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Ab initio Studies on the Structures and OH Vibrations of Small H-Bonded Systems*

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Ab initio SCF+MP2 calculations in the ESPB basis are reported for the systems $(H_2O)_2$, $(CH_3OH)_2$, H_2O–H_2CO and $(H_2O)_3$. Analysis of the methodology and comparison with experiment, where available, show that the binding energies are reliable to about 1 kJ/mol, and the O···O distances accurate to 0.01 Å, provided one employs the full counterpoise procedure to avoid the so-called basis set superposition error. If, on the other hand, one ignores the BSSE, then unrealistically short O···O distances are obtained. Distinctly bent OH..O geometries are found in some of the complexes, suggesting that the distance of the closest approach is determined by the H..O contacts and not by the O···O contacts involved. Non-additivity in $(H_2O)_3$ is found to shorten the O···O distance by 0.06 Å, and to enhance its OH vibrational frequency shift by some 50%.

INTRODUCTION

An impressively wide-ranging (and often surprisingly accurate) qualitative understanding of the phenomenon of hydrogen bonding was available already in the sixties thanks to the early contributions made by Coulson,[1] Pimentel,[2] Hadži[3] and many others. From the seventies onwards, *ab initio* studies have steadily increased our quantitative knowledge on specific issues, such as the directional character of H-bond formation[4] and the role of non-additivity[5] in molecular clusters. Yet, even in 1986, one of the conclusions of an extensive *ab initio* study of H-bonded dimers was that predicted energies were still uncertain by about 4 kJ/mol, and predicted O···O distances in the largest calculations were still off by some 0.1 Å.[6] This situation clearly precludes meaningful predictions on the subtle differences between H bonds such as those in $(H_2O)_2$, $(CH_3OH)_2$ and H_2O–OCH_2, even though these are clearly of interest if one were to attempt an accurate modelling of biomolecular systems.

* Dedicated to Prof. D. Hadži on the occasion of his 70th birthday.

COUNTERPOISE PROCEDURES

The main underlying reason for the limited accuracy attained in the *ab initio* studies was the problem of how to handle the non-physical energy-lowering occurring in supermolecular calculations on interacting systems, usually referred to as basis-set superposition error (BSSE). Already in 1970, Boys and Bernardi[7] argued that the effect of a perturbation (in this case: interaction) can best be evaluated by applying the counterpoise procedure (CP). That is, the variational parameters available in the calculations on the cluster and on the monomers should be the same. In the following years, the validity of the CP has been questioned time and again, and there has been a great reluctance to rely on this procedure in deriving accurate interaction energies. Based on the argument that apart from the BSSE there are other errors in calculated energies, associated with limitations in the basis set and in the configuration-interaction (CI) procedures, it was suggested[6,8] to circumvent the BSSE problem by increasing the basis set to the largest size that can be handled. If this advice were to be taken seriously, it would push the era of accurate calculations on molecular interactions well into the next century.

However a close inspection of the arguments against the CP showed each of them to be invalid.[9,10] Subsequent calculations on He_2 provided conclusive numerical evidence of the extreme accuracy (better than 0.05 K or 0.0004 kJ/mol)[11,12,13] that can be obtained both at the SCF and at the CI level when the CP recipe is adhered to. An unexpected result emerging from these studies[12,13] is that in supermolecular CI calculations the monomer description used in evaluating ΔE should include higher levels of excitation than those actually available to the monomer in the dimer calculation. The implications of this result are being investigated further. However, the available results suggest that in the studies on polar molecules a sufficient degree of counterpoise is attained if at least all singly and doubly excited configurations are included in the CI description of both the monomers and the dimer (or, alternatively, if the MP2-method is adopted for both).

AB INITIO METHODS SUITABLE FOR H-BONDED SYSTEMS

Given the reliability of the counterpoise recipe, the factors that determine the accuracy of a given calculation are the quality of the one-electron basis set (the atomic orbitals) and the size of the n-electron basis set (the type of CI). As for the latter aspect, it is well known that triply-excited configurations contribute significantly to the dispersion energy in a given complex,[14] and so in systems in which E_{disp} is a large fraction of the binding energy (such as in the noble gas-molecule complexes) they cannot be ignored if one aims at accurate results. However, in H-bonding systems E_{disp} contributes only some 20% of ΔE, and good accuracy may be expected already if one truncates the CI expansion at the double-excitation level. In fact, in a recent thorough study on $(H_2O)_2$, Szalewicz *et al.*[15] demonstrated that the CP corrected contributions to ΔE from terms beyond MP2 are of the order of 0.5 kJ/mol and moreover tend to cancel. Thus, MP2 calculations in a good basis will be sufficient for obtaining good interaction energies.

As for the question what constitutes a good basis set, basically one requires a basis that adequately represents the permanent moments as well as the polarizabilities of the separate monomers.[16] Moreover, the shape of the atomic 'tail'[17] is important because it determines the overlap dependent exchange-contributions and, hence, such

properties as equilibrium distances and intermolecular stretching force constants. There is a consensus that double-zeta or triple-zeta-type basis sets, augmented with diffuse polarization functions, meet the above requirements.[15,16,18,19] Some components of ΔE converge more readily to the basis set limit than others. In polar complexes, the first-order coulomb interaction energy and the second-order dispersion energy are the terms that converge most slowly.[18,20] Following up earlier findings for He_2,[19] it has recently been found[20] that a set of s,p bond functions located at the midpoint of a H···X hydrogen bond speeds up the convergence of E_{disp} in H-bonded systems, and allows a closer approach to the basis set limit than it was possible without such functions.

In the remainder of this paper, we summarize some of our results that were obtained using the ESPB basis (see below) at the CP-corrected SCF and MP2 level of theory. In order to assist in the interpretation of the results, the SCF interaction energy was partitioned in first- and second order contributions, and the MP2 interaction energy was obtained using Vos' non-canonical MP2-theory, which allows a partitioning in contributions due to intra and inter-molecular correlation.[21] Thus, we have

$$\Delta E = E^1 + E^2 + E^{intra} + E^{inter}$$

where E^{inter} corresponds to the dispersion energy (including the effects of antisymmetrization).

EFFECT OF CP ON OPTIMIZED O···O DISTANCES: THE CASE OF $(H_2O)_2$

The availability of program packages that allow geometry optimization using gradient techniques has led to the practice that geometries of H-bonded systems are determined by searching for the global minimum of the total energy of a dimer. This ignores the presence of BSSE. A better, but more laborious procedure is to search for the geometry which minimizes the CP-corrected interaction energy ΔE. A striking illustration of the very different results to which these two procedures may lead is given in Table I, which is taken from ref. 20. Table I shows optimized R_{OO} distances for

TABLE I

Equilibrium properties of $(H_2O)_2$ from ab initio SCF + MP2 calculations in several basis sets[20],[a]

Basis	Number of contracted AO's	ΔE/kJmol^{-1} CP corrected[b]	R_{OO}/Å CP corrected	R_{OO}/Å no CP	E^{inter}/kJmol^{-1} R_{OO} = 2.963 Å[b]
DZP'	50	−18.3	3.03	2.86	−5.1
ESP	52	−18.8	2.98	2.84	−6.8
ESPB	56	−19.7	2.97	2.55	−7.3
EZPPB	84	−19.3	2.96	2.63	−8.1
Estimated limit		−19.6±0.8	2.95	(2.95)	–
Experimental data		−22.6±3.0[22]	2.96±0.01[23]		

[a] Using donor and acceptor angles from a geometry optimization in basis DZP'.[21]
[b] At R_{OO} = 2.963 Å, except for basis DZP', where R_{OO} = 3.03 Å.

$(H_2O)_2$ in a number of basis sets. It is clear that the larger basis sets, which include bond functions, give O···O distances that considerably depart from reality if one minimizes the total dimer energy. Even fairly conventional sets, such as ESP, give O···O distances that are much too short. In contrast, a smooth and rapid convergence to the experimental O···O distance is observed if instead one searches for the minimum of the CP-corrected ΔE.

Another aspect of Table I is the convergence of the CP-corrected ΔE to the basis-set limit. Numerical experiments using various basis sets larger than EZPPB[20] suggest that for the final $(H_2O)_2$ geometry found in Table I, the limit for ΔE at the SCF+MP2 level is -19.6 ± 0.4 kJ/mol. Explicit inclusion of higher excitation levels might shift this number by another 0.5 kJ/mol and so the exact nonrelativistic limit at this geometry is estimated to be -19.6 ± 0.8 kJ/mol. This value is at the lower bound of the experimental ΔE estimate by Curtiss *et al.*.[22] Note that most pair potentials that are currently used in molecular dynamics simulations have ΔE about -23 kJ/mol, and so all of these significantly overestimate the pair attractive force. A smaller basis that gives results for OH···O H-bonded systems that are only slightly less accurate (ΔE to within 1 kJ/mol for $(H_2O)_2$) is the ESPB basis. This is an O(10s,5p,1d)→[5s,2p,1d]/H(4s,1p)→[2s,1p] basis, augmented with one s, p set of bond functions.[20] The ESPB basis is seen to reproduce the most accurate R_{OO} and ΔE-values of $(H_2O)_2$ quite accurately. This is due to a cancellation of small errors in E^1 (which is overestimated) and E^{inter} (which is underestimated, *cf.* final column of Table I). If one assumes a similar cancellation to occur for related O–H···O bonded systems, it follows that SCF + MP2 calculations in basis ESPB can produce accurate data on the subtle differences between such systems. Some of these are discussed in the next sections.

$(CH_3OH)_2$: ACCURATE MEASUREMENTS ON ITS ΔE

By a remarkable coincidence, Bizzarri *et al.*[24] recently succeeded in directly measuring the dissociation energy of this H-bonded system. They found that CH_3OH-dimers in He or Ne molecular beams behaved differently when excited by a single photon from a low-power CO_2 laser. The not-so-cold He-beam dimers dissociated, but the cooler Ne-beam dimers survived the excitation and delivered the absorbed energy at the bolometer detector. From this observation it was possible to deduce that D_0, the dissociation energy from the lowest vibrational level, is 13.4 ± 0.4 kJ/mol. After correcting for the zero-point vibration energy, one finds $\Delta E = -20.9\pm1.2$ kJ/mol. $(CH_3OH)_2$ appears to be the first OH···O H-bonded dimer for which ΔE is known at such high precision.

SCF + MP2 calculations were carried out in the ESPB basis, assuming that the donor and acceptor angles are the same as for $(H_2O)_2$. Variation of R_{OO} led to a minimum at R_{OO} = 2.91 Å, and ΔE was calculated to be -22.2 kJ/mol. The excellent agreement with the experimental value confirms the validity of the above error estimates for *ab initio* calculations at the SCF + MP2 level.

The larger ΔE, as well as the shorter R_{OO} in $(CH_3OH)_2$, as compared to $(H_2O)_2$, is caused by the additional dispersion attractions in the former system and these differences are absent if only the SCF is considered. No direct experimental evidence for this shortening is available, since a gas-phase structure for $(CH_3OH)_2$ has not been determined. However, there is indirect evidence in that OH···O H-bonded chains in crystals of alcohols tend to have O···O distances near 2.67 Å, whereas one has O···O distances of about 2.75 Å in various H_2O ices.

The *ab initio* calculations on $(CH_3OH)_2$ showed the C–O lengths to be slightly different. In the proton-donor molecules C–O is 0.004 Å shorter than in free CH_3OH (this makes the donor O–H more acidic), while in the proton-acceptor molecule the C–O is 0.004 Å longer (making the acceptor more basic). These changes lead to a calculated difference of 24 cm^{-1} between the two C–O stretching frequencies. They are in reasonable agreement with the molecular beam experiment where these two vibrational frequencies were found to differ by 25 cm^{-1}. These findings are also consistent with the crystal geometry of 2- ethynyl –2-adamantanol[25] in which the two C–O lengths differ by as much as 0.024 Å.

THE WATER–FORMALDEHYDE COMPLEX: A STRONGLY BENT HYDROGEN BOND

Geometry optimizations at the CP-corrected SCF + MP2 level have been carried out for this system by Vos *et al.*,[21] using the DZP'-basis set. Single-point calculations at the final geometries were done in the ESPB basis set in order to obtain more reliable ΔE-values. Assuming a planar geometry for the complex, an initial optimization was done in which the OH···O bond was constrained to be linear. The optimum structure (Figure 1a) reflected the directional properties usually ascribed to the C=O–group, *i.e.* the minimum occurs in the direction of one of the presumed sp^2-hybridized lone pairs of this group. However, when the constraint of linearity was lifted, a pronounced bending of the donor and acceptor molecules took place to yield the geometry in Figure 1b. The H-bond O–H···O angle is now only 150 °, and the angle between O–O and the C = O bond is as large as 82 °. This folding is caused primarily by the E^1 term in ΔE, and may be ascribed to the close antiparallel side-by-side approach that it allows between the H_2O and H_2C = O dipole moments.The folding is accompanied by a lowering in ΔE of about 2 kJ/mol, and the final ΔE for this complex is slightly less than that of $(H_2O)_2$. A striking feature of the bent structure (Figure 1b) is that the H···O

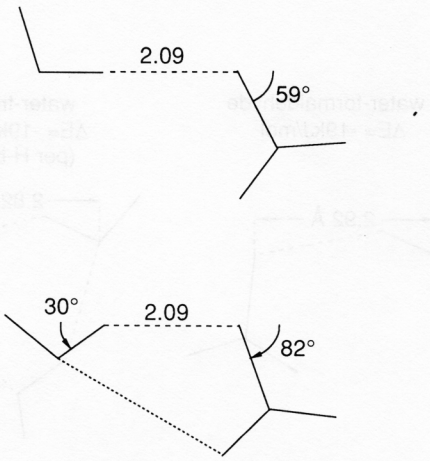

Figure 1. Optimized geometries for the water-formaldehyde complex at the SCF + MP2 level of theory. Basis set DZP'. (a) OH···O constrained to be linear, (b) unconstrained.

distance is virtually unchanged from that in Figure 1a. This strongly suggests that the distance of the closest approach is imposed by this H···O contact, and not, say, by the O···O contact, for the O···O distance is reduced from 3.04 Å (in Figure 1a) to 2.96 Å (in Figure 1b). (These optimizations will shortly be repeated using the ESPB basis, and we expect to find O···O distances that are shorter by about 0.05 Å).

The structure of water-formaldehyde has not yet been detected experimentally, but a less strongly bent H-bond with ∠FH···O = 164 ° has been reported for the FH–OCH_2 complex by Baiocchi *et al.*.[26]

CYCLIC WATER TRIMER: THE ROLE OF NON-ADDITIVITY

In this section, we present some preliminary results of a study at the SCF + MP2 level on cyclic $(H_2O)_3$.[27] The ESPB basis was employed. Following the usual procedure,[5,28] ΔE was evaluated not only for the trimer ABC, but also for the (individual) dimers AB, BC and CA, and the difference between these is the non-additivity contribution in ΔE_{ABC}. Assuming a planar structure with C_{3h} symmetry, the geometry was optimized by minimizing the total interaction-energy, ΔE_{ABC}, or, alternatively, the sum of the dimer energies ΔE_{AB} + ΔE_{BC} + ΔE_{AC}. Structures with strongly bent H bonds (OH···O angle 147°) were obtained in both cases. The bent OH···O bond allows a

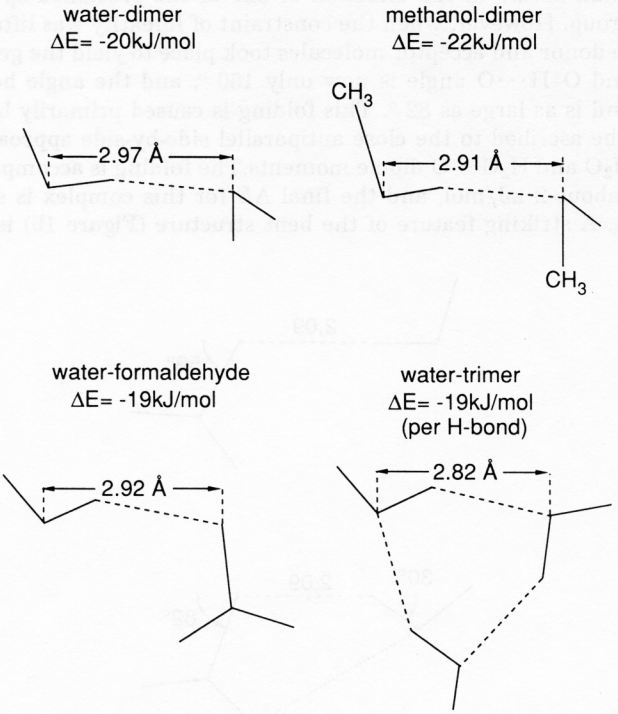

Figure 2. Optimized structures and energies for some OH···O hydrogen-bonded complexes at the SCF + MP2 level of theory, using the ESPB basis set. The O···O distance for water-formaldehyde is an estimate (see text).

short R_{OO} approach already at the pair level, just like in water-formaldehyde, even though ΔE per H-bond is rather small in the $(H_2O)_3$ case. The non-additivity term is strongly R-dependent and so inclusion of this term causes R_{OO} to contract by 0.06 Å, while ΔE per H-bond increases to the same value as that of water-formaldehyde. The large role of three-body non-additivity in producing short O···O distances has been pointed out previously in an SCF-study on the structure of ice.[29] Non-additivity contributions can be reliably obtained at the SCF level, for only the E^2 contribution to ΔE is markedly nonadditive.[28]

OH VIBRATIONAL FREQUENCY SHIFTS

H-bond formation causes a characteristic red shift of the infrared and Raman OH stretching bands of the OH groups involved.[2,3] Correlations between H-bond strength, R_{OO} and $\Delta\nu_{OH}$ have been established,[2,3] but many exceptions occur in practice and so one cannot simply assume that if $\Delta\nu_{OH}$ is large, R_{OO} *must* be short, or ΔE *must* be large. In order to achieve a better insight into these red shifts, we have calculated the change in the harmonic O–H stretching frequency, $\Delta\omega_e$, at a near-equilibrium geometry for several of the complexes considered here. This was done by considering the perturbation of a given high-accuracy anharmonic O–H potential by the first and second derivatives of the interaction energy ΔE with respect to the vibrational motion of the donor H atom. These derivatives were calculated at the SCF + MP2 level using the ESPB basis. Further details of this approach have been given in ref. 30. The resulting estimate of $\Delta\omega_e$ may be expected to have an accuracy of 10 cm^{-1}.

The results have been collected in Table II, together with some experimental frequency shifts, $\Delta\nu_{01}$, taken from Nelander's matrix isolation studies.[31,32] The data employed were taken (or estimated) from suitably deuterated systems, in order to reduce the effects of OH···OH vibrational couplings that were ignored in our calculations. Taking into account that our calculated shifts should be increased by some 15 cm^{-1} (for $(H_2O)_2$ and H_2O–OCH_2) up to some 40 cm^{-1} (for $(H_2O)3$) to allow for anharmonicity effects, the agreement with experiment is seen to be reasonably good. We are, hence, in a position to comment on the relation between ΔE, R_{OO} and $\Delta\nu_{01}$ in these complexes. All systems have roughly the same ΔE, and yet $\Delta\nu_{01}$ doubles when going

TABLE II

Properties of some OH..O hydrogen-bonded systems[a]

System	*Ab initio* results ΔE/kJmol^{-1}	R_{OO}/Å	O–H···O/°	$\Delta\omega_e$/cm^{-1}	Experiment $\Delta\nu_{01}$/cm^{-1}
$(H_2O)_2$	−19.7	2.97	173	−111	−120b
$(CH_3OH)_2$	−22.2	2.91	173 (ass.)	–	–
HOH..OCH_2	−19.2	[2.92]c	150	−93	−90[b]
$(H_2O)_3$ – pair approx.	−17.0[d]	2.88	147	−95[e]	–
– full treatment	−19.3[d]	2.82	147	−148[e]	−210[e,f]

[a]Based on *ab initio* SCF+MP2 calculations in basis ESPB.[20,21,24,27,30]
[b]Shifts of D*OH*..OHD and D*OH*..OCH_2 relative to free D*OH* in an N_2-matrix.[31]
[c]Estimated for basis ESPB from optimized result in basis DZP'.[21]
[d]Per H bond.
[e]Preliminary results, for the symmetric H-bonded OH-stretching mode.[27]
[f]Estimated from the observed OH modes of partially deuterated $(H_2O)_3$ in an Ar-matrix.[32]

to $(H_2O)_3$. No direct relation is, therefore, obtained between ΔE and $\Delta\nu_{01}$. The reason appears to be that in $(H_2O)_3$ there is a profound effect of the non-additivity on $\Delta\omega_e$, but not on ΔE.

At first sight, there does appear to be an inverse relation between R_{OO} and $\Delta\nu_{01}$, but even here one should not draw the conclusion that for $(H_2O)_3$ $\Delta\nu_{01}$ is large *because* R_{OO} is short. Rather, the short R_{OO} and the large $\Delta\nu_{01}$ are symptoms that have a common origin, *viz.* the large non-additivity in $(H_2O)_3$. However, the non-additivity may affect R_{OO} and $\Delta\nu_{01}$ to a different extent, depending on the geometry of the complex, and this leaves room for exceptions to a strict R_{OO} versus $\Delta\nu_{01}$ relation.

Finally, our calculated $\Delta\omega_e$-values allow us to comment on the OH vibrational bands that have recently been detected for water clusters in the gas phase.[33-35] The initial assignments of these bands implied a $\Delta\nu_{01}$ shift of about -200 cm^{-1} for the dimer. However, these assignments have been questioned,[36] and in fact our calculated values support Nelander's reassignment of these bands.

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REFERENCES

1. C. A. Coulson, *Research* **10** (1957) 149.
2. G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond*, W. H. Freeman, San Francisco, 1960.
3. *Hydrogen Bonding*, D. Hadži (ed.), Pergamon Press, London, 1959.
4. R. Bonaccorsi, C. Petrongolo, E. Scrocco, and J. Tomasi, *Theor. Chim. Acta (Berl.)* **20** (1971) 331.
5. D. Hankins, J. W. Moskowitz, and F. H. Stillinger, *J. Chem. Phys.* **53** (1970) 4544.
6. M. J. Frisch, J. E. Del Bene, J. S. Binkley, and H. F. Schaefer, *J. Chem. Phys.* **84** (1986) 2279.
7. S. F. Boys and F. Bernardi, *Mol. Phys.* **19** (1970) 553.
8. D. W. Schwenke and D. G. Truhlar, *J. Chem. Phys.* **82** (1985) 2418.
9. J. H. van Lenthe, J. G. C. M. van Duijneveldt-van de Rijdt, and F. B. van Duijneveldt, *Adv. Chem. Phys.* **69** (1987) 521.
10. M. Gutowski, F. B. van Duijneveldt, G. Chałasiński, and L. Piela, *Mol. Phys.* **61** (1987) 233.
11. R. J. Vos, J. H. van Lenthe, and F. B. van Duijneveldt, *J. Chem. Phys.* **93** (1990) 643.
12. R. J. Vos, F. B. van Duijneveldt, and J. H. van Lenthe, *Mol. Phys.* **67** (1989) 1011.
13. B. Liu and A. D. McLean, *J. Chem. Phys.* **91** (1989) 2348.
14. W. Meyer, P. C. Hariharan, and W. Kutzelnigg, *J. Chem. Phys.* **73** (1980) 1880.
15. K. Szalewicz, S. J. Cole, W. Kołos, and R. J. Bartlett, *J. Chem,. Phys.* **89** (1988) 3662.
16. J. G. C. M. van Duijneveldt-van de Rijdt, and F. B. van Duijneveldt, *J. Mol. Struct.* **89** (1982) 185.
17. M. Gutowski, G. Chałasiński, and J. G. C. M. van Duijneveldt-van de Rijdt, *Int. J. Quant. Chem.* **26** (1984) 971.
18. S. M. Cybulski, G. Chałasiński, and R. Moszyński, *J. Chem. Phys.* **92** (1990) 1.
19. M. Gutowski, J. Verbeek, J. H. van Lenthe, and G. Chałasiński, *Chem. Phys.* **111** (1987) 271.
20. J. G. C. M. van Duijneveldt-van de Rijdt and F. B. van Duijneveldt, submitted to *J. Chem. Phys.*
21. R. J. Vos, R. Hendriks, and F. B. van Duijneveldt, *J. Compt. Chem.* **11** (1990) 1.
22. L. A. Curtiss, D. J. Frurip, and M. Blander, *J. Chem. Phys.* **71** (1979) 2703.
23. J. A. Odutola and T. R. Dyke, *J. Chem. Phys.* **72** (1980) 5062.
24. A. Bizzarri, S. Stolte, J. Reuss, J. G. C. M. van Duijneveldt-van de Rijdt, and F. B. van Duijneveldt, *Chem. Phys.* **143** (1990) 423.

25. S. Y. Lin, Y. Okaya, D. M. Chiou, and W. J. le Noble, *Acta Cryst. B* (1982) 1669.
26. F. A. Baiocchi and W. Klemperer, *J. Chem. Phys.* **78** (1983) 3509.
27. J. G. C. M. van Duijneveldt-van de Rijdt, M. de Groot-den Hartogh, and F. B. van Duijneveldt, to be published.
28. G. Chałasiński, M. M. Szczęśniak, P. Cieplak, and S. Scheiner, *J. Chem,. Phys.* **94** (1991) 2873.
29. B. J. Yoon, K. Morokuma, and E. R. Davidson, *J. Chem. Phys.* **83** (1985) 1223.
30. J. G. C. M. van Duijneveldt-van de Rijdt, and F. B. van Duijneveldt, submitted to *J. Compt. Chem.*.
31. B. Nelander, *J. Chem. Phys.* **72** (1980) 77.
32. A. Engdahl and B. Nelander, *J. Chem. Phys.* **86** (1987) 4831.
33. R. H. Page, J. G. Frey, Y.-R. Shen, and Y. T. Lee, *Chem. Phys. Lett.* **106** (1984) 373.
34. D. F. Coker, R. E. Miller, and R. O. Watts, *J. Chem. Phys.* **82** (1985) 3554.
35. S. Wuelfert, D. Herren, and S. Leutwyler, *J. Chem. Phys.* **86** (1987) 3751.
36. B. Nelander, *J. Chem. Phys.* **88** (1988) 5265.

SAŽETAK

Studije *ab initio* o strukturi i vibracijama skupine OH u malim sustavima s vodikovom vezom

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Prikazani su proračuni *ab initio* SCF-MP2 za sustave $(H_2O)_2$, $(CH_3OH)_2$ i $(H_2O)_3$. Analiza metodologije i usporedba s eksperimentom, gdje je to moguće, pokazuju da su vezne energije pouzdane na oko 1kJ/mol, a udaljenosti O···O točne na 0.01 Å, pod uvjetom da se koristi postupak »protutežni« (»counterpoise«) da bi se izbjeglo zbrajanje pogrešaka u baznom skupu. Ako se pak, s druge strane, zanemare BSSE, dobivaju se nerealno kratke udaljenosti O···O. U nekim kompleksima nađene su jasno svinute geometrije OH···O, upućujući na to da je udaljenost najbližeg dosega određena kontaktima H···O, a ne onima O···O. Utvrđeno je da neaditivnost u $(H_2O)_3$ skraćuje udaljenosti O···O za 0,06 Å i povećava pomak vibracijske frekvencije OH za oko 50%.