Concerted hydrogen atom exchange between three HF molecules

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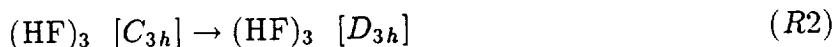Contribution No. 4558

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ABSTRACT

We have investigated the termolecular reaction involving concerted hydrogen exchange between three HF molecules, with particular emphasis on the effects of correlation at the various stationary points along the reaction. Using an extended basis, we have located the geometries of the stable hydrogen-bonded trimer, which is of C_{3h} symmetry, and the transition state for hydrogen exchange, which is of D_{3h} symmetry. The energetics of the exchange reaction were then evaluated at the correlated level, using a large atomic natural orbital basis and correlating all valence electrons. Several correlation treatments were used, namely, configuration interaction with single and double excitations, coupled-pair functional, and coupled-cluster methods. We are thus able to measure the effect of accounting for size-extensivity. Zero-point corrections to the correlated level energetics were determined using analytic second derivative techniques at the SCF level. Our best calculations, which include the effects of connected triple excitations in the coupled-cluster procedure, indicate that the trimer is bound by 9 ± 1 kcal/mol relative to three separated monomers, in excellent agreement with previous estimates. The barrier to concerted hydrogen exchange is 15 kcal/mol above the trimer, or only 4.7 kcal/mol above three separated monomers. Thus the barrier to hydrogen exchange between HF molecules via this termolecular process is very low.

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The HF trimer is known to adopt a C_{3h} equilibrium structure[4], while the transition state for concerted hydrogen exchange has been found to display D_{3h} symmetry. We shall consider the following three reactions:

$$3HF \rightarrow (HF)_3 \ [C_{3h}] \qquad\qquad (R1)$$

$$(HF)_3 \ [C_{3h}] \rightarrow (HF)_3 \ [D_{3h}] \qquad\qquad (R2)$$

$$3HF \rightarrow (HF)_3 \ [D_{3h}]. \qquad\qquad (R3)$$

Clearly, the energies of these three reactions are not independent, but it is convenient to retain all three for purposes of discussion.

There have been a number of recent calculations of the relative energies of the C_{3h} and D_{3h} forms of the hydrogen fluoride trimer, that is, the energy of ($R2$), generally at the self-consistent field (SCF) level. Gaw and coworkers[4] calculated this energy to be 29.5 kcal/mol using a double-zeta plus polarization (DZP) basis. From their data, the actual energy for reaction ($R3$) to proceed is 14.6 kcal/mol, uncorrected for vibrational effects. Heidrich[5] et al. employed a variety of basis sets with geometries obtained by optimization at the 4-31G split-valence level. Their best calculation gave $\Delta E(D_{3h}\text{-}C_{3h})=$ 37.1 kcal/mol ($R2$) and an activation energy($R3$) of 26.5 kcal/mol. An investigation of the relative stability of cyclic and open forms of the trimer by Karpfen[6] and coworkers has shown that the cyclic structure is more stable, while Liu et al. have investigated the stabilities of the trimer and tetramer relative to isolated fragments[7]. Most recently, Karpfen[8] has investigated equilibrium structures and concerted hydrogen exchange in (HF)$_3$ and several other HF clusters, using split-valence plus polarization basis sets and the averaged coupled-pair functional (ACPF) method. These results are compared to ours below.

In the present work we use large segmented Gaussian basis sets to locate the (HF)$_3$ stationary points at the SCF level, and then refine the energetics by performing extensive correlated calculations at the configuration-interaction and coupled-cluster levels, using large atomic natural orbital basis sets. Our computational methods are described in the next section, followed by a discussion of our results and conclusions.

Computational methods

The geometry of each stationary point was initially optimized at the SCF level using a triple-zeta plus polarization (TZP) basis of the form $[5s \ 3p \ 1d]/[3s \ 1p]$ contracted from a $(10s \ 6p \ 2d/5s \ 1p)$ primitive set[9]. The fluorine d set is a two-term fit to a Slater function with exponent 2.2 and the hydrogen p set has a Gaussian exponent of 1.0. Vibrational frequencies were evaluated at the SCF level using analytic second derivative methods[10]. The TZP basis was extended to $[5s \ 3p \ 2d]/[3s \ 2p]$ for use in MP2 calculations: an additional

d set was added (a two-term fit to a Slater function with exponent 0.7), while the original hydrogen p set was replaced by two functions with Gaussian exponents 1.4 and 0.35. Finally, in the largest of these MP2 calculations the $[5s\ 3p\ 2d]/[3s\ 2p]$ basis was augmented with an f set (exponent 1.9) on each of the fluorine atoms. All of these initial SCF and MP2 calculations utilized the program GRADSCF.[11]

For more elaborate studies of correlation effects, an atomic natural orbital (ANO) basis[12] of the form $[4s\ 3p\ 2d\ 1f/3s\ 2p\ 1d]$ was used. This was contracted from a $(13s\ 8p\ 6d\ 4f/8s\ 6p\ 4d)$ primitive set: the fluorine s and p exponents and the hydrogen s exponents are taken from van Duijeneveldt[13] and the polarization functions are even-tempered expansions $\alpha\beta^k, 0 \leq k \leq n$. The ratio β is 2.5 in all cases, with $\alpha(d) = 0.16$ and $\alpha(f) = 0.49$ on fluorine and $\alpha(p) = 0.1$ and $\alpha(d) = 0.26$ on hydrogen. The ANOs for fluorine were obtained from a single and double excitation CI (CISD) calculation on the atomic ground state, while those for hydrogen were obtained from a calculation on the molecule H_2.[12]

The first set of infinite-order correlated calculations was performed using the CISD method, including also Davidson's correction for higher excitations[14], denoted CISD+Q. The second method used was the coupled-pair functional (CPF) method of Ahlrichs and coworkers[15] which is nearly size-extensive. Finally, the coupled cluster method with single and double excitations (CCSD) was used — this is exactly size extensive[16] — together with the method denoted CCSD(T) in which a perturbational estimate of the effect of connected triple excitations is included.[17] In the correlated calculations SCF orbitals were used, and either 24 or 18 electrons were correlated: the former corresponds to neglecting fluorine $1s$ electron correlation while in the latter correlation is neglected for both fluorine $1s$ and $2s$. No virtual orbitals were deleted in any calculations, and in the ANO basis calculations only the spherical harmonic components of the basis functions were used. The CISD and CPF calculations were performed using the MOLECULE-SWEDEN suite of programs[18], while the coupled-cluster calculations were performed using the program VCCSD[19].

Results and Discussion

Geometry

Our optimized SCF bond distance in HF is 0.902 Å, compared to an experimental[20] value of 0.917 Å. In the calculated equilibrium structure for the trimer, the H-F bond increases slightly, to 0.910 Å, and the hydrogen-bonded H$-$F distance is 1.917 Å. Our calculated results are similar to those of Gaw and co-workers[4], who found $r(H-F)$ to be 0.912 Å in the monomer and 0.923 Å in the C_{3h} trimer. Their value for the H$-$F hydrogen bond distance is 1.860 Å, somewhat shorter than our value, which was determined using

a larger basis set. Our calculated H-F bond distance in the symmetric D_{3h} trimer is 1.136 Å, in excellent agreement with the value of 1.139 Å found by Gaw *et al.* As we noted above, Karpfen[8], has included correlation at the ACPF level using a split-valence plus polarization basis set. His optimum bond lengths are 0.919 Å in the monomer and 0.932 Å in the trimer. Correlation thus appears to have a rather small effect on the geometries, although the effect is larger on the trimer than on the monomer.

Vibrations:

For HF we calculate a harmonic frequency of 4455 cm^{-1} with an infrared intensity of 172 km/mol using the TZP basis set at the SCF level. The experimental value is 4138 cm^{-1}, while Gaw *et al.* calculated a value of 4440 cm^{-1}, and Karpfen[8], a value of 4182 cm^{-1} at the ACPF level. There is a strong dependence of the calculated vibrational frequency on the HF bond length: if the bond is elongated the computed "frequency" decreases sharply. The calculated trimer frequencies are given in Table I.

The hydrogen-bonded systems (HF)$_n$ have been extensively investigated experimentally, Some of these studies have included investigations of the higher species, although most have focused primarily on the dimer. Klemperer and coworkers[21] have shown that the trimer of HF is non-polar, consistent with a C_{3h} symmetry structure. Molecular beam predissociation experiments on the trimer have also been performed[22,23], as have infrared vibrational spectroscopy experiments in neon and argon matrices[24,25]. The vibrational predissociation spectrum of the trimer indicates that the e' band lies at 3712 cm^{-1}. Only one of the bands observed in matrix isolation spectra is consistent with a C_{3h} symmetry structure, the others are presumably due to open-chain forms that may be present in these experiments. This band is found at 3706 cm^{-1} in a neon matrix, and at 3702 cm^{-1} in an argon matrix.

Our C_{3h} structure is a minimum, based on the computed force constants. Of the twelve possible vibrational bands in this molecule there are three infrared active degenerate e' bands and one infrared active a'' band. Two of these bands, one of a' and the other of e' symmetry, correlate with the separated HF molecule fragment vibrations, while the remaining bands in the trimer correlate with translations and rotations in the separated fragments, that is to "intermolecular" modes in the trimer. The symmetric HF stretch is red shifted by 241 cm^{-1} while the degenerate HF stretch is red shifted by 175 cm^{-1} from the monomer. The red shift is consistent with the increase in the HF bond distance on going from monomer to trimer, although other factors also play a role, of course. Similar red shifts were computed by Karpfen. Our calculated frequencies are somewhat larger than those of Gaw and coworkers. The intensity of the degenerate e' stretch is predicted to be very large both in our calculations and in the other studies.
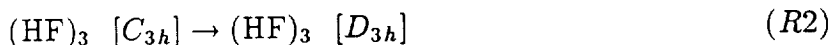
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The remaining harmonic frequencies are all below 1000 cm^{-1} and are associated with the intermolecular librational motions. The symmetric and degenerate hydrogen bond bends are at 879 and 531 cm^{-1}, respectively. The degenerate hydrogen bond bend is predicted to be very intense as is the out-of-plane motion of a'' symmetry.

In order to compare our computed trimer frequencies with experiment, we scale them by a factor of 0.93, which is the ratio of the experimental harmonic frequency of HF monomer to our computed value. Our scaled calculations thus predict a harmonic frequency of 3919 cm^{-1} for the symmetric H-F stretch and 3980 cm^{-1} for the degenerate H-F stretch. The experimental [23], gas phase result is 3712 cm^{-1} differing from our scaled result by almost 270 cm^{-1}, and suggesting a remarkably large anharmonicity for this mode. The assignment of the remaining bands appears to be in much better agreement with the available experimental data. We assign the band at 590 cm^{-1} to the a'' out of plane mode, calculated value of 596 cm^{-1}, while the band at 477 cm^{-1} is assigned as the degenerate bend in the C_{3h} trimer, calculated value 478 cm^{-1}. Both of these modes are predicted to be intense, while the lowest lying e' band is calculated to be very weak when compared to the other transitions.

Force constant calculations confirm that the D_{3h} symmetry structure is a transition state with the direction of negative curvature appropriate for the simultaneous exchange of hydrogens among the fluorines. The magnitude of the imaginary frequency is found to be $2224i$ cm^{-1}, consistent with the dominant motion involving hydrogens. The totally symmetric stretch is about half of its value when compared to the C_{3h} symmetry trimer. One of the degenerate stretches is much lower (1674 cm^{-1}) than the value found in the C_{3h} symmetry trimer (4280 cm^{-1}), and one is much higher, 1506 cm^{-1} versus 531 cm^{-1}.

Energetics:

Our discussion of the energetics of the concerted hydrogen exchange is based on the three reactions $R1$–$R3$ given in the Introduction: we repeat them here for convenience.

$$3\text{HF} \rightarrow (\text{HF})_3 \ [C_{3h}] \hspace{4cm} (R1)$$

$$(\text{HF})_3 \ [C_{3h}] \rightarrow (\text{HF})_3 \ [D_{3h}] \hspace{3cm} (R2)$$

$$3\text{HF} \rightarrow (\text{HF})_3 \ [D_{3h}]. \hspace{4cm} (R3)$$

Although ultimately the enthalpy changes are important chemically, we will first focus only on the electronic energy differences. Our results are summarized in Table II, where we present values for each of the three reactions given above with SCF, perturbation theory, CI, as well as the coupled-cluster methods. Our most accurate results suggest that the stable hydrogen bonded trimer is bound by slightly more than 14 kcal/mol relative to the

separated fragments, the barrier to reaction ($R3$) is predicted to be only 3.6 kcal/mol, and the energy separation between the transition state, and the stable trimer ($R2$) is 18 kcal/mol. This is in marked contrast to the results of most of the previous work cited in the introduction. There is also a substantial variation in the results depending on the correlation treatment employed, as we now discuss.

At the CISD+Q level of correlation treatment, the energy difference between three separated HF molecules and the transition state is found to be small: about 7 kcal/mol. A comparison of this reaction with the covalent exchange of hydrogens in the H_6 system indicates that introduction of ionic character into the molecular system by replacement of three hydrogens with three fluorine atoms reduces the effective barrier from some 70 kcal/mol to about 7 kcal/mol. An approximate quantitative measure of these changes can also be seen by an examination of the Mulliken charges calculated for the trimer and the transition state. At equilibrium the charge on hydrogen is found to be $0.3e^-$, whereas at the transition state this increases to $0.4e^-$.

As expected, the formation of the C_{3h} trimer from three monomers is found to be exothermic. The SCF value is found to be 12.4 kcal/mol while each of the correlated treatments predict that the complex is slightly more than 14 kcal/mol more stable than the reactants. The effect of correlation is found to be about 1.7 kcal/mol and roughly independent of the number of electrons correlated or the level of treatment. Liu and coworkers[7] have found that correlation contributed about 1 kcal/mol to this energy, somewhat less than we do. Their value was obtained with a TZP basis, while correlation effects were included at the ACCD level[26]. Karpfen obtains a somewhat larger binding energy (15.4 kcal/mol) at the ACPF level, with a rather small basis. We note, however, that consideration of basis set superposition error changes these observations, as we discuss in detail below.

The effect of correlation is most dramatically seen on the energy difference between the stable complex and the transition state. At the SCF level we find this energy difference to be over 35 kcal/mol, while the simplest correlation treatment (MP2) reduces this energy difference to 16 kcal/mol. More elaborate single and double excitation correlation treatments result in a difference of about 20 kcal/mol. The results are largely insensitive to whether 18 or 24 electrons are correlated, so it would not be unreasonable here to regard the fluorine $2s$ electrons to be part of an atomic core. On the other hand, there are significant differences between the CISD results and those of the various size-extensive or approximately size-extensive treatments; with such a large number of electrons correlated this would be expected. Thus the simplest CI treatment, CISD, predicts an energy separation of 23.9 kcal/mol, whereas inclusion of the +Q correction reduces this value to

21.1 kcal/mol. CPF reduces this separation by another 1.1 kcal/mol, but this appears to be an overestimate when compared to the CCSD result of 20.9 kcal/mol. Finally, inclusion of the (T) correction for the effects of connected triple excitations reduces the energy separation by almost 3 kcal/mol. This large triples contribution to the barrier height for hydrogen exchange deserves further comment.

On initial examination, such a large effect of triples is unexpected, and might be assumed to indicate that nondynamical correlation (near-degeneracy effects) might be important at the transition state. Recently, Lee et al.[27] have proposed the use of a diagnostic for the effects of nondynamical correlation, based on the magnitude of the norm of the t_1 amplitudes, denoted T_1. This T_1 diagnostic has been shown to be a good indicator of the applicability of a single-reference-based coupled-cluster method. It was suggested[27] that a value larger than 0.02 for T_1 indicates nondynamical correlation effects are large enough to cast doubt on the reliability of single-reference treatments limited to single and double excitations. For the D_{3h} geometry of $(HF)_3$ T_1 is 0.01, which would indicate that nondynamical correlation effects should not be a problem. The large triples contribution in fact arises from a different (and in some respects a simpler) cause. At the transition state we have three chemical bonds which are significantly elongated relative to their equilibrium value. We can examine the effect of triple excitations on this bond-lengthening by computing the triples contribution for a single HF moiety, at equilibrium bond length and at the bond length obtained for the transition state. The triples contribution to the energy difference between these two geometries was found to be a little less than 0.7 kcal/mol. Thus of the 2.9 kcal/mol triples correction to the barrier height, almost 2.1 kcal/mol originates in the simultaneous stretching of three HF bonds. Hence only 0.8 kcal/mol should be ascribed to a true "many-body" effect. Nevertheless, it is clear that in a system where even more bonds participate in the rearrangement, such as hydrogen exchange among higher oligomers of HF, such cumulative effects would be further magnified and would certainly require an appropriate correlation treatment.

We can now examine several sources of error in these calculations. The first is the use of SCF geometries in the correlation treatment. In order to address this question we have reoptimized the structure of the D_{3h} transition state at the MP2 level using the TZ2P basis augmented by a set of f-type functions on each of the fluorine atoms. The bond lengths increase slightly (less than 0.01 Å), while the energy is lowered by less than 0.8 kcal/mol relative to the MP2 result at the SCF geometry. Although we have performed only the easier task of reoptimizing the geometry of the D_{3h} symmetry structure with its two degrees of freedom, we expect the effects of electron correlation to be substantially less for the equilibrium structure than for the transition state, as discussed below. We are therefore confident that our choice of SCF geometries will not be a source of significant

error.

A quantitative assessment of our energetics must include an estimate of the basis set superposition error (BSSE). Ideally, this should be done for both the stable complex and the transition state. However, estimating the BSSE for polyatomic systems like $(HF)_3$ presents some conceptual difficulties. We have chosen to proceed by computing a counterpoise correction for the stable complex, using the SCF-optimized geometry and with both a single HF molecule with two HF ghost basis sets present and two HF molecules with a single ghost basis present as the fragments. The ANO basis was used in all BSSE investigations. At the SCF level the BSSE is less than 0.1 kcal/mol. However, at the CCSD level the BSSE is slightly greater than 0.5 kcal/mol for *each* HF moiety. We would thus assign a BSSE of 1.5 kcal/mol for the hydrogen-bonded trimer: this is likely to be an overestimate rather than an underestimate. Nevertheless, these results suggest that the effects of correlation on the binding of the trimer are grossly exaggerated, since most of the energy lowering is due to BSSE. This is consistent with the results of Karpfen, who (assuming an SCF result similar to ours) would obtain an even greater correlation contribution to binding: the split-valence plus polarization basis of Ref. 8 is likely to have a larger BSSE than our ANO basis. On the other hand, the results of Liu and co-workers are less consistent with this picture. Finally, the structure of the transition state is not qualitatively different from that of the stable complex, so we can reasonably assign the same (upper bound) value of 1.5 kcal/mol to the BSSE in the transition state.

The incompleteness of the one-particle space is also a source of error in these calculations. Comparison of the MP2 results, at least, in the TZ2P and ANO basis sets, suggests that the effect of basis set extension on the binding energy of the trimer is relatively small. Nevertheless, it is now well understood that the dominant contribution to hydrogen bonding is electrostatic, and so the basis set used should not only correctly describe the bonding in the monomer, but also provide a reasonable description of the multipole moments and polarizability. ANO basis sets are not always capable of meeting these requirements without further augmentation[28], which would make the present calculations too expensive. It is thus possible that the effect of basis set incompleteness on the binding energy is somewhat underestimated by our calculations. However, it seems unlikely that the remaining effects would contribute more than 1 kcal/mol. Since the bonding in the transition state is similar to that in the stable complex, we expect that the basis set effect on the barrier height would, if anything, be even smaller.

Enthalpy Changes

Our calculated ΔE values refer to the bottom of the potential energy well and need to be corrected by the difference in zero point vibrational energy, ΔZPE. Our correction

is done at the harmonic level using the experimental value for the HF frequency, while the trimer values are derived from our calculated frequencies scaled by 0.93 as indicated above. The stable trimer contains 4.5 kcal/mol more vibrational energy than the separated reactants which reduces its stability to 9.9 kcal/mol. Correcting this value for BSSE will further reduce the stability of the trimer: if the full counterpoise correction is applied the result would be as low as 8 kcal/mol. In view of our discussion of basis set incompleteness, it seems reasonable to assert that the trimer is bound by 9±1 kcal/mol.

The ΔZPE correction between the transition state and stable trimer is -3.5 kcal/mol, while it is 1.1 kcal/mol between the transition state and the reactants. Given these values our calculated barrier at 0 K is 4.7 kcal/mol, and the energy separation between the stable trimer and the transition state is 14.5 kcal/mol. Each of these values may then be further corrected for BSSE, which would raise the computed barrier to 6.2 kcal/mol.

These results require further correction for non-zero temperatures. For reaction R2 there are no corrections required to convert ΔE to ΔH if we neglect the dependence of the vibrational energy on temperature. For R1 and R3 the values must be corrected for differences in the translational and rotational energies and for the difference between ΔE and ΔH ($\Delta H = \Delta E + \Delta n RT$ with $\Delta n = -2$). The correction term is $-6.5RT$ and at 300 K this corresponds to a value of -3.9 kcal/mol for the correction, or a barrier of 2.3 kcal/mol, if the BSSE value for the barrier is used.

Conclusions

We have investigated the exchange of hydrogen atoms in a hydrogen-bonded system and have shown that such an exchange can proceed with an activation energy of ≈ 4 kcal/mol. In addressing this problem we have also demonstrated that the presence of ionic character in the bonding lowers the barrier relative to that found in a purely covalent system, such as H_6. The effects of electron correlation on the energetics once again demonstrate the magnitude of size-extensivity errors when many electrons are correlated. In addition, in $(HF)_3$ the effects of triple excitations significantly alter the barrier height from that predicted at the CCSD level, and we can expect this effect to become more important with increasing size of the system. Finally, since the barrier to concerted hydrogen exchange is small, we may anticipate a significant contribution from tunneling to the rate of the exchange reaction.

References

1. P. R. Taylor, A. Komornicki and D. A. Dixon, J. Am. Chem. Soc. **111**, 1259 (1989)

2. D.A. Dixon, R.M. Stevens, D.R. Herschbach,
   Faraday Disc. Chem. Soc. **62**, 110 (1977)
   J.S. Wright Chem. Phys. Lett. **6**, 476 (1970)
   J.S. Wright Can. J. Chem. **53**, 549 (1975)

3. D.R. Herschbach, Faraday Disc. Chem. Soc. **55**, 233 (1973)

4. J.F. Gaw, Y. Yamaguchi, M.A. Vincent and H.F. Schaefer III,
   J. Am. Chem. Soc. **106**, 3133 (1984)

5. D. Heidrich, M. Ruckert, H.-J. Kohler, Chem. Phys. Lett. **136**, 13 (1987)
   D. Heidrich, H.-J. Kohler, D. Volkmann, Int. J. Quantum Chem. **27**, 781 (1985)

6. A. Karpfen, A. Beyer, and P. Schuster, Chem. Phys. Lett. **102**, 289 (1983)

7. S. Liu, D.W. Michael, C.E. Dykstra, and J.M. Lisy, J. Chem. Phys. **84**, 5032 (1986)

8. A. Karpfen, Inter. J. Quantum Chem. Symp. **24**, 129 (1990)

9. T.H. Dunning Jr., J. Chem. Phys. **55**, 716 (1971)

10. H.F. King and A. Komornicki in *Geometrical Derivatives of Energy Surfaces and Molecular Properties* , ed. P. Jorgenson and J. Simons, NATO ASI series C. Vol 166. D. Reidel, Dordrecht 1986.
    H.F. King and A. Komornicki, J. Chem. Phys. **84**, 5645 (1986)

11. GRADSCF is an *ab-initio* gradient program system designed and written by A. Komornicki at Polyatomics Research Institute.

12. J. Almlof and P.R. Taylor, J. Chem. Phys. **86**, 4070 (1987)

13. F.B. van Duijeneveldt, IBM Res. Report RJ945 (1971)

14. S.R. Langhoff and E.R. Davidson
    Int. J. Quantum Chem. **8**, 61 (1974)

15. R. Ahlrichs, P. Scharf and C. Erhardt, J. Chem. Phys. **82**, 890 (1985)

16. S.A. Kucharski and R.J. Bartlett, Adv. Quantum Chem. **18**, 281 (1986)
    R.J. Bartlett, J. Phys. Chem. **93**, 1697 (1989)

17. K. Raghavachari, G.W. Trucks, J.A. Pople and M. Head-Gordon,
    Chem. Phys. Lett. **157**, 479 (1989)

18. MOLECULE-SWEDEN is a vectorized electronic structure suite of programs written
    by J. Almlof, C.W. Bauschlicher,Jr., M.R.A. Blomberg, D.P. Chong, A. Heiberg,
    S.R. Langhoff, P.A. Malmqvist, A.P. Rendell, B.O. Roos, P.E.M. Siegbahn, and P.R.
    Taylor.

19. T.J. Lee and J.E. Rice, Chem. Phys. Lett. **150**, 406 (1988)

20. K.P. Huber, G. Herzberg, *"Constants of Diatomic Molecules"*, (Van Nostrand, Rein-
    hold, New York, 1979)

21. T.R. Dyke, B.J. Howard and W.J. Klemperer, J. Chem. Phys. **56**, 2442 (1972)

22. J.M. Lisy, A. Tramer, M.F. Vernon and Y.T. Lee, J. Chem. Phys. **75**, 4733 (1981)

23. J.M. Lisy and D.W. Michael J. Chem. Phys. **85**, 2528 (1986)

24. L. Andrews, V.E. Bondybey, J.H. English, J. Chem. Phys. **81**, 3452 (1983)

25. L. Andrews, G.L. Johnson, J. Phys. Chem., **88**, 425 (1984)

26. K. Jankowski, J. Paldus, Int. J. Quantum Chem. **18**,1243 (1980)
    R.A. Chiles, C.E. Dykstra, Chem. Phys. Lett. **80**, 69 (1981)
    S.M. Bachrach, R.A. Chiles, and C.E. Dykstra, J.Chem. Phys., **75**, 2270 (1981)

27. T.J. Lee, J.E. Rice, G.E. Scuseria and H.F. Schaefer III,
    Theor. Chim. Acta **75**, 81 (989)
    T.J. Lee and P.R. Taylor, Int. J. Quantum Chem. Symp. **23**, 199 (1989)

28. J. Almlof and P.R. Taylor, Adv. Quantum Chem. In press.

Table I
Calculated harmonic vibrational spectra

Mode	ω (cm^{-1})	I(km/mol)	Description
C_{3h} Structure:			
a'	4214	0	symmetric HF stretch
a'	879	0	symmetric bend
a'	186	0	symmetric stretch -libration
a''	662	507	out of plane torsion
e'	4280	571	degenerate HF stretch
e'	531	382	degenerate angular def.
e'	157	17	degenerate stretch - libration
e''	475	0	degenerate out of plane torsion
D_{3h} Structure:			
a_1'	2212	0	symmetric breathing stretch
a_1'	788	0	symmetric HF str. and bend
a_2'	2194i	–	negative curvature stretch
a_2''	1449	466	out of plane torsion
e'	1674	21	degenerate stretch plus bend
e'	1506	4154	degenerate stretch + bend
e'	604	0.3	degenerate bend + stretch
e''	1135	0	degenerate out of plane torsion

Table II
Comparison of relative energies[a]

Calculation:	ΔE(R1)	ΔE(R2)	ΔE(R3)
SCF, CI, and CPF Results:			
ANO SCF	−12.4	35.8	23.4
ANO CISD 18 el	−14.2	23.8	9.6
ANO CISD+Q 18 el	−14.1	21.3	7.2
ANO CPF 18 el	−14.1	20.8	6.7
ANO CISD 24 el	−14.3	23.9	9.6
ANO CISD+Q 24 el	−14.2	21.1	6.9
ANO CPF 24 el	−14.1	20.0	5.9
SCF, MP2, and CC Results:			
TZ2P/SCF		35.1	
TZ2P/MP2		16.7	
ANO SCF	−12.4	35.8	23.4
ANO/MP2	−14.3	16.1	1.8
ANO CCSD 24 el	−13.9	20.9	7.0
ANO CCSD(T) 24 el	−14.4	18.0	3.6

a) Relative energies are given in kcal/mol.

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