

The reaction force. A scalar property to characterize reaction mechanisms

Jorge Martínez · Alejandro Toro-Labbé

Received: 13 September 2008 / Accepted: 6 October 2008 / Published online: 25 October 2008
© Springer Science+Business Media, LLC 2008

Abstract The reaction force is a global property of a chemical reaction that arises when applying the Hellmann–Feynmann theorem to the potential energy surface that links reactants, products and transition states. In the present work, the reaction force is defined rigorously from the cartesian components coming out from all forces exerted over each atom of a molecular system during the chemical reaction; it is demonstrated that the reaction force is a scalar property.

Keywords Reaction force · Reaction works · Reaction coordinate · Reactions mechanisms · Hellmann–Feynmann theorem

1 Introduction

The reaction force has been applied to understand the reaction mechanism of chemical reactions [1, 2], it has been used to define reaction regions along a reaction coordinate in which different mechanisms might be operating [3–10]. It also provides the basis for a rational partition of the activation energy which can be expressed in terms of two contributions that are associated to the energy change taking place at different regions along the reaction coordinate and being of different nature [5, 6, 9, 10].

J. Martínez (✉)

Materials Science Group, Southeastern Pacific Research Institute for Advanced Technologies (SEPARI), Universidad Técnica Federico Santa María, Avenida España 1680, Edificio T, Casilla 110 V, Valparaíso, Chile
e-mail: jorge.martinez@separi.cl

A. Toro-Labbé

Laboratorio QTC, Departamento de Química Física, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Correo 22, Santiago, Chile
e-mail: atola@uc.cl

The present paper establishes a formal definition of the reaction force, this concept differs from the classical force concept in the sense that the reaction force is an scalar quantity although it is rigorously defined from the Hellmann–Feynman theorem [11, 12].

2 Theoretical background

2.1 The reaction force

Any set of parameters characterizing the position of a mechanical system may be chosen as a suitable set of *generalized coordinates*, in particular the positions of M nuclei forming a molecule that are given by a set of cartesian coordinates, define a good set of coordinates [13]:

$$\{x_a, y_a, z_a\}_{a=1}^M$$

In general, a M -atoms molecule under m independent kinematical conditions can be characterized by $n = 3M - m$ independent parameters Q_1, Q_2, \dots, Q_n in such a way that the cartesian coordinates $\{x_a, y_a, z_a\}_{a=1}^M$ of all nuclei are expressible as functions of the variables $\{Q_\gamma\}_{\gamma=1}^n$:

$$\begin{aligned} x_1 &= f_1(Q_1, \dots, Q_n) \\ y_1 &= f_2(Q_1, \dots, Q_n) \\ z_1 &= f_3(Q_1, \dots, Q_n) \\ &\dots\dots\dots \\ x_M &= f_{3M-2}(Q_1, \dots, Q_n) \\ y_M &= f_{3M-1}(Q_1, \dots, Q_n) \\ z_M &= f_{3M}(Q_1, \dots, Q_n). \end{aligned}$$

The n parameters are the generalized coordinates that correspond to the $3M - 6$ and $3M - 5$ internal coordinates for non-linear and linear molecules, respectively. Note that any chemical reaction can be studied by analyzing the $\frac{M!}{(M-2)!2!}$ interatomic distances ($\forall M \geq 2$), or $\frac{M!}{(M-3)!3!}$ plane angles ($\forall M \geq 3$) or $\frac{M!}{(M-4)!4!}$ dihedral angles ($\forall M \geq 4$); however the present analysis will be carried out using the well-known set of $3M - 6$ internal coordinates [13].

A force acting over the a th-nucleus at $\mathbf{r}_a = x_a \hat{\mathbf{i}} + y_a \hat{\mathbf{j}} + z_a \hat{\mathbf{k}}$ is a vectorial quantity:

$$\mathbf{F}_a = F_{x_a} \hat{\mathbf{i}} + F_{y_a} \hat{\mathbf{j}} + F_{z_a} \hat{\mathbf{k}}, \quad (1)$$

where F_{x_a} , F_{y_a} and F_{z_a} are the cartesian components of \mathbf{F}_a , the action of a force is measured by the momentum produced by that force. The cartesian components of the force associated to the a th-nucleus are given by:

$$\left. \begin{aligned} F_{x_a} &= -\frac{\partial U}{\partial x_a} \\ F_{y_a} &= -\frac{\partial U}{\partial y_a} \\ F_{z_a} &= -\frac{\partial U}{\partial z_a} \end{aligned} \right\} \quad (2)$$

where $U (\{x_a, y_a, z_a\}_{a=1}^M)$ is the potential energy. The cartesian components of the force can now be expressed in terms of the internal coordinates $\{Q_\gamma\}_{\gamma=1}^{3M-6}$ since:

$$\left. \begin{aligned} -F_{x_a} &= \frac{\partial U}{\partial x_a} = \sum_{\gamma=1}^n \left(\frac{\partial U}{\partial Q_\gamma} \right) \cdot \left(\frac{\partial Q_\gamma}{\partial x_a} \right) \\ -F_{y_a} &= \frac{\partial U}{\partial y_a} = \sum_{\gamma=1}^n \left(\frac{\partial U}{\partial Q_\gamma} \right) \cdot \left(\frac{\partial Q_\gamma}{\partial y_a} \right) \\ -F_{z_a} &= \frac{\partial U}{\partial z_a} = \sum_{\gamma=1}^n \left(\frac{\partial U}{\partial Q_\gamma} \right) \cdot \left(\frac{\partial Q_\gamma}{\partial z_a} \right) \end{aligned} \right\} \quad (3)$$

Assuming that the reaction coordinate corresponds to a well known internal coordinate, Q_β , then the reaction force is:

$$\begin{aligned} F_\beta &= -\frac{\partial U}{\partial Q_\beta} \\ &= -\sum_{a=1}^M \left\{ \left(\frac{\partial U}{\partial x_a} \right) \cdot \left(\frac{\partial x_a}{\partial Q_\beta} \right) + \left(\frac{\partial U}{\partial y_a} \right) \cdot \left(\frac{\partial y_a}{\partial Q_\beta} \right) + \left(\frac{\partial U}{\partial z_a} \right) \cdot \left(\frac{\partial z_a}{\partial Q_\beta} \right) \right\} \\ &= -\sum_{a=1}^M \left\{ \frac{\partial U}{\partial x_a} \hat{\mathbf{i}} + \frac{\partial U}{\partial y_a} \hat{\mathbf{j}} + \frac{\partial U}{\partial z_a} \hat{\mathbf{k}} \right\} \cdot \left\{ \frac{\partial x_a}{\partial Q_\beta} \hat{\mathbf{i}} + \frac{\partial y_a}{\partial Q_\beta} \hat{\mathbf{j}} + \frac{\partial z_a}{\partial Q_\beta} \hat{\mathbf{k}} \right\} \\ &= \sum_{a=1}^M \left\{ F_{x_a} \hat{\mathbf{i}} + F_{y_a} \hat{\mathbf{j}} + F_{z_a} \hat{\mathbf{k}} \right\} \cdot \left\{ \frac{\partial x_a}{\partial Q_\beta} \hat{\mathbf{i}} + \frac{\partial y_a}{\partial Q_\beta} \hat{\mathbf{j}} + \frac{\partial z_a}{\partial Q_\beta} \hat{\mathbf{k}} \right\} \end{aligned}$$

and therefore the reaction force reduces to:

$$F_\beta = \sum_{a=1}^M \mathbf{F}_a \cdot \frac{\partial \mathbf{r}_a}{\partial Q_\beta} \quad (4)$$

As can be observed, the reaction force is not a vectorial quantity but an scalar one because of the dot product involved in its definition. The reaction force is a sum of products of all forces exerted on each nucleus ($\{\mathbf{F}_a\}_{a=1}^M$) times the relative change between the cartesian position \mathbf{r}_a and the internal coordinate Q_β . Equation 4 indicates that a functional relationship between each \mathbf{r}_a and Q_β should be known in order to determine F_β .

As an example of the scalar nature of the reaction force, consider a chemical process of dissociation (or formation) of a diatomic molecule, then the reaction coordinate is $Q_1 = R \equiv |\mathbf{r}_2 - \mathbf{r}_1|$, the interatomic distance, where \mathbf{r}_1 and \mathbf{r}_2 are the positions of each nucleus in the cartesian space. The forces \mathbf{F}_1 and \mathbf{F}_2 acting on atoms 1 and 2 are oriented in such a way that \mathbf{F}_1 is exerted from atom 1 toward atom 2 and \mathbf{F}_2 is exerted from atom 2 toward atom 1. According to Newton's third law of motion, $\mathbf{F}_2 = -\mathbf{F}_1$ during the whole dissociation process.

Let us now assume that the mathematical relationships between the pairs $\{\mathbf{r}_1; Q_1\}$ and $\{\mathbf{r}_2; Q_2\}$ is unknown, then Eq. 4 cannot be used, however the Virial Theorem [11, 14, 15] provides the equations to define the reaction force since:

$$Q \frac{\partial U}{\partial Q} = R \frac{dU}{dR} = \sum_{a=1}^2 \left\{ x_a \frac{\partial U}{\partial x_a} + y_a \frac{\partial U}{\partial y_a} + z_a \frac{\partial U}{\partial z_a} \right\} \quad (5)$$

Since the reaction force is defined as:

$$F_R = -\frac{dU}{dR}$$

then the Virial theorem leads to:

$$\begin{aligned} -F_R &= \frac{1}{R} \sum_{a=1}^2 \left\{ x_a \frac{\partial U}{\partial x_a} + y_a \frac{\partial U}{\partial y_a} + z_a \frac{\partial U}{\partial z_a} \right\} \\ &= \frac{1}{R} \sum_{a=1}^2 \left\{ x_a \hat{\mathbf{i}} + y_a \hat{\mathbf{j}} + z_a \hat{\mathbf{k}} \right\} \cdot \left\{ \frac{\partial U}{\partial x_a} \hat{\mathbf{i}} + \frac{\partial U}{\partial y_a} \hat{\mathbf{j}} + \frac{\partial U}{\partial z_a} \hat{\mathbf{k}} \right\} \\ &= -\frac{1}{R} \sum_{a=1}^2 \left\{ x_a \hat{\mathbf{i}} + y_a \hat{\mathbf{j}} + z_a \hat{\mathbf{k}} \right\} \cdot \left\{ F_{x_a} \hat{\mathbf{i}} + F_{y_a} \hat{\mathbf{j}} + F_{z_a} \hat{\mathbf{k}} \right\} \\ &= -\frac{1}{R} \sum_{a=1}^2 \mathbf{r}_a \cdot \mathbf{F}_a \\ &= -\frac{1}{R} (\mathbf{r}_1 \cdot \mathbf{F}_1 + \mathbf{r}_2 \cdot \mathbf{F}_2) \\ &= -\frac{1}{R} (\mathbf{r}_1 \cdot \mathbf{F}_1 - \mathbf{r}_2 \cdot \mathbf{F}_1) \\ &= -\frac{1}{R} (\mathbf{r}_1 - \mathbf{r}_2) \cdot \mathbf{F}_1 \\ &= \frac{1}{R} (\mathbf{r}_2 - \mathbf{r}_1) \cdot \mathbf{F}_1 \\ &= \frac{1}{R} |\mathbf{r}_2 - \mathbf{r}_1| \cdot |\mathbf{F}_1| \cdot \cos 0^\circ \\ &= \frac{R}{R} \cdot |\mathbf{F}_1| \\ &= |\mathbf{F}_1| \implies F_R = -|\mathbf{F}_1| = -|\mathbf{F}_2| \end{aligned}$$

As shown in this dissociation example, the reaction force is a scalar quantity because it is expressed in terms of a modulus of one of the forces acting over the nuclei. For this particular case F is always negative. This is a mathematical support for the analysis carried out by Politzer et al. [8] where it is mentioned that all dissociation process has a negative minimum in its reaction force profile; from the equilibrium point until the total dissociation, the reaction force profile exhibits negative values.

The validity of Eq. 4 should be tested in such a way that the same result obtained using the Virial theorem ($F_R = -|\mathbf{F}_1| = -|\mathbf{F}_2|$) be retrieved.

This is shown as follows for the same diatomic molecule:

$$\begin{aligned}
 F_R &= \sum_{a=1}^2 \mathbf{F}_a \cdot \frac{\partial \mathbf{r}_a}{\partial R} \\
 &= \mathbf{F}_1 \cdot \frac{\partial \mathbf{r}_1}{\partial R} + \mathbf{F}_2 \cdot \frac{\partial \mathbf{r}_2}{\partial R} \\
 &= \mathbf{F}_1 \cdot \frac{\partial \mathbf{r}_1}{\partial R} - \mathbf{F}_1 \cdot \frac{\partial \mathbf{r}_2}{\partial R} \\
 &= \mathbf{F}_1 \cdot \left(\frac{\partial \mathbf{r}_1}{\partial R} - \frac{\partial \mathbf{r}_2}{\partial R} \right) \\
 &= \mathbf{F}_1 \cdot \frac{\partial (\mathbf{r}_1 - \mathbf{r}_2)}{\partial R} \\
 &= -\mathbf{F}_1 \cdot \frac{\partial (\mathbf{r}_2 - \mathbf{r}_1)}{\partial R} \\
 &= -|\mathbf{F}_1| \cdot \left| \frac{\partial \mathbf{R}}{\partial R} \right| \cos 0^\circ \\
 &= -|\mathbf{F}_1|
 \end{aligned}$$

Therefore the reaction force corresponds to the negative of the modulus force exerted over one atom.

Similarly, for systems with $3M - 6$ degrees of freedom, the reaction force can be readily determined when the reaction coordinate coincides with one and only one internal coordinate, in such a case, the forces associated to the remaining internal coordinates do not take part in building up the reaction force.

Examples of those processes are torsional and inversion reactions, so that a total force (\mathcal{F}) can be considered as a vector of $3M - 6$ -components, one of them is the reaction force F_β associated to the β th-internal coordinate:

$$\mathcal{F} = (F_1, F_2, F_3, \dots, F_\beta, \dots, F_{3M-6})$$

It is worth to mention that Eq. 4 applies on reactions with non-reversal evolution of the reaction coordinate.

2.2 Reaction works

Having the reaction force at hand, activation and reaction energies are readily obtained, for instance the reaction energy is:

$$\Delta U^\circ = - \int_{Q_\beta^R}^{Q_\beta^P} F_\beta \, dQ_\beta$$

For an elementary step in which reactants are separated from the products by an energy barrier, the reaction force profile presents two critical points, a minimum at Q_β^{\min} and a maximum at Q_β^{\max} . The reaction coordinate is then divided into three reaction regions: the reactant region: $[Q_\beta^R; Q_\beta^{\min}]$; the transition state region: $[Q_\beta^{\min}; Q_\beta^{\max}]$; and the product region: $[Q_\beta^{\max}; Q_\beta^P]$. With this, specific amount of works can be calculated by selecting different intervals within the domain of the reaction coordinate, thus allowing a rational partition of the reaction energy and the energy barrier [4, 9, 16]. The relevant works involved during a chemical process are

$$\begin{aligned} W_1 &= - \int_{Q_\beta^R}^{Q_\beta^{\min}} F_\beta \, dQ_\beta ; & W_2 &= - \int_{Q_\beta^{\min}}^{Q_\beta^{\text{TS}}} F_\beta \, dQ_\beta \\ W_3 &= - \int_{Q_\beta^{\text{TS}}}^{Q_\beta^{\max}} F_\beta \, dQ_\beta ; & W_4 &= - \int_{Q_\beta^{\max}}^{Q_\beta^P} F_\beta \, dQ_\beta \end{aligned} \quad (6)$$

such that

$$\Delta U^\circ = W_1 + W_2 + W_3 + W_4$$

and

$$\Delta U^\ddagger = W_1 + W_2$$

3 Results and discussions

In this section different kind of chemical reactions depicted in Fig. 1 are analyzed in the light of the reaction force. It can be observed in Fig. 2 that the reactions under study are a highly diverse group. There are dissociations of polar and nonpolar molecules; inversions of isoelectronic molecules; internal rotations and a nucleophilic addition. All systems were fully optimized at appropriate level of calculation using the the GAUSSIAN 03 package [17].

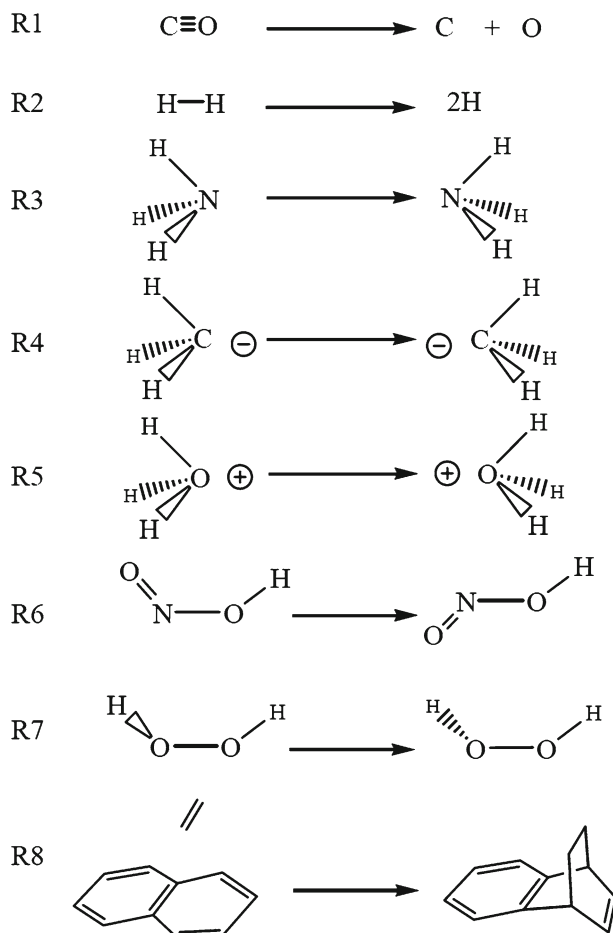


Fig. 1 Different kind of chemical reactions used to illustrate the reaction force concept

3.1 Dissociation processes: CO and H₂

Distinguished Reaction Coordinate (relaxed Scan) procedure at the UB3LYP/6-311++G(d,p) level of calculations was used to analyze the dissociation of CO (**R1**) and H₂ (**R2**) systems (Fig. 1). In both, **R1** and **R2**, the reaction coordinate corresponds to the bond distance R , Fig. 2.

Both reactions show similar shapes in their reaction energy and force profiles (Fig. 3). The reaction force profiles allows one to define the inflection point of the energy through detecting the position of the minimum located at Q_{β}^{\min} (Table 1). As shown recently [8], any dissociation process is divided into two phases: the initial stretching of the bond $X - Y$ implies a structural effect which is always followed by separation into the fragments X and Y , near 20% of the dissociation energy corresponds to the stretching process characterized by W_1 [8], Table 2. Despite the fact

Fig. 2 Reaction coordinates for the different reactions under study; note that all reaction coordinates coincide with one internal coordinate

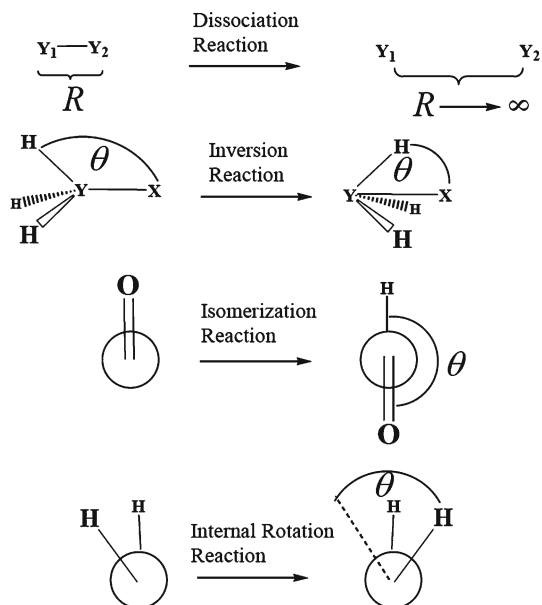


Table 1 Critical Q_γ points located on the reaction force profile. For **R1** and **R2**, are given in Å; from **R3** to **R7**, are given in rad and for **R8**, are dimensionless. Energies are given in kcal mol⁻¹

Reaction	$Q_\gamma^R(\xi_R)$	$Q_\gamma^{\min}(\xi_{\min})$	$Q_\gamma^{\text{TS}}(\xi_{\text{TS}})$	$Q_\gamma^{\max}(\xi_{\max})$	$Q_\gamma^P(\xi_P)$	ΔU^\ddagger	ΔU°
R1	1.15	1.45	8.45	8.45	8.45	368.010	368.010
R2	0.75	1.15	10.00	10.00	10.00	174.189	174.189
R3	1.197	1.365	1.571	1.776	1.945	4.069	0.000
R4	1.213	1.378	1.571	1.763	1.928	2.438	0.000
R5	1.304	1.422	1.571	1.720	1.834	1.079	-0.001
R6	0.000	0.754	1.508	2.293	3.142	11.804	-1.074
R7	0.000	1.227	2.116	2.963	4.232	8.466	0.000
R8	(0.000)	(0.535)	(0.585)	(0.651)	(1.000)	53.081	-1.316

that CO and H₂ are very different molecules, the calculated works indicate that they provide quite the same percentage of the reaction energy at the minimum of the reaction force [5, 9]; the vibrational state reached when applying the energy W_1 defines an activated reactant that is ready for dissociation [18]. The remaining 80% of the dissociation energy corresponds to W_2 which is needed to put the atoms very far to each other.

3.2 Inversions processes: NH₃, CH₃⁻ and H₃O⁺

RB3LYP/6-311++G(d,p) calculations were performed to analyze the inversion processes corresponding to reactions **R3**, **R4** and **R5** (Fig 1), energy and reaction force

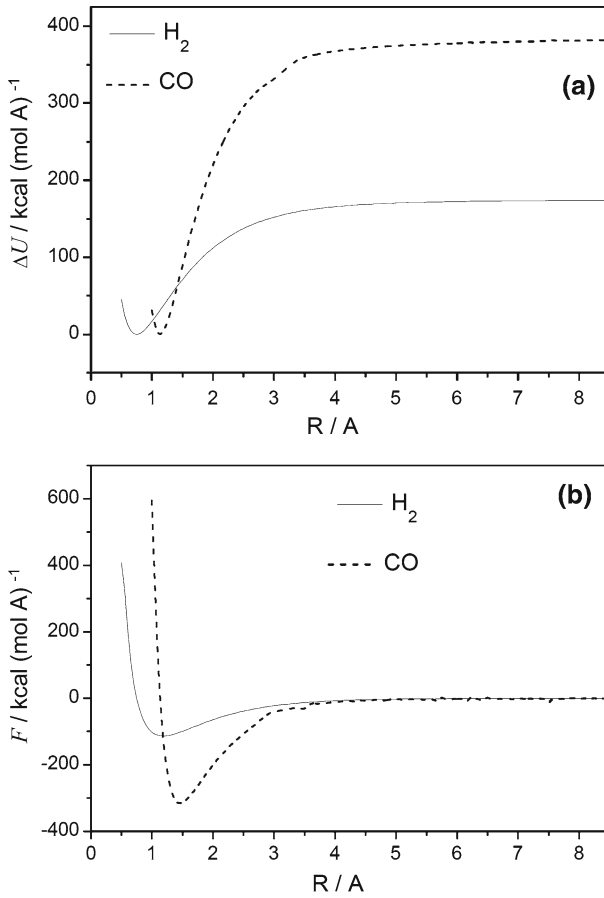


Fig. 3 **a** Energy and **b** reaction force profiles for dissociation reactions

Table 2 Works (kcal mol^{-1}) calculated from the reaction force profiles for the eight reactions under study

Reaction	W_1	W_2	W_3	W_4	ΔU^\ddagger	ΔU°
R1	72.12	295.90	—	—	368.02	368.02
R2	32.73	141.46	—	—	174.19	174.19
R3	1.87	2.20	-2.20	-1.87	4.07	0.00
R4	1.12	1.32	-1.32	-1.12	2.44	0.00
R5	0.49	0.59	-0.59	-0.49	1.08	0.00
R6	5.94	5.87	-6.30	-6.58	11.81	-1.07
R7	4.77	3.70	-3.70	-4.77	8.47	0.00
R8	43.155	9.926	-20.549	-33.848	53.081	-1.316

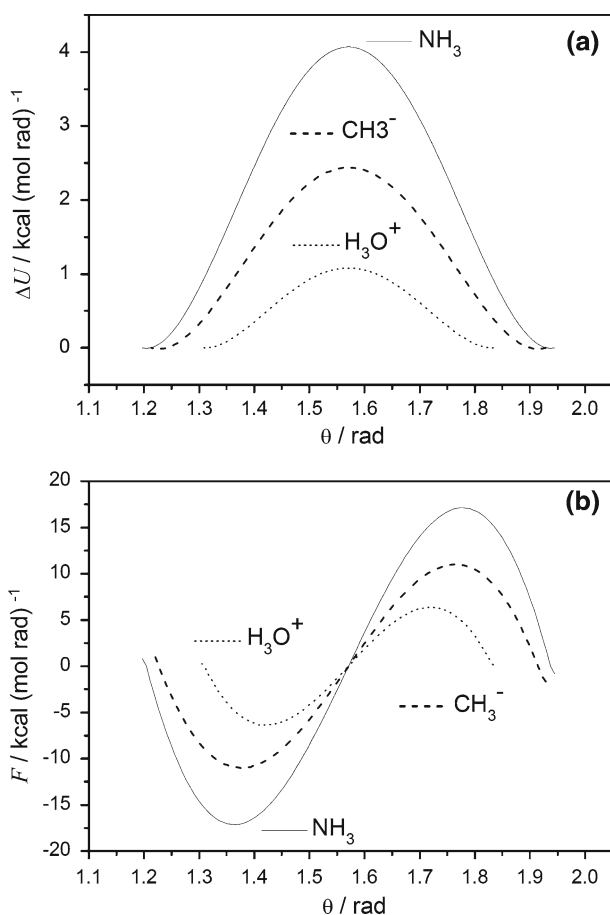


Fig. 4 **a** Energy and **b** reaction force profiles for inversion reactions

profiles are displayed in Fig. 4. A pure internal coordinate which is considered as a DRC was used as the reaction coordinate which corresponds to the angle θ defined in Fig. 2.

All systems involved in the inversion reactions are isoelectronic and the most noticeable difference among them is found in ΔU^\ddagger (Tables 1 and 2). Similarly to the dissociation reactions, the partition of ΔU^\ddagger according to the set of Eq. (6) provides a set of W_1 (Table 2) values which correspond to a specific percentage of ΔU^\ddagger , 46% ca. thus indicating that for an umbrella inversion process there is a common fraction from ΔU^\ddagger which is employed in order to overcome an specific amount of energy necessary to activate the process. Once the activated reactant is reached the system evolves to pass through the planar transition at Q_β^{TS} to achieve the inversion. After the transition state, the molecule experiences nuclear arrangements to reach the maximum on the reaction force profile whereas an energy W_3 is released in order to reach the activated product to finally relax to the product by releasing an energy W_4 .

Among the six internal coordinates, the total force is characterized by two components $\mathcal{F} = (F_r, F_\theta)$ in which F_θ is the reaction force. In all cases W_1 corresponds to 46% of the total activation energy and the ratio W_2/W_1 are 1.17, 1.18 and 1.20, respectively [8].

3.3 Rotational isomerization processes: HONO and HOOH

The same level of theory used for the inversion processes was used to determine the energy and reaction force profiles of the rotational isomerization processes, **R6** and **R7** displayed in Fig. 5. Although the total force has six components $\mathcal{F} = \{F_{r_1}, F_{r_2}, F_{r_3}, F_{\alpha_1}, F_{\alpha_2}, F_\theta\}$, F_θ can be distinguished as being the reaction force; the internal coordinate is the dihedral angle theta defined in Fig. 2. The energy and

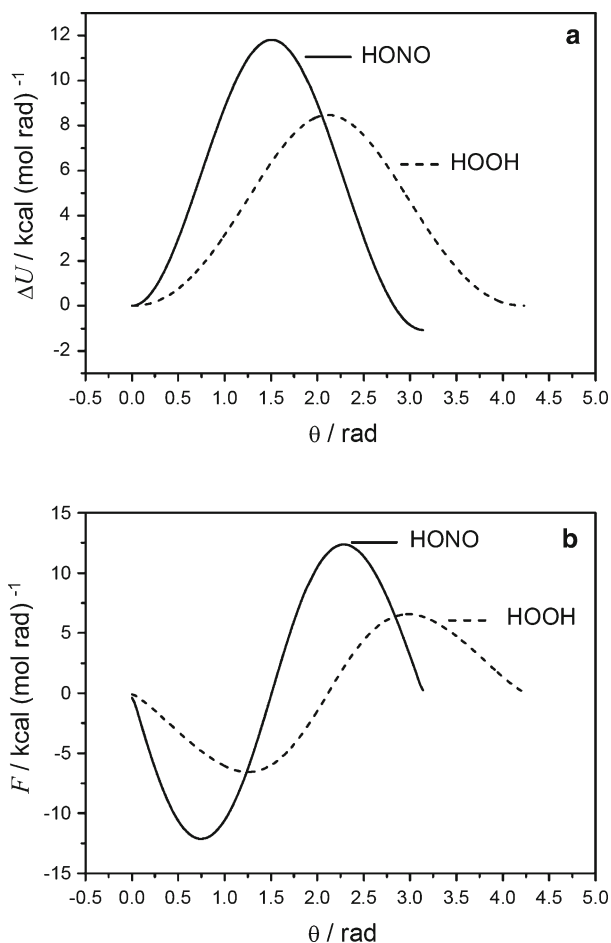


Fig. 5 **a** Energy and **b** reaction force profiles for internal rotation reactions

reaction force profiles show a big difference between **R6** and **R7** (Tables 1 and 2), reaction **R6** is slightly exoenergetic whereas reaction **R7** is isoenergetic the latter is characterized by symmetric work values, as indicated in Table 2. For reaction **R6**, W_1 is ca. 50% of ΔU^\ddagger ; whereas for **R7** it is ca. 56% of ΔU^\ddagger . Clearly, the kinetics aspects are manifested on these two torsional reactions. **R6** shows a higher ΔU^\ddagger value than **R7** and the works W_1 should be related in the same way: $W_1(\mathbf{R6}) > W_1(\mathbf{R7})$, thus indicating that the torsional process **R7** needs less energy to activate the reactant than **R6**. In reaction **R6**, $W_2/W_1 = 0.99$, whereas in **R7** is 0.78. Accordingly the electron rearrangements in **R6** are more important than in **R7**.

3.4 Diels–Alder Reaction: a complex case

Consider the one-step mechanism of the Diels–Alder reaction **R8**. Its energy and force calculated at the RHF/6-311G(d,p) level of theory following the internal reaction coordinate procedure [19–21] are displayed in Fig. 6, note that in Fig. 6 the IRC was normalized to a reduced reaction coordinate ξ in order to establish a reaction coordinate domain from 0 to 1 (Table 1). Despite the reaction coordinate is not easy to detect by monitoring the internal coordinates, three geometrical parameters are the more relevant in contributing to the reaction coordinate, these are shown in Fig. 7; these parameters were picked up because they show the best linear correlation with the intrinsic reaction coordinate (IRC), Fig. 8.

Due to the complexity of a Diels–Alder reaction, the reaction force can be expressed as a combination of local forces acting on different atoms and getting activated or inhibited at the different reaction regions, then

$$F = \sum_{\gamma=1}^M C_{\gamma} F_{\gamma}(Q_{\gamma})$$

in particular Fig. 8 shows that the relevant components are:

$$F(Q) = C_r F_r(Q) + C_{\delta} F_{\delta}(Q) + C_{\varepsilon} F_{\varepsilon}(Q) \quad (7)$$

where the coefficients can be determined by making use of the three boundary conditions [$F_{\text{reaction}}(0) = F_{\text{reaction}}(\xi_{\text{TS}}) = F_{\text{reaction}}(1) = 0$], under the condition $C_r + C_{\delta} + C_{\varepsilon} = 1$; so that a 3×3 linear system of equation has to be solved in order to get the coefficients. Those forces which are associated to the internal coordinates r , δ and ε can be obtained by a simple numerical differentiation of the same energy profile in relation to r , δ and ε , respectively. As a result, the coefficients are given by:

$$C_r = \frac{F_{\delta}(0) \cdot F_{\varepsilon}(1) - F_{\delta}(1) \cdot F_{\varepsilon}(0)}{F_r(0) \cdot F_{\delta}(1) - F_r(1) \cdot F_{\delta}(0) + F_{\delta}(0) \cdot F_{\varepsilon}(1) - F_{\delta}(1) \cdot F_{\varepsilon}(0) + F_{\varepsilon}(0) \cdot F_r(1) - F_{\varepsilon}(1) \cdot F_r(0)}$$

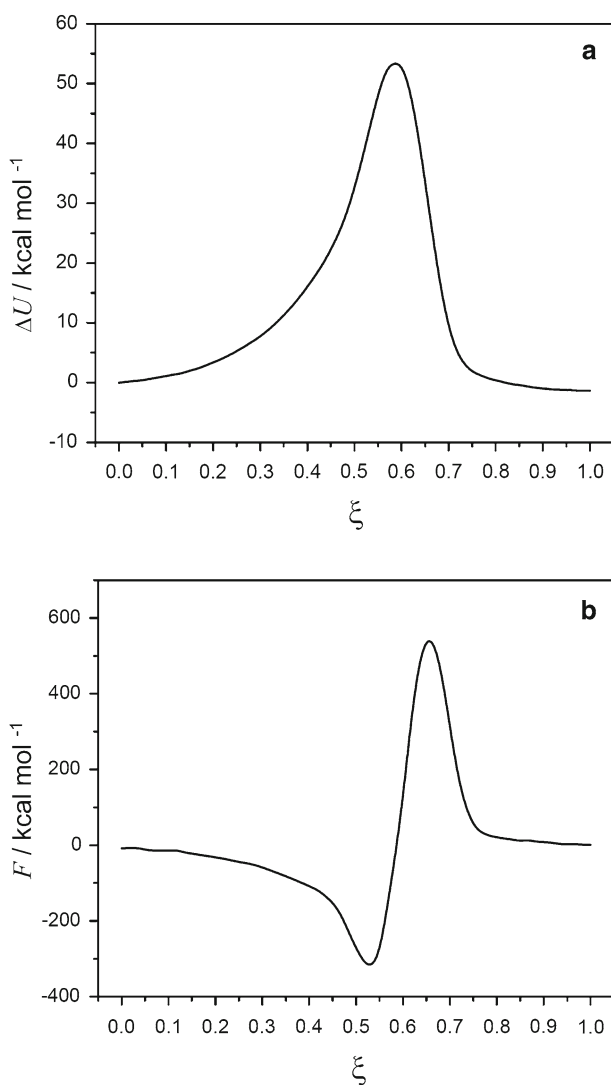
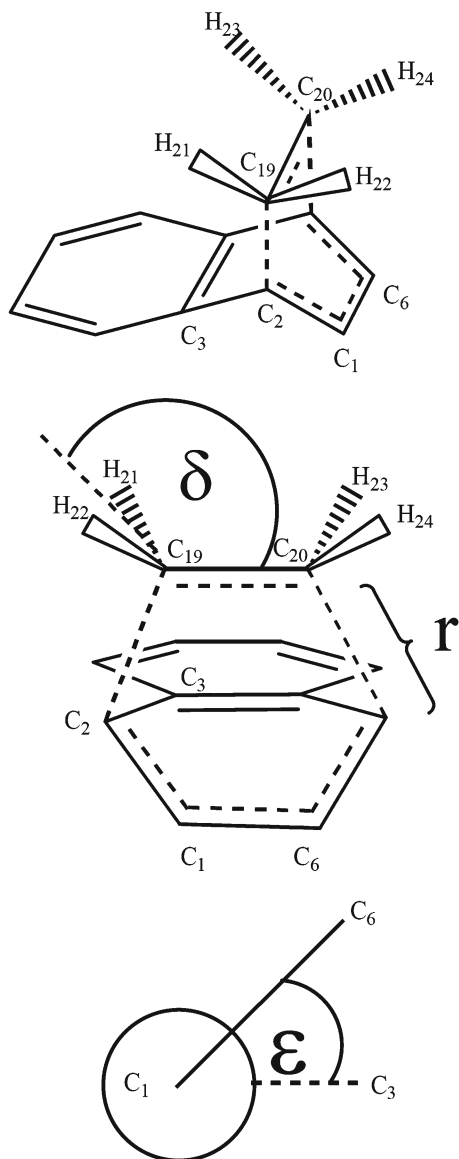


Fig. 6 **a** Energy and **b** reaction force profiles for Diels–Alder reaction; note that more than one internal coordinate is necessary for building up the actual reaction coordinate

$$C_{\delta} = \frac{F_{\varepsilon}(0) \cdot F_r(1) - F_{\varepsilon}(1) \cdot F_r(0)}{F_r(0) \cdot F_{\delta}(1) - F_r(1) \cdot F_{\delta}(0) + F_{\delta}(0) \cdot F_{\varepsilon}(1) - F_{\delta}(1) \cdot F_{\varepsilon}(0) + F_{\varepsilon}(0) \cdot F_r(1) - F_{\varepsilon}(1) \cdot F_r(0)}$$

$$C_{\varepsilon} = \frac{F_r(0) \cdot F_{\delta}(1) - F_r(1) \cdot F_{\delta}(0)}{F_r(0) \cdot F_{\delta}(1) - F_r(1) \cdot F_{\delta}(0) + F_{\delta}(0) \cdot F_{\varepsilon}(1) - F_{\delta}(1) \cdot F_{\varepsilon}(0) + F_{\varepsilon}(0) \cdot F_r(1) - F_{\varepsilon}(1) \cdot F_r(0)}$$

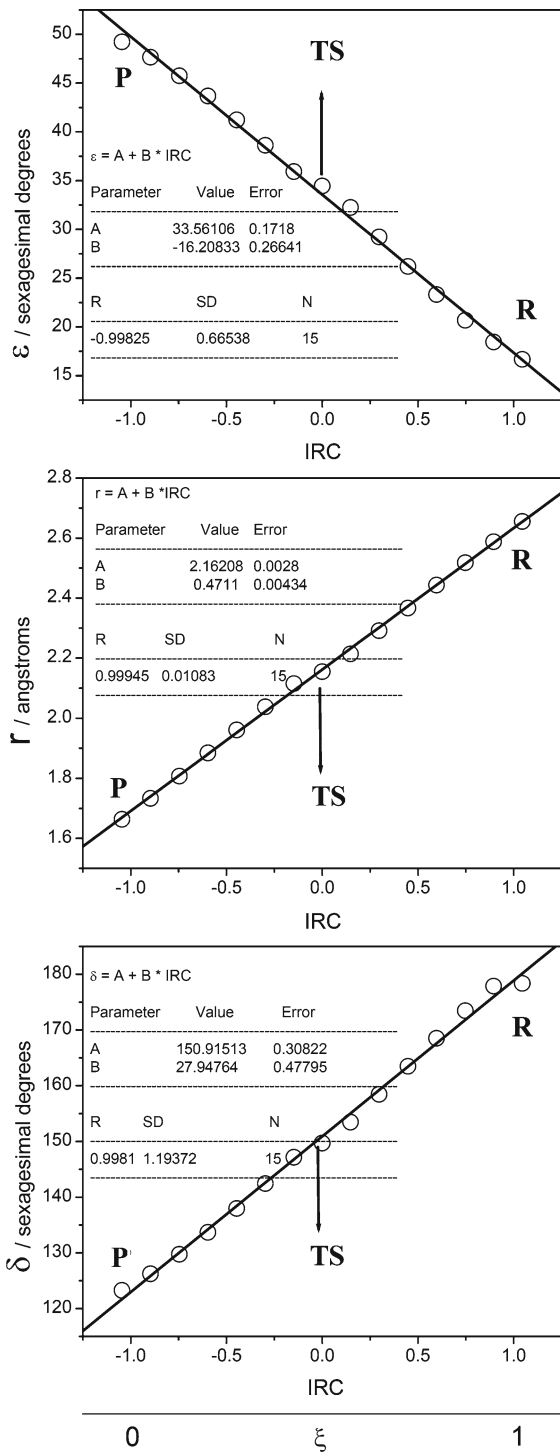
Fig. 7 Three geometrical parameters considered as main components of the reaction coordinate for the Diels Alders reaction



If more internal coordinates are involved, more boundary conditions should be considered, as an example, $\left(\frac{dF_{\text{reaction}}(\xi)}{d\xi}\right)_{\xi=\xi_{\min}} = \left(\frac{dF_{\text{reaction}}(\xi)}{d\xi}\right)_{\xi=\xi_{\max}} = 0$.

Although this reaction presents a ΔU° very close to zero, the energy profiles does not show a symmetric shape. This is due to the fact that more than one geometrical parameter can be considered as a reaction coordinate, as can be seen in Fig. 8.

Fig. 8 Relationships between $\{\delta, r, \varepsilon\}$ and IRC; positions of reactant, transition state and product along the intrinsic reaction coordinate, IRC (or reduced reaction coordinate ξ) are indicated as **R**, **TS** and **P**, respectively



Activation evolves smoother than relaxation and the work (Table 2) associated to reach the activated complex is $W_1 = 43.16 \text{ kcal mol}^{-1}$ that corresponds to the 81% of the total energy barrier; within the transition state region an energy $W_2 = 9.93 \text{ kcal mol}^{-1}$ is required to reach the transition state. Note that $W_3 \simeq 2W_2$, so the electronic reordering is more dramatic after the transition state when relaxing to reach the product of the reaction.

4 Concluding remarks

The reaction force concept has been defined as an scalar property of chemical processes, it helps understand reaction mechanisms and provides the basis for partitioning the activation and reaction energies. In most chemical reactions the reaction coordinate is given by the combination of two or more internal coordinates that can be chosen by analyzing the correlation among the internal coordinates and the actual IRC that comes out from the computational procedure.

Acknowledgments The authors wish to thank financial support from project FONDECYT 1060590, FONDAF No. 11980002 CIMAT (Centro para la Investigación Interdisciplinaria Avanzada en Ciencias de los Materiales).

References

1. A. Toro-Labbé, J. Phys. Chem. A **103**, 4398 (1999)
2. P. Jaque, A. Toro-Labbé, J. Phys. Chem. A **104**, 995 (2000)
3. B. Herrera, A. Toro-Labbé, J. Chem. Phys. **121**, 7096 (2004)
4. J. Martínez, A. Toro-Labbé, Chem. Phys. Lett. **392**, 132 (2004)
5. P. Politzer, A. Toro-Labbé, S. Gutiérrez-Oliva, B. Herrera, M.C. Concha, J.S. Murray, J. Chem. Sci. **117**, 467 (2005)
6. S. Gutiérrez-Oliva, B. Herrera, A. Toro-Labbé, H. Chermette, J. Phys. Chem. A **109**, 1748 (2005)
7. P. Politzer, J.V. Burda, M.C. Concha, P. Lane, J.S. Murray, J. Phys. Chem. A **110**, 756 (2006)
8. P. Politzer, J.S. Murray, P. Lane, A. Toro-Labbé, Int. J. Quantum Chem. **107**, 2153 (2007)
9. A. Toro-Labbé, S. Gutiérrez-Oliva, J.S. Murray, P. Politzer, Mol. Phys. **105**, 2619 (2007)
10. E. Rincón, P. Jaque, A. Toro-Labbé, J. Phys. Chem. A **110**, 9478 (2006)
11. R.P. Feynman, Phys. Rev. **56**, 340 (1939)
12. B.M. Deb, Rev. Mod. Phys. **45**, 22 (1973)
13. C. Lanczos, *The Variational Principles of Mechanics* (Dover Publications, Inc., New York 1970)
14. J.O. Hirschfelder, J. Chem. Phys. **33**, 1462 (1960)
15. J.H. Epstein, S.T. Epstein, Am. J. Phys. **30**, 266 (1962)
16. E. Rincón, A. Toro-Labbé, Chem. Phys. Lett. **438**, 93 (2007)
17. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision B.04. (Gaussian, Inc., Pittsburgh, PA, 2003)

18. P. Jaque, A. Toro-Labbé, P. Politzer, P. Geerlings, *Chem. Phys. Lett.* **456**, 135 (2008)
19. K. Fukui, *J. Phys. Chem.* **74**, 4161 (1970)
20. K. Fukui, *Pure Appl. Chem.* **54**, 1825 (1982)
21. C. González, B. Schlegel, *J. Chem. Phys.* **94**, 5523 (1990)