Analysis of diatomic bond dissociation and formation in terms of the reaction force and the position-dependent reaction force constant

Jane S. Murray · Alejandro Toro-Labbé · Tim Clark · Peter Politzer

Abstract Bond dissociation and formation in diatomic molecules are analyzed in terms of the reaction force $\mathbf{F}(\mathbf{R})$ and the reaction force constant $\kappa(\mathbf{R})$. These were determined for a group of 13 molecules from their extended-Rydberg potential energy functions $V(\mathbf{R})$, which are of near-experimental quality. From $\mathbf{F}(\mathbf{R})$ and $\kappa(\mathbf{R})$ comes a two-stage description of dissociation/formation. In dissociation, the first stage involves stretching of the bond, which is opposed by an increasingly negative retarding force $\mathbf{F}(\mathbf{R})$. This reaches a minimum and then begins to weaken in the second stage, which is the transition from stretched molecule to free atoms. Bond formation begins with the reverse transition, driven by a positive $\mathbf{F}(\mathbf{R})$ which reaches a maximum for the stretched molecule and then becomes a decreasing restoring force. In the stages in which the system is a stretched molecule, $\kappa(\mathbf{R})$ is positive with its maximum at the equilibrium bond length; it is zero at the minimum or maximum of $\mathbf{F}(\mathbf{R})$, and negative throughout the transition stages, going through a minimum. $\kappa(\mathbf{R}) < 0$ has been found to characterize the transition portion of a reaction. This description of dissociation/formation is reinforced by computed B3LYP and Hartree-Fock force constants at different atom separations for the singlet molecules. Hartree-Fock wave function stability assessments suggest that, for the single-bonded singlet molecules, the onset of electron unpairing in dissociation comes in the neighborhood of the $\mathbf{F}(\mathbf{R})$ minimum.

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The reaction force and the reaction force constant

Consider a chemical or physical process that is described by a potential energy function $V(\mathbf{R})$, where $\mathbf{R}$ is a reaction coordinate in the direction from reactants to products. Then there is an associated force $\mathbf{F}(\mathbf{R})$, given by

$$\mathbf{F}(\mathbf{R}) = -\frac{\partial V(\mathbf{R})}{\partial \mathbf{R}} \qquad (1)$$

This "reaction force" is characterized by maxima and minima at the inflection points of $V(\mathbf{R})$, where

$$\frac{\partial^2 V(\mathbf{R})}{\partial \mathbf{R}^2} = -\frac{\partial \mathbf{F}(\mathbf{R})}{\partial \mathbf{R}} = 0 \qquad (2)$$

and $F(R)$ is zero for the reactants, products, intermediates and transition states, where $\frac{\partial V(R)}{\partial R} = 0$.

For a one-step process A → B having $V(R)$ as in Fig. 1(a), $F(R)$ is shown in Fig. 1(b). The minimum and maximum of $F(R)$, at $R = \alpha$ and $R = \gamma$, provide a natural and universal partitioning of the process into three stages: A → α, α → γ and γ → B. Our experience in a series of

(a)

$V(R)$

A   β   B

(b)

$F(R)$

0.0

A   α   β   γ   B

(c)

0.0

$\kappa(R)$

A   α   β   γ   B

R
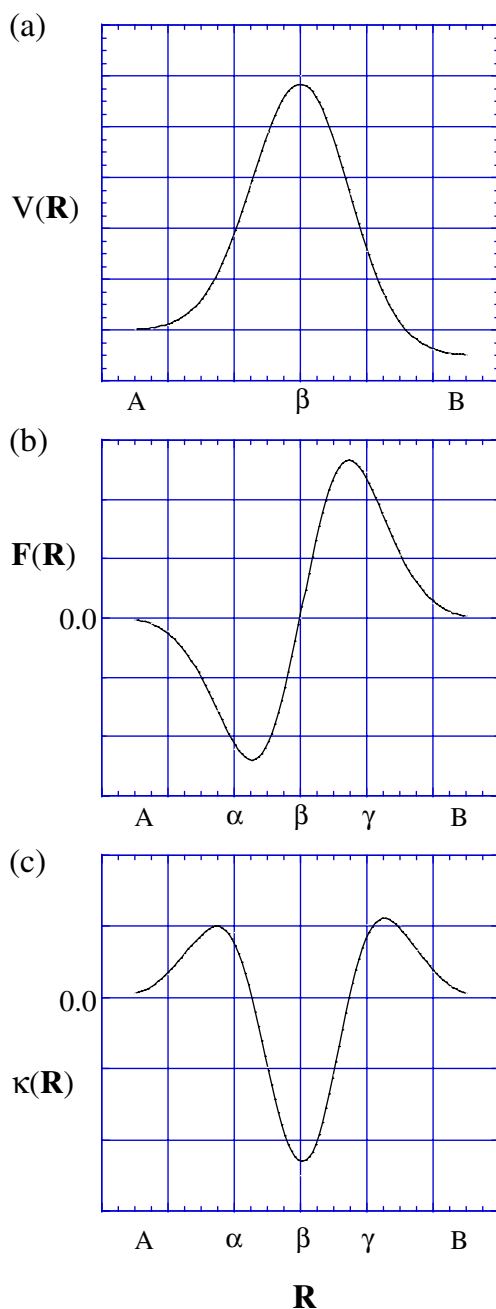
Fig. 1 Typical profiles of $V(R)$, $F(R)$ and $\kappa(R)$, (a) – (c) respectively, for a process A → B having an activation barrier in both forward and reverse directions. Same horizontal axis applies to all three plots. R = α and R = γ correspond to the minimum and the maximum of $F(R)$, and R = β to the transition state and the minimum of $\kappa(R)$

studies, summarized by Toro-Labbé et al. [1], has been that each stage tends to emphasize certain factors, although certainly not exclusively. The first, from A to α, is dominated by structural changes in the reactants – bond lengthening, angle bending, etc. – which are opposed by an increasingly negative retarding force $F(R)$. The second stage, α to γ, can roughly be viewed as a transition from distorted reactants to distorted products. It is in this stage that the most significant electronic effects, e.g., bond breaking/formation, are likely to occur. These are reflected in an increasingly positive driving force. The third stage, γ to B, again focuses upon structural changes, as the products approach their final states and $F(R)$ diminishes to zero.

It has been demonstrated that the reaction force can provide considerable insight into mechanisms, including the roles of solvents and catalysts in influencing activation barriers [2, 3]. For a summary of all of this work and a more extensive discussion of $F(R)$, see Toro-Labbé et al. [1].

The analysis can be extended further in terms of the second derivative of $V(R)$, which we interpret as the *position-dependent* reaction force constant, $\kappa(R)$ [4]:

$$\kappa(R) = -\frac{\partial F(R)}{\partial R} = \frac{\partial^2 V(R)}{\partial R^2} \qquad (3)$$

$\kappa(R)$ also shows a universal pattern in the stages of a process that are defined by the maxima and minima of $F(R)$. For the $V(R)$ and $F(R)$ in Fig. 1(a) and (b), $\kappa(R)$ is presented in Fig. 1(c). It is positive in the stages dominated by structural factors, A → α and γ → B, with maxima at the inflection points of $F(R)$. $\kappa(R)$ passes through zero at the minimum of $F(R)$, at $R = \alpha$, and then remains negative until reaching zero again at the maximum of $F(R)$, at $R = \gamma$. $\kappa(R)$ has a minimum at the transition state ($R = \beta$), where $F(R)$ has another inflection point. The fact that $\kappa(R)$ is negative from $R = \alpha$ to $R = \gamma$ is consistent with this entire stage of the process being one of transition, not just the single point $R = \beta$ that corresponds to the maximum of $V(R)$.

For the reverse process, B → A, the reaction coordinate vector **R** is in the opposite direction. Since $V(R)$ and $\kappa(R)$ are scalars, they retain the same forms as in Fig. 1(a) and (c). However $F(R)$ is now the negative of Fig. 1(b), the mirror image with respect to the horizontal. The minimum is at γ, the maximum at α.

Bond dissociation/formation

Our present focus will be upon a particular type of process, bond dissociation and formation. In the present paper, we deal specifically with diatomic molecules; in the future we will extend the analysis to polyatomic systems.

For a diatomic dissociation, A−B → A + B, the potential energy V(**R**) has the familiar form seen in Fig. 2(a). **R** is the vector measuring the increasing separation of A and B; R_e is the equilibrium bond length. Since V(**R**) is continually increasing, the reaction force **F**(**R**) is negative, a retarding force, throughout the course of the dissociation, Fig. 2(b). **F**(**R**) reaches its greatest magnitude at R = α.
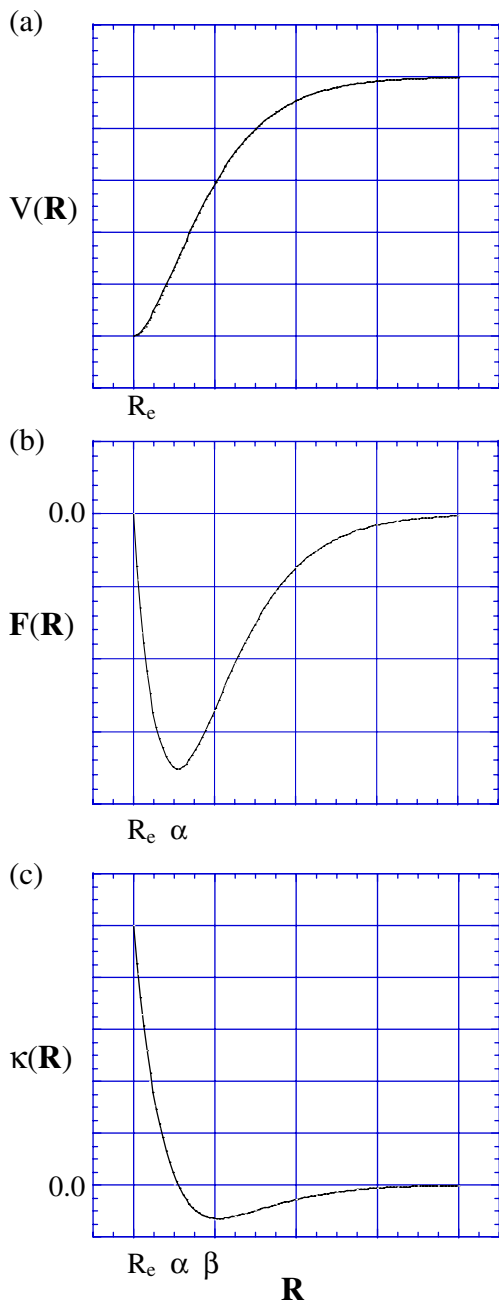

(a)

V(**R**)

R_e

(b)

0.0

F(**R**)

R_e α

(c)

κ(**R**)

0.0

R_e α β

R

Fig. 2 Typical profiles of V(**R**), **F**(**R**) and κ(**R**), (a) – (c) respectively, for the dissociation A−B → A + B. Same horizontal axis applies to all three plots. R = R_e corresponds to the equilibrium bond length of A −B, and R = α and R = β to the minima of **F**(**R**) and κ(**R**)

The reaction force constant, κ(**R**), is in Fig. 2(c). It has its maximum value (for R ≥ R_e) at R = R_e, where it is equivalent to the harmonic force constant k_e. Note however that k_e is defined only at R_e,

$$k_e = \left(\frac{\partial^2 V(\mathbf{R})}{\partial \mathbf{R}^2} \right)_{R_e} \quad (4)$$

whereas κ(**R**) is a position-dependent property. From R_e to α, it decreases in magnitude but remains positive, becoming zero at α, the minimum of **F**(**R**). For the rest of the dissociation, κ(**R**) is negative, with a minimum at the inflection point of **F**(**R**) and then approaching zero as R → ∞.

For the formation of the bond, A + B → A−B, **R** is directed from the separate atoms to the molecule. V(**R**) and κ(**R**) are the same as in Fig. 2(a) and (c), but **F**(**R**) is positive, a driving force, during the entire process.

Bond dissociation (formation) is thus divided by the minimum (maximum) of **F**(**R**) into two stages. This reveals some interesting features, which be discussed for diatomic molecules in the next section.

Properties of F(R) and κ(R) for diatomic molecules

In order to examine **F**(**R**) and κ(**R**) quantitatively for specific diatomic molecules, it is necessary to have accurate representations of their potential energies V(**R**). Huxley and Murrell have demonstrated that these are available via the extended-Rydberg function [5],

$$V(\mathbf{R}) = -D_e \left[1 + d_1(R - R_e) + d_2(R - R_e)^2 + d_3(R - R_e)^3 \right] \quad (5)$$

$$\exp[-d_1(R - R_e)].$$

In Eq. (5), D_e is the disssociation energy and the d_i are parameters that differ for each molecule and are determined from spectroscopic data.

We have used Eq. (5) to investigate **F**(**R**) and κ(**R**) for 13 diatomic molecules for which Huxley and Murrell found it to give very close agreement with experimental Rydberg-Klein-Rees V(**R**). The molecules are listed in Table 1. It should be noted that they are a highly diverse group. They range from quite polar (LiH, OH, HF) to nonpolar (C_2, N_2, O_2). They include singlet, doublet and triplet states. The bond lengths vary between 0.7414 A (H_2) and 1.9293 A (SiS), and dissociation energies between 2.515 eV (LiH) and 11.226 eV (CO). Second-row atoms are included as well as first-row.

Table 1 presents, for each molecule, some properties related to its **F**(**R**) and κ(**R**). These were obtained using the respective extended-Rydberg functions in conjunction with

Table 1 Molecular properties corresponding to extended-Rydberg representations of V($\mathbf{R}$)[a]

Molecule	R_e[a]	α	$(\alpha - R_e)$	β	$(\beta - R_e)$	$\frac{\beta - R_e}{\alpha - R_e}$	δ_1	δ_2
H$_2$	0.7414	1.130	0.389	1.555	0.814	2.09	0.279	0.648
LiH	1.5957	2.245	0.649	2.940	1.344	2.07	0.270	0.624
OH	0.9696	1.289	0.319	1.625	0.655	2.05	0.274	0.628
HF	0.9168	1.248	0.331	1.618	0.701	2.12	0.265	0.624
C$_2$	1.2430	1.539	0.296	1.831	0.588	1.99	0.285	0.635
CN	1.1718	1.460	0.288	1.745	0.573	1.99	0.287	0.639
CO	1.1283	1.435	0.307	1.756	0.628	2.05	0.254	0.582
CS	1.5349	1.915	0.380	2.310	0.775	2.04	0.266	0.607
N$_2$	1.0977	1.368	0.270	1.639	0.541	2.00	0.280	0.630
NO	1.1508	1.415	0.264	1.682	0.531	2.01	0.277	0.626
SiO	1.5097	1.890	0.380	2.295	0.785	2.07	0.253	0.585
SiS	1.9293	2.393	0.464	2.776	0.947	2.04	0.264	0.603
O$_2$	1.2075	1.488	0.280	1.757	0.549	1.96	0.300	0.658

[a] R_e and the parameters for the extended-Rydberg functions are from ref. 5.
All distances are in Angstroms.

Eqs. (1) – (3). The minimum of $\mathbf{F(R)}$ in dissociation (or maximum in bond formation) and the minimum of $\kappa(\mathbf{R})$ occur at atom separations of R = α and R = β, respectively, and the amount by which these differ from R_e changes considerably from one molecule to another, as is to be expected. Thus $(\alpha - R_e)$ goes from 0.264 to 0.649 A, and $(\beta - R_e)$ from 0.531 to 1.344 A, the extremes being for NO and LiH. What is notable, however, is that the ratio $(\beta - R_e)/(\alpha - R_e)$ is nearly constant; the average value is 2.04, with a standard deviation of 0.04. Thus, for all of these molecules, the increase in the atom separation, relative to R_e, is essentially twice as great at the minimum of $\kappa(\mathbf{R})$ as it is at the minimum of $\mathbf{F(R)}$. This confirms a recent prediction based upon the Rydberg potential energy function [6], which is a truncated version of Eq. (5), with $d_2 = d_3 = 0$ [7].

A particularly striking feature of diatomic V($\mathbf{R}$) that is revealed by $\mathbf{F(R)}$ and $\kappa(\mathbf{R})$ concerns the quantities δ_1 and δ_2, where

$$\delta_1 = \frac{V(\alpha) - V(R_e)}{D_e} \tag{6}$$

and

$$\delta_2 = \frac{V(\beta) - V(R_e)}{D_e} \tag{7}$$

δ_1 and δ_2 indicate what fractions of the dissociation energy have been reached when the separations of the atoms correspond to the minima of $\mathbf{F(R)}$ and $\kappa(\mathbf{R})$, respectively.

Both δ_1 and δ_2 display a remarkable uniformity for these 13 molecules (Table 1). This was mentioned already earlier for δ_1 [8]; its average in Table 1 is 0.273, with a standard

Table 2 Molecular properties of singlet diatomic molecules plus triplet O$_2$, as obtained from extended-Rydberg functions and from B3LYP and Hartree-Fock calculations

Molecule	Extended-Rydberg[a]		B3LYP/6-311G(3df,2p)			HF/6-311G(3df,2p)			
	α	β	R_0	R_{min}	$\frac{R_{min} - R_e}{R_0 - R_e}$	R_0	R_{min}	$\frac{R_{min} - R_e}{R_0 - R_e}$	Instab.[b]
H$_2$	1.130	1.555	1.17	1.66	2.1	1.20	1.71	2.1	1.22
LiH	2.245	2.940	2.32	3.12	2.1	2.40	3.19	2.0	2.28
HF	1.248	1.618	1.27	1.66	2.1	1.26	1.63	2.0	1.30
CO	1.435	1.756	1.46	1.79	2.0	1.45	1.81	2.0	1.35
CS	1.915	2.310	1.96	2.40	2.0	1.93	2.30	1.9	1.62
N$_2$	1.368	1.639	1.41	1.73	2.0	1.42	1.77	2.0	1.14
SiO	1.890	2.295	1.94	2.37	2.0	1.91	2.25	1.8	1.68
SiS	2.393	2.776	2.46	2.98	2.0	2.43	2.88	1.9	2.16
O$_2$	1.488	1.757	1.56	1.94	2.1	1.53	1.89	2.0	1.24[c]

[a] α and β are taken from Table 1.
[b] RHF $\rightarrow$ UHF instability.
[c] Internal instability.
All distances are in Angstroms.

deviation of 0.013. An analogous observation can now be made for δ_2; average value=0.622, standard deviation=0.022.

We see, therefore, a very noteworthy consistency in the dissociation patterns of these diatomics: the minima of the reaction force $\mathbf{F(R)}$ and the reaction force constant $\kappa(\mathbf{R})$ occur when the molecule has gained about 27% and 62%, respectively, of the energy needed for dissociation. (Conversely, in bond formation, the minimum of $\kappa(\mathbf{R})$ and the maximum of $\mathbf{F(R)}$ correspond to the interaction energies having reached 38% and 73% of the final value.)

The two stages of diatomic bond dissociation/formation

The preceding section has brought out the markedly close similarity between key features of bond dissociation or formation in a group of diatomic molecules of various types. In a recent preliminary analysis of what is taking place in these processes [6], we demonstrated that a dissociation is initially characterized by a negative retarding force that becomes stronger nearly linearly with atom separation until reaching its greatest magnitude at $R = \alpha$ (the reaction force minimum). It was suggested that this can be viewed essentially as a stretching of the bond, in which the molecule retains its intrinsic nature. At the same time, the reaction force constant $\kappa(\mathbf{R})$ is decreasing from its maximum at R_e to zero at $R = \alpha$. For atom separations greater than α, $\kappa(\mathbf{R})$ is negative, while $\mathbf{F(R)}$ begins to weaken. The dissociation has evidently entered a second stage.

We will now provide support for this interpretation from a different perspective. In Table 2 are listed eight singlet diatomic molecules from the group in Table 1, plus O_2, which is a triplet. For each of these, we have computed the force constant $k(\mathbf{R})$ at a series of atom separations, starting with $R = R_e$, using both the density functional B3LYP/6-311G(3df,2p) and the HF/6-311G(3df,2p) methods, and the Gaussian 03 code [9].

While a force constant is typically determined at energy minima and maxima, its definition as the second derivative of the energy with respect to position [10] does not impose such a restriction (except in the harmonic approximation). We use $\kappa(\mathbf{R})$ to represent the reaction force constant obtained via Eq. (3) from the near-experimental extended-Rydberg V(R), and $k(\mathbf{R})$ for the force constant coming from the B3LYP or Hartree-Fock procedure. Note that for a polyatomic molecule, there will still be only one reaction force constant $\kappa(\mathbf{R})$ but there can be many $k(\mathbf{R})$ [4].

The variation of $k(\mathbf{R})$ with R for these molecules is very much like that of $\kappa(\mathbf{R})$ in Fig. 2(c). This can be seen for CO in Fig. 3; $k(\mathbf{R})$ has its maximum at R_e, where $k(\mathbf{R}) = k_e$, then decreases to zero and becomes negative, going through a minimum before approaching zero as $R \rightarrow \infty$.

Table 2 gives, for each molecule, the computed atom separation at which $k(\mathbf{R})$ changes from positive to negative (R_0) and that where $k(\mathbf{R})$ has its minimum (R_{min}). The first point to note is that the B3LYP and the Hartree-Fock values of R_0 and R_{min} are in general quite similar. But what is particularly significant is that the calculated R_0 and R_{min} are usually close to the extended-Rydberg α and β, which are also included in Table 2. The computed force constants pass through zero and reach their minima at nearly the same atom separations as is predicted by the experimentally-based extended-Rydberg V(R) functions. Furthermore, the ratio $(R_{min} - R_e)/(R_0 - R_e)$ are almost all in the immediate vicinity of 2.0, again duplicating the extended-Rydberg.

Thus the calculated force constants $k(\mathbf{R})$ behave like the reaction force constant $\kappa(\mathbf{R})$ in changing from positive to negative near the minimum of the reaction force $\mathbf{F(R)}$ (in dissociation), and remaining so thereafter. In quantum chemistry, a negative force constant is used to identify a transition state. In diatomic dissociation, however, we see that negative $k(\mathbf{R})$ characterize the entire stage of the process after the $\mathbf{F(R)}$ minimum. Recently, for a proton transfer reaction that goes through an energy barrier such as that in Fig. 1(a) [4], the computed force constant for motion along the intrinsic reaction coordinate was found to be negative throughout the whole portion of the process between the minimum and the maximum of the reaction force. These observations support the concept that the reaction force minimum marks the start of a *transition stage*; in the case of diatomic dissociation, it is the transition from the stretched molecule to the free atoms.

How does this begin? What takes place in the neighborhood of the $\mathbf{F(R)}$ minimum? To address these questions, we
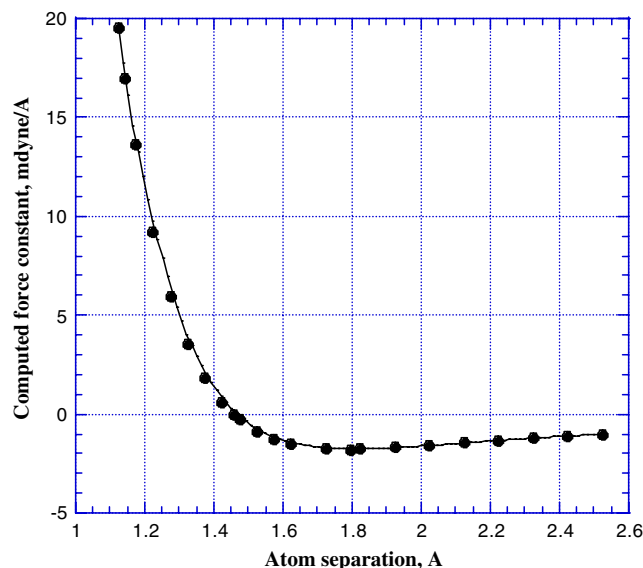

Fig. 3 Force constants computed for CO molecule at various atom separations, starting with equilibrium bond length. Calculations were at B3LYP/6-311G(3df,2p) level

give in Table 2 the atom separations at which Gaussian 03 reports "RHF → UHF instability." (For the triplet O_2, the message was "internal instability.") For the three singly-bonded molecules – H_2, LiH and HF – this occurs quite near to the $\mathbf{F(R)}$ minimum (i.e., α) and to R_0, and suggests the onset of electron unpairing. For the multiply-bonded singlet molecules, on the other hand, RHF → UHF instability is noted before the $\mathbf{F(R)}$ minimum; thus some electron unpairing is occurring already earlier.

For the doublet molecules in Table 1, the calculations of R_0, R_{min} and instability give erratic results with the computational methods that we are using, which is not surprising. These molecules are not included in Table 2, nor is C_2, for which both methods incorrectly predict the triplet to be the ground state.

In bond formation, α, β, R_0 and R_{min} have the same magnitudes as in dissociation, but α is now the atom separation at the maximum of the reaction force. The initial stage is the transition from separate free atoms to stretched diatomic molecule. $\mathbf{F(R)}$ is a positive and increasing driving force reflecting the growing interaction; $\kappa(\mathbf{R})$ is negative. $\mathbf{F(R)}$ reaches its maximum at $R = \alpha$, while $\kappa(\alpha)$ is zero. At this point we have basically a highly-stretched bond, and $\mathbf{F(R)}$ is essentially the restoring force, which diminishes as $R \rightarrow R_e$. $\kappa(\mathbf{R})$ is positive in this second stage, attaining its maximum at R_e. In both bond dissociation and formation, $\kappa(\mathbf{R})$ is positive in the stretched-molecule portion of the process, and negative during the transitions to or from the separate atoms.

Discussion and summary

From the analysis of the reaction force and the reaction force constant has evolved a two-stage description of the dissociation or the formation of a diatomic molecule. One of these involves the stretching or the relaxation of the bond, the other deals with the transition between the stretched molecule and the free atoms. This picture is fully consistent with what we have found for a variety of other processes [1], as mentioned at the beginning of this paper; the minima and maxima of the reaction force define stages emphasizing structural factors separated by transitional ones in which occur major electronic effects.

As part of this study, we have computed quantum-chemically the force constants $k(\mathbf{R})$ for eight singlet and one triplet diatomic molecules at different atom separations. Both the B3LYP and the Hartree-Fock force constants follow very much the same pattern as do those coming from the extended-Rydberg $V(\mathbf{R})$. They decrease from maxima at R_e, change from positive to negative near the atom separation corresponding to the reaction force minimum (in dissociation) and then remain negative. There are indications that the change from positive to negative $k(\mathbf{R})$ is associated, in singlets, with electron unpairing.

The analysis in terms of $\mathbf{F(R)}$, $\kappa(\mathbf{R})$ and the extended-Rydberg $V(\mathbf{R})$ is completely independent of the B3LYP and Hartree-Fock $k(\mathbf{R})$ calculations. It is significant, therefore, that these latter complement and reinforce the interpretation of diatomic bond dissociation and formation that comes from the reaction force $\mathbf{F(R)}$ and the reaction force constant $\kappa(\mathbf{R})$.

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