Forschung, Wissenschaft

Electronic and Molecular Structure of some Organic Radical Cations in Rigid Organic Systems *

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Abstract

Some recent investigations on organic radical cations $M^{\ddagger}$ obtained by γ-ray induced ionic processes in rigid organic systems are reviewed. Particular attention is paid to the strategy of comparing the electronic spectrum of $M^{\ddagger}$ with the UV-photoelectron spectrum of the parent neutral M, yielding insight into the nature of the electronic states of $M^{\ddagger}$, into medium effects influencing them, and into relaxation and isomerization processes undergone by $M^{\ddagger}$.

Introduction

Electron transfer is a key step in a variety of chemical processes. If the reactants are closed-shell neutrals (M), radical ions $M^{\ddagger}$ are produced. *Hamill* and *Shida* pioneered the use of rigid organic matrices for the spectroscopic study of such species, obtained by γ-ray induced ionic processes [1,2]. Improved methods for the identification of the cations $M^{\ddagger}$ have become available with the advent of UV-Photoelectron Spectroscopy (UPS). The virtue of simultaneously considering the electronic spectrum (ES) of $M^{\ddagger}$ and the UPS of M (for a collection of references see [3], [4]) lies in the fact the experiments start from two different ground state systems M and M^{+}, but reach the same excited state of the cation (Fig. 1). It follows that differences between the ionisation energies ΔI of M correspond to the excitation energies ΔE of $M^{\ddagger}$ provided:

a) that both transitions show up in the spectra. In UPS, transitions to states of $M^{\ddagger}$ which are strongly dominated by "Non-*Koopmans*" configurations Ψ_{NK} [5] (B-, C-type configurations in [6], A-, B-type configurations in [7]) are not observed; they would require a simultaneous movement of two electrons. Alternatively, for the ES of $M^{\ddagger}$ the electric dipole selection rules apply. A comparison between the two spectra thus allows, in principle, an experimental configuration analysis of the states of $M^{\ddagger}$;

b) that there is no solvation effect in passing from the gas phase UPS of M to the condensed phase ES of $M^{\ddagger}$. Observable shifts thus lead to an insight into the interaction of a charged species with the medium; such information is badly lacking in the literature (comp. [8]).

The above applies in principle to the respective adiabatic transition energies. Such data, however, are not easily available. A match of the vertical energies can be expected provided:

c) that the *Franck-Condon* (*FC*) factors for the corresponding UPS- and ES-transitions are equal. It follows that a mismatch of the *FC*-profiles provides insight into differences in bonding between the ground states of M and $M^{\ddagger}$. Such differences indicate a geometric relaxation of M on ionization, or even an activated chemical process with $M^{\ddagger}$ taking place. Such observations ultimately link the features of the ion $M^{\ddagger}$

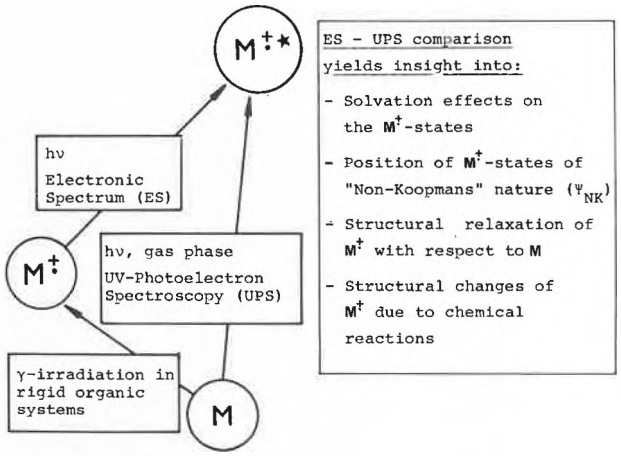

Fig. 1: Scheme to compare the electronic spectrum (ES) of $M^{\ddagger}$ and the UV-photoelectron spectrum (UPS) of M, and expected results.

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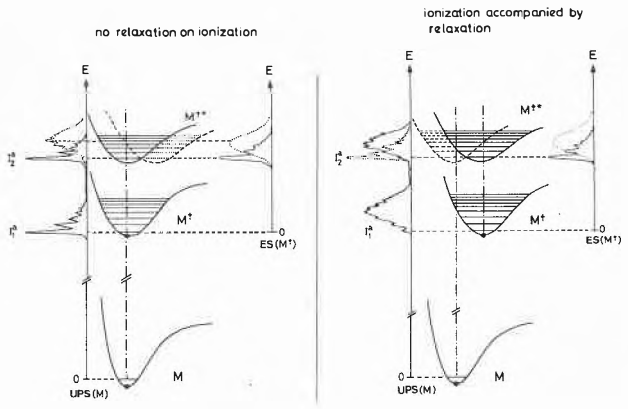

Fig. 2: Franck-Condon profiles of corresponding UPS- and ES-transition bands for "no relaxation" (left) and "relaxation" (right) in the course of $M \rightarrow M^+ + e^-$.

with the much better known molecular properties of the parent neutral M (Fig. 2).

The present paper describes some examples pertinent to the questions raised above.

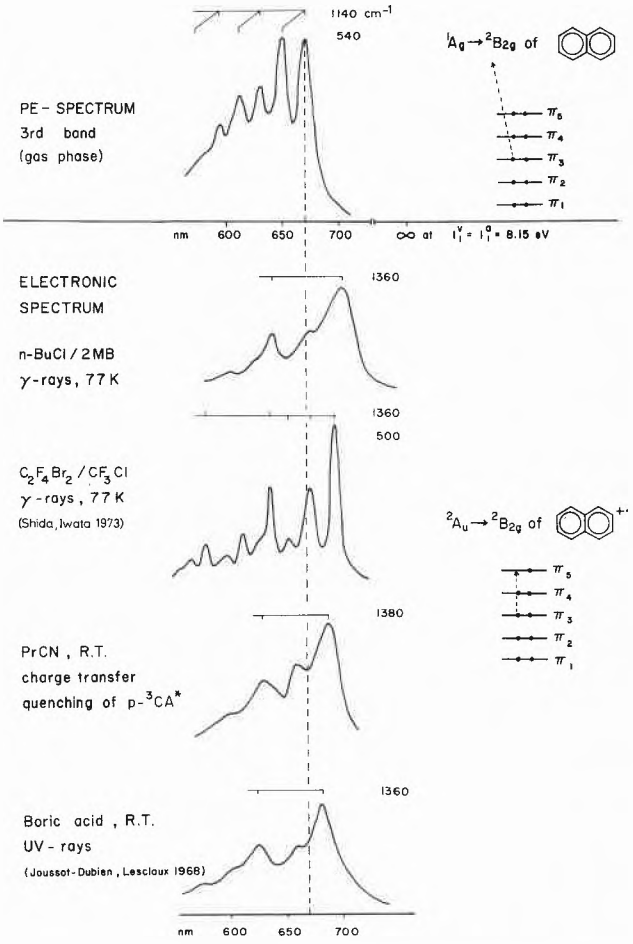

Fig. 3: Ionisation from π_3 of naphthalene (NP) ($^1A_g \rightarrow {}^2B_{2g}$) in comparison with $\pi_3 \rightarrow \pi_5$ excitation of NP^+ ($^2A_u \rightarrow {}^2B_{2g}$). Solvent shifts for the latter transition.

Solvation Effects

In a correlation between ES-data of M^+ and UPS-data of M *Shida* and coworkers [3] noted a general red shift of the condensed phase spectra, being slightly dependent on the matrix used. The same features are noted in Fig. 3 where the third UPS-transition $^1A_g \rightarrow {}^2B_{2g}$ of naphthalene (NP) is compared with the corresponding ES-transition $^2A_u \rightarrow {}^1B_{2g}$ of NP^+, prepared in four different media: in nBuCl/2MB [9] and $C_2F_4Br_2/CF_3Cl$ [7] by γ-irradiation at 77 K, in boric acid at R.T. by photoionization [10], and by charge transfer quenching of the p-chloranil (CA) triplet in PrCN at R.T. [11]. All condensed phase 0–0 transitions are red-shifted as a result of the higher polarizability of the excited ionic state. This observation parallels the experience with closed shell neutrals (such as NP itself) or ions whose ground states do not engage in specific interactions with the medium, and where the transition is not associated with significant charge transfer. If, however, these conditions are not fulfilled, blueshifts such as found for closed-shell ions in [8] or for $n \rightarrow \pi^*$ excitation of neutrales (e.g. acetone: 273 nm (gas), 265 (H_2O)) may also be expected. In this respect it is interesting to note that the NP^+ transitions shift slighthly to the blue with increasing polarity of the medium (the polarity order given in Fig. 3 was established using *Dimroth*'s dipole [12]). Apparently, excitation of NP^+ is (contrary to NP) accompanied by some charge transfer, leaving the upper state less optimally solvated. Inspection of the π-orbitals involved in the transition indicates that positive charge is transferred from the periphery to the central part of the ion (Fig. 4).

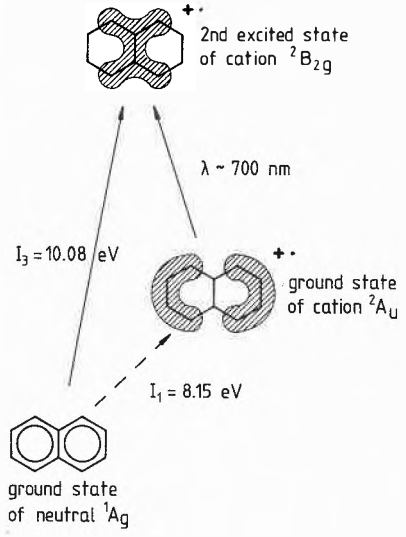

Fig. 4: Displacement of charge in NP^+ on $^2A_u \rightarrow {}^2B_{2g}$ excitation.

The results suggest that proper attention has to be paid to possible solvation effects if gas phase UPS and condensed phase ES are compared in a quantitative manner.

M^{+}-States of "Non-*Koopmans*" nature

Such states, involving heavy contributions of "Non-*Koopmans*" configurations Ψ_{NK}, are well known in XPS ("shake-up" configurations). Only few states of this type have been identified yet in UPS, mainly for smaller systems and in the high energy region of the spectrum. Clearly, an illuminating example would be a system where already the *first* excited state is dominated by Ψ_{NK}. Promising candidates require a HOMO-LUMO gap somewhat smaller than the gap between the first two doubly occupied levels. Inspection of HMO-tables led to the investigation of the o-xylylene

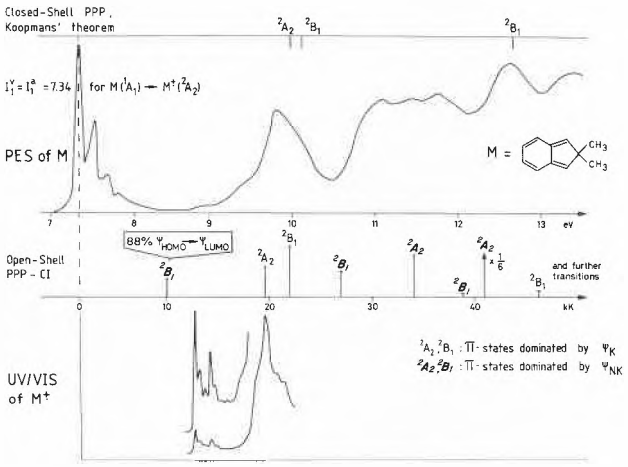

Fig. 5: Comparison between the photoelectron spectrum of dimethylisoindene (DMI) and the electronic absorption spectrum of DMI^{+}: Disclosure of the first excited doublet state of the ion of "Non *Koopmans*" nature.

derivative 2,2-dimethyl-isoindene (DMI). Fig. 5 shows its UPS, the assignement of the excited π-states being based on calculations of the transition energies from a) the closed-shell PPP-procedure and applying *Koopmans*' theorem (top), and b) the openshell PPP-CI procedure [6] (bottom). Many additional states for DMI^{+} result from the latter approach (italics), most notably a first excited $^2B_1$-state composed of ~88% Ψ_{NK} (HOMO → LUMO). It is situated at an energy where the UPS is empty; however, in DMI^{+} the $^2A_2 \rightarrow {}^2B_1$ (Ψ_{NK}) transition is allowed with $f_{calc.} = 0.03$. γ-irradiation of DMI in nBuCl/2MB at 77 K yields the ES shown in Fig. 5. The band system at ~20 kK corresponds to the allowed transitions predicted also by the UPS. *In addition* now, the band system at ~13 kK can be assigned to $^2A_2 \rightarrow {}^2B_1$ (Ψ_{NK}) predicted by theory.

On several occasions it has been stated that "the n-th UPS-ionization potential of M corresponds to the energy of the (n-1)th excited state of the parent ion M^{+}". Our example shows that this statement must be viewed with due caution; it fails in the present case already for n = 2! A full account of this work will be published in [13].

As a second contribution pertinent to this chapter we shall point out an open question regarding butadiene radical cation (BD^{+}) whose UPS is shown in Fig. 6.

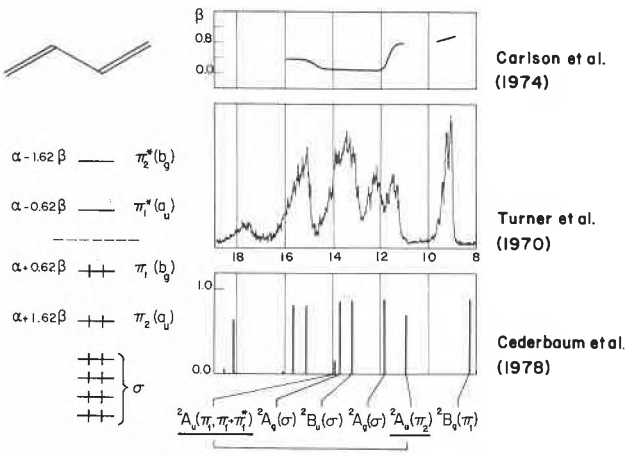

Fig. 6: Photoelectron spectrum of t-butadiene (BD) and its interpretation.

The assignment for the first three bands: $\pi_1(b_g)$, $\pi_2(a_u)$ and $\sigma(a_g)$ (in this order) is now firmly supported by the recent high quality calculations of *Cederbaum* et al. (below) as well as by the angular dependence of the photoelectron emission (above). Note that the theoretical pole strength for $^1A_g \rightarrow {}^2A_u$ (π_2) is significantly reduced; the remaining intensity is buried in the $^1A_g \rightarrow {}^2A_u$ ($\pi_1, \pi_1 \rightarrow \pi_1^*$) process, the upper state lying ~5.5 eV above the BD^{+} ground state and being dominated by Ψ_{NK} (HOMO → LUMO). Another estimate for this state energy (^2E), based on the singlet (^1E) and triplet (^3E) energies of BD [14] and using the formula $^2E = (^1E \cdot {}^3E)^{1/2}$ (valid for HOMO → LUMO excitations in alternant systems [15]), leads to 4.5 eV. We conclude that an (allowed) ES-transition to this state in BD^{+} is *not expected above ~300 nm.*

Fig. 7 shows a summary of earlier work dealing with the ES of BD^{+} (b), together with the predictions deduced from UPS (a). In addition our own results in nBuCl/2MB are shown, where

- minimal concentrations of BD were used to prevent $(BD)_2^{+}$-formation (d),
- photolysis of cyclobutene^{+} provided an independent source of BD^{+} (e).

Both the matrix and the gas phase photodissociation work (c) agree with the UPS-prediction of two allowed transitions at ~560 nm and ~300 nm. The intensity of the latter suggests that it is not due to the formally allowed transition to ^2B_u (σ) (which has a small moment) but to the transition to the Ψ_{NK}-dominated ^2A_u (π)-state mentioned above. Important, however, is that all matrix spectra show a band around *400 nm,* where a transition is not expected from UPS and where the gas phase photo-dissociation spectrum indeed is empty.

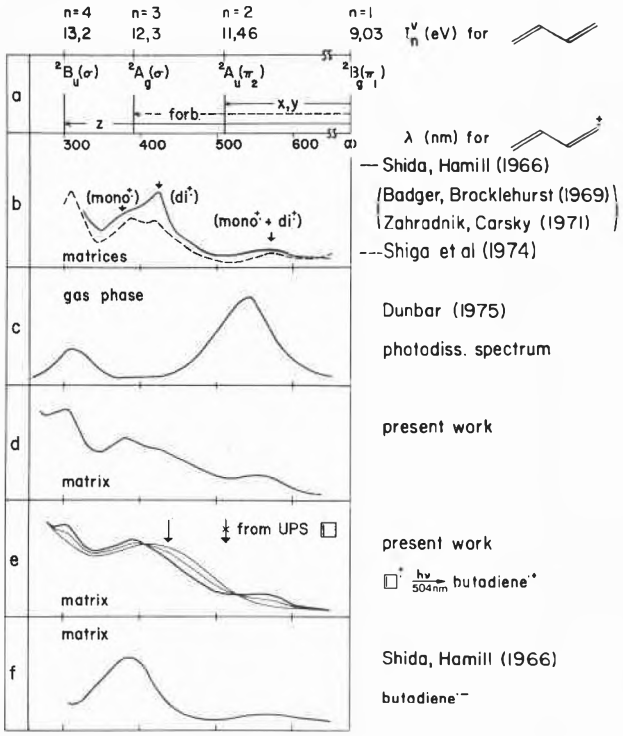

Fig. 7: Collection of the electronic absorption spectra of BD⁺ obtained under various conditions.

Note that also BD⁻ (f) exhibits this band as expected from the alternancy principle.

We have found no reasonable explanations (based on solvent shift or structural arguments) for the discrepancy between the matrix and the gas phase results and must therefore leave the question open to debate. As BD (or BD⁺) are key compounds in chemistry and spectroscopy, every effort should be put into finding an answer to this problem.

Structural Relaxation

Structural relaxation of M upon ionization to M⁺ is by definition a non-activated process for the isolated system. In a matrix, however, the rigid environment imposes an intermolecular potential which may prevent extensive relaxation. Thermally or light induced softening of the matrix removes this constraint.

Small differences in bonding between M and M⁺ are recognised in slightly different *FC*-profiles for corresponding UPS- and ES-transitions. An example is provided by NP and NP⁺ in Fig. 3; the two bands differ in the vibrational modes excited as qualitatively expected from the HMO-bond order changes for the two processes. A detailed analysis of the *FC*-factors is in progress.

Larger relaxation effects manifest themselves by strong changes in the ES. Pertinent examples were given by *Shida* [17], who studied M⁺ composed of π-systems connected by essential single bonds. Obviously, for such cases, UPS and ES should differ markedly. A nice example of this kind is the cation of [3]radialene (3R) which relaxes to X⁺ as shown in Fig. 8; the UPS of 3R and the ES of X⁺ bear now no resemblance (Fig. 9). Analysis showed that relaxation occurs by π-bond rotation yielding the species shown in Fig. 8.

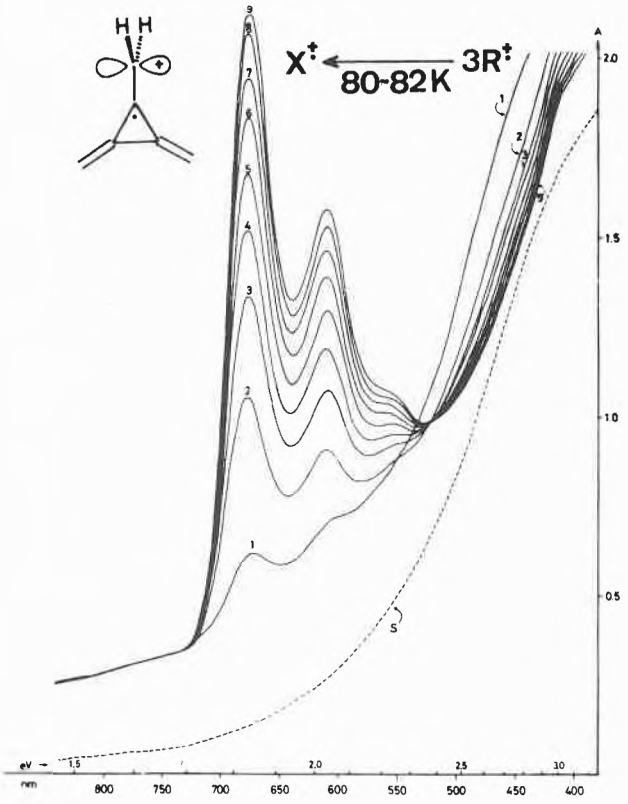

Fig. 8: Thermally induced process observed for the radical cation of [3]radialene.

The process is calculated to be favorable also in the gas phase, up to a torsional angle of ~45°. In the matrix used complete rotation may take place, which disconnects the p-AO at the exocyclic carbon atom from π-conjugation and allows full interaction with the alkyl halide component to form presumably a chloronium ion. For a complete account see [18].

Activated Processes (Isomerizations)

Several examples have been found where initially prepared M⁺ rearranges to an isomer, the transformations being either induced thermally or by light. With respect to the latter one may ask if the reaction really proceeds from excited M⁺, or if international conversion results in a local T-increase which softens the matrix, and also suffices to bring M⁺ across the ground state barrier. From theoretical considerations these barriers appear generally much lower than those for the corresponding neutrals; we have discussed such questions specifically for valence isomerizations [19]. It must also be recognised that M⁺ exhibit usually rather low

lying excited states which favors efficient internal conversion and therefore ground state processes. For work dealing with such questions we refer to [17], and for some details of the complexity of thermally induced cationic processes to [20].

Shida and *Hamill* have found that c-stilbene$^{+\cdot}$ (cS) in a rigid matrix is transformed into t-stilbene$^{+\cdot}$ (tS) by light [1]. We have repeated there work and have in addition observed (in nBuCl/2MB at 77 K) that the efficiency of the process increases drastically if irradiation occurs into the second band of cS$^{+\cdot}$ (~500 nm) instead of the first one (~800 nm). This, together with the earlier observation that the photoprocess for the neutrals (with high intrinsic ground state barrier) is very inefficient in a rigid environment, suggests that for the ionic process (with lower barrier) a local heating effect prevails being of course larger for the shorter wavelength.

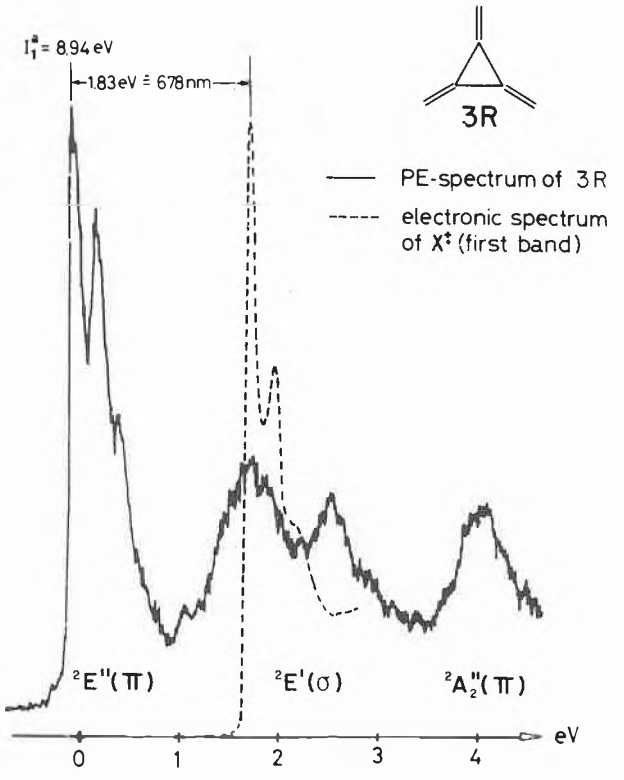

Fig. 9: Photoelectron spectrum of [3]radialene in comparison with the longest wavelength absorption of the product X$^{+\cdot}$ of the thermal process.

Similar irradiation of tS$^{+\cdot}$ leads to no detectable changes. Electron transfer quenching of several low lying acceptor triplets by either cS or tS at R.T. in polar fluid media results exclusively in tS$^{+\cdot}$ within the time scale of our laserflash photolysis apparatus (~20 ns). It appears that cS$^{+\cdot}$ is less stable than tS$^{+\cdot}$, in agreement with the findings for the corresponding radical anions [25] and also with ΔH_r^0 (cS$^{+\cdot}$ → tS$^{+\cdot}$) < 0 from ΔH_r^0 (cS → tS) < 0 and I_a^1(cS) > I_a^1(tS) for the gas phase.

For the radical anions an intrinsic barrier to isomerisation has been proven [21]. For the cations, however, this barrier – though quite likely – is not demonstrated by the above experiments. To our knowledge, no thermally induced rate process cS$^{+\cdot}$ → tS$^{+\cdot}$ could as yet be detected in matrix studies; in our matrix cS$^{+\cdot}$ bleaches at 85 K. Interestingly, tS$^{+\cdot}$ reacts under these conditions to red X whose spectrum bears some resemblance to that of cS$^{+\cdot}$ (Fig. 10). The efficiency of the process

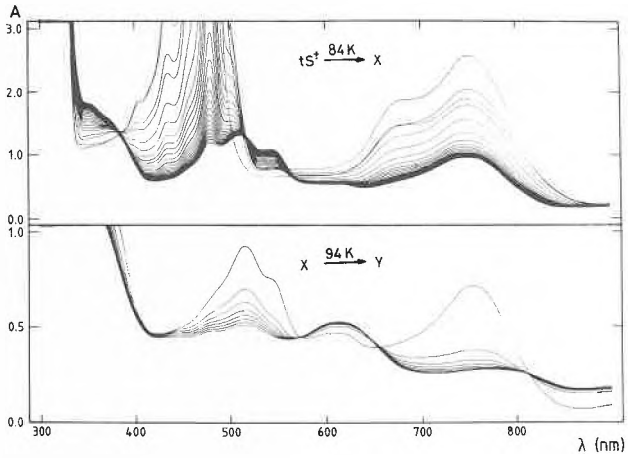

Fig. 10: Thermal processes of t-stilbene radical cation.

decreases with decreasing [tS] and bleaching becomes competitive. At 95 K X is converted to Y. Notably, tS$^{+\cdot}$ prepared by illumination of cS$^{+\cdot}$ does not exhibit X-formation but bleaches steadily. The observations are rationalized by assuming X = $(tS)_2^{+\cdot}$, i.e. dimer cation formation and subsequent collapse at higher T to an adduct Y. For cS, cS$^{+\cdot}$ steric factors prevent $(cS)_2^{+\cdot}$-formation and also the formation of a mixed dimer ion (cStS)$^{+\cdot}$ when tS$^{+\cdot}$ is prepared from cS$^{+\cdot}$ by light. Experience from exciplex chemistry suggests that hetero-dimer ions are anyway less stable than the

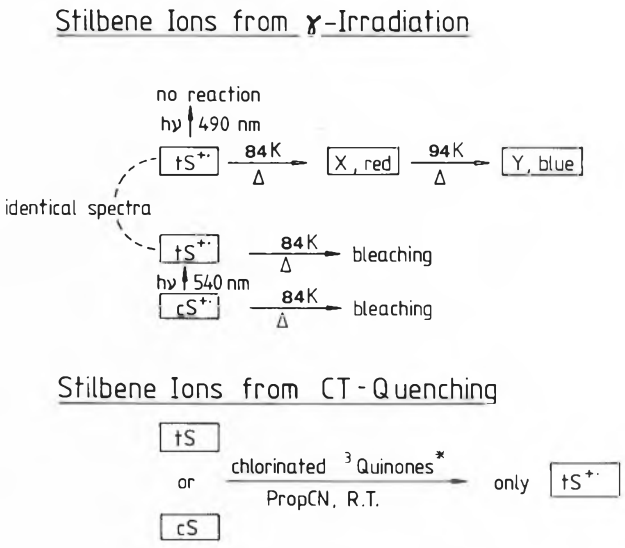

Fig. 11: Summary of preliminary results for stilbene radical cation processes.

homo-analogues. Support is also obtained from [22] where eximers were produced from oppositely charged radical ions: Only in the case of tS could emission be observed. Our preliminary results about this system are summarized in Fig. 11.

A truly electrocyclic radical cation process was reported by *Shida* and collaborators [23]: on illumination of 1,3-cyclohexadiene$^{+\cdot}$ ring opening to all-trans-1,3,5-hexatriene$^{+\cdot}$ takes place (Fig. 12). Analysis of the transient spectra revealed the intermediacy of the other three configurational triene isomers. We have found a similar light induced process for cyclobutene$^{+\cdot}$ as shown in Fig. 7. Unfortunately, no thermal activation could as yet be observed up to 90 K where bleaching sets in. The results could be taken as evidence for the presence of an intrinsic ground state barrier. Interestingly, however, the exothermicity of the hole transfer from matrix to CB (I(matrix)-I(CB) ~0.8 eV) does not suffice to initiate the reaction, whereas for the gas phase process a rather small barrier of < 0.3 eV has recently been claimed [24], in line with [19]. The energetic discrepancy between gas phase and matrix work suggests that for the latter "environmental hindrance" (understood in the most general sense) may play some role.

Contrary to the above system, for *Dewar* benzene$^{+\cdot}$ → benzene$^{+\cdot}$ (hexamethyl-derivatives) [25], and quadricyclane$^{+\cdot}$ (Q$^{+\cdot}$) → norbornadiene$^{+\cdot}$ (NBD$^{+\cdot}$) [26] only the more stable isomers were obtained (Fig. 12). Analysis shows that here the barriers should be lower and/or the change of molecular shape very modest. Evidently, "environmental hindrance" does not show up here; hole transfer is also more exothermic and may well lead to increased softening and/or a "hot" reaction. Addition of "hole transfer moderators" to the latter system still does not render Q$^{+\cdot}$, suggesting that the barrier can be overcome at 77 K even under nearly thermalized conditions.

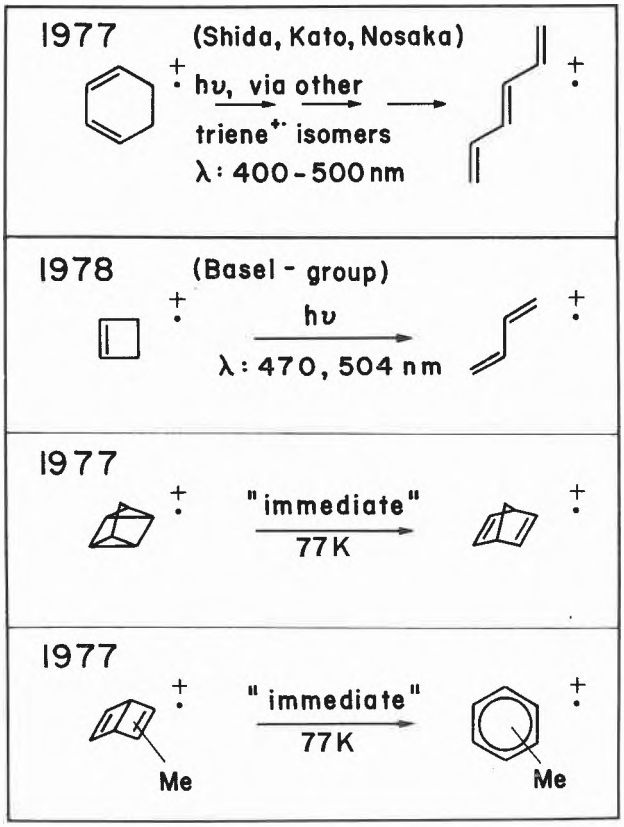

Fig. 12: Summary of electrocyclic radical cation processes.

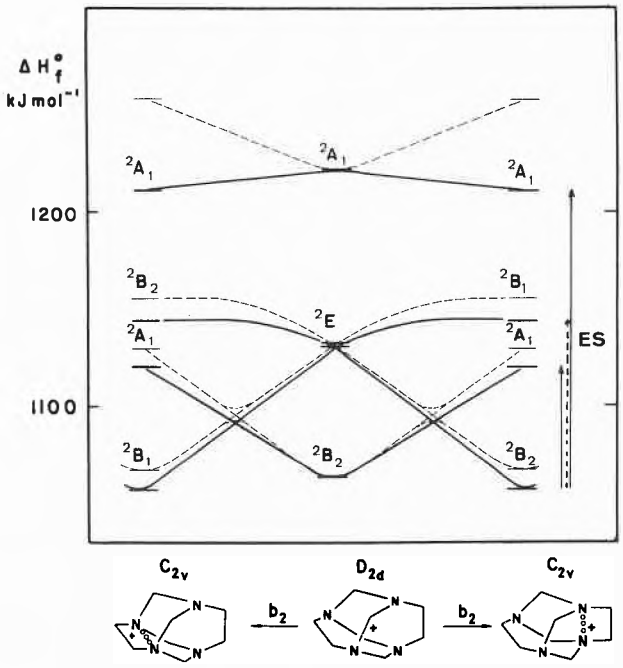

Fig. 13: State correlation diagram for the isomerization of 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane radical cation (TA$^{+\cdot}$).

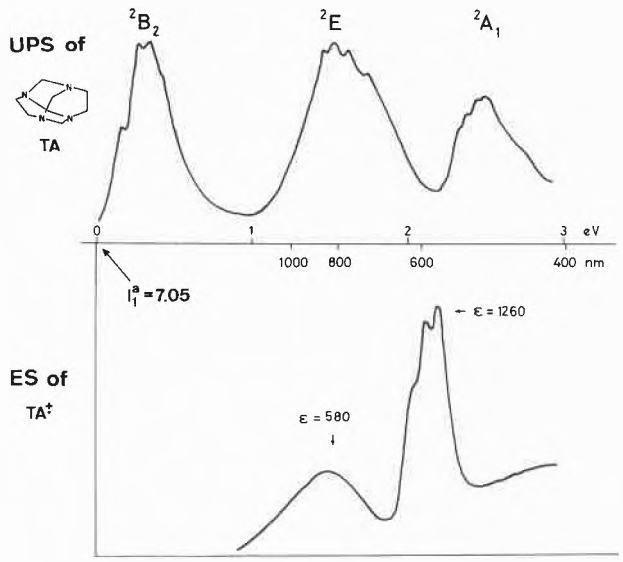

Fig. 14: Photoelectron spectrum of TA (D_{2d}) and electronic spectrum of the C_{2v}-isomer of TA$^{+\cdot}$.

A final example is the tetraamine system (TA) shown in Fig. 14. The UPS revealed a b_2-HOMO for TA (Fig. 14, top). As the ESR-spectrum of TA^+ (showing D_{2d}-symmetry also for the ion) favored an e-HOMO, an unprecedented "HOMO-inversion" between TA and TA^+ was postulated [27]. Subsequent MINDO/3-calculations (Fig. 13, dashed lines) resolved the puzzle: excited D_{2d}-TA^+ (^2E) is strongly Jahn-Teller active, the degeneracy being lifted by the b_2-mode. As the D_{2d}-ground state rises along this coordinate real crossing (no CI) occurs which renders a new ground state for TA^+ of C_{2v}-symmetry, exhibiting a 3 electron – 2 centre N-N-bond. In condensed phase the predicted energetic equality between the two gas phase isomers will be changed in favor of the C_{2v}-ion with more localized charge (full lines). The intervalence transition between the equivalent C_{2v}-isomers across the small barriers via the higher energy D_{2d}-intermediate is fast on the ESR-time scale and simulates effective D_{2d}-symmetry. On the other hand, the time averaged coupling constants arise from an electron moving in the $b_2(b_1)$-MO of the C_{2v}-ions which still exhibit the nodal characteristics of the e-MO of the D_{2d}-structure. These arguments were put forward in [28]. They subsequently found support (Fig. 14) by the discrepancy between the UPS of TA and the ES of TA^+ (prepared from TA by oxidation with an aminium salt, by CT-quenching of the triplet of p-dicyanobenzene, and by γ-irradiation in nBuCl/2MB): The latter spectrum exhibits a transition around 2 eV, where the UPS is empty. The example shows again the virtue of comparing the UPS of M and the ES of M^+ to disclose unexpected bonding situations in the ion. It also underlines the importance of medium effects on the structure of charged species. One might add that for the related system DABCO a perfect correspondence between its UPS and the ES of $DABCO^+$ exists [3,25]. Hence, speculations whether the ion perhaps exists in a [2,2,2]propellane-like structure with 3 electron – 2 centre N-N bond can be discarded.

Conclusions

In this paper, some aspects concerning the electronic and molecular structure of open-shell cations M^+ were discussed. It was emphasized that comparison between the UPS of M and the ES of M^+ is of great help in obtaining insight into the properties of the ion, conveniently prepared in rigid organic matrices by γ-irradiation. Mechanistic interpretation of observed ionic processes is, however, hampered by the fact, that – with respect to fluid media – the rigid environment poses additional constraints on the solute ion. Much work needs to be done towards disentangling its intrinsic properties from those of the bulk material.

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