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Properties of Organic Radical Ions in Rigid Media

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Abstract. This report describes the activities in the title field as carried out at the Institute of Physical Chemistry of the University of Fribourg over the past dozen years.

1. Introduction

When I received my undergraduate education, mechanistic organic chemistry was dominated by models whose basic paradigm was that electrons usually move in pairs. Unpaired electrons were mostly a nuisance which destroyed stereoselectivity and led to unwanted side products. These views have dramatically changed over the last 20 years, and today few chemists deny or ignore the pivotal role played by Single-Electron Transfer (SET) processes in chemical reactions ranging from imaging technology *via* stereoselective synthesis to photobiology [1].

Radical ions are the primary products of any SET process originating from closed-shell (neutral or multiply charged) molecules. An understanding of the properties of these species is a prerequisite for an understanding of SET reactions. By their very nature, radical ions are often too reactive to be studied in any detail under ambient conditions. Specifically, bimolecular reactions must be prevented, either by creating the radical ions in the gas phase under collision-free conditions or in inert matrices.

Building on the pioneering work of *Hamill* and *Shida* in the 1960's [2], we have adopted the latter approach to investigate in particular the electronic and molecular structure as well as the photochemistry of radical cations by optical spectroscopic methods [3]. It is the purpose of this account to briefly describe the techniques used in this program and to summarize some typical results thus obtained over the past dozen years at the University of Fribourg. No attempt is made to be comprehensive, and the interested reader is referred to the list of references for more in-depth information on individual topics.

2. Technical Background

To study radical cations embedded in rigid media, the following technical problems must be addressed: *a*) sufficient energy must be imparted onto a neutral precursor to effect ionization; *b*) a suitable electron scavenger must be provided in order to prevent charge recombination; *c*) the medium must be chosen such as to minimize interactions with the embedded radical cations, and it must be transparent in the spectral region of interest.

Concerning point *a*, the first studies on radical cations in condensed phase used UV light to ionize molecules in frozen organic solvents [4]. Today, this technique of *direct photoionization* is used mainly in experiments with Ne matrices which are transparent to the VUV light needed to effect ionization of small molecules (>10 eV) [5].

A more generally applicable approach consists in *ionization of the solvent* by X- or γ-irradiation as a primary step. Subsequently, the charges migrate through the medium, until they ultimately accumulate at sites with a lower ionization energy or a higher electron affinity, respectively, than the solvent atoms or molecules. Usually, these are the sites which contain the substrate to be ionized and/or the added electron scavenger, respectively (*cf.* point *b*)

It is perhaps important to point out that, although the entire sample is exposed to very high energy radiation, this hardly affects the substrate itself directly, because firstly it is present in rather low concentration (typically 10^{-2}–10^{-4} M in frozen solvents, 1:1000 in Ar matrices), and secondly it usually has a much smaller cross section for X- or γ-rays than the medium which is composed of (*i.e.*, Ar matrices) or contains heavy atoms (*i.e.*, Freon glasses). Thus, ionization of the substrate in such experiments occurs almost exclusively by *charge transfer* from the solvent, a process which may still be strongly exothermic and thus lead to unwanted secondary reactions in the incipient cations This is especially true in Ar matrices which are very inefficient at dissipating this excess energy.

Concerning point *b*, the most efficient way to trap electrons in such experiments is through dissociative electron capture [4] such as it is typical for alkyl chlorides:

$$R\text{–}Cl \xrightarrow{e^-} R^\cdot + Cl^-$$

If Freons are used as solvents (see below), these act also as electron scavengers, and the electrons are trapped right next to where they are formed. Luckily, due to the F substituents, the resulting radicals are nearly invisible both in optical as well as in ESR experiments. In Ar-matrix studies, we add CH_2Cl_2 to prevent migrating electrons from becoming attached to the substrate which would lead to a mixture of radical cations and anions. This particular electron scavenger has the advantage of a simple IR spectrum and does not produce optically obtrusive products upon X-irradiation.

With regard to point *c*, the ideal choice are noble gases, especially Ne, whose ionization energy is so much higher than that of all organic molecules, that charge-transfer type interactions with embedded radical cations are virtually negligible [5]. Unfortunately, Ne melts at *ca.* 6 K and thus necessitates the use of liquid He or unwieldy and expensive multistage closed-cycle cryostats. Furthermore, its virtual transparency to X-rays precludes the application of this practical method of ionization.

With regard to *chemical inertness*, Ar is equivalent to Ne for all practical purposes, but its lower ionization energy and higher polarizability lead to stronger physical interactions with embedded radical cations which may stand in the way of high-resolution spectroscopic studies, but never represented a serious impediment in our work. On the other hand, Ar has a large cross section for X-rays which makes it an ideal medium for the radiolytic generation of radical cations.

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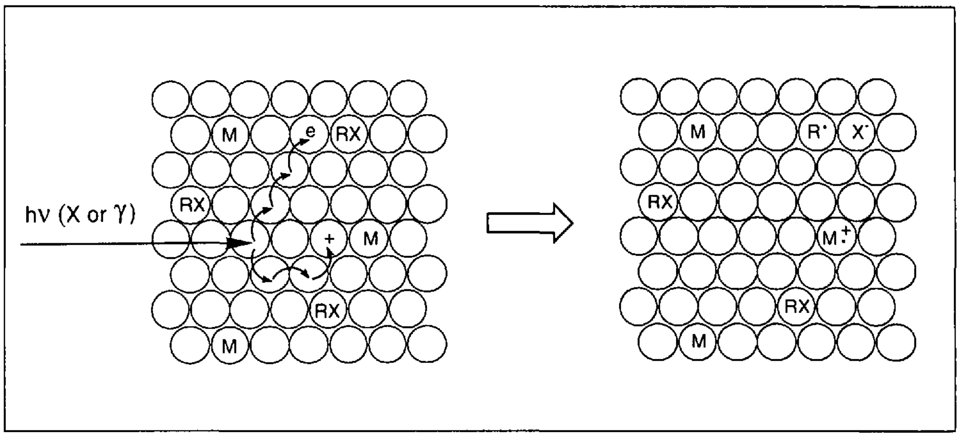


Fig. 1. *Mechanism of ionization by X- or γ-irradiation.* Circles denote solvent atoms (Ar), RX is the electron scavenger (alkyl halide) and M the substrate to be ionized.

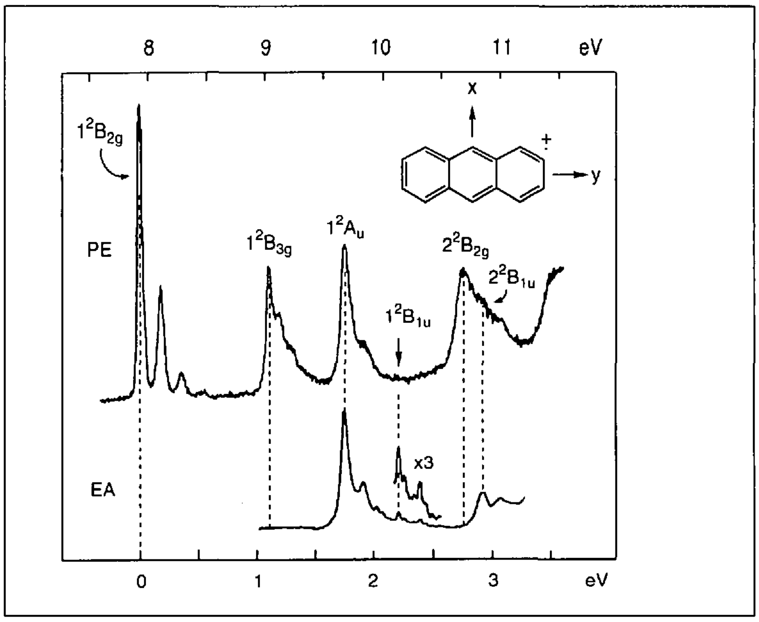


Fig. 2. *Partial PE and EA spectra of anthracene and its radical cation, respectively*

The main disadvantage of Ar in these experiments lies in the relatively high exothermicity of electron transfer to typical organic substrates (6–7 eV in the gas phase) and its poor ability to dissipate vibrational energy, two factors which may thwart attempts to stabilize primary cations. Finally, as in all matrix-isolation experiments, the substrate must be vaporizable without decomposition.

If the above factors constitute serious disadvantages, one may move to glassy solvents. In particular, chlorofluorocarbons (Freons) have proven to be well suited for studies of radical cations by a variety of spectroscopic methods. For optical studies, a mixture of $CFCl_3$ and $CF_2Br–CF_2Br$, which forms a transparent glass at 77 K [7], has gained acceptance as the solvent system of choice for electronic absorption (EA) spectrosocpy of radical cations [8] and has served well in a large number of such studies. Apart from the fact that it is of course not suitable for IR studies, its main drawback lies in its low melting point (*ca.* 80 K) which makes it impossible to conduct controlled annealing studies. For these, we resort to a mixture of BuCl and isopentane [9] which permits slow diffusion at temperatures between 80–100 K.

3. Typical Results

3.1. *Electronic Structure*

Building on the experience I had gained in the group of Prof. *Haselbach* during his tenure in Basel [10], and with his generous support and help after his move to Fribourg, my group and I concentrated initially on investigations concerning the *electronic structure* of organic radical cations. Previously, this field of research had been dominated by photoelectron (PE) spectroscopy, mainly because PE spectra can often be conveniently interpreted in terms of simple MO models by way of *Koopmans'* theorem ($I_i = -\varepsilon_i$) [11]. This link was so successful that it even entailed a blurring of the distinction between model and reality which expressed itself in the notion that the coincidence of PE-band positions with suitably scaled MO-energies represents a proof for the existence of MOs [12].

It is probably fair to say that EA spectroscopy of radical cations opened the way to a more comprehensive view of their electronic structure. In particular, it showed that other excited states than those accessible in the PE experiment exist (and may in certain cases even be the lowest excited ones). This becomes evident when EA spectra of radical cations are juxtaposed to PE spectra of the corresponding parent neutrals on the same energy scale. This is done in *Fig. 2* for the case of anthracene, whose cation shows a weak absorption band (1^2B_{1u}, corresponding essentially to HOMO → LUMO excitation) where the PE spectrum of the neutral is empty. The same example shows also the operation of electric dipole-selection rules as a consequence of which some of the states which are accessible in the PE experiment do not appear in the EA spectrum (namely, those corresponding to g → u transitions in the case of the D_{2h}-point group). This feature has in many cases permitted to resolve ambiguities in the assignments of PE spectra.

In a further step, EA spectroscopy has served to demonstrate quite directly that the independent particle approximation (states described by single configurations) at the basis of the above-mentioned PE-MO link is not universally valid and that – in the framework of MO models – configuration interaction must sometimes be taken into account even for a qualitatively correct description of the observed spectra [13]. A typical case in point are polyene radical cations which typically show a weak band in the VIS region and a very intense one in the near UV as shown in the center of *Fig. 3* for hexatriene.

In contrast to this observation, single configuration models invariably predict two closely spaced bands of nearly equal intensity for polyene-radical cations as shown for hexatriene by the PPP-SCF model at the bottom of *Fig. 3*. This situation is readily remedied by admitting interaction between the lowest two excited configurations which leads to a larger energy separation of the final states and – more importantly – to the vector addition and subtraction, respectively, of the transition moments μ_a and μ_v for excitations a and v in *Fig. 3*. This is needed to explain the disparity of the intensities of the two bands in the EA spectra of polyene radical ions. In general, higher excited configura-

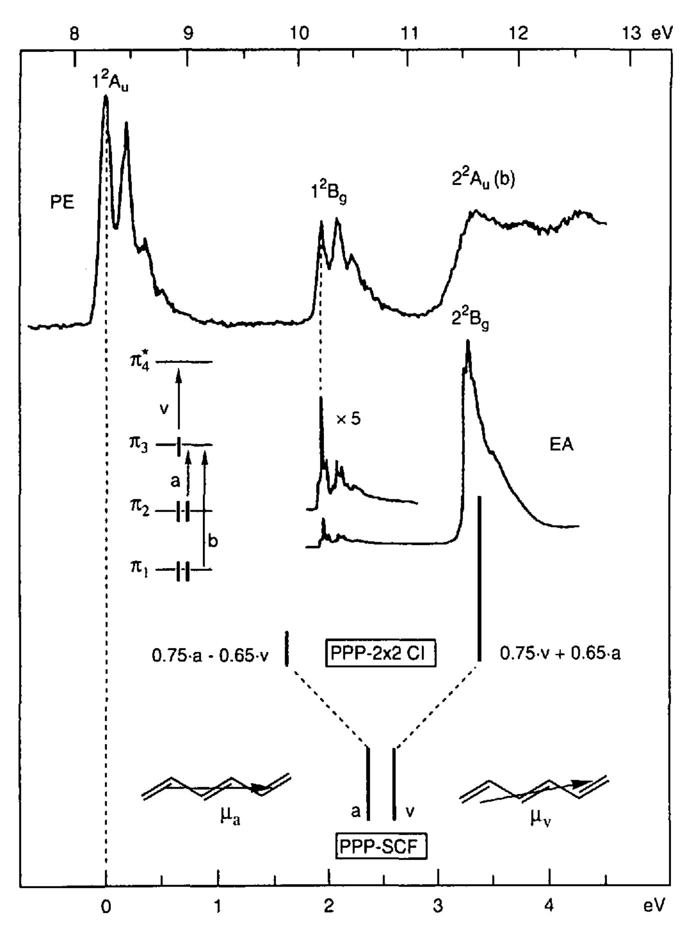


Fig. 3. *PE Spectrum of hexatriene* (top), *EA spectrum of its radical cation* (center), *and results of simple 2x2 CI calculation.* Discussion see text.

tions must be considered to arrive at quantitatively correct predictions, but the simple model calculations illustrated in *Fig. 3* show that a simple 2 x 2 CI already leads to a qualitatively correct picture in the case of polyene radical cations [14].

The example of hexatriene radical cation shows also that a good correspondence between EA and PE bands can be misleading. The states which give rise to the second, intense EA band (mainly excitation v) and to the third peak in the PE spectrum (mainly excitation b) cannot be the same due to dipole selection rules: the $1^2A_u \rightarrow 2^2A_u$ transition in the EA spectrum is dipole forbidden while the third PE band cannot be due to the (optically allowed but essentially non-*Koopmans'*) 2^2B_g state. Similar situations were found to prevail in several other conjugated hydrocarbons as documented in a series of papers in *Helv. Chim. Acta* [15]. The same concept can be extended with slight modifications to conjugated enynes and polyynes [16].

3.2. *Changes in Molecular Geometry upon Ionization*

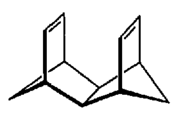
A mismatch between PE and EA bands does not necessarily indicate that different electronic states are observed in the two experiments, because it can also be caused by a change in geometry. This leads us into the realm of EA spectroscopy for the investigation of the changes in *molecular structure* upon ionization. We have encountered many examples where EA spectra proved to be quite insightful in this respect and have taught us a great deal about charge-transfer induced changes in the molecular structure of organic species.

As an example, consider norbornadiene (N) whose PE [17] and cation-EA spectrum [18] are shown in *Fig. 4*. Due to the broad *Franck-Condon* envelope of the first PE band, the placement of the origin of the energy scale of the cation spectrum is somewhat uncertain in this case, but it is clear that the visible EA band of $N^{+\cdot}$ is far from coinciding with the second PE band of N. Nevertheless, both bands must correspond to the same electronic state of $N^{+\cdot}$ because there is only one π state in this energy region (above 11 eV one sees the onset of ionizations from σ-MOs in the PE spectrum).

Ionization of N at 8.5 eV is effected by removing an electron from the antibonding combination of the two π-bond orbitals (the b_2 HOMO). This results in a *decrease* of the repulsive interaction between the ethylenic moieties which will express itself in a decrease of their distance *R*. The first excited state of $N^{+\cdot}$ is obtained by removing an electron from the bonding combination of the π-bond orbitals (the a_1 π-MO), or by promoting of an electron from the antibonding to the bonding combination (in terms of excitation from the ground state of $N^{+\cdot}$ as illustrated in *Fig. 5*. This leads to an *increase* of the repulsive interaction, hence to a widening of the distance *R*.

These structural changes, which are readily confirmed by quantum-chemical calculations, result in a disposition of the potential energy surfaces as illustrated in *Fig. 5*. From this it becomes immediately evident that $\Delta I_v = I_{v,2} - I_{v,1}$ in the PE spectrum (which is measured at the equilibrium geometry of neutral N) must be at lower energy than λ_{max} in the EA spectrum of $N^{+\cdot}$ (which is measured at the equilibrium geometry of ground-state $N^{+\cdot}$). The mismatch between these two quantities is in effect directly related to the importance of the structural changes suffered by N upon ionization and by $N^{+\cdot}$ upon excitation, respectively.

We have recently investigated several such cases of π systems interacting through space (see **1**–**4** below) and found that the above energy mismatch generally decreases with the rigidity of the σ framework in which the π moieties are embedded. For pagodiene (**3**) it has reduced to a few tenth of an eV and is nearly zero for dodecahedradiene (**4**) [19]. Actually, EA spectroscopy of radical cations has added an interesting new facet to the research area of through-space *vs.* through-bond interactions in that it allows to study these effects at two different geometries of the same compound and thus gain considerably more insight into the distance dependence of through-space interactions.



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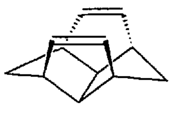

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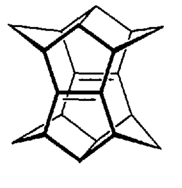

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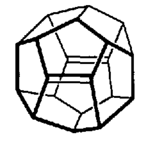


4

Another common electron-transfer induced structural change which occurs typically in polyenes consists in a *change in bondlengths* which reflects the changes in the π-bond orders upon removal of an electron from the HOMO. As the HOMO of all linear conjugated polyenes is antibonding along the essential single bonds and bonding along the double bonds, ionization leads to an attenuation of the bondlength alternation such that the single bonds become shorter and the double bonds longer (see also *Sect. 3.6* below).

Interestingly, in spite of the strong shifts in the orbital energies as a result of these geometry changes, they hardly affect the coincidence between PE and EA bands in the case of polyenes. This is due to a breakdown of the simple MO approximation for this class of compounds where many-electron effects strongly attenuate the energy differences between the two geometries which occur at the single-configuration level. As an example we show in *Fig. 6* how the excited-state energies at the neutral and the cation geometry of hexatriene evolve from a one-electron model (ROHF configurations) *via* a small CI level (CASSCF) all the way to a model which incorporates dynamic electron correlation (CASPT2). The large energy differences between the two geometries which prevail at the center of *Fig. 6* become almost negligible, if one compares the CASPT2 energies at the neutral and the cation geometry, energies which are actually in excellent agreement with the experimental observations (outermost columns) documented in *Fig. 3* above [20].

3.3. *Conformational Changes upon Oxidation or Reduction*

We have encountered numerous examples of *conformational changes* induced by ionization. Very often these changes are brought about by a change of π-bond orders. Thus, biphenyl which is twisted by *ca.* 45° in the gas phase [21] appears to become planar upon removal of an electron because the π_6-HOMO is antibonding along the 'interphenyl' bond and hence the corresponding π-bond order increases upon ionization. *Turner* and *Maier* had pointed out back in the early days of PE spectroscopy that the energy difference between the maxima of the first and the fourth PE band of biphenyl (which correspond to ionization from the HOMO π_6, and from π_3) is a direct measure of the twisting angle between the Ph rings [22]. In the PE spectrum $I_{v,4}$–$I_{v,1}$ is 1.44 eV while the band maximum of the first transition on the EA spectrum of the radical cation (which corresponds to the energy

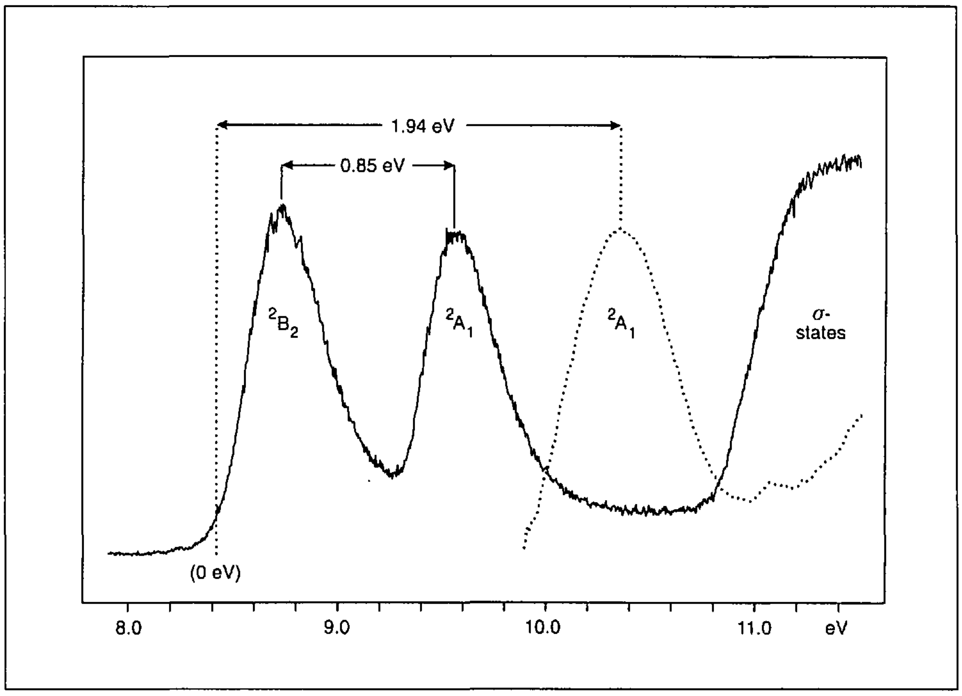


Fig. 4. *PE Spectrum of norbornadiene* (solid) *and EA spectrum of its radical cation* (dotted)

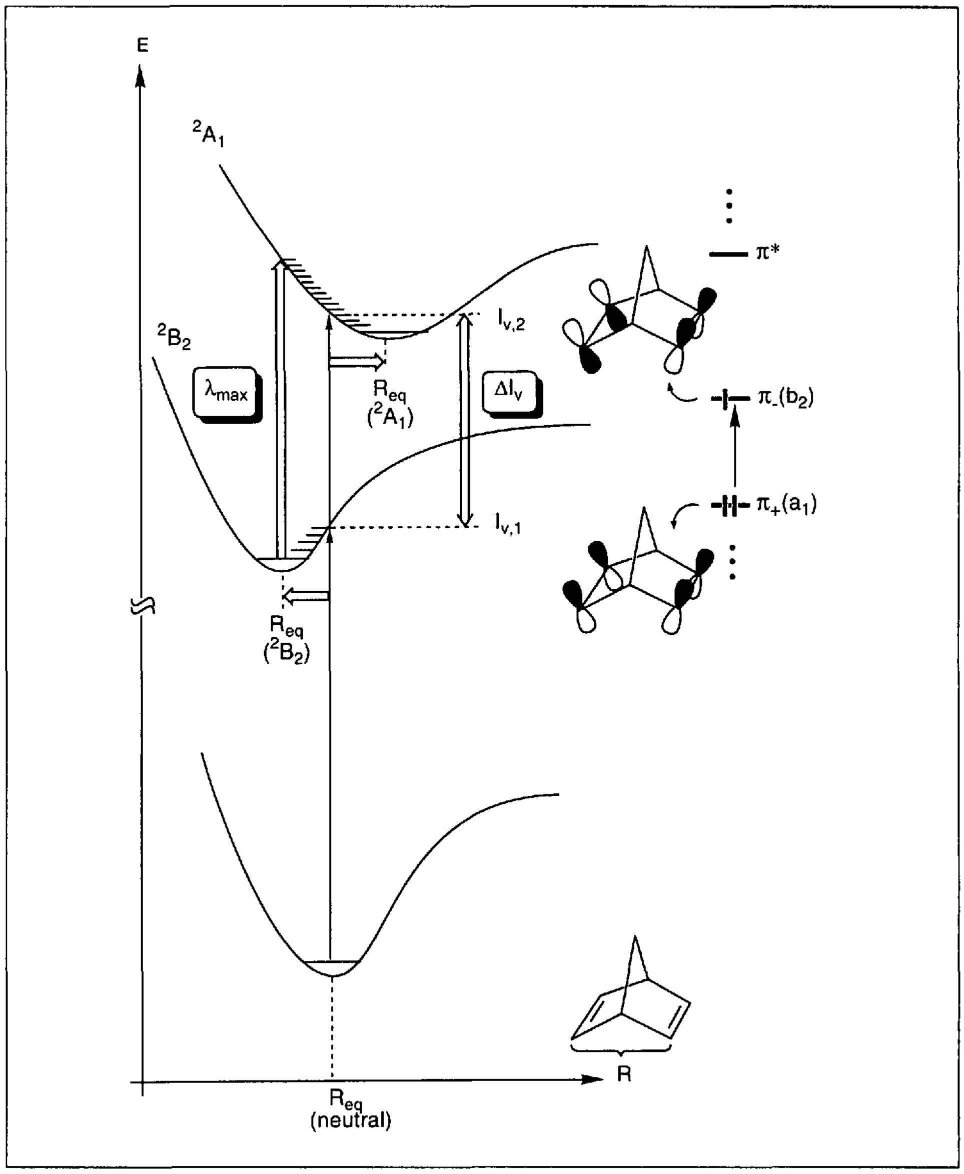


Fig. 5. *Disposition of potential-energy surfaces of norbornadiene and its radical cation illustrating the reason for the mismatch of the peaks in the PE and EA spectrum in* Fig. 4

difference between the same states) is at 1.81 eV, close to the value it assumes in the (perfectly planar) fluorene-radical cation (1.87 eV [2b] [22]).

This effect of planarization, which is a prerequisite for the doping-induced conductivity of polyphenyls and related polymers, is often rationalized in terms of an increasing importance of *p*-quinoid resonance structures in the radical cation, which amounts to explaining the same effect as above in the language of valence-bond theory instead of that of molecular orbitals [23].

Another interesting example of electron-transfer-induced conformational changes is found in cyclooctatetraene which in the neutral is folded by 136°. In the radical cation this angle is increased to *ca.* 150° [24], while the radical anion is found to be essentially planar [25]. Interestingly, the changes in π-bond orders on oxidation and reduction are identical at the *Hückel* level due to the pairing properties of alternant hydrocarbons, but for some reason the interplay between delocalization and σ-strain energy results in significantly different conformation in the two resulting radical ions.

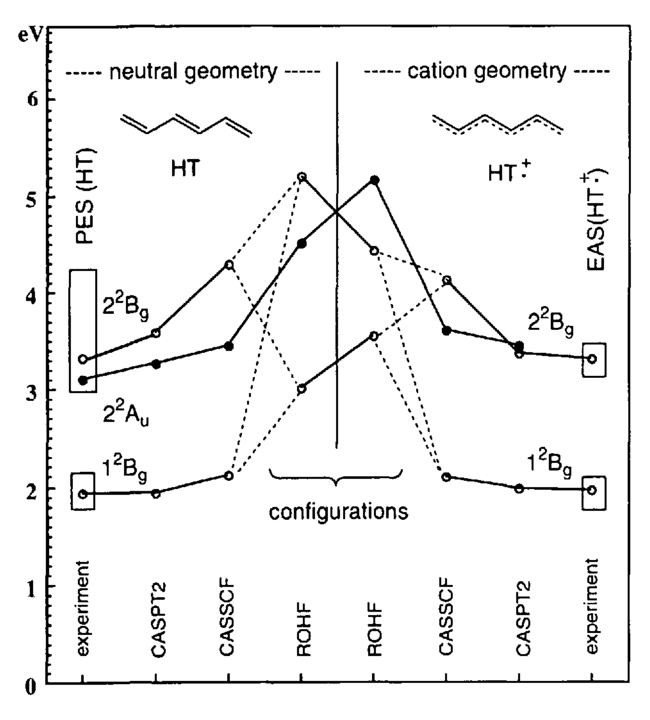
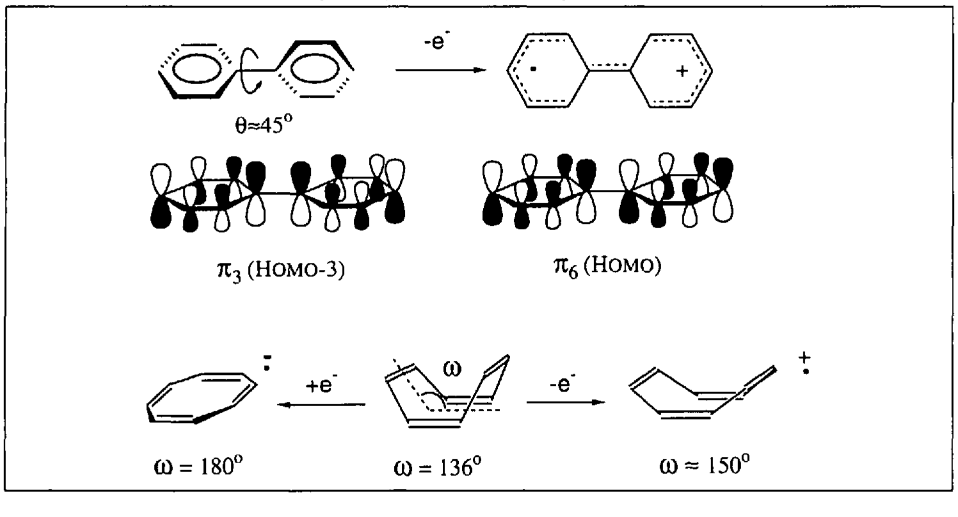
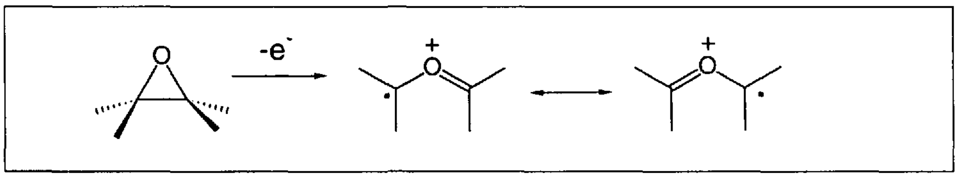


Fig. 6. *Excited-state energies of hexatriene-radical cation at the neutral and the cation geometry as obtained on different levels of theory.* Discussion see text.

Scheme 1. *Systems which Undergo Conformational Changes upon Ionization*





3.4. *Ring Opening Reactions Induced by Ionization*

Often, organic compounds undergo more profound structural changes upon ionization, and the elucidation of such processes where bonds are being (partially) broken or formed has moved increasingly into the focus of our research. For example, several instances of so-called '*inverted potential energy surfaces*' [26] were recently found, where structures which represent transition states on the neutral surface become equilibrium structures in the cations. One such case is semibullvalene which upon ionization collapses to a structure close to that of the transition state for the rapid *Cope* rearrangement [27][24] (*Fig. 7*).

Molecules which incorporate *small rings* are particularly prone to bond breaking upon ionization, especially in Ar matrices which are inefficient at dissipating the excess energy imparted onto the incipient radical cations. The first time we encountered this phenomenon was with ethylene oxide and its derivatives which upon ionization undergo spontaneous cleavage of the basal C–C bond, thus forming radical cations of carbonyl ylides [28]. These are theoretically interesting species due to their extremely facile antisymmetric distortion by virtue of vibronic interaction between the ground state and the excited state responsible for the broad VIS absorption which we found to be characteristic for these species.

In contrast to three-membered rings, *cyclobutanes* usually do not undergo cleavage of a single C–C bond. In fact, cleavage of cyclobutane derivatives rarely occurs already upon ionization (although the activation energy for such processes should not be large [29]) but it can usually be induced subsequently by visible photolysis. An interesting example of this is the radical cation of bicyclo[4.2.0]octa-2,4-diene ($\mathbf{3}^{+\cdot}$) [30] (see *Scheme 2*) which undergoes two different photoinduced cycloreversions: in Ar matrices, the rearrangement to octatetraene which already takes place partially upon ionization, can be completed photochemically [31]. Conversely, in Freon matrices, the dominant photochemical reaction is cleavage of the other pair of C–C bonds to yield benzene cation and ethylene which are observed in the form of their ion-molecule complex [32]. Similarly, the radical cation of cyclobutaacenaphthylene $\mathbf{4}^{+\cdot}$ is readily trans-formed into that of divinylnaphthalene by visible photolysis and that of the polycyclic cage compound **5** into the corresponding diene cation [33].

A notable exception to the above-stated rule that four-membered rings usually survive ionization intact are cyclobutabenzenes and -benzenones whose parent cations cannot be detected but appear to rearrange spontaneously to *o*-quinoid polyenes or ketenes, respectively. The characteristic IR bands of the latter permitted us to discover a phenomenon which appears to be quite universal but had previously gone unnoticed [34]: Once radical ions are formed in Ar matrices, they compete quite effectively with the added alkyl chloride for the electrons which are formed in the course of the continued X-irradiation, and are thus re-neutralized. Most of the time this process goes unnoticed, because it simply regenerates the starting material.

If prior to re-neutralization, a radical cation rearranges spontaneously to an isomer which is stable on the neutral potential energy surface, then a *net neutral rearrangement* is observed in the course of X-irradiation. Indeed, in the case of cyclobutabenzenone, a much higher yield of the neutral quinoketene is observed than can be built up in the photostationary equilibrium [34] (*Scheme 3*). Thus, in some cases, radical ions may serve as 'stepping stones' on the way to neutral high-energy isomers which are otherwise difficult to access. It is possible that such a mechanism is operative in the recently discovered method of photolysis of Xe matrices doped with halogen atoms for the formation of neutral transients [35].

3.5. *Electron-Transfer-Induced Tautomerizations*

In a joint project with the Technical University of Lodz (Poland), we are engaged in the study of compounds which upon ionization suffer spontaneous *tautomerization* [36]. Our first results concerned molecules which had previously been found to undergo photoinduced tautomerization, in particular photoenolization, such as *o*-alkyl substituted aromatic carbonyl compounds (*a*) [37], but more recently we discovered that the scope of this reaction is larger in that it encompasses also formyl (*b*) and OH groups (*c*) as hydrogen donors as well as NO_2 (*d*,*e*) and NO groups (*f*) as hydrogen acceptors [38] (*Scheme 4*).

In many cases, the neutral tautomers of such species are unknown, either because they cannot be formed photochemically, or because they revert too rapidly to the

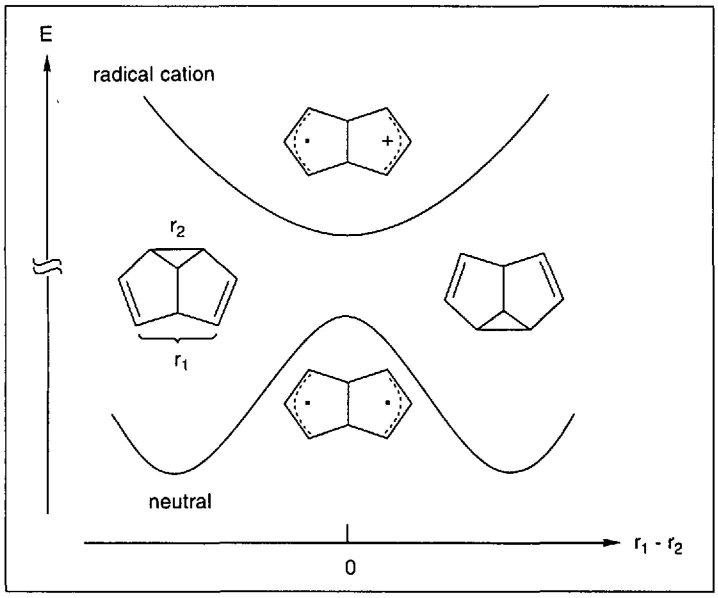
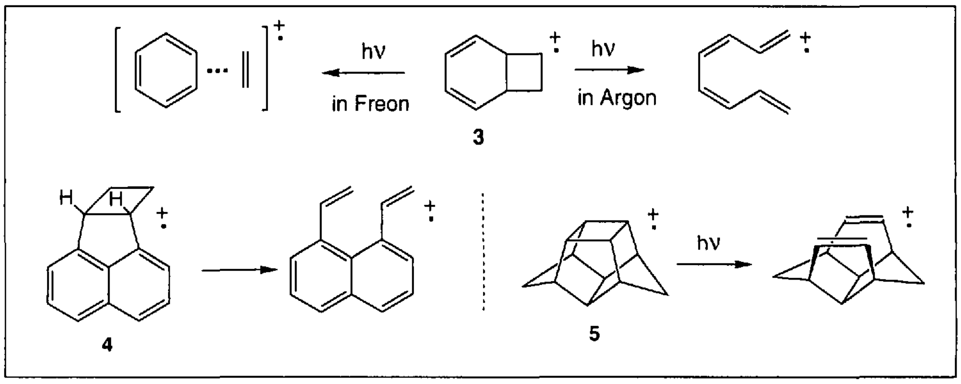
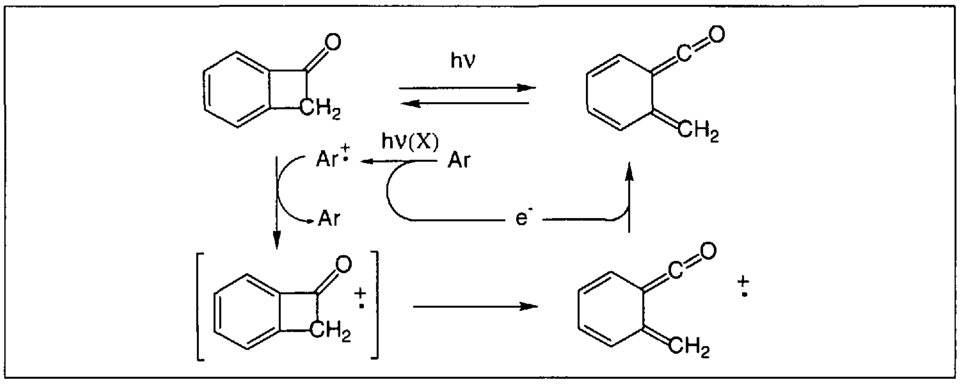


Fig. 7. *'Inverted potential-energy surface' for the radical cation of semibullvalene*

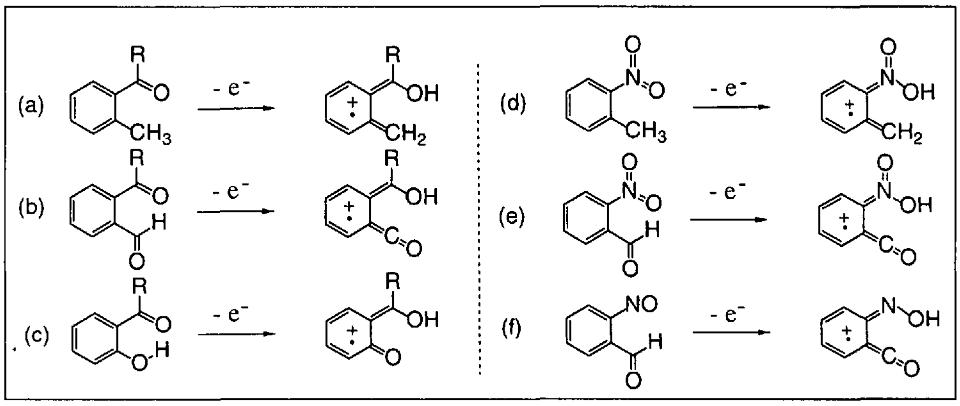
Scheme 2. *Photoinduced Cycloreversions of Radical Cations Containing Four-Membered Rings*



Scheme 3. *Generation of Neutral 'Photopoducts'* via *Radical Cations*



Scheme 4. *Different Classes of Compounds which Undergo Spontaneous Tautomerization upon Ionization*

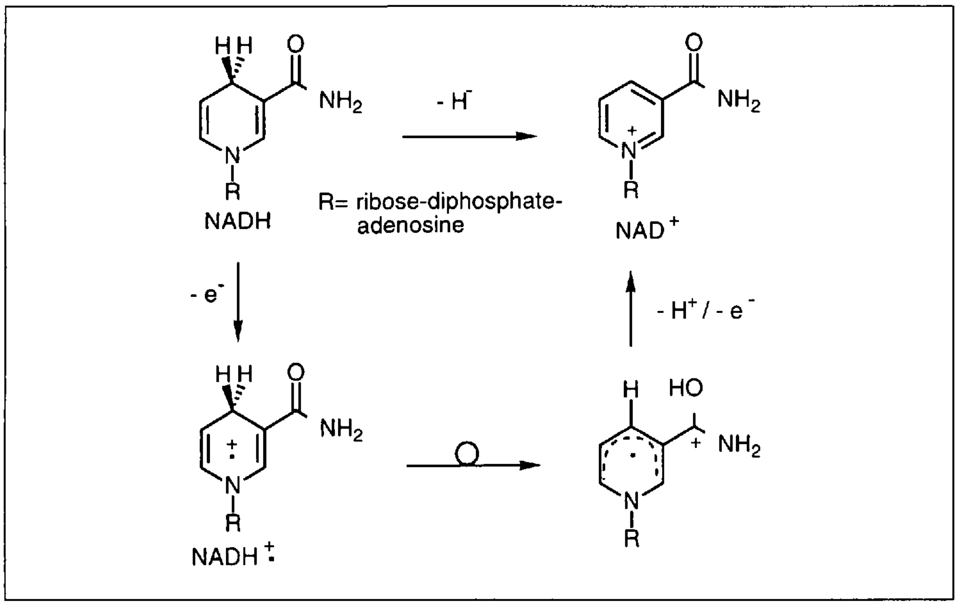


corresponding starting materials, a process which often involves quantum chemical H-atom tunnelling. Thus, only the *anti* conformers of the *o*-methyl-substituted aromatic carbonyl compounds have a sufficiently high lifetime for them to be observed spectroscopically, while, in the radical cations, all possible conformers can be observed and their photochemical interconversion be studied [39].

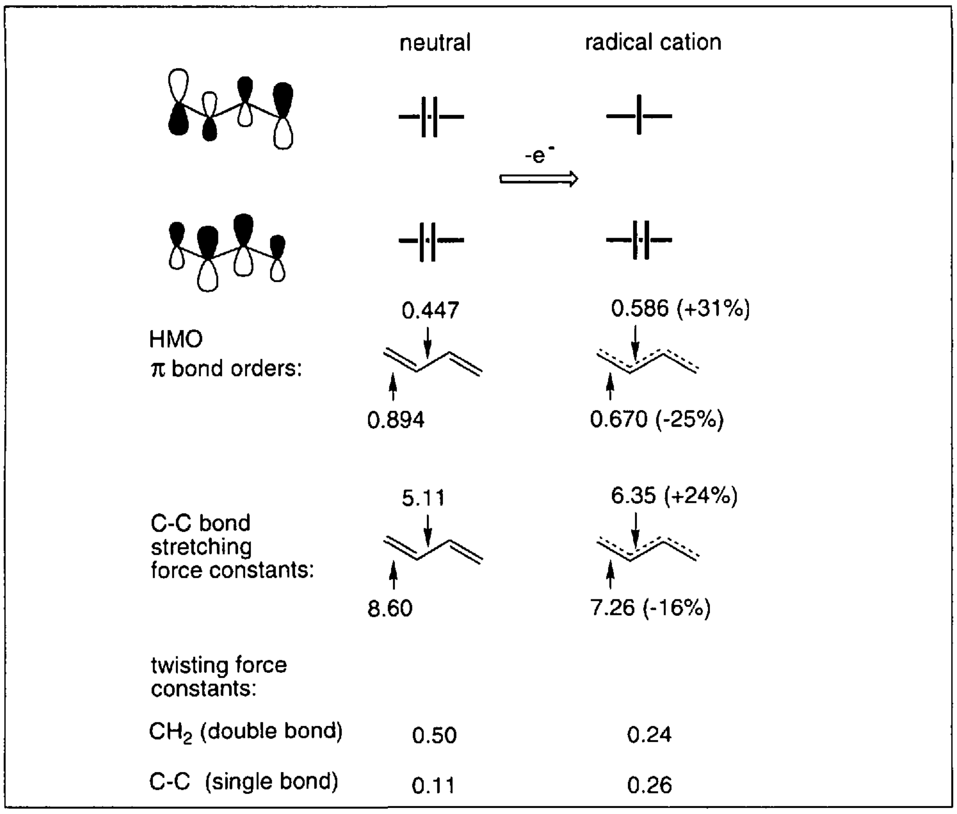
The importance of these reactions lies, however, in the field of molecular biology where several instances of such processes were observed, and where electron-transfer-induced tautomerization is a viable mechanistic possibility. Thus, the NADH → NAD^+ conversion which has usually been assumed to proceed *via* a single hydride-transfer could very well take place *via* stepwise electron/proton/electron transfer (*Scheme 5*).

We are currently investigating this possibility by generating the radical cations of synthetic NADH analogs (R = alkyl, aryl). The occurrence of an O–H stretch in the IR spectrum after ionization would constitute a direct proof for the feasibility of the $e^-/H^+/e^-$ pathway in the NADH → NAD^+ transformation.

Scheme 5. *Hydride-Transfer and Electron/Proton/Electron-Transfer Mechanism for the NADH → NAD^+ Interconversion*



Scheme 6. *Changes in π–Bond Orders and in Related Valence-Force Constants upon Ionization of Butadiene*



3.6. *Vibrational Structure of Organic Radical Cations*

The study of excited states represents a rather indirect way to gauge the changes in chemical bonding upon ionization. The study of ground state properties of radical ions by spectroscopic methods has been limited largely to Electron-Spin Resonance (ESR), a very powerful method indeed whose results we have repeatedly paired up with those obtained in our laboratory by EA spectroscopy. In national and international cooperations with ESR research teams, we have probed various molecular rearrangements and conformational changes induced by ionization which would have been impossible to fully elucidate by either of the two methods alone [40–43].

However, until recently we had no method at our disposition to directly probe the properties of individual chemical bonds before and after electron transfer. Ideally, one would like to do this by looking at changes in molecular structure (especially bond-lengths and -angles) but, unfortunately, this is not generally possible due to the high reactivity of radical ions. As an alternative, we launched a program targeted at the investigation of electron-transfer-induced changes in *valence-force constants*. To arrive at these, we measure complete IR spectra before and after ionization, assign as many fundamental normal modes as possible, and fit those to a quantum-mechanically computed force field by means of a set of scaling factors, building on techniques developed for and applied to neutral molecules mainly by *Pulay et al.* [44].

The present account leaves no room for a detailed description of the experimental and theoretical conditions which must be fulfilled for such studies to result in a trustworthy set of valence-force constants. Of course, complete IR spectra can only be measured in noble-gas matrices and usually a set of isotopomers is required to arrive at a reasonable approximation of the 'true' harmonic force field. Also, it is very useful in practice, if the radical cation can be fully bleached or photoisomerized after its formation so that one can monitor the rise and fall of IR bands of the target substrate and thus arrive at a clear distinction from those of possible side products.

For different practical and conceptional reasons, we chose the molecule of butadiene for a pilot study of this type [45]. We measured the IR spectra of six isotopomers of C_{2h} symmetry and were able to assign 43 of the 72 IR-active fundamentals of their radical cations. These were used to scale a force field calculated at a correlated level of *ab initio* theory, a procedure which resulted in accurate predictions for all relevant valence-force constants of butadiene radical cation (with the notable exception of the single bond stretch which, unfortunately, does not participate in any IR-active fundamentals of butadiene). At the same time we re-optimized the force field of the neutral [46] and were thus able to directly compare the changes induced by loss of an electron.

The most pertinent results of this study are summarized in *Scheme 6*: unsurprisingly, we found that the double bonds get weaker while the single bond gains strength upon removal of an electron from the HOMO of butadiene which is bonding along the former and antibonding along the latter. This expresses itself also in the force constants for twisting around the two types of bonds which are even more directly related to the changes in π-bond order, and which become nearly indistinguishable in the radical cation, thus justifying the drawing of dotted lines instead of localized double and single bonds for this species. The other force constants are not as strongly affected by ionization although subtle, but systematic changes in the properties of the C–H bonds were noted.

The program initiated by the above study continues and will be extended in two ways: firstly, longer polyenes as well as compounds with triple bonds will be investigated in order to arrive at an understanding of the electron-transfer-induced changes in chemical bonding in polyenes and related compounds as a function of chain length, and secondly, cooperations with groups who have complementary experimental techniques which permit the study of IR-inactive as well as low-energy vibrations of radical cations (ZEKE photoelectron spectroscopy, resonance *Raman* spectroscopy) are under way in order to arrive at a more comprehensive understanding of the vibrational structure of radical cations.

4. Conclusion

In this account, I have attempted to provide a rough survey of the methods available to my research group and the kinds of problems which we like to study with these. No attempt was made to be comprehensive, and in fact, many facets of our research which have been or still are dear to our hearts were passed over for space reasons. Thus, our numerous investigations concerning the *photochemistry* of radical cations [47], a research field full of surprises and challenges, were only touched upon in passing [48]. Also, our ongoing program for the investigation of the radical cations of carbenes and their diazo precursor cations which we undertake in cooperation with the groups of Prof. *Gerson*, Basel, and Prof. *Platz*, Ohio State University, and which is providing increasingly fascinating insights [42] went unmentioned. Also, I felt that a discussion of our efforts to apply modern quantum chemical techniques to the study of radical ions, which, by virtue of their open shell electronic structure, pose quite intriguing problems, may be beyond the scope of an article targeted at a general audience, although computational chemistry has become a tool of major importance to our research [49]. Finally, we are constantly involved in numerous side-projects, some of which may evolve into main lines of investigation.

More importantly, we must of course always pose the question where our research is headed and assess its relevance in the context of a changing world. As mentioned in the *Introduction*, our work is situated in the general context of single-electron-transfer chemistry, undoubtedly one of the pivotal areas of research in nearly all branches of chemistry at this time, and it will, therefore, remain relevant for a foreseeable future. Our activities in this field are well adapted to our situation as members of a small University with limited resources, in that we are not exposed to excessive competition in the field of condensed phase radical-ion spectroscopy. On the other hand, our contributions have served to initiate many national and international cooperations, most of which have proven very fruitful.

Following general trends, it is likely that in the future we will occupy ourselves increasingly with problems close to or at least of relevance to biological chemistry, in particular enzymatic processes where mechanisms involving single-electron transfer are increasingly being postulated. If the means for an expansion of our infrastructure become available, we will consider to extend our studies to include the probing of electron-transfer processes at surfaces and interfaces. Meanwhile, there are many more problems we would like to study (or colleagues of us would like us to study) than we can handle, especially in view of the declining number of Swiss students willing to take up chemistry as their branch of science.

First and above all I would like to express my gratitude to Prof. *Edwin Haselbach* for his continuing support and encouragement and his active participation in some of the studies mentioned in this account. Then, very little of what is described in *Sect. 3* would exist, were it not for the unflagging efforts of the graduate and diploma students with whom I had or still have the pleasure to cooperate. In particular, I am indebted to *Stephan Nitsche*, *Kuno Roth*, *Weilin Tang*, *Daniel Scherrer*, *Leo Truttmann*, *Stephan Matzinger*, and *Zhendong Zhu* for their perseverance and their important contributions. Thirdly, I would like to thank my colleagues *Tadmasa Shida* (Kyoto University), *Matthew Platz* (Ohio State University), *Ffrancon Williams* (University of Tennessee), *Jerzy Gebicki* and *Jacek Michalak* (Technical University of Lodz) as well as *Petr Čársky* and *Pavel Jungwirth* (Czech Academy of Sciences) for their invaluable contributions to our joint projects. Last, but not least, continued financial support by the *Swiss National Science Foundation* is gratefully acknowledged.

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[1] 'Photoinduced Electron Transfer', Eds. M.A. Fox and E. Chanon, Elsevier, Amsterdam, 1989 (3 Volumes).

[2] a) W.H. Hamill, in 'Radical Ions', Eds. E.T. Kaiser and L. Kevan, Wiley, New York, 1968; b) T. Shida, 'Electronic Absorption Spectra of Organic Radical Ions', Elsevier, Amsterdam, 1988.

[3] T. Bally, in 'Radical Ionic Systems', Eds. A. Lund and M. Shiotani, Kluwer, Dordrecht, 1991.

[4] See, *e.g.*, G.N. Lewis, D. Lipkin, *J. Am. Chem. Soc.* **1942**, *64*, 2801.

[5] See the chapters by T.A. Miller, V. Bodybey as well as by D. Klapstein, J.P. Maier, L. Misev, in 'Molecular Ions: Spectroscopy, Structure, and Chemistry', Eds. T.A. Miller and V. Bodybey, North Holland Publ. Co., Amsterdam, 1983.

[6] T. Shida, E. Haselbach, T. Bally, *Acc. Chem. Res.* **1984**, *17*, 180.

[7] C. Sandorfy, *Can. J. Spectrosc.* **1965**, *10*, 85.

[8] A. Grimison, G.A. Simpson, *J. Phys. Chem.* **1968**, *72*, 1776.

[9] B. Badger, B. Brocklehurst, *Nature (London)* **1968**, *219*, 261.

[10] See: E. Haselbach, T. Bally, R. Gschwind, U. Klemm, Z. Lanyiova, *Chimia* **1979**, *33*, 405, and ref. cit. therein.

[11] See, *e.g.*, H. Bock, B.G. Ramsay, *Angew. Chem.* **1973**, *85*, 773; H. Bock, *J. Chem. Educ.* **1974**, *51*, 507.

[12] D.S. Urch, *Eur. Spectrosc. News* **1980**, *28*, 55 quoted in: J. Spanget-Larsen, *Croat. Chim. Acta* **1984**, *57*, 1991.

[13] P. Cársky, R. Zahradník, *Topics Curr. Chem.* **1973**, *43*, 1.

[14] T. Bally, S. Nitsche, K. Roth, E. Haselbach, *J. Am. Chem. Soc.* **1984**, *106*, 3927; T. Bally, K. Roth, W. Tang, R.R. Schrock,

K. Knoll, L. Y. Park, *ibid.* **1992**, *114*, 2440.

[15] E. Haselbach, U. Klemm, R. Gschwind, T. Bally, L. Chassot, S. Nitsche, *Helv. Chim. Acta* **1982**, *65*, 2464; T. Bally, L. Neuhaus, S. Nitsche, E. Haselbach, J. Janssen, W. Lüttke, *ibid.* **1983**, *66*, 1288; T. Bally, D. Hasselmann, K. Loosen *ibid.* **1985**, *68*, 345; T. Bally, K. Roth, R. Straub, *ibid.* **1989**, *72*, 73.

[16] T. Bally, W. Tang, M. Jungen, *Chem. Phys. Lett.* **1992**, *190*, 453.

[17] P. Bischof, J.A. Hashmall, E. Heilbronner, V. Hornung, *Helv. Chim. Acta* **1969**, *52*, 1745. We thank *K. Asmis* for remeasuring the spectrum at 22 meV resolution for the purpose of *Fig. 4*.

[18] E. Haselbach, T. Bally, Z. Lanyiova, P. Baertschi, *Helv. Chim. Acta* **1979**, *62*, 583; spectrum remeasured in Freon mixture for the purpose of *Fig. 4*.

[19] H. Prinzbach, H.D. Martin, Z. Zhu, T. Bally, to be published.

[20] M. Fülscher, T. Bally, S. Matzinger, to be submitted to *Chem. Phys. Lett.*

[21] A. Almenningen, O. Bastiansen, L. Fernholt, B.N. Cyvin, S.J. Cyvin, S. Samdal, *J. Mol. Struct.* **1985**, *128*, 59; O. Bastiansen, S. Samdal, *ibid.* **1985**, *128*, 115.

[22] J.P. Maier, D. W. Turner, *Disc. Farad. Soc.* **1972**, *54*, 149.

[23] See, *e.g.*, D.S. Boudreaux, R.R. Chance, J.F. Wolf, L.W, Shacklette, J.L. Brédas, B. Thémans, J.M. André, R. Silbey, *J. Chem. Phys.* **1986**, *85*, 4584, where the related case of polyanilines is discussed in some detail.

[24] T. Bally, L. Truttmann, F. Williams, S. Dai, manuscript in preparation

[25] P.I. Kimmel, H.L. Strauss, *J. Phys. Chem* **1968**, *72*, 2813, and ref. cit. therein; see also: J.H. Hammons, D.A. Hrovat, W.T. Borden, *J. Am. Chem. Soc.* **1991**, *113*, 4500.

[26] F. Williams, *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1681. See also the related concept of 'nonvertical radical cations' proposed by H. Roth, *Acc. Chem. Res.* **1987**, *20*, 343.

[27] S. Dai, J.T. Wang, F. Williams, *J. Am. Chem. Soc.* **1990**, *112*, 2835.

[28] T. Bally, S. Nitsche, E. Haselbach, *Helv. Chim. Acta* **1984**, *67*, 86.

[29] See P. Jungwirth, T. Bally, *J. Am. Chem. Soc.* **1993**, *115*, 5783.

[30] T. Bally, K. Roth, R. Straub, *Helv. Chim. Acta* **1989**, *72*, 73.

[31] T. Bally, E. Haselbach, S. Nitsche, K. Roth, *Tetrahedron* **1986**, *42*, 6325.

[32] T. Bally, K. Roth, R. Straub, *J. Am.Chem. Soc.* **1988**, *110*, 1639.

[33] T. Bally, K. Roth, Z. Zhu, unpublished results.

[34] T. Bally, J. Michalak, *J. Photochem. Photobiol., A* **1992**, *69*, 185.

[35] G. Maier, S. Senger, *Angew. Chem.* **1994**, *106*, 605, and ref. 1 therein.

[36] J. Gebicki, A. Marcinek, J. Michalak, J. Rogowski, T. Bally, W. Tang,. *J. Mol. Struct.* **1992**, *275*, 249.

[37] A. Marcinek, J. Michalak, J. Rogowski, W. Tang, T. Bally, J. Gebicki, *J. Chem. Soc., Faraday Trans. 2* **1992**, 1353; J. Michalak, T. Bally, J. Gebicki, *Pol. J. Chem.* **1993**, *67*, 1403.

[38] J. Michalak, J. Gebicki, T. Bally, *J. Chem. Soc., Faraday Trans. 2* **1993**, 1321; J. Michalak, T. Bally, J. Gebicki, *Radiat. Phys. Chem.*, in press.

[39] W. Tang, T. Bally, to be published.

[40] F. Williams, S. Dai, L.D. Snow, X.-Z. Qin, T. Bally, S. Nitsche, E. Haselbach, S.F. Nelsen, M.F. Teasley, *J. Am. Chem. Soc.* **1987**, *109*, 7526.

[41] J.-N. Aebischer, T. Bally, K. Roth, E. Haselbach, F. Gerson, X.-Z. Qin, *J. Am. Chem. Soc.* **1989**, *111*, 7909.

[42] T. Bally, S. Matzinger, L. Truttmann, M.S. Platz, A. Admasu, F. Gerson, A. Arnold, R. Schmidlin, *J. Am. Chem. Soc.* **1993**, *115*, 7007.

[43] T. Bally, L. Truttmann, S. Dai, J.T. Wang, F. Williams, *Chem. Phys. Lett.* **1993**, *212*, 141.

[44] P. Pulay, G. Fogarasi, G. Pongor, J. E. Boggs, A. Vargha, *J. Am. Chem. Soc.* **1983**, *105*, 7037.

[45] W. Tang, X.-L. Zhang, T. Bally, *J. Phys. Chem.* **1993**, *97*, 4373.

[46] W. Tang, T. Bally, *J. Phys. Chem.* **1993**, *97*, 4365.

[47] E. Haselbach, T. Bally, *Pure Appl. Chem.* **1984**, *56*, 1203.

[48] For some typcial examples see: T. Bally, S. Nitsche, K. Roth, E. Haselbach, *J. Phys. Chem.* **1985**, *89*, 2528; Y. Fujisaka, M. Makino, T. Takahashi, T. Shida, K. Roth, R. Straub, T. Bally, *ibid.* **1992**, *96*, 2206 as well as Refs. 30, 31, 41, 43 above.

[49] See, *e.g.*, T. Bally, *J. Mol. Struct (Theochem)* **1991**, *227*, 249.

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Vibrational *Raman* Optical Activity Comes of Age

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Abstract. It is almost precisely 20 years since the first recording of an entire vibrational *Raman* optical activity (VROA) spectrum was accomplished. We describe some of the developments which by now have allowed the measurement of carbohydrates, peptides and even proteins, and nucleic acids. While we outline the enormous general potential of VROA for structural determinations of chiral molecules, our emphasis is on the particular potential the separate determination of the isotropic and anisotropic invariants of the optical activity scattering tensor has for the interpretation of VROA data.

1. A Historic Perspective which is also an Outlook

Two decades have elapsed since the modest experimental inception of vibrational *Raman* optical activity (VROA) [1][2]. What was looked at, by many chemists and physicists alike, with the notable exception of some stereochemists, as a curious little effect, almost impossible to measure and prone to misinterpretation and artefacts, is gradually revealing its potential of becoming the most powerful chiroptical method of the future. This achievement is owed to the perseverance of a small group of chemical physicists who never wavered in their belief in the potential of vibrational *Raman* optical activity.

We will elaborate in some detail on the potential of VROA in the following paragraphs and give a general argument here. Without wanting to take away from the merit of people working in the field of classical optical activity, our view can certainly be justified that the spectroscopic situation for determining chiral structures, apart from special X-ray techniques, has actually been for decades a dismal one, the only generally available techniques being the circular dichroism of electronic transitions and optical rotatory dispersion. This is equivalent to a situation where for ordinary structure determination the only spectroscopic method available would be visible and UV absorption spectroscopy and the measurement of the

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