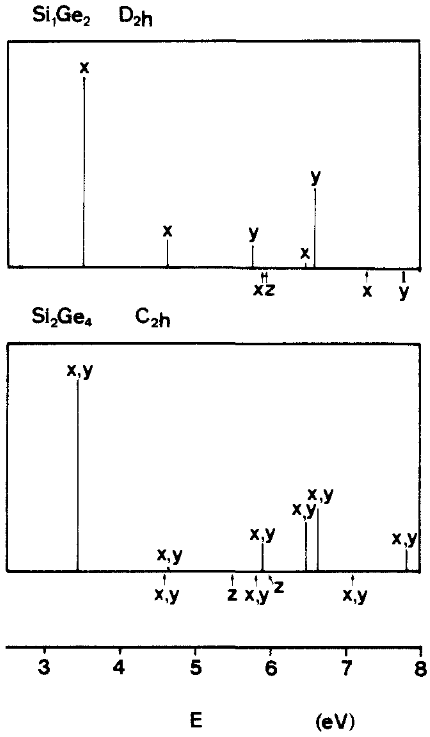

Figure 16. Optical transition profile for copolymers having same Si–Ge composition ratio: Si_1Ge_2 (a); Si_2Ge_4 (b). OTM values are normalized by the HOVB-LUCB transition. Symbols x, y, and z indicate the direction of polarization of the excitation light. The skeleton chain of polymers is configured in the x–y plane. The corresponding factor group is also shown in figure.

and Si_3Ge_1 copolymers. However, the corresponding band offsets in CB's are significant so as to concentrate electrons strongly in Ge block. Since the Si_3Ge_1 copolymer has only one Ge block in the unit cell, electrons tend to be confined in a smaller region than in the Si_3Ge_3 copolymer. This spatial confinement reduces the overlap of the wave functions between the initial (HOVB) and the final state and then results in the small OTM values found in the Si_3Ge_1 copolymer. On the contrary, the weak spatial separation between the HOVB and the CB's wave function lets Si_1Ge_3 copolymer be an optically active QW wire.

When copolymers have an equal Si–Ge reduced composition ratio, they show analogous OTM values (Figure 16) except for their OTM profiles. Since copolymers with the same composition ratio have an equal Ge block length entirely within the unit cell,[43] the spatial confinement of the wave function in CB's roughly coincides. This type of the coincidence preserves the value of the wave function overlapping between the initial (HOVB) and the final states equally among these copolymers. This is the reason why copolymers with the same composition ratio cause similar OTM values. Thus, for Si–Ge copolymers, the length of the Ge block, i.e., the electron pocket length, plays an important role in the OTM profile.

6. Conclusions

1. Polysilane and polygermane having a TP skeleton have a direct band gap of 3.89 and 3.31 eV, respectively. On the contrary, those having a GH skeleton have about 1.5 times larger values: 5.94 eV for GH polysilane and 5.13 eV for GH polygermane. However, the direct-type band structure is conserved independently of the skeleton forms of TP and GH.
2. TP Si_1Ge_1 alternating copolymer also has a direct band gap of 3.84 eV. The alternating copolymerization resolves the energy degeneracy at point X.
3. The ordered regular and/or block Si–Ge copolymerization introduces the zone-folding image in the copolymer band structures. Si_mGe_n ordered copolymers have the potential to be the 1D superlattice high polymers.
4. For Si–Ge copolymers having over five blocks, the band-edge electronic structure can be approximately estimated by using the effective mass theory and a picture of a 1D-QW wire model can be imaged.
5. Ge block plays the role of a electron pocket for HOVB and LUCB states in Si–Ge copolymers.
6. Si_mGe_n ordered copolymers might be expected to have E_g values different from those for Si_xGe_y disordered copolymers, even if their composition ratios are the same ($m/n = x/y$).
7. The ordered (regular and/or block) copolymerization introduces new states at point Γ, which are folded from point X. New optical transition processes occur from HOVB to these newly formed states. This increases the number of possible OTM peaks as well as changes the OTM profile.

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Registry No. $(SiH_2)_n$, 32028-95-8; $(GeH_2)_n$, 32028-94-7.

Automerization of Cyclobutadiene

R. Lefebvre*,[†] **and N. Moiseyev***

Contribution from the Department of Chemistry, Technion—Institute of Technology, Haifa 3200, Israel.

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Abstract: Two ways of calculating the tunneling rate for the automerization of cyclobutadiene are examined. One is based on an energy splitting and the other on a transmission probability. It is argued that the latter procedure is the appropriate one for a treatment of automerization in the condensed phase.

1. Introduction

Automerization of cyclobutadiene is usually considered to be an example of tunneling involving heavy atom motion. This suggestion was originally made by Carpenter,[1] following experiments by Whitman and Carpenter[2] with two differently deuterated cyclobutadienes as reaction intermediates. Carpenter[1] made an estimate of the tunneling rate by multiplying the frequency of the promoting mode for automerization (essentially the antisymmetric C–C stretch) by the transmission probability (TP)

[†] Address correspondence to this author at the Laboratoire de Photophysique Moléculaire, Campus d'Orsay, 91405 Orsay, France.

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through a barrier made of two truncated parabolas. This method for evaluating the rate (k_{TP}) has been subsequently criticized by Huang and Wolfsberg[3] as yielding too low values. These authors stated that it is preferable to regard the rate as being $2\Delta E_i/h$ for each level i of the initially populated well. ΔE_i is the energy splitting (ES) produced on this level by tunneling through the barrier. $h/2\Delta E_i$ is the hopping time between the two wells. A Boltzmann average can then be performed on such rates. At temperatures such that $k_BT \ll \hbar\omega_F$, where $\hbar\omega_F$ is the quantum of the promoting mode, the tunneling rate (k_{ES}) is thus directly related to the energy splitting of the zero-point level ΔE_0. A similar point of view was also taken up in other estimates of this tunneling rate.[4,5]

The fact that the energy splitting method yields a higher value for the rate cannot be invoked to choose between the two procedures since this is not a matter of discriminating between two reaction channels. Another strictly practical point of view would be to resort to experimental data. This is the route followed by Limbach and Hennig[6] in a study of hydrogen migration in *meso*-tetraphenylporphine based on NMR rates. They stated that the ES method gives a better understanding of the dynamics.

The question of choosing between the two methods to treat the double-well problem has also been approached from a more fundamental point of view. Brickmann and Zimmermann[7] have argued that the transmission method implies an unbound scattering situation that is not present in a double well. On the other hand Weiner[8] concluded that k_{TP} should be preferred to k_{ES} whenever the heat bath is perturbing the system on a time scale short in comparison with the period of oscillation deduced from the energy splitting. The introduction of the relaxation due to the coupling of the molecule to the bath (i.e. to its environment) is in fact the key point to understand how a concept from scattering theory can be applied to a bound situation: relaxation can prevent any recurrence from the final to the initial well and a first-order kinetic law is then appropriate to describe the time evolution of the system. This is the viewpoint adopted by Smedarchina, Siebrand, and Wildman in a recent reinterpretation[9] of the data for hydrogen transfer in porphines.[6,10] They are able to give a coherent picture on the basis of the Golden Rule, which amounts to a treatment of the final state as an effective continuum resulting from coupling between a molecular level and the dense solvent levels.

We will, in the following, consider the simplest quantum mechanical model that makes it possible to understand the transition from an oscillatory regime (typical of a tunneling problem in the absence of any relaxation) to the exponential regime produced by relaxation effects. We return, afterwards, to the question of estimating the tunneling rate in cyclobutadiene.

2. Quantum Mechanical Resonance with Damping

We consider quantum mechanical resonance between two states 1 and 2, of kets $|1\rangle$ and $|2\rangle$, of common energy $\bar{E}$ and presenting a coupling $V = \langle 1|H|2\rangle$ which induces an energy splitting $\Delta E = 2V$. The simplest way to describe a damping mechanism affecting state 2 is to impart an imaginary component $-i\Gamma$ to the energy of this state. $2\Gamma/\hbar$ is the decay rate of state $|2\rangle$ to the bath if $V = 0$. The time-dependent behavior of a system with this energy coupling scheme (or for models easily reducible to it) has been presented many times in the literature.[11] We quote the results relevant for the present discussion. The system is assumed to be in state 1 at time $t = 0$. The probability amplitude for finding the system in state 1 at time t is

$$A(t) = \langle 1|\Psi(t)\rangle \tag{1}$$

where $|\Psi(t)\rangle$ is the solution of the time-dependent Schrödinger equation. This amplitude obeys the equation

$$\ddot{A}(t) + \frac{\Gamma}{\hbar}\dot{A}(t) + \frac{V^2}{\hbar^2}A(t) = 0 \tag{2}$$

where the dot and double dot have the usual meaning of first- and second-order derivatives with respect to time. If the parameters V and Γ satisfy the inequality $2V > \Gamma$, $A(t)$ is given by

$$A(t) = \exp\left(-\frac{\Gamma t}{2\hbar}\right)\left[\cos\frac{\sqrt{\Delta}t}{2\hbar} + \frac{\Gamma}{\sqrt{\Delta}}\sin\frac{\sqrt{\Delta}t}{2\hbar}\right] \tag{3}$$

with $\Delta = 4V^2 - \Gamma^2$. This is a damped oscillation identical with that of a classical oscillator with a friction.[12] During the first periods of oscillation, the survival probability $P(t) = |A(t)|^2$ does not obey a first-order kinetic law. Averaging out the fast oscillations in the limit $2V \gg \Gamma$ yields an effective rate $\Gamma/\hbar$, which bears no relation to the energy splitting. If, however, the parameters V and Γ fulfill $2V < \Gamma$, the probability amplitude is

$$A(t) = \exp\left(-\frac{\Gamma t}{2\hbar}\right)\exp\left(\frac{\sqrt{\Delta'}t}{2\hbar}\right)\frac{(\Gamma + \sqrt{\Delta'})}{2\sqrt{\Delta'}} - \exp\left(-\frac{\Gamma t}{2\hbar}\right)\exp\left(-\frac{\sqrt{\Delta'}t}{2\hbar}\right)\frac{(\Gamma - \sqrt{\Delta'})}{2\sqrt{\Delta'}} \tag{4}$$

with $\Delta' = \Gamma^2 - 4V^2$. If we assume $2V \ll \Gamma$, the second term then has a small amplitude and relaxes very fast. A truncated binomial expansion of $\sqrt{\Delta'}$ to approximate the first term gives

$$A(t) \simeq \exp\left(-\frac{V^2t}{\hbar\Gamma}\right) \tag{5}$$

The classical oscillator presents also such a regime.[12] Equation 5 provides us with a first-order kinetic law for $P(t)$ with a rate $k = 2V^2/\hbar\Gamma$. The three different time scales that we can associate with the system fulfill the inequalities:

$$\frac{\hbar}{2\Gamma} \ll \frac{h}{2\Delta E} = \frac{\pi\hbar}{2V} \ll \frac{\hbar\Gamma}{2V^2} \tag{6}$$

Thus, as in Weiner's analysis,[8] the fact that there is bath relaxation on a time scale shorter than the time it would take for the system to oscillate between the two states leads to a rate that is smaller than the "rate" calculated from the splitting. This shows that a sequential type of reasoning (half oscillation followed by relaxation) does not apply in these circumstances. Another way to analyze the transition from oscillatory to decaying regime is to observe that a resonance picture is no longer valid when the uncertainty Γ in the energy of the final state is larger than the splitting. There are more elaborate treatments of the dynamics of a tunneling system coupled to a bath. For instance Nikitin[13] and Harris and Silbey[14] obtained equations similar to eq 2, either for the average of the coordinate (measured from the top of the barrier) or for the probability $P(t)$. A parameter is playing the role of Γ of eq 2, but with inclusion of temperature effects. The conclusions about the existence of the two regimes are essentially the same.

3. Tunneling Rates of Cyclobutadiene

The tunneling rates calculated from the splittings for cyclobutadiene are in the 10^{11} s^{-1} range.[3-5] For instance Dewar and co-workers[4] obtain 5.39×10^{11} s^{-1} while they estimate the classical rate to be 1.41×10^8 s^{-1} at 350 K. They conclude that at this

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temperature the rate of tunneling is still larger than the classical rate by 3 orders of magnitude. Even though the rate calculated from the transmission probability is necessarily smaller than the rate derived from the energy splitting, we now show that with the same parameters one may still reach the same conclusion concerning the role of tunneling. The two rates at zero temperature can be written[6] in terms of the transmission probability T and the frequency of the promoting mode ν_F

$$k^0_{TP} = \nu_F T \qquad k^0_{ES} = \frac{2\nu_F}{\Pi} T^{1/2} \tag{7}$$

or alternatively, introducing the energy splitting ΔE_0

$$k^0_{TP} = \frac{1}{4}\frac{(\Delta E_0)^2}{\hbar^2 \nu_F} \qquad k^0_{ES} = \frac{2\Delta E_0}{h} \tag{8}$$

The energy splitting enters k_{TP} through the transmission probability T. With the parameters of Dewar et al.[4] (barrier height, frequency of promoting mode) and their method for calculating the energy splitting, we obtain $k^0_{TP} = 1.4 \times 10^{10}$ s^{-1}. This is still two orders of magnitude larger than their classical rate.

Carpenter in his original work[1] obtained a much lower value for the tunneling rate estimated from the transmission probability ($k^0_{TP} \simeq 8 \times 10^4$ s^{-1}). We reconsider the calculation of this rate performed with a truncated parabolic barrier. With a reduced mass of 13 daltons to model the motion of the pseudoatoms, a barrier height equal to that of Dewar et al.[4] (8.14 kcal/mol), and a frequency of the promoting mode taken from Čarsky et al.[5] ($\nu_F = 4.7 \times 10^{13}$ Hz), we obtain $k^0_{TP} = 2.85 \times 10^8$ s^{-1}. This is much closer to the other estimates and allows us to conclude that there is a significant contribution from tunneling to the overall rate even if one accepts the classical estimate of Dewar et al.[4]

To summarize, first-order kinetics can only be obtained in the tunneling problem if one takes into account the relaxation in the final configuration of the system. This is in favor of the method based on a transmission probability which agrees with the concept of decay rate as being a probability per second (k_{TP} is a first-order rate constant while k_{ES} is not).

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Ab Initio Spin-Coupled Description of the Reactions $CH_2(^1A_1) + H_2 \rightarrow CH_4$ and $CH_4 \rightarrow CH_3(^2A_1') + H$

Maurizio Sironi,*,[1a] David L. Cooper,*,[1b] Joseph Gerratt,[1c] and Mario Raimondi[1a]

Contribution from the Dipartimento di Chimica Fisica ed Elettrochimica, Università di Milano, Via Golgi 19, 20133 Milano, Italy, Department of Chemistry, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, UK, and Department of Theoretical Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, UK. *Received June 19, 1989*

Abstract: Spin-coupled theory, which represents the modern development of valence bond theory, is applied to the singlet methylene insertion reaction $CH_2(^1A_1) + H_2 \rightarrow CH_4$ and to the hydrogen atom abstraction reaction $CH_4 \rightarrow CH_3(^2A_1') + H$. The spin-coupled wave function provides a highly visual model of the behavior of *correlated* electrons. Concepts such as directed covalent bonds, formed from the overlap of sp^x-like hybrids on carbon and 1s functions on hydrogen, are shown to arise naturally from minimizing the total energy without preconceptions. There are, however, some important differences from the ideas of classical VB theory. A new non-least-motion pathway with no activation barrier is proposed for the singlet methylene insertion reaction.

I. Introduction

The methane molecule is of fundamental importance to the whole of organic chemistry, and its elementary reactions are an obvious testing ground for any theory of chemical reactivity. In particular, the two connected potential energy surfaces

$$CH_2(^1A_1) + H_2 \rightarrow CH_4$$

and

$$CH_4 \rightarrow CH_3(^2A_1') + H$$

are of special importance as providing the simplest examples of singlet methylene insertion and of hydrogen atom abstraction reactions. The second reaction involves the breaking of a single bond only and is a relatively straightforward process. However, the singlet methylene insertion reaction is altogether much more complicated and is a prototype for a wide range of chemical processes.

The aim of the present work is to provide reliable orbital pictures for both reaction mechanisms and to understand the changes that occur in the coupling of the electron spins. We show that concepts such as directed covalent bonds, formed from the overlap of sp^x-like hybrids on carbon and 1s functions on hydrogen, arise naturally from our ab initio calculations simply by minimizing the energy without preconceptions. There are, however, some important differences from classical VB descriptions.

The central result of this paper is that our orbital picture for singlet methylene allows us to suggest a new non-least-motion pathway with no activation barrier for singlet methylene insertion. This reaction is very interesting from a theoretical point of view, as it involves the complex process of forming two new C–H bonds while breaking the strong bond in H_2. We examine least-motion and non-least-motion paths across this portion of the potential surface. For the hydrogen atom abstraction reaction, we concentrate on a least-motion path. A detailed dynamical treatment of both reactions, based on classical trajectories or on quantum scattering calculations, would require a rather more extensive study of the potential energy surfaces. However, such dynamical studies would be unlikely, on their own, to give detailed pictures of the

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[1] (a) Università di Milano. (b) University of Liverpool. (c) University of Bristol.

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