate⁸ for the ΔH at absolute zero is a modest 12.7 kcal/mol for the $N_2O_4 \rightarrow 2 NO_2$ reaction.

It is interesting to note the difference between the nitrogen-nitrogen bond in N_2O_4 and that of the conventional single bonded hydrazine (N_2H_4), which has a substantially shorter bond length of 1.47 Å.⁹ Several qualitative arguments for the seemingly anomalous N–N bond length in the planar N_2O_4 molecule have been introduced including Smith and

Hedberg's proposal¹⁰ of a “ π -only” bond, Pauling's arguments¹¹ for σ -contribution, and Bent's reasoning¹² using so-called “splayed” σ -bonds. However, the difficulty in describing the N–N bond in N_2O_4 has not been limited to conflicts in qualitative arguments. Previous *ab initio* studies^{7,13–15} using the Hartree–Fock self-consistent field (SCF) method have correctly described the planar nature of the molecule but have underestimated the N–N bond distance by as much as 0.2 Å and dictate the need for theoretical methods including electron correlation.

In 1983, Bauschlicher, Komornicki, and Roos¹⁵ studied the N–N bond in N_2O_4 in detail. Their calculations using configuration interaction with single and double excitations (CISD) within a double zeta basis set plus polarization functions (DZP) still resulted in a short N–N bond distance (1.62 Å). Those authors also reported that the SCF reference accounted for only 84% of the CI wavefunction, implying that a single reference wavefunction may be insufficient to correctly describe the weakly bound dimer. The principal effort of the study, however, was a series of complete active space SCF (CASSCF) calculations within a DZP basis set. Noting that the N–O bond distances and angles remained essentially identical to NO_2 , they fixed nearly all degrees of freedom and focused only on the N–N bond. Although the authors state their primary goal was only to provide a better *qualitative* assessment of the N–N bond, their value of 1.80 Å (using their most extensive CAS including 18 electrons correlated in 12 valence orbitals) is in much better agreement with the experimental values than single reference DZP-CISD, and they concluded that a multiconfiguration reference wavefunction may be needed for a proper description of N_2O_4 . On the other hand, they also point out one example where the CASSCF approach overemphasizes the effect of antibonding configurations in the wavefunction and produces bond lengths which are too long relative to the experiment.¹⁶

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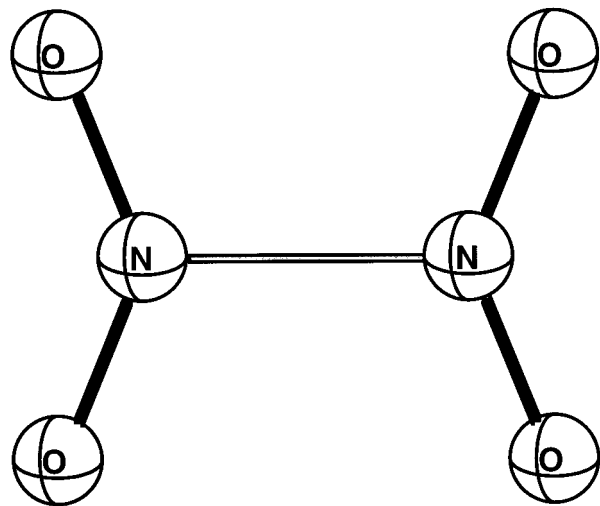


FIG. 1. Sketch of the D_{2h} structure of N_2O_4 .

Another theoretical study employing a multireference wavefunction is that of Koput,¹⁷ who used second order perturbation theory starting from a CASSCF reference function (CASPT2)^{18,19} within a correlation-consistent polarized basis set with as many as 230 contracted Gaussian functions. Like the CASSCF wavefunction of Bauchlicher *et al.*,¹⁵ the active space included 18 electrons in 12 orbitals. With no molecular orbitals held doubly occupied in the dynamical correlation treatment, the N–N bond distance was found to be 1.7940 Å, and the fragmentation energy ($N_2O_4 \rightarrow 2 NO_2$) was 9.6 kcal/mol. This fragmentation energy value includes an experimentally derived estimate of zero point vibrational energy difference and is in good agreement with the experimental value of 12.7 kcal/mol relative to the single reference 6-311 + G(2*d*,2*p*)-MP2 value of 23.9 kcal/mol obtained by Jursic.²⁰ However, the value for the N–N bond length is not substantially improved by the additional perturbative treatment of the CASSCF wavefunction.

Koput also calculated CASPT2 parameters within the frozen core approximation (the six 1*s*-like core orbitals of the two nitrogen and four oxygen atoms were held doubly occupied in the dynamical correlation treatment). These frozen core CASPT2 values were compared to single reference MP2 molecular parameters obtained within the same basis set and frozen core approximation. Interestingly, the values for the bond lengths and angles as well as the total energy for the single- and multireference calculations are virtually identical. For example, the two methods predict N–N bond lengths which differ by only 0.001 Å—the structural parameter for which a multireference description was thought to be necessary. The similarity in the single- and multireference values is somewhat surprising in light of the previous study by Bauchlicher *et al.*,¹⁵ in which the CI-expansion coefficient of the SCF reference configuration in the CASSCF wavefunction is 0.906 and there are 14 excited configurations with coefficients greater than 0.05. Koput further reports that, like Jursic, his single reference MP2 calculations

for the fragmentation energy fail, yielding “completely unreasonable” results.^{17,20} Although the similarity in single- and multireference geometrical parameters may very well be fortuitous, these findings initially suggest that inclusion of nondynamical correlation by using a multireference wavefunction may not be required to accurately predict molecular properties of N_2O_4 .

Dinitrogen tetroxide is the only molecule among the dinitrogen oxides (other than N_2O) for which the experimental vibrational assignments are well established.²¹ Dyer and Hendra²² recently produced the first gas phase Raman spectrum of NO_2/N_2O_4 and have made assignments for the N_2O_4 symmetric modes with slight shifts of frequencies relative to previous studies²³ in the solid phase. In 1993 Liu and Zhou²⁴ predicted harmonic vibrational frequencies for dinitrogen tetroxide using second order Møller–Plesset perturbation theory (MP2) within a 6-311G* basis set. A year later Stirling, Pápai, Mink, and Salahub²¹ conducted a density functional (DFT) study of various nitrogen oxides including N_2O_4 , and in 1996 Jursic²⁰ also performed both DFT and MP2 studies. The MP2 studies adequately describe the geometry and spectral features of dinitrogen tetroxide and establish the D_{2h} conformer as a true minimum on the potential energy surface. Within the DFT studies, the experimental geometry was well reproduced using the local spin density approximation (LSDA) of Vosko, Wilk, and Nusair.²⁵ Various nonlocal functionals formed from combinations of Becke’s exchange functional and the correlation functionals of Lee, Yang and Parr, and Perdew (e.g., Becke3LYP,^{26,27} BP86,^{28,29} Becke3P86^{26,29}) generally increase the N–N bond length to values slightly longer than that determined by experiment. However, the nonlocal functionals produce fragmentation energies and vibrational frequencies which are much closer to those obtained experimentally. For example, the widely used Becke3LYP functional yields an N–N bond length of 1.795 Å and a fragmentation energy of 13.65 kcal/mol within a 6-311 + G(2*d*,2*p*) basis set. Despite the sometimes promising results of these types of studies, a systematic approach toward a more accurate description of N_2O_4 is still needed and may also help assess the reliability of the functionals chosen in DFT studies.

Although experimental data concerning the molecular geometry of N_2O_4 vary by as much as 0.026 Å for the N–N bond length and 1.6 degrees for the O–N–O bond angle, theoretical reproduction of values which fall within this experimental range has proven to be a difficult task.^{7,13–15} Furthermore, until recently, many of the experimental studies have been performed in the solid or liquid phase,^{23,30,31} making direct comparisons to both theoretical studies and actual atmospheric conditions more difficult. In light of the new experimental study using gas phase Raman spectroscopy²² as well as the striking similarities in molecular property predictions of single- and multireference wavefunction calculations by Koput, we present here a theoretical reinvestigation of the equilibrium geometry, vibrational frequencies, and fragmentation energy of dinitrogen tetroxide using high level single reference wavefunctions.

TABLE I. Theoretical and experimental equilibrium bond lengths (Å) and bond angles (degrees) for N₂O₄.

| Basis set | | SCF | CISD | CCSD | CCSD(T) |
|----------------------|----------------------|-----------------|--------------------|-----------------------|---------|
| DZP | $r(\text{N-N})$ | 1.578 | 1.624 | 1.681 | 1.755 |
| | $r(\text{N-O})$ | 1.170 | 1.187 | 1.208 | 1.215 |
| | $\angle\text{O-N-O}$ | 132.8 | 133.5 | 133.8 | 134.3 |
| TZ2P | $r(\text{N-N})$ | 1.588 | 1.629 | 1.687 | 1.759 |
| | $r(\text{N-O})$ | 1.157 | 1.169 | 1.188 | 1.199 |
| | $\angle\text{O-N-O}$ | 133.2 | 133.7 | 134.0 | 134.3 |
| TZ2P+ <i>f</i> /TZ2P | $r(\text{N-N})$ | 1.588 | N/A | 1.681 | 1.752 |
| | $r(\text{N-O})$ | 1.156 | N/A | 1.185 | 1.195 |
| | $\angle\text{O-N-O}$ | 133.3 | N/A | 134.3 | 134.7 |
| Expt. data | | ED ^a | ND ^b | Infrared ^c | |
| | $r(\text{N-N})$ | 1.782±0.008 | 1.7562±0.0004 | 1.756±0.010 | |
| | $r(\text{N-O})$ | 1.190±0.002 | 1.191 ^d | 1.196±0.005 | |
| | $\angle\text{O-N-O}$ | 135.4±0.6 | 134.46±0.06 | 133.8±0.6 | |

^aElectron diffraction at 252 K (Ref. 5).

^bNeutron diffraction at 20 K (Ref. 7).

^cAnalysis of rotationally resolved infrared spectra at approximately 50 K (Ref. 6).

^dLinearly extrapolated zero point value. Value at 20 K was 1.1893 ± 0.0005 Å.

II. THEORETICAL METHODS

Three basis sets were employed in this study. The first was a DZP basis consisting of the standard Huzinaga–Dunning^{32,33} set of contracted Gaussian functions with one additional set of five *d*-type polarization functions on each atom.³⁴ The contraction scheme for the double zeta portion of this basis set was N(9*s*5*p*/4*s*2*p*), O(9*s*5*p*/4*s*2*p*). A triple zeta plus double polarization (TZ2P) basis set formed by augmenting the Huzinaga–Dunning^{32,35} triple zeta basis for both N and O with two sets of five *d*-type functions³⁶ on each atom was also implemented. With the further addition of seven *f*-type functions³⁷ on the nitrogen atoms the TZ2P + *f*/TZ2P basis set was formed. The contraction scheme for the triple zeta portion of this basis set was N(10*s*6*p*/5*s*3*p*), O(10*s*6*p*/5*s*3*p*). The DZP basis set contained 90 basis functions while the TZ2P and TZ2P + *f*/TZ2P contained 144 and 158 functions, respectively.

Energies were obtained using Hartree–Fock SCF wavefunctions as well as CISD, single and double excitation coupled-cluster (CCSD), and CCSD including perturbatively applied connected triple excitations [CCSD(T)]. At the correlated levels of theory the six lowest lying molecular orbitals corresponding to the N and O 1*s* orbitals were held doubly occupied, and the corresponding six highest virtual orbitals were deleted. The closed shell singlet ground state molecular orbital occupations in *D*_{2*h*} symmetry (with the molecule lying in the *x*–*y* plane) were designated as

$$[\text{core}]3a_g^2 3b_{3u}^2 2b_{2u}^2 2b_{1g}^2 4a_g^2 4b_{3u}^2 5a_g^2 1b_{1u}^2$$

$$3b_{2u}^2 3b_{1g}^2 1b_{2g}^2 5b_{3u}^2 4b_{2u}^2 4b_{1g}^2 1b_{3g}^2 1a_u^2 6a_g^2$$

though it should be noted that the TZ2P-CISD wavefunction was constructed in the *C*_{2*v*} subgroup of *D*_{2*h*}.

The stationary point structures were completely optimized at all levels of theory within the *D*_{2*h*} symmetry constraints using analytic gradient techniques, until residual Car-

tesian coordinate gradients were less than 10^{−6} a.u. The SCF force constants for all basis sets were determined via analytic second derivatives, while the CISD, CCSD, and CCSD(T) force constants were determined by finite differences of analytic gradients. For the fragmentation energy analysis, the open shell NO₂ structures for the coupled-cluster methods were optimized by energy points, and the force constants were determined by finite differences of the energy gradients. All computations were carried out using the PSI³⁸ program package.

III. RESULTS

The geometrical parameters of N₂O₄ at their optimized *D*_{2*h*} geometries for all basis sets and theoretical methods used are presented in Table I. The N–N bond length obtained using the TZ2P + *f*/TZ2P basis set at the CCSD(T) level is 1.752 Å while the N–O bond length and O–N–O angle are 1.195 Å and 134.7°, respectively. As is clear from Table I, expansion of the basis set size from DZP to TZ2P results in only small changes in the N–N bond distance, while the N–O bond length is shortened by approximately 0.02 Å at each level of theory. The addition of *f*-type functions to the nitrogen atoms refines the geometries by only thousandths of an Angstrom for both the N–N and N–O bond distances and tenths of a degree for the bond angle, suggesting that further additions to the largest basis set would not improve the molecular parameters significantly. It should be noted, however, that for a given basis set, there is a lengthening (≈0.07 Å) of the N–N bond between the CCSD and CCSD(T) levels of theory, suggesting that connected triple excitations are important for an accurate prediction of this geometrical parameter. It is expected that the inclusion of all triple excitations via a full CCSDT^{39,40} optimization might slightly elongate the N–N bond, perhaps placing it even closer to the 1.756 Å rotationally resolved infrared experimental value.⁶ In addition, the value of the *T*₁ diagnostic,⁴¹ which has been shown

to be a useful measure of the importance of nondynamical correlation, is slightly larger than 0.02 for all basis sets. This is at the upper limit of the value suggested by Lee and Taylor,⁴¹ indicating that perhaps a multireference wavefunction might be better suited to this problem. However, due to the close comparison with the experimentally determined geometry given in Table I, as well as the apparent near-convergence of these parameters with respect to basis set and level of correlation, it is unlikely that such a treatment will significantly alter the TZ2P + *f*/TZ2P-CCSD(T) geometries reported here.

The complete set of rotationally resolved infrared data is provided in Table I along with two additional sets of experimental data for the geometric parameters of N₂O₄ for comparison. The predicted bond lengths and angles are in excellent agreement (avg. error < 0.5%) with those determined via neutron diffraction⁷ and rotationally resolved infrared spectroscopy, and are also in good agreement (avg. error < 1%) with electron diffraction data.⁵ The experimental values are different as each technique determines the average bond lengths and angles in different ways; however, the variations are rather large especially for the N–N bond. The neutron diffraction and rotationally resolved ir data each give an N–N bond of 1.756 Å, whereas the electron diffraction value is 1.782 Å. As Koput¹⁷ and Bauschlicher *et al.*¹⁵ previously suggested, the discrepancy between the electron diffraction and ir values most likely arises from a large vibrational averaging effect of the N–N stretching motion. This view is in accord with a large vibrational amplitude evidenced by both the small fragmentation energy and weak vibrational frequency of the N–N stretching mode ($\approx 250 \text{ cm}^{-1}$). For this reason the gas phase rotationally resolved ir data were chosen to be the most directly comparable to theoretical values, despite the fact that the experimental uncertainty of the difficult N–N bond is substantial (0.01 Å).

A compilation of previous theoretical efforts to describe the geometrical parameters of N₂O₄ is provided in Table II along with the TZ2P + *f*/TZ2P-CCSD(T) values of this study for comparison. The SCF method predicts an N–N linkage which is 0.17 Å too short, as correlation effects are not taken into account. On the other hand, MP2 consistently overestimates the correlation effects and predicts an N–N bond which is too long by 0.05 to 0.08 Å. Multireference wavefunctions provide a better overall description of the bonding. However, the CASSCF method tends to overemphasize the effect of antibonding configurations and, therefore, overestimates the length of the N–N bond.¹⁶ Within the single reference realm, Thomas, DeLeeuw, Vacek, Crawford, Yamaguchi, and Schaefer⁴² have illustrated for a series of small molecules that a proper “balance” between basis set and level of theory can lead to bond lengths accurate to within 0.15% of experimental values. The TZ2P + *f*-CCSD(T) is one such combination, and it is quite clear that our TZ2P + *f*/TZ2P-CCSD(T) set of predictions for the N–O bonds as well as the O–N–O angle is in agreement with this balance. Furthermore, the length of the N–N bond (a *weak* interaction outside the set of bonding types studied

TABLE II. Comparison of previous and present theoretical predictions for N₂O₄ bond lengths (Å), bond angles (degrees), and fragmentation energies (kcal/mol).

| Method | <i>r</i> (N–N) | <i>r</i> (N–O) | ∠O–N–O |
|---|----------------|--------------------|--------------------|
| 6-31G*-SCF ^a | 1.583 | 1.168 | 132.8 |
| 6-311+G(2 <i>d</i> ,2 <i>p</i>)-MP2 ^b | 1.831 | 1.203 | 135.2 |
| <i>cc-pVQZ/cc-pVTZ</i> ^c -MP2 ^d | 1.8032 | 1.1954 | 135.16 |
| DZP-CASSCF ^a | 1.80 | 1.188 ^h | 133.3 ^h |
| Q/T-CASSCF ^d | 1.8033 | 1.1670 | 134.06 |
| Q/T-CASPT2 ^d | 1.7940 | 1.1906 | 134.90 |
| TZP-LSDA(DFT) ^e | 1.774 | 1.194 | 134.8 |
| 6-311+G(2 <i>d</i> ,2 <i>p</i>)-LSDA ^b | 1.766 | 1.186 | 135.2 |
| 6-311+G(2 <i>d</i> ,2 <i>p</i>)-BP86 ^b | 1.864 | 1.202 | 134.6 |
| TZ2P+<i>f</i>/TZ2P-CCSD(T)^f | 1.752 | 1.195 | 134.7 |
| Expt.(rotationally resolved ir) ^g | 1.756 | 1.196 | 133.8 |

^aReference 15.

^bReference 20.

^c*cc-pVQZ* on nitrogen, *cc-pVTZ* on oxygen (Q/T). See Ref. 17.

^dReference 17.

^eReference 21.

^fThis study.

^gReference 6.

^hFixed at the 4-31G SCF values.

by Thomas *et al.*⁴²) is reproduced with remarkable accuracy with respect to the rotationally resolved ir experimental parameters.

In addition to geometrical parameters, a limited analysis of the energetics associated with the fragmentation of dinitrogen tetroxide was performed using single reference wavefunctions. The classical fragmentation energies of the N₂O₄→2 NO₂ reaction at the SCF, CCSD, and CCSD(T) levels are presented in Table III. This table also shows that inclusion of zero point vibrational energy differences substantially reduces these values. At the CCSD(T) level with the largest basis set, the ZPVE-corrected fragmentation energy is 10.9 kcal/mol, in good agreement with the experimental value of 12.7 kcal/mol. The CASSCF and CASPT2 fragmentation energies predicted previously by Koput¹⁷ were 7.1 and 9.6 kcal/mol, respectively.

However, the calculation of fragmentation energies of weakly bound dimers and van der Waals complexes is well known to be subject to basis set superposition errors (BSSE).^{43–45} To address the question of BSSE, the full counterpoise correction of Boys and Bernardi⁴⁶ was performed at the TZ2P + *f*/TZ2P-CCSD(T) level. The energy of the NO₂

TABLE III. Classical and ZPVE-corrected^a fragmentation energies (kcal/mol) for the N₂O₄→2 NO₂ reaction.

| Basis set | SCF | CCSD | CCSD(T) |
|---|------|------|---------|
| Classical $\Delta E(\text{N}_2\text{O}_4 \rightarrow 2 \text{NO}_2)$ | | | |
| TZ2P | –4.6 | 11.3 | 15.0 |
| TZ2P+ <i>f</i> /TZ2P | –4.6 | 12.2 | 16.0 |
| ZPVE-corrected $\Delta E(\text{N}_2\text{O}_4 \rightarrow 2 \text{NO}_2)$ | | | |
| TZ2P | –9.3 | 7.5 | 9.9 |
| TZ2P+ <i>f</i> /TZ2P | –9.3 | 8.4 | 10.9 |

^aSCF values corrected for zero point vibrational energy using TZ2P/SCF values. All coupled-cluster values corrected using TZ2P/CCSD values.

TABLE IV. Theoretical harmonic vibrational frequencies (cm^{-1}) and SCF ir intensities (km/mol) for N_2O_4 (DZP basis). Experimental frequencies are fundamentals.

| Symmetry | Description | SCF | CISD | CCSD | CCSD(T) | Expt. freq. | Remarks ^a |
|----------|----------------------------|------------|------|------|---------|---------------------|----------------------|
| a_g | $\text{NO}_2\text{s-str}$ | 1608 (0) | 1535 | 1428 | 1385 | 1380 ^b | (Ra, G) |
| | $\text{NO}_2\text{s-bend}$ | 965 (0) | 904 | 834 | 798 | 806 ^b | (Ra, G) |
| | N-N str | 461 (0) | 408 | 349 | 278 | 254 ^b | (Ra, G) |
| a_u | torsion | 61 (0) | 76 | 80 | 86 | [79] ^c | (ir, G) ⁱ |
| b_{1g} | $\text{NO}_2\text{a-str}$ | 1993 (0) | 1951 | 1817 | 1760 | 1724 ^d | (Ra, S) |
| | $\text{NO}_2\text{a-rock}$ | 639 (0) | 599 | 545 | 495 | 498 ^b | (Ra, S) |
| b_{1u} | $\text{NO}_2\text{s-wag}$ | 918 (0) | 838 | 748 | 677 | 677 ^e | (ir, S) |
| b_{2g} | $\text{NO}_2\text{a-wag}$ | 599 (44) | 542 | 484 | 434 | 436 ^d | (Ra, S) |
| b_{2u} | $\text{NO}_2\text{a-str}$ | 2015(1335) | 1979 | 1844 | 1786 | 1757 ^{f,g} | (ir, G) |
| | $\text{NO}_2\text{s-rock}$ | 368 (0) | 326 | 285 | 240 | 265 ^h | (ir, S) |
| b_{3u} | $\text{NO}_2\text{s-str}$ | 1541 (437) | 1455 | 1346 | 1286 | 1261 ^{f,g} | (ir, G) |
| | $\text{NO}_2\text{a-bend}$ | 878 (220) | 825 | 770 | 738 | 751 ^g | (ir, G) |

^aRa denotes Raman spectroscopy and ir denotes infrared absorption. G and S denote gas and solid phase, respectively.

^bReference 22.

^cReference 49.

^dReference 23.

^eReference 30.

^fReference 6.

^gReference 50.

^hReference 31.

ⁱNeither ir nor Raman active. Experimental frequency inferred from combination band frequencies.

monomer was compared to that of NO_2 with additional basis functions located in the space where the other NO_2 monomer would have been in the equilibrium N_2O_4 structure. The difference of 1.85 kcal/mol results in a 3.70 kcal/mol counterpoise correction (close to one-third of the total fragmentation energy) producing a corrected fragmentation energy of 7.2 kcal/mol. Certainly a larger basis set is required to very accurately describe the relatively small energetic differences of the free NO_2 monomers and the weak dimer at the coupled-cluster levels without a sizable BSSE. Our finding is consis-

tent with the general observation that, once reasonable basis set sizes are reached (e.g., DZP), BSSE-corrected dissociation energies are in poorer agreement with experiment than the noncorrected results. Unfortunately, our BSSE-corrected fragmentation energy cannot be compared directly to those obtained previously by CASSCF and CASPT2 studies since counterpoise corrections for the multireference studies were not performed. Despite the modest agreement with experiment, a comparison of the CCSD(T) fragmentation energy neglecting BSSE and the CASSCF and CASPT2 values re-

TABLE V. Theoretical harmonic vibrational frequencies (cm^{-1}) and SCF ir intensities (km/mol) for N_2O_4 (TZ2P basis). Experimental frequencies are fundamentals.

| Symmetry | Description | SCF | CISD | CCSD | Expt. frequency | Remarks ^a |
|----------|----------------------------|------------|------|------|---------------------|----------------------|
| a_g | $\text{NO}_2\text{s-str}$ | 1588 (0) | 1527 | 1419 | 1380 ^b | (Ra, G) |
| | $\text{NO}_2\text{s-bend}$ | 977 (0) | 927 | 864 | 806 ^b | (Ra, G) |
| | N-N str | 458 (0) | 413 | 358 | 254 ^b | (Ra, G) |
| a_u | torsion | 66 (0) | 78 | 82 | [79] ^c | (ir, G) ⁱ |
| b_{1g} | $\text{NO}_2\text{a-str}$ | 1932 (0) | 1901 | 1765 | 1724 ^d | (Ra, S) |
| | $\text{NO}_2\text{a-rock}$ | 644 (0) | 607 | 552 | 498 ^d | (Ra, S) |
| b_{1u} | $\text{NO}_2\text{s-wag}$ | 940 (0) | 862 | 769 | 677 ^e | (ir, S) |
| b_{2g} | $\text{NO}_2\text{a-wag}$ | 610 (41) | 554 | 494 | 436 ^d | (Ra, S) |
| b_{2u} | $\text{NO}_2\text{a-str}$ | 1963(1324) | 1937 | 1799 | 1757 ^{f,g} | (ir, G) |
| | $\text{NO}_2\text{s-rock}$ | 365 (0) | 327 | 285 | 265 ^h | (ir, S) |
| b_{3u} | $\text{NO}_2\text{s-str}$ | 1499 (448) | 1427 | 1315 | 1261 ^{f,g} | (ir, G) |
| | $\text{NO}_2\text{a-bend}$ | 892 (229) | 848 | 792 | 751 ^g | (ir, G) |

^aRa denotes Raman spectroscopy and ir denotes infrared absorption. G and S denote gas and solid phase, respectively.

^bReference 22.

^cReference 49.

^dReference 23.

^eReference 30.

^fReference 6.

^gReference 50.

^hReference 31.

ⁱNeither ir nor Raman active. Experimental frequency inferred from combination band frequencies.

veals a better agreement with experiment by 3.8 and 1.3 kcal/mol, respectively.

The predicted harmonic vibrational frequencies and SCF ir intensities for N_2O_4 within the DZP and TZ2P basis sets are presented in Tables IV and Tables V, respectively. The determination of frequencies at the TZ2P + *f*/TZ2P-CCSD(T) level was deemed prohibitively expensive, however, Besler, Scuseria, Scheiner, and Schaefer⁴⁷ have shown that a good balance of basis set size and level of theory is also achieved at the TZ2P-CCSD level applied to harmonic vibrational frequencies. It should be noted, however, that their balance lies within the context of comparing theoretical *harmonic* frequencies to experimental *harmonic* frequencies. Although only experimental *fundamental* frequencies are available for the vibrational modes of dinitrogen tetroxide, valid comparisons between TZ2P-CCSD harmonic frequencies and experimental fundamental frequencies can still be made by attributing the differences primarily to anharmonic effects. For example, Galbraith and Schaefer⁴⁸ have successfully described the vibrational spectra of structures along the nitrosyl azide (N_4O) potential energy surface using the TZ2P-CCSD method, noting the lowering of experimental fundamental frequencies due to anharmonicity.

As seen from Table V, the TZ2P-CCSD frequencies for N_2O_4 are indeed slightly higher than the corresponding experimental fundamental frequencies, and these differences can be used as a measure of the anharmonicity of each mode. Of particular interest is the a_{1g} vibrational mode associated with the symmetric N–N stretch. This mode contains the largest deviation from experiment with much of the 104 cm^{-1} difference attributed to anharmonicity. However, such a large anharmonicity is still quite reasonable as modes with large vibrational amplitudes such as the weak N–N stretch are likely to deviate significantly from the harmonic approximation. Since the geometries of the NO_2 monomers remain essentially intact upon formation of the N_2O_4 dimer, the remaining vibrational modes are likely to be associated with more conventional bonding. This is evident quantitatively as the NO_2 stretching and bending harmonic frequencies are in much better agreement with the experimental fundamentals. For all twelve vibrational modes of the N_2O_4 system, TZ2P-CCSD harmonic frequencies were predicted with an average absolute error of 51 cm^{-1} relative to the experimental fundamental frequencies.

IV. CONCLUSIONS

Previous single reference *ab initio* studies of dinitrogen tetroxide (N_2O_4) have consistently underestimated the nitrogen-nitrogen bond length for variational methods and overestimated the N–N bond length using perturbative treatments. Several studies suggest that a multireference wavefunction is required in the description of this weakly bound NO_2 dimer. However, we have shown that the experimental structural parameters of N_2O_4 can be successfully reproduced using single reference coupled-cluster wavefunctions with large basis sets. At the TZ2P + *f*/TZ2P-CCSD(T) level

of theory, the N–N bond length, N–O bond length, and O–N–O bond angle were calculated to be 1.752 \AA , 1.195 \AA , and 134.7° compared to experimental values of 1.756 \AA , 1.196 \AA , and 133.8° , respectively.

The $N_2O_4 \rightarrow 2 NO_2$ fragmentation energy including corrections for zero point vibrational energy and basis set superposition error was 7.2 kcal/mol compared to the experimental value of 12.7 kcal/mol . The full counterpoise correction amounted to nearly one-third of the fragmentation energy and indicates that a larger basis set is required for very accurately predicting the reaction energetics using coupled-cluster methods. Harmonic vibrational frequencies were predicted with an average absolute error of 51 cm^{-1} relative to experiment with differences in part attributed to anharmonic effects.

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