

POTENTIAL ENERGY SURFACES AND THEORY OF UNIMOLECULAR
DISSOCIATION

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Reaction mechanisms can be determined from ab initio calculations of potential energy surfaces. Their complicated nature explains the frequent success of statistical theories, but nonstatistical behaviour is also accounted for. A certain correlation between structure and reactivity can be established, subject to many qualifications. Information on the nuclear motion on the potential energy surfaces of an ionized molecule can be extracted from a photoelectron spectrum by a Fourier transform operation.

REACTION MECHANISMS

Is the rate constant of a unimolecular reaction really determined by a single quantity, viz. the total intramolecular energy E , as assumed by QET, or does it depend on additional factors, related to the specificity of the initial excitation? This may well be the cardinal question of unimolecular reaction dynamics. An answer to that question is provided by the photoion-photoelectron coincidence spectroscopy. Most of the time, the evidence is in favour of the statistical model. PIPECO experimentation has revealed that, for most molecules, the ion yield curves are smooth functions of energy alone. This constitutes very convincing support of the validity of the assumption according to which the molecular ion has reached a state of microcanonical equilibrium. However, a few counterexamples are known, which are rather loosely referred to as "isolated state decay". The exact

meaning of this expression has become clear only recently.

A comparison between the cases of $C_2H_4^+$ and CH_3OH^+ has been attempted. The reaction paths of $C_2H_4^+$ have been determined by ab initio calculations. It has been shown that they are so complicated (i.e., the system has to fulfill such a large number of steps in a prescribed order) that a tendency towards energy redistribution follows naturally (1-3). Since the dissociation mechanism involves several nonadiabatic steps, an extension of QET had to be devised to calculate the ion yield curves (4). Agreement with experiment is very satisfactory (4).

CH_3OH^+ is known to offer a counterexample and the reasons of its behaviour have been understood only recently (5). The dissociation mechanism is here distinctly bimodal. Most of the ions are produced by a statistical RRKM/QET mechanism, except the CH_3^+ ions. This results from a branching in the reaction path brought about by an avoided crossing between two potential energy surfaces. One of the reactive paths gives rise to the RRKM/QET component, whereas the other leads directly to the $CH_3^+ + OH$ dissociation asymptote (Fig. 1). Production of CH_3^+ ions thus takes place by a fast, diatomic-like, non-statistical mechanism which escapes energy redistribution. "Isolated state decay" thus corresponds to dissociation of the non-randomized fraction of the population, and not to isolation, i.e., to lack of radiationless

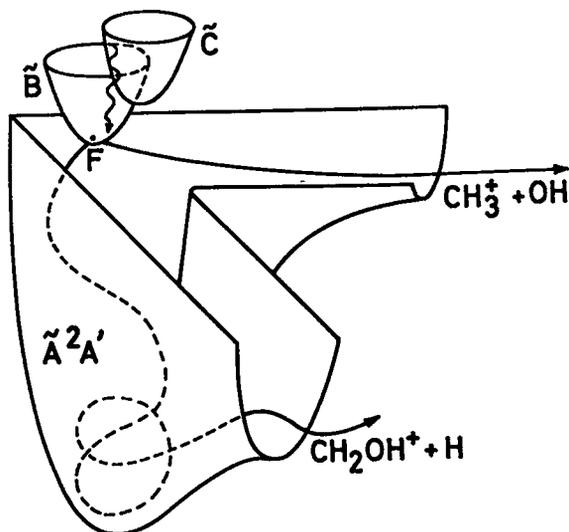


Fig. 1. Isolated state decay corresponds to a branching in the reactive flux between the statistical and non-statistical paths.

transitions to the lower electronic states.

STRUCTURE AND DYNAMICS

Do structural studies provide a shortcut to potential energy surface calculations and do they help to understand the reactivity of a particular ion? In principle (6), chemical reactivity is an inherently dynamic process which cannot be expected to reduce to a simple corollary of structural chemistry. A structure is an information concerning a particular point of the potential energy surface, whereas a reaction can be visualized as a trajectory leading from reactants to products, i.e., as a succession of structures. A structure can thus at most provide an initial tendency which may be altered and even reversed by the complicated nature of a reaction mechanism. Contrarily to what is often asserted in the literature, there is as a rule no correlation between the bonding or antibonding nature of a particular MO and the fragmentation of the ionic state which results from electron removal from this MO (6). The reason is that the bonding or antibonding nature is calculated at the equilibrium position of each state, whereas the nature of the wave function at the dissociation asymptote may be entirely different. In such a case, no correlation is to be expected between electronic structure and reactivity.

However, there exist cases in which, to a first approximation, the outcome of a chemical process is controlled by, or at least depends on the properties of a particular point of the potential energy surface or surfaces. This happens in two important circumstances: (i) when the transition state model is valid; (ii) in nonadiabatic processes (i.e., in which two electronic states are involved) which are governed by localized surface crossings or interactions. In such cases, chemical reactivity turns out to be controlled by specific points or regions of space of the potential energy surfaces. Photochemists, who have to deal with much of the same problems as mass spectrometrists have coined a new word and designate these particular points as "funnels" (6, 7). In brief, a funnel is a curve crossing or a localized region of strong nonadiabatic interaction between two potential energy surfaces.

Thus, a distinction has to be established between, on the one hand, equilibrium structures which provide a basis for the understanding of static properties, and, on the other hand, transition states and funnels which are the key features which control the dynamic properties and thus the chemical reactivity.

INTRAMOLECULAR DYNAMICS

Recently, a new experimental method has been developed (8, 9) to obtain information on the unimolecular processes in ionized molecules. It has been shown by Heller (10) that the Fourier transform of an electronic spectrum leads to an autocorrelation function $C(t)$ which describes the evolution in time of the wave packet created by the Franck-Condon transition, as it propagates on the potential energy surface of the electronic upper state. This correlation function is equal to the modulus of the overlap integral between the initial position of the wave packet and its instantaneous position at time t . When applied to a photoelectron spectrum, the method provides information about the nature of the nuclear motions on the potential energy surface of an ionized molecule. The original data resulting from an experimentally determined spectral profile must be corrected for finite energy resolution, rotational, and spin-orbit effects (8). The behaviour of the system can then be followed up to a time of the order of 10^{-13} s, i.e., during the first few vibrations which follow immediately the electronic transition. An oscillatory pattern of the correlation function indicates that the nuclear motion is taking place in a bound potential (Fig. 2).

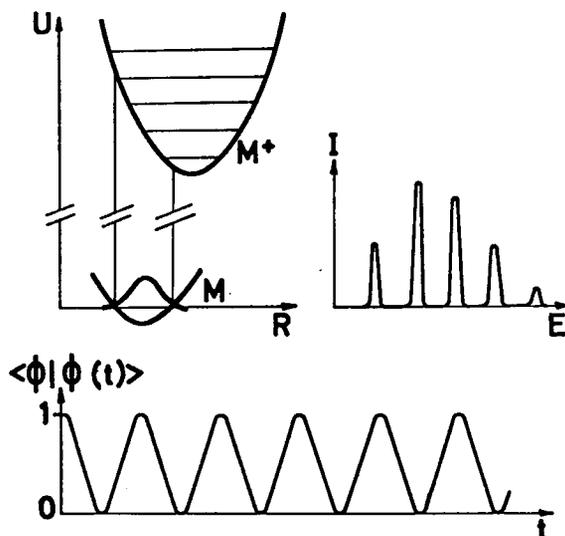


Fig. 2. A Franck-Condon transition to a stable electronic state leads to a well-resolved photoelectron spectrum whose Fourier transform gives a time-dependent correlation function with oscillatory character.

On the contrary, a time decrease of the correlation function is associated with an irreversible evolution. For a polyatomic molecule, the method provides a certain number of informations related to the multidimensional motion on a potential energy surface. The following problems can be studied :

- (1) Coupling among vibrational normal modes and rate of energy redistribution ;
- (2) Nonadiabatic interactions such as predissociations and internal conversions.

The correlation function is separable into a product of partial functions pertaining each to a single vibrational mode if the normal coordinates are identical for the initial and final states, except for a difference in the equilibrium positions ; in other words, if there is no Duschinsky effect. This is found to be the case for the \tilde{X}^2B_1 ground state of the H_2O^+ ion. The case of the \tilde{X}^2B_{3u} ground state of the $C_2H_4^+$ ion is more complex : although the separable approximation is acceptable, a slight but noticeable vibrational coupling takes place.

In the case of HCN^+ (8), the vibrational normal modes of the $\tilde{B}^2\Sigma^+$ state are entirely different from those of the ground state of the neutral molecule. One of them is an in phase stretching motion of the CH and CN bonds and the other is in fact a reaction coordinate. A measure of the rate of flux into the latter degree of freedom can be derived from the correlation function (8).

The method can be extended to study nonadiabatic processes (9). The predissociation of the $\tilde{A}^2\Sigma^+$ state of HBr^+ by a repulsive quartet can be monitored. Part of the wave packet has flowed into the continuum after half a vibrational period while the remainder remains trapped in the bound potential. A somewhat analogous wave packet splitting is brought about by a surface crossing in the case of the \tilde{B}^2B_2 state of H_2O^+ . A similar process, also brought about by a conical intersection takes place in the first excited state \tilde{A}^2B_{3g} of the $C_2H_4^+$ ion. From the correlation function, it can be deduced that the lifetime of state \tilde{A} with respect to internal conversion to the ground state \tilde{X}^2B_{3u} is of the order of $0.8 \cdot 10^{-14}$ s.

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