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When is H_3 stable to asymmetric distortion?

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The theory of the second-order Jahn-Teller effect is used to show that for sufficiently short bond lengths H_3 should be stable to asymmetric distortion. This prediction has been confirmed by *ab initio* MCSCF calculations.

Keywords: H_3—Second-order Jahn-Teller effect

1. Introduction

The theory of the second-order Jahn-Teller (SOJT) effect predicts that an asymmetric molecular distortion will be favored by a small energy gap between a filled and a partially filled or empty orbital that are mixed by the distortion [1]. Among its many applications SOJT theory has been used to explain molecular shapes [2-5], to predict the preferred modes of unimolecular reactions [6, 7], and to rationalize the unimportance of resonance in certain types of allylic radicals [8].

The instability of H_3 to a molecular distortion that shortens one H-H bond and lengthens the other may be seen as a consequence of the SOJT mixing of the singly occupied $1\sigma_u$ MO with the filled $1\sigma_g$ and the empty $2\sigma_g$ MO on this distortion. If the matrix elements that represent the mixing of the $1\sigma_u$ MO with the two σ_g MOs remain relatively constant, the theory of the SOJT effect predicts that the closer are the energies of these three orbitals, the more negative will be the force constant for asymmetric distortion to a hydrogen molecule plus a hydrogen atom.

Conversely, if the energy gaps between these MOs are somehow increased, the force constant for asymmetric distortion is expected to increase too. For sufficiently large energy gaps, the force constant for asymmetric distortion of H_3 should become positive.

The energy gaps between the MOs of H_3 depend on the overlap of the atomic orbitals of the two terminal hydrogen atoms with that of the central hydrogen. Since overlap varies with bond length, the force constant for asymmetric distortion should be a function of the bond length between the central and terminal hydrogens.

As the two identical H-H bond lengths in $D_{\infty h}$ H_3 decrease, the MO energy gaps increase. Provided that the matrix elements for MO mixing remain relatively constant with H-H bond length, SOJT theory allows one to predict that the force constant for asymmetric distortion will become more positive with decreasing bond length. For sufficiently short H-H bond lengths, the force constant for asymmetric distortion should change sign; and H_3 should become stable toward this type of molecular distortion.

2. Calculations

In order to test the SOJT prediction that, for sufficiently short H-H bond distances, H_3 should become stable to asymmetric distortion, *ab initio* calculations were performed. Dunning's $(4s/2s)$ double zeta Gaussian basis set for hydrogen [9] was augmented by a set of p orbital Gaussian polarization functions with orbital exponents of 1.2. In order to provide for electron correlation, MCSCF calculations were carried out, using all configurations that arise from all possible assignments of the three electrons to the three molecular orbitals of the conceptual minimal basis set. Calculations were performed using GAMESS [10].

Table 1 gives the results of calculations carried out for linear H_3 geometries with equal H-H bond lengths ranging from $R = 1.8$ to 1.4 bohr and for distorted variants in which one bond was lengthened by 0.1 bohr and the other was shortened by the same amount. In addition to the MCSCF energy at each geometry, the difference between the energies of the singly occupied $1\sigma_u$ MO and the doubly occupied $1\sigma_g$ is shown. The orbital energies were obtained from RHF calculations at geometries with equal bond lengths.

Table 1 shows that, as expected, the orbital energy difference increases with decreasing H-H bond length. Also as anticipated, as the orbital energy difference

Table 1. Energies (hartrees) of linear H_3

R (bohr)[a]	E^{b}_{sym}	ΔE^{c}_{asym}	$\Delta E(1\sigma_u - 1\sigma_g)^{d}$
1.80	−1.619944	−0.000576	0.241
1.70	−1.618150	−0.000199	0.270
1.60	−1.612469	0.000333	0.304
1.40	−1.583856	0.002090	0.388

[a] H-H bond length at symmetrical geometry

[b] Energy at symmetrical geometry

[c] Energy change after asymmetric distortion of bond lengths by ±0.1 bohr

[d] RHF energy difference between singly and doubly occupied MOs at symmetrical geometry

increases, the favorability of an asymmetric distortion of the H-H bond lengths decreases. At $R = 1.80$ bohr, which is very close to the interpolated, symmetrical energy minimum at $R = 1.796$ bohr in these calculations, an asymmetric bond length distortion of $\Delta R = \pm 0.1$ bohr lowers the energy by 0.6 mhartree. However, at $R = 1.40$ bohr, where the MCSF energy is 36.0 mhartree higher, the same asymmetric distortion of the H-H bond lengths raises the energy by 2.1 mhartree. The change in the sign of the force constant for asymmetric distortion occurs around $R = 1.67$ bohr at an energy that is only 3.0 mhartree higher than that at the symmetrical energy minimum (i.e., the transition state on the global H_3 surface).

3. Discussion

In order to verify that the computed change in the sign of the force constant for asymmetric distortion is not an artifact of the small basis set or of the limited treatment of electron correlation employed, the very accurate H_3 potential surface of Liu [11] was examined. From either the points tabulated by Liu or from the graphical representation of the fit to the surface by Truhlar and Horowitz [12], both the dependence of the asymmetric force constant on R and its change in sign at a value of R only slightly smaller than that at the symmetrical minimum were confirmed.

Physical insight into the reason why the force constant for asymmetric distortion in H_3 becomes positive for sufficiently small R can be gained by considering why SOJT theory predicts this change in sign to occur. For small R, because the MO energy gaps are large, SOJT theory predicts little orbital mixing. Thus, the wavefunction does not change significantly on asymmetric distortion, so that the two bonds tend to behave as independent oscillators. For values of R where this is the case, it is easy to show that the total energy is minimized when the two bonds have the same length. Indeed, if the energy of each bond is quadratic in R and independent of the other bond length, the force constants for symmetric and asymmetric distortion become identical.

The prediction of a positive force constant for asymmetric distortion of H_3 at sufficiently short R is obviously related to the transition from molecular to metallic hydrogen at high pressures [13] and to calculations that model this transition with finite chains [14] or rings [15] of hydrogens. In this regard it is interesting to note that Bender and Schaefer [14] found that, when linear H_4 is constrained to have equal bond lengths, the energy minimum occurs at $R = 1.67$ bohr. This is very close to the value at which the force constant for asymmetric distortion in H_3 is computed to change sign. However, it is clear from the data of Bender and Schaefer that at this value of R in H_4 shortening the two terminal bonds and lengthening the central one remains favorable.

Calculations on a 14-membered ring of hydrogen atoms find distorted geometries, consisting of seven hydrogen molecules, to be lower in energy than symmetrical geometries with equal bond length, until the intermolecular separation is reduced to the same value of 1.41 bohr as the H_2 bond length [15]. Thus, the present results on linear H_3 show it to become stable to asymmetric distortion of the H-H bond lengths at a larger value of R than the fourteen-membered ring. This finding suggests that, at identical values of R, SOJT stabilization on distortion is more effective in the symmetrical H_{14} ring than in $D_{\infty h}$ H_3. A larger SOJT effect in cyclic H_{14} than in linear H_3 is consistent with the relative size of the orbital energy gaps in these two systems, predicted by simple Huckel theory.

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References

1. Opik U, Pryce MLH (1957) Proc R Soc London A 238:425
2. Pearson RG (1969) J Am Chem Soc 91:4947
3. Salem L (1966) Molecular orbital theory of conjugated molecules. Benjamin, New York, pp 486-523
4. Cherry W, Epiotis N, Borden WT (1977) Acc Chem Res 10:167
5. Borden WT, Davidson ER, Feller D (1980) J Am Chem Soc 102:5302
6. Bader RFW (1962) Can J Chem 40:1164
7. Pearson RG (1976) Symmetry rules for chemical reactions. Wiley, New York
8. Feller D, Davidson ER, Borden WT (1984) J Am Chem Soc 106:2513
9. Dunning TH, Hay PJ (1977) In: Schaefer HF (ed) Methods of electronic structure theory, vol 2. Plenum Press, New York
10. Dupuis M, Spangler D, Wendelowski JJ (1980) NRCC Software Catalog, vol 1. Program GG01
11. Liu B (1973) J Chem Phys. 58:1925
12. Truhlar DG, Horowitz CJ (1978) J Chem Phys 68:2466
13. Hawke PS, Burgess TJ, Duerre DE, Huebel JG, Keeler RN, Klapper H, Wallace WC (1978) Phys Rev. Lett 41:994
14. Bender CF, Schaefer HF (1972) J Chem Phys 57:217
15. Seel M, Bagus PS, Ladik J (1982) J Chem Phys 77:3123, and references therein