

THE POSITION-DEPENDENT REACTION FORCE CONSTANT IN BOND DISSOCIATION/FORMATION

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It is a privilege to join in honoring Professor Rudolf Zahradník.

The concept of a position-dependent reaction force constant $\kappa(\mathbf{R})$ can be used to distinguish the two phases of bond dissociation or formation: stretched bond, $\kappa(\mathbf{R}) > 0$, and interacting but separate fragments, $\kappa(\mathbf{R}) < 0$. The transition between these phases is at $\kappa(\mathbf{R}) = 0$, which coincides with the minimum (for dissociation) or maximum (for formation) of the reaction force. As was shown earlier, all of these occur (for diatomic molecules) at the separation \mathbf{R} at which the system's energy relative to equilibrium is about 27% of its dissociation energy.

Keywords: Bond dissociation/formation; Reaction force; Position-dependent reaction force constant; Dissociation energy.

The potential energy $V(R)$ of a system undergoing a bond rupture,



typically varies in a manner such as is shown in Fig. 1a. The energy is a minimum when the A–B bond has its equilibrium length $R = R_e$, increases rapidly as A and B initially move apart, and then levels off as the A–B separation R becomes large and A and B essentially cease to interact. The quantity

$$D_e = V(\infty) - V(R_e) \quad (2)$$

is the dissociation energy of the bond.

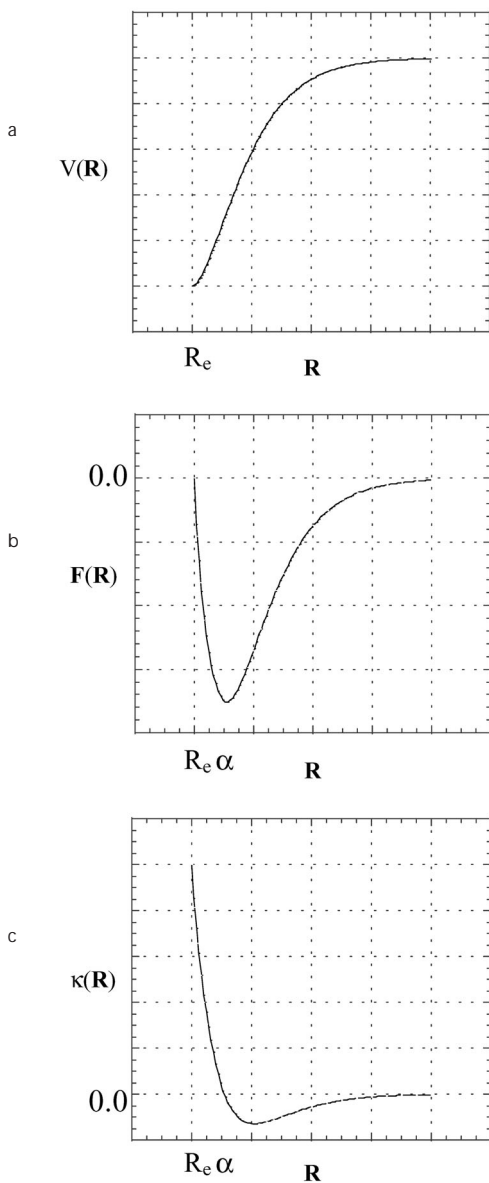


FIG. 1
Typical $V(\mathbf{R})$ (a), $\mathbf{F}(\mathbf{R})$ (b) and $\kappa(\mathbf{R})$ (c) profiles for dissociation of a bond A-B. The same horizontal axis applies to all three plots. $R = R_e$ corresponds to the equilibrium bond length of A-B, and $R = \alpha$ to the minimum of $\mathbf{F}(\mathbf{R})$

An additional perspective upon the process is provided by the reaction force $\mathbf{F}(\mathbf{R})$ that is associated with it:

$$\mathbf{F}(\mathbf{R}) = -\frac{\partial V(\mathbf{R})}{\partial \mathbf{R}}. \quad (3)$$

The A---B separation is now being treated as a reaction coordinate vector \mathbf{R} , along which is measured the progress of the dissociation. However, individual points along \mathbf{R} will still be denoted as scalars, e.g. R_e .

The reaction force concept has been used in recent years to examine a number of chemical reactions and conformational changes. (See overview by Toro-Labbé et al.¹) The maxima and minima of $\mathbf{F}(\mathbf{R})$ result in a natural partitioning of the process into a series of well-defined stages, differing in whether $\mathbf{F}(\mathbf{R})$ is driving or retarding and in the relative roles of structural vs electronic factors. Particularly important is the recognition that an activation barrier is comprised of two distinct components; this can lead to a much better understanding of the functions of external agents such as catalysts or solvents, which may affect primarily just one of these components.

The reaction force $\mathbf{F}(\mathbf{R})$ corresponding to the dissociation represented by $V(\mathbf{R})$ in Fig. 1a is shown in Fig. 1b. $\mathbf{F}(\mathbf{R}) = 0$ at $R = R_e$, which is a minimum of $V(\mathbf{R})$, and it approaches zero as $\mathbf{R} \rightarrow \infty$. Since $\partial V(\mathbf{R})/\partial \mathbf{R}$ is positive throughout a dissociation process, $\mathbf{F}(\mathbf{R})$ is negative, i.e. opposite in direction to \mathbf{R} at all times. $\mathbf{F}(\mathbf{R})$ has a minimum at $R = \alpha$, which is an inflection point of $V(\mathbf{R})$:

$$\left(\frac{\partial^2 V(\mathbf{R})}{\partial \mathbf{R}^2} \right)_{R=\alpha} = -\left(\frac{\partial \mathbf{F}(\mathbf{R})}{\partial \mathbf{R}} \right)_{R=\alpha} = 0. \quad (4)$$

Thus $\mathbf{F}(\mathbf{R})$ is a retarding force, opposing the separation of A and B, and reaching its greatest magnitude at $R = \alpha$.

For the reverse reaction, the formation of the bond,



$V(\mathbf{R})$ retains the same form as in Fig. 1a. However, the reaction coordinate vector is now directed from A + B to A-B. Thus, $\partial V(\mathbf{R})/\partial \mathbf{R} < 0$, and $\mathbf{F}(\mathbf{R})$ is positive, in the same direction as \mathbf{R} , with a maximum at $R = \alpha$; it is the mirror image, with respect to \mathbf{R} , of Fig. 1b. $\mathbf{F}(\mathbf{R})$ is therefore a driving force in the formation of the bond.

**POTENTIAL ENERGY FUNCTIONS; A UNIVERSAL FEATURE OF $V(\mathbf{R})$
FOR BOND DISSOCIATION/FORMATION**

A conceptually useful model for $V(\mathbf{R})$, but only in the immediate vicinity of $R = R_e$, is the harmonic oscillator, for which

$$V_{\text{HO}}(\mathbf{R}) = V_{\text{HO}}(R_e) + \frac{1}{2} k_e (R - R_e)^2. \quad (6)$$

The parameter k_e is the force constant; it governs the restoring force felt by the oscillator,

$$\mathbf{F}_{\text{HO}}(\mathbf{R}) = -\frac{\partial V_{\text{HO}}(\mathbf{R})}{\partial \mathbf{R}} = -k_e (R - R_e) \quad (7)$$

and can be expressed as

$$k_e = \left(\frac{\partial^2 V_{\text{HO}}(\mathbf{R})}{\partial \mathbf{R}^2} \right)_{R=R_e}. \quad (8)$$

Equation (7) is Hooke's law.

Being a parabola, $V_{\text{HO}}(\mathbf{R})$ cannot describe bond dissociation or formation. Even for R near R_e , it soon deviates from an actual $V(\mathbf{R})$. For the CO molecule, for example, the error in $V_{\text{HO}}(\mathbf{R})$ is about 0.86 eV already for $R - R_e = 0.2 \text{ \AA}$ (ref.²).

The harmonic function $V_{\text{HO}}(\mathbf{R})$ is simply the beginning of a Taylor expansion of $V(\mathbf{R})$ around $R = R_e$. Would a higher-order Taylor expansion of $V(\mathbf{R})$ provide a better representation of it? Murrell et al., following earlier work by Dunham³, found that a Taylor series does offer some improvement, but that even when taken to the fourth order, the predicted $V(\mathbf{R})$ for CO is "significantly in error" for $R - R_e = 0.2 \text{ \AA}$ (ref.²).

There have been many attempts to develop an accurate general representation of $V(\mathbf{R})$ for bond dissociation/formation⁴⁻⁶. One of the best known of these, due to Morse⁷, can be written as

$$V_{\text{M}}(\mathbf{R}) = D_e \{1 - \exp[-c(R - R_e)]\}^2 \quad (9)$$

in which $c = (k_e/2D_e)^{0.5}$, k_e being the force constant (Eq. (8)). Another function, proposed by Rydberg⁸, is

$$V_R(\mathbf{R}) = -D_e[1 + d(R - R_e)] \exp[-d(R - R_e)] \quad (10)$$

where $d = (k_e/D_e)^{0.5}$. Both $V_M(\mathbf{R})$ and $V_R(\mathbf{R})$ are good at reproducing known $V(\mathbf{R})$ curves², especially in the vicinity of $R = R_e$. Note that they differ with respect to the zero of energy, which is at R_e for $V_M(\mathbf{R})$ and at $R = \infty$ for $V_R(\mathbf{R})$.

We have recently shown that $V_M(\mathbf{R})$ and $V_R(\mathbf{R})$ have a very interesting feature⁹. They both predict that the point $R = \alpha$ at which $\mathbf{F}(\mathbf{R})$ has its minimum (for dissociation), and which can be determined by applying Eq. (4), corresponds to $V(\mathbf{R})$ having increased relative to its minimum by very close to 25% of the dissociation energy. Specifically⁹

$$\frac{V_M(\alpha) - V_M(R_e)}{D_e} = 0.250 \quad (11)$$

and

$$\frac{V_R(\alpha) - V_R(R_e)}{D_e} = 0.264. \quad (12)$$

These results are independent of the values of D_e , R_e and k_e , and thus of the particular bond A-B.

In order to test whether the predictions of Eqs (11) and (12) are approximately valid at a higher and more accurate level, we proceeded to the extended Rydberg function¹⁰:

$$V_{ER}(\mathbf{R}) = -D_e[1 + d_1(R - R_e) + d_2(R - R_e)^2 + d_3(R - R_e)^3] \exp[-d_1(R - R_e)]. \quad (13)$$

The parameters d_i in Eq. (13) differ for each molecule and are commonly determined spectroscopically. Huxley and Murrell concluded that Eq. (13) "appears to be an excellent representation of the ground-state potential of stable diatomics" in "the whole of the attractive well except for the long-range van der Waals region"¹⁰.

Due to the more complex form of Eq. (13) compared to Eqs (9) and (10), it does not yield a universal value for the quantity $[V_{ER}(\alpha) - V_{ER}(R_e)]/D_e$, as they do. For a group of 12 diatomic molecules, however, using parameters d_i that had been shown by Huxley and Murrell to reproduce very well the respective experimental $V(\mathbf{R})$ curves¹⁰, we found⁹

$$\frac{V_{\text{ER}}(\alpha) - V_{\text{ER}}(R_e)}{D_e} = 0.271 \text{ (average)} \quad (14)$$

with a standard deviation of 0.011. The 12 molecules are a very diverse group. They range from quite polar (LiH) to nonpolar (N_2), with R_e between 0.7414 and 1.9293 Å, and D_e between 2.515 and 11.226 eV. They include second-row atoms as well as first-row, radicals as well as closed-shell molecules. It is not surprising then that the distances $\alpha - R_e$ vary considerably, from 0.264 to 0.649 Å (ref.⁹).

What is noteworthy is the uniformity manifested in Eq. (14). The point at which the retarding force in a bond dissociation attains its greatest strength appears to universally correspond to the energy having increased by the same fraction (0.27) of the amount needed (i.e. D_e).

Also of interest is that for the diatomics not containing hydrogen, the quantity $(\alpha - R_e)/R_e$ was found to average 0.246, with a standard deviation of 0.004 (ref.⁹). Thus, the force minimum for these molecules comes at an A--B separation about 25% greater than the equilibrium bond length.

THE REACTION FORCE CONSTANT

In seeking to better understand what is happening between the equilibrium separation R_e and the force minimum at $R = \alpha$, we will make use of the recently introduced concept of the reaction force constant $\kappa(\mathbf{R})$ ¹¹:

$$\kappa(\mathbf{R}) = \frac{\partial^2 V(\mathbf{R})}{\partial \mathbf{R}^2} = -\frac{\partial \mathbf{F}(\mathbf{R})}{\partial \mathbf{R}}. \quad (15)$$

Equation (15) can be viewed as extending and complementing the idea of a reaction force, Eq. (3).

The definition of $\kappa(\mathbf{R})$, like that of $\mathbf{F}(\mathbf{R})$, is completely general; both apply to any process described by a potential energy $V(\mathbf{R})$. Thus Jaque et al. have analyzed $\kappa(\mathbf{R})$ for the proton transfer¹¹,



For a bond dissociation/formation such as that depicted in Fig. 1a, $\kappa(\mathbf{R})$ is as shown in Fig. 1c. It is a scalar, and will be the same for both the forward and reverse processes. A key feature of $\kappa(\mathbf{R})$ is that it is position-dependent,

in contrast to k_e , which is defined only for R_e , by Eq. (8). $\kappa(\mathbf{R})$ has its maximum value at $R = R_e$. It remains positive but decreasing for $R_e < R < \alpha$, and becomes zero at $R = \alpha$, the minimum of $\mathbf{F}(\mathbf{R})$, after which it is negative. $\kappa(\mathbf{R})$ reaches a minimum at the inflection point of $\mathbf{F}(\mathbf{R})$, and then approaches zero as $R \rightarrow \infty$.

Since our immediate interest is in the region between R_e and $R = \alpha$, we can work with the Rydberg potential function $V_R(\mathbf{R})$, Eq. (10), which is quite accurate in the vicinity of R_e (ref.²) and is simpler than the extended Rydberg. The corresponding reaction force, $\mathbf{F}_R(\mathbf{R}) = -\partial V_R(\mathbf{R})/\partial \mathbf{R}$, is

$$\mathbf{F}_R(\mathbf{R}) = -D_e d^2(R - R_e) \exp[-d(R - R_e)] . \quad (17)$$

It can easily be verified that Eq. (17) yields a force curve having the form of Fig. 1b, with its minimum, where $\partial \mathbf{F}_R(\mathbf{R})/\partial \mathbf{R} = 0$, at $R = \alpha = R_e + (1/d)$.

The reaction force constant, Eq. (15), is then

$$\kappa_R(\mathbf{R}) = D_e d^2[1 - d(R - R_e)] \exp[-d(R - R_e)] . \quad (18)$$

As in Fig. 1c, $\kappa_R(\mathbf{R})$ has its maximum at R_e , is zero at the force minimum, $R = \alpha = R_e + (1/d)$, and reaches a minimum at $R = R_e + (2/d)$. Thus, for the Rydberg function, the distance from R_e to the minimum of $\kappa_R(\mathbf{R})$ is twice the distance to the minimum of $\mathbf{F}_R(\mathbf{R})$.

It is evident in Fig. 1b that in much of the initial stage of a dissociation, $R < \alpha$, $\mathbf{F}(\mathbf{R})$ is dominated by the quantity $(R - R_e)$ in Eq. (17). What is occurring is essentially a stretching of the A-B bond accompanied by a nearly-linearly-increasing negative retarding force. At the same time, $\kappa(\mathbf{R})$ is decreasing from its maximum at R_e to zero at $R = \alpha$, the point at which $\mathbf{F}(\mathbf{R})$ has reached its greatest retarding strength. After $R = \alpha$, $\kappa(\mathbf{R})$ becomes and remains negative, and the nature of $\mathbf{F}(\mathbf{R})$ changes from a growing retarding force opposing the stretching of the bond to a gradually diminishing force of attraction between the separating A and B. The dissociation process has clearly entered a new stage.

DISCUSSION AND SUMMARY

The first part of a bond dissociation, before the minimum of the reaction force, can be viewed as largely a stretching of the bond, with the molecule retaining its intrinsic character. The next portion of the process presumably

emphasizes electronic factors: unpairing of electrons, relaxation of atomic valence states, etc. The two stages of the dissociation are distinguished by the sign of the reaction force constant; $\kappa(\mathbf{R})$ is positive during the bond stretching, and negative during the transition from stretched molecule to separate fragments, in which take place the major electronic changes.

In bond formation, we see the reverse of all this. As A and B initially approach each other, $\mathbf{F}(\mathbf{R})$ is the positive and increasing driving force that pulls them together. $\kappa(\mathbf{R})$ is negative in this part of the process. $\mathbf{F}(\mathbf{R})$ attains its maximum at $R = \alpha$, with $\kappa(\alpha) = 0$. After this point, the system takes on the character of a highly-stretched A–B bond. $\kappa(\mathbf{R})$ is positive, and $\mathbf{F}(\mathbf{R})$ can now be regarded as primarily the restoring force of the stretched A–B bond, diminishing as $R \rightarrow R_e$.

In both bond dissociation and bond formation, therefore, the reaction force constant $\kappa(\mathbf{R})$ is positive during the portion of the process in which the system is essentially a stretched molecule. It is negative in the more transitory phase in which two interacting but separate fragments are evolving toward either their ground states (dissociation) or the stretched molecule (bond formation).

Analogous behavior was observed in the proton transfer mentioned earlier¹¹ (Eq. (16)). This reaction has three stages (defined by the minimum and the maximum of the reaction force $\mathbf{F}(\mathbf{R})$ along the intrinsic reaction coordinate)^{1,11}. The first involves structural changes, primarily a lengthening of the O–H bond and a decrease in the ONS angle. The result can be viewed as a distorted HO–N=S molecule, comparable to a stretched pre-dissociation diatomic. This is followed by a transition stage, in which the O–H bond breaks and a lengthened S–H bond is formed, producing a distorted O=N–SH molecule, which can be compared to a stretched newly-formed diatomic. The last step is the relaxation to the final product, ground-state O=N–SH. In the stages that emphasize structural modifications (the first and the third), $\kappa(\mathbf{R})$ is positive. During the entire transition between these, in which one bond is being broken and another formed, $\kappa(\mathbf{R})$ is negative. Thus the pattern of $\kappa(\mathbf{R})$ for this proton transfer reaction is analogous to that in simply bond dissociation/formation.

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