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ON THE FRANCK–CONDON EFFECTS IN THE ABSORPTION SPECTRUM OF $C_{10}H_8$ ANION. THE ANALYSIS BASED ON THE *AB INITIO* MCSCF METHOD

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The near-IR, visible and UV regions of the absorption spectrum of naphthalene anion ($C_{10}H_8^-$) are studied in terms of full optimized reaction space multiconfiguration self-consistent field method applied with Dunning's double-zeta basis set including polarization and diffuse functions on the all hydrogen atoms. Computed Franck–Condon activity of the all (nine) totally symmetric vibrations in the seven low-energy transitions is discussed and compared to the available experimental data. The assignment for some electronic transitions in the visible part of the naphthalene anion absorption spectrum is corrected on the base of full optimized reaction space multiconfiguration self-consistent field computations. We have argued that two (overlapping) bands at 21700 cm^{-1} and 26800 cm^{-1} are due to $1^2B_{1g} \rightarrow 1^2A_u$ and $1^2B_{1g} \rightarrow 2^2A_u$ transitions rather than to the short-axis and long-axis polarized ones as was suggested in an earlier semiempirical treatment. An experimental method appropriate to verify this result is proposed.

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1. Introduction

Over the last few years an effort has been made to understand and explain the electronic structure of one-electron oxidated (or reduced) molecules with π-electron systems. Such molecules (ion radicals) are interesting and important at least for two reasons. The presence of these species in the cosmic space is most probably responsible for many infrared bands observed in the emission spectra of interstellar medium [1, 2]. On the other hand, it is well known that a conjugated anion–cation pair of an organic molecule offers the simplest model allowing us to study the charge transfer states in molecular crystals. Such crystals are photoconductive. Therefore, the proper understanding of ground and excited states properties of ion radicals may be helpful to answer several questions concerning the role of charge transfer states in a generation of the light induced electric charge [3, 4].

Except for a comprehensive study for series of polycyclic hydrocarbons cations [5], the detailed theoretical studies of ion radicals in terms of an *ab initio* quantum-chemical method are not very common in the literature, especially for the anion radicals. The older treatments concerning the optical properties of the hydrocarbons radicals [6–10] dealt with the electronic structure in terms of semiempirical self-consistent field molecular orbital configuration interaction (SCF–MO–CI) approaches and left aside the problem of vibrational structures in the electronic transitions. The survey of these data teaches us however that the absorption spectra of ion radicals show more or less resolved structures due to activity of the totally symmetric modes. Although an activity of the non-totally symmetric vibrations, due to vibronic coupling effects, may also be important in some cases [5, 11], the vibrational progressions seen in the experimental spectra of ion radicals are governed by the well-known Franck–Condon (FC) principle.

In our earlier paper [12] we investigated the absorption and the resonance Raman (RR) spectra for naphthalene cation in terms of the MCSCF method applied with minimal basis set. These somewhat simplified *ab initio* calculations reproduced quite correctly the intensity distributions in the RR spectra measured in the region corresponding to the lowest energy $^2B_{3g}$ state of the naphthalene cation. The satisfactory agreement between the theory and the experiment achieved earlier [12] encouraged us to use the same MCSCF methodology in order to discuss the absorption spectrum of the naphthalene anion.

The aim of this paper is to interpret the absorption spectrum of the naphthalene anion as far as possible in an nonempirical fashion. The absorption spectrum of that radical was measured in a wide range that encompasses the near-IR, the visible and the UV absorption regions [9]. Relatively simple electronic structure of that spectrum is due to promotions of electrons in the π-system of the naphthalene anion. To interpret electronic and vibrational structures of the absorption spectrum we employ full optimized reaction space (FORS) MCSCF method [13] applied with Dunning's double-zeta basis set [14]. Dealing with the vibrational structures of the electronic transitions we neglect the vibronic coupling effects and we treat the totally symmetric vibrations as the oscillators that are displaced but not distorted in the excited electronic states. It amounts to an assumption that neither vibrational frequency changes nor Dushinsky rotations are large enough to invalidate the conclusion of this paper.

2. Methods and computational details

The geometry of naphthalene anion radical and the orientation of Cartesian axes applied in the computations are depicted in Fig. 1. As the parent molecule, the naphthalene anion is flat so that Cartesian components x, y, and z belong respectively to B_{3u}, B_{2u}, and B_{1u} representations of the D_{2h} point group. It implies that following selection rules: $B_{1g} \rightarrow B_{2u}$ and $B_{3g} \rightarrow A_u$ (long-axis polarization) and $B_{3g} \rightarrow B_{2u}$ and $B_{1g} \rightarrow A_u$ (short-axis polarization) must apply for the in-plane dipole-allowed transitions.

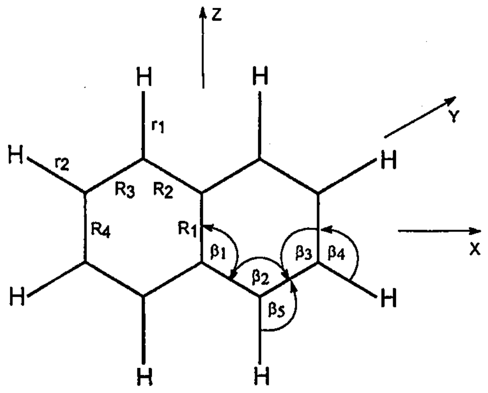

Fig. 1. The orientation of the axes used in the computations and the geometrical structure of the $C_{10}H_8$ anion radical. The values of bond angles and bond lengths are given in Table I.

TABLE I

The geometry of naphthalene anion in its ground state (1^2B_{1g}) and the five low-energy allowed excited electronic states obtained by FORS MCSCF method with Dunning's $(10s5p/5s1p)/[3s2p/3s1p]$ basis set. The symbols as in Fig. 1.

	1^2B_{1g}	1^2B_{2u}	1^2A_u	2^2A_u	2^2B_{2u}	3^2B_{2u}
R_1	1.4583	1.3949	1.4590	1.4674	1.5085	1.4818
R_2	1.4266	1.4596	1.4252	1.4294	1.4262	1.4345
R_3	1.4206	1.4036	1.4742	1.4331	1.4434	1.4328
R_4	1.3997	1.4272	1.3710	1.4491	1.4205	1.4428
r_1	1.0743	1.0717	1.0738	1.0744	1.0740	1.0742
r_2	1.0742	1.0749	1.0737	1.0725	1.0728	1.0723
β_1	118.57	120.55	118.61	118.77	118.17	118.57
β_2	121.36	118.31	121.86	122.12	122.04	121.93
β_3	120.06	121.14	119.53	119.10	119.80	119.50
β_4	120.24	118.73	121.32	120.51	120.49	120.36
β_5	119.82	121.66	118.96	119.24	119.19	119.41

The bond lengths r_i and R_i and the bond angles β_i defined in Fig. 1 are given in Table I. They were obtained by the optimization of the geometry in the 1^2B_{1g} ground state and in the five lowest energy allowed states. The optimizations were performed separately for each electronic state. These and the remaining results presented below were generated by GAMESS program applied at the FORS ([13]) MCSCF level with the active space provided by all (ten) π-orbitals: $3b_{2u}$, $2b_{1g}$, $3b_{3g}$, and $2a_u$. Dunning's $(10s5p/5s1p)/[3s2p/3s1p]$ double-zeta valence (DZV) basis set [14] was applied and the required polarization and the diffuse functions on the all hydrogen atoms were included in the calculations [15]. The orthogonal transition dipole moments were found from the CI calculations in which the active space was the same as that one used in the FORS MCSCF treatment.

In the subsequent section we discuss the absorption spectrum of the naphthalene anion observed in a wide range of the energy from near-IR to UV. In this range the naphthalene anion reveals several excited electronic states together with their vibrational manifolds; some of these may overlap on the energy scale. Such a situation creates various practical problems when dealing with the multimode and multistate effects at the same time. To reduce difficulties and to make the problem tractable for purpose of the quantitative analysis, we assume that the Born–Oppenheimer approximation is valid for every excited electronic state at issue. Therefore the corrections due to vibronic couplings [16] and non-Condon effects [17] are assumed to be small. At this level of approximation, the intensity distribution in the absorption spectrum can be evaluated from

$$\Omega \propto \sum_{x} \sum_{v_1} \sum_{v_2} \cdots \sum_{v_N} D(X)^2 |(v|0)_x|^2 \delta(E(X) + \omega_1 v_1 + \omega_2 v_2 + \ldots - \Omega), \quad (1)$$

where $D(X)$ is the transition dipole moment for $G \to X$ excitation and Ω is the energy of the absorbed light. The vectors $\mathbf{0} = \{0_1, 0_2, \ldots 0_N\}$ and $\boldsymbol{v} = \{v_1, v_2, \ldots v_N\}$ denote the sets of vibrational quantum numbers in the ground state and an excited electronic state, respectively. Further we will assume that vibrational frequencies do not change much upon going from one state to another one. Therefore the vibrational overlap integrals $|(v|0)_x|^2$ in Eq. (2) have simple familiar analytical form [16]. It reads

$$|(v|0)_x|^2 = \prod_{i=1}^{N} \frac{1}{v_i!} \left(\frac{B_{x,i}}{2}\right)^{2v_i} \exp\left(-\frac{1}{2} B_{x,i}^2\right). \quad (2)$$

The FC parameters, $B_{x,i}$, are directly available from the expression [5, 12]:

$$B_{x,i} = \boldsymbol{S}_i^{\mathrm{T}} \cdot \boldsymbol{F}(X, G) \left(\frac{\hbar}{\mu_i \omega_i}\right)^{-1} \quad (3)$$

in which $\boldsymbol{S}_i$ is a column vector containing the Cartesian nuclear displacements in Q_i (ground state) normal mode with the frequency ω_i and the reduced mass μ_i. $\boldsymbol{F}(X, G)$ is the column vector containing the differences of the nuclear position vectors in the excited X state and the ground G state equilibrium configurations.

Eventually, applying Eq. (1) to simulate the experimental spectrum we assume that an individual line in the absorption has the δ-function intensity distribution, instead of a Gaussian (or Lorentzian) function as usually assumed. Although this simplification is not rigorously needed, it is accepted here to minimize a number of (empirical) parameters not provided by our *ab initio* computations.

3. Results and discussion

Table II gives the (unscaled) frequencies of nine totally symmetric vibrations, the adiabatic excitation energies of a few low-energy transitions and the FC (dimensionless) parameters, $B_{x,k}$, of the k-th vibration in the X-th electronic

TABLE II

The vibrational frequencies, ω_i, the Franck-Condon parameters, $B_{n,i}$, the adiabatic excitation energies, $E(X)$, and the relative transition dipole moments, $D(X)/D(1^2B_{2u})$, for the naphthalene anion.

$1^2B_{1g} \to X$	1^2B_{3g}	1^2B_{2u}	1^2A_u	2^2A_u	2^2B_{2u}	2^2B_{3g}	3^2B_{2u}
E_n [eV]	0.59	1.76	2.86	3.68	4.25	4.40	4.97
$\frac{D(X)}{D(1^2B_{2u})}$ (a)	–	1	0.78	0.82	0.34	–	2.37
$\frac{D(X)}{D(1^2B_{2u})}$ (b)	–	1	0.67	0.91	1.20	–	1.25
$\omega_1 = 519$	0.16	0.88	-1.26	-0.51	-0.61	-1.74	-0.58
$\omega_2 = 806$	-0.19	-0.39	-0.34	-0.44	-0.94	-0.85	-0.79
$\omega_3 = 1082$	0.33	0.44	0.50	1.03	0.45	0.21	0.75
$\omega_4 = 1310$	0.64	-0.07	-0.33	0.31	0.10	-0.36	0.24
$\omega_5 = 1460$	-0.41	-1.40	0.84	0.08	0.65	-0.19	0.13
$\omega_6 = 1532$	-0.23	-0.22	-0.15	-0.17	-0.26	-0.60	-0.29
$\omega_7 = 1662$	-1.19	0.11	-0.97	-0.35	0.10	0.95	-0.31
$\omega_8 = 3343$	0.14	0.45	0.00	0.20	0.30	0.10	0.29
$\omega_9 = 3491$	-0.06	0.26	-0.74	-0.54	-0.51	-0.94	-0.54

(a) From the FORS CI computations; (b) from the spectral moments analysis. The frequencies in cm^{-1} unit.

state. For a comparison two sets of the (relative) transition dipole moments (a) and (b) are also given in Table II. The set (a) is that one obtained from FORS CI calculations whereas the set (b) was evaluated from a spectral moment analysis of the experimental absorption spectrum. A comparison between these two sets may serve as a quality test of the electronic functions used in the computations. As follows from Table II, the dipole moments for the three low-energy allowed transitions agree very well with the experiment and these found for the $1^2B_{1g} \to 2^2B_{2u}$ and $1^2B_{1g} \to 3^2B_{2u}$ transitions are only slightly worse in a comparison. Since the most apparent discrepancy occurs for the high-energy transitions, it is conceivable that the basis set applied in the actual calculations still requires an improvement to account in more complete fashion for an increasing influence of the Rydberg states.

With the numbers listed in Table II we can now discuss the absorption spectrum of naphthalene anion measured in the region of 10000–40000 cm^{-1} [9]. A comparison between the measured (curve) and the calculated (stick) spectra is presented in Fig. 2 together with the assignment of electronic transitions as it follows from our computations. The energies of these transitions were uniformly corrected down by *ca.* 1700 cm^{-1} to improve the presentation. For the same reason, the set (b) of transition dipole moments was employed to reconstruct the experimental data.

Although the calculated excitation energies of the allowed transitions are somewhat overestimated, a look at Fig. 2 reveals that the agreement between the

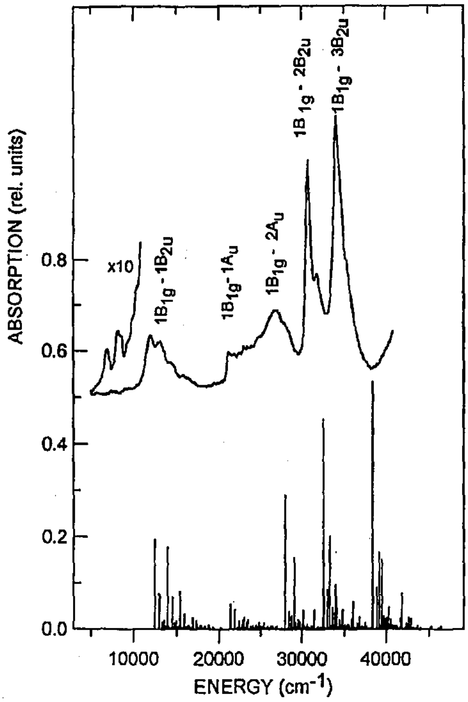

Fig. 2. The experimental (curves) and the calculated (sticks) absorption spectra of $C_{10}H_8$ anion radical.

theory and the experiment is in general satisfactory. Very weak (amplified) absorption features on the left wing of the $1^2B_{1g} \rightarrow 1^2B_{2u}$ band correspond to the optically forbidden but vibronically allowed 1^2B_{3g} state located at about 9500 cm^{-1} lower in energy than the allowed 1^2B_{2u} state. Therefore, the lowest energy part of the experimental spectrum can be unambiguously ascribed to (weak) vibronically induced progressions build on the false origin of the 1^2B_{3g} state. It should be noted that the position of the 1^2B_{2u} state relative to the 1^2B_{3g} state may be slightly corrected when more sophisticated *ab initio* treatment is tested. In fact, such a correction is needed to reduce upward shift of the calculated absorption spectrum comparing to the experimental one. A better approach should not drastically change the location of the 1^2B_{3g} state that was found to be the lowest excited state in agreement with the experiment and with the earlier semiempirical calculations [7, 9].

Viewing systematically the FC parameters in Table II and the stick spectrum in Fig. 2 we can see that only four of the nine a_g-symmetry modes with the frequencies: $\omega_1 = 519$ cm^{-1}, $\omega_2 = 806$ cm^{-1}, $\omega_3 = 1082$ cm^{-1}, and $\omega_5 = 1460$ cm^{-1} appear to be the most active in the optically allowed transitions. It is interesting to note that also the vibration with the frequency $\omega_9 = 3491$ cm^{-1}, which involves the OH motions, shows quite strong FC activity. The remaining totally symmetric vibrations show rather modest or very modest activity in the allowed transitions.

Therefore, their short FC progressions are overshadowed in the low-resolved experimental absorption spectrum. An inspection of Fig. 2 reveals that aforediscussed properties agree quite well with the experiment even when comparing the calculated absorption spectrum to the only partially resolved experimental one. Unfortunately, the feeble absorption in the near-IR region precludes the comparison between the theory and the experiment for the lowest-energy vibronically induced $1^2B_{1g} \rightarrow 1^2B_{3g}$ transition. On the base of our calculations we can state, however, that the two $\omega_4 = 1310$ cm^{-1} and $\omega_7 = 1662$ cm^{-1} modes are predicted to build the most prominent progressions that start from the false origin of 1^2B_{3g} state.

The assignment of two (overlapping) bands at *ca.* 25000 cm^{-1} has an interesting history of misinterpretation. In a first paper [18] Hoijtink et al. assigned these bands to a single short-axis polarized transition ($B_{1g} \rightarrow A_u$ in our axis convention). In their subsequent papers [19, 20] they expelled their earlier assignment concluding that the absorption at *ca.* 25000 cm^{-1} may be due to some impurity. That revised viewpoint was convincingly criticized by Shida et al. [9] who argued, on the empirical basis, that the absorption features at 21700 cm^{-1} and 26800 cm^{-1} should be assigned to two short-axis polarized transitions as they found from a semiempirical SCF-MO-CI treatment. Then, Jörgensen et al. [7, 21] showed that the absorption features in the visible region may consist of two electronic transitions of different polarizations as it followed from complete neglect of differential overlap/spectroscopic (CNDO/S) calculations. The results presented in this paper show that the debatable region is not spurious supporting Shida et al. arguments on the nonempirical ground. We wish to emphasize that the theoretical assignment proposed and discussed above is entirely based on the poorly resolved absorption spectrum. Therefore, for a better confidence, more experimental works based on the different spectroscopic methods should be done to verify the assignments for the transitions in question. Of many such methods, the resonance Raman spectroscopy [16, 22, 23] seems to offer a suitable tool to deal with the above-discussed problem. To our best knowledge, the RR studies of that kind are presently not available for the naphthalene anion. If they were available, say in the excitation region corresponding to the $1^2B_{1g} \rightarrow 1^2A_u$ and $1^2B_{1g} \rightarrow 2^2A_u$ electronic transitions, the sizes of FC parameters listed in Table II for the 2^2A_u and 1^2A_s states allow us to foretell that three fundamentals of $\omega_1 = 519$ cm^{-1} (CCC bending), $\omega_3 = 1082$ cm^{-1} and $\omega_5 = 1662$ cm^{-1} (CC stretching) modes of the naphthalene anion should show sizeable activity in the measured RR spectra.

4. Conclusion

We have studied the activity of totally symmetric modes in the low-energy part of the naphthalene anion absorption spectrum. Following earlier report [12] we have employed the FORS MCSCF method applied with Dunning's double-zeta valence basis set. At this level of approximation, the FC parameters derived from FORS MCSCF computations were found to be consistent with the available experimental data. We have also clarified some earlier conclusions regarding the assignment of two transitions in the visible part of the naphthalene anion absorption spectrum. Namely, we have ascribed two bands at 21700 cm^{-1} and 26800 cm^{-1} to two short-axis polarized transitions, in contrary to the assignment proposed previously on the base of the CNDO/S applied in the so-called ground canonical configuration interaction (GCCI) scheme [7, 21]. However, the present report and those two earlier ones [9, 21] are consistent in a conclusion that the two lowest-energy bands correspond to the dipole-forbidden $1^2B_{1\mathrm{g}} \rightarrow 1^2B_{3\mathrm{g}}$ and the dipole-allowed $1^2B_{1\mathrm{g}} \rightarrow 1^2B_{2\mathrm{u}}$ transitions. All these observations allow us to conclude that more experimental works based on a different technique are required to settle the assignment for electronic transitions in the debatable absorption region. One of such methods, namely the resonance Raman spectroscopy is suggested in this paper. This report is our second one which deals with the electronic structure of radicals by means of the MCSCF method. In a following paper we are going to show that the MCSCF method applied with formally less accurate Pople's basis set can account correctly for the available experimental RR spectra of pyromellitic diahydride (PMDA) anion radical [24].

Looking beyond the calculational methodology applied in this paper, we wish to note that the FORS MCSCF treatment yields reasonable, even if approximate first step to study the absorption spectrum of anion radicals in general and $C_{10}H_8^-$ radical in particular. The further improvement could be certainly done when considering more sophisticated quantum chemical methods based on the variational (MR-CI) [25, 26] or perturbational (CASPT2) [27, 28] scheme. In our opinion, an application of these time consuming methods might be justified when dealing with the experimental (absorption) spectra of sufficiently high-resolution to allow a better test of the quantum chemical tool. Since the experimental data of that kind do not currently exist in the literature, we hope to return to the problem in the future publications.

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