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The role of quantum intramolecular dynamics in unimolecular reactions†

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The dynamics of unimolecular reactions can be modelled by classical mechanics for the motion of nuclei on Born–Oppenheimer or other effective potential surfaces, by the corresponding quantum mechanical equations of motion and, perhaps, by quantum statistical treatments.

In this paper I provide a synopsis of fundamental, qualitatively important effects arising from the quantum nature of intramolecular dynamics, as opposed to classical mechanics, and illustrate these with theoretical predictions and experimental examples from the work of my group in Zürich. These include quantum nonlinearity in infrared (IR) multiphoton excitation and reaction, non-classical wavepacket spreading in the Fermi resonance coupled modes in CHX_3 molecules, effects of zero point energy and angular momentum in unimolecular reactions, nuclear spin symmetry conservation and interconversion and the hypothetical effects arising from the violation of parity and time reversal symmetry in unimolecular reactions. Specific applications to experiments include IR laser chemistry of CF_3I and CF_3Br , IR spectroscopy and dynamics of CHF_3 and predissociation spectra and dynamics of H_3^+ .

1. Introduction

One approach to the dynamics of unimolecular reactions of polyatomic molecules would be to describe only electronic motion by quantum mechanics, making use of the adiabatic or Born–Oppenheimer separation from nuclear motion. The heavy particle dynamics of the nuclei (or atoms?) on this effective potential might then be described by the classical mechanical equations of motion, for instance by the method of classical trajectories, pioneered by Bunker (1971, 1977). Although it is obvious that this approach cannot give quantitatively accurate results at energies corresponding to temperatures at which unimolecular reactions are ordinarily observed (Quack & Troe 1981), one might hope that at least most or all of the important qualitative aspects of the heavy particle dynamics in unimolecular reactions on one electronic potential surface are well described by these techniques.

It is the aim of the present paper to summarize those situations, where important qualitative differences exist between classical and quantum dynamics of intramolecular motion and unimolecular reactions. The goal is to clearly identify the central concepts, which will be illustrated with recent examples of experimental and theoretical evidence on the question mostly from work of my own laboratory, although in some cases excellent examples from other laboratories exist as well. This

† Dedicated to Paul von Ragué Schleyer on the occasion of his 60th birthday.

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is thus not an exhaustive survey, but exemplary and brief, with a necessary personal bias. To my knowledge, a consistent survey of this kind has not been given and in some cases striking predictions arise for future directions of experimental work.

To start, I define the way in which we shall view the distinction of classical and quantum dynamics: simply, as predicted by Newton's and Hamilton's equations or the superposition and uncertainty principles and as codified in typical texts (Landau & Lifchitz 1966; Goldstein 1980; Dirac 1967; Messiah 1969; Cohen-Tannoudji *et al.* 1977), in particular without additions that tend to merge classical and quantum dynamics such as semiclassical and related techniques. This restriction is important for conceptual reasons, because many of the rigorous theorems available for either classical dynamical systems or quantum mechanics are not valid for the 'intermediate theories' sometimes called semiclassical (Miller 1974, 1975; Marcus 1970; Child 1974). These usually tend to introduce quantization into classical dynamics according to some approximate scheme. They might thus be called 'semiquantal' as well as semiclassical. I shall illustrate these abstract remarks with a first, introductory example of a true quantum effect.

The fundamental example for the effect of the quantum uncertainty in unimolecular reactions is the decay of an isolated resonance as observed in radioactive decay. A pure quantum state describing an atomic or molecular system is described by an (approximately) lorentzian line shape function for the energy distribution $L(E)$ and an approximately exponential decay for the probability of the initial, bound state:

$$L(E) = \frac{1}{\pi} \frac{\frac{1}{2}\Gamma}{(E - E_0)^2 - (\frac{1}{2}\Gamma)^2}, \quad (1.1)$$

$$p(t) = p(0) \exp(-kt), \quad (1.2)$$

$$k = 2\pi\Gamma/h. \quad (1.3)$$

When one views quantum mechanics as a statistical theory for ensembles of identical atoms or molecules (all in the same pure quantum state), equations (1.1)–(1.3) provide the relevant distributions for the energy and time of decay in this ensemble. When viewed as a theory for an individual atom or molecule, the exact energy and decomposition time is strictly unpredictable and experimentally uncertain (but subject to the probabilities specified by (1.1)–(1.3)). In contrast, classical mechanics would allow an exact prediction of decomposition time at a given energy for the individual molecule. For an ensemble of molecules in exactly the same state there would be no exponential decay law, but a unique decomposition time. On the other hand we might introduce a statistical (classical) ensemble that mimics the quantum uncertainty in the initial state or one could even, by semiclassical S -matrix theory, calculate the width and life-time of the resonance and thus recover the quantum mechanical result, perhaps, approximately or exactly. But in doing so one introduces fundamental concepts from quantum mechanics (namely quantum uncertainty and superposition principle) into classical mechanics. Also it would have to be shown, for a given mechanical system, to what extent one obtains an accurate result. This introductory example is well-known textbook material (but still pertinent) and I shall turn now to examples from more recent research.

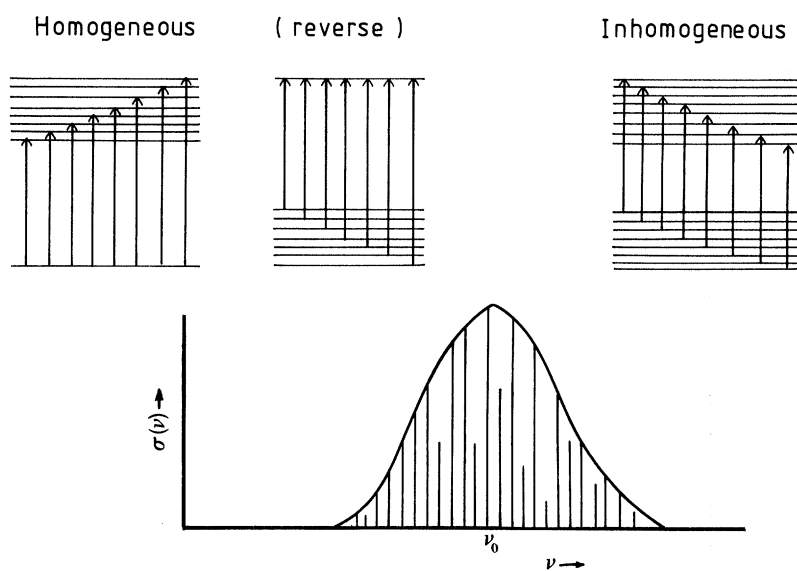


Figure 1. Schematic drawing of rovibrational band structure for IR multiphoton excitation of polyatomic molecules. Contributions for a one photon step in the ensemble are shown, that would give rise to a similar envelope $\sigma(\nu)$ but have fundamentally different origin and dynamical consequences.

2. Quantum nonlinearity in unimolecular reactions induced by monochromatic infrared radiation (URIMIR)

Among the more interesting recent additions to the general field of unimolecular reactions we find infrared laser chemistry as the basis of URIMIR. The general field has just recently been reviewed (Lupo & Quack 1987; Quack 1989). We shall address here one specific point: How does the nonlinear intensity dependence in the stepwise multiphoton process arise as a consequence of a true quantum effect?

Figure 1 illustrates schematically the band structure for a typical step (one-photon transition) in a sufficiently large polyatomic molecule with very complex level structures. In CO_2 laser induced URIMIR there are of the order of 10–50 steps of this kind, and coherence among these can be taken into account (Quack & Sutcliffe 1985). The absorption band may have a broad, more or less structured envelope centred at ν_0 , with width of about a few THz say. This would appear similarly in classical and quantum mechanics. However, the quantum structure really consists of narrow lines (natural bandwidths Hz to kHz in the infrared, assuming suppression of the Doppler effect by some appropriate technique, for simplicity). This quantized substructure can be homogeneous or inhomogeneous (Puttkamer *et al.* 1983), arising from the broad thermal distribution of initial states and from redistribution of line strength by Fermi resonances and many other, related effects. At 0 K only homogeneous structure remains, but in general both types occur together. The quantized substructure of the spectrum has a profound influence on the nonlinear intensity dependence of the stepwise multiphoton process (Quack 1978, 1979*b*, 1982). If the homogeneous structure dominates and is dense (line separations of the order of the optical coupling matrix elements or less), the rate constant for product formation after IR multiphoton excitation depends linearly upon intensity, (so called ‘case B’ even for a high-order stepwise multiphoton process), and this is the result

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Table 1. Nonlinear intensity dependence of the unimolecular rate coefficient in URIMIR (approximate steady state)

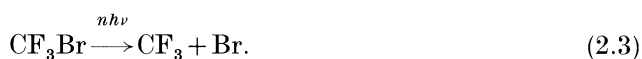
laser pulse type and approximate intensity	$k_{\text{uni}}/(10^6 \text{ s}^{-1})$	
	$\text{CF}_3\text{I} \rightarrow \text{CF}_3 + \text{I}^{\text{a}}$	$\text{CF}_3\text{Br} \rightarrow \text{CF}_3 + \text{Br}^{\text{b}}$
single mode $I \approx 50 \text{ MW cm}^{-2}$	60	3.4
mode locked $I \approx 300 \text{ MW cm}^{-2}$	750	66
2ns pulse $I \approx 1.5 \text{ GW cm}^{-2}$	3750	645

^a Dietrich *et al.* (1989)^b Quack *et al.* (1990)

also of the classical mechanical treatment. However, if inhomogeneous structure dominates or the line separations are large compared with the optical coupling matrix elements ('case C' of Quack (1978)) then one will observe a nonlinear intensity dependence of the stepwise n photon process about with $I^{\frac{1}{2}n}$. More precisely, if there are M steps following case C (and further possible steps following case B) then one finds

$$k_{\text{uni}} = \text{const.} \times I^{\frac{1}{2}(M+1)}. \quad (2.1)$$

Making use of the statistical theory of spectra with simple models for the distribution functions, analytical formulae have been derived for optical transition rates in master equations for the multiphoton process (Quack 1978, 1981, 1982). Accurate numerical (quantum Monte Carlo) results can be derived for realistic spectra (Quack & Sutcliffe 1985). I shall not review these here, but summarize in table 1 some recent experimental results from my laboratory that provide support for the quantum nonlinearity in URIMIR for the reactions



Because the rate constants have been evaluated by an indirect technique, which is quantitatively valid only for pulses of exactly constant intensity or else in the linear régime (case B), the nonlinear dependence of the rate constants shown are only semiquantitative. Nevertheless, the nonlinearity is demonstrated beyond doubt. Furthermore, the nonlinearity disappears at the highest intensities for CF_3I , in agreement with expectation (Quack *et al.* 1986).

One may wonder, whether the nonlinearity arises from direct multiphoton processes (nonlinear intensity dependence both in classical and quantum mechanics). This can be ruled out on several grounds. First, theoretical calculations indicate that direct (nonlinear) multiphoton processes play an insignificant role in IR laser chemistry under typical conditions (Quack & Sutcliffe 1985*b*). Secondly, the disappearance of the nonlinearity at the highest intensity for CF_3I is inconsistent with an explanation by direct multiphoton transitions. Thirdly, pressure broadening with inert gases allows us to remove the spectral line structure (figure 1) and such experiments, indeed, indicate a transition from the nonlinear case C to case B for the reactions considered (Quack 1981; Quack *et al.* 1990). We can thus consider the quantum nonlinearity for the stepwise multiphoton process to be safely established,

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although further work, particularly on a more quantitative intensity dependence and time resolution to shorter timescales is desirable (presently limited to greater than 1 ns).

3. Infrared multiphoton excitation and mode selective vibrational dynamics on the femtosecond and picosecond timescale: the non-classical Fermi resonance in CHX₃ molecules

We shall turn now to IR multiphoton induced intramolecular dynamics on a very short timescale, where on the one hand the statistical approximations of the previous section may become inappropriate and on the other hand the short-time coherent quantum wavepacket motion may perhaps be quasiclassical as observed for the one-dimensional harmonic and anharmonic oscillator (Marquardt & Quack 1989). I shall point out a recently discovered rather subtle quantum effect in the dynamics of coupled vibrations, which depends on details of molecular parameters (Marquardt *et al.* 1986; Marquardt & Quack 1987, 1990).

The route I have taken to study the subpicosecond dynamics of coupled vibrations is to derive an approximation to the molecular (partial) hamiltonian from an analysis of stationary high resolution molecular spectra and *ab initio* calculations (Amrein *et al.* 1988; Dübal *et al.* 1989) and compute the intermolecular dynamics on the basis of this hamiltonian \hat{H} ,

$$\Psi(t) = \hat{U}(t, t_0) \Psi(t_0), \quad (3.1)$$

$$i(\hbar/2\pi) \partial \hat{U} / \partial t = \hat{H} \hat{U}. \quad (3.2)$$

In the presence of an external perturbation $\hat{V}(t)$ (for instance by a coherent laser field) one has (Quack 1982)

$$i(\hbar/2\pi) \partial \hat{U} / \partial t = [\hat{H} + \hat{V}(t)] \hat{U}. \quad (3.3)$$

An alternative to this route would be femtosecond spectroscopy (Gruebele *et al.*, this Symposium).

Extensive spectroscopic investigations together with *ab initio* calculations and vibrational variational calculations have allowed us to characterize the 'universal' dynamics of the coupled CH stretching and bending motions in CHX₃ molecules (X = D, F, Cl, Br, CF₃), isotope effects on ¹²C, ¹³C and H, D, the work has been partly reviewed by Quack (1989); see also Hollenstein *et al.* (1990). On short timescales the heavy X₃ frame is approximately decoupled, adiabatically, and the quantum number l for the vibrational angular momentum of the degenerate bending vibrations is conserved. One has thus essentially a system of two coupled modes; the most important spectroscopic and potential parameters for the typical example CHF₃ (the other molecules are different in detail but similar in order of magnitude, which is important for the following discussion) are summarized in table 2. One may retain from table 2 the generally good agreement between experiment and *ab initio* theory. Furthermore one notes the enormous strength of the effective off-diagonal anharmonic coupling between stretching and bending modes, represented by the parameter k'_{sbb} , which exceeds the already large diagonal anharmonicity constant x'_{ss} of the CH stretching mode. In a low-order perturbation treatment the potential constant C_{sbb} should be equal to k'_{sbb} (Amat *et al.* 1971; Mills 1974, 1972; Papousek & Aliev 1982). This is satisfied qualitatively, but not quantitatively (Dübal *et al.* 1989). Thus C_{sbb} is a less adequate measure of the strength of the Fermi resonance, but gives some insight into the potential. However, as discussed in detail by Lewerenz & Quack (1988) about 30 terms in the Taylor expansion of the potential are

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Table 2. Spectroscopic and potential parameters for the coupled CH stretching and bending modes in $^{12}\text{CHF}_3$

parameter ^a	experimental Segal <i>et al.</i> (1987)	<i>ab initio</i> Dübal <i>et al.</i> (1989)
$\tilde{\nu}'_s/\text{cm}^{-1}$	3086	3126
$\tilde{\nu}'_b/\text{cm}^{-1}$	1370	1432
x'_{ss}/cm^{-1}	-64	-67
x'_{bb}/cm^{-1}	-5.6	-7.5
x'_{sb}/cm^{-1}	-29	-34
g'_{bb}/cm^{-1}	9.7	11.5
$ k'_{sbb} /\text{cm}^{-1}$	100 ± 10^c	99
C_{sbb}/cm^{-1}	187	187
C_{ssbb}/cm^{-1}	-92	-85
$F_{sbb}/(\text{cm}^{-1} \text{ A}^{-1})$	-5268 ^b	-20228
$F_{ssbb}/(\text{cm}^{-1} \text{ A}^{-2})$	-77424 (fix) ^b	-77424

^a The $\tilde{\nu}'_i$, x'_{ij} and g'_{ii} are spectroscopic wavenumbers and anharmonic constants for stretching (s) and bending (b) vibrations in essentially the ordinary term formula. k'_{sbb} is the effective Fermi resonance constant coupling constant, which is a good measure of the anharmonic coupling strength. C_{sbb} and C_{ssbb} are anharmonic potential constants in rectilinear normal coordinates (Lewerenz & Quack 1988). F_{sbb} and F_{ssbb} anharmonic constants in curvilinear internal coordinates (Carrington *et al.* 1987, Hollenstein *et al.* 1990). The usual definitions of force constants in different coordinate systems apply. The index indicates the order of the term in the Taylor expansion. For instance in rectilinear normal coordinates q the potential takes the form:

$$V/hc = \frac{1}{2}\omega_s q_s^2 + \frac{1}{2}\omega_b q_b^2 + C_{sbb} q_s q_b^2 + C_{ssbb} q_s^2 q_b^2 + \dots$$

^b These constants are only poorly determined by experiment. F_{ssbb} has been fixed to the *ab initio* value in this example (Dübal *et al.* 1989). F_{sbb} and F_{ssbb} are no good measure of the strength of the Fermi resonance, which can be strong with $F_{ssbb} = F_{sbb} = 0$ (Hollenstein *et al.* 1990).

^c An error estimate, including a cautious estimate also of systematic errors, is only given for this important constant. The statistical error (standard deviation) from the fit is much smaller.

necessary for a quantitative prediction of k'_{sbb} . In this interpretation, the Fermi resonance constant k'_{sbb} arises from potential coupling only. In the internal coordinate model, the Fermi resonance arises in general partly from kinetic energy coupling and partly from potential coupling. Thus the anharmonic force constants F_{sbb} and F_{ssbb} derived from the approximate, variational internal coordinate hamiltonian (Carrington *et al.* 1987) give no indication of the strength of the Fermi resonance. Even if they are zero, a strong Fermi resonance may exist by kinetic energy coupling, a situation found for CHBr_3 , approximately (Hollenstein *et al.* 1990). The reader should appreciate, that whereas the Fermi resonance coupling constant k'_{sbb} has a well-defined *definition* as a parameter measuring the strength of the tri-diagonal coupling, the *interpretation* of k'_{sbb} (as potential or kinetic energy coupling or both) is arbitrary and depends on the model used for the interpretation.

The parameters of the Fermi resonance define an anharmonic coupling potential and hamiltonian for the CH stretching and bending modes (see Lewerenz & Quack (1988) and Dübal *et al.* (1989) for quantitative representation of such potentials). I shall discuss the basic concepts of the dynamics for this Fermi resonance with the scheme of figure 2, which shows one equipotential line (say at 200 kJ mol⁻¹, corresponding to six quanta of CH stretching) as a function of the two coordinates x and y (say CH stretch and bend). For illustrative purposes the potential includes the possibility of reaction for large values of y .

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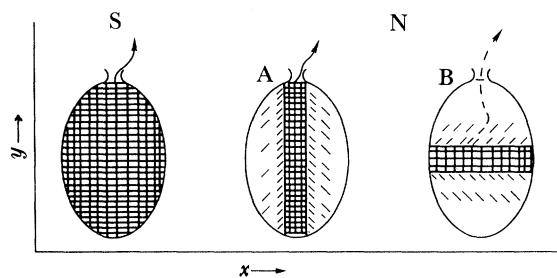


Figure 2. Scheme for two coupled oscillators with coordinates x and y . The probability density for the classically allowed space within the equipotential line is drawn following several models 'S' for statistical, 'N' for normal mode separable with two different initial conditions A and B (Quack 1984). Dashed lines indicate quantum tunnelling and the arrow the possibility of reaction. For weak anharmonic coupling one has periodic exchange between A and B, whereas strong Fermi resonance leads to quantum spreading of the density, more similar to S (Marquardt & Quack 1987, 1990).

For zero anharmonicity one would expect quasi-classical, coherent harmonic oscillator wave packets spanning either the space of stretching or of bending, depending on the initial state as shown in A and B. The dashed lines indicate minor penetration into the classically forbidden range by tunnelling. For weak anharmonic coupling (about $1\text{--}2\text{ cm}^{-1}$) one finds the expected slow, quasi-periodic, quasi-classical exchange between stretching and bending motions, quite similar to the motion of coupled classical pendula. However, for strong anharmonic coupling ($k'_{\text{sbb}} \approx 100\text{ cm}^{-1}$) one finds after less than 10 periods of the quasi-classical pure stretching vibration (about 100 fs) a spreading of the wave packet over most of the energetically accessible space without any excitation of a quasi-classical bending motion (Marquardt *et al.* 1986; Marquardt & Quack 1987, 1990). The wave-packet density for most times after 100 fs is rather similar to the time average and also to the statistical (microcanonical) density sketched by the scheme S. Whereas the equivalence of time average and microcanonical average exists for classically ergodic systems, only for a quantum system can we reach this state of affairs for a pure state at any given time (i.e. a state, which is described by a wavefunction $\Psi(t)$ and not by an ensemble or statistical mixture, describable only by a density operator). We note the drastic change of behaviour, when the anharmonicity is changed from a few cm^{-1} to 100 cm^{-1} . This change in the potential remains a minor perturbation in terms of overall quantization (fundamental wavenumber 3000 cm^{-1}). Non-classical spreading arises from anharmonicity but not from a drastic change in quantization.

One might speculate whether the change of behaviour is related to 'chaotic motion' in the corresponding classical system, which would then simulate the quantum spreading with an ensemble of classical trajectories corresponding to the initial conditions of the quantum wave packet. I stress, however, that similar to the decay of an isolated resonance mentioned in the introduction such an ensemble average is unnecessary in the quantum case. The behaviour illustrated by scheme S could be at the origin of the quantum statistical theory of unimolecular exponential decay of polyatomic molecules. This clearly depends on molecular coupling strengths and timescales, which opens the possibility of coherently driven, mode selective unimolecular reactions under certain conditions. In any case the redistribution process between CH stretching and bending modes is highly mode selective, as the

vibrational modes of the heavy atom CX_3 frame and rotation do not participate appreciably in the redistribution on the subpicosecond timescale.

I conclude this section with a discussion of whether some of the above experimental and theoretical results might be useful in the search for defining and understanding ‘molecular quantum chaos’. ‘Chaos’ is now a reasonably well-defined technical concept in the theory of (classical) dynamical systems (Berry 1978; Velo & Wightman 1983; Kunick & Steeb 1986; Schuster 1984), based in essence on the properties of classical trajectories in phase space. It is uncertain, and in fact unlikely, that this concept can be directly transferred to quantum mechanics. The situation of ‘classical chaos’ in quantum theory may be very similar to the question of a ‘classical orbit of the H atom at its ground state energy’, a meaningless quest (Quack & Sutcliffe 1983). Also the nature of the (linear) time-dependent Schrödinger equation should make us cautious when using concepts arising from the differential equations of nonlinear dynamics. Nevertheless, one would like to believe that ‘molecular chaos’ as a physical phenomenon exists in the quantum world. The hint from our results would be to define it by parameters of the time dependent quantum mechanical trajectory $\Psi(\mathbf{q}, t)$ or $\Phi(\mathbf{p}, t)$ or a combination of these, and the fast spreading of the probability density observed with strong Fermi resonance is such a parameter, albeit qualitative. For a system of three coupled oscillators I have shown that a quantum entropy can be used as a quantitative parameter of the time evolution, increasing quasi-irreversibly to values close to maximum and I shall come back to this point below.

4. Zero point energy and angular momentum in intramolecular dynamics and unimolecular reaction

The quantization of the lowest state, which gives the zero point energy, and of angular momentum J , are obvious quantum effects, which one might deal with just by mentioning them. However, in practice these two effects enter into the theory of unimolecular processes in a somewhat subtle way, which deserves a few further considerations. In a large molecular system, we wish to describe unimolecular reaction dynamics in general with reference to just the few, most relevant, coordinates. Indeed, very often just one coordinate, the reaction coordinate q , is retained. In this approximate description, the zero point energy in the other coordinates and the conserved part of the rotational energy generate an effective potential for the q -motion, giving rise to special ‘quantum’ zero point and angular momentum effects on the dynamics. These have been treated in the framework of the adiabatic channel model (Quack & Troe 1974).

Figure 3 illustrates these effects. V_e is the electronic (Born–Oppenheimer) potential. For a given total angular momentum J of the many particle system, conservation of J leads to a centrifugal (classical) potential V_{cc} , where q might be defined in such a way that the barrier in this potential is minimized. However, taking quantization into account, one must calculate this centrifugal energy of the asymmetric rotor by quantum mechanics (that is the lowest rotational energy for a given J) and at the same time add the zero point energy from all but the q modes. This defines the lowest adiabatic channel potential $V_{acm}(J, a = 0)$ shown also in figure 3. The zero point energy results in the states above the classical zero of energy being stable (i.e. the lowest six in the example, not just the lowest two). The highest level drawn predissociates through the combined zero point and angular momentum barrier by

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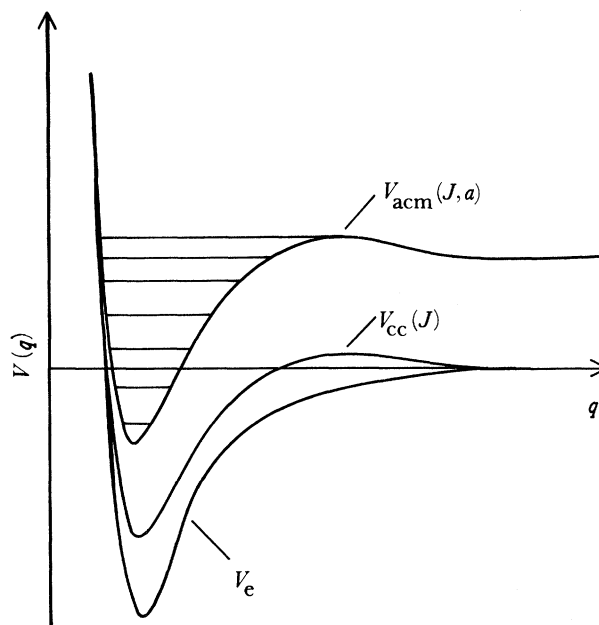


Figure 3. Effect of zero point energy and angular momentum on polyatomic reaction dynamics as illustrated by the adiabatic channel model. V_e is the electronic (Born–Oppenheimer) potential in the reaction coordinate q , $V_{cc}(J)$ the effective, classical centrifugal potential (for a total angular momentum quantum number J , and $V_{acm}(J, a)$ the effective adiabatic channel potential including zero point energy for J and channel a (for example the lowest channel).

tunnelling and both the effective quantum channel potential and tunnelling must be calculated, if accurate results are to be achieved.

The one-dimensional adiabatic channel potentials can be used both for calculations of reaction (Quack & Troe 1974, 1981) and of bound states (Quack 1981). Recent experimental and theoretical results on bound states indicate a surprisingly good validity of the fundamental approximations involved, if the calculation of channel potentials is carried out accurately (Quack & Suhm 1990). Our considerations of these effects in the framework of the adiabatic channel model has a wide range of applications and we mention here the predissociation spectra of H_3^+ (Carrington & Kennedy 1984). Quasi-bound state densities $\rho(E, J)$ above threshold have been calculated by crude estimates quite some time ago (Quack 1979), more accurately recently (Miller & Tennyson 1988) and classical rotational effects on the dissociation have been discussed (Schlier 1987), as well as approximate barrier effects (Chambers & Child 1988). An accurate treatment in the framework of the adiabatic channel model retaining the quantum effects mentioned above is possible and may help to resolve some of the questions that remain about the dynamics of this interesting system.

5. Nuclear spin symmetry conservation and interconversion from nanoseconds to seconds

As with electrons, the nuclei in molecules can have an internal contribution to angular momentum, generally called ‘nuclear spin’, although it sometimes contains

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Table 3. Character table for S_3 with the subduced representation $\Gamma(S_3) \downarrow S_2$

	E	(123)	(12) (23) (13)	$\Gamma(S_3) \downarrow S_2$
A_1	1	1	1	A
A_2	1	1	-1	B
E	2	-1	0	A+B

contributions from internal orbital angular momentum in the nucleus. Nuclear spin contributes in interesting ways to intramolecular dynamics and chemical reactions (Quack 1977, 1983, 1985), although these effects have usually been neglected in discussions. Nuclear spin is a true quantum phenomenon, having no classical analogue, and because of the recent interest in the experiments of Carrington & Kennedy (1984), Pollak (this Symposium) and Tennyson *et al.* (this Symposium), I shall discuss some of the striking consequences for the example H_3^+ (as discussed before). The considerations apply to other X_3 systems and also to NH_3 , for example (Quack 1983, 1986; Ashfold *et al.*, this Symposium). The foundations of the theory have all been presented in (Quack 1977), but it seems useful to discuss a specific experimental example in more detail, as so far there has been little acceptance of the concepts of nuclear spin symmetry conservation in an experimental context (predictions on the simple case of photodissociation of formaldehyde by Quack (1983) have been in part verified experimentally by Schramm *et al.* (1983)).

The photodissociation experiment by Carrington and co-workers (Carrington *et al.* 1982; Carrington & Kennedy 1984) has both spectroscopic and dynamical aspects. The following symmetry considerations could help to assign the spectra, particularly if use is made of hyperfine structure, but we shall concentrate on the quantum effects arising from the symmetry of the reaction dynamics. Consider the reaction



The group for our purpose is a direct product

$$S_{2,3}^* = S_{2e} \times S_3 \times S^*, \quad (5.2)$$

where S_{2e} is the group of permutations of the two electrons, S_3 the group of permutations of the three protons and S^* the reflection group (space inversion invariance assumed, see below). For simplicity, we shall consider reactions in the electronic ground state (1A_1 for H_3^+ and ${}^1\Sigma^+$ for H_2) and need not consider S_{2e} explicitly, in the following. The character table for S_3 is given in table 3 and because of the direct product nature with S^* we can label each species by + (positive parity) or - (negative parity) depending on whether it is symmetric with respect to reflection at the origin or antisymmetric. The symbols for the irreducible representations are chosen in such a way that they are rather similar to the isomorphous point group $D_{3h}(A_1^+, A_1^-, A_2^+, A_2^-, E^+, E^-)$. The nuclear spin functions are ${}^4A_1^+$ ($I = \frac{3}{2}$) and ${}^2E^+$ ($I = \frac{1}{2}$). They combine with the rovibronic functions to Pauli allowed levels A_2^+ or A_2^- , that is ${}^4A_1^+$ with A_2^+ and A_2^- (rovibronic) and ${}^2E^+$ with E^+ and E^- (rovibronic). Each combination gives just one final non-degenerate level (A_2) and rovibronic levels of species A_1^\pm are Pauli forbidden.

We next need to relate simple rovibronic quantum numbers to symmetry species.

This is practically useful, although rigorously neither possible nor necessary, in general. We shall first consider scattering channels $H^+ + H_2(v, j)$

$$|J, M_J, I, M_I, v, j, l\rangle, \quad (5.3)$$

J, M_J are the total angular momentum quantum numbers (except spin), I, M_I are the total nuclear spin quantum numbers. The species in S_3^* is determined by parity (+, -).

$$\Pi = (-1)^{j+l} \quad (5.4)$$

and by the induced representation $\Gamma(S_2) \uparrow S_3$ to be read from the subduced representation in table 3, i.e.

$$\text{para } H_2: \quad j = \text{even}, \quad A \uparrow S_3 = A_1 + E, \quad (5.5a)$$

$$\text{ortho } H_2: \quad j = \text{odd}, \quad B \uparrow S_3 = A_2 + E. \quad (5.5b)$$

It is obvious that for para H_2 we have $I_{H_2} = 0$ and thus $I = \frac{1}{2}$, whereas for ortho H_2 we have $I_{H_2} = 1$ and $I = \frac{1}{2}$ or $\frac{3}{2}$.

For H_3^+ we may derive rovibronic species

$$\Gamma_{\text{evr}} = \Gamma_{\text{elec}} \times \Gamma_{\text{vib}} \times \Gamma_{\text{rot}}, \quad (5.6)$$

$\Gamma_{\text{elec}} = A_1^+$, whereas for Γ_{vib} we may have A_1^+ , A_2^+ and E^+ . Table 4 summarizes the number of vibrational energy levels of given symmetry species calculated by a direct count using a separable Morse oscillator model with inaccurate frequency estimates before precise experimental and theoretical knowledge (Quack 1977, 1979) and from accurate vibrational variational calculations on the *ab initio* potential surface by Meyer *et al.* (1986). This table illustrates nicely the dependence of the densities and sums of states upon the potential model. It also shows how slowly the classical statistical limit $W(A_1^+): W(A_2^+): W(E^+) = 1:1:2$ is approached for such highly quantized vibrations (Quack 1985). We shall not give specific tables for Γ_{rot} but note several cases. For $J = 0$, one has $\Gamma_{\text{rot}} = A_1^+$, a Pauli forbidden level in the ground state. For $J = 1, K = 0$, we have A_2^+ and for $J = 1, K = 1$, we have E-rotational species. For large values of J and high excitation, K may not be a good quantum number, but the $2J+1$ levels (associated approximately with K) generate the following representation.

Non-degenerate vibronic state, even $J = 6m$

$(12m+1)$ levels,

$$m \times (A_1^+ + A_2^+ + A_1^- + A_2^- + 2E^+ + 2E^-) + A_1^+ \text{ (or } A_2^+). \quad (5.7)$$

Non-degenerate state with odd $J = 6m+1$

$(12m+3)$ levels,

$$m \times (A_1^+ + A_2^+ + A_1^- + A_2^- + 2E^+ + 2E^-) + E^- + A_2^+ \text{ (or } A_1^+). \quad (5.8)$$

Degenerate vibronic state with even or odd $J = 6m (+1)$

$(24m+2)$ (6) levels,

$$2m \times (A_1^+ + A_2^+ + A_1^- + A_2^- + 2E^+ + 2E^-) + E^+ (+ A_1^- + A_2^- + E^-). \quad (5.9)$$

The option in parentheses in (5.7) and (5.8) is for an A_2^+ vibronic level and in (5.9) it is for odd J . The equations show, how for the more classical rotational degree of freedom the regular density is quickly approached as a function of increasing energy and J , also for the negative parity following Quack's (1985) theorem (for the triatomic H_3^+ the vibrational wavefunctions are all of even parity). The formulae for

Table 4. Sums of vibrational states W of given symmetry for H_3^+

E hc/cm^{-1}	$W(\text{A}_1^+)$	$W(\text{A}_2^+)$	$W(\text{E}^+)$
	3000	1 (1) ^a	0 (0)
6000	3 (3)	0 (0)	2 (3)
9000	6 (7)	1 (1)	5 (6)
12000	10 (12)	2 (3)	10 (13)
15000	17 (22)	5 (6)	19 (26)
18000	24 (35)	8 (14)	30 (46)

^a The numbers in parentheses are from accurate variational calculations (Whitenell & Light 1989; Tennyson & Henderson 1989), the others from a simple weakly anharmonic separable Morse oscillator model using $\omega_{\text{A}_1} = 3470 \text{ cm}^{-1}$ and $\omega_{\text{E}} = 2810 \text{ cm}^{-1}$ before the knowledge of accurate frequencies for this molecular ion and a direct count algorithm from Beyer & Swinehart (1973) but taking anharmonicity and symmetry into account (Quack 1977, 1979). W is the number of levels below the energy E .

the reduction of rotational wavefunctions are given as an illustration; for other values of J , similar formulae can be derived and, if K is a good quantum number, each K can be assigned a reduction into the species. In the most general case we cannot assign the rotational levels of a given J to a particular vibrational state but can define $W(E, J)$ and $\rho(E, J) = dW(E, J)/dE$, which at high energy (averaged over an interval containing many states) can be reduced approximately according to the regular representation of S_3^* (Quack, 1977, 1985) for H_3^+ . Thus, at high energy, above the dissociation threshold there will be plenty of rovibronic pre-dissociating levels of any given symmetry, except A_1^+ , which are Pauli forbidden for H_3^+ (see Quack (1979), for a first, crude estimate of such densities $\rho(E, J)$ at about 3900 cm^{-1} above threshold, of the order of one state per cm^{-1} , strongly dependent upon E and J , and the rovibrational model used).

I am now ready to discuss some dynamical consequences of the selection rules for the dissociation of H_3^+ , equation (5.1). We shall first consider dissociation into the lowest channels with $j = 0$ and $j = 1$, separated by about 120 cm^{-1} (1.4 kJ mol^{-1}) for a low value of total angular momentum $J = 1$ with practically zero centrifugal barrier, and some large J , with a large centrifugal barrier, as schematically shown in figure 4. I shall discuss first a predissociating level of H_3^+ , numbered '1' in figure 4, at $J = 1$, with no centrifugal barrier. For the product with $j_{\text{H}_2} = 0$ we have $l = 1$ and hence symmetry $\text{A}_1^- + \text{E}^-$ (A_1^- is Pauli forbidden and E^- has $I = \frac{1}{2}$ as it must). The dynamical properties of the level '1' depend on its symmetry. For completeness, we shall consider in turn all possible symmetries for the predissociating level '1'. A_1^+ and A_1^- are Pauli forbidden for H_3^+ . An A_2^+ rovibronic level may arise from an A_1^+ vibronic state. It cannot predissociate (except for the very weak parity violation discussed in the next chapter) and will have thus much more than the microsecond lifetime discussed in the predissociation experiment. The same conclusion arises for E^+ levels (arising from E^+ vibronic states). On the other hand, an E^- level (arising from A_1^+ vibronic state) will have a very quick, allowed predissociation (perhaps picosecond lifetime). The most interesting case are A_2^- levels. These have $I = \frac{3}{2}$ and can only decompose by a nuclear spin flip and symmetry change for $j_{\text{H}_2} = 0$. This is possible, but will lead to long lifetimes, of the order of microseconds (times as short as 1 ns and even longer than a millisecond cannot be excluded without a detailed calculation, which is possible if accurate wavefunctions are known). The conclusion is thus, that

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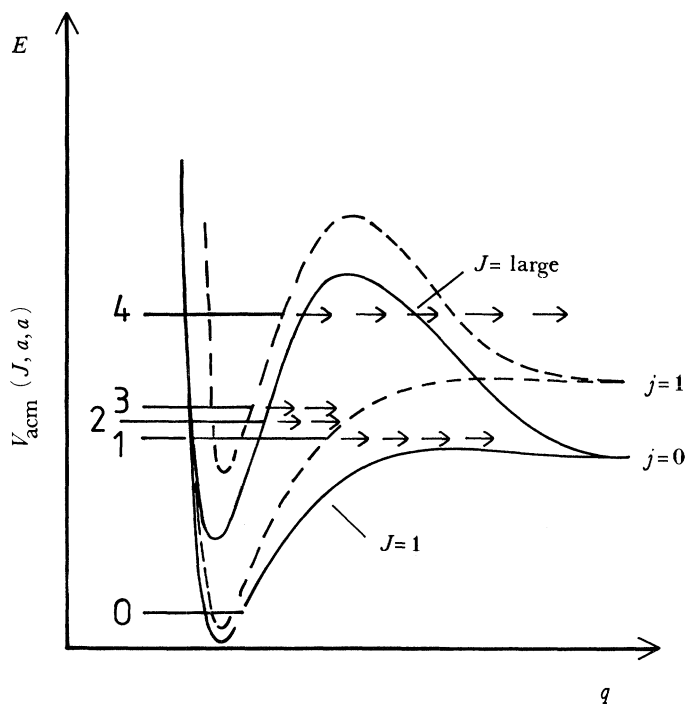
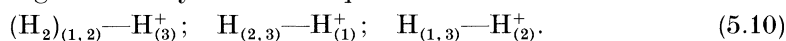


Figure 4. Schematic drawing of adiabatic channel potentials for the predissociation of H_3^+ (see detailed discussion in the text, the electronic potential is omitted, see figure 3).

metastables in mass spectrometry in general, and in the Carrington & Kennedy (1984) experiment in particular, can arise by this quantum effect in the absence of a centrifugal barrier and ‘tunnelling’ (quite in contrast to some conclusions drawn in the literature, which require high J tunnelling).

It is useful to consider the hyperfine aspects of this effect. For $J = 1$ and A_2^- level with an $I = \frac{3}{2}$ ($^4A_1^+$) nuclear spin function will be split by a hyperfine structure into a $F = \frac{1}{2}$, $F = \frac{3}{2}$ and $F = \frac{5}{2}$ triplet, observable in the spectrum. These have all the same nuclear spin symmetry, which is approximately conserved under this interaction (but see below). Similarly the product channel with $J = 1$, $l = 1$, $j = 0$, $I = \frac{1}{2}$ gives a hyperfine structure (degenerate, though) with $F = \frac{1}{2}$ and $\frac{3}{2}$. One might then think that the $F = \frac{5}{2}$ level in H_3^+ cannot predissociate. But with I non-conservation one has J non-conservation and $F = \frac{5}{2}$ can predissociate into a channel $J = 3$, $l = 3$, $j = 0$, $I = \frac{1}{2}$, $F = \frac{5}{2}$ respecting parity ($-$) and total angular momentum conservation (F).

We shall now consider a mechanism that may render nuclear spin symmetry violation more prominent. For specific states the D_{3h} symmetry of H_3^+ may be dynamically broken, for instance by a large amplitude ‘local’ vibration of H^+ with respect to H_2 or by a fast rotation of H_3^+ around a C_2 axis, giving a C_{2v} distortion, or finally by centrifugal trapping of the proton, separating it from a freely rotating H_2 . The full symmetry is generated by the three equivalent ‘structures’



‘Tunnelling’ or simply exchange between the dynamical structures will generate a multiplet structure, namely

$$A(S_2) \uparrow S_3 = A_1 + E, \quad (5.11a)$$

$$B(S_2) \uparrow S_3 = A_2 + E, \quad (5.11b)$$

S_2 is the symmetry group for the two protons that have remained dynamically equivalent. When the splitting between A_2 and E levels in such a pair becomes small, of the order of the hyperfine splitting, there will be hyperfine mixing and strong violation of nuclear spin symmetry conservation. If the levels are more distant (also ‘accidentally close’) the mixing will be weak but accounts for the long time predissociation. In principle, situations may arise with only ‘non-equivalent’ protons. The corresponding induced representation would then be $\Gamma(S_1) \uparrow S_3$. A trivial example is the fully dissociated state $H + H + H^+$.

Figure 4 shows levels at high J , bound by a large centrifugal barrier (‘2,3’). Whether or not these can dissociate in a symmetry allowed fashion will greatly influence their lifetime, following the above considerations. Furthermore, even level 4, which can decompose energetically to both $j_{H_2} = 0$ and 1 will ‘feel’ whether the $j = 0$ channel is forbidden or not. If it is an A_2 level, it will give only $j = 1$ products. At very high energies, when many product channels are open, there will be competition for dissociation into allowed and ‘forbidden’ channels. The selection rules predict, in the absence of strong violation, for example, that A_2^+ levels will generate only odd j of H_2 . By accurate measurements of the kinetic energy release on a given resonance or by spectroscopy of the H_2 produced, one would be able to assign the A_2 and E character of a resonance. Similarly, when H_3^+ is initially produced from para $H_2 + H_2^+$, in practice by ionization in pure para hydrogen, there will be no A_2^+ levels (Quack 1977).

There are numerous possible further applications to this particular system and others based on the general principle of nuclear spin symmetry and parity conservation in chemical reactions put forward by Quack (1977, 1983). I have given this somewhat pedestrian analysis for H_3^+ to show the multitude of useful effects. There could be even practical applications, based on the non mass dependent isotope effect arising even for nuclear isomers of almost equal mass, when breaking this symmetry.

6. Parity conservation and interconversion in unimolecular reactions of chiral molecules and the possible violation of time reversal symmetry for hours and longer

We turn now to what are perhaps the most fundamental quantum aspects of intramolecular dynamics and unimolecular reactions; the asymmetry of time and space, giving a unique preferred chirality to certain molecules (and, perhaps, life) and as a speculation also to the time direction of the course of chemical reactions. I shall be brief on this point and refer to Quack (1989) for details and extensive references.

In newtonian mechanics inverting particle positions in the centre of mass (‘space inversion’) or inverting momenta (‘time reversal’) lead to symmetrically equivalent solutions of the equations of motion, rigorously. In quantum mechanics the former symmetry would result in the quantum number parity to be conserved, but quantum effects connected with the weak nuclear interaction lead to non-classical violation of this symmetry (Lee & Yang 1956; Wu *et al.* 1957). In molecular physics this results, for instance, in a slight shift of energy levels of left and right handed chiral molecules, calculated to be of the order of about $\Delta E_{PV} \approx 10^{-13} \text{ J mol}^{-1}$ in certain cases (Mason & Tranter 1984). One would usually consider this to be too small for experimental verification. However, it has been shown that this small energy difference should be

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measurable (Quack 1986), and furthermore that racemization reactions under certain conditions may show drastic effects from parity violation (Quack 1989). When calculated by statistical thermodynamics or the ordinary statistical theory of specific unimolecular rate coefficients forward and backward rate constants of racemization are related by

$$k_{\text{RL}}/k_{\text{LR}} \approx 1 \pm \Delta \quad (6.1)$$

with Δ being of the order of 10^{-18} . However, under certain special conditions for moderately large ΔE_{PV} drastic deviations from this small effect are predicted for the initial relaxation in the racemization of well isolated molecules effectively breaking in appearance microscopic reversibility in (6.1) (Quack 1989). In classical mechanics this would not arise, the chiral symmetry violation being only *de facto* and not *de lege*. I shall not further elaborate on this here, as there is no experimental verification. We mention also possible effects of ΔE_{PV} in the kinetics of biological systems (Quack 1989). One possible hypothesis about chiral selection in the evolution of life invokes kinetic effects from ΔE_{PV} . A much more drastic hypothesis would be, that the mirror image form of an existing living species such as *E. coli* would be non-functioning or very different, because of catastrophic kinetic failure induced by ΔE_{PV} . This contradicts the biochemist's intuition but could be tested by a total synthesis of the complete mirror image form of a simple living system such as *E. coli*. A quantitative theory is difficult, though.

Rather, I turn now towards a question in intramolecular dynamics about which nothing is known for sure, neither experimentally nor theoretically. That is, I shall conclude by a few remarks of pure speculation. The weak nuclear interaction leads to a remarkable connection between space inversion asymmetry (P) and time reversal violation (T). Indeed, in the decay of the neutral K meson CP violation has been demonstrated experimentally (C for charge conjugation), leading to a strong hypothesis for T violation by CPT symmetry (Christenson *et al.* 1964; Casella 1969). Ordinarily, for instance in the complex 'chaotic' intramolecular dynamics discussed in §3, one may have a *de facto* T violation, defining a parameter entropy increasing with time (Quack 1984). However, by changing initial conditions this could be reversed, the *de lege* time reversal symmetry being preserved. This is the traditional view of the origin of the second law of classical statistical thermodynamics, following Maxwell, Gibbs and Boltzmann. Quantum intramolecular dynamics (with T violation) could change this. While this is a perfectly open question, it might be amenable to being answered experimentally (on rather long timescales) by the molecular physicochemist, not just a philosophical speculation as old as the word entropy (Clausius 1865).

7. Conclusion

Motto. Were it not for matters of practicality, the application of quantum mechanics to chemistry would be straightforward and its impact immediate and dramatic (Hehre *et al.* 1986).

I have tried in this paper to provide a synopsis of my work – some experiments and some thoughts – on important quantum effects in intramolecular dynamics and unimolecular reactions. Some effects, such as nonlinear intensity dependence in IR laser chemistry or the non-classical wave packet spreading in a strong Fermi resonance, can be considered as perfectly established by experiment. Others, such as those arising from nuclear spin symmetry and parity conservation discussed in §5, should be safe and useful predictions for experiment. Some effects discussed in §6 are

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still speculative. But all these non-classical effects are exciting when confronting experiment and theory.

Many members of my group in Zürich have contributed importantly to the advances reported here, as can be seen from the references. The discussion of H_3^+ in §5 has profited from correspondence with A. Carrington. S. Kaufmann helped with the manuscript. My work is supported financially by the Schweizerischer Schulrat and the Schweizerischer Nationalfonds.

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