

# DOES A MOLECULE REMEMBER THE WAY IT WAS ENERGIZED?

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Intramolecular vibrational redistribution (IVR) is the key phenomenon in unimolecular decomposition of polyatomic molecules energized in collisions, by photon absorption, or formed by association of radical particles. On an ultrashort time scale, the excitation energy is localized at some place (bond) of the molecule. On a middle time scale, energy irreversibly flows from the excited place to the rest of the molecule. On a long time scale fluctuations of the internal energy are reminiscent of a quasiperiodic process. Almost all the relevant experimental data and model calculations suggest that the information concerning the place of excitation in the molecule is lost during 100 fs – 10 ps after excitation. It seems that due to the rapid IVR the laser selective chemistry has in general no promising perspectives.

## 1. INTRODUCTION

At present, several good experimental methods are available which make it possible to prepare highly vibrationally excited molecules with internal energy exceeding the threshold energy for their dissociation. In addition to the classical activation in collisions with inert particles – which represent a thermal bath with a canonical energy distribution – there exist chemical activation (where an excited molecule is formed by association of radical particles) and single photon and multiphoton excitation. Collisional excitation provides an ensemble of molecules with a practically equal population of all accessible microstates of a given energy; on the other hand, chemical activation and photon excitation localizes energy initially in a specific part of the molecule (Fig. 1).

Kinetics of decomposition of the energized particles (both under many-collision

and collisionless conditions) and the nature of fragments depend on the relaxation time of delocalization (redistribution, reorganization) of the molecular internal energy over all accessible degrees of freedom. In connection with the collisional activation the problem of localization of the excitation energy was formulated during the fifties and sixties as a problem of choice between the Rice–Ramsperger–Kassel (RRK) and Slater theories of unimolecular reactions<sup>1</sup>.

In the seventies and the eighties this problem has come up in connection with the possibility of selective breaking of a chemical bond<sup>2,3</sup> and with the nature of intramolecular dynamic chaos<sup>3–5</sup>. The process of internal energy delocalization, resulting from anharmonic interactions, has been referred to as IVR (intramolecular vibrational redistribution).

## 2. RRK vs SLATER THEORY

From the point of view of the IVR rate, the statistical RRK and the dynamical Slater theories represent two extreme cases: the former assumes a fast, continuous redistribution of excitation energy within the entire molecule (the resulting rate equation corresponds to the rate of  $\text{IVR} \rightarrow \infty$  and, therefore, to a molecule without memory), in the latter theory the rate of IVR is zero (a molecule with persistent memory).

In a more realistic model of unimolecular reactions<sup>6,7</sup> the IVR rate is introduced as a parameter  $\omega$  (reciprocal value of the redistribution relaxation time). For  $\omega > 10^{13} \text{ s}^{-1}$  the final equation for the dependence of the logarithm of the rate constant on the logarithm of the inert component concentration,  $\log k_{\text{uni}}$  vs  $\log [M]$ , coincides with the RRK prediction. For  $\omega < 10^{13} \text{ s}^{-1}$  this dependence is less steep in the region between the low-pressure and high-pressure limit: in case the number of modes participating in the reaction coordinate is substantially lower than the number of vibrations participating in the IVR, there is a more or less pronounced

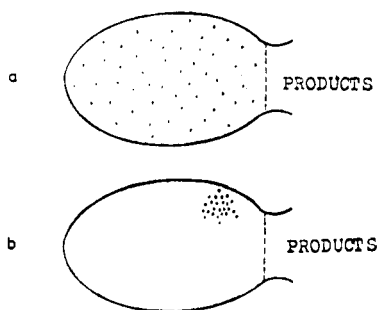


FIG. 1

Phase space density of representative points after a collisional and b chemical or photon activation

plateau between two inflection points on this dependence for  $\omega < 10^{10} \text{ s}^{-1}$ , the so called "false" high-pressure limit (Fig. 2). The expansion of the middle-pressure region was predicted also by Borkovec et al.<sup>8</sup> for a hypothetic molecule with a model Hamiltonian which includes potential interactions between two representative oscillators, and by Thiele et al.<sup>9</sup> for a molecule with a limited IVR between two oscillator groups.

The literature provides several sets of data which indicate the existence of inflexion points on the curve  $\log k_{\text{uni}}$  vs  $\log [M]$ . They involve decomposition of cyclobutane<sup>10</sup>, methylcyclobutane<sup>11</sup>, ethylchloride<sup>12</sup>, and isomerization of cyclohexane<sup>13</sup>. However, it is probable that in case of the first three reactions the low-pressure data were influenced by wall-effects (experimentally identified by Thomas et al.<sup>11</sup>) and the data from paper by Ross and True<sup>13</sup> may lack enough accuracy. Thus, the existence of the inflexion points cannot be regarded as reliably proved so far. Also, analysis of the high-pressure data does not indicate that the measured high-pressure limit,  $\lim_{M \rightarrow \infty} k_{\text{uni}} = k_{\infty}$ , is only a "false" limit<sup>14,15</sup>.

Data are available over a span of three or more orders of magnitude of pressure of the inert which show a less steep dependence of  $\log k_{\text{uni}}$  vs  $\log [M]$  than RRK or Slater theory predicts. In particular, this concerns the following reactions: nitrous oxide<sup>16</sup> and nitrylchloride<sup>17</sup> dissociation, methylisocyanide<sup>18</sup>, tetrafluorocyclobutane<sup>19</sup>, cyclobutene<sup>20</sup> and *cis*-2-butene<sup>20</sup> isomerization. Comparison of curvatures of measured and calculated dependences  $\log k_{\text{uni}}$  vs  $\log [M]$  (refs<sup>6,21,22</sup>) leads to an estimation of the minimum value of  $\omega$  to  $10^{11} - 10^{12} \text{ s}^{-1}$ . This value indicates that the energy redistribution in collisionally activated molecules (excitation energy of 10 to  $10^2 \text{ kJ/mol}$ ) occurs on the time scale of picoseconds and that the RRK model is more realistic than the strict non-ergodic Slater model, where energies of various modes are constants of motion during the time between collisions.

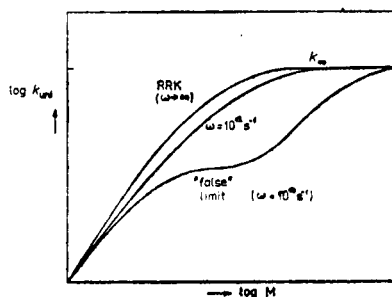


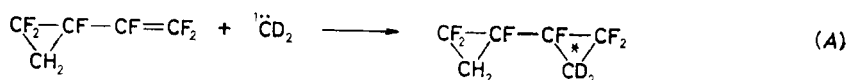
FIG. 2

The influence of IVR on the curvature of  $\log k_{\text{uni}}$  vs  $\log [M]$  dependence

### 3. IVR AFTER CHEMICAL BOND FORMATION

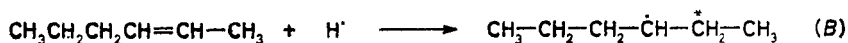
In the sixties, J. N. Butler and G. B. Kistiakowski and, in particular, B. S. Rabinovitch developed a new method to study IVR – the chemical activation method. Highly vibrationally excited molecules (several hundreds of kJ/mol) are formed in a bimolecular association of particles of which at least one is a radical. Energy released as a result of the new bond formation is for a certain time localized in the bond or in its nearest vicinity. The energy delocalization rate may be estimated from the qualitative and quantitative analysis of products of this molecule decomposition and from the dependence of the decomposition rate constant on the mean time between deactivation collisions (i.e. on the inert gas pressure). There are three mutually competing processes: collisional deactivation, dissociation and IVR. The dependence of the decomposition rate constant on the inert gas pressure can be linear (with a slope close to zero) or curved. A curvature indicates non-ergodic behaviour, i.e. a detectable IVR.

In a classical experiment<sup>23</sup>, excited methylcyclopropane was prepared both by an addition reaction between methylene radical and propene and by an insertion reaction of methylene radical with cyclopropane. Population of reaction products (butene isomeres) did not depend on the method of methylcyclopropane preparation and it was an evidence of a fast vibrational energy delocalization (lost information on the way the molecule was formed). A very fast IVR follows from a series of other data derived from measurements of decomposition rates of chemically activated molecules. Vibrationally excited butyl radical formed in reaction of atomic hydrogen with *cis*-2-butene decomposes to methyl radical and propylene with a pressure-independent (up to 11 MPa) rate constant. This indicates that the energy redistribution is accomplished after a few tenths of a picosecond<sup>24</sup>. In another experiment, Ryndbrandt and Rabinovitch<sup>25,26</sup> prepared a vibrationally "hot" dideuteriohexafluorobicyclopropyl in a reaction of a deuterated singlet methylene radical with hexafluorovinylcyclopropane:

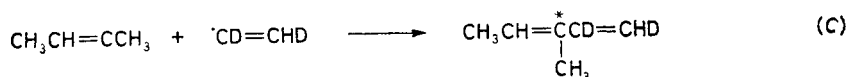


(\* denotes the initial localization of the vibrational energy). The "hot" molecule can dissociate by breaking the newly formed ring, or – after energy delocalization – also by a split in the original ring. Evaluation of the experiment (products composition) lead to an IVR rate constant of the order of  $10^{12} \text{ s}^{-1}$ , similarly as in other analogous reactions of fluoroalkylcyclopropanes<sup>27</sup> and alkylcyclobutanes<sup>28</sup>.

The 3-hexyl radical prepared by a reaction of H-atom with *cis*-2-hexene

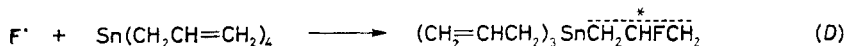


(\* indicates energy localization) decomposes both to 1-pentene and the methyl radical, and — after energy delocalization — to 1-butene and ethyl radical. The population of products in dependence on the inert gas pressure showed that  $\omega \approx 2 \cdot 10^{12} - 7 \cdot 10^{12} \text{ s}^{-1}$ . In this reaction the excitation energy (180 kJ/mol) is about one third of that one in reactions of cyclopropanes and cyclobutanes; the estimated value of  $\omega$  is, however, practically the same<sup>29,30</sup>. Ibuki and Sugita<sup>31</sup> derived IVR rates about two orders of magnitude smaller ( $\omega \approx 2 \cdot 10^{10} \text{ s}^{-1}$ ) from measurements of isomerization rates of 1,2-dideuterated *cis*-3-methyl-1,3-pentadiene formed in reaction



The low value was ascribed to the fact that in this reaction only one C—C bond was formed, while in the above mentioned reactions of cyclopropanes and cyclobutanes two or more bonds were formed; this may make the energy delocalization more convenient.

Conflicting opinions exist on energy delocalization in chemically activated molecules of the type  $\text{M}(\text{R}_i)_4$  where  $\text{R}_i$  denotes polyatomic aliphatic ligands and M is a heavy atom (Sn, Ge, Pb)<sup>32</sup>. Kinetics of decomposition of fluorotetraallylstannic radical<sup>33</sup> prepared in reaction



indicates that energy does not flow from the excited ligand (\*) over the Sn atom into other ligands even after hundreds of picoseconds and that the heavy atom represents a significant barrier for IVR (refs<sup>33,34</sup>). This finding was corroborated by a calculation of dynamics of the linear chain C—C—C—Sn—C—C—C, modelled by Morse oscillators including mixed momentum terms<sup>35</sup>. However, experiments carried out by Rabinowitch et al.<sup>36,37</sup> with 4-(trimethyltin)-2-butyl, 4-(trimethyllead)-2-butyl and 5-(trimethyltin)-2-pentyl radicals indicate a fast IVR (on the picosecond scale) over the entire molecule. It is possible that the IVR barrier is not caused by the mere presence of a heavy atom blocker, but also by properties of  $\text{R}_i$  ligands; theoretical quasiclassical trajectory studies of analogous model systems show a considerable sensitivity of the IVR rate to chosen potential interactions<sup>38</sup>.

Delocalization of energy in a long aliphatic chain was studied on a reaction of decomposition of the decyl radical prepared by the reaction of a H atom with a 1-decene molecule<sup>39</sup>. The excitation energy of 170 kJ/mol is concentrated first in the part of the radical containing 2 terminal C atoms



The decyl radical decomposes to propylene and heptyl radical after a partial energy delocalization (over 3 terminal atoms) and this decomposition is in competition with a full energy delocalization over the entire molecule ( $\omega \approx 5 \cdot 10^{12} \text{ s}^{-1}$ ). This picture of sequential motion of the excitation along the chain was supported by Lami and Villani<sup>40</sup> using model calculations (Morse oscillator coupled to the chain of normal modes). The excitation moves from one bond to the adjacent one and the time interval between the maxima in two consecutive bonds is approximately 50 fs.

#### 4. IVR AFTER PHOTON ABSORPTION

Development of laser techniques has opened in the seventies a new way of preparation of highly vibrationally excited molecules — infrared multiphoton absorption<sup>41</sup>. As the energy of an infrared photon (typical frequency  $3 \cdot 10^{13} \text{ s}^{-1}$ ) corresponds to 12 kJ/mole, dissociation of a molecule requires absorption of about 20 to 30 photons<sup>42</sup>. Intensive research effort in this area has been motivated mainly by hopes of using lasers in developing vibrationally selective chemistry — breaking specific bonds in a molecule by using a suitable radiation wave length<sup>3,43</sup>. These hopes relied on an implicit assumption that delocalization of energy from a specific excited bond will be slow in comparison with accumulation of photons during absorption (in principle possible to accomplish within a few picoseconds) and subsequent bond dissociation (lower time limit for excited bond dissociation is of the order of tenths of a picosecond<sup>44</sup>).

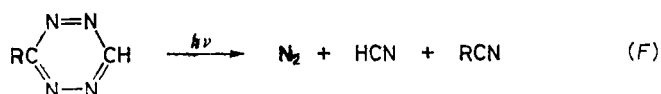
A frequently quoted experiment in this connection is that one of Hall and Kaldor<sup>45</sup>: cyclopropane was excited by light of two different lasers; one activation caused only isomerization (a low activation energy process) while the other led to fragmentation (a high activation energy process). This result was interpreted by the authors as a proof of an energy selective reaction mechanism. Thiele et al.<sup>2,9</sup> regarded this interpretation as a plausible one and in agreement with IVR rates of the order of  $10^{10} \text{ s}^{-1}$  or greater. However, other views questioned the selectivity of excitation in this experiment<sup>42</sup>.

By the end of the seventies a large series of experimental results concerning IR multiphoton induced decomposition has been published, in all cases confirming a fast IVR in a molecule. The data were summarized and discussed by Oref and Rabinovitch<sup>15</sup>. As an example, one can quote dissociation of  $\text{CH}_2\text{FCH}_2\text{Br}$  in collisionless conditions upon irradiation by light leading to C—F bond excitation<sup>46</sup>. In case of selective decomposition, HF ought to be preferentially split off; the experiment showed a preferential splitting of HBr, in agreement with the statistical redistribution prediction.

Therefore, during the last ten years hopes concerning the feasibility of laser-induced selective chemistry turned to the use of ultra-short (picosecond) laser

pulses. If the time of excitation (pulse length) is short in comparison with the delocalization relaxation time, then indeed only one vibrational mode is excited and only afterwards the energy redistribution over other modes takes place. If the excitation time is long, a superposition of modes is most probably excited. The pulse intensity does not seem to be important, as it determines only the number of excited molecules. The time profile of the pulse determines the nature of the excited state. Because the interactions between excited modes and other modes may vary, a certain degree of selectivity cannot be a priori excluded<sup>47</sup>. However, in mid-eighties the chances for mode-selective laser chemistry were regarded rather skeptically (William P. Reinhardt: "Bond-selective chemistry is not here. There is no doubt about that"<sup>48</sup>.); though IVR makes infrared multiphoton absorption possible, it works against the localization of energy in a molecule.

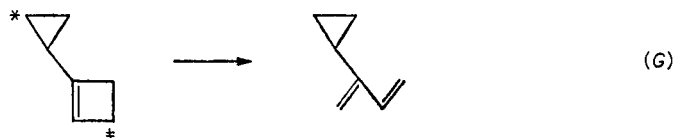
Important information on IVR has been obtained from single-photon excitation experiments. A vibrationally "hot" molecule can be formed by internal conversion from a molecule originally excited by a visible or ultraviolet photon to a higher electronic state. Windisch et al.<sup>49</sup> measured the rate of photodissociation of *s*-tetrazine and 3-phenyl-*s*-tetrazine:



(where R is a hydrogen atom or a phenyl ring) prepared by excitation of photons of 531 or 515 nm. They found that the phenyl group addition to the tetrazine ring very substantially lowers the decomposition rate (by four orders of magnitude). Because the role of the phenyl group consists only in increasing the number of accessible vibrational degrees of freedom, it is clear that there exists energy flow from one ring (tetrazine) over the single bond into the other ring (phenyl) before the molecule decomposes. As the rate constant of the *s*-tetrazine decomposition is of the order of  $10^9 \text{ s}^{-1}$ , the IVR rate must be substantially larger than this value. Taylor et al.<sup>50</sup> employed femtosecond laser pulses (of the order of tens of fs) to excite large organic molecules to optically accessible vibrational states of the first excited electronic state and measured the ensuing intramolecular relaxation into all other vibrational states. The results were interpreted as being due to an extremely fast ( $10^{13} \text{ s}^{-1}$ ) IVR.

A fast IVR has been also confirmed by results on decomposition of molecules after single-photon overtone excitation to vibrational states ( $v = 4-7$ ) of higher energy than the threshold energy of one of the bond dissociation. By this method an ensemble of excited molecules with a narrow distribution of localized vibrational energy is obtained; it was assumed that this could be an alternative approach to a bond-selective molecular decomposition<sup>51</sup>. Chandler et al.<sup>52</sup> used a dye-laser to excite an OH vibration in *t*-butylhydroperoxide to  $v = 5$  and measured the rate of

the OH radical formation which occurs after a partial energy delocalization. This process is in competition with the energy delocalization over the entire molecule. It follows from the dependence of the decomposition rate on pressure that the rate of complete delocalization is  $5 \cdot 10^{11} \text{ s}^{-1}$ . Jasinski et al.<sup>53</sup> excited by laser 1-cyclopropylcyclobutene to the  $v = 6$  vibrationally excited state of the C—H methylen type bond in cyclobutenyl ( $15\,650 \text{ cm}^{-1}$ ) or cyclopropyl ( $16\,475 \text{ cm}^{-1}$ ). The rate constant of isomerization to 2-cyclopropyl-1,3-butadiene (\* and † are alternating



positions of the excited CH bonds) depended only on the total energy in molecule, and not on the type of excited C—H bond; this shows an energy redistribution before the cyclobutene ring opening. The authors concluded that IVR in the molecule was completed during a time interval shorter than 4 ps. Lishan et al.<sup>54</sup> produced by laser excitation a molecule of quadricyclane in the vibrationally excited states  $v = 5, 6$  of the CH bond either of the cyclopropanoid or methylene type. This excitation energy was higher than the threshold energy for isomerization to norbornadiene. Even in this case the reaction rate did not depend on the type of excitation and the authors expressed their skeptical opinion on whether vibrational specific photochemistry could be accomplished. Segall and Zare<sup>55</sup> reinterpreted the kinetics of isomerization of allylisocyanide activated by a single-photon excitation  $v = 5, 6$  (CH vibration). Using their own experiments they showed that the reaction can be satisfactorily described without introducing nonstatistical effects considered by Reddy and Berry<sup>56</sup> (they assumed that vibrational energy delocalization is not due to a fast IVR, but to a redistribution of energy in elastic collisions).

Specific effects were observed in dissociations of some weakly-bound complexes<sup>57</sup>. The  $(\text{NO})_2$  molecule has a low dissociation energy,  $\sim 9.2 \text{ kJ/mol}$ . By picosecond excitation pulses of two different wave lengths either the symmetric or asymmetric N—O vibration was excited. Again, the deposited energy was larger than the dissociation energy of the dimer to two monomers. The experiments revealed a strikingly different kinetic behaviour of the excited dimer: the mean lifetimes were 880 ps in the former and 39 ps in the latter case.

Theoretical trajectory studies of hydrogen peroxide with the O—H bond excited to  $v = 5$  and, at the same time, with a single-quantum excitation in the O—O stretching and O—O—H bending vibration showed that dissociation lifetime of the molecule may, according to the type of excitation, differ approximately by an order of magnitude<sup>58</sup>. This result may be interpreted in terms of a gradual delocalization in the time scale of tens of picoseconds. In the hydrogen peroxide molecule excited



in the OH bond ( $\nu = 6$ ) the energy flows into the bending vibration O—O—H in the time scale of 0.1 ps, but into other vibrations about 100 times slower<sup>59,60</sup>. This observation is in agreement with the interpretation of the unimolecular decay kinetics of chemically activated decane radicals in terms of gradual energy delocalization along the chain or among normal modes<sup>61</sup>.

Experimentally observed absorption lines of a single-photon transition from  $\nu = 0$  to  $\nu = 5, 6, 7$  of the local mode C—H in benzene have a width of 80–100  $\text{cm}^{-1}$ . Assuming that this width is not due to an inhomogeneous broadening, it corresponds to an energy relaxation from the C—H mode into the other modes during 50–100 fs (see ref.<sup>61</sup>). Thus two originally rather separated branches – chemical dynamics and spectroscopy – begin to overlap and pure spectral data emerge in this sense as a potential source of information important for detailed understanding of chemical reaction kinetics<sup>32,62–64</sup>. An important concept which appeared as a result of views of the two disciplines is the concept of local modes<sup>3,65,66</sup>. Normal modes were introduced to describe vibrations of polyatomic molecules with low excitation (harmonic approximation); they have been successfully used in interpretation of single-quantum transitions. However, application of this concept to molecules of medium and high excitation has been connected with many problems<sup>67</sup>. It turns out that under these conditions energy has a tendency of localization in particular bonds – in local modes. For example, the C—H vibration in benzene molecule has a highly local character and behaves like a vibration of a diatomic molecule being little dependent on other modes<sup>3,62</sup>. Spectra of the polyatomic molecules containing an X—H bond (where X represents a heavier atom like C, N, O or Si) exhibit a series of vibrational bands which fit the relations for the Morse oscillator energy<sup>62,68</sup>. This has been interpreted as a “diatomic” behaviour of the local mode. In fact, the concept of local modes is close to a chemist’s view of a reaction: in case of chemical activation the energy released during the bond formation is localized in this bond, not in a normal mode.

Quite recently, a revision of the concept of an instantaneous transition from the ground state to an excited state upon interaction with electromagnetic radiation was suggested. According to Hutchinson<sup>69</sup> the wave function describes the behaviour of an individual molecule in an ensemble. During the excitation the molecular state is described by a superposition of the ground and the excited states with time-dependent amplitudes, in principle accessible from solutions of the Schrödinger equation. This makes it possible to compare the rates of mutually competing processes – excited state preparation, IVR and unimolecular decomposition. However, the superposition of states is not an observable quantity (measurements can offer only eigenvalues) and thus the wave function provides a time dependent fraction of excited molecules in the ensemble. By employing long laser pulses tuned to relatively low-energy vibrational transitions ( $\nu = 4, 5$ ) the excited state preparation occurs on the time scale of nanoseconds. As IVR occurs within 0.1 ps and the decomposi-

tion itself takes picoseconds, it is clear that the prepared state cannot correspond to an excitation of a local mode. However, using laser pulses shorter than 100 fs results in completing the excitation earlier than complete intramolecular redistribution takes place and the state prepared in this way may have energy localized in a specific bond<sup>68</sup>.

### 5. MECHANISM OF IVR

The simplest model of IVR (refs<sup>6,7,70</sup>) assumes that a molecule excited to a state characterized by energies of representative oscillators  $\varepsilon_1, \dots, \varepsilon_n$  ( $n$  is the total number of oscillators) remains in this state for a time  $\tau$ ; thereafter, during a short time interval  $\Delta\tau$  energy redistribution takes place which results in a new state  $\varepsilon'_1 \dots \varepsilon'_n$ ; there the molecule resides for a time  $\tau'$ , then another redistribution follows, etc. The states  $\varepsilon_1, \dots, \varepsilon_n$  and  $\varepsilon'_1, \dots, \varepsilon'_n$  are not correlated and they have all the same probability (Fig. 3). The residence time  $\tau$  in a given state is a random quantity characterized by an exponential probability density and the time sequence of reorganizations represents a Poisson process<sup>6,70</sup>. The mean lifetime of a state,  $\bar{\tau}$ , is substantially longer than the reorganization time,  $\Delta\tau$  (Fig. 4). Such a model resembles the model of collisional activation and deactivation: interactions between oscillators are concentrated into small time intervals, intramolecular "collisions". In a qualitative way, the IVR rate can be characterized by a mean lifetime of a state,  $\bar{\tau} : \omega = 1/\bar{\tau}$ .

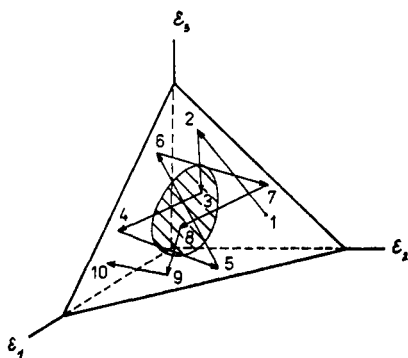


FIG. 3

Collisional model of IVR pictured as a random walk on the surface  $\varepsilon_1 + \varepsilon_2 + \varepsilon_3 = \text{const}$ . Dashed area corresponds to the states satisfying a sufficient and necessary condition for dissociation; 1, 2, ... are subsequent states

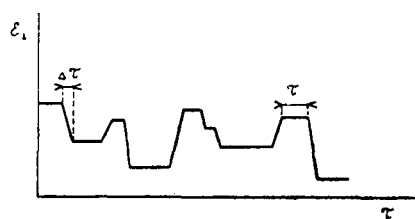


FIG. 4

Time dependence of the  $i$ -th oscillator energy in the collisional model of IVR;  $\Delta\tau$  duration of the reorganization,  $\tau$  time between reorganizations

The Markovian model of IVR is based on an assumption that the energy of a critical oscillator does not change randomly in the reorganizations (modelled also as intramolecular "collisions"), but the state after the reorganization depends on the state before the reorganization<sup>71</sup>. As a result of limitations following from the application of the microscopic reversibility principle, this model does not lead to significantly different results than the RRK model of random fluctuations.

Several models have been formulated which assume that the energy redistribution is limited only to certain oscillators or to certain groups of oscillators. Such models have been suggested<sup>72-74</sup> and theoretically studied<sup>9,75-78</sup>; they were applied, e.g., to molecules containing a heavy atom which separates several ligands<sup>79,80</sup>. However, experiments with chemically activated molecules (namely those from Rabinovitch's laboratory) indicate that these limitations are either weak or scarce.

In the energy exchange between groups of oscillators (e.g., in a chemically activated molecule of hexafluorobicyclopentadiene or a photoexcited molecule of phenyltetrazine) two mechanism can be considered<sup>81</sup>: a relaxation mechanism (energy localized initially in one group is equally distributed among other groups and a microcanonical distribution results) and an oscillatory mechanism (excitation energy periodically oscillates between the originally excited oscillator group and other groups). This latter mechanism is, however, improbable and contradicts the contemporary understanding of intramolecular chaos.

In the relaxation mechanism treatment, of course, fluctuations have to be considered; these may lead to a concentration of energy in an arbitrary part of the molecule, including the part originally excited. These fluctuations in particular, causing energy concentration in the reaction coordinate, are of key importance in the RRK theory<sup>82</sup> and they can be modelled by the above mentioned reorganizations of the "collisional" type. The requirements of the microcanonical energy distribution of representative oscillators (which is equivalent to the ergodic hypothesis) in the RRK theory includes the assumption of a constant probability density of all states with the energy of oscillators  $(\varepsilon_1, \varepsilon_1 + d\varepsilon_1), \dots, (\varepsilon_n, \varepsilon_n + d\varepsilon_n)$  (where  $\varepsilon < \varepsilon_1 + \dots \varepsilon_n \leq \varepsilon + d\varepsilon$ ); this is equal to  $\Gamma(n) d\varepsilon_1 \dots d\varepsilon_n / \varepsilon^{(n-1)} d\varepsilon$ .

The probability of fluctuation into the region of states determined by  $f(\varepsilon_1, \dots, \varepsilon_n) > 0$  is

$$\text{Prob} \{f(\varepsilon_1, \dots, \varepsilon_n) > 0\} = \Gamma(n) \int_I \dots \int \eta(f(\varepsilon_1, \dots, \varepsilon_n)) d\varepsilon_1 \dots d\varepsilon_n / \varepsilon^{n-1} d\varepsilon,$$

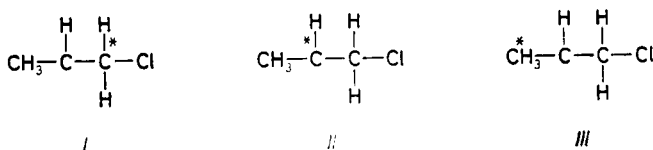
where  $\int_I \dots \int$  denotes integration over  $\varepsilon < \varepsilon_1 + \dots \varepsilon_n \leq \varepsilon + d\varepsilon$  and  $\eta(\dots)$  is the step (Heaviside) function. Thus, e.g., for  $f(\varepsilon_1, \dots, \varepsilon_n) = \varepsilon_k - \varepsilon_0$ ,  $1 \leq k \leq n$ , from Eq. (1) the classical RRK expression can be obtained.

$$(\varepsilon - \varepsilon_0)^{n-1} / \varepsilon^{n-1}, \varepsilon > \varepsilon_0,$$

and for  $f(\varepsilon_1, \dots, \varepsilon_n) = \varepsilon_k + \varepsilon_j - \varepsilon_0$ ,  $1 \leq k, j \leq n$  the right side of Eq. (1) equals to

$$(\varepsilon - \varepsilon_0)^{n-1} / \varepsilon^{n-1} + \varepsilon_0(\varepsilon - \varepsilon_0)^{n-2} (n-1) / \varepsilon^{n-1}, \varepsilon > \varepsilon_0.$$

The vibrational energy relaxation from the originally excited mode can occur in several stages: first, the energy flows into the closest (and therefore strongly coupled) vibrations and afterwards gradually to more distant vibrations<sup>39,61</sup> (Fig. 5). To elucidate the process of sequential delocalization, a theoretical and experimental investigation of dissociation was suggested<sup>61</sup> of systems depicted in Scheme 1,



SCHEME 1

where the asterisk denotes the energy localization immediately after the radical formation. In the third case (energy initially located in the C—H bond of the CH<sub>3</sub>

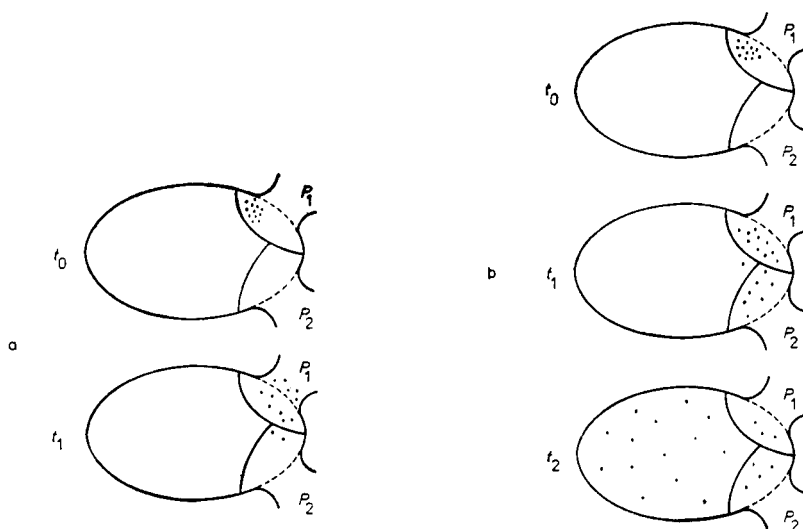


FIG. 5

Phase space density of representative points after local activation (two-channel decomposition): a locally excited molecule with slow sequential IVR and rapid decomposition ( $t_1 > t_0$ ); b locally excited molecule with rapid sequential IVR and slow decomposition ( $t_2 > t_1 > t_0$ ).  $P_1$ ,  $P_2$  are different products

group) the energy is fairly far away from the reaction coordinate (C—Cl) and a question arises, if the lifetime distribution of this excited radical with respect to the dissociation in the time interval (0,  $\sim 10$  ps) is zero or non-zero. Intuitively one would expect that the lifetime distribution for *I*, *II*, and *III* would differ close to the time zero, but after a certain time interval the memory of the activation site vanishes and the lifetime probability densities for all three types of excitation would decrease exponentially<sup>70</sup>. Such a gradual energy delocalization cannot be characterized by one single rate parameter of the IVR. The existence of several relaxation times in the intramolecular dynamics of a polyatomic molecule, differing by as much as orders of magnitude, implies the existence of a time interval during which the intramolecular motion is quasiperiodic or even chaotic, but not ergodic<sup>80,83</sup>.

Theoretical studies indicate that rotational-vibrational interactions are important in the rate of IVR. Sumpter and Thompson<sup>84</sup> investigated the influence of rotation on the dissociation rate of the  $\text{H}_2\text{O}_2$  molecule excited in the O—H bond ( $\nu = 6$ ) analyzing a set of 50 trajectories both of rotating and not-rotating molecules. The lifetime of non-rotating molecule was 8.8 ps, while rotating molecules (rotational energy corresponding to  $T = 1500$  K) decomposed much faster, with the lifetime of 3.5 ps. The effect of rotational-vibrational interactions could play a significant role in mutual comparisons of results of IVR rates on molecules excited by radiation with those on collision complexes produced in beam experiments (high rotational excitation).

The considerations mentioned above are based on the classical mechanical view of the reaction dynamics combined with the concept of phase-space trajectories. From the quantum mechanical view point the IVR may be characterized as follows<sup>80</sup>: an excitation process brings the molecule to a state which is described by a non-stationary wave function  $\Psi(t)$ ; this function may be represented by a superposition of functions of a zeroth order basis set,  $\Phi_j$  (normal modes, local modes)

$$\Psi(t) = \sum_j c_j(t) \Phi_j \exp(-i\varepsilon_j t/\hbar), \quad (2)$$

where  $c_j(t)$  are expansion coefficients and  $\varepsilon_j$  is the energy of the state  $j$ . The initial state  $\Psi(0)$  depends on the type of the excitation process (e.g., during photoexcitation it depends on the radiation source bandwidth and on the degree of interaction between the radiation and various molecular degrees of freedom); some coefficients  $c_j(0)$  may be large, some close to zero. Upon single-photon excitation to a higher vibrational state  $\Psi(0)$  may be identical with the excited local mode. The time dependence of the coefficients  $c_j(t)$  is given by the solution of differential equations (deduced from the time-dependent Schrödinger equation)

$$dc_j(t)/dt = -(i/\hbar) \sum_k c_k(t) V_{jk} \exp(-i(\varepsilon_k - \varepsilon_j) t/\hbar), \quad (3)$$

where  $V_{jk}$  is the coupling element between states  $j$  and  $k$ . The probability that the molecule is in the state  $\Phi_i$  is  $|c_i(t)|^2$ . The measure of the energy delocalization rate from  $\Psi(0) \approx \Phi_i$  is the rate of change of  $|c_i(t)|^2$  with time. Sibert, Reinhardt and Hynes<sup>85</sup> studied a model of the benzene molecule in which the local mode C—H was represented by a Morse oscillator coupled (through interactions of the Fermi resonance) to planar delocalized normal modes of the benzene ring. The initial state corresponded to the excitation of the local C—H mode. The quantum mechanical treatment showed an exponential decrease of the probability  $|c_i(t)|^2$  for  $\Phi_i$ , corresponding to the C—H mode, in the time scale of tenth of picoseconds, in agreement with the classical calculations<sup>86</sup>.

The main conceptual difficulty of quantum mechanical treatments of intramolecular processes is that the concept of quantum ergodicity is not clear<sup>3</sup>. According to Jancel's first ergodic theorem<sup>87</sup> the system is ergodic if and only if the spectrum of energy eigen values is not degenerated. However, this definition is too broad, as — according to it — even a system of two independent oscillators of frequencies independent in the region of rational numbers is an ergodic one. New ideas in this respect were published in the seventies by S. A. Rice and co-workers<sup>88,89</sup> who introduced notions as "global" or "local" states in dependence on the populations (abundance) of the basis functions (normal modes) in the wave function of the state. However, it is not evident, if global states can be regarded as ergodic (stochastic)<sup>90</sup> in the classical sense of the word<sup>3</sup>. The concepts of intramolecular chaos and ergodicity are still a matter of debate<sup>91</sup>.

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