Molecular Spectroscopy and Molecular Dynamics: Theory and Experiment

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Current aspects of the field of research are summarized, as defined by the title of this article and the theme of the related, recent discussion meeting, which is the subject of this special issue of Berichte der Bunsengesellschaft für Physikalische Chemie.

1. Introduction

Molecular spectroscopy has an outstanding tradition in relation to the determination of *molecular structure*, this topic being the theme of the monumental set of volumes written by Gerhard Herzberg during the decades situated at the center of our century [1–4]. Of course, dynamical aspects have also been an important topic of molecular spectroscopy for a long period. However, the traditional "dynamical" aspects were mostly related to the determination of spectra and structure of unstable species, again importantly pioneered by Herzberg [5]. We may mention here as an example the discovery and analysis of the spectrum of the methyl radical [6] with many "dynamical" applications including high temperature kinetics and multiphoton ionization [7], infrared laser chemistry [8] and chemical vapour deposition [9]. Another "dynamical" application of spectroscopy is related to the analysis of linewidths. The methyl radical may again serve as an example. Its predissociation linewidth of about 60 cm^{-1} in the 216 nm absorption band [5–7] can be related to a predissociation lifetime of about 88 fs (for CD_3 the corresponding quantities are 8 cm^{-1} or 663 fs, showing a large isotope effect). After four decades of experimental research in these areas an enormous number of similar examples could be given, ranging from femtosecond to microsecond time scales. Finally, the "dynamics" of *molecular motion* has been related traditionally to rotational and vibrational spectra by means of the harmonic oscillator and semi rigid rotor theory of molecular spectra [1–3, 10].

More recently "molecular dynamics" has become a central theme of spectroscopic research along slightly different lines. Now, one is interested in the real time quantum dynamics of polyatomic molecules, isolated in the gas phase, perhaps also including the interaction with a radiation field. One starting point for this development can be found in the experiments and theories of radiationless transitions in polyatomic molecules [11–13]. The concepts developed in the late sixties still influence the whole field.

A second source for the new developments is the experimental and theoretical investigation of the time dependent dynamics of polyatomic molecules under the influence of intense, coherent laser radiation, particularly with infrared lasers, a field which emerged in the seventies initially stimulated by laser isotope separation [14, 15], subsequently as a fundamentally new branch of reaction dynamics [16, 17]. In particular the explicit, time dependent quantum theoretical treatment of the interaction of complex molecular spectra with intense laser fields, introducing concepts such as Floquet-Liapounoff theory, short time, and long time quasiresonant approximations in conjunction with statistical theories [18] have been fruitful until the most recent years. The importance of understanding the complex spectra and dynamics of highly excited molecules has been particularly clear in this branch of research.

Finally, the development of femtosecond molecular spectroscopy and reaction dynamics, particularly in conjunction with molecular beams has had great impact since about the second half of the decade of the eighties of this century [19–21]. The three developments mentioned are, of course, not independent from each other, but have had strong interactions among each other as well as with traditional spectroscopy.

In the preparations for this discussion meeting (originally planned for 1993) it became soon clear that there was enormous enthusiasm from the participants for the theme of the conference, which led to a substantially larger participation than originally expected. This can be traced to the merging of two active fields of research: molecular dynamics and high resolution spectroscopy. While the interaction between theory and high resolution spectroscopy has been traditionally very strong, the new impetus arising from the interplay with kinetics at the most detailed, dynamical level leads also to an increased role for theory in unifying concepts and approaches from the different fields. Also, ab initio quantum chemistry [22] receives a new role, not just as a complement to experiment, but as a unifying theoretical approach to these different areas of endeavour.

The history of this merging of the fields of reaction dynamics and high resolution spectroscopy can be seen quite well by following the evolution of some discussion meetings which may be considered to some extent as predecessor meetings to the present one, and of which there is printed record. The 1981 Faraday Discussion on High Resolution Spectroscopy covered essentially the traditional field in the invited papers [23], with reference to detailed dynamics arising mostly from a few interchanges during the discussion sessions. On the other hand, the meeting on "Energy

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Storage and Redistribution in Molecules" at about the same time was largely dominated by dynamics, although contacts to spectroscopy were established, mostly through theory [24]. A similar statement may be made about the 1982 Jerusalem Symposium of "Intramolecular Dynamics" [25]. The interaction between spectroscopy and dynamics becomes much more visible in the Faraday Discussions 75 on "Intramolecular Kinetics" [26], and 82 on the "Dynamics of Molecular Photofragmentation" [27]. Dynamics and spectroscopy were largely merged by 1987 in the Bunsen Discussion Meeting on "Intramolecular Processes" [28], although theory, particularly ab initio electronic structure quantum chemistry and related developments played only a minor role there. Finally, laser induced short time dynamics emerged in all its beauty in the 1993 Berlin conference on Femtosecond Chemistry, of which there is twofold printed record [21, 30].

The present Discussion Meeting offered a platform for extensive interaction between all branches of theory, high resolution spectroscopy, detailed molecular reaction dynamics and intramolecular kinetics, which was obviously quite extensively used. Although the printed record of the meeting in this issue gives only a partial picture, as obviously not all papers presented orally or as posters were received for print [29], it nevertheless provides a good insight into some of the developments.

The aim of this little survey of the field in our introductory article to this issue is to provide a short personal overview, including in particular also some historical perspectives and the conceptual background. We shall refer also to some work, which is not represented in this special issue, perhaps was not even presented at the conference. We do not at all aim at completeness nor do we provide the record of original papers, when reference to review articles seems to provide a more useful entrance into a subfield. We completely refrain from summarizing or repeating work represented in this special issue. Even less do we wish to give marks to the individual papers which seems sometimes to be a popular habit. Indeed we feel that the work represented in this special issue by the contributing authors speaks for itself extremely well, indeed. We draw attention also to a particularly complete report about this Discussion Meeting, which has been produced quite independently with much enthusiasm by Jörn Manz and which appears separately with many references to work presented actually at the meeting, whether this work is included in this issue or has been published elsewhere [31]. With such a complete and well evaluated literature survey appearing already separately, we can restrict our attention to the more fundamental, complementary aspects.

2. Experimental Developments

Novel spectroscopic experiments and their results have always had a great impact on our understanding of molecular dynamics as derived from spectroscopy. Broadly one may classify advances as arising from the introduction of either *conceptually* new approaches or else new *technology*, which itself may sometimes involve new concepts, of course.

2.1 Experimental Concepts for Deriving Molecular Dynamics from Spectroscopy

2.1.1 Time Resolved "Classical" Kinetic Spectroscopy

By far the most obvious approach to time dependent molecular processes is the short time application of an external perturbation and observation of subsequent changes in time by spectroscopic techniques. If the external perturbation results in a change of temperature, pressure, or electric field and related, macroscopic parameters, one has the now "classic" techniques of $T(P,E)$ jump relaxation kinetics [32, 33]. Shock wave techniques [7, 36] may be broadly classified to fall into this class.

If, on the other hand, one introduces microscopic, molecular changes by an optical excitation, one establishes the similarly "classic" method of flash photolysis, which can be used for studies in reaction kinetics [34, 35], as well as for investigations on the structure of unstable species [5, 6]. Flash photolysis has originally been applied on microsecond time scales and has changed qualitatively by the transition to short time, coherent laser excitation down to the femtosecond domain.

2.1.2 Short Time, Possibly Coherent Spectroscopy into the Femtosecond Domain

While the "classic" techniques investigate global, macroscopic kinetic changes, to the limit of measuring rates of chemical elementary reactions, laser spectroscopy of gases and molecular beams with short time, coherent nanosecond to femtosecond pulses opens a window to measuring detailed molecular and intramolecular processes. While in some cases "slow" nanosecond processes have been found with infrared excitation of gases [37], the true domain of this research is femtoseconds combined with molecular beams [19, 20, 38 – 40]. However, studies in the condensed phase should not be overlooked [41 – 43]. The race for short times is to some extent more dominated by technology than by concepts. However, the femtosecond photolysis studies have allowed us a fresh look at the dynamics of photodissociation from excited electronic states [27, 44, 45]. Often considerable ambiguity arises in the interpretation of time resolved experiments: One knows the fast rates, but not which process they are related to.

2.1.3 Competitive Rate Methods using Fluorescence Spectroscopy

The competitive rates method using the kinetics of change in fluorescence spectra has been a "classic" in the early days of proton and electron transfer kinetics in solution [46]. In relation to intramolecular kinetics and vibrational redistribution in excited electronic states of polyatomic molecules, this concept was widely exploited by Parmenter and coworkers [47, 48]. The competitive rates method has also been used in chemical activation experiments on intramolecular relaxation processes [49] and in high pressure stationary photolysis, using inert gas collisions as a clock [50]. Often it is difficult to be certain about which competing processes are observed.

2.1.4 Stationary Line Shape Analysis in Optical Spectra

Lorentzian optical linewidths Γ(FWHM) can often be related to fast kinetic processes by the simple equation for rate constants k of exponential decay

$$k = \frac{2\pi\Gamma}{h} . \tag{1}$$

Predissociation and related processes are common examples [1 – 4]. More recently, high overtone [51] and molecular beam infrared spectra have been systematically analyzed in terms of vibrational relaxation rates using Eq. (1) [52]. The difficulty again arises from lack of knowledge of the underlying processes leading to some linewidth. Also, homogeneous and inhomogeneous contributions to line shapes must be carefully distinguished [53, 54]. Often it is incorrectly assumed that the Fourier transform of the observed absorption spectrum contains all the relevant information about time dependent molecular dynamics. A critical discussion of this assumption of, mildly speaking, very limited validity can be found in [55] (see also Sect. 5).

2.1.5 Line Shape Analysis in Dynamical NMR Spectroscopy

NMR spectra depend indirectly upon the dynamics of the molecular framework in which they arise. There analysis may reveal kinetic processes [56, 57].

2.1.6 Effective Hamiltonian Analysis of Individual Line Resolved Infrared and Visible Spectra

So-called "eigenstate resolved" spectra may be analyzed by means of simple level coupling model schemes. Such schemes arose already in the theory of electronic radiationless transitions [11 – 13]. Fig. 1 shows such a scheme, which is among the most widely used models, often reproduced. More recently a variety of other coupling situations including statistical coupling models from random matrix theory have been applied to intramolecular dynamics [58 – 62]. Fig. 2 shows another example of such a scheme, which is now often called a tier model. Such models have been used in conjunction with perturbation theory for the analysis of spectra [63, 64]. Since in such level scheme models the actual molecular wavefunction corresponding to a given level is not at all or not accurately known, the "effective" hamiltonian is defined in algebraic terms by means of a coupling matrix but not in terms of a real molecular hamiltonian with basis functions in coordinate and momentum space. The translation from the effective to the true hamiltonian is often not carried out or remains ambiguous.

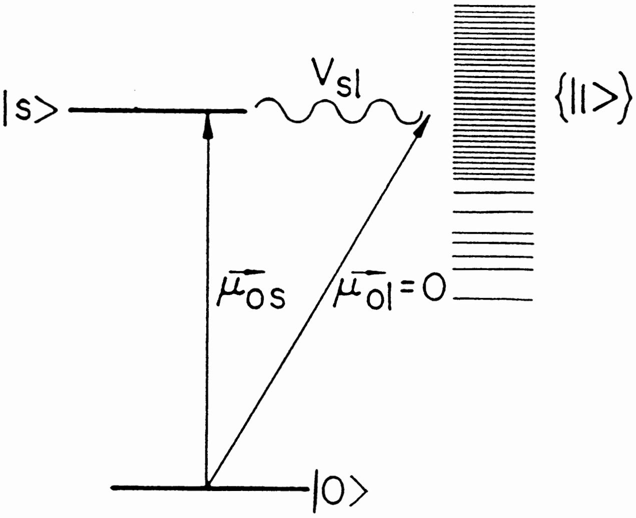


Fig. 1
Level coupling scheme (effective Hamiltonian model) for various types of intramolecular couplings between a ground state $|0\rangle$, with radiative dipole coupling μ to an excited state $|s\rangle$, which is coupled by intramolecular (radiationless) coupling matrix elements to a set of levels $|l\rangle$ (after Bixon and Jortner [11], see also cover paper to Jortner birthday issue of J. Phys. Chem. *98*, 3228 – 3554 (1993) and ref. [13])

In that sense, time dependent processes derived by such schemes (usually as survival probability of some initial state) cannot be related unambiguously to real physical processes, although sometimes an approximate relation can be established by low order perturbation theory.

2.1.7 Extraction of Full Molecular Quantum Dynamics from Spectroscopic Hamiltonians

With the limitations of other approaches having been mentioned, the obvious ultimate goal of spectroscopy might be to derive the complete hamiltonian dynamics from the analysis of high resolution spectra following the abstract scheme

$$\text{Spectra} \rightarrow \text{Hamiltonian} \rightarrow \begin{matrix}\text{Stationary states}\\ \text{and time dependent}\\ \text{dynamics}\end{matrix} \rightarrow \begin{matrix}\text{general}\\ \text{rate processes}\\ \text{and reactions}\end{matrix} . \tag{2}$$

The difficulty with this scheme is to actually realize it accurately. High resolution spectroscopy has often concentrated on stationary state, time independent dynamics, but the more general time dependent dynamics is accessible as well. Some progress towards this goal has been made [65] and we refer to Sect. 5 for more detail.

2.2 Experimental Art and Technology

Experimental technology has greatly evolved as well in molecular sample preparation as well as in the handling of the electromagnetic radiation. While molecular gases in thermal equilibrium are still the routine samples of molecu-

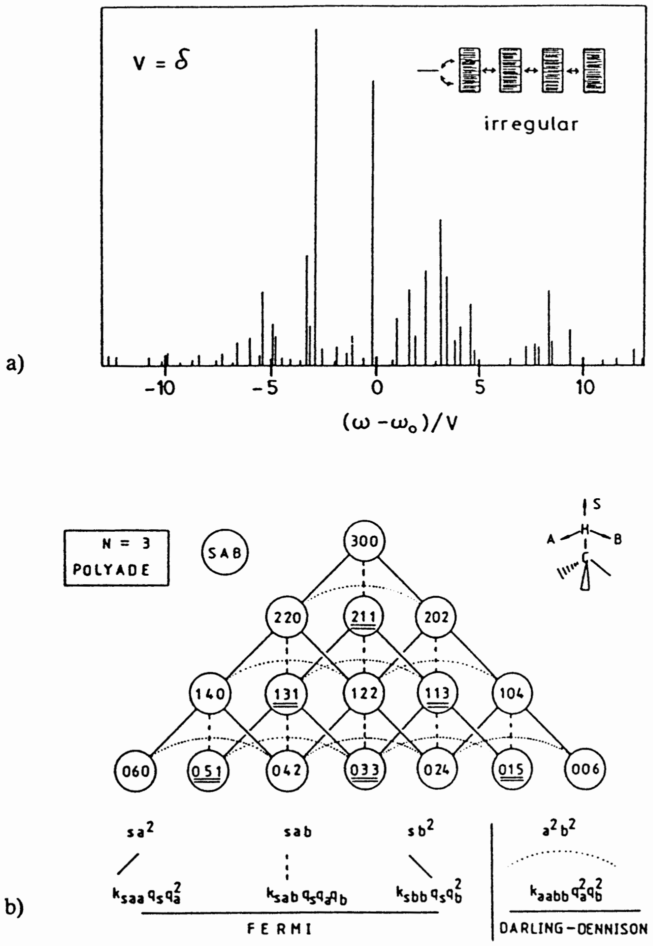


Fig. 2
Sequential level coupling schemes for intramolecular couplings (IVR, intramolecular vibrational redistribution, "tier model"). a) Abstract coupling scheme from an irregular ("random") sequential coupling model with resulting eigenstate-resolved line spectrum (reproduced by permission from Faraday Discuss. Chem. Soc. *71* (1981) 359, Ref. [58]). b) Realization of the abstract level coupling model for IVR in real CHXYZ molecules in a vertical representation of the couplings. The levels are represented by one CH stretching (S) and two CH bending quantum numbers (A and B). The state with radiative coupling to the ground state is $|S,A,B\rangle = |3,0,0\rangle$ on top of the pyramid. This is anharmonically coupled by sequential low order Fermi resonances to other levels with high CH bending excitation as shown. There are also "horizontal" Darling Dennison resonances and symmetry restrictions for C_s molecules (reproduced by permission from Mol. Phys. *53* (1984) 257, Ref. [64])

lar spectroscopy, much progress has been made in the systematic use of molecular beams and supersonic jets as also exemplified by several papers in this issue [66 – 72]. This approach has, in particular, rendered possible the study of gas phase molecular clusters, at the borderline between isolated molecules and liquid or solid phase aggregates, which is among the most fruitful areas of spectroscopic research today [66 – 70, 75, 93]. However, also spectroscopic studies of molecules in low temperature solid matrices or, less widely used, low temperature rare gas solutions [74] should be mentioned.

Experimental generation "treatment", and detection of electromagnetic radiation is obviously a central issue in spectroscopy. Compared to the traditional art [1 – 4] advances may be broadly associated with two major technological advances.

(i) Extension of the use of quasiclassical, coherent electromagnetic radiation generated by means of electronic devices in the radiofrequency and microwave ranges to the optical domain of the spectrum with the invention of MASERS and LASERS.

(ii) Extension of the traditional interferometric spectroscopic techniques by means of computers to become a most powerful spectroscopic tool in the framework of Fourier transform spectroscopy.

Among the many qualitative jumps that have been made by laser spectroscopy, we may just mention the extreme sensitivity reached by laser induced fluorescence [76] in conjunction with beams, MHz resolution, now accessible in the visible [77] or infrared, with particular ease using diode lasers [77 – 81]. Novel spectroscopic schemes using the advantages of lasers are being invented and named with acronyms, such as coherent antistokes Raman scattering CARS, laser induced fluorescence LIF, resonantly enhanced multiphoton ionization REMPI, vibrational predissociation spectroscopy VPS [86], zero kinetic photoelectron spectroscopy ZEKE [82], FDS [89], IRLAPS [71], OSVADPI [72], ICLAS [84], SEP [91], and whatever their names may be. On the detection side, one may also name photoacoustic spectroscopy [83], bolometric detection in beams [52, 73] and, more recently, cavity ring down spectroscopy [9, 85] as sensitive techniques for weak absorptions. The combinations of new techniques such as high resolution FTIR-spectroscopy with supersonic jets [54, 66, 69] also offer obvious possibilities, to name just one example. It is easy to foresee that future experimental art will in part be evolving by invention of various combination schemes and we refer to the papers and reviews cited. The field for inventions of novel spectroscopic tools using lasers and Fourier transform methods is not closed, rather just opened and is one of the most promising for young scientists to enter.

Clearly, also the short time spectroscopy mentioned under the conceptual advances depends largely upon technological developments of short pulse lasers. While the 10 to 100 fs and ps ranges have been reached with some effort using pulsed dye lasers [38 – 42], recent developments in solid state lasers promise much greater ease of application [87]. Also, the zero femtosecond poulse should not be omitted [88], but at this point it may be useful to turn to theory.

3. The Traditional Interplay of Theory and Experiment in Molecular Spectroscopy

There is hardly a branch of physical chemistry for which the interaction of experimental studies with theoretical approaches based on quantum mechanics has been as intense as for molecular spectroscopy. Many pioneers of molecular spectroscopy such as Herzberg, Mulliken, Mecke, Weizel were both experimentalists and theoreticians. Special reference to the work of Mecke has been made in the EUCMOS 22 conference [92]. Besides Herzberg, in particular also R.S. Mulliken had a great impact both on the evolution of molecular spectroscopy and the theory of the chemical bond. One of the most important centers of early computational chemistry was the Laboratory of Molecular Structure and Spectra at the University of Chicago [90].

At a time when electronic computers entered the scene, but were still too slow to allow ab initio calculations on molecules of chemical interest, so-called semiempirical methods were developed, among which that of Pariser-Parr and Pople (PPP) [94, 95] became particularly popular, in which only the π-electron system in conjugated molecules was treated explicitly. The importance of the PPP approach to our understanding of the UV-VIS spectra of conjugated molecules can hardly be overestimated [96–98].

The success of photoelectron (PE) spectroscopy in chemistry [99] was largely based on the fact that it allowed a rather direct theoretical interpretation. In view of Koopman's theorem [100, 101] ionisation potentials could to a first approximation be identified with orbital energies. This identification was often done in a too naive and uncritical way, but it was fortunate that orbital energies can be evaluated relatively easily by standard quantum mechanical methods and that this arose an interest in such calculations. Moreover, methods were developed to go beyond the Koopmans approximation and to get better agreement between experiment and theory [102].

The progress of ab initio theory made also the calculation of force constants and hence of vibrational spectra possible. An increased computational effort was necessary because many points of the potential surface had to be calculated, before one could fit the energy near the minimum as a polynominal in the internal coordinates. A big step forward came with the direct calculation of energy gradients [103] and later even of second and higher derivatives of the energy [104–106]. Force constants obtained from molecular SCF-calculations did not agree too well with the experimental counterparts, but scaling rules were found to enforce the agreement for diagonal force constants [106–108]. The computed off-diagonal force constants turned out to be very useful, because there is often not enough information to get them from experimental data. The comparison between experiment and theory is still today mostly done at the level of harmonic force constants, but there is an increased tendency to shift the comparison to observable vibrational frequencies, or rather rovibronic spectra, at least for small (diatomic to 4-atomic) molecules. For more detail see Sec. 4.2.

Today quantum chemical methods are available that allow the ab initio calculation of rovibronic spectra without adjustable parameters, to almost *spectroscopic* accuracy. For the H_2 molecules this has been possible long ago [109, 110], both for the ground and excited states, although the accuracy is still being pushed further [111–113]. Meanwhile calculations of the H_3^+ ion to cm^{-1} accuracy have become possible [114]. Taking care correctly of adiabatic and nonadiabatic corrections still higher accuracy appears possible [115]. The assignment of the rovibronic transitions in H_3^+ accepted at present [116, 117], is largely based on earlier ab initio calculations [118, 119].

UV-VIS spectra are nowadays accessible to ab initio calculations as well, at least for sufficiently small molecules [120]. One must be able to describe all the electronic states involved in the transition that one is interested in. Interesting complications arise in the presence of crossing of different potential surfaces, e.g. in the case of conical intersections, a topic that is much studied theoretically [121]. Further difficulties arise if relativistic effects such as spin-orbit interactions have to be taken care of [122, 123].

Important aspects in the theory have to do with the fact that the absorption or emission of light is a dynamical process. This has been understood in principle rather early. A rather classical example of dynamic aspects in the theory of molecular spectra is a radiationless transition, which occurs when the energy of an initially populated vibronic level of an excited state is close of a set of high vibrational levels of the ground state [11–13].

Very recently a big challenge to theory came from spectroscopy and photochemistry on the femtosecond time scale, which lead to numerous new applications [21].

4. Ab Initio Theory of Spectra and Dynamics

Although semiempirical methods are still used for the theoretical calculation of spectra of especially large molecules, spectroscopic accuracy is only possible with ab initio methods, although sometimes the results from these are subject to empirical corrections.

4.1 Rotational Spectra

In order to reproduce or to predict rotational spectra theoretically, one mainly needs the moments of inertia and permanent electric dipole moments. These depend usually on the molecular equilibrium geometry and on the energy and the wave function in the neighborhood of the equilibrium geometry. The relevant quantities do not require extremely sophisticated wave functions, although the identification of an unknown species, especially in interstellar space, requires high accuracy. A classical example is the so-called Xogen [124], identified as COH^+ [125].

The rotational spectra of van der Waals complexes are the subject of thorough current studies [68, 93]. Here, it is necessary to relate rotational transitions and the related effective spectroscopic "rotational" constants to properties of a multidimensional potential hypersurface by means of an accurate solution of a multidimensional Schrödinger equation. This is possible, for instance, by Quantum Monte Carlo methods [126]. A similar approach has also been used for the rather more rigid methane molecule, necessitating a treatment in 9-dimensional hyperspace, and resulting in a new understanding of the rotational constants of this molecule as well as the permanent dipole moments of its isotopomers [127].

4.2 Vibrational Spectra

Comparison of theory and experiment is usually done at the level of harmonic vibrational frequencies. Theoretically the harmonic force constants are given as

$$f_{k\lambda} = \left(\frac{\partial^2 E}{\partial S_k \partial S_\lambda} \right)_{S_k = 0, S_\lambda = 0} , \tag{3}$$

where S_k and S_λ are the deviations of some internal coordinates from their equilibrium value 0. From the harmonic force constants the harmonic frequencies are easily obtained by classical mechanics [3, 10]. What one needs to know is hence the energy E as function of the S_k , i.e. the potential hypersurface near the equilibrium geometry. The harmonic vibrational frequencies are not directly observable, but they must be obtained by some harmonization procedure from experimentally observed fundamental frequencies as well as overtone and combination frequencies [128]. This is quite straighforward for diatomic molecules, but nontrivial for polyatomic molecules. It would therefore be desirable to make the comparison not at the level of the harmonic frequencies, but rather at the measurable IR or Raman frequencies. One thus avoids the *harmonization procedure*, but on the theoretical side the dynamics of the nuclei must be treated quantum mechanically in terms of the accurate potential hypersurface rather than its harmonic approximation. This is much harder and so far only possible for rather small (2 to 4 atomic) molecules [129 – 131]. There is currently considerable effort in developing new methods of treating rovibrational dynamics on multidimensional potential hypersurfaces, where we mention numerical grid and DVR techniques [132, 133], as well as quantum Monte Carlo methods, which are applicable at very high dimensions.

If one uses the Hartree-Fock (SCF) approximation for the calculation of harmonic force constants, one usually overestimates the diagonal force constants by something like 10%. Since this error arises rather consistently, a scaling procedure has become popular, if one wants to predict force constants (and harmonic frequencies) [106, 107, 135].

Empirically determined harmonic force constants are usually problematic, since there is not enough input from spectra to determine all diagonal and off-diagonal force constants. Therefore plausible assumptions are made concerning some of the latter. In view of these uncertainties theoretically determined off-diagonal force constants are often very helpful, even if they are from crude calculations and therefore not very accurate, although progress has been made towards more accurate results [135, 136].

The theoretical determination of vibrational (and rovibrational) spectra with spectroscopic accuracy (and without scaling rules or other empirical adjustment) requires highly sophisticated quantum chemical methods. For H_2 and its isotopomers perfect agreement between theory and experiment has been achieved, i.e. the differences are of the order of $10^{-2}\,\mathrm{cm}^{-1}$ [111, 112]. In order to achieve this not only extremely accurate Born-Oppenheimer wave functions with explicit r_{12}-dependent terms were necessary, but also the evaluation of adiabatic and non-adiabatic corrections, and even relativistic effects.

For the next-more complicated molecule, the H_3^+ ion with 2 electrons and three nuclei one has by now achieved an accuracy of the Born-Oppenheimer surface of about $1\,\mathrm{cm}^{-1}$ and got the lower rovibronic intervals accurate to a few tenth of $1\,\mathrm{cm}^{-1}$ [114, 130, 137]. The agreement between theory and experiment will presumably be improved if non-adiabatic corrections are taken care of appropriately [115].

The calculation of infrared intensities requires the knowledge of the dipole moment as function of the internal coordinates, while for Raman intensities the electron polarizability as function of the S_k is needed. Such calculations are currently being done more frequently than in the past [127, 138].

4.3 UV-VIS Spectra

While for rotational vibrational spectra only the potential energy surface of the ground state is needed, the electronic spectra depend on the potential energy surface of ground and excited states. This is computationally much more demanding and it is therefore not surprising that accurate theoretical studies of these spectra are limited to very small (mostly diatomic molecules). The construction of wave functions and energies of the ground state and various excited states can either be done in one step – by means of configuration interaction (CI) [120, 139] – or from independent calculations. In either case it is very important to start with a balanced basis and a balanced selection of configurations. Independent calculations of ground and excited states are recommended only if these states have different symmetry. There are approaches where instead of computing two states one tries to get the energy difference of these states directly [140 – 143]. Such methods have been more popular in the theory of PE rather than UV-VIS spectra.

For very small molecules entire vibrational contours of electronic transition bands can be calculated. It is more common, especially for large molecules, to calculate only the vertical transition energies and to correlate these with maxima of observed bands.

Although the distinction is not always clearcut, it makes sense to distinguish between valence- and Rydberg excited states. The two kinds of states are often better characterized by theoretical than by experimental data [144].

In chiral molecules the absorption intensity of some UV-VIS bands are different for left or right circular polarized light. This arises if the electric and magnetic transition vectors are not perpendicular [146]. The qualitative and quantitative theory of this "circular dichroism" looks rather promising [147]. Much progress has also been made in the understanding of vibrational circular dichroism (VCD [146, 158]).

Particularly interesting are excitations from a low lying state to excited states, which are not bound but can rather be classified as resonances. The traditional quantum chemical methods then fail, but other, powerful techniques are available, like that of complex scaling.

4.4 Photoelectron Spectra (PE, XPE)

Photoelectron spectra relate the ground states of neutral molecules to the ground state and the excited states of its ion. In principle, similar theoretical techniques as for UV-VIS spectra can be used. A nice feature of PE spectra is that in view of Koopman's theorem the measured ionization potentials can to first order be identified with the orbital energies of the Hartree-Fock approximation for the neutral ground state. Corrections to the Koopman's energies can then rather conveniently be obtained by propagator methods [102].

4.5 ESR, NMR and NQR Spectra

The theory of the parameters of ESR, NMR or NQR spectra is highly developed. However, since these aspects have not been discussed at the present meeting, we shall not go into details.

The hyperfine splitting of ESR spectra of radicals is directly related to the spin density at the respective nuclei [148]. In the theoretical evaluation of the spin density two difficulties arise. The one is that in terms of Gaussian basis sets, which are currently used, the wave functions at the position of the nuclei are not very accurate and converge only slowly with increase of the basis size. The other, more serious difficulty is that especially in π-radicals on the lowest level of theory the spin density at the respective nucleus vanishes, such that higher order effects, mainly so-called spin polarization and effects of nuclear motion become decisive. Various contributions to spin-polarization have often opposite sign and cancel each other to a large extent [149]. Nevertheless, substantial progress in the theoretical calculations of hyperfine interaction has been achieved recently [150–152].

The key quantities in NMR are the chemical shift and the indirect spin-spin coupling. Very reliable calculations of the chemical shift (or more generally the nuclear shielding tensor) have become possible in the last ten years and have served as a powerful tool for the elucidation of molecular structure [153, 154]. Attempts towards a quantitative theory of spin-spin coupling constants are more recent, but promising as well [155].

NQR experiments are mostly done in the solid state, so NQR is not genuinely "molecular" spectroscopy. However, a molecular property is often measured, namely the interaction of the field gradient at a nucleus with its quadrupole moment. The ab initio calculation of field gradients is rather straightforward. The least certain quantity has often been the nuclear quadrupole moment, such that from a combination of measured NQR spectra and theoretical field gradients improved values of the nuclear quadrupole moments could be obtained [145, 156].

4.6 Dynamical Aspects of Molecular Spectra

In the mathematical theory of quantum mechanics the *spectrum* of an operator is the set of its eigenvalues, i.e. of the expectation values of its stationary states [157]. The traditional interpretation of spectroscopy is accordingly a technique to measure differences between eigenvalues. In this interpretation spectroscopy is essentially time independent. A first hint of the limitation of this interpretation came from fluorescence spectroscopy. Often excited molecules – unlike isolated atoms – do not decay by emission of light, but prefer a *radiationless* decay. Sometimes the radiationless transition leads back to the ground state, but often a photochemical process like dissociation or isomerization takes place. There are obviously various processes that compete on a real time scale. Hence molecular spectroscopy cannot be considered independently of photochemical or photophysical dynamics. Of particular recent importance are the efforts related to the understanding of very highly excited electronic "Rydberg" states, where electronic and nuclear dynamics occur on similar time scales or even with electrons becoming the "slow" partners in the motion [13, 159].

5. Time Dependent Intramolecular Quantum Dynamics: Spectroscopic Experiment and Theory

The stationary states ideally observed by spectroscopy are obviously, even by definition, time independent except for natural line broadening by spontaneous emission or perhaps predissociation and related effects, if applicable, which in the low energy part of the spectrum take place on very long time scales, often seconds to milliseconds at best. Yet, short time molecular processes do exist, and we shall provide here a brief summary of some current aspects of such short time phenomena as derived from spectroscopy.

Time Dependence can Arise in two Ways

(i) By choice of an appropriate initial condition in the ideally isolated molecule;

(ii) By interaction with an external perturbation, in particular the radiation field.

We use the theoretical description with the time evolution operator $\hat{U}$, which indeed solves all the relevant quantum mechanical equations of motion, such as time dependent Schrödinger equation for the wave function $\Psi(t)$, Liouville-von Neumann equation for the density operator $\hat{\rho}$ or Heisenberg equation of motion for some observable $\hat{Q}$ such as generalized coordinates and momenta.

$$\Psi(t) = \hat{U}(t, t_0)\,\Psi(t_0) \tag{4}$$

$$\hat{\rho}(t) = \hat{U}(t, t_0)\hat{\rho}(t_0)\,\hat{U}^{\dagger}(t, t_0) \tag{5}$$

$$\hat{Q}(t) = \hat{U}^{\dagger}(t, t_0)\hat{Q}(t_0)\,\hat{U}(t, t_0)\ . \tag{6}$$

$\hat{U}(t, t_0)$ results from the solution of the differential equation

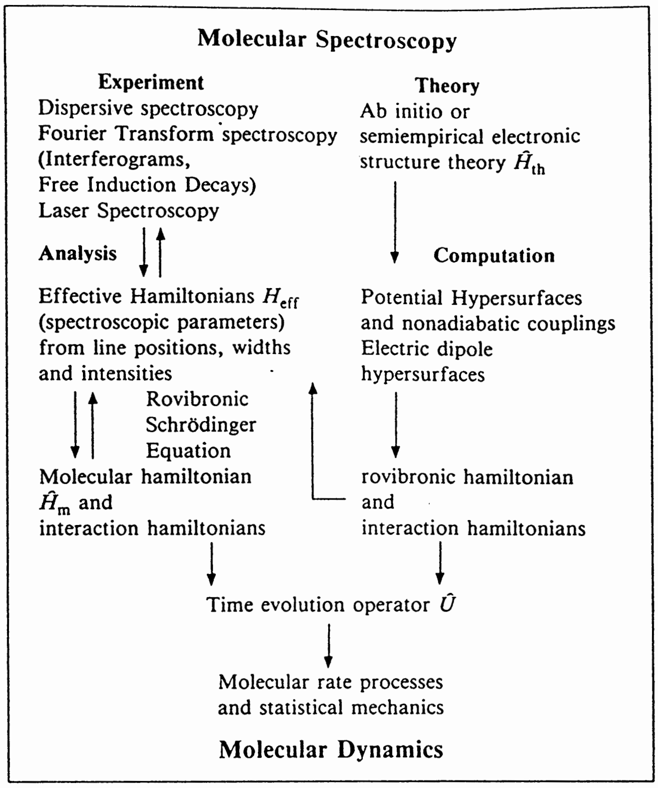
$$\mathrm{i}\left(\frac{h}{2\pi}\right)\frac{\partial \hat{U}}{\partial t} = \hat{H}\hat{U} \; . \tag{7}$$

For the isolated molecule case (i), $\hat{H}_\mathrm{m}$ *is time independent*, and thus one finds simply

$$\hat{U}(t,t_0) = \exp\left(-2\pi\mathrm{i}\hat{H}_\mathrm{m}t/h\right) \; . \tag{8}$$

For the case (ii) with a general *time dependent Hamiltonian* from an external perturbation, one must solve Eq. (7) explicitly by some means.

Eqs. (4 – 8) contain the essence of what needs to be said about time-dependent molecular quantum dynamics in general, and it is now necessary to enter into some more detailed consideration of the relation to molecular spectra. For the isolated molecule case, the key to understanding time dependent dynamics according to Eq. (8) is obviously the hamiltonian $\hat{H}_\mathrm{m}$. For the case of the interaction with some external perturbation, one needs in addition to $\hat{H}_\mathrm{m}$ the interaction hamiltonian, which mediates the interaction with the environment. For radiative excitation in the optical domain, this is usually dominated by the electric dipole contribution, to give a specific example, but one may also have magnetic dipole, electric quadrupole and higher order interactions. $\hat{H}_\mathrm{m}$ as well as the various interaction hamiltonians can, indeed, be derived from spectra.



Scheme 1

5.1 High Resolution Spectra and their Theoretical Analysis in Time Dependent Terms

Scheme 1 summarizes the general approach from either experiment or theory, much of which is self explanatory (see also [160] for a related scheme). It may be useful to comment on some steps in this scheme. In experimental molecular spectroscopy we start from the spectrum obtained either in the frequency domain or in the corresponding Fourier transform domain, either time Fourier transform (free induction decays [57]) or interferograms as space Fourier transforms [54] or other, related observations. Already at this step often serious misconceptions arise in that the Fourier transform representations of the frequency spectrum are assumed to be "molecular dynamics", which is definitely not the case. All these representations are simply equivalent forms of the empirical molecular spectrum. This has been known to some for a very long time, our comment being nevertheless necessary, because the literature is full of misleading statements in this respect.

In order to extract *dynamics* from the spectrum (or also *structure*, for that matter), an *analysis* of the spectrum is necessary, leading usually to an understanding in terms of the effective hamiltonian parameters, or spectroscopic constants. These parameters include usually a partly predictive description of line positions, line intensities, possibly also effective linewidths. In most cases spectroscopic analysis for semirigid molecules stops here and relates these parameters by low order Taylor expansions of the potential around the equilibrium position and perturbation theory to molecular structure and dynamics including adequate, careful formulations of the underlying molecular hamiltonian [1 – 4, 161 – 166]. This procedure has been understood to fail for highly nonrigid molecules, van der Waals and hydrogen bond clusters, where one must proceed to a complete variational or other solution of the multidimensional rovibronic Schrödinger equation [65, 75, 93, 132]. A striking discovery of the last decade was the finding [54, 65, 167], that the standard perturbation theory approach fails badly also for rather common, rigid but strongly anharmonic systems, such as the coupled CH stretching and bending motions, where again complete rovibrational dynamics must be considered in order to establish the "true" spectroscopic molecular hamiltonian $\hat{H}_\mathrm{m}$, related to the potential hypersurface in the Born-Oppenheimer approximation. It is still not clear, whether for more weakly anharmonic "typical" molecular systems perturbation theory is not perhaps more generally valid [135]. Once $\hat{H}_\mathrm{m}$ (and the electric dipole and other interaction hamiltonians) are established, and *only then*, may we proceed to obtain complete molecular dynamics through the time evolution operator. An early result in terms of "spectroscopic" femtosecond wavepacket motion in coordinate space may be cited here [191], but there are still relatively few complete experimental investigations along those lines (reviewed in [54, 55, 65]). Most experimental results on dynamics have still been obtained along the more traditional lines from effective hamiltonians, line widths and related quantities. The frequently presented "survival probability" of some zero order "bright state" can be formulated in terms of an effective hamiltonian level scheme [55, 58, 61]. Also, the step from experiment to some molecular hamiltonian is usually not straightforward or unambiguous.

The theoretical route in contrast is much more straightforward, starting with the formulation of some ab initio or semiempirical electronic structure theory and proceeding to potential hypersurfaces and nonadiabatic couplings, if desired. From there one may proceed to compare with experimental spectra either through low order Taylor expansions of the potential and perturbation theory or by means of the complete solutions of the rovibronic Schrödinger equation, obtaining in the end energy levels and stationary state wave functions. Alternatively, one may proceed to obtain time evolution again through $\hat{U}$. Of course, classical [168, 169] and semiclassical [170 – 172] approximations to dynamics can be useful.

Numerous types of rate processes can be investigated following this general abstract scheme. We shall turn here to one current example intramolecular vibrational (rotational) redistribution (IVR and IVRR).

5.2 IVR and IVRR: Redistribution or Relaxation?

The question of IVR and IVRR originated from the kinetics of unimolecular reactions, vibrational predissociation and the theory of mass spectra [4, 173 – 180]. To start with, it can be formulated in very simple terms: Given some initial vibrational excitation in a vibrational mode (which may be a normal mode) of a polyatomic molecule, how does the amplitude of vibration change with time, if anharmonic coupling is important, how does the amplitude of vibration in another mode change with time during this process? How does the extension of some coordinate change, which may lead to reaction (predissociation or isomerization)? This is the question of *vibrational redistribution* of the initial excitation. In statistical theories of unimolecular reactions, such as quasi-equilibrium theory (QET) [175], RRKM theory [174], or the adiabatic channel model (ACM) [177, 179, 180], one furthermore assumes that after some time a microcanonical intramolecular quasi-equilibrium is attained, with a characteristic relaxation time τ_{relax} for establishing this equilibrium. This is the question of intramolecular vibrational *relaxation*. The microcanonical quasiequilibrium is characterized by average populations $\langle p_k \rangle$ for all nondegenerate quantum states at energy E being proportional to the reciprocal density of states

$$\langle p_k \rangle = \alpha \rho(E)^{-1} \ . \tag{9}$$

While this expression was first understood to apply to *vibrational* equilibration and vibrational (and vibronic) densities of states [174, 175], a more careful consideration of rovibrational couplings (due to Coriolis and related forces) lead to a similar formulation with a density of states for a given total angular momentum J and other good quantum numbers Γ, as originally presented in [179]:

$$\langle p_k(E, J, \Gamma \ldots) \rangle = \beta \rho(E, J, \Gamma \ldots)^{-1} \ . \tag{10}$$

We may talk about intramolecular vibrational-rotational redistribution (IVRR). As good quantum numbers Γ on short time scales one should mention in particular also nuclear spin symmetry and parity [181]. This is now widely accepted knowledge. The approximate calculation of the relevant densities of states does not pose any serious problems [181 – 183]. Also, the question of the possibility of relaxation towards a quasimicrocanonical equilibrium in a discrete spectrum of bound states has found its practical answer [11, 184, 185], as a phenomenon on time scales short compared to the recurrence time, the latter being exceedingly large for polyatomic molecules of even rather modest size.

Still the question recurs, what IVR might mean in the case of a stationary state. The anwer to this is twofold. First, if the density of states is low enough to talk in a meaningful way about stationary states, then IVR(R) is reflected by the wavefunctions for these states resulting in a "redistributed" widely delocalized probability density, which is very different from a density resulting from separable oscillator dynamics. The concept of the "global vibrational state" has been introduced in this context [58]. It is clear that for stationary states, "redistribution" in this sense can be defined, while time dependent relaxation cannot. This is one of the reasons why "redistribution" as term is being preferred by part of the community in reading the symbol IVR, because it is more general.

Second, for large polyatomic molecules the densities of states become so high that the concept of a stationary state looses its usefulness (their energies overlap within their natural linewidths) and relaxation may become a general phenomenon.

The fundamental existence of IVR in polyatomic molecules still leaves the question of the detailed mechanisms and rates open. We shall comment here just on a few results from current discussion. One mechanism *inhibiting* IVR is discussed to be the heavy atom blocking effect [186] resulting in *slow* IVR. This effect can be understood already in terms of a simple normal model of a molecule XY_n with identical light atoms Y and heavy central atom X [3]. It is easily seen that a local excitation of an XY bond will remain localized for relatively long time if the mass of X is increased. This phenomenon has been discussed widely also in the local mode model of molecular vibrations [187, 188]. Since this "redistribution" happens also in a completely separable oscillator system (or in a "stable" oscillator system in the KAM sense [58, 189]), one may question its association with IVR. However, in practice, it will occur in conjunction with the other mechanisms for nonseparable systems, and then it will contribute to IVR. A second mechanism leading to *fast* IVR is the sequential coupling through a series of low order resonances [58, 63]. This has been shown to operate on the 100 fs time scale for highly excited CH stretching vibrations [58, 63] and has been used also for longer time processes, using low order

Taylor expansions [60]. While there is little doubt about the *qualitative* mechanistic validity of such expansions, the quantitative treatments need relatively sophisticated approaches, showing the importance of very high order terms in the potential expansion in rectilinear normal coordinates (or otherwise in the kinetic energy) [54, 55, 167].

One of the most important developments of the last decade is the understanding of the wide range of possible time scales for IVR. Whereas two decades ago, the common assumption in the reaction kinetics of highly excited molecules was universally fast redistribution on the subpicosecond to a few ps timescale, we have learned that there are substantial variations with a strong separation of time scales within one molecule [71, 190] and also very different behaviour for different types of chemical groups [65, 160]. We may refer here just to the great difference between the highly excited alkylic and acetylenic CH, which have found the attention of several research groups. In the original investigations it was suggested that the dominant channel in producing fast IVR, was the 1 : 2 CH stretch bend Fermi resonance, mediating further redistribution [63, 64]. If one could suppress this channel, for instance by strongly decreasing the CH bending frequency, as is the case in acetylenes with $\tilde{\nu}_{\text{bend}} \lesssim 700\,\text{cm}^{-1}$, then one should decrease the efficiency of IVR, an effect which was promptly established experimentally [53], on the basis of this perhaps somewhat simplistic reasoning. Fig. 3 shows spectra of the high overtone regions of heavily substituted fluorinated alkyl and acetylenic compounds [192, 193]. Whereas the alkyl CH overtone shows a very broad resonance structure, extended over more than $500\,\text{cm}^{-1}$, the acetylene gives a single vibrational band of less than about $10\,\text{cm}^{-1}$ largely inhomogeneous width, still showing shoulders from the rotational PQR envelope. In the CH stretching fundamental of the acetylenic compound a bound to the lifetime could be given from a temperature dependent analysis, $\tau \gtrsim 10$ to 20 ps with considerable uncertainty towards longer times [53, 194]. More recently this bound could be much extended by the beautiful bolometric molecular beam spectroscopy of the Princeton group [52] to $\tau \gtrsim 60$ ps [195]. This is to be contrasted with the subpicosecond lifetimes of the alkyl CH stretching due to Fermi-resonance with bending (the time evolution being nonexponential). Table 1 provides a summary of some current alkyl and acetylene CH lifetimes. While there is also some individuality to the evolution (not exhibited in detail in the table for the alkyl compounds), the differences between alkyl and acetylene CH are clearcut. The mechanism blocking fast IVR for the acetylenes has been discussed to be an effective, vibrationally adiabatic separation of the high frequency CH stretching mode from the low frequency modes [53, 200]. This adiabatic separation breaks down due to Fermi-resonance, if the CH bending frequency is raised to be close to about half the stretching frequency. The anharmonic coupling constants are otherwise rather similar for both cases. It may be noted, that a similarly efficient adiabatic separation of high frequency HF stretching modes ($4000\,\text{cm}^{-1}$) from the low frequency bending motions ($\lesssim 400\,\text{cm}^{-1}$) has been discussed

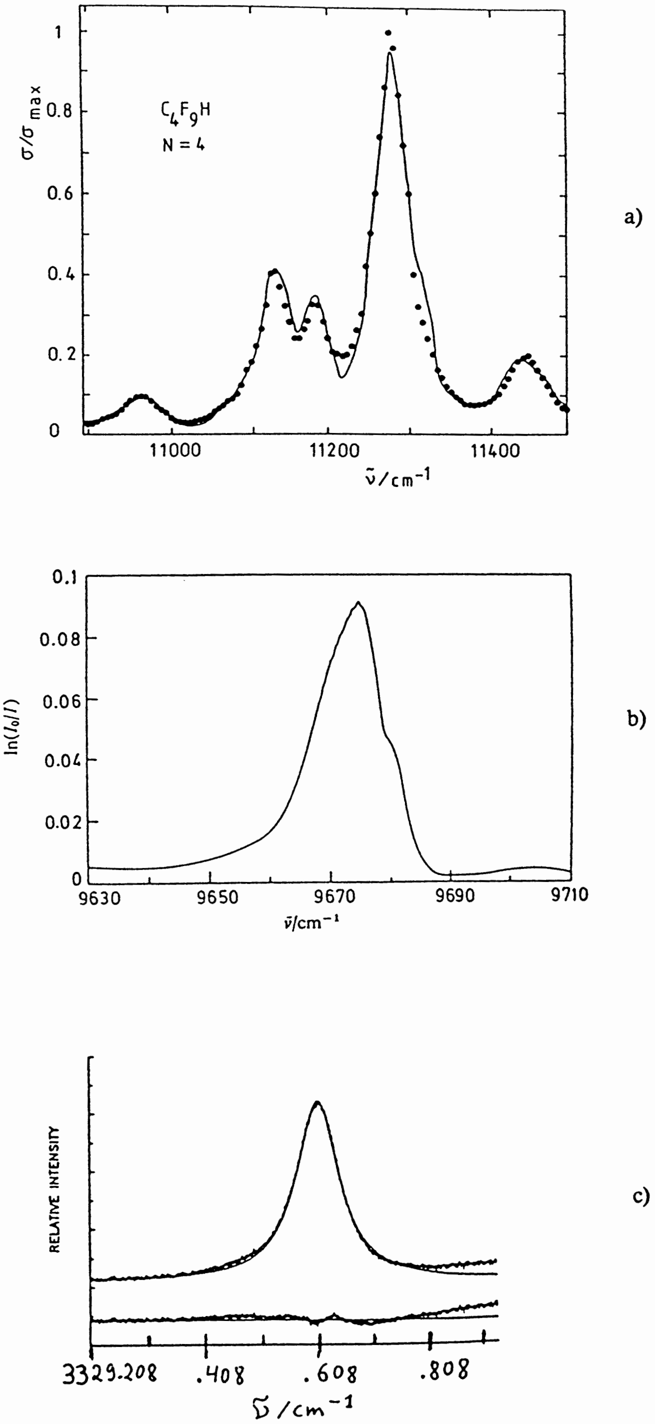


Fig. 3
Spectra of the CH chromophore in large, fluorinated molecules (note the very different wavenumber scales for the examples). a) N = 4 polyad (corresponding to 4 quanta of CH stretching) in $(CF_3)_3CH$, showing the characteristic very wide and broad mostly homogeneous multiplet structure arising from ultrafast fs IVR in the alkyl-CH chromophore (the points are from a theoretical fit procedure), (from Ref. [192]). b) N = 3 acetylenic≡CH stretching overtone in $(CF_3)C-C{\equiv}C-H$ showing a single, relatively narrow band, with reminiscences of PQR structures at room temperature, the remaining width being still largely inhomogeneous, corresponding to a long lifetime of CH stretching excitation (from Ref. [193]). c) N = 1≡CH stretching fundamental Q-branch in $(CF_3)_3C\ C{\equiv}CH$ measured in a beam at low temperature, the full line being a fit with a Lorentzian of a width of about $0.1\,\text{cm}^{-1}$ FWHM (after Ref. [195] by permission)

Table 1
Typical IVR lifetimes of initial CH stretching excitation in alkyl and acetylene compounds estimated from spectroscopic data (see reviews [52, 54, 160] for further tables)

Example	τ_{IVR}/ps	Method and reference
alkyl CH	<0.1^{a})	effective hamiltonian H_{eff} dynamics
X_3CH		[54, 160, 192] or real molecular
$(X=D, F, Cl, Br, CF_3)$		hamiltonian dynamics H_{mol} in subspace [160, 191, 196]
XF_2CH	<0.1^{a})	H_{eff} [63, 64, 160]
X_2FCH	<0.1^{a})	or
$(X=D, Cl, (CF_3))$		H_{mol} [133, 160, 197)
Acetylene CH		
$(CX_3)_3CC{\equiv}CH\,(X=F)$	≥ 10 to 20	temperature dependent lineshape [194]
$(v=1)$ $(X=F)$	≥ 60	molecular beam linewidth, bolometric [195], [52]
$X=H$	>200	molecular beam, bolometric [52] linewidth
$X=D$	≥ 40	molecular beam, bolometric [52] linewidth
$(CH_3)_3Si-C{\equiv}C-H$ $(v=1)$	inhomogeneous ≥ 2000	FTIR, temperature dependent [216] bolometric [217]
$CH_3CH_2C{\equiv}C-H$	≥ 269	Statistical H_{eff} (band structure [198, 199])

^{a}) Detailed dynamics (nonexponential) obtained from 10 to 1000 fs.

to be the origin of long lifetimes for vibrational predissociation in $(HF)_2$ [201].

Another mechanism promoting IVR has been related to the presence of internal rotors (such as methyl rotors) in the molecules exhibiting IVR in the electronic ground or excited states [47, 48, 61]. It is clear also from Table 1, that the mere presence of the internal rotor in the molecule is insufficient for promoting IVR. Some close neighborhood with the group under consideration, steric or special electronic effects must be present, and we refer to [48, 61] (in this issue) for further detail and references. In any case IVR(R) is expected to be a fruitful field of research in the future, due to the variety effects to be discovered still.

5.3 Outlook on Coherent Optical Excitation in Molecular Spectra and Possibilities for Control of Molecular Dynamics

The control of molecular dynamics by frequency selective and coherent laser excitation in complex molecular spectra has been a goal from the early days of laser chemistry [202]. While the control of *intermolecular selectivity* [203] has been achieved, with the example of isotope separation [14, 15], much subsequent work being reviewed in [203], *intramolecular selectivity* (or "mode selectivity") was searched for but repeatedly rejected (see [16, 203] for reviews). More recently there has been some experimental success [204] and a very large body of theoretical work. Broadly the approaches can be classified according to two types

(i) Selective excitation of spectroscopic "eigenstates" or at least selected vibrational states with specific properties, using one photon [204] excitation or multiphoton excitation [205–207].

(ii) Coherent generation of superpositions according to some selection scheme with localization of the molecular wavepacket either in electronic ground [196, 208] or excited states [45, 209].

These general schemes have more recently been supplemented by very specific considerations concerning optimized pulse shapes of the exciting radiation to achieve control [210–212]. In this issue we find the work by de Vivie [213] and Manz and coworkers on this topic [214]. Often, simply going to short times may lead to success [19]. For quite a different aspect of control we refer to the article by Letokhov [225]. One may expect in the future much progress in this field. When one wants to go beyond simple theoretical models, a good understanding of the response of the truly complex spectra of real molecules under the influence of coherent radiation is primordial including methods of solving the explicitly time dependent Eq. (7) for the molecular dynamics as has been noted early on [17, 18]. Without such understanding, there will be no systematic control.

With respect to theoretical numerical methods of solving the quantum dynamical equations of motion, there has been much work over the last two decades. We may mention the treatments allowing for explicit inclusion of the interaction with coherent radiation fields both for long and short time propagation [18], part of which exists as program package [218] (see also the review of the early work in [17]). Other work includes mostly aspects of short time propagation [219–221]. Since there has been growing interest in numerical methods for time dependent quantum dynamics, there are books and special issues available covering the work of several research groups [222, 223]. With reference to [21] and [215], where several chapters provide in depth reviews of the current status of this field we close this section.

5.4 Outlook on Past and Future Phases in Research on Molecular Dynamics and Kinetics

The first phase of molecular kinetics can be broadly classified as the elucidation of reaction mechanism and rates by the traditional indirect methods of reaction kinetics: Mechanism can be suggested and tested but not proven, rate constants for elementary chemical reactions are obtained indirectly from overall rate constants and described by the Arrhenius law. All such knowledge remained uncertain, although in simple cases rather firm conclusions on molecular mechanisms and rates were possible. Unstable intermediates were inferred indirectly.

The second phase of molecular dynamics started about in 1950 with the work of Eigen, Norrish and Porter, and Herzberg. Spectroscopy is used to detect unstable intermediates directly and it is possible, sometimes, to measure directly the rate of elementary reactions, proving certain reaction mechanisms directly, in simple cases.

The third phase of molecular dynamics was governed by molecular beam techniques. Single molecular collision events are the central theme in this phase, but also unimolecular photodissociation and collision free multiphoton excitation and dissociation of individual molecules. In this phase certainly most of the overall *molecular* mechanism in an elementary reaction could be inferred from the reaction products detected long after the reaction by molecular beam time of flight, laser induced fluorescence and other sensitive detection schemes. Molecular spectroscopy has a secondary role here, mostly as a detection technique. While the observations from detailed detection of reaction products certainly provide much information about the reaction process itself, this information is indirect, very much like observing children from a marriage in order to conclude about the properties of a marriage – certainly a useful method, but certainly indirect [226].

The fourth phase of molecular dynamics, which we have entered now, deals with direct observations, again by spectroscopy, of the detailed molecular quantum dynamics, by either by analysis of hamiltonian dynamics or by inferring properties of molecular potentials near transition structures governing the rate determining steps at the most detailed molecular level. As is to some extent becoming clear also from the record of this meeting, at this stage molecular spectroscopy will provide the deepest insights into dynamics including possibilities for detailed molecular control by radiation. The questions we ask today are: what is the nature of molecular quantum motion in highly excited molecular states or collision complexes? What is the relation between molecular structure and chemical properties and such motion? Can one use knowledge of this motion to construct molecular machines? Are such construction principles already used in natural biochemical processes? Answering some of these questions is the challenge for the coming years.

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Appendix: On a aspect of language in spectroscopy and a proposal of an SI unit and name for the quantity wavenumber.

The quantity wavenumber (1/wavelength) has the commonly used unit cm^{-1} in molecular spectroscopy. In a humorous evening session a statistics of the speaker's usage was presented, showing that cm^{-1} is most frequently pronounced "wavenumber" again, which is an abuse of language (the "wavenumber of the radiation is 10 wavenumbers" is clearly as meaningless as "the wavelength of the radiation is 350 wavelengths"). As a remedy it was suggested to introduce an easy to pronounce unit, at best being consistent with SI [224]. Also one would wish to distinguish between wavenumber $\tilde{\nu} = 1/\lambda$ and wavenumber $k = 2\pi/\lambda$.

A closely analogous situation (but not as bad) existed with respect to frequency in the past. This was solved by introducing the now accepted Hertz ($1\ \mathrm{Hz} = 1\ \mathrm{s}^{-1}$) exclusively for ordinary frequency ν (not for angular frequency $\omega = 2\pi\nu$). The choice was an easily pronounced name of a highly regarded physicist.

In molecular spectroscopy on obvious choice of a name for the unit of the quantity wavenumber would be Herzberg, who has shaped our field. However, it will not be possible to have this in use parallel to Hertz for frequency, because of obviously problematic confusions. A possible useful name might be $1\ \mathrm{Berg} = 1\ \mathrm{m}^{-1}$ for the SI unit of regular wavenumber $\tilde{\nu} = 1/\lambda$ (not to be used with $k = 2\pi/\lambda$, for which the use of m^{-1} would be continued). One may note that Berg (Bg) has the meaning "mountain" (in German), which lends itself to counting the number of "mountains" of the wave per unit length. It also retains at least some relation to Herzberg. The cm^{-1} will be the hectoberg, using standard prefixes ($1\ \mathrm{cm}^{-1} = 1\ \mathrm{hBg}$). One can easily extend this to kiloberg, megaberg and even gigaberg (but also milliberg and femtoberg will be possible at ultimate resolution). Even if this proposal is not ultimately accepted it provides some fun. If it is accepted the most frequently used units will be Hertz and Berg.

References

[1] G. Herzberg, Molekülspektren und Molekülstruktur, Theodor Steinkopff Verlag, Dresden/Leipzig, 1939.

[2] G. Herzberg, Molecular Spectra and Molecular Structure Vol. I, van Nostrand, Toronto, 1950.

[3] G. Herzberg, Molecular Spectra and Molecular Structure Vol. II, van Nostrand, Toronto, 1945.

[4] G. Herzberg, Molecular Spectra and Molecular Structure Vol. III, van Nostrand, Toronto, 1966.

[5] G. Herzberg, The Spectra and Structures of Simple Free Radicals. An Introduction to Molecular Spectroscopy. Cornell University Press, Ithaca, N.Y. 1971 (Einführung in die Molekülspektroskopie. Die Spektren und Strukturen von einfachen freien Radikalen, Dietrich Steinkopff Verlag, Darmstadt 1973).

[6] G. Herzberg and J. Shoosmith, Can. J. Phys. *34*, 523 (1956); G. Herzberg, Proc. R. Soc. (London) *262A*, 291 (1961).

[7] a) K. Glänzer, M. Quack, and J. Troe, 16th Symposium (International) on Combustion, p. 949–960, The Combustion Institute, Pittsburg 1977; Chem. Phys. Lett. *39*, 304 (1976).
b) J. Danon, H. Zacharias, H. Rottke, and K.H. Welge, J. Chem. Phys. *76*, 2399 (1982).

[8] H. Groß, Y. He, M. Quack, A. Schmid, and G. Seyfang, Chem. Phys. Lett. *213*, 122–130 (1993).

[9] F. Zalicki, Y. Ma, R.N. Zare, E.H. Wahl, J.R. Dadamino, T.G. Owano, and C.H. Kruger, Chem. Phys. Lett. *234*, 269 (1995).

[10] E.B. Wilson, J.C. Decius, and P.C. Cross, Molecular Vibrations, McGraw Hill, New York 1955.

[11] M. Bixon and J. Jortner, J. Chem. Phys. *48*, 715 (1968).

[12] J. Jortner, S.A. Rice, and R.M. Hochstrasser, Adv. Photochem. *7*, 149 (1969).

[13] J. Jortner and M. Bixon, Berichte Bunsenges. Phys. Chem. *99*, 296 (1995).

[14] R.V. Ambartzumian, Y.A. Gorokhov, V.S. Letokhov, and G. Makarov, JETP Lett. *21*, 171 (1975); R.V. Ambartzumian and V.S. Letokhov, Acc. Chem. Res. *10*, 61 (1977).

[15] J.L. Lyman, R.J. Jensen, J. Rink, G.P. Robinson, and S.D. Rockwood, Appl. Phys. *27*, 87 (1975).

[16] P.A. Schulz, A.S. Sudbo, D.J. Kraijnovitch, H.S. Kwok, Y.R. Shen, and Y.T. Lee, Annu. Rev. Phys. Chem. *30*, 379 (1979).

[17] M. Quack, Adv. Chem. Phys. *50*, 395 (1982).

[18] M. Quack, J. Chem. Phys. *69*, 1282 (1978).

[19] A.H. Zewail, Ber. Bunsenges. Phys. Chem. *99*, 474 (1995).

[20] M. Gruebele, G. Roberts, and A.H. Zewail, Phil. Trans. R. Soc. London *A332*, 223 (1990).

[21] J. Manz and L. Woeste (eds), Femtosecond Chemistry, Proc. Berlin Conf. Femtosecond Chemistry, Berlin (March 1993), Verlag Chemie, Weinheim 1994.

[22] W. Kutzelnigg, Einführung in die Theoretische Chemie Bd. 1 und 2, Verlag Chemie 1992, 1994.

[23] Faraday Discussion No. 71, High Resolution Spectroscopy, J. Chem. Soc. Faraday Discuss 71 (1981).

[24] J. Hinze (ed), Energy Storage and Redistribution in Molecules (Workshop 1980), Plenum Press, New York 1983.

[25] J. Jortner and B. Pullmann (eds), Intramolecular Dynamics, (15th Jerusalem Symposium), Reidel, Dordrecht 1982.

[26] Faraday Discussion No. 75, Intramolecular Kinetics, J. Chem. Soc. Faraday Discuss *75* (1983).

[27] Faraday Discussion No. 82, The Dynamics of Molecular Photofragmentation, J. Chem. Soc. Faraday Discuss *82* (1986).

[28] Bunsen Discussion Meeting on Intramolecular Processes, E.W. Schlag and M. Quack (eds), Ber. Bunsenges. Phys. Chem. *92*, 209 – 443 (1988).

[29] Bunsen Discussion Meeting on Molecular Spectroscopy and Molecular Dynamics: Theory and Experiment, Grainau 1994, W. Kutzelnigg and M. Quack (eds), Ber. Bunsenges. Phys. Chem. *99*, 231 – 570 (1995). A more complete record can be found in "Final Program and Book of Abstracts", Grainau (1994), R. Marquardt and M. Quack (eds).

[30] J. Manz and W.A. Castleman (eds), J. Phys. Chem. *97* 12423 (1993).

[31] J. Manz, in: Nachr. Chem. Techn. Labor *43*, 219 (1995).

[32] M. Eigen, Z. Phys. Chem. *203*, 176 (1954); Disc. Farad. Soc. *17*, 194 (1954).

[33] M. Eigen, Angew. Chem. *75*, 489 (1963); *80*, 892 (1968).

[34] G. Porter, Discuss Faraday Soc. *9*, 60 (1950).

[35] G. Porter, in [21] page 3.

[36] J. Troe, in: Modern Developments in Shock Tube Research, G. Kamimoto (ed.), Shock Tube Research Society, Japan 1975; H.A. Olschewski, J. Troe, and H.Gg. Wagner, Ber. Bunsenges. Phys. Chem. *70*, 450 (1966); 1060.

[37] M. Quack, R. Schwarz, and G. Seyfang, J. Chem. Phys. *96*, 8727 (1992).

[38] A.H. Zewail, in [21] page 15.

[39] P.M. Felker and A.H. Zewail, in [21] page 193.

[40] T. Baumert, R. Thalweiser, V. Weiss, and G. Gerber, in [21] page 397.

[41] G.R. Fleming, Chemical Applications of Ultrafast Spectroscopy, Oxford University Press, Oxford 1986 (reviewing many techniques of condensed-phase work).

[42] W. Kaiser (ed.), Ultrafast Laser Pulses and Applications, Springer Verlag, Berlin 1988 (second ed. 1993).

[43] A.G. Joly, S. Ruhmann, B. Kohler, and K.A. Nelson, in: Ultrafast Phenomena VI, p. 506 – 510, T. Yajima, K. Yoshihara, C.B. Harris, and S. Shionoya (eds), Springer Verlag, Berlin 1988.

[44] J.P. Simons, Gas Kin. Energy Transf. *2*, 58 (1977).

[45] R. Schinke, Photodissociation Dynamics, Cambridge U.P. (1993).

[46] A. Weller, Z. Phys. Chem. N.F. *13*, 335 (1957); Nobel Symposia *5*, 413 (1967).

[47] C.S. Parmenter, Faraday Discuss Chem. Soc. *75*, 7 (1983).

[48] Z.-Q. Zhao, C.S. Parmenter, Ber. Bunsenges. Phys. Chem. *99*, 536 (1995).

[49] W. von E. Doering, J.C. Gilbert, P.A. Leermakers, Tetrahedron *29*, 6863 (1968); J.D. Rynbrandt and B.S. Rabinovitch, J. Phys. Chem. *75*, 2164 (1971); M. Quack and H.J. Thöne, Chem. Phys. Lett. *135*, 487 (1987).

[50] J. Troe, Ber. Bunsenges. Phys. Chem. *73*, 906 (1969).

[51] R.G. Bray and M.J. Berry, J. Chem. Phys. *71*, 4909 (1979).

[52] K. Lehmann, G. Scoles, and B.H. Pate, Annu. Rev. Phys. Chem. *45*, 241 (1994).

[53] K. v. Puttkamer, H.R. Dübal, and M. Quack, Faraday Discuss Chem. Soc. *75*, 263 (1983).

[54] M. Quack, Annu. Rev. Phys. Chem. *41*, 839 (1990).

[55] M. Quack, in [21] page 781.

[56] H.S. Gutowsky and C.H. Holm, J. Chem. Phys. *25*, 1228 (1956).

[57] R.R. Ernst, G. Bodenhausen, and A. Wokaun, Principles of NMR in One and Two Dimensions, Oxford U.P. 1987.

[58] M. Quack, Faraday Discuss Chem. Soc. *71*, 359 (1981).

[59] E.L. Sibert, J.T. Hynes, and W.P. Reinhardt, J. Chem. Phys. *81*, 1135 (1984).

[60] A.A. Stuchebrukov, A. Mehta, and R.A. Marcus, J. Phys. Chem. *97*, 12491 (1993).

[61] D.S. Perry, G.A. Bethardy, and X. Wang, Ber. Bunsenges. Phys. Chem. *99*, 530 (1995).

[62] M.A. Suhm, J.T. Farrell, S.H. Ashworth, and D.J. Nesbitt, J. Chem. Phys. *98*, 5985 (1993).

[63] H.R. Dübal and M. Quack, J. Chem. Phys. *81*, 3779 (1984); Mol. Phys. *53*, 257 (1984).

[64] A. Amrein, H.R. Dübal, and M. Quack, Mol. Phys. *56*, 727 (1985).

[65] M. Quack, J. Mol. Struct. *292*, 171 (1993).

[66] D. Luckhaus, M. Quack, U. Schmitt, and M.A. Suhm, Ber. Bunsenges. Phys. Chem. *99*, 457 (1995).

[67] W.E. Ernst and S. Rakowsky, Ber. Bunsenges. Phys. Chem. *99*, 441 (1995).

[68] U. Dahmen, H. Dreizler, and W. Stahl, Ber. Bunsenges. Phys. Chem. *99*, 434 (1995).

[69] C.L. Hartz, B.A. Wofford, A.L. McIntosh, R.F. Meads, R.R. Lucchese, and J.W. Bevan, Ber. Bunsenges. Phys. Chem. *99*, 447 (1995).

[70] T. Droz, T. Bürgi, and S. Leutwyler, Ber. Bunsenges. Phys. Chem. *99*, 429 (1995).

[71] O.V. Boyarkin, R.D.F. Settle, and T.R. Rizzo, Ber. Bunsenges. Phys. Chem. *99*, 504 (1995).

[72] M. Hippler and M. Quack, Ber. Bunsenges. Phys. Chem. *99*, 417 (1995).

[73] J.E. Gambogi, M. Becucci, C.J. O'Brian, and K.K. Lehmann, Ber. Bunsenges. Phys. Chem. *99*, 548 (1995).

[74] V.M. Blunt, A. Brock, and C. Manzanares I., Ber. Bunsenges. Phys. Chem. *99*, 520 (1995).

[75] R.C. Cohen, and R. Saykally, Annu. Rev. Phys. Chem. *42*, 369 (1991).

[76] M.P. Sinha, A. Schulz, and R.N. Zare, J. Chem. Phys. *58*, 549 (1973).

[77] A. Habib, R. Lange, G. Brasen, and W. Demtröder, Ber. Bunsenges. Phys. Chem. *99*, 265 (1995).

[78] K. Sugawara, F. Ito, T. Nakanaga, and H. Takeo, Ber. Bunsenges. Phys. Chem. *99*, 352 (1995).

[79] J. Waschull, B. Sumpf, Y. Heiner, V.V. Pustogov, and H.-D. Kronfeldt, Ber. Bunsenges. Phys. Chem. *99*, 381 (1995).

[80] T.-K. Ha, Y. He, J. Pochert, M. Quack, R. Ranz, G. Seyfang, and I. Thanopoulos, Ber. Bunsenges. Phys. Chem. *99*, 384 (1995).

[81] R.E. Weston and G.W. Flynn, Annu. Rev. Phys. Chem. *43*, 559 (1992).

[82] C.E. Alt, W.G. Scherzer, H.L. Selzle, and E.W. Schlag, Ber. Bunsenges. Phys. Chem. *99*, 332 (1995); K. Müller-Dethlefs and E.W. Schlag, Annu. Rev. Phys. Chem. *42*, 109 (1991).

[83] D. Cavagnat, L. Lespade, and C. Lapouge, Ber. Bunsenges. Phys. Chem. *99*, 544 (1995).

[84] H. Ben Kraiem, A. Campargue, M. Chenevier, and F. Stoeckel, J. Chem. Phys. *91*, 2148 (1989).

[85] A. O'Keefe, J.J. Scherer, A.-L. Cooksy, R. Sheeks, J. Health, and R. Saykally, Chem. Phys. Lett. *172*, 214 (1990); D. Romanini and K.K. Lehmann, J. Chem. Phys. *99*, 6287 (1993); P. Zalicki and R.N. Zare, J. Chem. Phys. (1995), in press; G. Meijer, M.G.H. Boogaarts, R.T. Jongma, D.H. Parker, and A.M. Wodtke, Chem. Phys. Lett. *217*, 112 (1994).

[86] T.R. Rizzo, C.C. Hayden, and F.F. Crim, Faraday Discuss Chem. Soc. *75*, 223 (1983); T.M. Ticich, M.D. Likar, H.R. Dübal, L.J. Butler, and F.F. Crim, J. Chem. Phys. *87*, 5820 (1987); F.F. Crim, Annu. Rev. Phys. Chem. *35*, 657 (1984); T.R. Rizzo, C.C. Hayden, and F.F. Crim, J. Chem. Phys. *81*, 4501

(1984); T.M. Ticich, T.R. Rizzo, H.R. Dübal, and F.F. Crim, J. Chem. Phys. *84*, 1508 (1986); H.R. Dübal, H. Hollenstein, and M. Quack, Faraday Discuss Chem. Soc. *75*, 272 (1983).
[87] U. Keller, W.H. Knox, and G.W. t'Hooft, IEEE J. Quant. Electron. *28*, 2123 (1992); U. Keller, Appl. Phys. *B58*, 347 (1994).
[88] W.H. Knox, R.S. Knox, J.F. Hoose, and R.N. Zare, Opt. Photonics News (April) 1990.
[89] U.K.A. Klein, Ber. Bunsenges. Phys. Chem. *99*, 402 (1995).
[90] D.A. Ramsey and J. Hinze (eds), Selected papers of R.S. Mulliken, The University of Chicago Press, Chicago 1975.
[91] C. Kitrell, E. Abramson, J.L. Kinsey, S.A. McDonald, D.E. Reisner, D.A. Field, and D.H. Katayama, J. Chem. Phys. *75*, 2056 (1981); W.D. Lawrance and A.E.W. Knight, J. Chem. Phys. *76*, 5637 (1982); *77*, 570 (1982); H.L. Dai, C.L. Korpa, J.L. Kinsey, and R.W. Field, J. Chem. Phys. *82*, 1688 (1985); C.E. Hamilton, J.L. Kinsey, and R.W. Field, Annu. Rev. Phys. Chem. *37*, 493 (1986); S.A.B. Solina, J.P. O'Brien, R.W. Field, and W.F. Polik, Ber. Bunsenges. Phys. Chem. *99*, 555 (1995); A. Gleers, J. Kappert, F. Temps, and J.W. Wiebrecht, J. Chem. Phys. *101*, 3618, 3634 (1994).
[92] EUCMOS 22, J. Mol. Struct. (1995) special issue, see in particular W.A. Lüttke and G.A.A. Nonnenmacher, J. Mol. Struct. (1995) in press.
[93] W. Klopper, H.P. Lüthi, Th. Brupbacher, and A. Bauder, J. Chem. Phys. *101*, 9747 (1994); Th. Brupbacher, J. Makarewicz, and A. Bauder, J. Chem. Phys. *101*, 9736 (1994); J. Makarewicz, T.K. Ha, and A. Bauder, J. Chem. Phys. *99*, 3694 (1993).
[94] R. Pariser, R.G. Parr, J. Chem. Phys. *21*, 466, 767 (1953).
[95] J.A. Pople, Trans. Faraday Soc. *49*, 1375 (1953).
[96] R.G. Parr, Quantum Theory of Molecular Electronic Structure, Benjamin, New York 1964.
[97] L. Salem, The Molecular Orbital Theory of Conjugated Systems, Benjamin, New York 1966.
[98] R.L. Ellis and H.H. Jaffe, in: Modern Theoretical Chemistry, Vol. 8, G.A. Segal (ed) Plenum, New York 1977.
[99] D.W. Turner, C. Baker, A.D. Baker, and C.R. Brundle, Molecular Spectroscopy, Wiley, New York 1970.
[100] T. Koopmans, Physica *1*, 104 (1933).
[101] R.S. Mulliken, J. Chim. Phys. *46*, 497, 675 (1949).
[102] L.S. Cederbaum and W. Domcke, Adv. Chem. Phys. *36*, 205 (1977).
[103] P. Pulay, Mol. Phys. *17*, 197 (1969).
[104] J. Gerrat and I.M. Mills, J. Chem. Phys. *49*, 1719 (1968).
[105] R. Moccia, Chem. Phys. Lett. *3*, 260 (1970).
[106] J.F. Gaw and N.C. Handy, R. Soc. Chem. Ann. Rep., 291 (1984).
[107] P. Pulay, G. Fogarasi, G. Pongor, J.E. Boggs, and A. Vergha, J. Am. Chem. Soc. *105*, 7037 (1983).
[108] P. Pulay, G. Fogarasi, and J.E. Boggs, J. Chem. Phys. *87*, 2564 (1987).
[109] W. Kolos and C.C.J. Roothaan, Rev. Mod. Phys. *32*, 219 (1960).
[110] W. Kolos and L. Wolniewicz, Rev. Mod. Phys. *35*, 473 (1963); J. Chem. Phys. *99*, 3663, 3674 (1964).
[111] L. Wolniewicz, J. Chem. Phys. *99*, 1851 (1993).
[112] W. Kolos and J. Rychlewski, J. Chem. Phys. *98*, 3960 (1993).
[113] K. Dressler and L. Wolniewicz, Ber. Bunsenges. Phys. Chem. *99*, 246 (1995).
[114] R. Röhse, W. Kutzelnigg, R. Jaquet, and W. Klopper, J. Chem. Phys. *101*, 2231 (1994).
[115] B.M. Dinelli, C.R. Le Sueur, J. Tennyson, and R.D. Amos, Chem. Phys. Lett. (1995) in press.
[116] T. Oka, Rev. Mod. Phys. *64*, 1141 (1992).
[117] S. Miller and J. Tennyson, Chem. Soc. Rev. 281 (1992).
[118] W. Meyer, P. Botschwina, and P.G. Burton, J. Chem. Phys. *8*, 899 (1986).
[119] B.M. Dinelli, S. Miller, and J. Tennyson, J. Mol. Spectrosc. *153*, 718 (1992).
[120] S.D. Peyerimhoff and R.J. Buenker, Adv. Quantum Chem. *9*, 69 (1975).
[121] H. Köppel, W. Domcke, and L.S. Cederbaum, Adv. Chem. Phys. *57*, 59 (1984).
[122] C.M. Marian, J. Chem. Phys. *93*, 1176 (1990).
[123] C.M. Marian, Ber. Bunsenges. Phys. Chem. *99*, 254 (1995).
[124] E. Herbst and W. Klemperer, Astrophys. J. *188*, 35 (1974).
[125] P.J. Bruna, Astrophys. Lett. *16*, 107 (1975) and references quoted therein.
[126] M. Quack and M.A. Suhm, J. Chem. Phys. *95*, 28 (1991).
[127] H. Hollenstein, R. Marquardt, M. Quack, and M.A. Suhm, J. Chem. Phys. *101*, 3588 (1994); Ber. Bunsenges. Phys. Chem. *99*, 275 (1995).
[128] I.M. Mills, Farad. Discuss Chem. Soc. *62*, 7 (1977).
[129] S. Carter and W. Meyer, J. Chem. Phys. *93*, 8902 (1990); *94*, 2424 (1992); S. Carter and N.C. Handy, Comput. Phys. Rep. *5*, 115 (1986); B.T. Sutcliffe and J. Tennyson, Int. J. Quant. Chem. *29*, 183 (1991).
[130] A. Alijah, J. Hinze, and L. Wolniewicz, Ber. Bunsenges. Phys. Chem. *99*, 251 (1995).
[131] P. Botschwina, Chem. Phys. *68*, 41 (1982).
[132] Z. Bacic and J.C. Light, J. Chem. Phys. *85*, 454 (1986); *86*, 3065 (1987); Annu. Rev. Phys. Chem. *40*, 469 (1989).
[133] D. Luckhaus and M. Quack, Chem. Phys. Lett. *190*, 581 (1992); D. Luckhaus, M. Quack, and J. Stohner, Chem. Phys. Lett. *212*, 434 (1993).
[134] M.A. Suhm and R.O. Watts, Phys. Rep. *204*, 203 (1991).
[135] A. Gelessus and W. Thiel, Ber. Bunsenges. Phys. Chem. *99*, 514 (1995); A.F. Borro, I.M. Mills, E. Venuti, J. Chem. Phys. (1995) in press; J. Breiding, H. Bürger, M. Senzlober, W. Thiel, Ber. Bunsenges. Phys. Chem. *99*, 282 (1995).
[136] R.D. Amos, J.F. Gaw, N.C. Handy, and S. Carter, J. Chem. Soc. Faraday Trans. 2, *84*, 1247 (1988); T.K. Ha, M. Lewerenz, and M. Quack, ibid. p. 1556.
[137] R. Röhse, W. Klopper, and W. Kutzelnigg, J. Chem. Phys. *99*, 8830 (1993).
[138] P. Botschwina, Chem. Phys. *81*, 73 (1983); Chem. Phys. Lett. *105*, 535 (1984).
[139] S.D. Peyerimhoff and R.J. Buenker, Theoret. Chim. Acta *35*, 33 (1974).
[140] P.J. Rowe, Rev. Mod. Phys. *40*, 153 (1968).
[141] D. Mukherjee, R. Moitra, and A. Mukhopadhja, Mol. Phys. *30*, 1861 (1975).
[142] H. Reitz and W. Kutzelnigg, Chem. Phys. Lett. *66*, 111 (1979).
[143] W. Kutzelnigg, H. Reitz, S. Durmaz, and S. Koch, Proc. Ind. Acad. Sci. *96*, 1172 (1986).
[144] R.J. Buenker and S.D. Peyerimhoff, Chem. Phys. Lett. *36*, 415 (1975).
[145] E.A. Lucken, Nuclear Quadrupole Coupling Constants, Academic Press, London 1969.
[146] D.J. Caldwell and H. Eyring, The Theory of Optical Activity, Wiley Interscience, New York 1971; L.D. Barron, Molecular Light Scattering and Optical Activity, Cambridge University Press 1982.
[147] M. Carnell, S.D. Peyerimhoff, A. Breest, K.H. Gödderz, P. Ochmann, and J. Hormes, Chem. Phys. Lett. *180*, 477 (1991).
[148] H. McConnell, J. Chem. Phys. *24*, 632, 764 (1956).
[149] W. Meyer, J. Chem. Phys. *51*, 5149 (1969).
[150] D.M. Chipman, Theoret. Chim. Acta *76*, 73 (1989).
[151] H.U. Suter, M.B. Huang, and B. Engels, J. Chem. Phys. *101*, 7686 (1994) and references therein.
[152] B. Engels, S.D. Peyerimhoff, and E.R. Davidson, Mol. Phys. *62*, 109 (1987).
[153] W. Kutzelnigg, U. Fleischer, and M. Schindler, in: NMR Basic Principles and Progress, Springer, Berlin 1990, Vol. 23.
[154] J. Tossell (ed), Nuclear Magnetic Shielding and Molecular Structure, Kluwer, Dordrecht 1993.
[155] J. Oddershedde, J. Geerben, and G.E. Scuseria, J. Phys. Chem. *92*, 3056 (1988); S. Ajit Perera, H. Sekino, and R.J. Barlett, J. Chem. Phys. *101*, 2186 (1994).
[156] T.-K. Ha, Chem. Phys. Lett. *107*, 117 (1984).
[157] T. Kato, Perturbation Theory for Linear Operators, Springer, Berlin 1966.

[158] Faraday Discuss Chem. Soc. *99* (1994) on Vibrational Optical Activity.

[159] E. Rabani, R.D. Levine, and U. Even, Ber. Bunsenges. Phys. Chem. *99*, 310 (1995).

[160] M. Quack, Jerusalem Symp. *24*, 47 (1991).

[161] J.K.G. Watson, Mol. Phys. *15*, 479 (1968).

[162] H.H. Nielsen, Phys. Rev. *60*, 794 (1941); Rev. Mod. Phys. *23*, 90 (1951); Handb. Phys. *37* (1959).

[163] G. Amat, H.H. Nielsen, and G. Tarrago, Rotation, Vibration of Polyatomic Molecules, Marcel Dekker, New York 1971.

[164] I.M. Mills, Specialist Per. Rep. Theor. Chem. *1*, 110 (1974) (The Chemical Society, London).

[165] D. Papousek and M.R. Aliev. Stud. Phys. Theor. Chem. *17*, 160 (1982).

[166] S. Califano, Vibrational States, Wiley, New York 1976.

[167] M. Lewerenz and M. Quack, J. Chem. Phys. *88*, 5408 (1988).

[168] D.L. Bunker, Classical Trajectory Methods, Methods Comput. Phys. *10*, 287 (1971), Ber. Bunsenges. Phys. Chem. *81*, 155 (1977).

[169] W.F. van Gunsteren und H.J.C. Berendsen, Angew. Chem. *102*, 1020 (1990).

[170] W.H. Miller, Adv. Chem. Phys. *25*, 69 (1974).

[171] M.S. Child, Semiclassical Mechanics with Molecular Applications, Oxford University Press 1991.

[172] F. Stechel, E.J. Heller, Annu. Rev. Phys. Chem. *35*, 563 (1984); E.J. Heller and J.C. Brown, J. Chem. Phys. *79*, 3336 (1983); E.J. Heller, in: Potential Energy Surfaces and Dynamics Calculations, D. Truhlar (ed) Plenum, New York 1981; E.J. Heller and M.J. Davis, J. Phys. Chem. *84*, 1999 (1980); E.J. Heller, Phys. Today 1994; G. Hose and H.S. Taylor, Chem. Phys. *84*, 375 (1984).

[173] N.B. Slater, Theory of Unimolecular Reactions, Cornell University Press, Ithaca, New York, 1959.

[174] R.A. Marcus, O.K. Rice, J. Phys. Colloid. Chem. *55*, 894 (1951); R.A. Marcus, J. Chem. Phys. *20*, 359 (1952).

[175] H.M. Rosenstock, M.B. Wallenstein, A.L. Wahrhaftig, and H. Eyring, Proc. Nat. Acad. Sci. USA *38*, 667 (1952); J.C. Giddings and H. Eyring, J. Chem. Phys. *22*, 538 (1954).

[176] J. Troe, in: Phys. Chem. an Advanced Treatise, *6B*, 835 (1975) (ed) W. Jost, Academic Press, New York.

[177] M. Quack and J. Troe, in: Theor. Chem. Adv. Persp. *6B*, 199 (1981) (ed) D. Henderson, Academic Press, New York.

[178] R.G. Gilbert and S.G. Smith, Theory of Unimolecular and Recombination Reactions, Blackwell, Oxford 1990.

[179] M. Quack and J. Troe, Ber. Bunsenges. Phys. Chem. *78*, 240 (1974); *79*, 469 (1975).

[180] J. Troe, Ber. Bunsenges. Phys. Chem. *99*, 341 (1995).

[181] M. Quack, Mol. Phys. *34*, 477 (1977); J. Chem. Phys. *82*, 3277 (1985).

[182] A. Sinha and J.L. Kinsey, J. Chem. Phys. *80*, 2029 (1984).

[183] S.M. Lederman and R.A. Marcus, J. Chem. Phys. *81*, 5601 (1984).

[184] A.H. Zewail, Faraday Discuss Chem. Soc. *75*, 424 (1983).

[185] M. Quack, Faraday Discuss Chem. Soc. *75*, 425 (1983).

[186] R.A. Marcus, Faraday Discuss. Chem. Soc. *75*, 103 (1983).

[187] R. Mecke, Z. Phys. *99*, 217 (1936); Z. Elektrochem. *54*, 38 (1950).

[188] M.S. Child and R.T. Lawton, Farad. Discuss Chem. Soc. *71*, 274 (1981).

[189] A. Kolmogorov, Doklad. Akad. Nauk. SSSR *98*, 525 (1954); V.I. Arnold, Russ. Math. Survey *18*, 85 (1963); J. Moser, Nachr. Akad. Wiss. Göttingen Math. Phys. Klasse (1962) page 1.

[190] J. Segall, R.N. Zare, H.R. Dübal, M. Lewerenz, and M. Quack, J. Chem. Phys. *86*, 634 (1987).

[191] R. Marquardt, M. Quack, J. Stohner, and E. Sutcliffe, J. Chem. Soc. Faraday Trans. 2, *82*, 1173 (1986).

[192] J. Baggott, M.C. Chuang, R.N. Zare, H.R. Dübal, and M. Quack, J. Chem. Phys. *82*, 1186 (1985).

[193] K. von Puttkamer and M. Quack, Faraday Discuss Chem. Soc. *75*, 343 (1983).

[194] K. von Puttkamer, H.R. Dübal, and M. Quack, Chem. Phys. Lett. *95*, 358 (1983).

[195] J.E. Gambogi, K.K. Lehmann, B.H. Pate, and G. Scoles, J. Chem. Phys. *98*, 1748 (1993).

[196] R. Marquardt and M. Quack, J. Chem. Phys. *95*, 4854 (1991).

[197] M. Quack and J. Stohner, J. Phys. Chem. *97*, 12574 (1993).

[198] A. McIllroy, D.A. Nesbitt, J. Chem. Phys. *92*, 2229 (1990).

[199] G.A. Bethardy, D.S. Perry, J. Chem. Phys. *98*, 6651 (1993).

[200] H.R. Dübal and M. Quack, Chem. Phys. Lett. *90*, 370 (1982).

[201] K. von Puttkamer and M. Quack, Chem. Phys. *139*, 31 (1989).

[202] M.C. Bordé, A. Henry, M.L. Henry, and C.R. Séances, Acad. Sci., Ser. B *263B*, 619 (1966).

[203] D.W. Lupo and M. Quack, Chem. Rev. *87*, 181 (1987).

[204] F.F. Crim, Annu. Rev. Phys. Chem. *44*, 397 (1993).

[205] M. Quack and E. Sutcliffe, Isr. J. Chem. *24*, 204 (1984).

[206] G. Paramonov, chapter 23 in [21].

[207] M. Holthaus, chapter 24 in [21].

[208] M. Quack and E. Sutcliffe, Chem. Phys. Lett. *105*, 147 (1984).

[209] R. Schinke and R.J. Huber, chapter 8 in [21].

[210] D.J. Tannor and S.A. Rice, J. Chem. Phys. *83*, 5013 (1985); R. Kosloff, S.A. Rice, P. Gaspard, S. Tersigni, and D.J. Tannor, Chem. Phys. *139*, 201 (1989); see also A.H. Zewail, J. Phys. Chem. *97*, 12427 (1993), and T. Baumert, R. Thalweiser, G. Gerber, in [21] for real experiments.

[211] S. Shi and H. Rabitz, Chem. Phys. *139*, 185 (1989).

[212] J.L. Krause, R.M. Whitnell, K.R. Wilson, and Y. Yan, chapter 26 in [21].

[213] R. de Vivie and B. Reisch, Ber. Bunsenges. Phys. Chem. *99*, 485 (1995).

[214] M. Dohle, J. Manz, and G.K. Paramonov, Ber. Bunsenges. Phys. Chem. *99*, 478 (1995).

[215] J. Manz and C. Parmenter (eds), Chem. Rev. *139*, 1–229 (1989).

[216] K. von Puttkamer and M. Quack (1983), unpublished work cited in [160].

[217] Th. Kerstel, K.K. Lehmann, T.F. Mentel, B.H. Pate, and G. Scoles, J. Phys. Chem. *95*, 8282 (1991).

[218] M. Quack and E. Sutcliffe, URIMIR Programs, Quantum Chemistry Program Exchange, Program 515, QCPE Bulletin *6*, 98 (1986).

[219] R. Kosloff and D. Kosloff, J. Comp. Phys. *52*, 35 (1983).

[220] M.D. Feit and J.A. Fleck, J. Chem. Phys. *78*, 301 (1983).

[221] R.H. Bisseling, P. Kosloff, and J. Manz, J. Chem. Phys. *83*, 993 (1985).

[222] K.C. Kulander (ed) Time dependent methods for quantum dynamics, North Holland, Amsterdam 1991.

[223] K. Broeckhove and L. Lathouwers (eds), Time dependent quantum molecular dynamics, NATO ASI Series B, *299* (1992) Plenum Press.

[224] I.M. Mills, T. Cvitas, K. Homann, N. Kallay, and K. Kuchitsu, Quantities, Units and Symbols in Physical Chemistry, 2nd Ed. 1993, Blackwell Scientific Publ. Oxford.

[225] V.S. Letokhov, Ber. Bunsenges. Phys. Chem. *99*, 498 (1995).

[226] M. Quack, Chimia *40*, 386 (1986).

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