

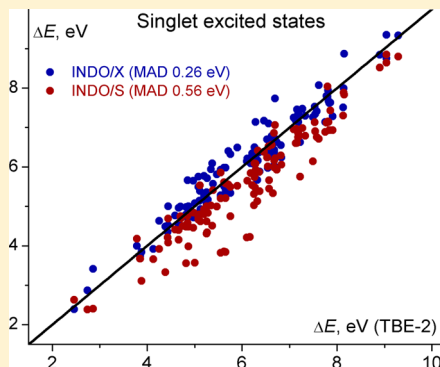
INDO/X: A New Semiempirical Method for Excited States of Organic and Biological Molecules

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ABSTRACT: The semiempirical method INDO/S is a well-known computational tool for calculating spectroscopic properties of molecular systems. This scheme has been modified and reparameterized using the TBE-2 benchmark excitation energies and oscillator strengths. The developed method referred to as INDO/X provides significant improvements over INDO/S. The mean absolute deviations of the INDO/X excitation energies relative to the TBE-2 data is 0.26 eV for singlet states and 0.33 eV for triplet states. The corresponding values for INDO/S are 0.56 and 0.64 eV. Also, the oscillator strengths estimated with INDO/X are in good agreement with the benchmark data. The proposed method is very fast and may be applied to large organic and biological molecules.



INTRODUCTION

The semiempirical method INDO/S (Intermediate Neglect of Differential Overlap—spectroscopic parametrization) was designed 40 years ago to compute excited state properties of π conjugated organic molecules.¹ Later, this approach based on the CIS scheme (Configuration Interaction of Singles) was extended to systems containing other main-group elements and transition metals.^{2,3} INDO/S and its variant INDO/S2⁴ reparameterized for oxygen-containing compounds are widely used to calculate spectroscopic and electron transfer properties of biological molecules and advanced materials.⁵ An accurate solvation model was proposed for INDO/S.⁶

Rapid progress in the computer power and numerical algorithms in the two last decades allows one to apply sophisticated theoretical methods like MR-(S)DCI,⁷ MS-CASPT2,^{8–10} coupled cluster (CC),^{11–14} and SAC-CI¹⁵ to molecules containing up to 50 atoms. Because the bottleneck due to molecular size is much more restrictive for calculations of excited states than for calculations of ground-state properties, many biological systems and even their reasonable models lie still far beyond the high-level approaches. Time-dependent density functional theory (TDDFT) is computationally less expensive and gives reasonable results for medium-size molecules.^{16,17} A good performance in calculation of excited state properties is demonstrated by the DFT/MRCI scheme.¹⁸ Advantages and limitations of these methods to compute spectroscopic parameters and photochemical reactions have been overviewed in several papers.^{19–22} Semiempirical schemes are computationally much less demanding than the *ab initio* and DFT methods, and often they provide rather accurate estimates for the ground- and excited-state properties of large molecules.^{23,24} Several semiempirical methods have been developed to compute excited states of organic molecules.^{25–27}

Still, INDO/S is widely used to calculate excited states of organic molecules.⁵

A benchmark set for vertical singlet and triplet excitation energies, theoretical best estimates (TBE-1),²⁸ was developed several years ago and has been intensively used to assess different computational strategies including *ab initio*,^{28,29} TDDFT,¹⁷ and semiempirical³⁰ methods. Later, this set was upgraded by replacing the data computed with the TZVP basis set by the results obtained using the augmented correlation-consistent basis set aug-cc-pVTZ.³¹ Also, CASPT2 excitation energies for several molecules were replaced by the corresponding results from CC/aug-ccpVTZ calculations. This upgrade yielded a new reference set TBE-2.³¹ For most singlet excited states, the TBE-2 oscillator strengths were computed with the CASPT2 method. It is known that CASPT2 estimates may be quite sensitive to the basis set, the active space, and the averaging procedure employed within the CASPT2 scheme.³¹ In contrast, the oscillator strengths computed with the couple cluster method appear to be quite robust.³² The TBE-2³¹ and CC3 (couple cluster triples)³² oscillator strengths are found to be in good agreement. Thus, the TBE-2 set provides excellent reference data for excited singlets (both energies and oscillator strengths) and triplets (excitation energies) that can be employed to parametrize and/or to assess semiempirical methods.

It was shown that the OM3 Hamiltonian in combination with the CISDTQ and MRCISD schemes provides good estimates for excited-state properties of organic molecules. The standard deviation (SD) of singlet and triplet excitation energies calculated for nitrogen and oxygen containing

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compounds (CHO and CHNO molecules) is 0.52 and 0.57 eV, respectively.³⁰ The commonly used OM3/MRCISD is computationally costly, which limits the size of systems that can be treated. The INDO/S CIS approach is much faster and can be applied to large molecules. However, it does not provide accurate data for CHO and CHNO species. The standard deviation for singlet excitation energies is found to be quite large, 0.88.³⁰ Furthermore, the standard INDO/S method is not applicable to triplet states because the predicted excitation energies are much too low. To solve this problem, INDO/S calculations of triplets are carried out using a modified Hamiltonian.³³ Because of that, the singlet and triplet excited states are related to different ground states and constructed using different molecular orbitals. Even so, the standard deviation for the INDO/S triplet states is still large.³⁰ The INDO/S2 variant gives better estimates for low-lying singlet states but makes the results worse for higher singlets.³⁰

In the present work, a new semiempirical scheme referred to as INDO/X (INDO for eXcited states) is developed on the basis of the INDO/S model. Like INDO/S, INDO/X employs the CIS method, which is much faster than CI schemes that include double and higher excitations.¹⁹ In contrast to INDO/S, the same semiempirical Hamiltonian is used for both singlet and triplet excitations. The TBE-2 data³¹ are employed as reference values for excitation energies and oscillator strengths. INDO/X results are shown to be significantly more accurate as compared to the INDO/S data. The standard deviation (SD) for singlet excitation energies is found to be 0.35 and 0.71 eV for INDO/X and INDO/S, respectively. The corresponding SD values for triplet energies are 0.37 and 0.80 eV. The oscillator strengths computed with INDO/X are in good agreement with the TBE-2 values. The proposed scheme is shown to be quite robust to the choice of the CIS active space. INDO/X is designed for spectroscopic applications and cannot be applied to compute excited state surfaces.

METHOD

As already noted, the CIS scheme is employed to generate excited states. This technique is based on diagonalization of a CI matrix built from singly excited configurations Φ_i^a that are obtained by replacing an occupied spin-orbital ψ_i by a virtual spin-orbital ψ_a in the ground state determinant Φ_0 .²⁰ For closed-shell systems, the CIS matrix elements for singlet and triplet excitations are defined as

$$\langle \Phi_i^a H^1 \Phi_j^b \rangle = \delta_{ij} \delta_{ab} (\epsilon_a - \epsilon_i) - (ialjb) + 2(ijlba) \quad (1a)$$

$$\langle \Phi_i^a H^3 \Phi_j^b \rangle = \delta_{ij} \delta_{ab} (\epsilon_a - \epsilon_i) - (ialjb) \quad (1b)$$

where ϵ_i and ϵ_a are the orbital energies of ψ_i and ψ_a , and $(ialjb)$ and $(ijlba)$ are the Coulomb and exchange integrals computed in the MO basis. Scaling of these integrals improves the excitation energies computed with DFT/SCI.³⁴ Our calculations showed that using different scaling factors for singlets and triplets as suggested in ref 27 may lead to physically erroneous results. In particular, the lowest triplet excited states may become higher than the corresponding excited singlets (see, for instance, the excitation energies for molecules with the C=O bond provided in Tables 3 and 4 of ref 27). To avoid such inconsistencies, the standard CIS method without any scaling factors is employed within INDO/X. Note that CIS cannot deliver accurate estimates for excited states with large contributions of double and higher excitations.¹⁹ This problem

cannot be solved by parametrization.³⁰ In many cases, however, the nature of low-lying excited states, especially in large systems, is well described in terms of single excitations.

Like other semiempirical schemes based on the NDO approximation,²³ INDO/X employs orthonormalized atomic orbitals (AOs). The Fock equation for a closed-shell system can be written as

$$FC = CE \quad (2)$$

where E contains the orbital energies and columns of the square matrix C merge coefficients of the corresponding MOs. The Fock matrix F is defined by

$$F_{\mu\mu} = U_\mu + \sum_B V_{\mu\mu,B} + \sum_\nu P_{\nu\nu} (g_{\mu\nu} - 1/2 h_{\mu\nu}) + \sum_B \sum_\lambda (\mu\mu, \lambda\lambda) \quad (3a)$$

$$F_{\mu\mu} = 1/2 P_{\mu\nu} (3h_{\mu\nu} - g_{\mu\nu}) \quad (3b)$$

$$F_{\mu\nu} = \beta_{\mu\nu} - 1/2 P_{\mu\nu} (\mu\mu, \lambda\lambda) \quad (3c)$$

The indices μ and ν denote AOs of the same center A , whereas AO λ belongs to another center B . The one-center term U_μ describes the sum of the kinetic and potential energy of an electron in AO μ . Within INDO/X, these quantities are treated as optimized parameters. The resonance integral $\beta_{\mu\lambda}$ is proportional to the overlap $S_{\mu\lambda}$:

$$\beta_{\mu\lambda} = (\beta_A + \beta_B) S_{\mu\lambda} f_{\mu\lambda} \quad (4)$$

The parameters β_A and β_B depend only on the type of the atom; three scaling factors f_{ss} , $f_{\sigma\sigma}$, and $f_{\pi\pi}$ modify $\beta_{\mu\lambda}$ for s - s , p_σ - p_σ , and p_π - p_π orbital overlaps for X–Y atomic pairs (X, Y = C, N, and O); otherwise $f_{\mu\lambda} = 1$. The overlap integrals $S_{\mu\lambda}$ are calculated using Slater-type orbitals with exponents ζ_s and ζ_p . The spectroscopic values³⁵ are used for the atomic Coulomb and exchange integrals $g_{\mu\nu}$ and $h_{\mu\nu}$. Two-center two-electron repulsion integrals $(\mu\mu, \lambda\lambda)$ are assumed to be independent of the type of AOs μ and λ , $(\mu\mu, \lambda\lambda) = g_{AB}$

$$g_{AB} = \frac{e^2}{\sqrt{R_{AB}^2 + (\rho_A + \rho_B)^2}} \quad (5)$$

where R_{AB} is the interatomic distance, and ρ_A and ρ_B are adjustable parameters. The core-electron attraction $V_{\mu\mu,B}$ is defined by $V_{\mu\mu,B} = -Z_B g_{AB}$.

For H, there are four parameters U_s , ζ_s , β , and ρ to be optimized. For each of the atoms C, N, and O, six parameters (the core energies U_s and U_p , the exponents ζ_s and ζ_p , the resonance parameter β , and the additive term ρ) are to be determined. Also, three factors f_{ss} , $f_{\sigma\sigma}$, and $f_{\pi\pi}$ in eq 4 are treated as adjustable parameters. Our test calculations showed that excited states for molecules with the N=N bond (like pyridazine and tetrazine) cannot be satisfactorily described with the defined parameter set. Because of that, three bond-specific parameters f_{ss} (N–N), $f_{\sigma\sigma}$ (N–N), and $f_{\pi\pi}$ (N–N) are introduced to describe more accurately the resonance interaction between nitrogen atoms.

The parameters for H, C, N, and O were adjusted to best reproduce the TBE-2 excitation energies and oscillator strengths. The reference data were augmented by the CC/AVTZ results³¹ for several bright excited states. A nonlinear least-squares method was employed. The following weighting

factors w were taken: $w = 1$ and $w = 0.5$ for lower and higher singlet state energies, $w = 0.33$ for triplet energies, $w = 3$ for strong oscillator strengths, $f > 0.2$, and $w = 10$ for $f \leq 0.2$. Several parametrization runs were carried out starting from different parameter values and using different training sets. During the optimization, the orbital exponents ζ_s and ζ_p of N and O converged to similar values and thus were set to be equal. The optimized parameters were tested in extensive survey calculations in order to find the most balanced description of the TBE-2 data. The values found by fitting were rounded off so that there is no effect on the accuracy of the method. The final parameters are listed in Table 1.

Table 1. INDO/X Atomic Parameters for H, C, N, and O

	H	C	N	O
U_s (eV)	−12.184	−49.338	−79.811	−106.849
U_p (eV)		−39.102	−57.460	−79.026
ζ_s (au)	1.180	2.133	2.320	2.400
ζ_p (au)		1.893	2.320	2.400
β (eV)	−11.367	−18.605	−33.709	−34.883
ρ (au)	0.570	1.454	1.611	0.858
Parameters f for N–N and X–Y Pairs (X,Y=C, N, O) ^a				
	f_{ss}	$f_{\sigma\sigma}$	$f_{\pi\pi}$	
N–N	2.008	0.717	0.880	
X–Y	1.382	0.773	0.902	

^aParameters f are used for scaling of resonance integrals, eq 4.

Computational Details. Geometries. Atomic coordinates for all molecules have been taken from the Supporting Information of ref 28. The molecular structures were optimized at the MP2/6-31G* level and used to compute the TBE-2 benchmarks.³² INDO/X calculations were also performed for B3LYP/6-31G* optimized structures computed with the program Gaussian 09.³⁶

CIS Calculation. Singlet and triplet excitations for each molecule were computed using the same CIS scheme. The numbers of occupied and unoccupied MOs included into the active space are specified in Table 2. As shown below, INDO/X excitation energies are not very sensitive to the choice of the active space. All calculations were carried out with the program SIBIQ.³⁷ We note that SIBIQ and Gaussian 09 provides identical results for INDO/S calculation of singlet excited states.

RESULTS AND DISCUSSION

Vertical Singlet Excitations. Vertical excitation energies and oscillator strengths computed with INDO/X for 28 standard molecules are listed in Table 2 along with the corresponding benchmarks.³² The mean absolute deviation (MAD) and the standard deviation (SD) for INDO/X are found to be 0.26 and 0.35 eV, which are significantly smaller than the corresponding INDO/S values, MAD = 0.64 eV and SD = 0.80 eV. Figure 1 shows the INDO/X and INDO/S singlet excitation energies with respect to the reference data. The INDO/X energies are close to the ideal correlation line with unit slope, whereas the INDO/S values show a larger scatter.

In general, the oscillator strengths computed with the INDO/X scheme agree well with the reference values (see Table 2). We note that the performance of the INDO/X scheme remains almost unchanged when all possible singly

excited configurations are included in CI; the MAD and SD values are found to be 0.27 and 0.36 eV. The effect of the active space on the INDO/X results will be considered in more detail later in this paper. Now we briefly discuss spectroscopic parameters predicted by INDO/X for different classes of molecules.

Ethene, Butadiene, Hexatriene, and Octatetraene. The INDO/X method provides accurate values for the excitation energy and oscillator strength of the $\pi\pi^*$ state in ethene. In linear polyenes, the $\pi\pi^*$ state 2^1A_g has a large contribution from double and higher excitations and cannot be properly described within CIS. As seen from Table 2, INDO/X overestimates considerably the energy of the 2^1A_g states in butadiene, hexatriene, and octatetraene. In contrast, the energy of the bright state 1^1B_u in these molecules is in excellent agreement with the TBE-2 data. The oscillator strength for this transition is predicted too strong.

Cyclopropene, Cyclopentadiene, Norbornadiene, Benzene, and Naphthalene. Reasonable estimates are obtained for the $n\pi^*$ and $\pi\pi^*$ energies in cyclopropene. These two states are almost degenerate in TBE-2 (CC/AVTZ calculation) but split by 0.30 eV in TBE-1 (CASPT2/TZVP data, see ref 31 for details). INDO/X predict the $n\pi^*$ state to be 0.40 eV lower than the $\pi\pi^*$ state. In cyclopentadiene, the results for the B_2 and $3A_1$ states are in excellent agreement with the reference data. INDO/X overestimates by 0.9 eV the energy of the $2A_1$ state, which has a considerable contribution, $\sim 20\%$,³² from double and higher excitations. The first excited state energy in norbornadiene is predicted to be 0.7 eV higher than the TBE-2 value. The excitation energy and the oscillator strength of three other states in this molecule are well reproduced. The INDO/X results for benzene and naphthalene are in good agreement with the reference data. In particular, the spectroscopic parameters for all bright states (E_{1u} in benzene and $1B_{2u}$, $2B_{3u}$ and $2B_{2u}$ in naphthalene) are very close to the reference values. However, large errors, 0.7–1.4 eV, are found for higher $\pi\pi^*$ dark states (E_{2g} in benzene and $2B_{1g}$ and $3A_{1g}$ in naphthalene).

Furan, Pyrrole, Imidazole, Pyridine, Pyrazine, Pyrimidine, Pyridazine, s-Triazine, and s-Tetrazine. The first excitation energy in heterocycles furan and pyrrole are underestimated by ~ 0.6 eV, whereas the higher states are accurately described. The INDO/X results for imidazole are close to the TBE-2 values. Overall, a good agreement is found for four heterocycles pyridine, pyrazine, pyrimidine, and pyridazine. INDO/X describes properly azobenzenes with the N=N bond, pyridazine and tetrazine. The first $n\pi^*$ transition energy decreases by 0.60 eV when passing from pyrimidine to pyridazine, which is in perfect agreement with the TBE-2 estimate of 0.58 eV. Also in s-tetrazine, the low-energy state $1B_{3u}$, 2.46 eV, is well reproduced by INDO/X, 2.39 eV. Three lowest excitations corresponding to the $n\pi^*$ transitions in s-triazine are nearly degenerate. INDO/X describes accurately the energy of the $1^1A_2''$ and E'' but overestimates the energy of the $1^1A_1''$ state by 0.3 eV. The first $\pi\pi^*$ transition is predicted too high by 0.7 eV. The excitation energies of other $\pi\pi^*$ states and the E'' $n\pi^*$ state are close to the benchmark values.

Formaldehyde, Acetone, p-Benzoquinone, Formamide, Acetamide, and Propanamide. According to TBE-2,³² the lowest $n\pi^*$ excited state in formaldehyde is found at 3.88 eV, whereas the $\sigma\pi^*$ and $\pi\pi^*$ states lie much higher, at 9.17 and 10.44 eV. As seen from Table 2, the INDO/X method describes properly these states in formaldehyde as well as in

Table 2. Vertical Singlet Excitation Energy ΔE (eV) and Oscillator Strength f

molecule	state	TBE-2 ^a		INDO/X		
		ΔE	f	ΔE	f	CI ^b
ethene	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	7.80	0.356	7.77	0.381	4-4
E-butadiene	1 ¹ B _u ($\pi \rightarrow \pi^*$)	6.18	0.635	6.09	0.905	6-6
	2 ¹ A _g ($\pi \rightarrow \pi^*$) ^c	6.55		7.85		
all-E-hexatriene	1 ¹ B _u ($\pi \rightarrow \pi^*$)	5.10	0.981	5.14	1.387	8-8
	2 ¹ A _g ($\pi \rightarrow \pi^*$) ^c	5.09		6.89		
all-E-octatetraene	1 ¹ B _u ($\pi \rightarrow \pi^*$)	4.66	1.307	4.54	1.885	10-10
	2 ¹ A _g ($\pi \rightarrow \pi^*$) ^c	4.47		6.19		
cyclopropene	1 ¹ B ₁ ($\sigma \rightarrow \pi^*$)	6.67	0.009	6.02	0.002	5-5
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	6.68	0.241	6.41	0.146	
cyclopentadiene	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	5.55	0.117	5.27	0.145	7-7
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.28	0.000	7.12	0.027	
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$) ^d	8.14	0.642	8.00	0.671	
norbornadiene	1 ¹ A ₂ ($\pi \rightarrow \pi^*$)	5.37		6.08		8-8
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	6.21	0.131	6.34	0.088	
	2 ¹ A ₂ ($\pi \rightarrow \pi^*$) ^d	7.22		6.64		
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$) ^d	7.49	0.342	7.26	0.370	
benzene	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	5.08		5.48		8-8
	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	6.54		5.98		
	1 ¹ E _{1u} ($\pi \rightarrow \pi^*$)	7.13	0.787	7.18	0.773	
	1 ¹ E _{2g} ($\pi \rightarrow \pi^*$)	8.15		8.86		
naphthalene	1 ¹ B _{3u} ($\pi \rightarrow \pi^*$)	4.25	0.001	4.63	0.001	12-12
	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	4.82	0.099	4.79	0.124	
	1 ¹ B _{1g} ($\pi \rightarrow \pi^*$)	5.75		6.32		
	2 ¹ A _{1g} ($\pi \rightarrow \pi^*$)	5.90		6.48		
	2 ¹ B _{3u} ($\pi \rightarrow \pi^*$)	6.11	1.514	6.24	1.672	
	2 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	6.36	0.354	6.45	0.600	
	2 ¹ B _{1g} ($\pi \rightarrow \pi^*$)	6.46		7.16		
	3 ¹ A _{1g} ($\pi \rightarrow \pi^*$) ^c	6.49		7.88		
furan	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	6.32	0.239	5.71	0.150	7-7
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.57	0.006	6.47	0.009	
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	8.13	0.546	7.57	0.518	
pyrrole	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.37	0.002	5.88	0.134	7-7
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	6.57	0.167	6.30	0.003	
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	7.91	0.396	7.28	0.555	
imidazole	2 ¹ A' ($\pi \rightarrow \pi^*$)	6.25	0.207	6.08	0.162	8-8
	1 ¹ A'' ($n \rightarrow \pi^*$)	6.65	0.009	6.60	0.013	
	3 ¹ A' ($\pi \rightarrow \pi^*$)	6.73	0.052	6.63	0.013	
	2 ¹ A'' ($n \rightarrow \pi^*$) ^d	7.57	0.006	7.42	0.005	
pyridine	1 ¹ B ₁ ($n \rightarrow \pi^*$)	4.59	0.007	4.78	0.004	8-8
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	4.85	0.025	5.66	0.034	
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	5.11		5.41		
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.26	0.004	6.24	0.055	
	3 ¹ A ₁ ($\pi \rightarrow \pi^*$)	7.18	0.848	7.36	0.563	
pyrazine	2 ¹ B ₂ ($\pi \rightarrow \pi^*$)	7.27	0.267	7.47	0.649	
	1 ¹ B _{3u} ($n \rightarrow \pi^*$)	4.13	0.009	3.95	0.006	8-8
	1 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	4.97	0.127	5.65	0.100	
	1 ¹ A _u ($n \rightarrow \pi^*$)	4.98		4.76		
	1 ¹ B _{2g} ($n \rightarrow \pi^*$)	5.65		5.98		
	1 ¹ B _{1g} ($n \rightarrow \pi^*$)	6.69		7.75		
	1 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	6.83	0.176	6.25	0.148	
	2 ¹ B _{2u} ($\pi \rightarrow \pi^*$)	7.81	0.598	7.92	0.483	
pyrimidine	2 ¹ B _{1u} ($\pi \rightarrow \pi^*$)	7.86	0.620	7.70	0.263	
	1 ¹ B ₁ ($n \rightarrow \pi^*$)	4.43	0.010	4.36	0.007	8-8
	1 ¹ A ₂ ($n \rightarrow \pi^*$)	4.85		4.73		
	1 ¹ B ₂ ($\pi \rightarrow \pi^*$)	5.34	0.054	5.94	0.044	
	2 ¹ A ₁ ($\pi \rightarrow \pi^*$)	6.82	0.189	6.57	0.076	
pyridazine	3 ¹ A ₁ ($\pi \rightarrow \pi^*$) ^d	7.53	0.530	7.69	0.452	
	2 ¹ B ₂ ($\pi \rightarrow \pi^*$) ^d	7.82	0.742	7.55	0.434	
	1 ¹ B ₁ ($n \rightarrow \pi^*$)	3.85	0.008	3.75	0.007	8-8

Table 2. continued

molecule	state	TBE-2 ^a		INDO/X		CI ^b
		ΔE	f	ΔE	f	
triazine	1 ¹ A ₂ (n→ π^*)	4.44		4.53		
	2 ¹ A ₁ (π → π^*)	5.20	0.041	5.77	0.030	
	2 ¹ A ₂ (n→ π^*)	5.66		5.39		
	2 ¹ B ₁ (π → π^*) ^d	6.33	0.006	6.15	0.002	
	1 ¹ B ₂ (π → π^*) ^d	6.68	0.051	6.40	0.020	
	2 ¹ B ₂ (π → π^*) ^d	7.33	0.655	7.29	0.496	
	3 ¹ A ₁ (π → π^*) ^d	7.54	0.676	7.38	0.503	
	1 ¹ A ₂ ' (n→ π^*)	4.71	0.024	4.71	0.017	8-8
	1 ¹ A ₁ ' (n→ π^*)	4.70		5.02		
	1 ¹ E'' (n→ π^*)	4.75		4.76		
	1 ¹ A ₂ ' (π → π^*)	5.71		6.39		
	2 ¹ A ₁ ' (π → π^*) ^d	7.18		7.17		
	1 ¹ E' (π → π^*) ^d	7.84	0.566	7.67	0.397	
	2 ¹ E'' (n→ π^*) ^d	7.78		7.79		
s-tetrazine	1 ¹ B _{3u} (n→ π^*)	2.46	0.010	2.42	0.009	8-8
	1 ¹ A _u (n→ π^*)	3.78		4.03		
	1 ¹ B _{1g} (n→ π^*)	4.87		5.15		
	1 ¹ B _{2u} (π → π^*)	5.08	0.123	5.75	0.115	
	1 ¹ B _{2g} (n→ π^*)	5.28		5.56		
	2 ¹ A _u (n→ π^*)	5.39		4.98		
	1 ¹ B _{3g} (n,n→ π^* , π^*) ^b	5.76				
formaldehyde	1 ¹ A ₂ (n→ π^*)	3.88		3.85		4-4
	1 ¹ B ₁ (σ → π^*)	9.04	0.012	9.34	0.007	
	2 ¹ A ₁ (π → π^*)	9.29	0.242	9.32	0.067	
acetone	1 ¹ A ₂ (n→ π^*)	4.38		4.54		6-6
	1 ¹ B ₁ (σ → π^*)	9.04	0.009	8.83	0.010	
	2 ¹ A ₁ (π → π^*)	8.90	0.357	8.85	0.056	
p-benzoquinone	1 ¹ B _{1g} (n→ π^*)	2.74		2.91		8-8
	1 ¹ A _u (n→ π^*)	2.86		3.43		
	1 ¹ B _{3g} (π → π^*)	4.44		5.03		
	1 ¹ B _{1u} (π → π^*)	5.47	0.731	5.94	0.963	
	2 ¹ B _{3u} (n→ π^*)	5.55	0.000	5.92	0.008	
	2 ¹ B _{3g} (π → π^*)	7.16		7.47		
	2 ¹ B _{1u} (π → π^*) ^d	7.62	0.353	8.10	0.667	
	1 ¹ A'' (n→ π^*)	5.55	0.000	5.22	0.000	5-5
formamide	2 ¹ A' (π → π^*)	7.75	0.331	7.16	0.168	
	1 ¹ A'' (n→ π^*)	5.62	0.002	5.53	0.002	6-6
acetamide	2 ¹ A' (π → π^*)	7.14	0.299	7.26	0.193	
	1 ¹ A'' (n→ π^*)	5.65	0.000	5.45	0.002	7-7
propanamide	2 ¹ A' (π → π^*)	7.09	0.284	7.24	0.160	
	1 ¹ A'' (n→ π^*)	5.65	0.000	5.45	0.002	7-7
cytosine	2 ¹ A' (π → π^*)	4.66	0.053	4.94	0.109	10-10
	1 ¹ A'' (n→ π^*)	4.87	0.003	4.87	0.000	
	2 ¹ A'' (n→ π^*)	5.26	0.000	5.71	0.001	
	3 ¹ A' (π → π^*)	5.62	0.238	5.95	0.109	
	4 ¹ A' (π → π^*) ^d	6.29	0.546	6.29	0.676	
thymine	5 ¹ A' (π → π^*) ^d	6.62	0.406	6.76	0.143	
	1 ¹ A'' (n→ π^*)	4.82	0.000	4.99	0.001	10-10
	2 ¹ A' (π → π^*)	5.20	0.278	5.26	0.329	
	2 ¹ A'' (n→ π^*)	6.16	0.000	6.15	0.000	
	3 ¹ A' (π → π^*)	6.27	0.067	6.37	0.139	
uracil	4 ¹ A' (π → π^*)	6.53	0.283	6.70	0.202	
	1 ¹ A'' (n→ π^*)	5.00	0.000	5.09	0.001	10-10
	2 ¹ A' (π → π^*)	5.25	0.276	5.35	0.290	
	2 ¹ A'' (n→ π^*)	6.10	0.000	6.14	0.000	
	3 ¹ A' (π → π^*)	6.26	0.045	6.49	0.087	
adenine	4 ¹ A' (π → π^*)	6.70	0.259	6.71	0.206	
	3 ¹ A'' (n→ π^*)	6.56	0.000	7.10	0.002	
	1 ¹ A'' (n→ π^*)	5.12	0.002	4.95	0.000	12-12
	2 ¹ A' (π → π^*)	5.25	0.398	5.05	0.309	

Table 2. continued

molecule	state	TBE-2 ^a		INDO/X		CI ^b
		ΔE	f	ΔE	f	
	3 ¹ A' ($\pi \rightarrow \pi^*$)	5.25	0.015	5.14	0.079	
	2 ¹ A'' ($n \rightarrow \pi^*$)	5.75	0.007	5.35	0.002	
	4 ¹ A' ($\pi \rightarrow \pi^*$) ^c	6.25	0.510	6.28	0.397	
count ^f				116		
mean				0.06		
abs. mean				0.26		
SD				0.35		
max. (−) dev				−0.65		
max. (+) dev				1.02		

^aThe TBE-2 reference data are taken from ref 31. ^bThe active space (the number of HOMOs and LUMOs) used to generate excited configurations.

^cThe state has a large contribution of double excitations and cannot be described within CIS; it is excluded from statistics. ^dCC/AVTZ results from ref 31. ^eCASPT2/AVTZ results from ref 31. ^fNumber of excited states included in statistics.

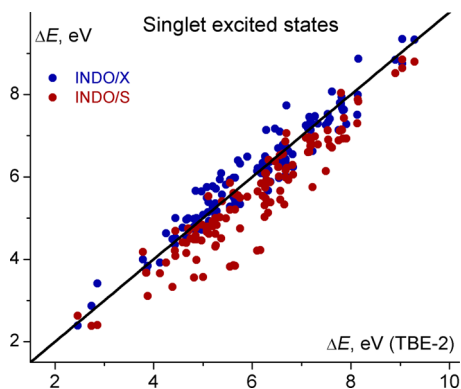


Figure 1. Correlation plot for the singlet excited states computed using the INDO/X and INDO/S methods with respect to the TBE-2 reference energies.

acetone. In *p*-benzoquinone, the energy of the first excited state, 2.91 eV, estimated with INDO/X is close to the TBE-2 value of 2.74 eV. The energy of higher $n\pi^*$ and $\pi\pi^*$ states is, however, overestimated by ~ 0.5 eV. The results for $n\pi^*$ and $\pi\pi^*$ excited states in formamide, acetamide, and propanamide are found to be in good agreement with the reference data.

Cytosine, Thymine, Uracil, and Adenine. Overall, the excited state properties of nucleobases are well reproduced by INDO/X. In cytosine, the energy of lowest $\pi\pi^*$ and $n\pi^*$ states, 4.94 and 4.87 eV, are close to the reference values of 4.66 and 4.87 eV, although the order of these states is reversed. The energy and oscillator strength for the bright states 2 ¹A', 3 ¹A', and 4 ¹A' are well reproduced. Thymine (5-methyluracil) and uracil have similar excitation spectra. For most transitions, the INDO/X energies deviate from the TBE-2 values by less than 0.20 eV; also, the oscillator strengths are found to be in good agreement. The results for adenine agree perfectly with the reference data. INDO/X predicts correctly the order of all excited states including three lowest states, one $n\pi^*$ and two $\pi\pi^*$, which are close in energy.

It is known that vertical excitation energies extracted from experimental spectra (especially for large chromophores) may be uncertain for several reasons.²⁸ In particular, when vibronic effects are not accounted for, the computed spectra of organic molecules are shifted by 0.1–0.3 eV to higher energy.³⁸ Nevertheless, a comparison of calculated and experimental excitation energies provides useful information about the performance of the computational scheme. Figure 2 compares TBE-2 and INDO/X singlet excitation energies with exper-

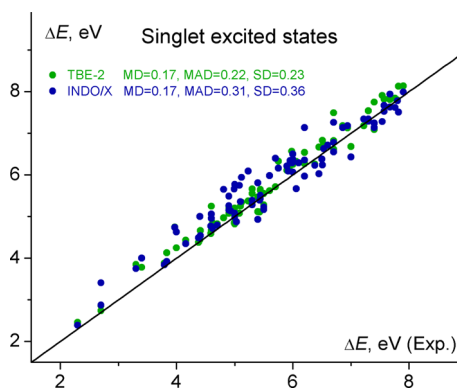


Figure 2. Correlation plot for the INDO/X and TBE-2 singlet excited states with respect to experimental data.

imental data for 84 transition taken from the Supporting Information of ref 31. As seen, both TBE-2 and INDO/X overestimate the transition energies by 0.17 eV. The standard deviation of the TBE-2 and INDO/X excitation energies from the experimental data are 0.23 and 0.36 eV.

Vertical Triplet Excitations. Table 3 compares 63 vertical triplet excitation energies computed using INDO/X with the TBE-2 reference data.^{30,31} A correlation plot for the triplet excited states is shown in Figure 3. Statistical evaluation of the data suggests that INDO/X underestimates the triplet excitation energies by 0.15 eV. The largest deviation of -0.92 eV is found for the ¹³A₁ state in furan. The MAD and SD values are 0.35 and 0.37 eV, respectively. Comparison of these data with the MAD and SD for INDO/S, 0.64 and 0.80 eV, shows that also for triplet states INDO/X is significantly more superior than its predecessor. The energy of the lowest triplet states (one state per molecule) is reproduced by INDO/X more accurately. In this case (20 comparisons), the MAD and SD values are 0.23 and 0.27 eV.

Some Practical Points on INDO/X Calculations. *CIS Active Space.* First we consider how INDO/X results depend on the CIS scheme employed in the calculation. To this end, singlet excitations in uracil were computed using different numbers of excited configurations. In the valence orbital approximation, uracil has 21 occupied and 15 unoccupied molecular orbitals (MOs). Ten highest occupied MOs (HOMO, HOMO−1, ..., HOMO−9) are π , π , n , n , π , σ , σ , π , σ , and π MO; they are followed by 11 occupied σ MOs. Five lowest unoccupied MOs (LUMO, LUMO+1, ..., LUMO+4) are π , π , σ , σ , and π MO followed by σ orbitals. The smallest

Table 3. Vertical Excitation Energies for Triplet States (eV)

molecule	state	TBE-2 ^a	INDO/X	molecule	state	TBE-2 ^a	INDO/X
ethene	1 ³ B _u ($\pi \rightarrow \pi^*$)	4.50	4.24		1 ³ B ₁ ($n \rightarrow \pi^*$)	4.25	4.25
E-butadiene	1 ³ B _u ($\pi \rightarrow \pi^*$)	3.20	3.09		1 ³ B ₂ ($\pi \rightarrow \pi^*$)	4.64	4.89
	1 ³ A _g ($\pi \rightarrow \pi^*$)	5.08	4.64		2 ³ A ₁ ($\pi \rightarrow \pi^*$)	4.91	5.05
all-E-hexatriene	1 ³ B _u ($\pi \rightarrow \pi^*$)	2.40	2.49		1 ³ A ₂ ($n \rightarrow \pi^*$)	5.28	5.26
	1 ³ A _g ($\pi \rightarrow \pi^*$)	4.15	3.84		2 ³ B ₂ ($\pi \rightarrow \pi^*$)	6.08	5.93
all-E-octatetraene	1 ³ B _u ($\pi \rightarrow \pi^*$)	2.20	2.14	s-tetrazine	1 ³ B _{3u} ($n \rightarrow \pi^*$)	1.87	1.84
	1 ³ A _g ($\pi \rightarrow \pi^*$)	3.55	3.25		1 ³ A _u ($n \rightarrow \pi^*$)	3.49	3.66
cyclopropene	1 ³ B ₁ ($\sigma \rightarrow \pi^*$)	4.28	3.89		1 ³ B _{1g} ($n \rightarrow \pi^*$)	4.18	4.21
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	6.40	5.75		1 ³ B _{1u} ($\pi \rightarrow \pi^*$)	4.36	3.59
cyclopentadiene	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	3.26	2.99		1 ³ B _{2u} ($\pi \rightarrow \pi^*$)	4.39	4.37
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	5.09	4.43		2 ³ A _u ($n \rightarrow \pi^*$)	4.96	4.71
norbornadiene	1 ³ A ₂ ($\pi \rightarrow \pi^*$)	3.68	3.79		1 ³ B _{2g} ($n \rightarrow \pi^*$)	4.89	4.97
	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	4.16	3.78		2 ³ B _{1u} ($\pi \rightarrow \pi^*$)	5.32	5.60
benzene	1 ³ B _{1u} ($\pi \rightarrow \pi^*$)	4.15	3.80	formaldehyde	1 ³ A ₂ ($n \rightarrow \pi^*$)	3.50	3.43
	1 ³ E _{1u} ($\pi \rightarrow \pi^*$)	4.86	4.87		1 ³ A ₁ ($\pi \rightarrow \pi^*$)	5.87	6.61
	1 ³ B _{2u} ($\pi \rightarrow \pi^*$)	5.88	5.48	acetone	1 ³ A ₂ ($n \rightarrow \pi^*$)	4.05	4.13
	1 ³ E _{2g} ($\pi \rightarrow \pi^*$)	7.51	7.02		1 ³ A ₁ ($\pi \rightarrow \pi^*$)	6.07	6.78
naphthalene	1 ³ B _{2u} ($\pi \rightarrow \pi^*$)	3.09	2.93	p-benzoquinone	1 ³ B _{1g} ($n \rightarrow \pi^*$)	2.51	2.64
	1 ³ B _{3u} ($\pi \rightarrow \pi^*$)	4.09	4.19		1 ³ A _u ($n \rightarrow \pi^*$)	2.61	3.11
	1 ³ B _{1g} ($\pi \rightarrow \pi^*$)	4.42	4.16		1 ³ B _{1u} ($\pi \rightarrow \pi^*$)	3.02	3.29
	2 ³ B _{2u} ($\pi \rightarrow \pi^*$)	4.56	4.53		1 ³ B _{3g} ($\pi \rightarrow \pi^*$)	3.37	3.57
	2 ³ B _{3u} ($\pi \rightarrow \pi^*$)	4.92	4.63	formamide	1 ³ A'' ($n \rightarrow \pi^*$)	5.28	4.89
	1 ³ A _g ($\pi \rightarrow \pi^*$)	5.42	5.14		1 ³ A' ($\pi \rightarrow \pi^*$)	5.69	5.23
	2 ³ A _g ($\pi \rightarrow \pi^*$)	6.17	6.37	acetamide	1 ³ A'' ($n \rightarrow \pi^*$)	5.35	5.22
	2 ³ B _{1g} ($\pi \rightarrow \pi^*$)	6.12	6.56		1 ³ A' ($\pi \rightarrow \pi^*$)	5.71	5.25
	3 ³ B _{1g} ($\pi \rightarrow \pi^*$)	6.67	7.11	propanamide	1 ³ A'' ($n \rightarrow \pi^*$)	5.38	5.14
	3 ³ A _g ($\pi \rightarrow \pi^*$)	6.65	6.92		1 ³ A' ($\pi \rightarrow \pi^*$)	6.08	5.29
furan	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	4.11	3.44	count ^b			63
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	5.43	4.57	mean			−0.17
pyrrole	1 ³ B ₂ ($\pi \rightarrow \pi^*$)	4.44	3.72	abs mean			0.33
	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	5.42	4.63	SD			0.38
imidazole	1 ³ A' ($\pi \rightarrow \pi^*$)	4.65	3.89	max. (−) dev			−0.92
	2 ³ A' ($\pi \rightarrow \pi^*$)	5.64	4.98	max. (+) dev			0.74
	1 ³ A'' ($n \rightarrow \pi^*$)	6.25	5.98	^a The TBE-2 reference data are taken from ref 31. ^b Total number of states included in statistics.			
	3 ³ A' ($\pi \rightarrow \pi^*$)	6.38	5.46				
pyridine	1 ³ A ₁ ($\pi \rightarrow \pi^*$)	4.06	3.93				

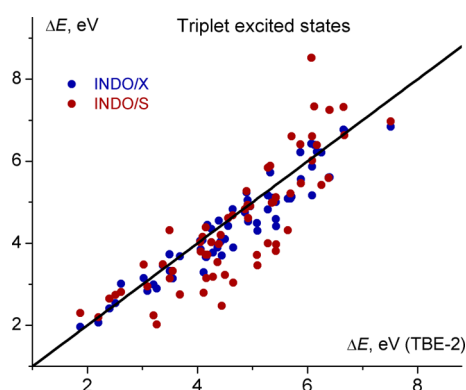


Figure 3. Correlation plot for the triplet excited states from INDO/X and INDO/S with respect to the TBE-2 reference energies.

reasonable active space 4-4 contains 16 configuration functions generated by using 4 HOMOs (π, π, n, n) and 4 LUMOS ($\pi^*, \pi^*, \sigma^*, \sigma^*$). More extended CIS schemes 8-8 and 10-10 include 64 and 100 excited configurations. All $\pi\pi^*$ excitations are accounted in the last scheme. Finally, the active space 21-15 corresponds to full CIS.

As expected, the estimated transition energies become smaller with the increasing number of configurations taken into account. The mean deviation reduces from 0.62 to 0.09 eV. The active space 4-4 is too small to properly describe vertical excitation energies in uracil; the calculated energies are significantly overestimated (the mean deviation is 0.62 eV); however, the oscillator strengths are correctly reproduced (see Table 4). The 8-8 and 10-10 CIS calculations give similar results. The energy of the $n\pi^*$ states remains unchanged, whereas the $\pi\pi^*$ energies decrease by 0.05 eV. Extension of CIS from 100 to 315 configurations does not significantly alter the results; MAD and SD reduce by 0.06 eV. Note that calculations with full CIS do not necessarily improve the results as found for uracil. If computed energies are smaller than the reference values, a further extension of the active space will lead to larger deviations. For instance, INDO/X calculation with CIS 12-12 underestimates singlet excitation energies in adenine, MD = −0.17 eV and SD = 0.25 eV. If all excited configurations are accounted for, CIS 25-20, the SD value becomes larger, 0.30 eV. Conversely, a decrease of the active space improves the results, the use of CIS 8-8 reduces the SD value to 0.20 eV. Overall, the performance of the INDO/X scheme does not substantially depend on the CIS active space. A thumb rule to

Table 4. Singlet Excitation Energies ΔE (eV) and Oscillator Strengths f Computed Using Different Numbers of Excited Configurations

state	TBE-2		4-4 = 16		8-8 = 64		10-10 = 100		21-15 = 315	
	ΔE	f	ΔE	f	ΔE	f	ΔE	f	ΔE	f
1 $^1A''$ ($n \rightarrow \pi^*$)	5.00	0.000	5.74	0.002	5.10	0.001	5.09	0.001	5.06	0.001
2 $^1A'$ ($\pi \rightarrow \pi^*$)	5.25	0.276	5.58	0.344	5.42	0.317	5.35	0.290	5.25	0.286
2 $^1A''$ ($n \rightarrow \pi^*$)	6.10	0.000	6.88	0.000	6.15	0.000	6.14	0.000	6.11	0.000
3 $^1A'$ ($\pi \rightarrow \pi^*$)	6.26	0.045	6.73	0.106	6.55	0.107	6.49	0.087	6.33	0.059
4 $^1A'$ ($\pi \rightarrow \pi^*$)	6.70	0.259	6.92	0.269	6.76	0.226	6.71	0.206	6.65	0.207
3 $^1A''$ ($n \rightarrow \pi^*$)	6.56	0.000	7.75	0.000	7.10	0.002	7.10	0.002	7.01	0.000
mean dev			0.62		0.20		0.17		0.09	
mean abs dev			0.62		0.20		0.17		0.11	
SD			0.77		0.29		0.27		0.21	

choose the active space is that N HOMOs and N LUMOs can be used in CIS for a molecule containing N heavy (non-hydrogen) atoms. For large systems ($N > 20$), the number of configurations may be reduced.

Input Geometry. Vertical excitation energies depend on the ground state molecular geometries used in the calculation. As already noted, the structures from ref 28 optimized at the MP2/6-31G* level were employed for the INDO/X parametrization. For large molecules, however, more efficient methods, e.g. B3LYP/6-31G*, are usually applied to optimize molecular geometry. We recalculated the excited states using the B3LYP geometries instead of the MP2 data. Figure 4 and

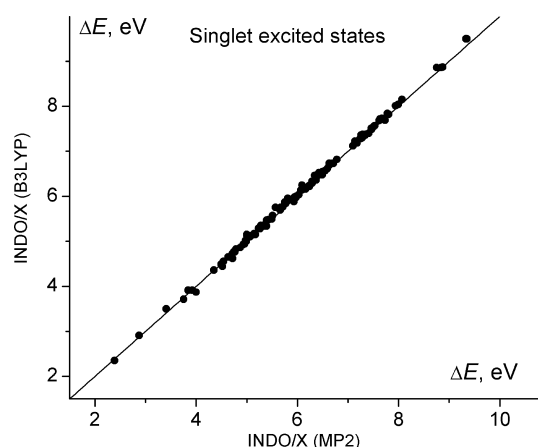
**Figure 4.** Correlation plot for the INDO/X singlet excitation energies obtained for the MP2/6-31G* and B3LYP optimized structures.

Table 5 show that the INDO/X results do not practically change when the MP2 geometries are replaced by the corresponding B3LYP data. A correlation coefficient between the vertical singlet excitation energies is found to be 0.9992 (Figure 4). The estimated energies differ by more than 0.1 eV for three molecules (norbornadiene, s-tetrazine, and p-

Table 5. Statistical Evaluation of the INDO/X Excitation Energies Computed Using MP2/6-31G* and B3LYP/6-31G* Optimized Geometries

geometry	singlet (116 entries)		triplet (63 entries)	
	MP2	B3LYP	MP2	B3LYP
MD, eV	0.06	0.09	−0.17	−0.18
MAD, eV	0.26	0.27	0.33	0.35
SD, eV	0.35	0.36	0.38	0.39

benzoquinone). The maximum deviation of 0.18 eV is found for the 2^1A_u ($n \rightarrow \pi^*$) state in s-tetrazine. Thus, the differences in MP2 and B3LYP optimized geometries are not significant for the spectroscopic parameters computed with INDO/X.

CONCLUSIONS

A new semiempirical method INDO/X has been developed to calculate vertical singlet and triplet excited states. Unlike INDO/S where two different Hamiltonians are employed for singlet and triplet excitations, both types of excited states are calculated within the same INDO/X scheme. The method has been parametrized using the TBE-2 benchmark excitation energies and oscillator strengths as reference data. The performance of INDO/X is significantly superior as compared to INDO/S. The mean absolute deviations of the INDO/X excitation energies relative to the theoretical best estimates is 0.26 eV for singlet states and 0.33 eV for triplet states. The corresponding values for INDO/S are 0.56 and 0.64 eV. Also, the oscillator strengths estimated with INDO/X are in good agreement with the reference data. An appealing feature of the developed scheme is its “black box” behavior: the results are not very sensitive to the employed active space. The method has been designed for spectroscopic applications and can be applied, for instance, to assign absorption bands of large organic and biological molecules or to explore the effects of structural fluctuations on the excited-state properties. However, INDO/X cannot be used to compute excited state surfaces and to study photochemical reactions.

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Notes

The authors declare no competing financial interest.

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