Energy hypersurface local properties of the O_2HF^- rearrangement

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This work analyses a case where Murrell's proposal, stating that a second-order point must lie above a first-order one, is apparently violated. Study at the SCF-UMP2 level within the D95++ basis set, of one critical point of the O_2HF^- anion, previously proposed to be of order two by Lopez, shows the importance of the electronic correlation. The critical point associated with the $^2\Pi$ state should rather be considered as a superposition of two first-order ones. The present analysis reveals that this contradistinction can be explained by three unconsidered elements: the local symmetry, the electronic correlation and the internal variables description.

1. Introduction

In his study of the ion O_2HF^- in a 4-31G basis set [1,2] augmented with 4 sp diffuse functions on each oxygen, Lopez [3] mentioned the existence of a second-order critical point that was 0.835 kcal/mol lower in energy than another trapped first-order saddle point. These two extrema lie on two different paths connecting two symmetric minima (see fig. 1). Lopez's result is in opposition to Murrell's proposal [4] according to which a minimum energy reaction path cannot pass through a critical point of order higher than 1. Since the wavefunction for the linear geometry of the second-order point is a $^2\Pi$ state, the Renner–Teller effect, i.e. the splitting of the two degenerate electronic states by a coupling with a π nuclear vibration [5], is expected. Given that a linear nuclear arrangement characterizes itself by $3N-5$ and not $3N-6$ normal modes, the linear symmetry breaking π vibrations contain a rotational-like component. The question thus arises as to whether the Hessian eigenvectors are associated with equivalent deformations, one in a given plane and the other in the perpendicular one.

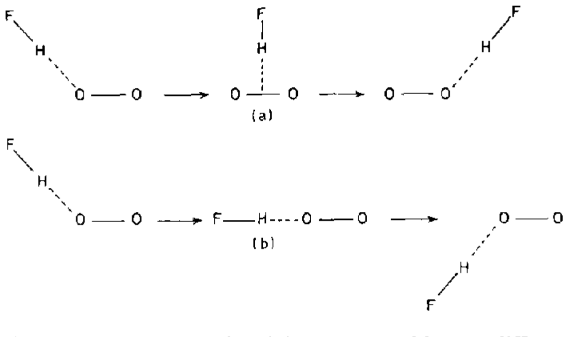

Fig. 1. The two symmetric minima connected by two different reaction paths through either the first-order critical point (a) or the second-order critical point (b).

The aim of this work is twofold: first to investigate the variation of the Hessian matrix during a non-linear deformation of the $^2\Pi$ state in order to determine the order of the critical point, and second to study the influence of electronic correlation.

2. Method of calculation

All the calculations were performed with GAUSSIAN 86 [6] on a FPS 264 attached to a Digital VAX 11/780.

The geometry optimizations were performed at the full UMP2 level with the Dunning D95 [7] basis set extended with diffuse functions on all the atoms (4 sp on the heavy atoms and 1 s on the hydrogen), and

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hereafter noted D95++. The work also includes 4-31G+ calculations for the $C_{\infty v}$, C_s and C_{2v} conformers.

In the course of the optimization, oscillations between the expected $^2A_2$ state and a close $^2B_2$ state occurred in such a way that the final result was obtained in the $^2B_2$ state, and not in the $^2A_2$ state. To solve this problem, a guess for the $^2A_2$ state was determined by drawing energy curves, in C_2 symmetry, for the two $^2A''$ and $^2A'$ states up to the C_{2v} geometry (see figs. 2 and 3).

Following the optimizations, frequencies and Hessian analytical calculations were performed in $C_{\infty v}$ and C_{2v} symmetry groups with different numbers of internal coordinates to emphasize the influence of freezing some symmetry deformations.

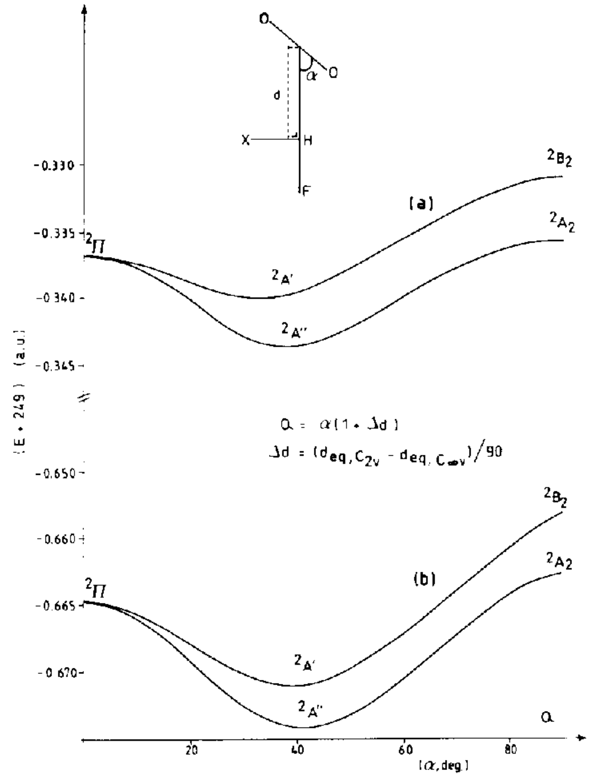

Fig. 2. SCF energy curves in the 4-31G+ [3] (a) and D95++ (b) basis sets, connecting the $^2\Pi$ state to the $^2A_2$ and $^2B_2$ states via the $^2A''$ and $^2A'$ states. The bond lengths O–O and H–F are the mean values between the optimized ones for the $^2\Pi$ and $^2A_2$ (in 4-31G+) or $^2B_2$ (in D95++) states. The coordinate used to connect $C_{\infty v}$ to C_{2v} is a linear combination of the angle α and the distance d.

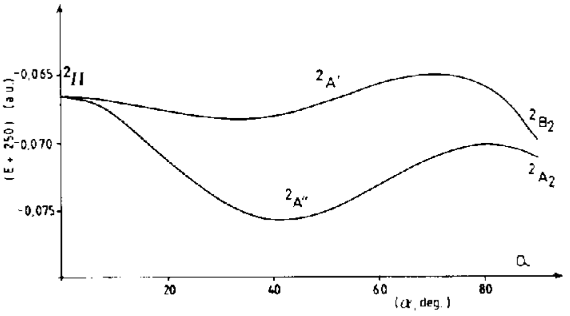

Fig. 3. UMP2 curves within the D95++ basis set, connecting the $^2\Pi$ state to the $^2A_2$ and $^2B_2$ states. See legend of fig. 2.

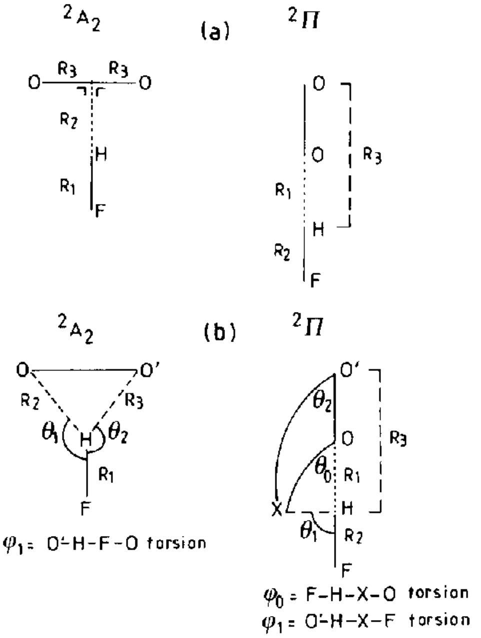

Fig. 4. Definition of the internal coordinates for the $^2A_2$ and $^2\Pi$ electronic states, for the geometry optimization (a) and the frequencies calculation (b).

3. Results and discussion

The geometries of the extrema were optimized with symmetry constraints, using only three internal variables ($R1$, $R2$, $R3$) either for C_{2v} or for $C_{\infty v}$ (see fig. 4a). That the extrema thus obtained (table 1) were

Table 1
Optimized $R1$, $R2$, $R3$ values (Å) for the $^2A_2$, $^2B_2$ and $^2\Pi$ electronic states (see fig. 4a), at the SCF and SCF+UMP2 levels, within the D95++ basis set

Variables	D95++//(SCF+UMP2)			D95++//SCF		
	$^2A_2$	$^2B_2$	$^2\Pi$	$^2A_2$	$^2B_2$	$^2\Pi$
$R1$	0.98406	0.97208	1.61788	0.94087	0.94064	1.56332
$R2$	1.74269	1.80710	0.98163	1.80162	1.88090	0.95348
$R3$	0.74271	0.74183	2.97628	0.67467	0.67568	2.90569

minima, was confirmed by the three positive eigenvalues of the Hessian.

Although the existence of the imaginary frequencies (one in C_{2v}, two in $C_{\infty v}$) is independent of the choice of the internal coordinates, the negative eigenvalues of the Hessian appear only when the additional symmetry breaking internal coordinates are introduced in the molecular description.

3.1. *The critical point of the $^2\Pi$ state*

In the linear conformation of the $^2\Pi$ state, seven frequencies are calculated (table 2), two of which are imaginary, i.e. correspond to negative eigenvalues of the usual force constants and metric matrices product FG [8]. These two vibrations are the components of a π normal mode. The non-equality of the two associated frequencies is due to the fact that the calculation is made with real numbers. Thereby the questions are whether or not the Hessian can correctly reproduce the order of the critical point [9] and whether or not the two imaginary frequencies remain when the symmetry is broken down.

If the $3N-5$ vibrational prescribed motions (seven variables) are taken into account – i.e. three bond lengths and four angles (valence and torsional) – two negative eigenvalues are always found and the motions represented by their associated eigenvectors correspond to out-linearity deformations. It is already well know that, at a critical point, the number of negative Hessian eigenvalues is independent of the choice of the coordinates in which it is calculated as long as the coordinate set is complete. As an example, we investigated how the number of negative Hessian eigenvalues, at the critical point of the $^2\Pi$ state, could be accounted for by different choices (all the possible combinations were envisaged) of only $3N-6$ variables. It was found that the number of negative eigenvalues is not always two. There are two cases for which only one negative eigenvalue is found. The suppression of one angle, i.e. of one out-linearity deformation, leads to the disappearance of one π-like component among the Hessian eigenvectors and thus to the possibility of loosing one negative eigenvalue.

Furthermore, only one imaginary frequency is found for the very nearly linear C_s conformations or for the C_1 one of the $^2\Pi\rightarrow{}^2A_2$ electronic state (table 2), thus clearly indicating that the so-called second-order critical point can be considered as a superposition of two first-order ones. It remains that the description in terms of the Hessian can lead to two negative eigenvalues, depending on the choice on the internal coordinates. This fact is already well known [9–12] that, away from the critical points, the Hessian properties can vary substantially as a function of the coordinates choice.

One point to be noted in table 2 is the following. For the out-equilibrium C_s and C_1 conformations, the highest frequency (≈ 4000 cm^{-1}) appears to be associated with a deformation mode. This is quite unphysical and is related to the fact that the frequency analysis refers to an unstable nuclear arrangement very near linearity. If one admits that the combination of the two π deformations (≈ 645 and ≈ 911 cm^{-1}) could be viewed as the composition of one scissoring and one rotation (even though, at the linear conformation, these are not at all rotational modes), one can understand this ($\nu_{\text{"rot"}}\rightarrow\infty$) discontinuity.

Table 2
Frequencies (ν) (cm^{-1}) for: the linear $C_{\infty v}$ case ($^2\Pi$ state) (case 1), two C_s cases ($^2A''$) (cases 2 and 3) with different choices of the variables as defined in fig. 4b, and one C_1 case ($^2A \rightarrow {}^2A''$) (case 4) [a]

case 1: $\theta_1=\theta_2=90°$, $\phi_1=180°$						
ν (symmetry)	i×389.80 (π)	i×85.26 (π)	251.51 (σ)	645.37 (π), 911.05 (π)	1836.04 (σ)	3214.44 (σ)
deformation	scis.	bend.	rel. str.	2 ⊥ scis. = 1 scis. + 1 rot	O2 str. + rel. str.	HF str. + rel. str.
case 2: $\theta_1=\theta_2=90°$, $\phi_1=179.25°$						
ν (symmetry)	i×289.48 (a′)	252.47 (a′)	659.78 (a′)	1834.55 (a′)	3215.31 (a′)	4358.28 (a″)
deformation	in pl. scis.	rel. str.	in pl. scis.	O2 str. + rel. str.	HF str. + rel. str.	out pl. scis.
case 3: $\theta_1=90°$, $\theta_2=89.5°$, $\phi_1=179.5°$						
ν (symmetry)	i×289.91 (a′)	252.46 (a′)	659.60 (a′)	1834.70 (a′)	3215.34 (a′)	4206.90 (a″)
deformation	in pl. scis.	rel. str.	in pl. scis.	O2 str. + rel. str.	HF str. + rel. str.	out pl. scis.
case 4: $\theta_1=\theta_2=89.5°$, $\phi_1=179.5°$						
ν	i×375.19	251.28	664.03	1833.62	3200.23	3657.73
deformation	scis.	rel. str.	scis.	O2 str. + rel. str.	HF str. + rel. str.	scis.

[a] $\theta_0=90°$, $\phi_0=90°$, for all cases. Abbreviations: rel. = relative, str. = stretch, bend. = bending, scis.-scissoring, ⊥ = perpendicular, pl. = plane.

3.2. Energy curves connecting the $^2\Pi$ state to the $^2B_2$ and $^2A_2$ states

At the SCF level (see fig. 2), the 4-31G+ and D95++ basis sets produce qualitatively similar curves. The $^2B_2$ and $^2A_2$ states are separated by approximately 3 kcal/mol.

The energies for the optimized states are given in table 3. As already stated [3], the $^2\Pi$ energy of the so-called second-order point is 0.835 kcal/mol lower than the energy of the optimized $^2A_2$ first-order point in the 4-31G+ basis set. At the SCF level, a similar variation is observed with D95++, for both the SCF and the SCF+UMP2 optimized geometries. The differences are equal to 1.5 and 9.8 kcal/mol, respectively. In contrast, at the SCF+UMP2 level, within the D95++ basis set, the $^2\Pi$ state lies 10.5 kcal/mol higher than the $^2A_2$ state. As seen in figs. 2 and 3, the correlation is much more important in the C_{2v} conformation than in the $C_{\infty v}$ one, the difference being around 20 kcal/mol (table 3). It can be calculated straightforwardly from the data of table 1, that on the average, the two oxygens are nearer HF in C_{2v} than in $C_{\infty v}$. Hence, it seems obvious that the correlation correction is greater in the former than in the latter symmetry arrangement.

4. Conclusions

In the linear conformation of the O_2HF^- ion, the two imaginary frequencies that define a second-order critical point are due to the symmetry degeneration. This statement is highlighted by the occurrence of a single imaginary frequency in the nearly linear C_s and C_1 geometries. Under this condition, the $^2\Pi$ state should be considered rather as a superposition of two first-order saddle points.

The energies associated with the optimized $^2\Pi$ and $^2A_2$ states clearly emphasize the importance of the electronic correlation. At the SCF level, the $^2\Pi$ state is lower in energy than the $^2A_2$ state whereas this feature is inverted at the UMP2 level.

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Table 3
Energies (hartree) of the $^2\Pi$, $^2A_2$ and $^2B_2$ states for the optimized geometries in the D95+ + basis set, at the SCF+UMP2 level, and in the 4-31G+ basis set at the SCF level

	4-31G+ [3] SCF	D95+ +			
	4-31G+//SCF	SCF D95+ +//SCF	SCF+UMP2 D95+ +//(SCF+UMP2)	SCF D95+ +//(SCF+UMP2)	correlation correction [a] D95+ +// (SCF+UMP2)
$^2\Pi$	−249.3368104	−249.6637268	−250.0728007	−249.6624643	−257.5
$^2A_2$	−249.3354796	−249.6612588	−250.0895302	−249.6467892	−277.8
$^2B_2$	−249.3308317	−249.6570084	−250.0823325	−249.6440237	−275.0

[a] In kcal/mol.

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Note added

The Hessian eigenvalues, and their associated deformation characterization, corresponding to table 2, are available on request.

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