THE SINGLET-TRIPLET TRANSITIONS INTENSITY CALCULATION IN FULLERENE BY DENSITY FUNCTIONAL THEORY WITH ACCOUNT OF QUADRATIC RESPONSE METHOD

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Introduction

The singlet-triplet (S -T) transitions in fullerene, calculated in the present work, are important not only for fundamental assignment of electronic structure and symmetry of wave functions of the ground state and a number of low-lying exited states condition of the C_{60} molecule, but also for many applied problems.

Results and discussion

Fullerene C_{60} and its analogues have found wide application in molecular electronics, in phototherapy (sensibilizators of singlet $^1\Delta_g$ oxygen), in devices of nonlinear optics, and in particular - in optical limiting devices [1]. All these aspects are connected with specific properties of the lowest triplet state (T_1) of the C_{60} molecule. The life time of the T_1 state is rather large (0.4 ms in the frozen matrix), and its quantum yield is close to unit. Fullerene C_{60} has very weak absorption in visible region (it is almost transparent) at low intensity of the incident light, when almost all molecules are basically the ground state (S_0). At more powerful illumination the fullerene molecules are excited into the metastable T_1 state; they are accumulated there under the singlet-singlet absorption (S_0 - S_n) with subsequent intersystem conversion (S_1 -T_1). Under accumulation of sufficient concentration of the triplet molecules C_{60} the intensive triplet-triplet absorption (T_1- T_n) is rising in the visible region of a spectrum and the transparent substance grows dull, becomes opaque at bright light.

A large number of theoretical and experimental studies is devoted to spectra of absorption and fluorescence of fullerenes (reviews are given in [1-3]). The molecule C_{60} in the ground state has a high symmetry I_h and the exited states are highly degenerate. The optimization of geometry of a molecule is carried out with the help hybrid density functional B3LYP [1] in the 6-31 G basis. Our calculation has given the C-C bond lengths equal to 1.395 A and 1.453 A, in a good agreement with experiment (1.391 A and 1.455 A, respectively) [1]. The spectra of the S_0 - S_n and T_1- T_n absorption are calculated by the time-dependent density functional theory (DFT), [2], which represents a method of the linear response [3], made in a frameworks of DFT. The energy of the T_1 state (1.7 eV) is received in a good agreement with experiment (1.6 eV). The account predicts, that the lowest T_1 state has the symmetry 1^3T_{2g} and is separated from other triplets by a significant energy gap (0.4 eV). The optimization of geometry in the T_1 state confirms presence of the Yahn-Teller effect for the degenerate state. With the account of spin we have 9 sublevels, which are very poorly split in a zero magnetic field. The term 1^3T_{2g} is split in five degenerate spin sublevels of the H_g-type and four degenerate spin sublevels of the Gg type. The account of spin - spin interaction gives parameter of splitting in a zero field (ZFS) equal D = 0.034 cm^{-1} in a reasonable agreement with the EPR data (D = 0.045 cm^{-1}) [6]. The S_0 - T_1 transition ($1^1Ȧ_g$ - 1^3T_{2g}) in the undistorted molecule with the symmetry I_h remains forbidden even at the account of spin- orbit interaction (SOI). In the study [2] the account of vibronic interaction by the Herzberg-Teller mechanism together with the account of SOI for an explanation of a phosphorescence spectrum is carried out. Such spectrum received in a Xe matrix, contains an intense 0-0 band [2,6], that speaks about strong SOI perturbation induced by effect of external heavy atom. Even in a cyclohexane-decaline (CD) matrix, where the spectrum is strongly broaded, the presence of the 0-0 band testifies the influence of intermolecular electrostatic interactions, which reduce the symmetry of C_{60}, on removal of a spin forbiddness of the S_0 - T_1 transition.

The authors of job [2] have reduced however the problem of the S_0 - T_1 transition intensity to a problem of spin-vibronic interaction in the symmetry I_h. Its solution in a framework of a CNDO/S method [2] seems to us rather unreliable. The first step to decoding a phosphorescence spectrum of C_{60} can be solved by the non-empirical calculation of the S_0 - T_n transitions probability allowed by symmetry by account of SOI, within the framework of the quadratic response method [5]. The results of such calculation with a method B3LYP are given in the Table, where the electric dipole S_0 - T_n transition moments, their energy (eV), rate constant ($K_n^{av.}$), and radiative life times ($\tau_n^{av.}$) are given, designed in basis 3-21G at equilibrium structure of the ground state

T_n	E_n(эВ)	$M_{o-n}(ea_0)$	$K_n^{cp.}(c^{-1})$	$\tau_n^{cp.}$ (c)
1^3T_{1u}	2.961	0.00011	0.22	4.54
1^3H_u	3.130	0.00020	0.83	1.20
2^3H_u	3.518	0.00021	1.20	0.84
3^3H_u	3.605	0.00081	32.2	0.03

For radiation 1^3T_{1u} - 1^1A_g all three spin sublevels should be averaged for each of three orbitally degenerate states. For the ^3H_u - 1^1A_g transitions all 15 components are averaged. The radiative life time of all triplets, given in the Table, can not be measured, as all of them lay above the T_1 level. However the calculated S_0 - T_n transition moments can be taken into account for estimation of the phosphorescence lifetime in a framework of the Herzberg-Teller theory. Taking into account results of accounts of vibronic interaction by a CNDO/S method [3] one can notice, that the T_1 state is effectively mixed with the ^3H_u triplets by the t_u vibrational mode of frequency 1435 cm^{-1}. Thus the 1^3T_{2g} - 1^1A_g transition can borrow intensity from the S_0 - T_n transitions given in the table. Vibronic band 1435 cm^{-1} is really active in the C_{60} phosphorescence spectrum in CD matrix [2,6].

The calculated phosphorescence lifetime is equal to 452 s. This is larger than the observed C_{60} phosphorescence lifetime in CD matrix [2,6], which indicates a strong nonradiative deactivation of the lowest triplet state of fullerene C_{60}.

References

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