Theor Chim Acta (1994) 88: 425–435

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Chimica Acta

A theoretical determination of the dissociation energy of the nitric oxide dimer

Remedios González-Luque[1], Manuela Merchán[1], and Björn O. Roos[2]

[1] Departamento de Química Física, Universitat de València, Dr. Moliner 50, Burjassot, E-46100 València, Spain

[2] Department of Theoretical Chemistry, Chemical Centre, P.O.B. 124, S-221 00 Lund, Sweden

Received September 14, 1993/Accepted February 7, 1994

Summary. Multi-reference CI methods have been applied to determine the dissociation energy and structure of the *cis*-N_2O_2 molecule. The convergence of the theoretical result has been checked with respect to a systematic expansion of the one-electron basis set and the multi-reference CI wave function. The best calculated value, 13.8 kJ/mol, is in agreement with the experimental value, 12.2 kJ/mol. It has been obtained with an extended ANO-type basis set [$6s5p3d2f$], including the effect of the basis set superposition error (BSSE) in the geometry optimization, and additional effects, such as the electron correlation of core electrons and relativistic corrections, using the average coupled pair functional (ACPF) approach. The optimal geometry computed at this level was found to be: $r(\mathrm{NN}) = 2.284$ Å, $r(\mathrm{NO}) = 1.149$ Å, and $<\mathrm{NNO} = 96.1°$. Employing the [$6s5p3d2f$] basis set, the BSSE was found to be ≈ 2 kJ/mol.

Key words: Nitric oxide dimer – Dissociation energy – Structure, ACPF Method

1 Introduction

The nitric oxide dimer has been characterized in condensed and gas phases using many types of techniques [1–13]. It plays an important role in the chemistry of nitrogen oxides as a possible intermediate in a variety of chemical reactions [14]. The most stable form of the molecule is a *cis* planar structure with a bond between the nitrogen atoms. The ground electronic state of the (*cis*) dimer ($^1A_1$) is formed by singlet coupling of the odd electron of the NO monomers. In terms of the energetics of the interaction, the gas-phase NO dimer can de facto be classified as a van der Waals complex [4, 9, 11]. The best current estimate [11] of the experimental dissociation energy, D_0, is $710 \pm 40\,\mathrm{cm}^{-1}$. The weak N–N σ bond is consistent with a long bond length. Structural determinations of *cis*-N_2O_2 from X-ray crystallographic and gas-phase experiments have been reported [1, 3, 5, 6]. The geometries obtained from different experiments are, however, quite different. For the N–N distance in particular, the reported values fall within the range from 1.75 to 2.33 Å. The gas-phase geometry (r(NN) Å; r(NO) Å; $<$NNO°) obtained by Kukolich [6] (2.236(1); 1.161(4); 99.6(2)) can probably be considered to be the most accurate. This geometry is quite close to the crystal structure reported by Lipscomb et al. [1].

A number of theoretical studies have been performed for the NO dimer. Most of them have been attempts to determine the equilibrium geometry [15–24]. RHF calculations give, as expected, an N–N distance much shorter than experiment [6]. The closed-shell SCF wave function and the corresponding potential curve have the wrong asymptote at large distances yielding as a consequence a too short equilibrium distance. Electron correlation contributions to the geometry were first taken into account by Ha [17]. In this CI study an N–N bond length of 2.39 Å was obtained, which in turn is considerably longer than the experimental value. The performance of single-reference based methods in geometry predictions has also been investigated [22]. However, as far as we are aware, the dissociation energy of the NO dimer has not yet been determined with high quality theoretical methods.

In the present communication, we discuss results for the equilibrium geometry and dissociation energy of *cis*-N_2O_2 obtained from multi-configurational *ab initio* calculations. In order to predict a reliable geometry and dissociation energy for this weakly bonded system an extended basis set and a proper treatment of electron correlation effects are required. A specific reason for using extended basis sets is the need to reduce as much as possible the basis set superposition error (BSSE). An accurate calculation of D_e further requires a sophisticated treatment of the correlation problem. We exclude here treatments in which agreement with experiment derives from cancellations of errors or from basis set superposition effects. Systematic convergence studies have been carried out with respect to the one-electron basis using extended atomic natural orbital (ANO) sets [25, 26]. The effect of improving the basis set by extending the primitive set and number of contracted *s*-, *p*-, *d*-, and *f*-type functions is analyzed. Computation of the correlation energy is carried out in two steps. First, a qualitatively correct dissociation is assured by a multiconfigurational SCF wave function. Secondly, using as one-electron basis the MOs so obtained, remaining correlation effects are accounted for by means of multi-reference CI techniques. Different multi-reference methods are analyzed for this purpose.

A brief description of the computational methods is given in the next section. Details of wave functions, basis sets, together with an analysis of results and possible sources of remaining errors are next considered. Our conclusions are presented in the last section.

2 Methods and computational details

In order to properly describe molecular correlation effects, basis sets derived from correlated atomic calculations which include functions of high angular momentum are required. The one-particle basis sets employed in this study are constructed using general contractions based on ANOs [25]. They have been derived from a density matrix averaged over several atomic states, positive and negative ions, and the atom in a polarising field [26]. The different density matrices have been obtained from correlated atomic wave functions. These basis sets have been specifically designed to account for as much correlation as is possible within a given size. They are, therefore, particularly suited for the type of calculations performed in the present work. Initially [4*s*3*p*2*d*] ANOs were selected from the primitive set (14*s*9*p*4*d*3*f*), hereafter labelled the BS1 set. Larger basis sets are built by progressively increasing the number of ANOs. The effect of adding new primitive *s*- and *p*-type functions in an even-tempered way has been also checked. Only the pure spherical harmonic components of the *d* and *f* functions were used.

The orbitals were optimized using the complete active space (CAS) SCF method [27], or in some case with the restricted active space (RAS) SCF method [28, 29]. Dynamic correlation effects were subsequently computed, either using the multi-reference CI (MRCI) method or by using the average coupled pair functional (ACPF) approach [30]. The coupled pair functional (CPF) method [31] and CASPT2 approach [32, 33] were also used as valuable intermediate tools. The magnitude of the occupation numbers of the corresponding CPF natural orbitals (CPF-NOs) was employed as criterion to choose the inactive and active orbitals for the CASSCF and RASSCF calculations. In order to simplify the demanding large basis sets MRCI and ACPF calculations, a procedure was designed to truncate the virtual space. Guided by the occupation numbers of the quasi-natural orbitals from a CASPT2 calculation, the size of the virtual space could be reduced considerably with only a very small loss in precision. As will be discussed below the procedure is quite efficient, making feasible calculations which would otherwise exceed the technical limits.

In the RASSCF method [28, 29], the inactive and secondary spaces have the same properties as for the CAS wave function. The RAS1 space consists of orbitals in which a certain maximum number of holes may be created. The RAS2 space has the same properties as the active space in CAS type wave functions. The RAS3 space is allowed to be occupied with up to a given number of electrons. All CSFs which fulfil these restrictions are included in the RAS wave function.

The MRCI wave functions comprise all singly and doubly (SD) excited configuration functions (CFs) from a given set of reference functions. To the MRCI energies we have also added the multi-reference analogue [34] of the Davidson correction [35] to estimate the effects of unlinked contributions from multiple excitations, which is denoted by $+Q$. Compared to other CI techniques, in the single-reference CPF [31] and multi-reference ACPF [30] methods the functional is modified to be approximately size-extensive. The CPF approach is known to give accurate results where the wave function is dominated by a single configuration. The ACPF wave function can be considered an extension of the CPF method to allow more than one reference configuration.

The CASPT2 method [32, 33] computes the first order wave function and second order energy with a CASSCF function as the unperturbed state. The zeroth order Hamiltonian is defined as a Fock type one electron operator such that Möller–Plesset (MP) perturbation theory is obtained in a closed-shell determinant case. Two different formulations of the zeroth order Hamiltonian are possible: using only the diagonal part of the Fock matrix (called PT2D), and including also the non-diagonal elements (PT2F) which is invariant to rotations of the molecular orbitals. The CASPT2 approach has been used in calculations of many different properties of molecular systems [36]. Relative energies are reproducd with errors of the order of a few kcal/mol. Such an accuracy is usually satisfactory in cases where the error is only a small fraction of the bond energy. This is not the case here, however, since the total bond energy is of the order of 3 kcal/mol. It is therefore not expected that the CASPT2 method will yield results of high enough accuracy. Still, it might be of interest to study the behaviour of this new approach and compare it with more advanced methods used in the present study.

Geometry optimizations were carried out by point wise calculations with the energies fit to a second order polynomial in the three degrees of freedom (assuming C_{2v} symmetry for the *cis*-form of $(NO)_2$).

All calculations have been performed on the IBM 9021/500-2VF computer at the University of Valencia using the MOLCAS-2 quantum chemistry software [37].

3 Results and discussion

The main interest in this work is the interaction energy between two NO monomers. This involves a careful comparison of the dimer and the monomers at each stage of the calculation. For the investigation of the effect of changing the basis sets and correlation treatment, the dissociation energy was computed, in the supermolecule approach, as the difference between the total energy of the dimer at the optimized geometry and the two subunits separated 100.0 a.u. Unless otherwise stated the core electrons occupying the 1*s*-derived molecular orbitals (MOs) were not correlated.

Initial calculations were carried out using the BS1 [4*s*3*p*2*d*] basis set. The trends for the equilibrium parameters at the SCF and CPF levels were found to be in agreement with previous findings [15–22]. The NO dimer has a complex electron structure. One very weak NN bond, with 1.6 and 0.4 in occupation numbers of the CPF σ_{NN} and σ_{NN}^* NOs, respectively, and a near-degenerate π system. Two configurations are required to properly describe the bond breaking process: the Hartree–Fock and the doubly excited $(\sigma_{NN})^2 \rightarrow (\sigma_{NN}^*)^2$ configurations. Dynamic correlation energy, which is important for the quantitative description of the dissociation energy, is estimated by considering all singly and doubly excited CFs from those two reference configurations. These calculations are labelled MRCI(2). In order to employ as optimal MOs as possible, RASSCF MOs were used as the one-electron basis for the MRCI calculations. In the RASSCF calculations the 22 valence electrons were active. The active space was chosen as follows: lone-pairs plus NO σ bonds (8 orbitals) in RAS1; NN bond plus π bonds and the anti-bonding counterparts (6 orbitals) in RAS2; and RAS3 having the corresponding correlating orbitals for RAS1. At most one hole was allowed in RAS1 and two electrons in RAS3.

The potential energy curve vs. the NN distance (using experimental data [6] for the remaining geometrical parameters) revealed that the dissociation energies computed at the SCF, CPF, and SDCI($+Q$) levels are highly overestimated due to the incorrect behaviour of single-reference based approaches at large distances. As soon as the correct qualitative dissociation is allowed by including the doubly excited configuration $(\sigma_{NN})^2 \rightarrow (\sigma_{NN}^*)^2$, either by the RASSCF or the MRCI(2) methods, the dissociation energy becomes negative. Thus, the anti-bonding contribution to the NN bond is overestimated by these methods. Including the effect of higher excitations by the multi-reference analogue [34] of the Davidson correction [35], MRCI(2)$+Q$ results, leads to a bound dimer. Therefore, geometry optimization was carried out at the MRCI(2)$+Q$ level, employing the BS1 basis set, resulting in the following optimal values: r(NN)$=2.253$ Å, r(NO)$=1.149$ Å, and $<$NNO$=97.3°$. This geometry is indeed consistent with the experimental evidence [6] and the previous CI result [17]. The dissociation energy (D_e) at the MRCI(2)$+Q$ level of theory was computed to be 16.8 kJ/mol. For comparison with experiment, the experimental value of D_0 (8.5 ± 0.5 kJ/mol) [11] must be corrected for the zero-point energy (ZPE). Using the experimental fundamental frequencies together with the available vibrational anharmonic constants (symmetric and anti-symmetric NO stretch) of the dimer [7, 9] and the corresponding data for NO

[38] leads to a D_e value of 12.2 kJ/mol. It might be noted that the anharmonic corrections have only been partially included, due to lack of data. Also fundamental instead of harmonic frequencies have been used. Thus the true D_e value is probably slightly larger than the present estimate. The difference should, however, be very small and certainly outside the accuracy of the present study. Consequently, it may be concluded that the computed dissociation energy is in agreement with the experimental value. The obtained overestimation could possibly be ascribed to the BSSE, since a rather limited basis set was used.

Although there seems to be a consensus that one has to correct for the BSSE in the study of weak intermolecular complexes, there is still some controversy regarding the proper method [39]. The full counterproise correction [40] (CPC) has been used in this investigation. The BSSE contribution to the dissociation energy, that is, twice the energy lowering obtained by including a ghost basis in a monomer calculation, was computed to be 13.2 kJ/mol at the SDCI $+Q$ level. Even taking into account that this value can be considered as an upper limit of the actual BSSE occurring with the BS1 basis set, due to the inherent overestimation obtained by the CPC, the result is not satisfactory. The corrected dissociation energy $CD_e = D_e - \mathrm{BSSE}$ is only 3.6 kJ/mol, i.e., about one third of the experimental value. It is clear that a more extended basis set has to be used in order to obtain a quantitative result for CD_e.

But using large basis sets ultimately yields MRCI expansions that are prohibitively large. The bottleneck of the computation is actually the integral transformation step of the BSSE calculations, because of the reduction of symmetry from C_{2v} in the dimer to C_s in the NO($^2A'$)-ghost-basis system. In order to overcome this technical difficulty, the virtual space was reduced in a way that minimises the loss in correlation energy. Second-order perturbation theory was applied to obtain the approximate occupation numbers for the secondary orbitals [36]. The CASSCF wave function built with the 2*p*-derived MOs active (12 active orbitals, 14 active electrons) was used as reference function in the second-order treatment of the dimer. In the BSSE calculations, the valence CASSCF wave function of the monomer was used as reference function. The calculations will be denoted as *p*-CASSCF (or *p*-CASPT2) and val-CASSCF (or val-CASPT2). The *p*-CASPT2 and val-CASPT2 quasi-natural orbitals were used as one-electron basis for the MRCI(2) $+Q$ calculations of the dimer and SDCI $+Q$ computation of the BSSE, respectively. Orbitals corresponding to the lowest occupation numbers were deleted. A exploratory study was performed using the BS1 basis set. In this study the virtual space was systematically reduced and the BSSE calculated. The result of this analysis is presented in Table 1. System A denotes the NO($^2A'$) molecule in the full basis set of N_2O_2 at the equilibrium geometry of the dimer. System B denotes the NO($^2A'$) molecule, in the full basis set of N_2O_2, with an NN distance of 100 a.u.

It is obvious that a strong reduction of the virtual space is possible without significantly affecting the accuracy of the BSSE result. To delete secondary orbitals with occupation numbers less than 10^{-7} is appropriate for the BS1 basis set. Using the 72% and 50% of the total secondary space for the system A and System B, respectively, the same BSSE result is obtained as without deleting virtual orbitals. It is worth noting that the total energies for both systems are not significantly affected by the reduction of the secondary space. The success in removing a large portion of the virtual space in the computation of the BSSE in N_2O_2 is mainly due to the fact that a large number of ghost orbitals with small occupation numbers is present in the calculation. A threshold of 10^{-7} was used also with the larger basis

Table 1. Convergence pattern of the SDCI, SDCI+Q, and basis set superposition error (BSSE) energies with respect to the truncation of the virtual space, using the BS1 [$4s3p2d$] basis set

Calculation[a]	System A[b]	System B[c]	BSSE (kJ/mol)[d]
Threshold = 10^{-5}			
SDCI	–129.636460	–129.634205	11.8
SDCI+Q	–129.670354	–129.667946	12.6
No. virtual MOs	50	46	
No. real conf.	32891	26877	
Threshold = 10^{-6}			
SDCI	–129.636537	–129.634205	12.2
SDCI+Q	–129.670447	–129.667946	13.1
No. virtual MOs	56	46	
No. real conf.	42837	26877	
Threshold = 10^{-7}			
SDCI	–129.636549	–129.634205	12.3
SDCI+Q	–129.670462	–129.667946	13.2
No. virtual MOs	66	46	
No. real conf.	62505	26877	
Threshold = 0.0			
SDCI	–129.636551	–129.634205	12.3
SDCI+Q	–129.670465	–129.667946	13.2
No. virtual MOs	92	92	
No. real conf.	130835	130835	

[a] The quasi-natural val-CASPT2 orbitals with occupation numbers less than the given threshold were deleted.

[b] The NO(^{2}A′) molecule in the full basis set of N_2O_2 at the optimal BS1 MRCI(2)+Q geometry of N_2O_2.

[c] The NO(^{2}A′) molecule, in the full basis set of N_2O_2, separated from the ghost functions 100.0 a.u.

[d] The BSSE is computed as twice the interaction between one NO monomer and the ghost basis set.

sets and accurate calculations of the BSSE and D_e could be carried out with significantly reduced virtual spaces.

The convergence pattern of D_e, BSSE, and CD$_e$ with respect to a systematic increase of the one-electron basis is examined in Table 2. The optimal geometry obtained at the MRCI(2)+Q level with the BS1 basis set was employed.

The comparison between the BS2 and BS1 results shows that f-type functions added to BS1 increase the CD$_e$ value by one 1.6 kJ/mol, and the BSSE is still large. It is thus clear that the s, p, and d spaces have to be increased in order to significantly reduce the BSSE. When BS1 is enlarged with an additional set of s-, p-, and d-type functions (the BS3 results), the BSSE is considerably reduced. Since the D_e value also decreases, the CD$_e$ keeps about the same value, 4.7 and 5.2 kJ/mol for BS3 and BS4, respectively. The addition of an f-type function (BS5 results) gives an additional improvement in D_e and reduces the BSSE, according to the trends noted when enlarging BS1 to BS2. The effect of a second f-type function is not negligible. The final result for CD$_e$, using the BS6[$6s5p3d2f$] basis set, 8.7 kJ/mol, is 3.5 kJ/mol smaller than the experimental value. All the basis sets included in Table 2 have been built from the original primitive set [26]. This procedure was found more efficient than introducing additional diffuse functions. For instance, adding s and p primitives in even-tempered way to BS3, resulting in the [$5+1s$, $4+1p$, $3d$]

Table 2. Estimation of the dissociation energy, D_e, basis set superposition error, BSSE, and corrected dissociation energy $CD_e = D_e - \text{BSSE}$ for N_2O_2. MRCI(2)+Q values for D_e and SDCI+Q results for BSSE. The optimal geometry obtained at MRCI(2)+Q level with the BS1 basis set was employed[a]

Basis set	D_e (kJ/mol)	BSSE (kJ/mol)	CD_e (kJ/mol)
BS1[4*s*3*p*2*d*]	16.8	13.2	3.6
BS2[4*s*3*p*2*d*1*f*]	17.2	12.0	5.2
BS3[5*s*4*p*3*d*]	9.5	4.8	4.7
BS4[6*s*5*p*3*d*]	8.6	3.4	5.2
BS5[6*s*5*p*3*d*1*f*]	9.0	2.6	6.4
BS6[6*s*5*p*3*d*2*f*]	10.6	1.9	8.7
Exp.[b]			12.2

[a] r(N–N) = 2.253 Å; r(N–O) = 1.149 Å; <NNO = 97.3°

[b] The experimental value [11] of D_0 has been corrected for the ZPE using the experimental frequencies for the dimer [9] and NO [38].

contraction, the BSSE was computed to be 4.8 kJ/mol, i.e., 1.4 kJ/mol larger than the BS4 value.

The convergence of the D_e, BSSE, and CD_e results is slow. Further reduction of the BSSE is without doubt a challenging task. Inclusion of *g*, *h*, *i*, and higher angular momentum functions would probably be required. Nevertheless, the present results can be regarded as reasonably satisfactory. In our largest calculations, the BSSE does not exceed ≈2 kJ/mol. The slow convergence of BSSE at the correlated level seems to be a general problem in theoretical calculations of dissociation energies. It becomes more relevant within the context of weakly bonded systems, and here quite often represents the major source of error in the computation of the binding energy, but it is also present in molecules with strong chemical bonds. For instance, in a detailed investigation of the dissociation energy of N_2 reported by Almlöf et al. [41], the contribution of the BSSE to the calculated dissociation energy was computed to be 1.2 kJ/mol, using a 6*s*5*p*4*d*3*f*2*g*1*h* contracted basis set.

While it is feasible to saturate the basis set at the SCF level to obtain a BSSE-free result, this cannot be easily done for the correlation energy. The ghost orbitals have here a larger effect and the BSSE for the correlation energy only slowly decreases with increasing basis set. At the SCF level the BSSE decreases from 2.3 (BS1) to 0.3 (BS6) kJ/mol. The val-CASSCF values are very similar to the SCF results. As noted in Table 2, the BSSE becomes around six times larger at the SDCI+Q level. The CPF and SDCI+Q results are within 0.2 kJ/mol of each other. On the other hand, as a by-product of the calculation, the second-order perturbation theory result for the BSSE is also obtained. Compared to the corresponding SDCI+Q result, its value is of rather poor quality. At the val-PT2D level the results are in the range 17.6 (BS1) to 10.2 (BS6) kJ/mol. The BSSEs are therefore overestimated. Similar results have earlier been obtained at the MP2 level [39]. A second-order perturbation treatment does not seem to be accurate enough for calculating such small energy differences. The BSSE obtained with the SDCI+Q or the CPF methods decrease with increasing basis set size as expected. The correction obtained with the CASPT2 method shows, on the other hand, poor convergence.

In order to analyze possible sources of remaining errors in the calculation of the dissociation energy, a sequence of MRCI calculations was performed, where the number of reference configurations was progressively increased. Considerable attention was paid to enlarging the number of reference configurations in a consistent and balanced manner for the two molecular geometries: at the equilibrium geometry, and at 100 a.u. separation between the two monomers. Analysis of the *p*-CASSCF wave function, comprising 42 756 configurations, revealed that the additional most important candidates to be included as references in the MRCI calculations should be: single excitations within the valence π system, MRCI(6) + Q calculations, and doubly excited valence configurations within the π system, MRCI(10) + Q results. For the sake of comparison with the previous MRCI(2) + Q result, the geometry employed was fixed at the optimized structure obtained with the BS1 basis set. Using this moderate basis set, the D_e was computed to be 17.0 and 17.2 kJ/mol at the MRCI(6) + Q and MRCI(10) + Q level, respectively. Compared to the MRCI(2) + Q result, 16.8 kJ/mol, the D_e value shows to be quite insensitive to the extension of the MRCI expansion. In other words, dynamic correlation effects are well accounted for by means of the less demanding MRCI(2) + Q wave function. Even with the smallest basis set used, the number of CFs generated in the MRCI(10) wave functions was about 1.2 million. Therefore, one is forced to assume that the same improvement of D_e would be obtained with the largest basis. This assumption is reasonable, based on previous experience of similar convergence studies [42]. Further enlargement of the reference space is not possible in a consistent way because of the many singly excited configurations from the σ and π valence MOs that should have to be included at the same time in the next step, since they all are equally important.

The geometry was now re-optimised using the largest basis set with BSSE included in the energy, that is, the maximum value of CD_e was searched. This study could not be performed at the MRCI(2) + Q level, since this calculation is not size-consistent. As a result, a too large NN distance is obtained. The computed energy of the supermolecule (two monomers at 100.0 a.u. treated as a dimer) at the MRCI(2) + Q level differs from twice the SDCI + Q energy of the monomer. Instead the multi-reference ACPF method was used, since this method fulfils the size-consistency requirement better (in particular when the two monomers are the same). The results of the optimization using the BS6 basis set and two configurations as reference, ACPF(2) calculations, are listed in Table 3, together with information from previous experimental and theoretical studies.

Inspection of Table 3 shows that the issue of the detailed geometry of N_2O_2 is still a question open to debate. Analysis and comparison of the previous results can be found elsewhere [15–22] and it will not be repeated here. There is a strong coupling between the NN distance and the NNO angle. The structural determination is very sensitive to the one-electron basis set and type of correlation treatment. Using the BS6 basis set the NN bond distance is somewhat larger than with the BS1 basis set, and 0.048 Å larger than the value reported by Kukolich [6]. The computed NO distance is 0.012 Å shorter and the NNO angle 3.5° smaller than the same set of experimental data [6]. At the ACPF(2) level, 15.6 kJ/mol was obtained for D_e. The contribution to the dissociation energy of the BSSE was computed to be 2.2 kJ/mol at the ACPF level. Therefore, at the ACPF(2) level, the CD_e result is 13.4 kJ/mol.

Additional corrections were also included at the ACPF(2) level, using the BS6 basis set and the final optimal geometry, in order to arrive at a final estimate of the dissociation energy of the nitric oxide dimer. The core–valence and core–core correlation energy and relativistic effects were computed to check their influence on

Table 3. Theoretical and experimental geometry parameters for N_2O_2

Technique	r(NN) (Å)	r(NO) (Å)	<NNO (°)	Ref.
Experimental structures				
X-ray	2.18 ± 0.06	1.12 ± 0.02	101 ± 2	[1]
IR	1.75	(1.15)[a]	90	[3]
MBER	2.33 ± 0.12	(1.15 ± 0.01)[a]	95 ± 5	[5]
FTM	2.236 ± 0.001	1.161 ± 0.004	99.6 ± 0.2	[6]
Theoretical results				
SCF (GLF, DZ)	1.768	1.162	106.5	[15]
SCF (DZ)	1.615	1.182	112.0	[16]
CI (DZP)	2.39	1.19	90	[17]
MP2 (TZ2Pf)	2.186	1.170	91.3	[22]
CISD (TZ2P)	1.772	1.140	105.6	[22]
CPF (TZ2P)	2.160	1.154	98.1	[22]
CCSD (DZP)	1.928	1.176	102.2	[22]
CCSD(T) (DZP)	2.354	1.180	95.3	[22]
MRCI(2)+Q [$4s3p2d$]	2.253	1.149	97.3	This work
ACPF(2) [$6s5p3d2f$] +BSSE	2.284	1.149	96.1	This work

[a] Assumed value in the analyses.

Table 4. Final estimate of the dissociation energy of the nitric oxide dimer using the optimal ACPF(2)+BSSE geometry obtained with the BS6 [$6s5p3d2f$] basis set

Level of theory	D_e (kJ/mol)	BSSE (kJ/mol)	CD_e (kJ/mol)
ACPF(2)	15.6	2.2	13.4
additional corrections[a]			
Core–core and core–valence corrections	8.3	7.8	0.5
Relativistic effects	0.0	0.1	−0.1
Final value	23.9	10.1	13.8
Exp.[b]			12.2

[a] See details in text.

[b] Present estimate of the experimental D_e (see text for details).

the computed D_e, BSSE, and CD_e values. Table 4 collects the results obtained for these corrections.

A net contribution to the CD_e value of 0.5 kJ/mol was found correlating the core electrons. Relativistic effects were estimated using first-order perturbation theory [43]. The relativistic corrections were found to decrease CD_e by 0.1 kJ/mol. Adding together these contributions we arrive at a final value of 13.8 kJ/mol for the dissociation energy of the nitric oxide dimer.

4 Summary and conclusions

The best calculated value for the dissociation energy of the nitric oxide dimer is 13.8 kJ/mol. It has been obtained using an extended ANO-type basis set

[6*s*5*p*3*d*2*f*]. Requirement of size-consistency was found decisive for a proper treatment. The ACPF method was selected to be the most reliable approach for this purpose. Geometry optimization including the effect of the BSSE yielded a geometry in good agreement with experiment.

The core–valence and relativistic corrections have an opposite influence on the dissociation energy and are of minor importance (0.4 kJ/mol). The remaining error should then be mainly due to deficiencies of the basis set. A small improvement is expected from remaining dynamic correlation effects taken into account by enlarging the number of reference configurations in the multi-reference CI method.

Acknowledgements. The research reported in this communication has been supported by a grant from the Swedish Natural Science Research Council (NFR), by IBM Sweden under a joint study contract, by the Cooperación Científica-Técnica (Ministerio de Assuntos Exteriores) of Spain, and by the DGICYT Project No. PB91-0634. We are grateful to Dr. M. P. Fülscher for valuable discussions and suggestions.

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