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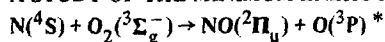
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A STUDY OF THE MINIMUM ENERGY PATH OF THE REACTION
$N(^4S) + O_2(^3\Sigma_g^-) \rightarrow NO(^2\Pi_u) + O(^3P)$ *

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A new method of calculating polyatomic surfaces is used to obtain minimum energy paths for the reaction $N + O_2 \rightarrow NO$ + O. The calculated barrier height is nearly 14 kcal/mole for the doublet surface whereas that of the quartet surface 18 kcal/mole.

1. Introduction

The reaction $N + O_2 \rightarrow NO + O$ is an important contributor in the upper atmospheric processes. One important question has been the height and location of the barrier of the exothermic reaction. There exists a number of experimental results giving an activation energy in the vicinity of 8 kcal/mole [1]. We reported a calculation [2] (to be referred to as I in the rest of the paper) sometime ago on the minimum energy path in the potential surface of this reaction proceeding via a $^2A'$ state. The calculations were based on an extensive MC SCF treatment followed by an exhaustive "valence" CI. However, the main emphasis of the work was more on determining the importance of various factors of the method: the basis set selection, the choice of configurations and the method of MC SCF + CI itself. The primary conclusions in this regard were that (i) a double-zeta level basis set is a good first choice, (ii) changing to a large basis set containing d functions does not alter the barrier height significantly and (iii) more configurations than those of the "valence-only" type are needed, particularly those representing at least one order of excitation in virtual orbitals in order to make an accurate determination of the barrier height. (iv) In general the "MC SCF + CI" approach was demonstrated to be a direct and accurate way of exploring the reaction surface. However, extension to excitations involving virtual orbitals needs thousands of configurations in the CI step. This is not intractable, considering the recent advances in the theory of large CI matrices. However, in this work we adopt a more economical approach based on the following observation: Excitations representing various kinds of correlation can be broken up into small groups of configurations such that matrix elements connecting members of different groups are small. These groups can therefore be optimized separately. The corresponding improvements in energy are then added to the valence CI energy leading to the total energy versus R curve.

As we have noted in I there exist in the literature suggestions of which some favor the doublet state, while the others favor the quartet for the potential surface of the reaction $N + O_2 \rightarrow NO + O$. While Clyne and Thrush [1] suggest that the reaction proceeds through a linear or bent transition complex $N-O-O$ with the bent complex most probably in a doublet state, a semi-empirical diatomics-in-molecule calculation by Wilson [3] rules out the doublet state. We have already noted in I serious discrepancies in the latter work. Here we undertake to calculate both the doublet- and the quartet-state barrier heights using in each case wavefunctions of the kind described in the last paragraph.

2. Configuration-group approach to the evaluation of various types of correlation in reaction surface study

There are three distinct types of correlation to be considered in an accurate reaction surface study.

(i) Valence type. This is defined to consist of terms arising from various kinds of occupation of the valence orbitals, other than those used in the Hartree—Fock term.

(ii) "First-order" type. This arises from an electron undergoing excitation into a virtual orbital while other electrons redistribute themselves amongst the valence orbitals.

(iii) "Second-order" type. This type of correlation, predominant in long-range effects, also manifests itself in chemical systems in the following way. If in the interactive region there is a substantial charge transfer, then the sum of local electron correlations at each center can be significantly different from that at the dissociation limit. Since there is a significant fraction of the charged state N^-O^+ and N^+O^- in the interactive region, the predominant double excitations in characterizing N^- and O^- electron correlation have to be taken into account.

2.1. Calculation of the valence and first-order correlation by configuration-group approach

The first two types of correlation can be computed in the following stepwise manner·

(1) Obtain the zeroth-order multi-configuration (MC) function Ψ_0 that dissociates to Hartree—Fock or MC constituents.

(2) Perform an accurate "valence-only" CI, considering all important possible excitations amongst the valence orbitals.

(3) Using the dominant configurations and orbitals of step (1) above, obtain corrections coming from terms representing core excitations into unfilled or partially filled valence shells.

(4) Define configuration groups representing first-order excitations of each valence shell. Perform MC SCF on the wavefunction consisting of these configurations with the following approximation: The matrix elements between configurations belonging to different groups are arbitrarily set to zero. Also only the virtual orbitals are optimized, leaving the valence orbitals frozen. This approximation simplifies and economizes the MC SCF process drastically since the "contractions" of supermatrices have to be done only once and that too only over the valence-shell density matrices.

(5) Perform a conventional first-order CI using the above orbitals.

Obviously the approximation in step (4) is acceptable only if the configuration groups involved interact weakly. It will be demonstrated later that this is truly the case.

For the interactive region the important terms of the zeroth-order function of step (1) are the four orbital products

$$\Phi_0 = \{core\}Y^2_{O1}Y^2_{NO,b}Z^2_{OO1,b}Z_N X_{O1}X^2_O X_N, \qquad \Phi_1 = \{core\}Y^2_{O1}Y^2_{NO,a}Z^2_{OO1,b}Z_N X_{O1}X^2_O X_N,$$

$$\Phi_2 = \{core\}Y^2_{O1}Y^2_{NO,b}Z^2_{OO1,a}Z_N X_{O1}X^2_O X_N, \qquad \Phi_3 = \{core\}Y^2_{O1}Y_{NO,b}Z_{OO1,b}Y_{NO,a}Z_{OO1,a}Z_N X_{O1}X^2_O X_N$$

$$(1)$$

There are other configurations that have to be included in order to dissociate the molecule correctly. However, their role at the barrier region, especially for steps (3)—(5), is small. In the above, the core consists of fully occupied 1s and 2s orbitals, O1 refers to the more distant oxygen atom from N, Y_{O1} is a $2p_y$-like orbital centered at O1 and similarly for X_O, X_{O1}, X_N and Z_N, $Y_{NO,b}$ is a bonding MO made of N and O $2p_y$ orbitals; similarly $Z_{OO1,b}$ is a bonding MO made of O1 and O $2p_z$ orbitals; $Y_{NO,a}$ and $Z_{OO1,a}$ are the corresponding antibonding ones. The orbital products $\Phi_1-\Phi_4$ are written in excitation notation. In step (3) we construct the configuration groups in the following manner: We first assign one virtual orbital to every orbital occupied in step (1). Each of the configuration groups is now formed as consisting of excitations representing an electron excited from each occupied orbital into its assigned virtual followed by either no other excitation or one that corresponds to transfer of another electron

from one valence shell to any of the valence shells other than the one already excited. There are therefore nine configuration groups to be considered corresponding to the excitations

$$Y_{O1} \rightarrow Y'_{O1}, \quad Y_{NO,b} \rightarrow Y'_{NO,b}, \tag{2}$$

etc.

For the asymptotic region the configurations in steps (1) and (2) for a dissociated $N + O_2$ system (apart from the O_2 core and the N atomic function) are

$$\sigma_g^2 \pi_u^4 \pi_g^2, \quad \sigma_g^2 \pi_u^2 \pi_g^4, \quad \sigma_u^2 \pi_u^4 \pi_g^2, \quad \sigma_u^2 \pi_u^2 \pi_g^4, \quad \sigma_g \sigma_u \pi_u^3 \pi_g^3. \tag{3}$$

In step (4), the total first-order correlation is calculated by performing MC SCF on a first-order CI set of configurations involving the virtuals π'_u, π'_g.

2.2 Calculation of the second-order correlation

The most straightforward way of computing the second-order correlation is to consider all types of double excitations of the valence electrons in a large basis and solve the corresponding CI problem for all geometries. This, however, is a gigantic task even for a small interactive system, involving tens of thousands of configurations. Instead we consider only that part of the second-order correlation that is associated with a bond and vanishes upon dissociation of the bond. Since in the present work we are interested only in the reaction channel of the reaction $N + O_2 \rightarrow NO + O$, the only bond of interest is that associated with $Y_{NO,b}$ orbital [see eq. (1)]. The excitations required to represent the second-order correlation in this bond are double excitations into virtual orbitals and couple weakly with the first-order correlation excitations described above. The second-order terms can therefore be calculated separately and added to the energy obtained previously.

3. Computational details and results

As in I we select the points for the minimum energy path by keeping the distance R_{NO} fixed while varying the distance between the oxygen atoms as well as the angle $\angle$ NOO1 for an energy minimum. This method, obviously, does not lead to the exact minimum energy path. However, providing that the interaction between the internal coordinates chosen in the above fashion is small the path traced out according to the above is very close to the minimum energy path. Furthermore, it can be shown (see appendix) that if a maximum results from this technique, the maximum indeed corresponds to the transition point.

Also, our selection of points will still be on the basis of valence CI. Since the corrections coming from the first- and second-order correlation are expected to be much more slowly varying with respect to variation of geometry than the valence-CI energies themselves, we do not expect a significant error in the location of the minimum energy path resulting from this approximation.

We shall continue to use the 4-31G basis set used in I. As we have already mentioned, this basis set appears to be satisfactory insofar as the height of the barrier is concerned, although the geometry is likely to be somewhat different with a larger basis set. The basis is also found to be adequate for the calculation of the first-order correlation. However, for calculating the second-order correlation involving the p shells, d functions are found to be important. The d functions already described in I are used for this purpose. They seem to represent $\approx 70\%$ of the contribution that an optimized STO d function yields.

In table 1 are presented the results for the asymptotic limit. We include the nitrogen atom energy for easy comparison with the results for the interaction region. The total first-order contribution of 0.037 hartree is to be compared with the value 0.043 for the same quantity obtained with a near-saturated basis set [4]. This implies that our basis set is able to represent the dominant virtual orbitals required for the computation of the first-order correlation in the asymptotic region. Since in the interactive region the change in the first-order correlation effect is brought

Table 1

Asymptotic region energies for the reactants of the reaction
$N(^4S) + O_2(^3\Sigma_g^-) \rightarrow NO + O$

Various terms of the wavefunction	Energy contributions (hartree)
"valence-only" CI wavefunction	−203 8166
terms representing excitation of the $2s\sigma_g$ and $2s\sigma_u$ electrons in the valence shells	0.0020
first-order correlation	0.0373
total	−203 8559

Table 2

Minimum energy path "valence-only CI" energies for the doublet and quartet surface of the reaction $N + O_2 \rightarrow NO + O$

Doublet surface				Quartet surface			
geometry			valence-only CI energies (hartree)	geometry			valence-only energies (hartree)
d_{NO} (bohr)	d_{OO1} (bohr)	θ_{NOO1} (deg)		d_{NO} (bohr)	d_{OO1} (bohr)	θ_{NOO1} (deg)	
3 5	2 46	114.7	−203.7878	3 5	2.52	109 8	−203.7807
3.3	2.56	111.3	−203.7824	3.3	2 64	105.2	−203.7751
3.1	2 61	109 8	−203.7821	3.1	2.78	102 4	−203.7752
2.9	2 68	108 8	−203.7839	2.9	2.95	102.6	−203.7791
2 7	2.73	110 5	−203 7861	2.71	2 92	103 0	−203.7803

about mostly by the breaking of old bonds and building of new rather than the polarization of the bonding orbitals, we expect that the basis set found adequate at large separation will also be acceptable over the whole interesting range of interaction.

In table 2 are presented the doublet- and quartet-state total valence-only CI energies for the interactive region. The doublet-state results have already been reported in I. On the basis of these "valence-only" results we select the transition-state geometries for the doublet and quartet states as respectively $(d_{NO}, d_{OO1}, \theta_{NOO1}) = (3.5, 2.61, 109.8°)$ and $(3.3, 2.64, 105.2°)$, all distances in bohrs.

In computing the first-order correlation terms, we first demonstrate in table 3 that the configuration groups selected *do* indeed interact weakly. The first-order corrections shown in table 3 correspond to inclusion of the groups discussed in step (4) of section 2.1. The energies calculated with or without the intergroup matrix elements differ by less than 1 mhartree. In table 4 the first (i.e. the result of step (5) of section 2.1) and second-order correlation terms as well as those coming from core excitations into valence [step(3)] are shown for both the doublet- and quartet-state transition points at the geometries mentioned above. The total correlated energies are also presented in table 4. The barrier heights calculated as the differences of these energies and the asymptotic energy are respectively 13.8 and 18.1 kcal for the doublet- and quartet-state surfaces respectively.

On the basis of our calculations we arrive at the following conclusions:

(i) The configuration-group approach is useful in determining to an acceptable accuracy the higher-order corrections coming from electron correlation.

Table 3
First-order correlation energies with and without the intergroup matrix elements (all energies in hartree and distances in bohr)

State	Geometry	Intergroup matrix elements set to zero	Intergroup matrix elements retained
$^2A'$	$d_{NO} = 3.1$ $d_{OO1} = 2.61$ $\theta_{NOO1} = 109.8°$	0.0401	0.0395
$^4A'$	$d_{NO} = 3.3$ $d_{OO1} = 2.64$ $\theta_{NOO2} = 105.2°$	0.0400	0.0395

Table 4
Various correlation corrections to the doublet- and quartet-state energies at the transition state geometries (all energies in hartree)

State	First-order correlation	Second-order correlation	2s-to-valence excitation correlation	Total energies	Barrier heights
$^2A'$	0.0432	0.0038	0.0048	−203.8339	0.0220
$^4A'$	0.0445	0.0030	0.0044	−203.8270	0.0289

(ii) The reaction $N + O_2 \rightarrow NO + O$ proceeds primarily via the doublet surface rather than the quartet surface as concluded by Wilson [3].

(iii) The barrier height, according to our calculations, is nearly 13.8 kcal. However, on the basis of the fact that our d space is not optimized, this can be considered to be an upper bound to the actual theoretical height to be expected from our model. Taking into account an estimated 2–3 kcal of zero-point energy difference, the calculated barrier height is in fiar agreement with the experimental activation energy of 7–8 kcal.

Appendix

For simplicity let us consider the collinear collision $A + BC \rightarrow AB + C$. The internal coordinates for this reaction are r_{AB} and r_{BC}. Assume that the energy versus r_{AB} curve obtained by optimizing the coordinate r_{BC} exhibits a barrier. Then it can be shown that *the point X where $\partial V/\partial r_{AB}|_{curve} = 0$ is indeed the saddle point*. For

$$0 = \partial V/\partial r_{AB}|_{curve} = \lim_{\delta r_{AB} \to 0} [V(r_{AB} + \delta r_{AB}, r_{BC} + \delta r_{BC}) - V(r_{AB}, r_{BC})]/\delta r_{AB}$$

$$= \lim_{\delta r_{AB} \to 0} [V(r_{AB} + \delta r_{AB}, r_{BC} + \delta r_{BC}) - V(r_{AB} + \delta r_{AB}, r_{BC}) + V(r_{AB} + \delta r_{AB}, r_{BC}) - V(r_{AB}, r_{BC})]/\delta r_{AB}$$

$$= \partial V/\partial r_{AB} + \lim_{\delta r_{AB} \to 0} [V(r_{AB} + \delta r_{AB}, r_{BC}) - V(r_{AB} + \delta r_{AB}, r_{BC})]/\delta r_{AB}.$$

However, δr_{AB} and δr_{BC} are related as follows: Let $f(r_{AB}, r_{BC}) \equiv \partial V/\partial r_{BC}$; then

$$(\partial f/\partial r_{AB})\,\delta r_{AB} + (\partial f/\partial r_{BC})\delta r_{BC} = 0 \tag{A1}$$

if both $(r_{AB} + \delta r_{AB}, r_{BC} + \delta r_{BC})$ as well as (r_{AB}, r_{BC}) lie on the curve. Expanding

$$V(r_{AB} + \delta r_{AB}, r_{BC}) = V(r_{AB} + \delta r_{AB}, r_{BC} + \delta r_{BC}) - K\,\delta r_{BC} + \mathcal{O}(\delta r_{BC}^2),$$

where

$$K = \partial V/\partial r_{BC}\big|_{r_{BC} + \delta r_{BC}, r_{AB} + \delta r_{AB}}.$$

However $K = 0$, since $(r_{BC} + \delta r_{BC}, r_{AB} + \delta r_{AB})$ is a point on the curve. Thus we have $0 = \partial V/\partial r_{AB} + \mathcal{O}(\delta r_{AB})$, using (A1), which along with $\partial V/\partial r_{BC} = 0$ satisfied the requirements of a transition point.

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