

**IDENTIFICATION OF SHAKE-UP SATELLITES
IN VALENCE PHOTOELECTRON SPECTRA OF ORGANIC COMPOUNDS
BY COMPARISON WITH ELECTRONIC ABSORPTION SPECTRA OF RADICAL CATIONS.
CASE STUDY: OCTAFLUORONAPHTHALENE**

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Electronic absorption spectroscopy of chemically prepared octafluoronaphthalene radical cations is used to identify a shake-up transition in the valence photoelectron spectrum of the same compound excited by HeI radiation. It is shown by comparison with theoretical calculations that in photoemission a two-electron process populating a state of B_{1g} symmetry borrows intensity from a close-lying hole state of the same symmetry. Absorption of a photon by the radical cation populates the same state by a one-electron excitation with rather large oscillator strength ($\epsilon \approx 1.6 \times 10^4$).

1. Introduction

It is usually assumed that the photoelectron spectra of the outer valence region of aromatic hydrocarbons, i.e. those ionizations connected with π electrons, can be interpreted and assigned in terms of a single-particle picture. In other words, up to an energy of about 5 eV above the first ionization potential, extra structure due to ion states that are not hole or hole-excited states (see below) is not expected. This is why semi-empirical one-electron theories have been used rather successfully in assigning the valence photoelectron spectra of an extended series of catacondensed benzenoid hydrocarbons [1].

Although the breakdown of the one-particle picture for the inner valence electron region is now a well established phenomenon, both experimentally [2] and theoretically [3], it was only recently recognized that one has to expect interference between shake-up structure and hole or hole-excited states even in the outer valence

region of aromatic hydrocarbons and other molecules [4–13].

Lindholm and Asbrink [5] showed that, for benzene, a shake-up structure is observed near the $2e_{2g}$ and $2e_{1u}$ ionization. They supported their assignment by calculations using the HAM-3 algorithm, thus providing additional evidence for a result reported earlier by von Niessen et al. [6] who used the so-called two-particle–hole Tamm–Dancoff (2ph TD) approximation to calculate ionization potentials on the basis of ab initio SCF neutral ground-state Hartree–Fock wavefunctions.

We report in this Letter experimental and theoretical evidence for shake-up structure in the outer valence ionization region of octafluoronaphthalene [14] by comparing independent spectroscopic methods, namely photoelectron and optical spectroscopy. Such a comparison is useful in this connection, since in photoemission a transition from the ground state of the neutral system to a shake-up state is a two-electron transition with, usually, low probability, while the transition from the ground state of the cation to the corresponding excited state of the radical cation is a one-electron

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transition with, possibly, large oscillator strength. We show that such a situation is actually met in octafluoronaphthalene.

We have chosen octafluoronaphthalene for two reasons:

(i) The "perfluoro effect" [14,15] shifts σ ionizations more strongly to higher binding energies than π ionizations. In the PE spectrum, this leads to a clear separation of most of the π ionizations from the σ ionizations.

(ii) Perfluorinated naphthalene can be chemically oxidized to form the radical cation in solution.

Our experimental results are supplemented by calculations on the absorption spectrum of the radical cation as well as on the photoelectron spectrum of the neutral molecule.

2. Experimental

The photoelectron spectrum was taken with a Leybold-Heraeus gas-phase spectrometer equipped with a spherical condenser analyser. Before the electrons enter the analyser, they are deflected by means of a cylindrical deflector and pre-retarded by three tube lenses. The transmission of the system is essentially constant for the recorded kinetic energies. The overall resolution was 20 meV, as checked by the line-

widths of the two components of the Ar 3p doublet, which at the same time was used as calibration gas with HeI radiation.

The electronic absorption spectra were taken on a Zeiss PMQ II spectrophotometer. Octafluoronaphthalene was completely oxidized in pure oleum (conc. H_2SO_4 with 60% SO_3) [16]. Due to the large slit width and the absorption of SO_3 with a threshold at about 30000 cm^{-1} , we only compare the low-energy part of the UV spectrum (up to 3.5 eV) with the photoelectron spectrum. The photoelectron spectrum (HeI) as well as the absorption spectrum of octafluoronaphthalene are shown in fig. 1.

3. Calculations

To calculate the photoelectron spectrum, we used the CNDO/S algorithm developed by Del Bene and Jaffe [17] in its final parameterization [18] to derive the one-electron states of neutral naphthalene and then treated the effects of final-ion-state relaxation and shake-up excitation using the diagonal 2ph TD approximation introduced by Cederbaum and co-workers [3].

We also tried to incorporate electron-vibration coupling using a linear coupling model [19], where the coupling constants for the ion state γ with energy E_γ and the normal mode Q_i with frequency ω_i are

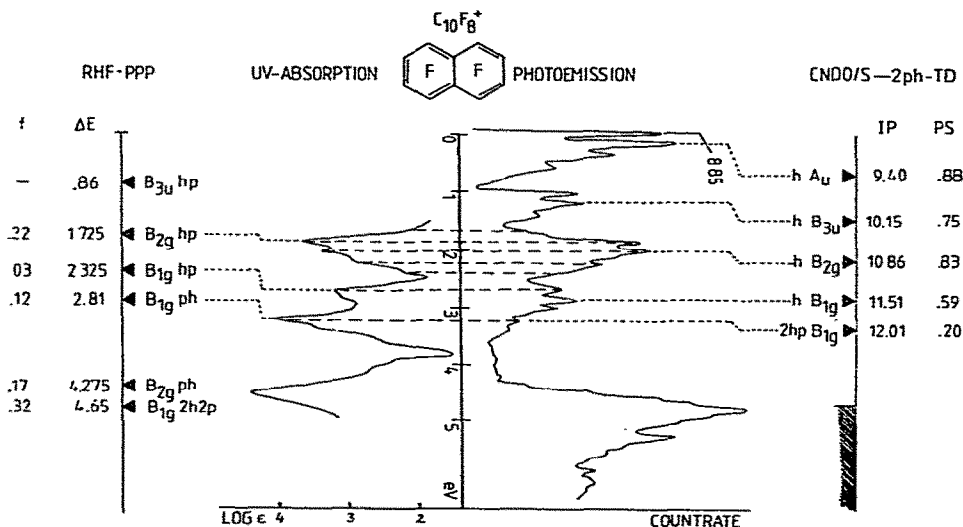


Fig. 1. Experimental photoelectron and electronic absorption spectra of octafluoronaphthalene. The calculated excitation energies, oscillator strengths, ionization potentials and pole strengths are also indicated.

$$G_{\gamma i} = (2\hbar\omega_i)^{-1/2} \partial E_\gamma / \partial Q_i. \quad (1)$$

The energy lowering of a given state γ due to its interaction with vibrations, often referred to as "polaron binding energy", is given by

$$\Delta E_\gamma = \sum G_{\gamma i}^2 / (\hbar\omega_i). \quad (2)$$

The coupling constants applied in our calculations are taken from Sheka [20].

In order to include vibrational structure for the shake-up states, we used the one-particle approximation given by Cederbaum and Domcke [3], namely

$$G_{(\gamma\delta\epsilon)i} = (2\hbar\omega_i)^{-1/2} \partial (E_\epsilon - E_\gamma - E_\delta) / \partial Q_i, \quad (3)$$

where ϵ refers to the unoccupied orbital that becomes occupied in the excitation process, while δ refers to the occupied orbital from which the electron is excited. γ indicates the orbital that is ionized. Using this relation, we can estimate the coupling constant for a shake-up state from the sum of the coupling constants of the participating orbitals.

To calculate the excitation energies and oscillator strengths of the radical cation, we employed an open-

shell RHF PPP algorithm including the lowest singly excited π excitations. An extensive review of this procedure was given by Zahradnik et al. [21].

4. Results

The results of our experimental and theoretical investigations on octafluoronaphthalene are collected in fig. 1. On the left-hand side, the optical absorption spectrum measured in concentrated sulfuric acid containing 60% dissolved SO_3 is shown. The excitation energy (in eV) is plotted versus the logarithm of the extinction coefficient. The energies of the maxima are summarized in table 1. Parallel to the experimental spectrum we give the calculated excitation energies (ΔE) and oscillator strengths (f). The symmetries of the electronic states are indicated and the assignment of the three most pronounced maxima in the experimental spectrum can be followed by the dotted lines. On the right-hand side of fig. 1, the photoelectron spectrum is shown. The energy scale refers to the ground state of the gaseous radical cation. The absolute ioniza-

Table 1

Comparison of experimental and theoretical results. $\Delta\tilde{\nu}$ gives the vibrational frequencies observed in the absorption and photoelectron bands, ΔE the excitation energy, f the oscillator strength, and ϵ_{max} the extinction coefficient at the maximum of the vibrational progression. IP_{ad} is adiabatic ionization potential, the values given in parentheses being the energies relative to the ground state of the ion. $I_{\text{rel}}^{\text{max}}$ is the relative intensity of the maximum of the vibrational progression, IP the calculated ionization potential, and PS the pole strength

Theory RHF-PPP		Experiment				Theory CNDO/S-2ph TD	
ΔE (eV)	f	absorption		photoemission		IP (eV)	PS
		ΔE (eV)	ϵ_{max}	IP_{ad} (eV)	$I_{\text{rel}}^{\text{max}}$		
—	—	—	—	8.85 (0.0) $\Delta\tilde{\nu} = 1530 \text{ cm}^{-1}$	1.0	9.40	0.88
0.86	—	—	—	9.90 (1.05) $\Delta\tilde{\nu} = 1450 \text{ cm}^{-1}$	0.57	10.15	0.75
1.725	0.22	1.84 $\Delta\tilde{\nu} = 1400 \text{ cm}^{-1}$	5.8×10^3	10.78 (1.93) $\Delta\tilde{\nu} = 1400 \text{ cm}^{-1}$	0.87	10.86	0.83
2.325	0.03	2.71 $\Delta\tilde{\nu} = 800 \text{ cm}^{-1}$	2.2×10^3	11.57 (2.72) $\Delta\tilde{\nu} = 1450 \text{ cm}^{-1}$	0.53	11.51	0.59
2.81	0.12	3.20 $\Delta\tilde{\nu} = 800 \text{ cm}^{-1}$	1.6×10^4	12.08 (3.23) $\Delta\tilde{\nu} = 1400 \text{ cm}^{-1}$	0.26	12.01	0.20

tion energy of the 0–0 transition of the first band is 8.85 eV, as indicated. The calculated ionization potentials (IP) obtained from the 2ph TD corrected CNDO/S eigenvalues are given on the right margin. As a theoretical measure of the intensity of the different transitions, we have included the calculated pole strengths. As in the case of the absorption spectrum, we have indicated the symmetries of the final states. Assignments again are shown by dotted lines.

To rationalize the similarities and differences appearing in the spectra shown in fig. 1, we use the orbital scheme depicted in fig. 2. On the left, the four highest occupied and the two lowest unoccupied π orbitals of the neutral system are shown. For each orbital, localizations of the LCAO coefficients as viewed from above the aromatic ring system are given. The orbitals are classified according to the point group of the system, D_{2h} , and the irreducible representations are added. Since in the neutral ground state with N electrons all orbitals below the dashed line are doubly occupied, the state is totally symmetric with irreducible representation A_g . If we ionize the N -electron system with the lowest possible energy, we end up in the ground state of the $(N-1)$ -electron system, i.e. the radical cation. Due to the change in the potential, the one-electron states change their relative and absolute energies and their LCAO coefficients. The relative change in energy is indicated in fig. 2 while the absolute

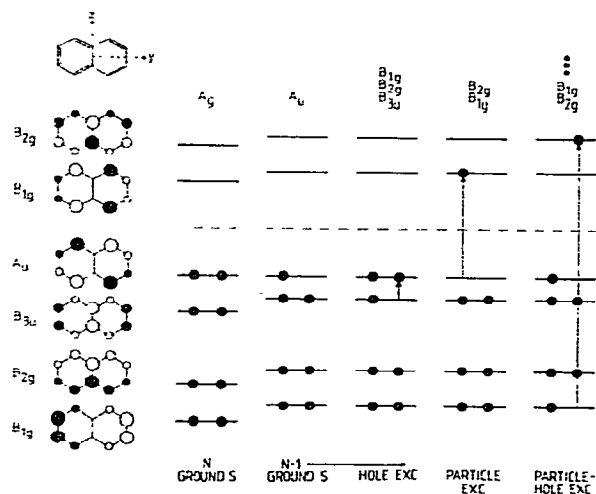


Fig. 2. Orbital scheme for the neutral and valence ionized π system of naphthalene topology.

change is compensated for by referring to the dashed line as energy zero. If we disregard hole localization or vibrational coupling, the ion belongs to the same point group as the neutral molecule. The ground state of the $(N-1)$ -electron system can now be looked at as having lost one electron from the highest occupied molecular orbital with symmetry A_u . Since all other orbitals are doubly occupied, the symmetry of the ion ground state is A_u .

The excited states of the radical cation can be described by configurations resulting from various types of electron–hole excitations (ph/hp) as shown in fig. 2. The first type of excitation is called “hole excitation”: electrons from the lower occupied orbitals are excited into the singly occupied orbital which means that the hole is excited towards higher binding energy. By this mechanism, the same ion states are reached that are formed by one-electron emission from each occupied orbital. For a nine-electron system (naphthalene cation in the π approximation), four states result from this mechanism. (The lowest occupied π orbital is not shown in fig. 2, due to its very low energy.)

A second type of excitation leads to configurations characterized as “particle excitations”. In these excitations the unpaired electron in the highest occupied orbital is excited to various unoccupied orbitals. Within the scheme of fig. 2, possible configurations of this type have B_{2g} and B_{1g} symmetry. The third type of excitation is the most general one: any electron in the occupied orbitals can be excited to an orbital unoccupied in the ionic ground state. This type of configuration is called “particle–hole excitation”, because with respect to the ion ground state the hole as well as an electron is excited, although only one particle–hole pair has been created.

Within this scheme, the first four band systems in the photoelectron spectrum are assigned to the ground state of the radical cation with symmetry A_u and three hole-excited states of symmetry B_{3u} , B_{2g} and B_{1g} . Due to the strong relative stability of the lowest occupied π orbital, and due to the stabilization of the σ ionizations by perfluorination, the first four ionization bands are followed by a rather large gap. This gap allows us to identify some extra, rather low-intensity structure on the high-binding-energy side of the fourth ionization band. According to the calculation, there is a two-particle–hole excitation (2ph) with symmetry B_{1g} close in energy to the third hole excita-

tion. The energy of the 2ph excitation is determined by the ejection of an electron out of the occupied a_u orbital with simultaneous excitation of the second a_u electron to the unoccupied b_{1g} orbital. This state, therefore, involves a two-electron process with respect to the neutral ground state and consequently only leads to a band of low intensity in the photoelectron spectrum. The state borrows its intensity from the neighbouring hole state of same symmetry (B_{1g}). The calculation reveals that the hole and the two-particle-hole state are rather strongly mixed by configuration interaction. The pole strength of the hole state is reduced to 0.59. The rather low intensity of the parent band in the spectrum is in agreement with this prediction.

Let us now turn to the absorption spectrum and discuss the nature of the observed bands. The lowest optical transition between the ground and the first excited doublet state of the radical cation would be expected at 1.1 eV (0-0 band) according to the photoelectron spectrum. However, this transition would lead to a B_{3u} state and is therefore dipole-forbidden (u-u transition). The transition will most likely gain some intensity by vibronic coupling but a band with $\log \epsilon < 2$ cannot be detected in the medium used to prepare the radical cation. Transitions from the ground state of the radical cation to the three higher-lying excited states, including the "shake-up" state of the photoelectron spectrum, are dipole allowed and thus can be observed in the absorption spectrum. For the optical absorption process, the population of the B_{1g} ph does not involve a two-electron process, as in the case of the ionization spectrum, but rather a "normal" one-electron transition. In fact, the extinction coefficient is the largest among the low-lying transitions. The higher excited states calculated are not assigned to the observed features since in this energy range the absorption of oleum (SO_3) influences the extinction coefficients.

We are now in a position to compare in some detail the optical absorption spectrum with the photoelectron spectrum. The first excited state observed in the absorption spectrum is the third doublet state of the ion. This is not only supported by the energy of the corresponding transition but also by its vibrational structure. The dashed lines indicate that the spacing of vibrations observed in the optical and in the ionization spectrum is practically the same. The frequency ($\approx 1400 \text{ cm}^{-1}$) is close to an a_{1g} mode of the naphtha-

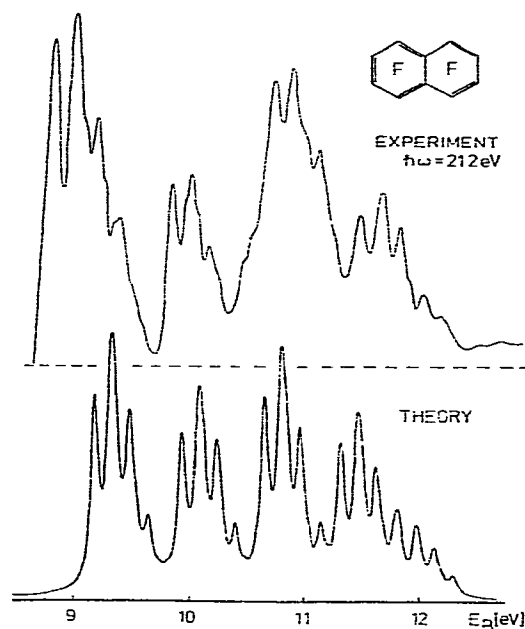


Fig. 3. Calculated photoelectron spectrum including vibrational structure in comparison with the observed spectrum.

lene carbon-ring system observed for perhydronaphthalene [14,15]. In the limit of experimental resolution, the spacing of frequency levels is similar for the other bands also. It has to be realized, however, that most likely it is not only a single vibration that couples to the electronic states. Of course, this leads to a more complicated vibrational sub-structure. We calculated a theoretical PE spectrum in order to show how it would look if we considered only the coupling of two vibrations with frequencies of about 1400 and 1530 cm^{-1} , representing a carbon skeleton vibration and a C-F valence stretching vibration with identical coupling constants [20]. Fig. 3 shows the result of such a calculation in comparison to experiment. In the calculation, it was assumed that the coupling constants for the shake-up transition are a factor of 1.5 larger than for the hole excitations[‡]. The result is in astonishingly good agreement with the experimental spectrum, although the details are not completely reproduced,

[‡] This is reasonable according to eq. (3): the two-electron process involves the a_u orbital twice and the unoccupied b_{1g} orbital once. The coupling constant for this b_{1g} orbital is taken as half of the a_u coupling constant due to its larger anti-bonding character.

since there are certainly more than two coupling vibrations. A more detailed analysis must await better resolved experimental data.

The important point of our study is that the combined information of optical absorption and photoelectron spectroscopy allows us to identify the fifth band of the photoelectron spectrum as a shake-up peak involving a two-electron process. The study shows that shake-up peaks in valence photo-emission are not uncommon and that it is necessary to consider such states for the assignment of photoelectron spectra of the valence-electron region.

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