Ionization, Excitation and Electron Affinity of Naphthalene, Studied with HAM/3

L. Åsbrink, C. Fridh and E. Lindholm
Department of Physics, Royal Institute of Technology, S-100 44 Stockholm, Sweden

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The electronic structure of naphthalene is calculated using the new semiempirical method HAM/3. The calculated photoelectron spectrum is in reasonable agreement with the measured spectrum. The excitation energies are obtained directly in HAM as the difference of the energies of the unoccupied and the occupied orbitals, and the calculated UV spectrum is in good agreement with experiment. The electron affinities are also obtained directly and are also in agreement with recent measurements. The absorption spectrum of the naphthalene anion is in reasonable agreement with experiment also regarding intensities. All calculations did not require more 76 seconds computer time although no advantage was taken of the symmetry of the molecule.

1. Introduction

Electron affinities of organic molecules have traditionally been considered as difficult to measure. Recently, however, the transmission method [1, 2] has opened possibilities to successful measurements of negative electron affinities of a number of molecules.

The calculation of electron affinities has also been difficult [3, 4] and very few molecules have been studied. Two reasons for the difficulties can be mentioned.

First, in the usual Hartree-Fock type calculations the self-repulsion has not been eliminated for the unoccupied orbitals. These orbitals are partially filled when the negative ion is formed. The calculation gives therefore "virtual" orbitals whose energies deviate from those of "excited" orbitals.

Second, the correlation energy error is usually very difficult to eliminate, and this is especially important in the calculation of electron affinities.

It may therefore be of interest for the study of electron affinities that the new semiempirical method, HAM/3, [5—9], seems to have small or essentially negligible errors due to self-repulsion or correlation energy. The self-repulsion is avoided since the method is founded upon Slater's [10, 11] study of atoms, using shielding constants. The correlation energy error is compensated in the same way as in other semiempirical methods by a suitable choice of the parameters, but in HAM/3 this is performed in a different way. Usually, the molecular orbital theory is deduced and completed before a comparison with experiment is performed, and the errors are compensated afterwards by a change of parameters. The result is that such a semiempirical method is corrected only for a certain type of experiments. In HAM/3 the comparison with experiment is performed for the atoms before the theory is extended to molecules. The resulting molecular orbital method can therefore be expected to be useful for many types of experiments simultaneously.

In this paper naphthalene is studied by *one* HAM/3 calculation. All calculations did not require more than 76 seconds on an IBM 370/165 computer although no advantage was taken of the symmetry of the molecule. The calculation consists of two parts. The first gives all ionization energies (photoelectron spectrum) and all excitation energies and oscillator strengths (UV spectrum, electron impact spectrum). The second gives all ionization and excitation energies of the negative ion (electron affinity, anion UV spectrum).

2. The HAM/3 Method

The HAM/3 method is based upon a study of the atoms from which the molecule is composed. The atoms are treated according to an idea introduced by Slater 1930 [10, 11]. He calculated the total energy of the atom from the effective nuclear charge for each of its electrons by the use of certain shielding constants.

In the HAM/3 method this idea has been extended by the observation that if the shielding constants $\sigma_{\nu\mu}$ are replaced by functions

$$\sigma_{\nu\mu} = a_{\nu\mu} - (b_{\nu\mu} + c_{\nu\mu} Z)/\zeta_{\mu}$$

(a, b and c are parameters, Z is the nuclear charge and ζ_{μ} the orbital exponent of the shielded electron) a very good agreement can be obtained with the

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Reprint requests to Prof Dr. E. Lindholm, Physics Department, The Royal Institute of Technology, S-10044 Stockholm 70.

total energies from atomic spectroscopy, not only for atoms but also for a large number of ionized and excited atoms. The average error for 311 atomic states from H to Ne is only 0.16 eV.

This good accuracy for atoms makes it desirable to treat molecules in the same manner. The goal can certainly be attained in many ways and the HAM/3 method constitutes only the first effort.

In the molecule the total energy is estimated by use of shielding constants. The atomic shielding parameters a, b and c are used also in molecules. In this way a major part of the total energy of the molecule is determined, but of course also molecular parameters are necessary.

From the total energy E the Fock matrix elements $F_{\mu\nu}$ are obtained by use of the following formula, which can easily be proved [5],

$$F_{\mu\nu} = \partial E / \partial P_{\mu\nu} .$$

Here $P_{\mu\nu}$ is the density matrix element. The MO-SCF calculation proceeds then as usual.

Since the correlation energy errors are supposed to have been avoided through the choice of a, b and c in the shielding "constants", it is necessary to calculate the ionization energies of a molecule not by the use of Koopmans' theorem but by treatment of the reorganization. This can be done by the ΔE_{SCF} method, but the same result is more conveniently obtained by the transition state method.

Since Slater's idea meant that the shielding was caused only by "the other" electrons, no self-repulsion is introduced neither in the atomic nor in the molecular expressions. The unoccupied orbitals, which are obtained from the calculation, are therefore excited orbitals, and an excitation energy can be obtained directly from the calculation as the difference between the energies of the unoccupied and the occupied orbitals. It must then be split to give the singlet and triplet energies separately, but no advanced methods are necessary to achieve this.

A negative molecule ion is formed if an extra electron enters an unoccupied orbital in the molecule. A transition state calculation gives then eigenvalues which are interpreted as the negative ionization energies of the negative ion.

3. Calculated and Experimental Ionization Energies

The geometry of naphthalene is shown in Figure 1. Due to the symmetry the molecular orbitals are sufficiently described by the coefficients for only part of the atoms together with the node planes. The same internuclear distances as in a previous ab initio study were used [12].

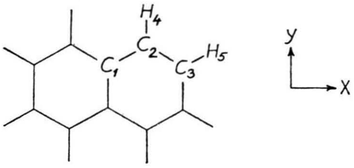

Fig. 1. Schematic diagram and atom labelling of naphthalene.

The results of the HAM/3 calculation are shown in Table 1. The calculation is performed for a transition state in which $\frac{1}{2}$ electron has been removed in order to obtain the ionization energies (IP). They are given in the top line of the table for the orbitals 6—30. The orbitals 1—24 are doubly occupied. The columns give the molecular orbitals themselves.

The molecular orbitals of naphthalene have already been presented in a schematic way [13] from a SPINDO calculation [14]. The connections with the orbitals of benzene were also discussed in detail.

The calculated ionization energies are compared in Fig. 2 with the photoelectron spectrum of naphthalene [15]. It can be seen that the distribution of the orbital energies corresponds well to the measured spectrum. The agreement with the SPINDO calculation is also satisfactory. It was pointed out earlier [15] that the SPINDO calculation gives nearly the same energetic order as ab initio calculations [12, 16] and other studies [17—20].

It can be seen from Fig. 2 that the HAM/3 calculation is in error by about 0.4 eV for the first two bands (orbitals 23 and 24).

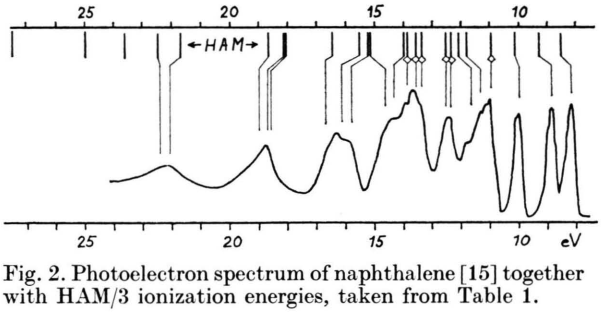

Fig. 2. Photoelectron spectrum of naphthalene [15] together with HAM/3 ionization energies, taken from Table 1.

Table 1. HAM/3 calculation for naphthalene. The table gives the ionization energies (eV) and the orbitals. Due to the symmetry it is sufficient to present the coefficients for only part of the atoms. The species and the node planes are shown below the table. The number of occupied orbitals is 24. The orbitals 25 … are excited orbitals with energies corresponding to excitation energies. In the bottom line, marked "Anion", the ionization energies for the negative naphthalene ion are given.

Naphthalene	One half electron diffusely removed. Filled orbitals give ionization energies											
	6	7	8	9	10	11	12	13	14	15	16	17
	−18.774	−18.138	−18.121	−16.463	−15.637	−15.278	−15.194	−13.996	−13.993	−13.676	−13.450	−12.618
1 C 1	0.0	0.188	0.172	0.0	0.0	0.109	−0.200	0.018	−0.000	0.0	−0.100	0.0
2 C 1	−0.151	0.0	0.0	0.143	−0.112	0.0	0.0	0.002	0.192	−0.327	0.0	0.132
3 C 1	0.0	0.110	−0.193	0.0	0.0	−0.024	−0.062	−0.319	0.003	0.0	−0.101	0.0
4 C 1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5 C 2	−0.219	0.033	−0.150	0.153	0.011	−0.054	0.000	0.007	0.045	−0.017	0.095	−0.008
6 C 2	0.038	−0.166	−0.020	−0.106	0.033	−0.122	0.044	0.185	−0.001	0.258	0.200	0.059
7 C 2	−0.059	0.005	−0.149	0.068	0.196	0.105	0.287	0.002	−0.308	0.017	−0.071	−0.211
8 C 2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
9 C 3	0.142	−0.196	0.065	−0.164	−0.044	−0.042	−0.088	−0.040	0.061	0.050	−0.009	−0.040
10 C 3	0.127	−0.055	0.059	−0.131	0.155	0.271	0.022	−0.034	−0.139	−0.207	−0.292	0.008
11 C 3	−0.081	−0.121	−0.078	−0.103	0.157	0.066	−0.024	0.269	−0.004	0.060	−0.011	0.327
12 C 3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
13 H 4	−0.153	0.016	−0.208	0.130	0.150	0.059	0.237	0.012	−0.188	−0.003	0.002	−0.143
14 H 5	0.127	−0.187	0.037	−0.215	0.146	0.187	−0.040	0.061	−0.057	−0.083	−0.194	0.104
	$4\,b_{3u}$	$5\,b_{2u}$	$6\,a_g$	$4\,b_{1g}$	$5\,b_{3u}$	$7\,a_g$	$6\,b_{2u}$	$8\,a_g$	$5\,b_{1g}$	$6\,b_{3u}$	$7\,b_{2u}$	$7\,b_{3u}$
	|	—		+	|		—		+	|	—	|
Anion:	−14.32	−13.68	−13.63	−12.14	−11.22	−10.87	−10.77	−9.52	−9.37	−9.04	−9.02	−8.17

	18	19	20	21	22	23	24	25	26	27	28	29	30
	−12.451	−12.088	−11.876	−10.976	−10.145	−9.333	−8.594	−4.835	−4.013	−2.833	−1.426	1.109	12.698
1 C 1	0.0	0.0	−0.008	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2 C 1	0.0	0.303	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	−0.614
3 C 1	0.0	0.0	−0.378	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4 C 1	−0.380	0.0	0.0	0.0	0.312	−0.397	0.0	0.0	0.489	−0.387	0.0	−0.565	0.0
5 C 2	0.0	0.012	−0.037	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.311
6 C 2	0.0	−0.296	0.044	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	−0.445
7 C 2	0.0	−0.029	0.219	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	−0.098
8 C 2	−0.243	0.0	0.0	0.238	0.359	0.008	0.401	−0.455	−0.006	0.461	−0.327	0.384	0.0
9 C 3	0.0	−0.004	0.012	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.132
10 C 3	0.0	0.238	−0.004	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	−0.046
11 C 3	0.0	−0.019	−0.242	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.110
12 C 3	−0.190	0.0	0.0	0.363	0.162	0.373	0.260	0.299	−0.439	−0.214	0.501	−0.315	0.0
13 H 4	0.0	−0.009	0.159	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	−0.136
14 H 5	0.0	0.139	−0.081	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	−0.004
	$1\,b_{1u}$	$6\,b_{1g}$	$9\,a_g$	$1\,b_{2g}$	$1\,b_{3g}$	$2\,b_{1u}$	$1\,a_u$	$2\,b_{2g}$	$2\,b_{3g}$	$3\,b_{1u}$	$2\,a_u$	$3\,b_{3g}$	$8\,b_{3u}$
		+		|	—		+	|	—		+	—	|
Anion:	−7.78	−7.53	−7.33	−6.45	−5.53	−4.74	−4.07	−0.36	0.49	1.68	2.94	5.60	17.10

4. Excitation of Naphthalene

In the HAM/3 calculation, mentioned in the introduction, the excitation of naphthalene was calculated in the following way.

The excitation energies are obtained directly from Table 1 as the difference (ΔIP) of the energies of the unoccupied (a) and the occupied (i) orbitals. The exchange integral (K) is then calculated using ordinary PPP (ZDO) theory [21] (see also [6]) as

$$K_{ia} = \sum_{A} \sum_{B} E_{ia}^{A} \, E_{ia}^{B} \, \gamma_{AB}$$

with

$$E_{ia}^{A} = \sum_{\mu}^{A} c_{\mu i} \, c_{\mu a}$$

and with γ_{AB} taken from MINDO [22].

The singlet and triplet excitation energies are then obtained by adding or subtracting the exchange integral K. The intensities (f-values) are finally calculated in conventional ways [23].

In our present HAM/3 calculation 204 transitions of naphthalene are calculated and printed. Since most of them have negligible intensity or very high energy only 17 transitions can be considered to be of interest, and the corresponding printout is reproduced in Table 2. N denotes the number of the excitation in energetic order.

The HAM/3 program continues now with a configuration interaction study. The 46 lowest energy singlet excitations interact through the configuration interaction matrix elements [24]

$$G_{iajb} = 2\,(i\,a \,|\, j\,b) - (i\,j \,|\, a\,b)\,, \quad i \neq j \neq a \neq b .$$

(A previous HAM/3 calculation with 90 excited configurations and also a comparison with Pariser's [25] PPP study of naphthalene indicated that all interesting excitations are included if the study comprises 46 configurations. Since the diagonalization of a large determinant is expensive (2 minutes of computer time), this choice should be done carefully.)

Part of the resulting print-out is reproduced in Table 3. The top line gives the final singlet excitation energies (in eV), and the second line gives the resulting f-values (oscillator strengths). The left column gives the number of the excitation which has been defined in Table 2. The remaining columns show the contributions of the different excited configurations to the final excited states.

The triplet excitations are treated in the same way but with another matrix element. Our results are not given here since they agree very well with Pariser's results [25] and no new experimental data seem to be available.

5. Experimental Excitation Studies

The singlet excitation of naphthalene has been studied by electron impact energy loss spectroscopy by Huebner, Mielczarek and Kuyatt [26]. Their result is presented in the lower part of Figure 3. In the upper part two UV spectroscopic studies are shown. Between 5 eV and 10 eV Koch, Otto and Radler [27, 28] have studied the absorption using synchrotron radiation. Their curve exhibits a large number of Rydberg transitions. Between

Table 2. Energies and intensities of some transitions in naphthalene, calculated with HAM/3. The occupied orbital is denoted i and the unoccupied a. $\Delta IP = IP_a - IP_i$ is the difference between the energies of the unoccupied and occupied orbitals in Table 1. The singlet and triplet energies are obtained as $\Delta IP \pm K_{ia}$.

N	i	a	ΔIP	K_{ia}	Singlet	Triplet	F-values
1	24	25	3.7586	0.7615	4.5201	2.9971	0.463126
2	23	25	4.4978	0.6040	5.1018	3.8938	0.973214
3	24	26	4.5805	0.6040	5.1845	3.9765	0.994632
4	22	25	5.3099	0.4446	5.7544	4.8653	0.000000
5	23	26	5.3197	0.7499	6.0696	4.5699	0.533039
6	24	27	5.7610	0.4521	6.2130	5.3089	0.000000
7	22	26	6.1318	0.4786	6.6104	5.6532	0.000000
8	21	25	6.1408	0.4810	6.6218	5.6598	0.000000
9	23	27	6.5002	0.4605	6.9607	6.0397	0.000000
14	22	27	7.3122	0.4766	7.7889	6.8356	0.539608
15	18	25	7.6159	0.2613	7.8771	7.3546	0.000002
20	21	27	8.1431	0.2390	8.3821	7.9042	0.060576
21	18	26	8.4378	0.3300	8.7677	8.1078	0.000517
24	22	28	8.7191	0.2308	8.9499	8.4883	0.056090
31	21	28	9.5500	0.3405	9.8906	9.2095	0.010521
34	24	29	9.7024	0.2722	9.9746	9.4303	0.001091
39	23	29	10.4416	0.3160	10.7577	10.1256	0.000000

Table 3. Energies and intensities of some singlet transitions in naphthalene, calculated from Table 2 by configuration interaction. (Since the calculation was performed with single precision, the excitations 1 och 2 became accidently degenerate. They have therefore been transformed to correspond to the given species.)

Naphthalene	Singlet excitations								
	1	2	3	4	5	6	13	17	22
	3.85990	3.85995	5.18047	5.45433	6.01716	6.20981	7.42232	7.91200	8.50168
	0.00000	0.10331	0.00000	0.00000	2.30120	0.64741	0.09686	0.72237	0.32200
1	0	0.854	0.000000	0.000002	0.000040	0.514594	0.000002	−0.012676	0.050022
2	−0.705	0	0.000012	−0.000015	0.651027	−0.000049	0.219206	−0.000000	0.000004
3	0.675	0	−0.000007	0.000010	−0.691966	0.000050	−0.174763	0.000005	−0.000002
4	−0.000004	0.000005	0.785281	0.000009	−0.000021	−0.000114	0.000003	−0.000009	−0.000001
5	0	−0.479	−0.000011	0.000021	0.000060	0.779420	0.000000	−0.232111	0.281451
6	0.000005	0.000012	−0.477096	0.000001	−0.000003	−0.000194	−0.000002	−0.000004	0.000003
7	0.000006	0.000006	−0.000005	0.627869	0.000030	−0.000015	−0.000038	−0.000058	−0.000002
8	0.000008	−0.000006	−0.000005	0.509752	−0.000022	−0.000001	0.000004	0.000128	−0.000004
9	−0.000003	−0.000005	0.000002	−0.535484	−0.000020	0.000012	−0.000043	0.000369	−0.000001
14	0	−0.139	−0.000003	0.000006	0.000021	0.296948	0.000016	0.859317	−0.385918
15	−0.011	0	−0.000000	0.000003	−0.158551	0.000007	0.806260	−0.000006	−0.000011
20	0.167	0	0.000001	0.000008	−0.197721	0.000007	0.456093	−0.000009	0.000019
21	0	−0.021	0.000006	0.000001	−0.000005	−0.071397	0.000000	0.394357	0.774998
24	0.141	0	−0.000000	−0.000006	0.169393	−0.000016	−0.223486	0.000011	−0.000006
31	0	0.149	0.000005	−0.000005	−0.000016	−0.180865	−0.000001	0.189153	0.378337
34	0.009	0	−0.000001	0.000001	−0.067015	0.000006	0.115883	−0.000005	0.000014
39	0	0.008	0.000003	0.000001	0.000003	0.042150	−0.000000	−0.127456	−0.160074
	$^1B_{3u}$	$^1B_{2u}$	$^1B_{1g}$	^1A_g	$^1B_{3u}$	$^1B_{2u}$	$^1B_{3u}$	$^1B_{2u}$	$^1B_{2u}$

3.5 eV and 5 eV two valence transitions have been studied by George and Morris [29].

In Fig. 3 the calculated excitation energies and intensities from Table 3 are plotted at the top of the figure. The agreement between calculation and experiment can be considered as satisfactory. The high-intensity band at 5.89 eV is interpreted as due to $^1B_{3u}$ with a smaller contribution from $^1B_{2u}$ in agreement with some other MO studies [25, 30—33] and interpretations [26, 29, 28].

The strong band at 7.6 eV is due to $^1B_{2u}$ for energy and intensity reasons. This conclusion is in agreement with Pariser's [25] values 8.182 eV and $f = 0.851$ and with Hummel and Ruedenberg's [30] values 8.24 eV and $f = 1.013$ (the IRX calculation). In the study by Koch et al., however, this band is denoted as $^1B_{3u}$. In the MO work by Hofer and Hedges [34] this band was interpreted as due to the lower $^1B_{2u}$ transition.

The band around 8.3 eV was interpreted by Koch et al. as due to Rydberg transitions. It is clear, however, that according to HAM/3 there is a $\pi\pi^*$ transition here of $^1B_{2u}$ type with a reasonable intensity. Its energy and wave function agrees well with Pariser's energy 8.778 eV and wave function (presented in Table III A in Ref. [25]) but unfortunately Pariser did not give any f-value. In Hummel and Ruedenberg's work the TBX and IRX methods give quite different and irregular results and no transition above 7.76 eV can be identified. The valence character of the band at 8.3 eV has been proven by Angus and Morris [35] by a study of naphthalene in a rare gas matrix.

The bands around 8.8 eV and 9.9 eV were interpreted by Angus and Morris [35] as due to valence transitions and by Koch et al. [27] as due to Rydberg transitions. It is shown in Table 2 and Fig. 3 that the HAM/3 calculation gives valence transitions with approximately correct energies. With the present method to handle the configuration interaction, however, the calculated intensities are too small.

In the low energy region the weakest band at 3.97 eV is successfully treated by the HAM calculation, but the energy of the $^1B_{2u}$ band at 4.6 eV is calculated 0.8 eV too low. This large error is due to our choice of γ_{AB} in the CI calculations and was also observed in our study of pyridine [5] (see also [36]).

By use of low energy electron impact forbidden transitions can be observed. Compton, Huebner, Reinhardt and Christophorou [37] obtained a

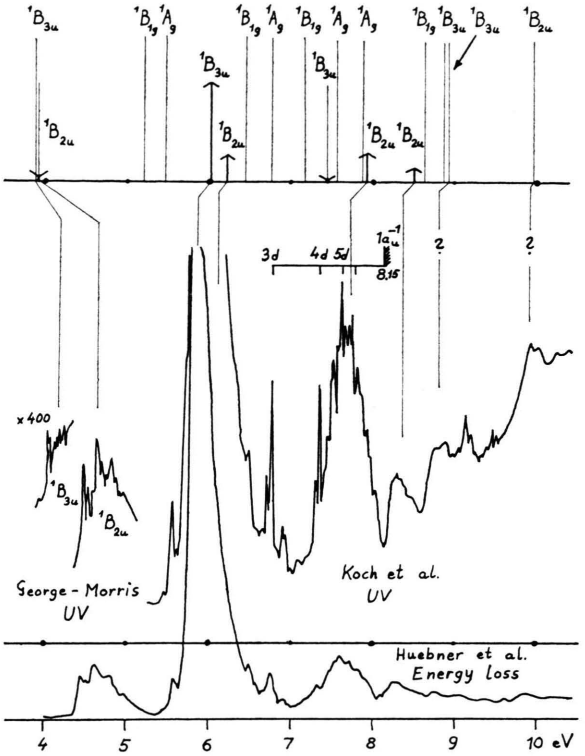

Fig. 3. Excitation spectrum of naphthalene. The UV spectra [27, 29] and electron impact energy loss spectrum [26] are compared with the HAM/3 singlet energies and intensities from Table 3. The allowed transitions are marked as arrows whose height indicates the intensity. The transitions in the top line are forbidden or have small intensity.

threshold excitation spectrum by use of SF_6 scavenging. They found a triplet band at 3.0 eV in good agreement with the calculations by Pariser [25] and with HAM/3 for $^3B_{2u}$ and $^3B_{3u}$. Further, they found two very strong and narrow peaks at 4.8 eV and 5.4 eV which could not be given a satisfactory explanation. It is possible that one or both of these peaks are due to the forbidden excitations to $^1B_{1g}$ and/or ^1A_g (see Fig. 3) in spite of the experimental observation by Birks, Christophorou and Huebner [38] that *g*-*g* transitions are never observed. With this explanation the allowed $^1B_{2u}$ transition appears as only a shoulder at 4.6 eV in the threshold spectrum.

It is perhaps appropriate to stress that the results of the HAM/3 calculations of singlet excitations are very similar to those of the fundamental work by Pariser both regarding energies and intensities. This agreement therefore supports our new method of study. For the triplets the agreement is still better.

6. Electron Affinities of Naphthalene

In the HAM/3 calculation, mentioned in the introduction, the electron affinities of naphthalene were calculated in the following way.

The electron affinity is simply the ionization energy of the negative ion and the calculation is therefore performed for a transition state in which $\frac{1}{2}$ electron has been added to the molecule. A separate SCF calculation must therefore be done. The resulting eigenvectors are very similar to the molecule orbitals presented in Table 1 and only the eigenvalues are therefore given in the lowest line in Table 1 (marked "Anion").

The electron affinities of naphthalene are given in Table 4 and compared with other work.

Transmission measurements have been made by Mathur and Hasted [39] and Burrow, Michejda and Jordan [40] (mentioned in [41]). The threshold electron excitation spectrum has been studied by Compton et al. [37] using the SF_6 scavenger technique, and Pisanias, Christophorou and Carter [42] have used a trapped electron experiment.

A comparison of the calculated and experimental energies in Table 4 shows a rather satisfactory agreement. For orbital 27 the agreement is more or less exact, and for the orbitals 26 and 28 the HAM/3 energy seems to be in error by about 0.4 eV (in the same direction as the error in Fig. 2 for the orbitals 23 and 24).

For orbital 25 the situation is less clear. When the electron affinity is about zero it may happen that a vibrational band is observed in the transmission study. It is therefore probable that neither the HAM/3 calculation nor the transmission experiments can be used to determine the first electron affinity of naphthalene.

The only theoretical study of the electron affinities of naphthalene seems to be the work by Younkin, Smith and Compton [43] in which Koopmans' theorem is applied by the following linear correlation

$$EA = -0.95\,\varepsilon - 1.9 \text{ (eV)}.$$

Here ε is the orbital energy of the unoccupied orbital, which is obtained in a special PPP calculation. The experimental affinity -0.20 eV was used for parametrization but the procedure gav finally -0.06 eV. If the theoretical procedure can be trusted, it indicates that the electron affinity is higher than -0.20 eV.

Table 4. Electron affinities of naphthalene (eV), calculated with HAM/3 as ionization energies of the naphthalene anion, which are tabulated in Table 1. Some experimental values are also given together with results from a semiempirical treatment.

Orbital	Species	HAM/3	Transmission exp. [39]	[41]	Threshold exp. [37]	[42]	Semiemp. [43]
25	$^2B_{2g}$	+ 0.36	−0.20	−0.17			−0.06
26	$^2B_{3g}$	− 0.49	−0.75	−0.88	−0.8	−0.8	−0.78
27	$^2B_{1u}$	− 1.68	−1.50	−1.65		−1.3	−1.69
28	^2A_u	− 2.94		−3.39			
29	$^2B_{3g}$	− 5.60	−5.3 −7.5	−4.72			
30	$^2B_{3u}$	−17.10					

7. Excitation of the Naphthalene Radical Anion

The absorption spectrum of the naphthalene radical anion, in which an extra electron occupies the lowest unoccupied molecular orbital in naphthalene (orbital 25), was studied first by Balk, Hoijtink and Schreurs [44] and measured later by several authors [45—48].

The spectrum was immediately explained by Balk, de Bruijn and Hoijtink [49] and has been the object of several detailed calculations [45, 50—57].

In spite of these efforts there is no agreement regarding the quantitative interpretation of the spectrum. The excitation energies (wavelengths) seem all to be more or less correct, but the intensities differ usually so strongly from the experimental intensity distribution that the correlation between the experimental and theoretical transitions is difficult to recognize.

The reason why the intensities appear to be difficult to calculate is possibly that the "virtual" orbitals from the usual SCF calculations deviate from the "excited" orbitals in nature. We have reasons to suspect this (cf. [58, 59]), since the "virtual" eigenvalues deviate strongly from the "excited" values.

Since the HAM/3 method gives eigenvalues for unoccupied orbitals which correspond to what is expected for "excited" orbitals, it would be of interest to calculate the anion spectrum of naphthalene by HAM/3, using the anion energies in the bottom line of Table 1 to get the excitation energies and using the orbitals in Table 1 to get the intensities. The calculations are presented in Table 5.

It is easy to calculate the transition energies from Table 1 by forming the difference of the energies there (see Table 5). For a transition of type 25 → 28 we start with a single electron in 25 and none in 28. No exchange integral should therefore be included. For a transition of type 23 → 25 we have already a single electron in 25, and also here the exchange integral should be omitted. For a transition of type 24 → 26 the situation is similar to that in a neutral molecule and the exchange integral must be added to obtain the allowed transition. These simple rules were given already by Hoijtink et al. [50]. We will assume that the configuration interaction between x_2 and x_3 (see Table 5) can be neglected due to the large energy difference.

Table 5. Absorption spectrum of the naphthalene anion, calculated with HAM/3 from the energies and orbitals in Table 1.

Transition	Polarisation	Transition energy (eV)	*f*
$25 \rightarrow 26$		$0.36 + 0.49 = 0.85$	0
$25 \rightarrow 27$	x_1	$0.36 + 1.68 = 2.04$	0.61
$25 \rightarrow 28$	y_1	$0.36 + 2.94 = 3.30$	0.54
$25 \rightarrow 29$		$0.36 + 5.60 = 5.96$	0
$24 \rightarrow 25$	y_2	$4.07 - 0.36 = 3.71$	0.45
$23 \rightarrow 25$	x_2	$4.74 - 0.36 = 4.38$	0.97
$22 \rightarrow 25$		$5.53 - 0.36 = 5.17$	0
$21 \rightarrow 25$		$6.45 - 0.36 = 6.09$	0
$24 \rightarrow 26$	x_3	$4.07 + 0.49 + K = 5.17$	0.99
$23 \rightarrow 26$	y_3	$4.74 + 0.49 + K = 5.99$	0.53

In Figure 4 the calculated transitions are compared with the experimental spectrum obtained by Shida and Iwata [45]. We prefer their spectrum since Shida and Iwata were able to prove that the strong absorption at 3.3 eV is not spurious. It can be seen that the general agreement is satisfactory both regarding transition energies and intensities.

The energy of the transition 25 → 27 is, however, in error by about 0.4 eV in Figure 4. The explanation is, of course, that the energies in Table 1 are not quite correct. We have already pointed out that it is necessary to apply a correction of about 0.4 eV

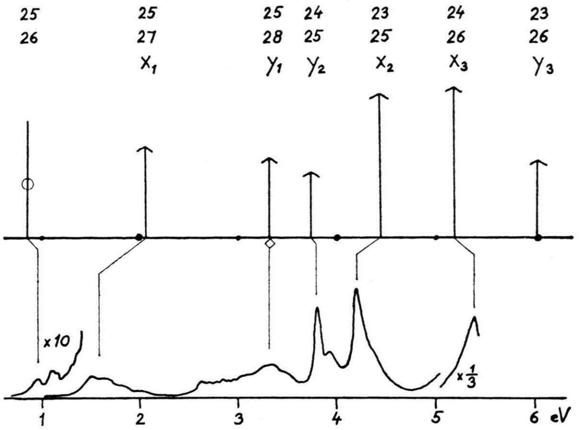

Fig. 4. Absorption spectrum of the naphthalene anion [45] together with calculated transition energies and intensities from Table 5. The intensity is proportional to the height of the arrow.

to the orbitals 23, 24, 26 and 28. The error in Figure 4 proves that it is necessary to apply the same correction also to orbital 25. After the application of these corrections *all* experimental data in this paper are treated essentially correct by the HAM/3 calculation.

We have now arrived at a value for the electron affinity of naphthalene. It is $0.36 - 0.4 \approx 0.0$ eV. The value -0.20 eV from the transmission experiments is then probably due to the formation of a vibrationally excited ion.

The electron affinity ≈ 0.0 eV is in good agreement with the estimation by Younkin et al. [43] and explains also why naphthalene negative ions are stable and easy to form [44], which cannot be understood from the previously accepted value -0.20 eV for the electron affinity.

8. Conclusions

In quantum-mechanical studies of molecules the eigenvalues are related to the most fundamental observables, and it is therefore of utmost importance to be able to calculate them in agreement with experiment. One must then require that different experiments should be handled in *one* calculation, and it is not satisfactory if different theoretical methods are necessary for different experiments.

In the present paper naphthalene has been studied in *one* calculation, and the results from probably all experimental methods related to eigenvalues have been compared with the results from this calculation. The agreement is generally satisfactory, and it is shown that only small improvements in the parametrization of HAM/3 are necessary to give a very reasonable agreement for ionization energies, excitation energies and electron affinities of naphthalene.

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