Theoret. Chim. Acta (Berl.) 59, 251–279 (1981)

THEORETICA CHIMICA ACTA

Comments About the Representation of Rydberg and Ionic Excited States and Their Photochemistry

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This paper discusses the conditions for representing Rydberg and ionic excited states of molecules. It especially shows the intrinsic difficulties of MO methods to treat the weak resonances between strongly polarized situations in highly polarizable symmetric systems; such situations occur in the long distance region for Rydberg excited states of homonuclear molecules, and for the 90° twisted singlet excited states of polyenes. The valence/Rydberg mixing is discussed, and some principles for the understanding of Rydberg photochemistry are proprosed, based on a few examples. The present knowledge of the photochemistry of zwitterionic excited states of polyenes is summarized.

Key words: Excited states – Photochemistry – Sudden polarization – H-F instability.

1. Introduction

Theoretical photochemistry is so productive now that a few pages review is impossible and we have chosen to study a minor part of it, namely the somewhat exotic excited states;

(i) "Rydberg" excited states (i.e. those which cannot be represented using valence AOs) [1]).
(ii) "Ionic" excited states, according to Valence Bond Theory. The lowest excited states of polyatomic molecules (especially the unsaturated molecules) usually are "neutral" in the sense of this theory; the lowest triplet states for instance are obtained by breaking covalent bonds to give diradicals (eventually dissociative),

0040-5744/81/0059/0251/$05.80

but in these states the molecule avoids ionic stituations in which two electrons, due to orthogonality constraints to the lower neutral states, must stay on the same atom, creating strong *instantaneous* dipoles with large fluctuation; these situations characterize the ionic states.

These excited states are not accessible to the intuitive description of electronic properties; they even are not treatable through *ab initio* monoelectronic methods, the parametric algorithms seem rather insecure to follow the events which occur in these highly versatile excited states [2], and some specific problems are difficult to overcome, even with *ab initio* CIs.

This partial review is devoted to an illustration of the difficulties to represent correctly the properties of such states, and their photochemical properties. We hope to underline a few unexplored questions.

2. Rydberg States Representability

Rydberg states may be calculated by adding appropriate diffuse AOs to the usual basis set. For diatomic molecules, they may be chosen through an optimization of the separated atoms Rydberg states; this procedure insures a correct dissociation limit; it may underestimate specific molecular changes at short distances. For polyatomic molecules minimal basis sets with one exponent ($\simeq$0.03, 0.025, 0.020 for O, N, C respectively) have been proposed [3] and are widely used.

These representations arise a few questions:

(i) what is the relationship between the best exponent for a Rydberg state of the carbon atom, and for the Rydberg state of CH_4; what is the influence of the H atoms shell on the Rydberg state of the molecule? In other words, is the united atom for the molecule the central heavy atom?
(ii) is a single gaussian sufficient, even when there is only one heavy atom, as in hydrides XH_n? The exponent will be chosen to realize a good balance between potential and kinetic energy on one hand, and orthogonality constraints on the other hand. The overall energy will be reasonable and, since in the energy xpression

$$\Delta E = \varepsilon^*_{\mathscr{R}} - \varepsilon_v - J_{\mathscr{R}v},$$

the distance between valence and Rydberg electrons appears through the coulombic integral, one may hope that the mean distance between the Rydberg electron to its centroid r_0,

$$\langle \mathscr{R} | (r - r_0)^2 | \mathscr{R} \rangle, \text{ will be correct.}$$

Experience confirms that the minimum of the curve of the energy E as a function of the exponent is rather flat [4],

$$\frac{d^2E}{d\zeta^2} \text{ small near the minimum,}$$

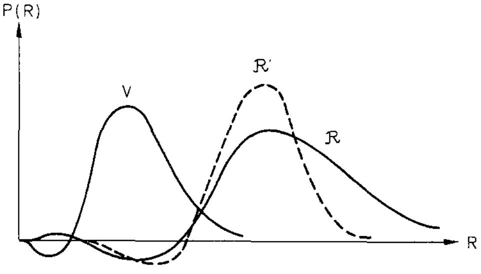


Fig. 1. Qualitative defects of a poor representation R' of the Rydberg orbital R, namely a bad long distance behaviour and a bad differential overlap with the valence AOs V

and one may consider further improvements as unnecessary. Actually the photochemical events usually concern the crossing with a valence dissociative state, and the main problem concerns a correct location of this crossing in energy and distance.

One cannot forget however the strong defects of such a minimal description of the Rydberg cloud (cf. Fig. 1).

The long distance part of the density is meaningless and the intermolecular properties of the excited state cannot be treated (especially the pressure effects on the spectra, which are so important to determine the Rydberg/valence character of an excited state). van Hemert and van der Avoird recently calculated the $H_2O\cdots H_2O$ and $H_2O\cdots Ne$ interactions [5]; they used a single set of diffuse Gaussians on oxygen, but also on the H atoms; this choice insures some plasticity to their basis set, but the long range repulsion should be underestimated.

In a diatomic problem (A_2 or AB), the potential curves which dissociate into A^*+A or A^*+B where A^* is a Rydberg state are not correct at long distances due to a bad differential overlap between the Rydberg function of A and the valence AOs of its partner.

The internal part of the orbital is not precisely reproduced, and the differential overlap between the Rydberg ($\mathcal{R}^*$) and Valence (v) orbitals of the same atom is bad [6].

$J_{\mathcal{R}^*v}$ may be correct→correct transition energy and $\int|\mathcal{R}^*v|\,dv$ uncorrect→ $\langle\mathcal{R}^*|\mathbf{r}|v\rangle$ bad→bad transition moment; $K_{\mathcal{R}^*v}$ bad→bad singlet-triplet splitting.

One may notice immediately from the energy expression

$$\Delta E^{(1,3)}_{v\mathcal{R}^*} = \varepsilon_{\mathcal{R}^*} - \varepsilon_v - J_{\mathcal{R}^*v} + \{2, 0\}\, K_{\mathcal{R}^*v}$$

that the best exponent is different for the triplet and the singlet states, the singlet being more diffuse, due to the repulsive exchange term. The difference between optimal ζ is important (15% difference for the $3p^5 4s$ configuration of Ar; Spiegelmann, F., private communication).

The errors on the S.T. separation prevent a correct treatment of the spin–orbit effects, which result from a balance between the spin–orbit parameter and the S.T. separation. For instance spin–orbit will mix ${}^1\Sigma_u$ and ${}^3\pi_u$ states through the equation

$$\begin{vmatrix} E(^1\Sigma_u)-\mathscr{E} & \sqrt{2}\xi \\ & E(^3\pi_u)-\xi-\mathscr{E} \end{vmatrix} = 0$$

and an error in the Singlet Triplet difference before spin–orbit interaction $(E(\Sigma_u)-E(^3\pi_u)\rightarrow 2K_{3p,4s}$ when $R\rightarrow\infty)$ may introduce spurious barriers near the curve crossing between the attractive $^1\Sigma_u$ and repulsive $^3\pi_u$ states [7] (cf. Figs. 2 and 3).

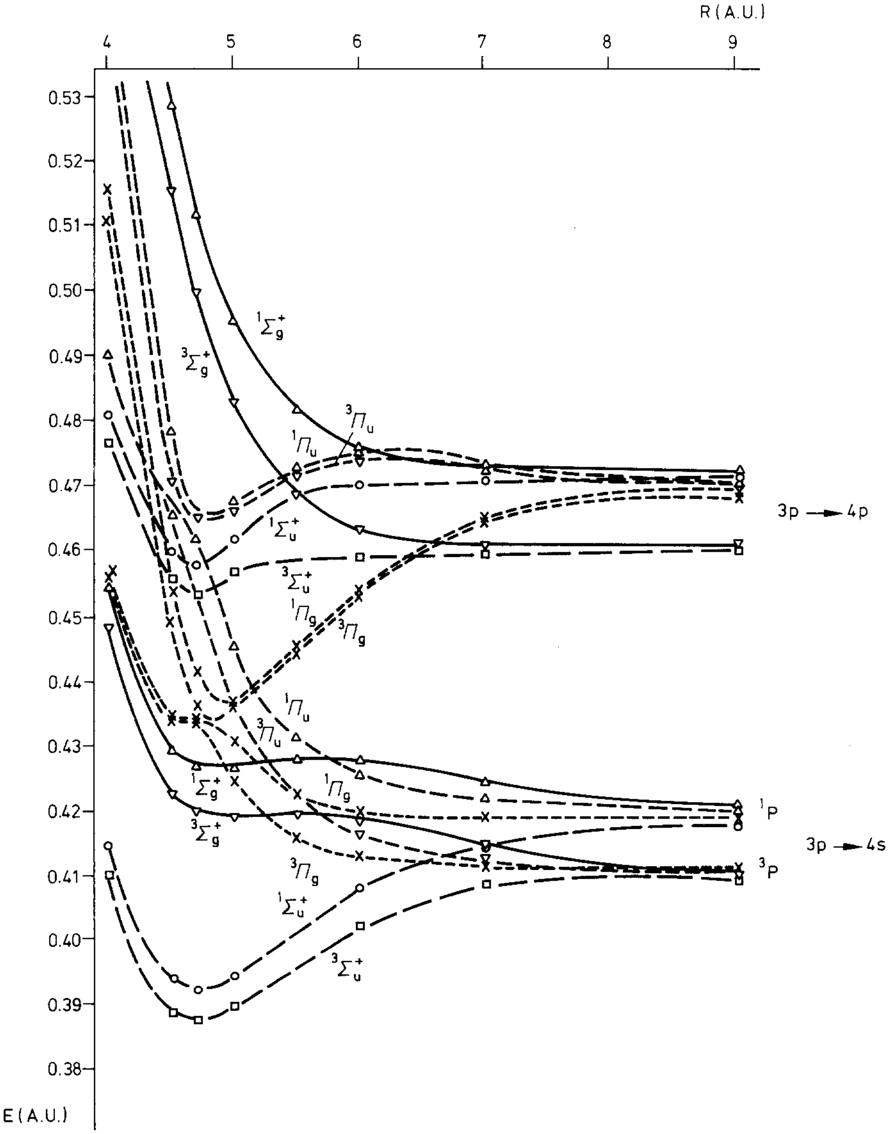


Fig. 2. Ar_2 potential curves before spin–orbit coupling. Notice the strongly avoided crossings in the Σ_g^+ states (from F. Spiegelmann, Thesis, Toulouse (1978))

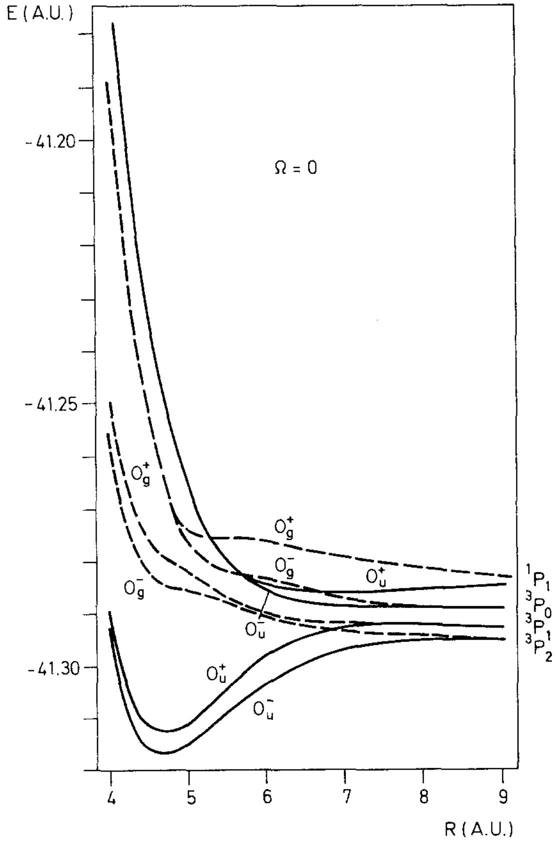


Fig. 3. $\Omega = 0$ Ar_2 potential curves dissociating in the $3p \rightarrow 4s$ configuration after spin–orbit coupling. Notice the weak 0_u^+ long distance hump (same Ref. as for Fig. 2.)

The conclusion is clear: it is almost necessary to use at least a double ζ representation of Rydberg orbitals to improve both the long distance decrease of the density and the valence–Rydberg overlap. If one only deals with the singlet *or* the triplet state one may contract these two AOs.

(iii) for a molecule containing several "heavy" atoms, should one introduce several sets of diffuse AOs, one on each heavy atom, or introduce only a unique basis in the center of the molecule? The latter solution [8] seems in better agreement with the proper definition of the Rydberg state (based on the united atom model), but it is more rigid and may neglect some important physical-features: in a lone pair containing polyatomic molecule, (involving N and O atoms for instance), the lowest Rydberg excited states are obtained from the pure p lone pairs of the heteroatoms, and the hole-particle attraction $J_{\mathcal{R}v}$ distorts the Rydberg orbital towards the atom bearing the hole.

Some authors introduce diffuse AOs on the heteroatoms only (and not on the C atoms) but this practice may be unbalanced.

The opposite solution [9] (one set of diffuse AOs on each atom) may face near dependance problems, due to the large overlap between diffuse AOs on neighbouring atoms. The coefficients of the diffuse MOs become very large, and the calculation of bielectronic repulsion integrals (ij, kl) for the CI step involves multiplications of large numbers (and cancellations) resulting in a loss of accuracy. Such large basis sets of diffuse AOs (for instance double ζ on each heavy atom) may encounter tremendous numerical difficulties. Ref. [11] compares two CI calculations on the vertical spectrum of formamide, one with a single set of diffuse AOs located on the C atom [10], the other one [11] introducing three sets (for N, C, O). At the SCF level (Fock operator of the Ground State) the second calculation gives 11 virtual Rydberg MOs below the lowest valence π^* antibonding MO, instead of four in the first calculation; in this calculation the Rydberg states were not calculated as accurately as the valence states, but it only predicted 2 Rydberg singlet states under the ${}^1\pi\pi^*$ valence state, while the second calculation predicts 5 such states under the valence singlet state, and 2 Rydberg triplet states, ($n \rightarrow \sigma_R^*$ and $\pi \rightarrow \sigma_R^*$), under the lowest valence ${}^3\pi\pi^*$ triplet state. It is likely that in such heteroatomic molecules, the lowest diffuse MOs keep an important local (or anisotropic) character, with different weights on the different centers, and it becomes impossible to simply hierarchize (ns or np) these MOs according to their number of nodes. In other words, even if they are diffuse, these MOs keep some memory of the heterogeneity of the molecule.

The use of diffuse AOs on a single center may be correct for the study of the vertical spectrum, but does not allow the description of the dissociation. The best extensive studies of Rydberg states potential curves concern the rare gas dimers (see Ne_2 [12], Ar_2 [13], Kr_2 [14] and Xe_2 [15]); the qualitative behaviour of their lowest excited states have been well understood by Mulliken [16]. The lowest ${}^{3,1}\Sigma_u^+$ excited states are associated to the stable ground state ${}^2\Sigma_u^+$ of the molecular ion, obtained by ejecting one electron from the σ_u combination of p_z doubly occupied AOs which strongly repell each other in the ground state of the neutral molecule. For Ar_2^+ for instance the ${}^2\Sigma_u^+$ ground state potential curve presents a 1.3 eV well at short distance [17] (4.7 a.u.; the van der Waals minimum for the neutral ${}^1\Sigma_g^+$ ground state being at 7.2 a.u.). The attractive excited states of the neutral molecule are obtained by adding one electron in a $4s$ or $4p$ diffuse AO to the ${}^2\Sigma_u^+$ core. The Rydberg electron diminishes to some extent the depth of the potential well (0.75 eV for the ${}^{3,1}\Sigma_u^+$ of the $3p^5 4s$ configuration), without changing the position of the minimum; the Rydberg state closely resembles its parent ion (with increasing similarity for higher n).

To represent the excited state minimum region, a single s or p diffuse MO centered in the middle of the bond would be sufficient. For the dissociative part of the curve one must introduce, for the $3p \rightarrow 4s$ atomic configuration, one $4s$ AO on each center, which give, besides the $4s$ molecular MO,

$$4s_M = \mathcal{N}(4s_A + 4s_B),$$

a molecular "$4p_z$" MO (with a higher number of nodes than a canonical $4p$ MO, but a similar spatial extent)

$$4p_{zM} = \mathcal{N}'(4s_A - 4s_B)$$

which will have a very large overlap with the symmetry MO built from the $4p_z$ AOs centered on each atom

$$4p'_{zM} = \mathcal{N}''(4p_{zA} + 4p_{zB})$$

$$\langle 4p_{zM} | 4p'_{zM} \rangle \gg 0.$$

This illustrates a typical trouble of the atom ↔ molecule change for Rydberg states. The SCF MOs progressively change their nature when R varies, strongly avoided crossings occur between various configurations, which prevent a well defined identification of molecular situation to a peculiar atomic configuration ($3p \to 4s$ *or* $3p \to 4p$ for Ar_2; see for instance in Fig. 2a the lowest ${}^{1,3}\Sigma_g^+$ potential curves). The semiempirical treatment of Spin–Orbit effects linked to special atomic configurations, such as the well-known Cohen and Schneider scheme [12], fails for such states.

2.1. *Failure of the MO Schemes for the Treatment of Resonance Between Rydberg Excitations* [4]

One may prove that the long range part of the potential curves for an homonuclear diatom Rydberg excited state is very difficult to calculate in an MO scheme. The departure from the atomic limit $A^* + A$ is due to the left/right resonance of the excitation

$$\psi = 1/\sqrt{2}\,(A^*A' \pm AA'^*).$$

At large $R_{AA'}$ distances, the excitation fluctuates, it is at each moment *either* on the left atom *or* on the right one, but in the excited atom the valence MOs are more concentrated than in the neutral one (valence shell repolarization in the Rydberg state). This is physically evident.

Turning back now to the MO description

$$\left.\begin{aligned} \sigma_u &= 3p_{zA} + 3p_{zB} = (p + p') \\ \sigma_g &= 3p_{zA} - 3p_{zB} = (p - p') \end{aligned}\right] \quad \text{Valence}$$

$$\left.\begin{aligned} \sigma_g^* &= 4s_A + 4s_B = (s + s') \\ \sigma_u^* &= 4s_A - 4s_B = (s - s') \end{aligned}\right] \quad \text{Rydberg}$$

the Σ_u molecular state will be obtained as a mixture of excitations $\lambda(\sigma_u \to \sigma_g^*) + \mu(\sigma_g \to \sigma_u^*)$. As λ, $\mu \to 1/\sqrt{2}$ when $R_{AA'} \to \infty$, the excitation becomes $[(p \to s) + (p' \to s')]/2$, as necessary. But whatever the choice of the Fock operator to determine the MOs (even an MC SCF one), the closed shell MOs, built from $3p_x^2$, $3p_y^2$ and $3s^2$ AOs, are calculated in an *average* field, with a one electron hole spread on both centers. They therefore are calculated, for long distances, in a field of half-electron hole, these MOs are *half polarized*, intermediate between the ground-state and the excited state situation. The MO picture without sufficient CI does not tend toward the correct dissociative limit, A^*A', with one ground state and one excited atom, but toward a physically meaningless picture. A lot of CI will be necessary to introduce the physical contraction and diffusion of the electron clouds which follow the left–right jump of the excitation.

One may conclude that:

(i) the SCF or MC SCF energy of the diatom does not converge to the sum of the SCF energies of the separated atoms A^*+A'

$$E_{\mathrm{SCF}}^{\mathrm{sym}}(AA')^* > E_{\mathrm{SCF}}(A)+E_{\mathrm{SCF}}(A'^*) \text{ when } R\to\infty.$$

(ii) for large enough distances, a Hartree–Fock instability should occur by breaking the symmetry with respect to the inversion center

$$\exists R_0 \text{ so that } R>R_0 \Rightarrow E_{\mathrm{SCF}}^{\mathrm{sym}}(AA')^* > E_{\mathrm{SCF}}^{\mathrm{unsym}}(AA'^*) = E_{\mathrm{SCF}}^{\mathrm{unsym}}(A^*A').$$

(iii) the precise conditions for this instability remain to study, but they clearly depend on the resonance interaction amplitude

$$|\langle\psi(A^*A')|H|\psi(AA'^*)\rangle|.$$

The largest interaction is the R^{-3} dependant interaction between the transition dipoles if the $A\to A^*$ transition is dipole-allowed, but it necessarily must become smaller, for large enough distances, than the valence shell repolarization that one obtains by leaving the symmetry.

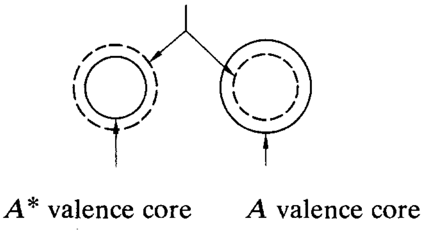
(iv) One might be tempted to start from symmetry broken solutions (excitation on one side), but the resonance no longer appears as a degeneracy, as it should; using the MOs obtained for the A^*A' situation, the AA'^* state is no longer degenerate since the valence MOs are too contracted on A and too diffuse on A'^*

$$E(AA'^*)>E(A^*A') \text{ if the MOs are calculated for } A^*A'.$$

The situation may be summarized as follows, the closed shell valence MOs being labeled "valence core",

Symmetry MOs

→half polarized "valence core"

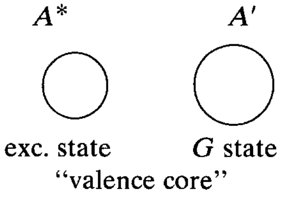


→ bad (MC) SCF dissociation limit, large CI necessary to reach it,

but degeneracy OK, correct long distance behaviour (ex: R^{-3})

Symmetry broken (*localized*) MOs

one ground state "core", one excited state "core"



→ good SCF dissociation limit,

but no degeneracy between A^*A' and AA'^*; incorrect shape of long distance potential curves, except for very large CIs.

HF instability will occur as soon as the polarization energy lacking in the symmetry treatment is larger than the resonance energy

$$E_{\mathrm{SCF}}^{\mathrm{sym}}(AA')^* - E_{\mathrm{SCF}}^{\mathrm{unsym}}(AA'^*) > |\langle\psi(AA'^*)|H|\psi(A^*A')\rangle|$$

The dissociation limit is then correct at the SCF level but the asymptotic behaviour is not, the expected R^{-3} dependance is distorted by the non degeneracy. Such a defect is very bad if one wants to treat the collisional processes which are responsible for the broadening of atomic spectral lines.

This phenomenon and its methodologic dilemma are typical; it occurs as soon as one may consider a resonance between two local events occuring in a highly polarizable environment. Such a phenomenon is well known for the ionization of the core electrons of polyatomic symmetrical molecules [18]; in this case the resonance between the localized hole situations is very weak, much weaker than the energy lowering obtained by leaving symmetry and polarizing the valence shells in the field of a localized hole. In such a case the localized description gives a correct ionization energy at the SCF level, while the symmetry treatment requires extensive CIs to reach it.

Ionic states of symmetrical molecules furnish another example of this general phenomenon.

3. Representability of Ionic States

Ionic excited states may occur in heteronuclear and homonuclear systems. Remembering the ground state Cl Na problem, one may think of the almost isoelectronic ArCl or KrCl diatomics. The ground state is almost purely repulsive (except for a long distance Van der Waals minimum) while one may conceive an ionic excited state Kr^+, Cl^- much lower than the Kr ionization potential since Cl has a large (3.6 eV) electron affinity, and the electrostatic attraction leads to a deep hole (5.6 eV [19]) from which an intense laser emission takes place to the repulsive ground state continuum (Fig. 4).

Ionic states occur in the simplest two electron two center problem, namely for H_2, X_2 or the ethylenic π bond, in the lowest antisymmetric singlet, when treated

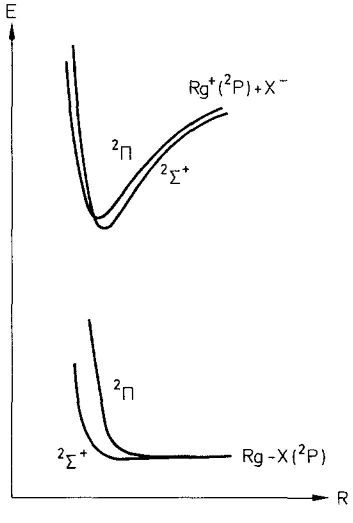


Fig. 4. Potential curves of the neutral and ionic states of rare gas halides (cf. Ref. 19)

in the valence minimal basis set

$$\varphi_g = (a+b)/\sqrt{2}, \qquad \varphi_u = (a-b)/\sqrt{2}$$

$$^1\psi_u = [|\varphi_g\overline{\varphi_u}| + |\varphi_u\overline{\varphi_g}|]/\sqrt{2} = [|a\bar{a}| - |b\bar{b}|]/\sqrt{2}.$$

Ionic states again appear as a resonance between strongly polar (zwitterionic) situations, one with two electrons on the left center (and a hole on the right one) and the reverse one. These states have a zero net atomic charge, and a zero mean dipole moment, but the charges and dipole moment exhibit large fluctuations.

$$\langle\psi|(\mu-\mu_0)^2|\psi\rangle \quad \text{large.}$$

They dissociate into an ion pair A^-B^+ or A^+B^- (except for the curve crossing with a lower Rydberg state), and they are stabilized by the R^{-1} component appearing in each localized $|a\bar{a}|$ or $|b\bar{b}|$ determinant energy. The $^1\Sigma_u^+$ excited state of H_2 is a good example; the equilibrium distance is significantly larger than for the ground state (perhaps due to the diffuseness of the negative center cloud), and this result is general; it is verified on the halogen X_2 ionic excited states as analyzed by Mulliken [20], or calculated for Cl_2 by Delbecq and Lefour [21] and by Peyerimhoff et al. [22] at a higher level of accuracy.

A correct treatment of ionic states requires:
(i) a large enough basis set to reproduce the instantaneous contraction and expansion of the electronic clouds of the atoms when they become positively and negatively charged. A double ζ basis set selected for the G.S. of the atom appears rather poor, even for the MOs which remain closed shell in the resonance process.
(ii) a large enough basis set to correlate the two electrons occupying the instantaneous lone-pair $|a\bar{a}|$; this requires polarization type AOs, but with sufficiently high exponents to introduce sufficient angular correlation (the usual polarization functions chosen for SCF calculation to give polarizability are not necessarily relevant). H_2 will require concentrated p AOs, Cl_2 and ethylene will require concentrated d AOs to obtain the angular correlation of the two electrons in the same p AO.
(iii) diffuse AOs since the ionic/Rydberg mixture may be important (see next section).

For homonuclear problems, the SCF treatment will face the same difficulties as for Rydberg excited states when the resonance between the two ionic components ($A^-A'^+$ and $A^+A'^-$) becomes weak. The symmetry MOs are calculated in a mean field, i.e. in a neutral field AA and the instantaneous polarization effects of the closed shells are only introduced through difficult correlation corrections, or by leaving symmetry. Again when resonance becomes weak, i.e. when

$$\langle|a\bar{a}||H||b\bar{b}|\rangle = K_{ab}$$

becomes small enough with respect to the polarization energy obtained by leaving symmetry

$$E_{\mathrm{SCF}}^{\mathrm{sym}}(^1\Sigma_{\mathrm{u}}) - E_{\mathrm{SCF}}^{\mathrm{unsym}}(A^-A^+)(\simeq\Delta E_{\mathrm{SCF}}(A^-)+\Delta \mathrm{E}_{\mathrm{SCF}}(A^+)),$$

(sum of the Koopmans defects for the positive and negative ions), an HF instability occurs.

This phenomenon would occur for large R_{AB} distances in Cl_2, and for a weakening of K_{ab} due to a small differential overlap in twisting the excited state of ethylene, the a and b $2p_z$ AOs becoming orthogonal at $\theta = 90°$. The Hartree–Fock instability has been noticed first by Berthier et al. [23] for the latter problem.

A real perturbation may stabilize one of the zwitterionic components with respect to the other one, and completely destroy symmetry, as if will be discussed in some length in Sect. 6.

4. Rydberg/Valence Mixing and Crossings

Such a crossing is easily predicted for the $^1\Sigma_u^+$ state of H_2, since the ionic attractive potential curve, the minimum of which lies at $91\,700\ \text{cm}^{-1}$ above the G.S. minimum, should dissociate into $H^-(10^2) + H^+$ at $140\,000,\ \text{cm}^{-1}$, while a Rydberg $^1\Sigma_u^+$ state dissociates into $H(2s) + H(1s)$ at $120\,000\ \text{cm}^{-1}$ only. A long distance curve crossing necessarily occurs in H_2.

A more complex and wonderful example is given by Cl_2 in its lowest excited state of the $^1\Sigma_u^+$ symmetry, as treated in a very powerful work by Peyerimhoff et al. [22]. This result may be understood from qualitative considerations. Let us recall that

$$\text{for } Cl_2 \quad X\,^1\Sigma_g^+ \quad (\text{G.S.}) \qquad De = 2.48\ \text{eV}, \qquad re = 1.988\ \text{Å},$$

$$\text{for } Cl_2^+ \quad X\,^2\Pi_g \quad (\text{G.S.}) \qquad De = 4.30\ \text{eV}, \qquad re = 1.892\ \text{Å}.$$

The deeper minimum in the positive ion is due to the fact that the σ covalent bond is not destroyed while an electron is removed from the π repelling clouds. Starting from the G.S. of the ion, one may build an attractive $^1\Pi_g$ Rydberg state by adding one electron in a $4s$ type diffuse MO; this is the lowest attractive singlet, which dissociates *a priori* into the $Cl^*\ (3p \rightarrow 4s) + Cl^0$ limit. From this limit one may also build $^1\Pi_u$ excited state by an antisymmetric combination of the $4s$ AOs. To build $^1\Sigma_u^+$ attractive Rydberg state one may use a diffuse π_u orbital built from $4p$ AOs and dissociating into the $Cl^*\ (3p \rightarrow 4p) + Cl^0$ limit. This $Cl^*(^2D) + Cl^0(^2P)$ limit is 12.8 eV above the $^1\Sigma_g^+$ G.S. minimum of Cl_2. By analogy with Ar_2, one may predict that for these states

$$r_e \simeq r_e(Cl_2^+) \simeq 1.89\ \text{Å},$$

the equilibrium distance is *shorter* than for the G.S., while the "dissociation energy" (before Valence/Rydberg mixing) may be evaluated to

$$D_e(Cl_2^+) > D_e(Cl^*_{2\text{Rydberg}}) \simeq 4.0\ \text{eV}.$$

There exist several configurations of the ion pair (Cl^+, Cl^-); the G.S. ^3P of Cl^+ ($3p^5$) only generate triplet states with (^1S) Cl^- ($3p^6$), while the ^1D state allows to build $^1\Sigma_u^+$ state. The $Cl^-(1D)$, $Cl^+(^1S)$ pair is 13.34 eV above the Cl_2 G.S.

minimum. As predicted by Mulliken [20], the equilibrium distance for the ionic state is larger than for the G.S.

$$r_e(\text{ionic}) \simeq 2.5\ \text{Å}$$

in both calculations [22, 23]. The minimum is lower than for the Rydberg $^1\Sigma_u^+$ state, and a curve crossing necessarily occurs at intermediate distances, near the G.S. r_e. This situation is in some sense opposite to that of $H_2\ ^1\Sigma_u^+$, the Rydberg/Valence crossing occuring here at short distances to give a double well potential.

But another Rydberg/ionic crossing will occur at large distances since one may build a $^1\Sigma_u^+$ state from $Cl^*(2P)$ $(3p \rightarrow 4s) + Cl^0(^2P)$ located at 11.4 eV above the G.S. minimum, i.e. below the previously mentioned dissociation limits. This $^1\Sigma_u^+$ state is not associated with the Cl_2^+ G.S., and is not attractive, but it will cross the ionic $^1\Sigma_u^+$ curve for large enough distances.

The lowest $^1\Sigma_u^+$ potential curve therefore results from two curve crossings and starts from a Rydberg hole at short distances, goes to an ionic minimum through a barrier at intermediate distances and finishes into a repulsive Rydberg state at long distances (through a new barrier?) (see Fig. 5).

The Rydberg/valence mixture in the vertical ionic $^1\pi\pi^*$ singlet state of ethylene has been so widely studied [24] that it is not necessary to repeat the now well established conclusions. The Rydberg character had been overestimated when the correlation was not taken into account sufficiently, especially through the use of 3*d* AOs to correlate the 2*p* electron pair of the instantaneous C^- center [24 (*g*)]. However no accurate calculation has followed the Valence/Rydberg mixing evolution when the molecule is distorted to its excited state equilibrium geometry (rotation around the C—C bond, C—C bond lengthening and pyramidalization of a carbon center) but it is likely that by stabilizing one of the zwitterionic forms

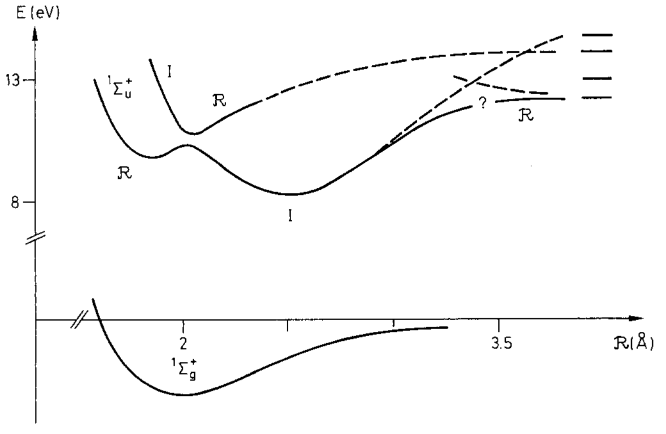


Fig. 5. Schematic representation of the Rydberg/ionic mixings in the lowest $^1\Sigma_u^+$ state of Cl_2 (from Ref. 22)

– especially through pyramidalization – these deformations should diminish the Rydberg character of this state.

An open question concerns the region of the V/R crossing. (These crossings may involve *neutral* states in photodissociation processes, cf. next section). Is it sufficient to mix the Valence and Rydberg configurations

$$\psi = \lambda V + \mu R$$

where the Rydberg state is described through diffuse AOs chosen for atomic situations? Should not intermediate AOs be necessary to allow a progressive return of the outer electron in the valence region? In other words are not the Valence/Rydberg curve crossings potential barrier systematically overestimated?

5. Photoreactions From Rydberg Excited States (without intermediate ionic states)

(A) Most of these reactions are dissociative (half collision)

$$AB^* \rightarrow A + B.$$

One may quote however a true reaction

$$A^* + BC \rightarrow AB + C.$$

The laser excited Cs atom reacts in a cell on molecular hydrogen, giving the so-called "laser snow" [25]. These white crystals seem to be built from CsH or

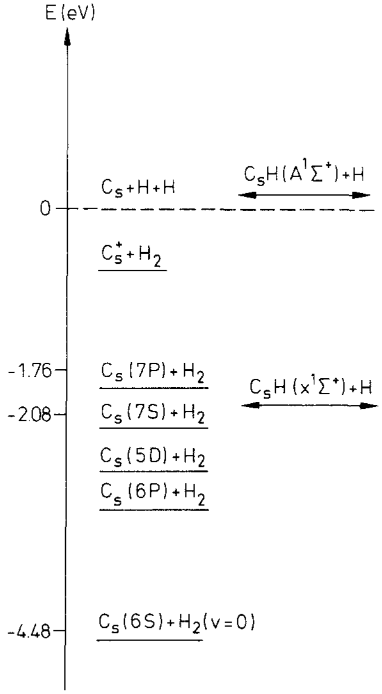
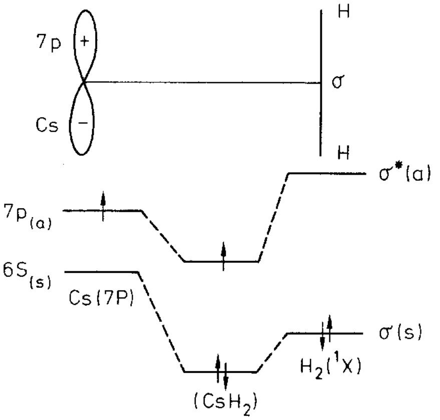


Fig. 6. Energy diagram for the $Cs^* + H_2 \rightarrow CsH + H$ reaction

$(CsH)_n$. A recent study [26] *i*) identified CsH as a photoproduct; CsH was obtained in its $^1\Sigma^+$ ground state and studied by Laser Induced Fluoresence through its $^1\Pi$ lowest excited state *ii*) showed that the lowest active excited state of the Cs atom is the $7p(^2P)$ one, the lower ($6p$, $5d$ and $7s$) excited states being inactive. Assuming a

$$Cs^* + H_2 \rightarrow CsH + H$$

reaction, this result is easily rationalized (cf. Fig. 6), since the $7p$ excited state is the first one to have enough energy to overcome the strong endothermicity (2.48 eV) of the G.S. reaction. The initial state of the photoreaction is only 0.3 eV above the final state. Such a small energy excess makes the reaction rather strange since the potential surface initially reached is the 11th one! How does the reaction proceed from the 11th potential surface to the lowest one without losing more than the 0.3 eV in excess? In the $(CsH_2)^*$ excited state a stable minimum may occur for an isocele triangular geometry through a double $\langle 7p|F|\sigma^*_{u_{H_2}}\rangle$ and $\langle \sigma_{g_{H_2}}|F|6s\rangle$ stabilizing interaction.



From this potential hole a non radiative excitation might occur to the ground state surface, the end of the reaction occuring on the ground state surface. An alternative mechanism would involve the formation of such an excited complex and a second reactive collision with G.S. atomic Cs

$$Cs^* + H_2 \rightarrow (CsH_2)^*$$

$$(CsH_2)^* + Cs \rightarrow 2CsH.$$

The problem is under study through supersonic crossed beams experiment and quantum mechanical calculations [27].

The photodissociation of Rydberg excited states have been well explored for the series of hydrides XH_n. It is not necessary to recall the H_2O photodissociation and its well known conic intersection [28]. Methane and ammonia are simple examples which illustrate the passage from the vertical Rydberg state to a neutral dissociative valence excited state which breaks one or two XH bonds.

(B) $CH_4 \xrightarrow{h\nu} CH_2 + H_2$ [29].

The lowest vertical excited state is a degenerate Rydberg state obtained by exciting one electron from the degenerate t_2 highest MO to 3*s* type a_1 orbital. Due to its degeneracy, this excited state is stabilized by a Jahn–Teller distortion to the C_{2v} symmetry, lengthening two CH bonds and diminishing their HCH angle; this Jahn–Teller distortion is already present in the parent CH_4^+ ion [30] and anticipates the photoreaction.

The reaction occurs through the energy decrease of an *a* valence MO built on the lengthened CH bonds, their σ^* antibonding MOs being lowered

$$\begin{aligned} a_1^v &= \sigma^*_{CH_1} + \sigma^*_{CH_2} \\ &= \lambda S_C + \mu x_C - \nu(s_{H_1} + s_{H_2}). \end{aligned}$$

This orbital will cross the Rydberg orbital of almost constant energy, and will become the singly occupied virtual MO. During the CH bonds elongation the singly occupied MO

$$\begin{aligned} b_1 &= \sigma_{CH_1} - \sigma_{CH_2} \\ &= \lambda' y_c + \mu'(s_{H_1} - s_{H_2}) \end{aligned}$$

will tend to localize on its y_c component, the a_1 doubly occupied MO

$$\begin{aligned} a_1 &= \sigma_{CH_1} + \sigma_{CH_2} \\ &= \lambda'' \mathrm{S}_C + \mu'' X_C + \nu''(s_{H_1} + s_{H_2}) \end{aligned}$$

tends to localize on the $s_{H_1} + s_{H_2} = \sigma_g(H_2)$ component, while a_1^v concentrates on the σ AOs of the carbon atom. One gets there a $^1B_1$ carbene photoproduct, which is known to lie 1.3 eV above the $^3B_1$ ground state. The evolution of the MOs is summarized in Fig. 7. The reaction has been well studied by Gordon [31], keeping the C_{2v} geometry but optimizing all geometrical parameters. He demonstrated:

(i) the progressive change of the virtual a_1 MO, which loses all Rydberg character as soon as $R_{CH} \geq 1.5$ Å;
(ii) the lack of any barrier in this reaction.

He also studied the analogous $SiH_4 \rightarrow SiH_2 + H_2$ reaction, which behaves similarly [32].

Other alkanes present analogous gas phase photolysis reactions,

$$CH_3{-}CH_3 \xrightarrow{h\nu} CH_3{-}CH + H_2$$

$$CH_3{-}CH \rightarrow CH_2{=}CH_2$$

which are likely to proceed through the singlet state [33] (see however [34]). Going to larger and larger molecules the excitation energy diminishes (and

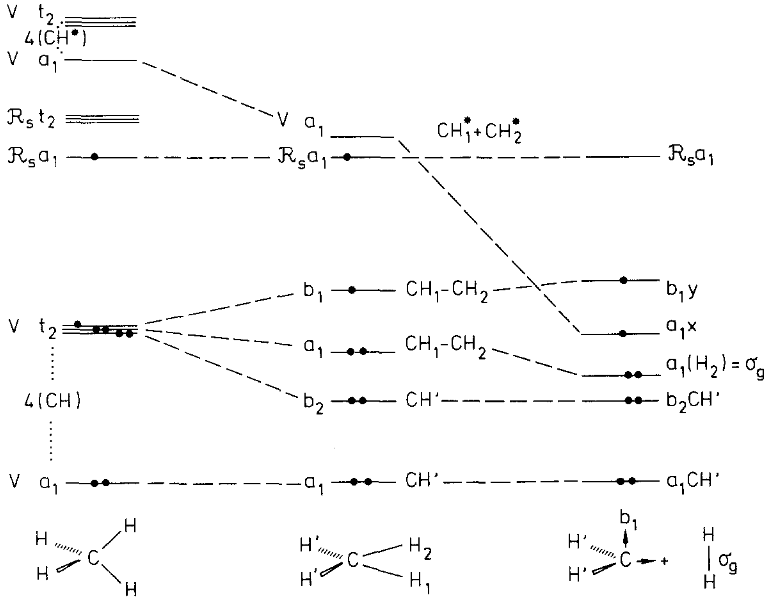


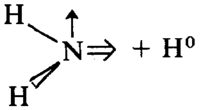
Fig. 7. Orbital correlation diagram for the $CH_4^* \rightarrow CH_2 + H_2$ reaction

therefore the excess energy available to break the CH bonds) but the valence character of the virtual MO increases.

(C) $NH_3 \xrightarrow{h\nu} NH_2 + H$.

The electronic spectrum [35] and photochemical disssociation [36] ammonia have been well studied. The first singlet excitation would lead to NH_2 $(X^2B_1) + H(^2S)$ while a higher excitation gives $NH_2(^2A_1) + H(^2S)$. Other photochemical reactions leading to NH in various states [36, 37] and H_2 or H+H are certainly complex processes. A recent study on PH formation from the "iso" electronic PH_3 molecule demonstrated a two photon mechanism [38]. Runau, Peyerimhoff and Buenker perfectly clarified the $NH_3 \xrightarrow{h\nu} NH_2 + H$ reaction [39].

The highest occupied MO is the a_1 lone pair, while the lowest virtual MOs are *s* and *p* Rydberg MOs. The excitation from the a_1 lone pair makes the molecule planar (as do NH_3^+). Then a lengthening of a NH bond may occur, the corresponding σ a_1MO will mix with the Rydberg virtual MO and tends to localize on the moving proton, while the singly occupied a_2'' (previously a_1 in the pyramidal geometry) keeps his symmetry and occupation, while the doubly occupied $a_1\sigma_{NH}$, MO tends to localize on the most electronegative center (N atom) to give a lone pair, and one obtains the photoproducts.



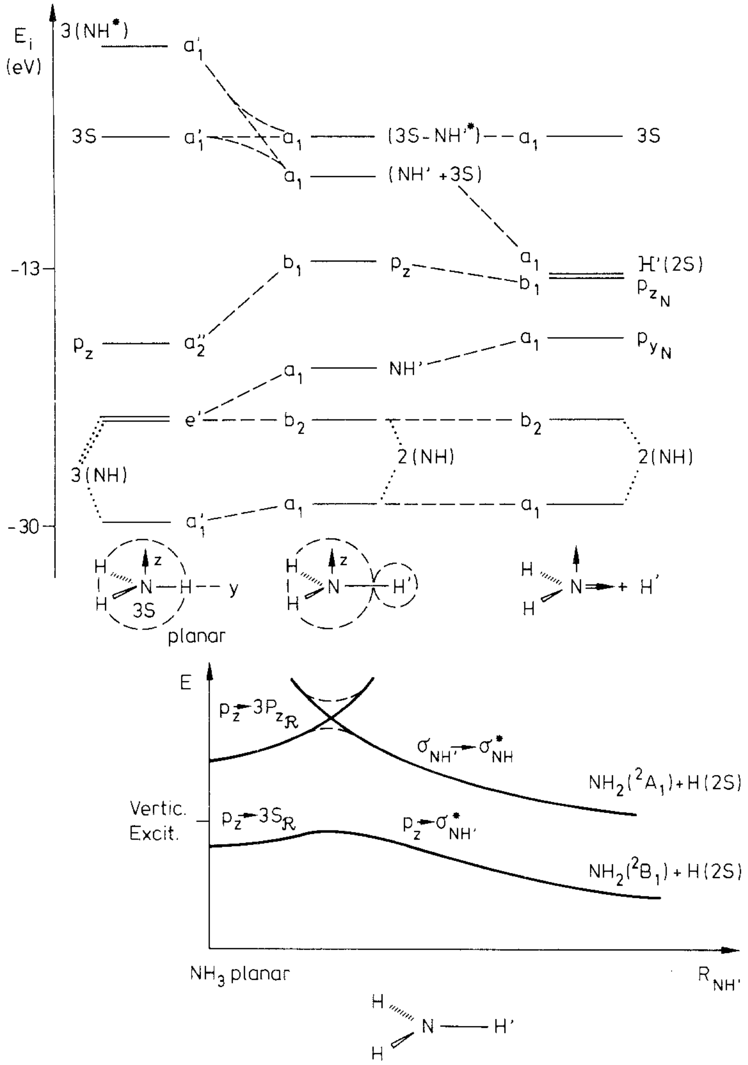
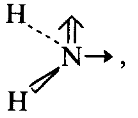


Fig. 8. $NH_3^* \rightarrow NH_2 + H$ correlation diagram and potential curves (from Ref. 39)

The process occurs without curve crossing since between virtual MOs of the same symmetry, and is already involved at the SCF level for the excited state [39]. The calculation predicts however a weak barrier (<0.57 eV) for $NH = 2.5$ a.u. while $\Delta H = -1.2$ eV. The barrier is lower than the excess vibrational energy (0.67 eV) given by the depyramidalization of the molecule from the vertical excitation, which explains the lack of emission from the Rydberg state.

To explain [39] the formation of $(A_1)NH_2$



the next $B\ {}^1E''(3a_1 \rightarrow 3p_{x,y})$ excited state of NH_3 is not candidate since it does not allow an in plane rupture, while the C state ${}^1A_1\ (3a_1 \rightarrow 3p_z)$ is totally symmetric, as are the photoproducts. But in such a case the $(2p_z \rightarrow 3p_z)\ {}^1A$ excited Rydberg state will cross the $\sigma_{NH'} \rightarrow \sigma^*_{NH'}$ valence excited state which differs by two orbitals and the process cannot be reproduced without CI.

S. Canuto and J. Muller [40] extended the analysis previously reported for the ${}^1A''_2$ state to the corresponding triplet without significant differences.

(D) $CH_3OH \xrightarrow{h\nu} CH_3O + H$.

Chaillet et al. [41] have extensively studied (large CI and extended basic set) this photoreaction from the vertical Rydberg state (already treated by Wadt and Goddard [6]) which results from an excitation from the $2p_zO$ lone pair to a $3s$ type orbital. They stress on the qualitative difference between the photofragmentation and the bond rupture occuring in the parent positive ion

$$CH_3OH^+ \rightarrow CH_2OH^+ + H.$$

The equilibrium geometries of the Rydberg state and of its parent ion are often very similar. The difference noticed here comes from the existence of the Rydberg electron which remains strongly attracted by the well localized hole on the oxygen atom, and will move into an antibonding σ^* orbital of low energy, i.e. located in the region of the hole, while the ionic rupture led to the most stable (conjugated) fragment. The $2p_{z(O)} \rightarrow \sigma^*_{(OH)}$ excitation has low energy,

$$\Delta E = \varepsilon_{\sigma^*(OH)} - \varepsilon_{2p_z(O)} - J_{\sigma^*(OH)2p_z(O)}$$

due to the large coulombic integral, and has a large overlap with a $3s$ type AO centered on the oxygen atom.

During the reaction the $2p_z$ singly occupied MO remains qualitatively unchanged, while σ_{OH} doubly occupied bond MO polarizes, the two electrons going on the electronegative O atom to give a σ (and later on p_y) lone pair, the other lone pair becoming s^2, while the previously Rydberg electron enters the σ^*_{OH} MO and localizes on the H atom which is leaved by the two electrons of the σ_{OH} bond MO.

(E) General Comments.

In his excellent review article devoted to far UV spectra of organic molecules, G. Sandorfy [42] tempted – in a very prudent way – to formulate some basic principles of Rydberg photochemistry, based on the spatial and nodal properties of the Rydberg orbitals. We believe that one cannot think in terms of Rydberg MO only, neither in terms of Rydberg state only:

(1) one must think in terms of a *(hole/particle) pair*, the possible localization of the hole being decisive for the behaviour of the Rydberg particle;

(2) one cannot think in terms of Rydberg state only, but in terms of *Rydberg state/valence state coupling*; the Rydberg state may be viewed as a reservoir (of energy) "waiting" for a mixture with a low lying valence state, and the question is: "due to the *symmetry* and *space* characters of the Rydberg state (i.e. the $(h/\mathscr{R})$ pair), what is the valence excited state ((h'/V^*), $h' \neq$ or $= h$) which may become low enough in energy in the region of the stabilizing deformation of the Rydberg state, and which may interact sufficiently with the "waiting" Rydberg state?"

One may distinguish two possibilities:

(1) The $(h/\mathscr{R})$ Rydberg state mixes with a (h'/V^*) valence state which only differs by the antibonding MO, the hole remaining qualitatively the same. Most of the previous examples belong to this case. Then V^* must be stabilized either by the proper deformation of the Rydberg state (case $CH_4 \rightarrow CH_2 + H_2$), or by another deformation of the skeletton, and must be located in the same region as $\mathscr{R}$, i.e. near the hole h. In this case of mixing, a single determinantal MO treatment is sufficient to describe the $\mathscr{R}/V$ change.
(2) The $(h/\mathscr{R})$ Rydberg state mixes with a (h'/V^*) valence state differing by both the hole and the particle, as occurs in the reaction $C(^1E'')NH_3^* \rightarrow NH_2 + H$. Again the valence state must be strongly localized by the deformation and the (h'/V^*), pair must be located in the same region of space as the Rydberg pair, to avoid a high barrier. CI is required to treat such mixings.

Once the valence state is created, the destiny of the MOs in the breaking bonds is easily established by considering:
- first the doubly occupied MOs which tend to localize by creating the most stable bond or lone pair;
- then the antibonding singly occupied MO which goes in the complementary direction.

Before leaving the subject of Rydberg states photochemistry one should mention the relevant remarks of Sandorfy [42] concerning the applicability of the topicity rules formulated by Dauben, Salem and Turro [43] to valence states which are above Rydberg states. A similar conclusion was obtained by Evleth and Kassab [44]. One should also mention the ring opening reactions from the Rydberg states of three membered rings [45, 46].

6. Reactivity of Ionic Excited States

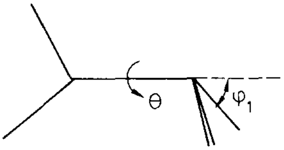
6.1. *Singlet cis-trans Isomerization of Linear Polyenes*

The question has been extensively studied after the discovery by Salem et al. [47] of the so-called "sudden-polarization" effect. In order to establish on firm grounds the validity of some conclusions concerning the suddeness of the polarization, its possible biological implications [48], the reliability of the Born–Oppenheimer description [49], all these problems being discussed on large systems, using rather crude descriptions, it is worthwhile to move back to the simplest problem, for which extensive studies are not available.

6.1.1. Ethylene V state minimum

The already mentioned H.F. instability for the first singlet excited state in the perpendicular form of ethylene suggests that the resonance between the two ionic forms is so weak that the molecule might prefer a deformation of the skeleton which destroys the resonance but strongly stabilizes one of the ionic forms [50]. Salem et al. thought of a pyramidalization of one carbon atom, since a negative carbon (isoelectronic to NH_3) tends to become pyramidal. Other perturbations might be sufficient to destroy the degeneracy between the ionic forms, such as a methylation of ethylene [47] or the lack of symmetry of the *cis-trans* hexatriene [47] rotating around its central bond. These perturbations are rather weak and illustrate the weakness of resonance in the $\theta = 90°$ region, they are specific of a given problem, while the pyramidalization of a carbon atom of the rotating bond may be a general feature.

Once carbon A is pyramidalized, it keeps the negative charge, and the A^-B^+ structure is much lower in energy than the previously resonant A^+B^- form, which dislikes a planar negative carbon and a pyramidal positive carbon. Recent *ab initio* works [51–54] with large CI establish that the pyramidalization of one carbon (i.e. a symmetry breaking deformation) actually stabilizes the singlet excited state with respect to the best C_{2v} geometry. The ${}^1\pi\pi^*$ singlet state potential surface presents four minima [$\theta = 90°$, $\varphi_1 = \pm(30 \text{ to } 60°)$, $\varphi_2 = 0$, or $\varphi_1 = 0$, $\varphi_2 = \pm(30$ to 60°)]. Brooks and Schaefer [51] compelled their MOs to be non polarized, in order to treat correctly the region of exact degeneracy ($\varphi_1 = \varphi_2 = 0°$); this is not favorable for the strongly zwitterionic minimum. Yet they obtained a well defined minimum ($\varphi = 30°$) and a large dipole moment, as did V. Bonačić-Koutecký et al. [52] independently, also using non polar MOs. Trinquier and Malrieu extensively studied the minimum of this surface, [53] taking benefit of the strong symmetry breaking (which keep however the orthogonality to the diradicalar ground state, thus allowing a closed shell ground state description of the excited state, before performing large CIs). The polarization of the MOs in the stable zwitterionic form is then included at the SCF level. Our R_{CC} value (1.426 Å) is in good agreement with the result obtained by Brooks and Schaefer (1.416 Å), while our pyramidalization ($\varphi = 60°$), made easier by a proper rotation of the CH_2^+ group, is larger than their ($\varphi = 30°$). Analogous results have been obtained by Tennyson [54] in a rather different procedure (see also Ref. in Fig. 9).



The pyramidalized minima are well defined, strongly polar ($\mu \simeq 4D$) and they lie about 133 kcal/mole above the ground state minimum [51, 53]. The fact that they are well defined appears from Fig. 9. The depyramidalization barrier to go from one minimum ($\varphi = +(30-60°)$) to the other ($\varphi = -(30-60°)$) is large enough

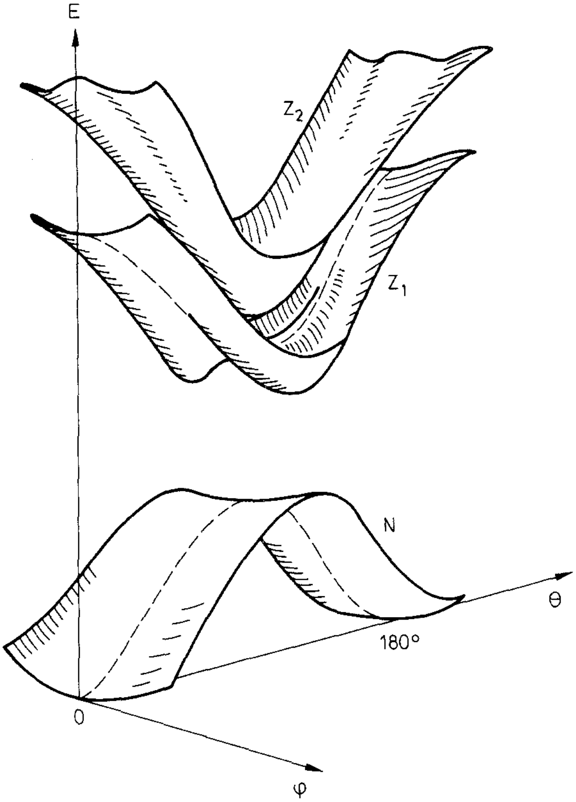


Fig. 9. Energy dependance of the ethylenic ground state N and ionic singlets as a function of θ (torsion around the double bond) and φ (pyramidalization angle of one carbon atom). A very recent paper from Buenker, R. J., Bonačić-Koutecký, V. and Pogliani, L.: J. Chem. Phys., **73**, 1836 (1980) suggests that the upper surface is more inserted in the second one, and that a conic intersection occurs for $\theta = 82°$, $\varphi = 0°$

($\simeq$6–10 kcal/mole) to consider that in dense media the molecule keeps a given shape during a rather long time.

In view of the near degeneracy between the symmetric and antisymmetric ionic states for $\theta = 90°$, $\varphi = 0°$ (weakness of the resonance)

$$\psi_g = A^-B^+ + A^+B^- \quad \text{and} \quad \psi_u = A^-B^+ - A^+B^-$$

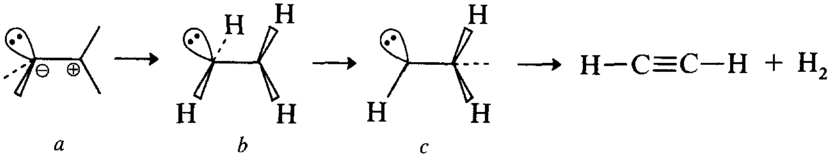
the legitimity of the Born–Oppenheimer description was dubious and vibrational mixing might occur [49], destroying the so called sudden polarization effect noticed on weakly perturbed double bonds (such as propene). Once pyramidalization is included, the upper state is no longer degenerate, and the dipole moment will remain important [55a], but progressive pyramidalization may destroy the suddeness of the polarization.

The strong polarity of these minima imply that they cannot be reached easily from non polar MOs such as those of the diradicalar ground or lowest triplet states.

To approach them one must perform large CIs or use localized symmetry broken MOs.

Their low energy (130 kcal/mole) serves as a criterion to estimate the accuracy of approximate calculations on larger systems, which should have lower minima (see below), and it explains the photochemical role of these zwitterionic excited states, which well appear as deep holes in the flatter surfaces of neutral states.

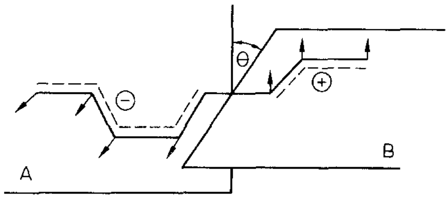
Evleth and Sevin have established [55b] the possibility of an H migration from the twisted pyramidalized singlet excited state ethylene



The barrier corresponding to step *b* ($\simeq$1 eV) is lower than the excess energy delivered by the torsion of the double bond.

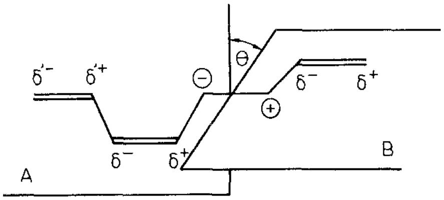
6.1.2. Larger polyenes

The ethylene problem may be considered as solved. The situation is less clear for higher conjugated polyenes. The 90° torsion of a double bond defines two nearly orthogonal subsystems with odd numbers of carbon atoms, and the G.S. calculation gives delocalized MOs on each fragments (some delocalization may even occur between the two fragments through small overlaps between non neighbouring atoms [56]). If α and β are the highest singly occupied MOs obtained in the calculation of the diradical ground state, α being on the left side and β on the right subsystem, the ionic states described as $|\alpha\bar{\alpha}|$ and $|\beta\bar{\beta}|$ delocalize the negative and positive charge on the whole skeleton of their respective fragments; the centroids of the + and − charges in $|\alpha\bar{\alpha}|$ are located near the central atom of fragments *B* and *A* respectively.



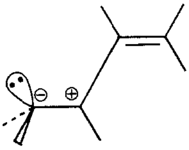
The subsequent 3×3 CI of the $|\alpha\bar{\beta}+\beta\bar{\alpha}|$, $|\alpha\bar{\alpha}|$ and $|\beta\bar{\beta}|$ determinants can mix the ionic forms but it does not describe correctly any one of them. The + and − charges are not realistically distributed, they should attract each other and concentrate on the carbon atoms of the rotated bond, while the σ MOs, which are non polar in the open shell+3×3 CI procedure, should polarize to screen the π field [57, 58].

The localized description

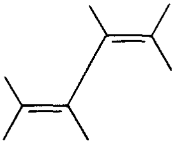


in which the rotation in the excited state is considered as an essentially local event, with concentrated charges on the rotating bond, is certainly more valid; the + and − charges may slightly delocalize through charge transfer excitations in the adjacent π bonds, they will polarize these π bonds and the σ distribution. Moreover a pyramidalization should further stabilize this localized excited state [58].

For conjugated polyenes these localized zwitterionic excited states should be lower than the 133 kcal/mole obtained for ethylene. For butadiene the delocalization in the next π bond and the polarization of the double bond stabilizes the excited state minimum by 18 kcal/mole with respect to ethylene [58].



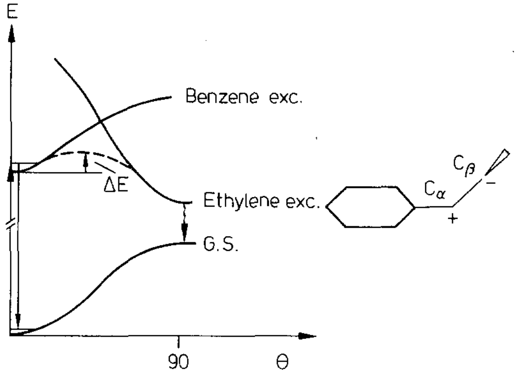
is 116 kcal/mole above



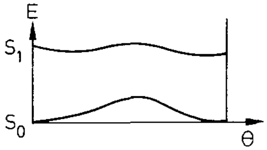
The stabilization of the negative fragment by another double bond in the central bond rotation of hexatriene should give an equivalent stabilization and a localized minimum should lie at about 100 kcal/mole above the G.S. minimum, while the delocalized description for this molecule (open shell + 3 × 3 CI) only gives a 180 kcal/mole estimate, which is physically meaningless. One should consider with some scepticism the conclusions obtained by such crude delocalized methods concerning the occurrence of sudden polarization for conjugated polyenes [56].

Momicchioli et al. [59] have nicely interpreted the rotation around the extra benzenic double bond of styrene as the crossing between the vertically formed benzenic excited state and the *Z* state of the ethylenic bond. The rotation of the double bond in the benzenic excited state is difficult (as in the G.S.), but the zwitterionic excited state of the double bond is strongly stabilized by the delocalization of the conjugated + or − charge in the benzenic system, and by polarization of this highly polarizable ring. (Notice that the $C_\alpha^+ - C_\beta^-$ state is necessarily orthogonal to the diradical G.S. even if C_β is pyramidal). The minimum of the zwitterionic excited state should be significantly lower than

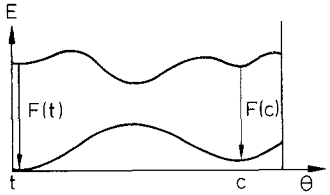
100 kcal/mole, i.e. than the 4.35 eV of the vertical excitation.



This mechanism allows to interpret the temperature effect (necessary to go through the small barrier near $\theta \simeq 45°$). It has been criticized by Orlandi et al. [60] who prefered to involve a weak barrier in the excited surface, the *cis-trans* isomerization occuring in the excited state, and not through the zwitterionic funnel. Their calculation is done with limited CI from non polarized MOs and is not able to give a correct description (and correct energy) of the zwitterionic state,



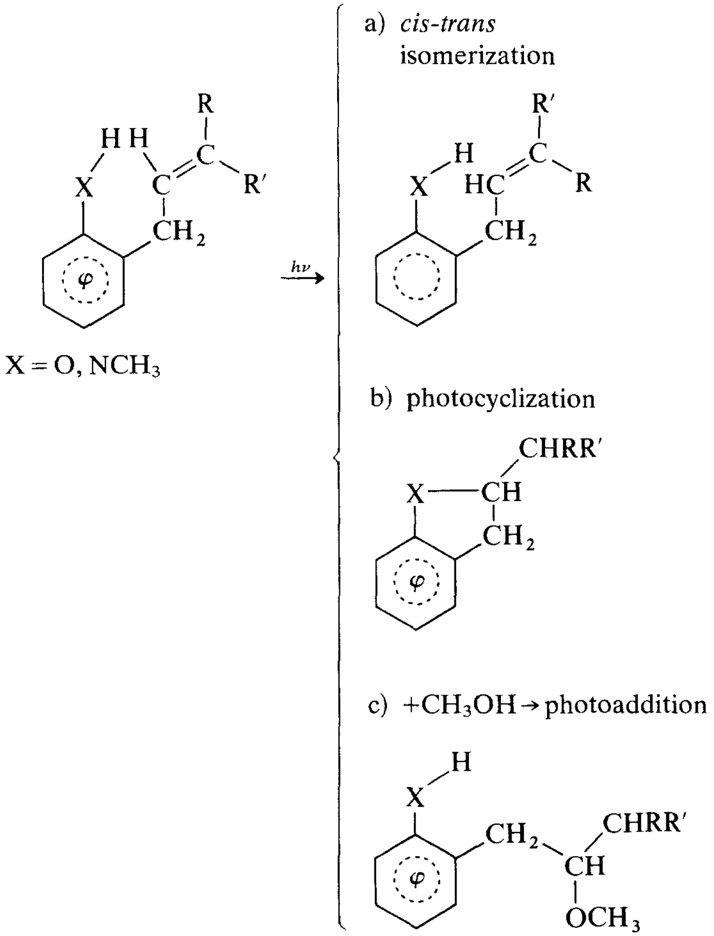
One may suppose analogous mechanisms for the rotation around the central double bond of stilbene in its excited state. In that case the two *cis-* and *trans-* isomers having different energies, the *cis-* minimum of S_1 will be less pronounced



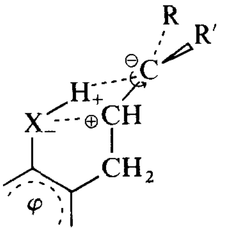
that the *trans* one (protected by a smaller barrier) and the fluorescence yield will be lower for the *cis* isomer ($\phi_F = 0.00$) than for the *trans* isomer ($\phi_F = 0.05$) at room temperature. At low temperatures ($T = 77°K$) ϕ_F increases to 0.75 for both isomers. The rigid analogs for which the rotation of the double bond is forbidden have a high fluorescence quantum yield ($\phi_F = 1.00$) at all temperatures.

6.1.3. Photocyclization Through a Zwitterionic Excited State?

Zwitterionic excited states have been invoked to explain a surprising set of photochemical reactions [61] involving a *non conjugated* double bond in ortho allyl anilines and phenols.



The reaction proceeds from the lowest singlet of the benzenic fragment (100 kcal/mole) and does not go through triplet states [62]. To explain a possible transfer of the excitation to the ethylenic singlet state, one may imagine that the polar X–H group, already linked to the double bond in the G.S. through an XH···π hydrogen bond, stabilizes the zwitterionic excited state through electrostatic interaction



Semi empirical (PCILO) calculations support this hypothesis [62].

6.2. Direct Reaction From an Ionic State

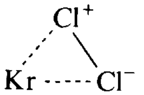
Recent experiments [63] show that by exciting Cl_2 to the ${}^1\Sigma_u^+$ excited state ($\lambda = 1.355$ Å) in presence of Kr, one obtains the laser emission of KrCl (2 220 Å)

$$Cl_2^* + Kr \rightarrow KrCl^* + Cl.$$

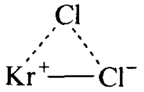
This reaction may be interpreted in the following qualitative way – the vertical state is Rydberg according to the theoretical predictions (cf. Ref. 22) in a vibrational level which should allow the passage to the ionic potential well:

– The collision with a Kr atom should unfavour the more diffuse Rydberg state and facilitate the passage to the ionic form.

– In the ionic valley the lack of symmetry during the collision with Kr may stabilize one of the ionic forms



allowing a further transfer of the positive charge and the Kr^+Cl^- formation.



However one must remember that the Kr^* lowest Rydberg configuration is almost degenerate with the ${}^1\Sigma_u^+$ state and excitation transfer also may occur. A further mechanism might invoke a charge transfer Kr^+ $(Cl_2)^-$ excited state.

7. Conclusion

This paper discusses in some length the conditions for a correct reproduction of Rydberg and ionic excited states (and of their mixing). A lot of efforts remains to be done in order to test and improve the presently most used practices, which remain by far less accurate than for ground state problems. This paper points out an intrinsic difficulty which concerns both valence *ionic* and *Rydberg states* of *symmetrical molecules*. This difficulty appears for all situations in which a weak resonance occurs between two equivalent highly polar (or contrasted) components in a given shell surrounded by other highly polarizable shells. To our knowledge, it also concerns the *ionization of* 1*s shells* [18], the *ionization* of very distant *equivalent lone pairs* in symmetrical molecules and the *valence excitation from equivalent lone pairs* [64]. As soon as the resonance between the two local equivalent components becomes lower than the surrounding shells polarization energy gain obtained by localizing the excitation, a symmetry breaking of the approximate wave function stabilizes the energy through H.F. instability; a further nuclear symmetry breaking may occur when more than two atoms are present, which stabilizes one of the local forms, breaking the resonance. If one leaves the problem of the stationary states, the time evolution becomes a further problem, since the time of the resonance between the two local polarized forms may be evaluated to be larger than the time of the observation [18, 65].

Acknowledgements. This review article corresponds to a conference given at the 11th congress of the "Chimistes Théoriciens d'Expression Latine", Pau (1980). We would like to thank Dr M. C. Castex and F. Spiegelmann for numerous and helpful discussions.

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Received December 22, 1980