СЕКЦІЯ 1. КВАНТОВО-ХІМІЧНЕ МОДЕЛЮВАННЯ ТА ПРАКТИЧНЕ МАТЕРІАЛОЗНАВСТВО

ANALYSIS OF SOC EFFECTS IN THE NITROGEN DISCHARGE SPECTRUM AS A USEFUL EXAMPLE FOR SPIN VIBRONIC PERTURBATION TREATMENT IN OLED MATERIALS

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OLED technique often requires sintersystem crossing measurements and spin-orbit coupling (SOC) study between singlet (S) and triplet (T) states. The N_2 molecule provides a good example of numerous S-T transitions since it possesses the most stable singlet ground state (S_0) among diatomics and a rich manifold of photostable T states. Being abundant component of air, N_2 plays a crucial role in many photochemical processes in the upper atmosphere demonstrating bright and expressive S–T perturbations [1–5].

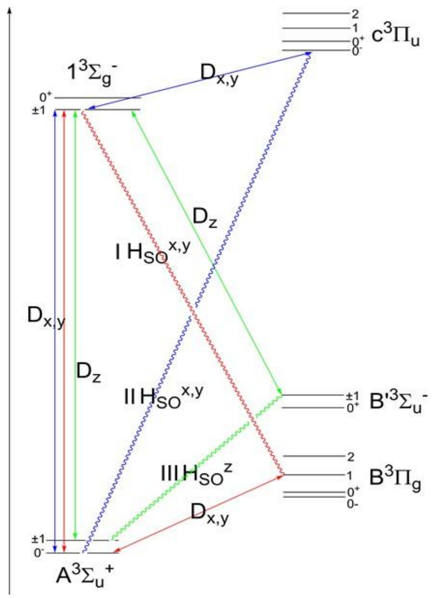

Fig. 1. Enhanced intensity borrowing for the forbidden transition $1^3\Sigma_g^- \rightarrow A^3\Sigma_u^+$. The first (I H_{SO}) and second mechanisms (II H_{SO}) of SOC account provide perpendicular polarization of ED transitions ($D_{x,y}$), and the third one is responsible for parallel polarization (D_z) along the N–N axis. We see that T-T transition can be induced by SOC (Never has been accounted for OLED)

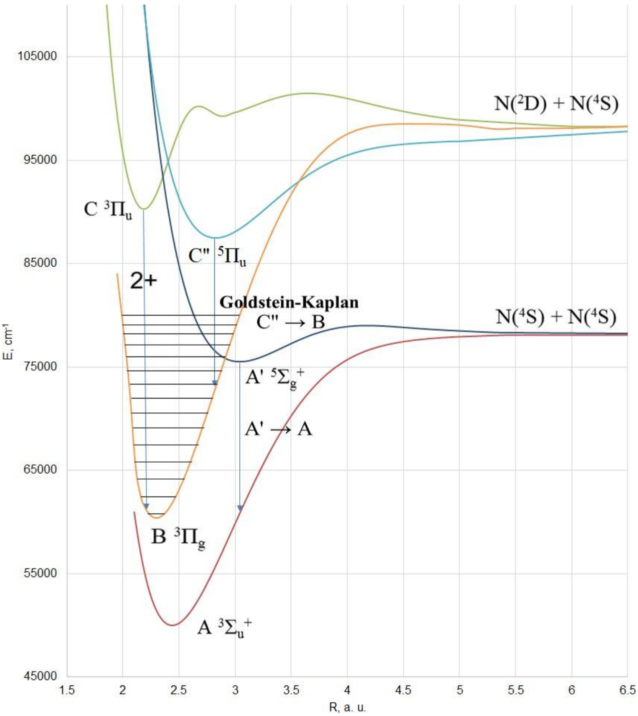

Fig. 2. PECs of several excited states of the N_2 molecule, calculated by MRCI/aug-cc-pV5Z approach. Vibrational levels for the $B^3\Pi_g$ state are shown to present the second positive C→B system and new assignment of the C”→B emission as the Goldstein-Kaplan band

The triplet excited states manifold of N_2 is well studied in the far-UV $S_0 \rightarrow T_n$ absorption and in numerous T_1-T_n transitions involved in Aurora Borealis and Rayleigh afterglow [1]. The discovery of new spin-forbidden transitions of N_2 induced by SOC perturbations is an important part of optical tracking of nitrogen at different altitudes [4]. The origin of intensitie borrowing of the known N_2 emission bands forbidden by the electric dipole (ED) selection rule provides a high standard of spin selection.

Fig. 1 illustrates a strict selection between spin sublevels of the triplet states. The solid lines denote ED transitions, waved lines denote SOC-induced mixing between spin sublevels. The SOC calculations are getting popular now in OLED theory often in connection with structural analysis of dye luminophores. Meanwhile, the spin sublevels selectivity of SOC perturbation is often neglected together with light-emitted polarization and color chromaticity of OLED device.

The correct assignment of the quintet-quintet transition $C''^5\Pi_u \rightarrow A'^5\Sigma_g^+$ to the Herman IR band system of N_2(Fig. 2) was a great achievement, which put an end to a long fifty-years history of contradictory hypotheses [5]. Now it paves the way for new discoveries of the quintet (Q) states involvements into N_2 spectroscopy [2–5]. It has long been suggested that the triplet states of N_2 undergo predissociation, being perturbed by quintet analogues of the same parity [2– 6].Fig. 2 shows a number of such Q–T PEC crossings. The $A'^5\Sigma_g^+$quintet state crosses the $B^3\Pi_g$ triplet, which is manifested by the high v'–v" lines broadening of the second positive C→B system (Fig. 2). The Herman IR transition is not shown by arrow in Fig. 2 (there is no space); instead, the new predicted $C''^5\Pi_u \rightarrow B^3\Pi_g$band is denoted close to the Herman IR region [2]. Now we assign this Q-T transition to the well-known Goldstein-Kaplan band in the range 508– 286 nm [2–6], which was assigned tentatively to the C' → B emission. It is a relatively weak rotational-vibronic system consisting of a number of complex red-degraded bands. Kaplan identified them as probably belonging to a transition from an unknown state to the $B^3\Pi_g$state [7]. Our assignment of this complicated weak system corresponds to the calculated intensity of the Q–T transition (C"–B band). At least the green-blue part of the Goldstein-Kaplan band system may be identified as the calculated spin-forbidden C"–B band strongly enhanced by SOC perturbation and efficient intensity borrowing from the $B^3\Pi_g \rightarrow A^3\Sigma^+$ transition of the First Positive System [2].

Thus, the detailed analysis of spin-selected SOC effects with exact assignment of spin sublevel according to the total angular momentum quantum number J=L+S in the symmetric diatomic N_2 molecule affords to make new discoveries of the spin-forbidden Q-T and S-T transitions [1–4]. This experience indicates how to apply the similar grate amount of information extracted from the SOC-induced optical transitions in electroluminescent devices accounting for the radiative lifetime, polarization and quantum yield of S-T transitions in the new OLED engineering depending on spin-sublevels selection. Our review of intersystem crossing in nitrogen afterglow published in a special issue devoted to the triplet states harvesting in molecular electronics [5] is now augmented by new discoveries in the N_2 spectroscopy [2–4]. Diatomic molecules with high spectral resolution of their rovibronic spin-forbidden transitions and modern MRCI methods conjugated with DUO program represent useful experience for the OLED community being so far not in a large demand by electroluminescence.

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References

1. B. Minaev, P. Norman, D. Jonsson, H. Ågren.Response theory calculations of singlet-triplet transitions in molecular nitrogen. *Chemical Physics*, 1995, Vol. 190, № 1, P. 11–29.

2. B. F. Minaev, R. S. da Silva, O.O. Panchenko, H.Ågren. Prediction of a new spin-forbidden transition in the N_2 molecule - $C''^5\Pi_u \rightarrow B^3\Pi_g$. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 2023, P. 108701.

3. Б. Мінаєв, О. Панченко, Х. Майдi. Prediction of New Emission Band in the Spectrum of Nitrogen Molecule. *Наука і техніка сьогодні*, 2022,№ 4(4), С. 321–338.

4. B. Minaev, R.S. Da Silva, O. Panchenko, H. Ågren. Prediction of newspin-forbiddentransitions in the N_2molecule—theelectricdipole $A'\ ^5\Sigma_g^+ \rightarrow A^3\Sigma_u^+$ and magnetic dipole $a'\ ^1\Sigma_u^- \leftarrow A^3\Sigma_u^+$transitions. The Journal of Chemical Physics, 2023, 158 (8) 084304.

5. B. F. Minaev, O. O. Panchenko, V. A. Minaeva, H. Ågren. Tripletstateharvesting and search for forbiddentransitionintensity in the nitrogenmolecule. *Frontiers in Chemistry*, 2022,Vol. 10, 1005684.

6. K. P. Huber, M. Vervloet. High-resolution Fourier transforms spectroscopy of supersonic jets. The $C''^5\Pi_{ui} \rightarrow A'^5\Sigma_g^+$ Herman infrared bands of $^{14}N_2$ *J. Mol. Spectrosc*. 1992, Vol. 153, P. 17–25.
DOI: 10.1016/0022-2852(92)90453-U.

7. J. Kaplan. New bands in nitrogen. Phys. Rev. 1934, Vol. 46, P. 534.

8. L. Xiao, S. An, B. F. Minaev, H. Ågren, B. Yan. Therovibronicspectra in UV absorption of S_2. Astronomy & Astrophysics, 2025, 702, A98.