DISSOCIATION TIME OF CHEMICAL BOND I.
DISSOCIATION OF THE MORSE OSCILLATOR

Ladislav VALKO

Department of Physical Chemistry, Slovak Technical University, 812 37 Bratislava

By solving the equation of motion, the formula was derived for the dissociation time of the Morse oscillator. The dissociation time of oscillator is a characteristic physical parameter of chemical bond whose value depends on the parameters of potential curve. It is important for the selective excitation of chemical bond in a molecule in connection with the progress in femtosecond laser technique. The time required to break the bond must be of the order of a few hundred femtoseconds.

It would seem at first sight that the dissociation of chemical bond takes place instantaneously, i.e., that its time course is unmeasurable. Such notions of academic nature have been substantiated only until recently. Today the state of knowledge is already different. The dissociation time of chemical bond has acquired a particular importance especially recently in connection with the progress in laser chemistry and above all in connection with arising and applying the femtosecond spectroscopy of transition state[1-3]. Considering that the femtosecond pulses are shorter than the dissociation time of chemical bond (which can be accounted for on the basis of simple relations), the real basis has been formed for the experimentation in this region. This has a direct relation to the possibility of realizing the selective excitation of bonds in a molecule, which is the basic aim of vibration laser photochemistry[4]. The problem of selective excitation of the given bond or the corresponding normal mode of molecule consists in the fact that the molecules with a rapid redistribution of internal energy can be considered as ergodic systems. In such systems, the intramolecular energy redistribution takes place in the picosecond time scale, and in the framework of such a scale, it is little probable to induce selectively the molecule decomposition before the energy dissipation over the whole molecule takes place[5]. It is evident that only such systems which are internally non-ergodic (e.g., molecules containing an atom of heavy element) are an exception. In the framework of the femtosecond scale, the selective excitation of the I—C bond in the I—CN molecule[1-3] has been successful.

In this paper we present, in the classical approximation, the derivation of a relation for the dissociation of chemical bond on the basis of solution of the equation of motion of atoms moving in the Morse potential field.

PROBLEM FORMULATION

Let us denote the reduced mass of atoms forming the chemical bond in molecule by μ, the potential energy of their interaction $V(x)$, where $x = r - r_e$ is the displacement of nuclei from the equilibrium position (r_e is the equilibrium distance of nuclei). For such a pair of atoms, in agreement with the law of energy conservation, it is possible to write[6]

$$E = \frac{\mu}{2} \dot{x}^2 + V(x) . \tag{1}$$

Equation (1) represents the first-order differential equation which is integrated on separating variables. Thus

$$dx/dt = [(2/\mu)(E - V(x))]^{1/2} . \tag{2}$$

On the basis of this equation we define the dissociation time of chemical bond τ_d in the following form

$$\tau_d = \left(\frac{\mu}{2}\right)^{1/2} \int_{x_1(E)}^{x_2(E)} \frac{dx}{[E - V(x)]^{1/2}} , \tag{3}$$

where $x_1(E)$ and $x_2(E)$ are the turning points ($V(x_i) = E, i = 1, 2$), by means of which the limits of motion of atoms in potential field $V(x)$ are determined. (Bersohn and Zewail[2] defined the dissociation time of chemical bond for the repulsive potential of atom interaction in the ICN molecule in different way.)

Limits or boundaries of motion of atoms are points of inflexion of atoms because the velocity of atomic motion is zero at these points. If the region of atomic motion s limited by such two points, the motion occurs in a limited region of space (Fig. 1).
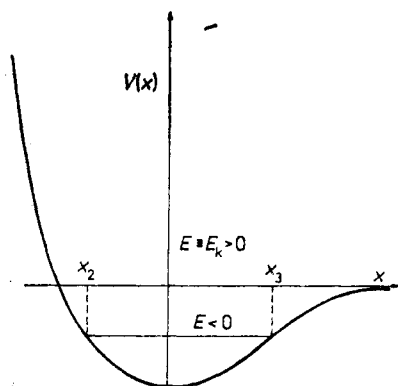

FIG. 1

The shape of potential curve of the Morse oscillator and the designation of single regions of energy

For instance, if $E < 0$, atoms move in region $x_2 \leq x \leq x_3$, the motion is finite. If the region of motion is not limited by such two points or if it is limited from one side only, accordingly if $E \geq 0$, the atoms move in the region $x = \infty$. In this region the motion of atoms is infinite — unbounded. The molecule has already dissociated to atoms which can move away to infinity. After dissociating, the atoms are characterized by kinetic energy, E_k, only, therefore $E \equiv E_k > 0$.

The selective photophysical and photochemical processes arouse great interest at the present time, originating from nonlinear resonance interaction of laser radiation with atoms and molecules. In this connection, the photochemistry of strongly excited molecules in the ground electron state or also the multiphoton vibrational photochemistry[4] gain importance with progress in laser chemistry beside the photochemistry of excited electron states or electron photochemistry. In connection with its intense progress, the dissociation time of chemical bond or the corresponding normal mode may be of great importance. For this reason, the formula for the dissociation time of chemical bond in its ground electron state of molecule will be derived in this work.

If the potential energy of bounded state of atoms in the ground electron state of molecule is considered in the form of the Morse potential

$$V(x) = D(e^{-2ax} - 2\,e^{-ax})\,, \tag{4}$$

where D is the dissociation energy of bond and a is the Morse parameter, for the region of bounded motion of atoms, for which $E < 0$ in agreement with the Morse potential, we get from the condition $V(x_1) \equiv E$:

$$z_{(+,-)} = \frac{D \pm (D^2 - |E|\,D)^{1/2}}{|E|} \tag{5}$$

or

$$x_{(+,-)} = \frac{1}{a}\ln z_{(+,-)}\,, \tag{6}$$

where the substitution $z \equiv \exp(ax)$ has been used.

Considering that the kinetic energy is always positive, total energy E of atom motion in integral (3) must be always higher than potential energy $V(x)$. Therefore, the bounded motion of atoms may take place only in the region of space for which $V(x) < E$. This condition determines the limits of integral (3). The lower limit is chosen as $x_1(E < 0) = 0$ and $z_1(E < 0) = 1$. The upper limit, x_2, cannot be identified with $x_2 = \infty$ because for $x_2 = \infty$, energy E is already $E > 0$, and the solution of Eq. (3) with the initial condition $E < 0$ does not satisfy for $E > 0$. Way out of this situation is to express E in the form $|E| = D/n$, where n is a positive integer,

from experimental conditions being deduced that $n \geqslant 1$. For the given value of $|E| = D/n$, the final value $z_{(+)}(|E| = D/n) = n + n[(n - 1)/n]^{1/2}$ follows from Eq. (4) for the upper limit of dimensionless variable z. The chosen limits are in agreement with the quantum-mechanical virial theorem determining the interrelation between the total kinetic and potential energy of diatomic molecule expressed in the form of the Morse potential[7].

The solution of the integral of motion, Eq. (3), for the condition $E < 0$ can be expressed by means of ref.[8] in the form

$$\tau_d = \left(\frac{\mu}{2a^2}\right)^{1/2} \int_1^{n + n[n(n-1)/n]^{1/2}} \frac{dz}{(Ez^2 + 2Dz - D)^{1/2}} =$$

$$= -\left(\frac{\mu}{2a^2}\right)^{1/2} \left(\frac{1}{-E}\right)^{1/2} \arcsin \frac{-|E|z + D}{(D^2 - |E|D)^{1/2}} \Bigg|_1^{n + n[(n-1)/n]^{1/2}}, \quad E < 0. \quad (7)$$

It is evident that the solution in the form of Eq. (7) does not fulfil the condition $|E| = D$ for the lower limit of integral. To save the situation, we choose D as follows. Let $D = 1 \cdot 0 \ldots m1|E|$, where m is the number of ciphers (0) after the decimal point before number one. With this choice of E it is already possible to find the final solution of integral (3). After inserting the corresponding limits

$$\tau_d = -\left(\frac{\mu}{2a^2}\right)^{1/2} \left\{ \left(\frac{n}{D}\right)^{1/2} \arcsin(-1) - \right.$$

$$\left. - \lim_{m \to \infty} \left(\frac{1 \cdot 0 \ldots m1}{D}\right)^{1/2} \arcsin \left[\frac{10^{-(m+1)/2}}{(1 \cdot 0 \ldots m1)^{1/2}}\right] \right\}$$

or

$$\tau_d = \frac{\pi}{2} \left(\frac{\mu n}{2a^2 D}\right)^{1/2} \quad (8)$$

It is advantageous to consider the Morse parameter a in the form

$$a = \tilde{\nu}_e \left(\frac{2\pi^2 c^2 \mu}{D}\right)^{1/2},$$

where $\tilde{\nu}_e$ is the equilibrium wave number of normal mode. After substituting for a into Eq. (8) we get

$$\tau_d = \frac{\pi}{2} \frac{n^{1/2}}{2\pi\tilde{\nu}_e c} = \frac{\pi}{2} \frac{n^{1/2}}{\omega_e}, \quad (9)$$

where ω_e is the equilibrium angular frequency of vibration. Now we carry out the

estimation of the magnitude of τ_d. We ask, what defines a dissociation time τ_d. Here we define it as the time for two fragments (atoms) to reach a separation at which their interaction energy is negligible. We restrict ourselves to fragments interacting via a short-range van der Waals forces. Thus, the dissociation time τ_d depends on the sensitivity with which the energy can be measured. The measure of this interaction energy is the magnitude of the n parameter $(n = D/|E|)$. With this in mind, we might ask the question: how long does it take break a chemical bond, i.e., I—C bond in the elementary reaction

$$\text{ICN} + h\nu \rightarrow \text{I} + \text{CN}$$
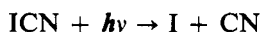
Thank to the recent advances in ultrafast laser spectroscopy of chemical reactions[1-4], the direct clocking of I—C bond breaking time in the above elementary reaction was allowed. Rosker et al.[1-3,9] experimentally observed that the bond between I and CN breaks 205 ± 30 fs after photoexcitation. By fitting known properties of the ICN molecule, taking $n = 150$, the I—C stretch $451 \cdot 5$ cm^{-1} (ref.[2]), then for the dissociation time we obtain $\tau_d \approx 225$ fs. Assuming that the dissociation of I—CN bond in its ground state is $3 \cdot 21$ eV (ref.[9]), then $|E| = 2 \cdot 14 \cdot 10^{-2}$ eV is order of van der Waals interaction energy.

On the basis of the Floquet analysis, Tanner and Maricq[10] have recently investigated the dynamics of the Morse oscillator represented by the ionic molecule I_2^+ in the intense laser field and in a highly excited state. From the comparison of results of the Floquet analysis with the results of accurate quantum simulations, the authors have judged that the molecular dissociation may take place only on the assumption of an extensive internal dynamics of motion of the molecule nuclei and electrons in the framework of the space of its bounded states. The dynamics of internal motion manifests itself in the excitation of vibration bounded states near the dissociation continuum. The actual dissociation of molecule will take place only in the second stage after the transition from these states into the states of dissociation continuum. At that, the starting excitation process plays a key role in determining how the dissociation probability depends on the initial state of oscillator, intensity of laser radiation and its frequency. It is therefore clear that the determination of number n requires a deeper analysis.

VIBRATION PERIOD OF NUCLEI OF CHEMICAL BOND

Further we shall try to compare the dissociation time of chemical bond, τ_d, with the period of vibrational motion of nuclei of the bond considered. By solving the integral of motion (3) for path $x(t)$, we get

$$x(t) = \frac{1}{a} \ln \left\{ \frac{D - [D(D - |E|)]^{1/2} \cos([2|E|/\mu]^{1/2} at + C)}{|E|} \right\}, \quad E < 0. \quad (10)$$

The constant of integration, C, in Eq. (10) is determined from the initial value $x(0)$ for condition $\dot{x}(0) > 0$. Therefore

$$C = \arccos\left\{\frac{D - |E| e^{ax(0)}}{[D(D - |E|)]^{1/2}}\right\}. \tag{11}$$

The motion of atomic nuclei of molecule under the condition $E < 0$ in agreement with Eq. (11) is periodical with period

$$T = \pi\left(\frac{2\mu}{a^2|E|}\right)^{1/2}. \tag{12}$$

If E is near the minimum value $V(x)$, i.e., if $V(x) \rightarrow V_{min}$, $D - |E| \ll D$, then we can write for the vibration period:

$$T \approx \pi\left(\frac{2\mu}{Da^2}\right)^{1/2}\left(1 - \frac{D - |E|}{2D}\right). \tag{13}$$

We can see that period T depends weakly on E. Taking into account the above-mentioned expression $D = 1\cdot0\ldots m1|E|$, then

$$T \approx \pi\left(\frac{2\mu}{Da^2}\right)^{1/2}\left(1 - \frac{10^{-(m+1)}}{2\cdot0\ldots m2}\right) \tag{14}$$

and for sufficiently large m, T can be approximated by the formula

$$T \approx \pi\left(\frac{2\mu}{Da^2}\right)^{1/2}. \tag{15}$$

Under the given conditions, the law of path $x(t)$ can be written in the form

$$x(t) = \frac{1}{a}\ln\frac{D}{|E|} + \frac{1}{a}\ln\left[1 - \left(\frac{D - |E|}{D}\right)^{1/2}\cos\left(\frac{2\pi t}{T} + C\right)\right] \approx$$

$$\approx \frac{1}{a}\ln\frac{D}{|E|} - \frac{1}{a}\left[\frac{D - |E|}{D}\right]^{1/2}\cos\left(\frac{2\pi t}{T} + C\right), \tag{16}$$

or

$$x(t) = \frac{1}{a}\ln(1\cdot0\ldots m1) + \frac{1}{a}\ln\left\{1 - \left[\frac{10^{-(m+1)}}{1\cdot0\ldots m1}\right]^{1/2}\cos\left(\frac{2\pi t}{T} + C\right)\right\} \approx \tag{17}$$

$$\approx \frac{1}{a}\ln(1\cdot0\ldots m1) - \frac{1}{a}\left[\frac{10^{-(m+1)}}{1\cdot0\ldots m1}\right]^{1/2}\cos\left(\frac{2\pi t}{T} + C\right). \tag{18}$$

Under the given conditions, the nuclei vibrate harmonically in the vicinity of point $a^{-1} \ln 1 \cdot 0 \dots m1$ with the amplitude defined by the difference $E - V_{min}$ with the frequency dependent on energy. Such a character of motion of the nuclei, on condition that E is near $V_{min} = 0$, is proper to the motion of atoms in an arbitrary potential field of molecule[6].

Now it is already possible to compare mutually the dissociation time of chemical bond, τ_d, expressed in the form of Eq. (8) with the vibrational period of nuclei in the form

$$\tau_d = \frac{T}{4} (n)^{1/2}, \quad n^{1/2} > 4. \tag{19}$$

Thus, the dissociation time of chemical bond τ_d is longer than the period of vibrations of nuclei T in the vicinity of the potential curve minimum.

The dissociation time of chemical bond is now an important parameter of progress in infrared laser chemistry but it may be of importance for the dynamics of molecular reactions[11].

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