A quantum chemical study of the hydrogen bonding in the $CO_2 \cdots HF$ and $N_2O \cdots HF$ complexes

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Summary. Quantum chemical *ab initio* calculations have been performed for the complex $CO_2 \cdots HF$ and $N_2O \cdots HF$. The interaction energies were computed through fourth order MBPT and were corrected for basis set superposition errors. Extended polarized basis sets were used which are constructed to give accurate values for electric moments and polarizabilities. The complex $NNO \cdots HF$ was found to be bent, while $OCO \cdots HF$ is linear, in agreement with experiment. The MBPT calculations give evidence for a second linear isomeric structure $FH \cdots NNO$, a possibility which has also been suggested by recent experimental data. The computed binding energies are: 2.5 kcal/mol for $OCO \cdots HF$, 2.4 kcal/mol for $NNO \cdots HF$, and 3.0 kcal/mol for $FH \cdots NNO$. At the SCF level, the $FH \cdots NNO$ complex is less stable than $NNO \cdots HF$, but correlation has a large effect on the geometry and energetics of the latter complex. The $NNO \cdots HF$ complex seems to be a system where the positive intramolecular correlation correction prevails over the negative intermolecular component.

Key words: Hydrogen bonding — CO_2-HF complex — N_2O-HF complex

1. Introduction

Structures and potential energy surfaces of van der Waal's and hydrogen bonded complexes are matters of much current experimental and theoretical interest. To a large extent this is a result of the development of experimental techniques for

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the production of dimers and the determination of their spectra. Examples of such techniques are molecular beam electric resonance spectroscopy and pulsed nozzle Fourier-transform microwave spectroscopy [1, 2], as well as microwave spectroscopy of gas mixtures and high resolution infrared spectroscopy [3, 4].

Occasionally, spectroscopic evidence has been presented for multiple isomers of weakly bound hydrogen bonded complexes [5], but only the HCN···DCN and DCN···HCN isomeric pair has actually been observed [6]. More recently, two distinct minima have been suggested for the complex between hydrogen fluoride (HF) and nitrous oxide (NNO). Joyner et al. [7] have previously reported evidence for a bent NNO···HF complex from microwave data. The complex can be characterized by a hydrogen bond to one of the non-bonding electron pairs of oxygen with O···HF at the angle of $64°$ to the NNO axis. Dayton and Miller [8] and Andrews and Jonsson [9] have reported the infrared spectrum of the bend isomer; however, recent infrared measurements by Lovejoy and Nesbitt [10] have shown that an approximately linear ONN···HF isomer, featuring a hydrogen bond to the terminal nitrogen, also exists.

The CO_2 molecule is isoelectronic with N_2O. The molecules display other similarities, but also many differences: N_2O behaves as an anesthetic [11] while CO_2 is an almost inert compound. Microwave studies have shown that the CO_2···HF complex is nearly linear, while NNO···HF is bent [12]. Both molecules are important atmospheric components. The CO_2···HF complex is used as a catalyst in several organic reactions. A deeper understanding of the structure of these complexes is therefore of general interest.

Theoretical studies of hydrogen bonded complexes have essentially followed two directions. The first partitions the interaction into terms such as electrostatic, repulsion, polarization, induction, and dispersion, and evaluates the contribution to the interaction separately for each term. The second approach is the super-molecule method which treats the complex as a single molecule [13].

The experimental geometries for the CO_2···HF and NNO···HF complexes [7, 12] have been confirmed by the SCF supermolecule calculations (no BSSE corrections made) of Sapse and Howell [14], using 6-31G and 6-31G** basis sets. The question has been raised whether the bent structure of NNO···HF could be predicted from electrostatic theory alone. On the basis of SCF and electrostatic calculations Baiocchi et al. [15] suggest that the electrostatic minimum for both CO_2···HF and NNO···HF corresponds to a linear structure. However, the calculations by Rendell et al. [16] and Spackman [17], which were performed with a fixed O···F separation, are consistent with Buckingham and Fowler's idea of H-bonding [18], and predict the NNO···HF complex to be bent.

The observation of both the isomers NNO···HF and ONN···HF [10] provides important new clues regarding the nature of the interactions involved. In view of these results it is clear that the N_2O···HF potential has at least two distinct minima of comparable depth. The ONN···HF structure is also surprising in that the dipole moments of the N_2O and HF moieties are opposed, leading to a destabilization of the complex from the dipole-dipole interaction term.

The theoretical understanding of these hydrogen-bonded complexes is thus limited, and there is a need for calculations at a higher order of theory. The

purpose of the present study is to provide such an understanding on level which includes electron correlation and the use of extensive AO basis sets.

During the preparation of this article a paper appeared [19] which presents results for $CO_2\cdots HF$ and $N_2O\cdots HF$ (both isomers) that are in many respects parallel to the results obtained in the present work; the method used is MP2 with full geometry optimization. The present study is performed to full fourth order many body perturbation theory (MBPT) and therefore should treat the correlation effects more accurately. Full geometry optimization has not been performed here; only the intermolecular degrees of freedom have been varied. On the other hand the present geometry optimizations take full account of the basis set superposition error (BSSE), while Alberts et al. [19] only add BSSE at the finally optimized geometry. This difference between the two studies is certainly significant since the BSSE is considerable in both cases, in spite of the fact that extended basis sets have been used. In future this problem can to a large extent be remedied by using ANO type basis sets, which are known to give very small BSSEs [20].

2. Method of calculation

The aim of this work is to provide advanced calculations on the ground electronic state of the $CO_2\cdots HF$ and $N_2O\cdots HF$ complexes. The fourth order MBPT method has been used to include electron correlation effects. Geometry optimization was performed for the intermolecular degrees of freedom only, with the subunits fixed at their experimental structures. As has been shown by Alberts et al. [19], the changes of intramolecular structure parameters are small and most certainly insignificant for the calculation of the structure and binding energy of the complex. They are, of course, significant for the interpretation of the IR spectrum of the complex.

Calculations of intermolecular interactions by means of MBPT have several advantages compared to other methods. Besides the size-consistency of the supermolecule MBPT approach, the favorable accuracy/cost ratio should also be noted [21]. All contributions to the total energy up to fourth order in the electron correlation perturbation series (due to single (S), double (D), triple (T) and quadrupole (Q) excitations) are included. The work by Alberts et al. [19] was carried only to second order in the perturbation expansion and the present results will therefore be of value for estimating the accuracy of their results. As is well known, N_2O is a molecule which is not well described at the Hartree–Fock level, and one would expect this to lead to slow convergence of the perturbation expansion. That is true for the monomer properties, and also strongly affects the convergence of the intermolecular properties, contrary to the assumption made by Alberts et al. [19].

The BSSE, which is especially large for the electron correlation contribution [21], has been treated with the full Boys–Bernardi counterpoise correction [22, 23], and corrections determined by means of the function counterpoise method [22]. Thus, the energy of each subunit was computed with its own basis set as well as with the basis set of the other subunit.

The MBPT calculations have been carried out with an extensive polarized basis set of the CGTO type, which has been described in detail by Sadlej and Diercksen [24]. For C, N, and O a $10s$, $6p$, $4d$ basis was contracted to $5s$, $3p$, $2d$, and for hydrogen a $6s$, $4p$ basis was contracted to $3s$, $2p$. This basis set has been designed to reproduce the electric properties of molecules accurately, an important factor for a correct calculation of the electrostatic forces between them. This property also leads to a negligible secondary BSSE. Thus the standard counter poise correction for the basis set effect on the total energy becomes justified.

All calculations have been performed with the MBPT program system program system of the Bratislava group [25] interfaced with the quantum chemistry program system of this laboratory. Dipole and quadrupole moments and polarizabilities were obtained from the numerical derivatives of the total energy. A convenient check of the precision of this method can be obtained by comparing the first derivative of the SCF energy with the expectation value for the SCF dipole moment: with the external field strengths employed in these calculations the two values differ only by $\sim 10^{-4}$ a.u. The MBPT polarizability data are expected to be accurate to within ± 0.01 a.u.

Geometry optimizations were carried out for the complexes only with respect to the intermolecular parameters: $R(X \cdots H)$ and the angles. The geometries of the subunits have been kept unchanged. All linear structures were studied with all contributions to the total energy through fourth order, but due to limitations in available computer resources, the final results for the non-linear structures of the complexes have been obtained at the SDQ-MBPT4 level, that is, without triple excitations.

3. Monomers properties

Prior to reporting the results for the complexes, we list in Table 1 the relevant properties of the isolated HF, CO_2 and N_2O molecules, calculated with the same basis set; total energies of the molecules calculated at the experimental distances are also given. The results at different levels of approximation in the MBPT expansion are compared with both the SCF energy values and earlier published results. The total energy values are accompanied by the same set of results for the dipole moment, quadrupole moments and polarizabilities. It is well known that electrostatic effects play a major role in H-bonding, and so it is therefore extremely important that the calculations reproduce the electric properties of each subunit accurately. For this reason, the generally close agreement found between MBPT4 calculated dipole and quadrupole moments and the corresponding experimental estimates is satisfying.

There is a number of accurate calculations of properties of the hydrogen fluoride using a variety of techniques including MSCF, CI, CASSCF, and MBPT [26-30]. The present results are comparable with the MBPT calculations published in [29].

The dipole moment at the SCF level is 7% too big, while the second order value is close to the experiment. The third order contribution has the opposite

Table 1. Total energy, dipole moment, μ, quadrupole moment, θ, and polarizability, α, calculated at different levels of approximation, for the molecules FH, CO_2, and N_2O. Basis set used for C, N, O, and F is [10, 6, 4/5, 3, 2], and for H is [6, 4/3, 2][a]. Calculations were performed at experimental geometries[b]

	HF	CO₂		NNO	
Energy	+ 100 a.u.	+ 187 a.u.		+ 183 a.u.	
SCF	−.053465	−0.691839		−0.729875	
MBPT2	−.263687	−1.188976		−1.271893	
MBPT3	−.264983	−1.176589		−1.246874	
SDQ-MBPT4	−.268926	−1.189286		−1.263796	
MBPT4	−.273690	−1.214338		−1.298732	
Dipole moment[c] (Debye)					
SCF	1.92	−		0.62	
MBPT2	1.80	−		−0.06	
MBPT3	1.81	−		0.36	
SDQ-MBPT4	1.79	−		0.21	
MBPT4	1.77	−		−0.14	
exp	1.83 [44]			−0.17 [34]	
	1.80 [43]				
Quadrupole moment Q_{zz} (a.u.)					
SCF	1.742	−3.796		−2.756	
MBPT2	1.741	−3.112		−2.744	
MBPT3	1.720	−3.336		−2.752	
SDQ-MBPT4	1.721	−3.275		−2.697	
MBPT4	1.720	−3.145		−2.654	
exp	1.75 ± 0.02 [43]	−3.2 ± 0.02 [33]		−2.45 [42]	
		−3.34 ± 0.11 [32]			
Polarizabilities α_{xx} and α_{zz} (a.u.)					
SCF	4.446 5.731	11.80	23.87	12.40	30.63
MBPT2	5.292 5.393	12.85	27.82	13.21	33.17
MBPT3	5.000 6.190	12.51	26.33	12.93	31.69
SDQ-MBPT4	5.213 6.369	12.64	27.32	13.11	32.94
MBPT4	5.370 6.511	12.83	27.76	13.33	34.01
exp	5.10 6.59	12.88 ± 0.03	29.91 ± 0.03	14.54	34.38
$\bar{\alpha}$(exp)	5.60 [26]	17.56 ± 0.01 [14]		21.15 [42b,c]	
$\Delta\alpha$(exp)	1.48 ± 0.14 [40]	14.03 ± 0.04 [41]		19.84 [42b,c]	

[a] [24]

[b] R_{FH} = 1.7329 a.u.; R_{CO} = 2.1944 a.u.; R_{NN} = 2.132 a.u.; R_{NO} = 2.238 a.u. All molecules are linear with the atoms along the z-axis

[c] Convention of the dipole moment: μ is positive in the direction $A^{(-)}CB^{(+)}$

sign and worsens agreement with experiment. SDQ-MBPT4 fits experiment slightly better than the full fourth order treatment. Singles and triples appear in the perturbation expansion for the first time in the fourth order, and as occurs with doubles at the second and third orders, some compensation of their relatively large contribution at fourth order can be expected; however, such cancellations are obviously system dependent.

The SCF quadrupole moment of HF is overestimated by only 1.3% (the experimental value, corrected for the zero-point vibration, is 1.72 ± 0.02 a.u.). The second and fourth order contributions are almost negligible and the whole correlation correction arises from third order only. We note that Alberts et al. MP2 treatment overestimates both the dipole and quadrupole moments [19].

The correlation contributions to the polarizability components of subsequent orders have an oscillating character. The final full fourth order results are in excellent agreement with experiment.

The electric properties of the CO_2 molecule have been extensively studied at the SCF level [31]. It is, however, clear that the polarizability is underestimated at this level of theory. The correlation corrections of subsequent orders display the characteristic sign alternation, with good agreement with experiment already obtained at the second order. The SCF value of the quadrupole moment of CO_2 overestimates experiment by 12%. Correlation corrections for the quadrupole also show the normal oscillatory behaviour, with substantial contributions from triple excitations. The final fourth order results are in close agreement with experiment [32, 33].

The electronic structure of the N_2O molecule has been carefully studied by Hopper [34a]. The experimental dipole moment which is close to zero [34], is grossly overestimated at the SCF level, but the correlation correction at second order does shift the value closer to experiment. Higher order perturbation treatment shows a strong oscillatory behaviour with a fourth order value in fortuitously good agreement with experiment. It follows from the results in Table 1 that triples contribute extensively to the dipole moment of NO_2. In contrast, the quadrupole moment is more stable and contains only small correlation corrections. The same is true for the polarizability components where the full fourth order results are in excellent agreement with experimental values.

Results obtained for the electric properties of the monomers show that the basis set and the level of treatment are adequate for an accurate description of the electrostatic interactions between the subunits.

4. The complex $CO_2 \cdots HF$

The experimental results [12] show that the $CO_2 \cdots HF$ complex has a linear structure, in agreement with the theoretical results [14, 19, 35, 36], and so the present calculations were first carried out for the linear structure ($\alpha = 0°$ in Fig. 1). At a later stage the angular dependence was studied by varying $R(O \cdots H)$ and α simultaneously. At all levels of theory the angular dependence of the total energy was found to be very flat, with the minimum lying between $\alpha = 0°$ and
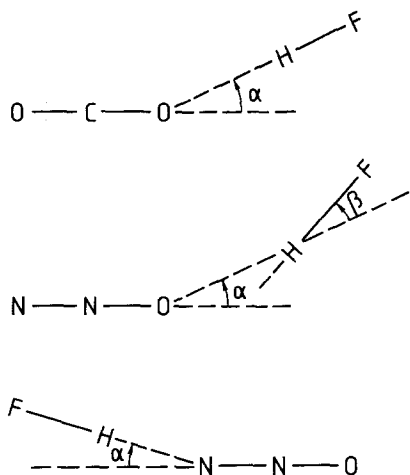
Fig. 1. Geometrical structure of the hydrogen bonded complexes $CO_2\cdots HF$, $NNO\cdots HF$, and $FH\cdots NNO$

$10°$, which is within the error limits of the experimental angle: $0° \pm 30°$ [12]. This is also in agreement with the results of Alberts et al., who find a bending frequency of $10\ cm^{-1}$ [19].

The results of the present study for the linear $CO_2\cdots HF$ system are given in Table 2. Two aspects of these results are of special interest, especially when referring to the results obtained by Alberts et al. [19]: the effect of higher order correlation terms, and the way the BSSE correction modifies the structure and bonding.

Studying the results in Table 2, we notice first that the BSSE is large with the present basis set; as expected, the correction is more moderate at the SCF level. Thus the bond distance is shifted $0.07\ Å$ by the BSSE corrected at the SCF level, while the shift is as large as $0.13\ Å$ at the MBPT2 level. Similar shifts are obtained at higher orders of electron correlation. Alberts et al. obtain a BSSE uncorrected OH distance of $1.94\ Å$ in agreement with the experimental value. Their BSSE is somewhat smaller than in this work, but large enough to affect the prediction of the bond distance. Hence their agreement with experiment is probably fortuitous, and the correct R_e value is more likely to be about $2.00\ Å$. Correlation has the effect of shortening the bond distance by $0.05-0.07\ Å$. Most of this effect is already obtained at the MBPT2 level, while higher order corrections are small.

The computed binding energy is $2.5\ kcal/mol$, which is very close to the MP2 value of $2.4\ kcal/mol$ reported by Alberts et al. [19]. We note that the second and fourth order results are very similar, with higher order correlation effects accounting for only about $0.1\ kcal/mol$ of the binding energy. The BSSE for D_e is about $0.8\ kcal/mol$ at the SCF level, but increases to around $3\ kcal/mol$ on the correlated levels. Alberts et al. report a somewhat smaller BSSE of $0.8\ kcal/mol$ at the MP2 level.

We also report the intermolecular stretching frequency in Table 2. This has been obtained by treating the complex as a diatomic system, with only one degree of freedom. The full potential curve has, however, been used, and the result has been obtained by solving the corresponding Schrödinger equation for

Table 2. Comparison of calculated and experimental geometry parameters, binding energy, stretching frequency, and dipole moment for the linear $CO_2\cdots HF$ complex. BSSE uncorrected values within parenthesis

	This work		[14][a]	[35][b]	[19][c]		exp. [12]
$R(O\cdots H)$ (Å)							
SCF	2.10	(2.03)	1.94	2.08			
MBPT2	2.04	(1.91)			1.94		
MBPT3	2.05	(1.92)					1.91
SDQ-MBPT4	2.05	(1.92)					
MBPT4	2.03	(1.91)					
D_e (kcal/mol)							
SCF	2.19	(2.95)	4.95	2.89			
MBPT2	2.45	(5.53)			2.42	(3.22)	
MBPT3	2.45	(5.44)					
SDQ-MBPT4	2.46	(5.50)					
MBPT4	2.55	(5.84)					
Stretch freq. (cm^{-1})							
SCF	82	(105)					
MBPT2	97	(147)			125		
MBPT3	96	(149)					
SDQ-MBPT4	96	(149)					
MBPT4	100	(150)					
Dipole moment (D)							
SCF		2.45	3.02	–	2.78	(MP2)	2.25

[a] Full optimization with a 6-31G basis set: no BSSE correction
[b] As above, but with a 6-31G** basis set
[c] Full optimization at the MP2 level; BSSE correction only for D_e

the reduced motion. The reported frequencies correspond to $\Delta G_{1/2}$ of the 'diatomic' system.

The large effect of the BSSE is clearly noticeable here, since it leads to a deeper well with a higher stretch frequency. Results obtained without a BSSE correction must therefore be viewed with some caution [19]. The anharmonic contributions to $\Delta G_{1/2}$ are not negligible: at the MBPT4 level the harmonic frequency is $116\ cm^{-1}$, which is 16% larger than the result obtained from the full potential curve. The use of the harmonic approximation for treating weak interactions is thus of limited value.

To summarize, the use of a BSSE correction potential curve in the present work is responsible for the major differences between our results and those of Alberts et al. [19]: the longer bond distance and the lower stretch frequency obtained in our calculations.

5. The complex NNO···HF

The experimental result [7, 9] show that the NNO···HF complex has a bent structure. The three published *ab initio* calculations [14, 19, 35] are in agreement with these experimental results.

Optimization of the energy of the complex NNO···HF was carried out as a function $R(O···H)$ and angles α and β as defined in Fig. 1b. The results are presented in Table 3, where a comparison is made with earlier theoretical results and also with the experimental data of Joyner et al. [7]. Only BSSE corrected values are reported in Table 3, the BSSE corrections being similar to those in the CO$_2$···HF complex.

The most striking result in Table 3 is probably that the binding energy, D_e, is larger at the SCF level than at the correlated level. This fact is not surprising, however, as it can be directly related to variations in the N$_2$O dipole moment with the order of the MBPT (cf. Table 1). Actually the binding energy at the correlated level is very nearly a linear function of the value of the dipole moment of N$_2$O. It was not possible, for technical reasons, to perform full fourth order calculations for the non-linear geometries of NNO···HF. However, full MBPT4 calculations were performed for linear geometries. The MBPT4 results are very close to MBPT2, and it can be expected that this will also be true for the optimal

Table 3. Comparison of calculated and experimental geometry parameters, binding energy, stretching frequency and dipole moment for NNO···HF[a]

	This work	[14][b]	[35][b]	[19][b]	exp.
$R(O···H)$ (Å)					
SCF	2.22	1.91	2.09		
MBPT2	2.15			1.95	
MBPT3	2.11				1.94 [12]
SDQ-MBPT4	2.13				2.13 [37]
$\alpha°$ (see Fig. 1)					
SCF	53	58	76		
MBPT2	55			59	
MBPT3	55				64 [12]
SDQ-MBPT4	55				
$\beta°$ (see Fig. 1)					
SCF	12	3.5	45		
MBPT2	12			−	
MBPT3	12				13 [12]
SDQ-MBPT4	12				
D_e (kcal/mol)					
SCF	2.50	9.29	5.75		
MBPT2	2.11			2.65	0.29 [37]
MBPT3	2.63				
SDQ-MBPT4	2.41				
Dipole moment (D)[c]					
SCF	3.13	3.69	−		2.07
MBPT2	2.33			2.91	
MBPT3	2.76				
SDQ-MBPT4	2.60				
MBPT4	2.23				

[a] All values BSSE corrected
[b] See footnotes a–c in Table 2
[c] For a linear structure with $R(OH) = 4.00$ a.u.

geometry. The strong correlation effects on the dipole moment of N_2O result in a positive correlation contribution to the binding energy in $N_2O\cdots HF$ at all orders of perturbation except MBPT3, where $\mu(N_2O)$ is large and has the wrong sign. Thus, this complex constitutes a case where the positive intrasystem component prevails over the negative intersystem component.

The calculated non-linear equilibrium geometry for $NNO\cdots HF$ agrees well with the experimental result [12]. The computed value for the angle α is slightly smaller than the value reported by Alberts et al. [19]. They do not give a value for β, but our result is essentially the same as Joyner et al. have reported [12]. As was the case for $CO_2\cdots HF$, we found a larger value for the OH bond distance than that quoted in [12]. The difference is again due to the neglect of BSSE in their geometry optimization. A recent microwave study [37] of the $NNO\cdots HF$ and $ONN\cdots HF$ complexes estimates the distance between the centre of mass of the two subunits in $NNO\cdots HF$ to be 3.69 Å. Using our computed equilibrium angles, this corresponds to an OH distance of 2.13 Å, in excellent agreement with the present result. It should, however, be emphasized that the estimates of geometry parameters and binding energies from experimental data are very uncertain.

6. The ONN···HF complex

Recent infrared [10] and microwave [37] measurements have demonstrated the existence of an approximately linear isomer, $ONN\cdots HF$, which is hydrogen bonded on the nitrogen side of N_2O. The only previous theoretical study of this complex is the recent MP2 calculation of Alberts et al. [19].

Our results for this complex are presented in Table 4. Optimization of the energy was carried out as a function $R(N\cdots H)$ and angle α (Fig. 1c). The complex proved to be linear ($\alpha = 0°$) at all levels of theory.

Examining the results in Table 4 we see, as for the non-linear isomer, large variations in the $N\cdots H$ distance and bond energy with the order of perturbation theory, but now the situation has reversed: the bond energy at the SCF level is much lower than at the correlated levels. This is again related to the variations of the dipole moment and polarizability, especially of the NNO part of the complex, with the perturbation order.

Lovejoy and Nesbitt have reported a centre of mass distance between the subunits of 4.14 Å [10], leading to an NH distance of 2.07 Å in good agreement with the present result 2.04 Å (MBPT4). The recently reported centre of mass distance 4.46 Å [37] corresponds to a much larger NH distance (2.39 Å) and is not consistent with the present theoretical result.

On the other hand, the MBPT4 value for the dissociation energy, 3.05 kcal/mol, is in excellent agreement with the value 2.94 eV obtained from the microwave spectrum [37]. The computed binding energy for $ONN\cdots HF$ is 0.8 eV larger than the value obtained for the non-linear isomer $NNO\cdots HF$ at the MBPT2 level of theory; a similar difference was obtained by Alberts et al. in their MP2 study. We notice, however, that the difference in binding energy fluctuates

Table 4. Comparison of calculated and experimental bond distance, binding energy, stretching frequency and dipole moment for the linear $ONN\cdots HF$ complex. All values BSSE corrected

	This work	[19][a]	exp.
$R(N\cdots H)$ (Å)			
SCF	2.35		
MBPT2	2.04	1.99	
MBPT3	2.13		2.07 [10][b]
SDQ-MBPT4	2.09		2.39 [37][b]
MBPT4	2.04		
D_e(kcal/mol)			
SCF	1.08		
MBPT2	2.95	3.66	
MBPT3	2.02		0.74 [10]
SDQ-MBPT4	2.32		
MBPT4	3.05		2.94 [37]
Stretch freq. (cm^{-1})			
SCF	61		
MBPT2	105	126	
MBPT3	83		
SDQ-MBPT4	89		
MBPT4	107		96 [37]
Dipole moment (D)[c]			
SCF	1.93		
MBPT2	2.29	2.27	
MBPT3	2.11		
SDQ-MBPT4	2.61		
MBPT4	2.25		

[a] Full optimization at the MP2 level; BSSE correction only for D_e
[b] Estimated from centre of mass distances using experimental subunit values for bond distances in N_2O and HF
[c] At $R(NH) = 4$ a.u.

strongly with the order of perturbation theory. The MBPT4 value could not be computed for $NNO\cdots HF$ but is probably very close to the MBPT2 value. The fluctuations of the binding energies make it difficult to draw any final conclusions from the present investigation regarding the relative stabilities of the two isomers.

7. Conclusions

The NNO molecule is not well described by methods based on a single reference configuration. Near degeneracy configurational mixing is clearly important. In the present work this manifests itself by a slow convergence of the properties with the order of perturbation theory.

This feature of the electronic structure of NNO was also noted by Alberts et al. [19], who calculated the NN distance to be 0.028 Å too long on the MP2 level

of theory. They state, however, that: "Since the wave function deficiency will be almost the same in the monomer and in the complex, it is believed that it should not have a serious effect on these calculations". This is clearly a misjudgement of the situation. A valid description of the monomer properties is essential for a correct calculation of the intermolecular interactions. The dipole moment of NNO especially is crucial, and its magnitude will, to a large extent, determine the strength of the interaction. As illustrated in Table 1, the calculated value of the NNO dipole moment converges only slowly with the perturbation order. Also, the dipole moment of NNO in the complex is different from that of the monomer. Tables 3 and 4 give the dipole moment of the NNO···HF and ONN···HF complexes at all levels of theory used. These dipole moments are not the sum of the moments of the subunits, due to the mutual polarization. NNO has the larger polarizability and thus contributes the major part of the induced effect.

The dipole moment of the complex varies considerably with the order of perturbation and it cannot a priori be claimed that even the fourth order result is converged. However, comparison with experiment strongly indicates that such a view is too pessimistic. As indicated in Table 1, all monomer properties computed at the MBPT4 level are in excellent agreement with experiment. Especially important in this context are the results for the dipole moments and polarizabilities. With these properties correctly computed we also believe the other properties of the complexes are essentially correct. However, this result is, to some extent, fortuitous. It is a general rule that the contribution from triple excitations is overestimated at the fourth order of perturbation theory [38, 39], and one therefore expects to find the converged result somewhere between full MBPT4 and SDQ-MBPT4. It is therefore possible that the agreement with experiment found on the MBPT4 level is a result of cancellation between different types of errors. On the other hand, the rule itself may not be applicable in the NNO case, where the contribution from the triples are very important due to near degeneracies between different electronic configurations. How important they are is well illustrated by the dipole moment, for which SDQ-MBPT4 results in a value having the wrong sign while the MBPT4 result is in good agreement with experiment.

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