

Ground-state reduced density matrices, effective Hamiltonians, and optical properties of Schiff bases of retinal

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Abstract

The optical properties of Schiff bases of retinal are determined from their *ab initio* Hartree–Fock ground-state reduced single-electron density matrices. This is achieved by extracting the effective Hamiltonian of the π electrons in the systems from their ground-state reduced density matrices. The linear and non-linear optical properties of these molecules are thus calculated by employing the time-dependent Hartree–Fock (TDHF) method. Structure dependence of the optical properties is examined by comparing the values of linear and non-linear polarizabilities of *all-trans* and various *cis* isomers. The effect of protonation is studied as well. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Schiff bases of retinal are important molecules in biological processes. For instance, the 11-*cis* retinal in rhodopsin converts to its 11-*trans* isomer after absorbing a photon, and this process triggers a nerve impulse sent to the brain which leads to vision. The isomerization of *all-trans* conformation to the 13-*cis* in bacteriorhodopsin triggers a series of protein structural changes that convert the solar energy into biological energy. Picosecond transient UV/VIS spectroscopy has been used to postulate the structures of intermediates after absorption of lights [1] and the mechanism of the photoisomerization [2]. Fourier transform infrared (FTIR) and time-resolved Raman spectroscopy have been used to elucidate information about the intermediates [3–6]. The stability of various isomers has been investigated theoretically. Molecular dynamics (MD) simulations suggested that the product of the photoisomerization is 13-*cis* retinal [7] or 13,14-*dicis* [8]. Morokuma et al.

carried a hybrid density functional B3LYP calculation and concluded that for the protonated Schiff bases the *all-trans* conformation is the most stable, and while for the non-protonated systems the 6-*s-cis* conformation is the ground-state configuration [9]. The protonated 9-, 11- and 13-*cis* conformations are 1.6, 5.2, and 2.1 kcal/mol above the *all-trans* conformation respectively. The wavelength of absorption maximum λ_{\max} depends the conformation, and this may be utilized to determine the structures of photoisomerization intermediates. Theoretical calculations have been carried out to investigate linear and non-linear optical spectra of retinal and its derivatives [10–19].

More than three decades ago Hohenberg and Kohn proved that the three-dimensional distribution of electron density of a system has one-to-one correspondence to its potential, and thus to its electronic Hamiltonian [20]. The Hamiltonian of a system determines the properties of its ground state as well as its excited states. Therefore, in principle the ground-

state three-dimensional electron density distribution determines both the ground state and the excited states. The density functional theorem of Hohenberg and Kohn has been applied to the local density approximation (LDA) theory which calculates the ground state properties of an electronic system. Attempts have been made to calculate the properties of excited states, e.g. the optical spectra, from the ground state. The memory-function formalism may evaluate linear optical spectrum from the ground-state wave function [21]. Mukamel et al. started from the ground-state reduced density matrix, and calculated the optical responses of conjugated polymers using a set of sum rules [22]. The electronic Hamiltonian is required explicitly in these calculations.

Chen and Mukamel have proved that the one-electron part of Hamiltonian may be determined from the ground-state reduced single-electron density matrix under certain conditions [23]. Subsequently they devised a constrained density matrix variation (CDMV) approach at the Hartree–Fock level to determine the effective Hamiltonian for π electrons in polyacetylene [24]. The CDMV approach has been generalized and applied recently to polymethineimine (PMI), polyazine (PAZ) and polyazoethene (PAE) to determine the effective Hamiltonian for the π electrons in these systems [25]. The reduced density matrix was extracted from the result of ab initio Hartree–Fock molecular orbital calculation. After the effective Hamiltonian is obtained, the excited states may be calculated readily. This thus provides a way to determine the properties of excited states from the ground-state properties. Since the input is merely the ab initio Hartree–Fock ground-state reduced density matrix, which is relatively easy to calculate, it becomes realistic to calculate accurately the properties of excited states of large molecular systems like the Schiff bases of retinal.

In this paper we use the CDMV approach to determine the effective Hamiltonians for the π electrons of various Schiff bases of retinal. These Hamiltonians are subsequently employed to calculate the linear and non-linear optical spectra of these systems. In Section 2 we describe the CDMV approach briefly and use it to calculate the effective Hamiltonians for the π electrons of several Schiff bases of retinal. The ab initio Hartree–Fock ground-state reduced single-electron density matrices are used as

inputs. In Section 3 we use the TDHF method to calculate their optical properties, i.e. the optical absorption, the second harmonic generation (SHG) and the third harmonic generation (THG) spectra, and investigate their structural relationships and the effects of protonation. In Section 4, we compare our results with those of the existing methods.

2. Effective Hamiltonian

The structures of the Schiff bases of retinal that we have chosen to study are shown in Fig. 1 and Fig. 2. Two of them are non-protonated systems, and they are *all-trans* and 6-*cis* Schiff bases of retinal, which are denoted respectively as **1a** and **5a**. The rest of the

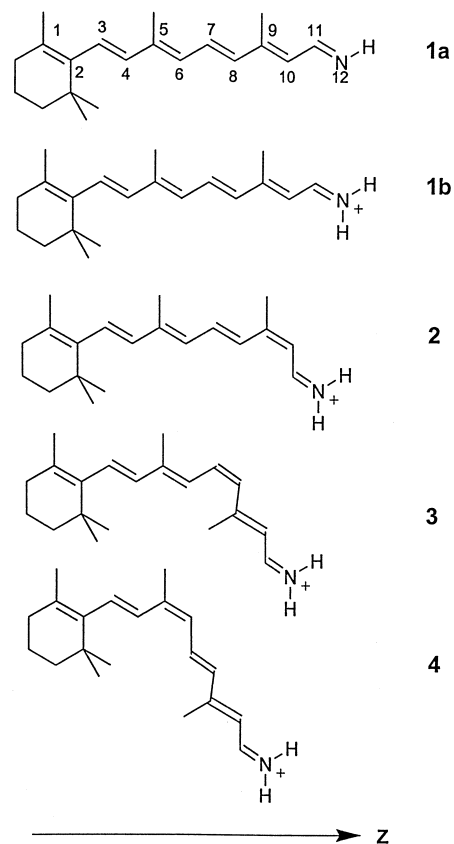


Fig. 1. Structures of non-protonated and protonated Schiff bases of retinal **1a**, **1b**, **2**, **3** and **4**. The arrow at the bottom indicates the *z*-direction, i.e. the polarization direction of the external field $E(t)$.

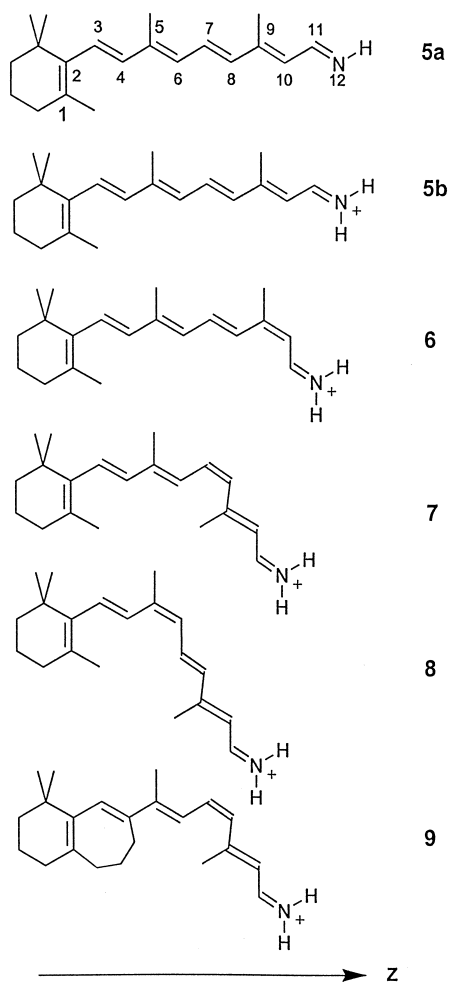


Fig. 2. Structures of non-protonated and protonated Schiff bases of retinal **5a**, **5b**, **6**, **7**, **8** and **9**. The arrow at the bottom indicates the z -direction, i.e. the polarization direction of the external field $E(t)$.

molecules are protonated Schiff bases of retinal. **1b**, **2**, **3** and **4** are *all-trans*, *13-cis*, *11-cis*, and *9-cis* protonated Schiff bases of retinal, respectively. **5b**, **6**, **7** and **8** are *6-cis*, *6,13-cis*, *6,11-cis* and *6,9-cis* isomers respectively. **9**, *6,9-cis-8,18-ethanoretinol*, may be constructed by attaching an ethylene group to **3** through its C-8 and C-18 positions. Since the π electrons are accountable for most of the optical response in conjugated systems, we concentrate only on the π electrons in the Schiff bases of retinal. We label numerically the atoms which have π atomic orbitals for each molecule. In Figs. 1 and 2 we show

only the numerical labels for **1a** and **5a**. The labels for other molecules are assigned similarly but not shown in Figs. 1 and 2.

The effective Hamiltonian H for the π electrons can be written as follows:

$$H = H_e + H_{ee},$$

$$H_e = \sum_{m\sigma} t_{mn} a_{m\sigma}^+ a_{n\sigma},$$

$$H_{ee} = \sum_{mn\sigma\sigma'} V_{mn} a_{m\sigma}^+ a_{m\sigma} a_{n\sigma'}^+ a_{n\sigma'},$$

where $a_{m\sigma}^+$ ($a_{n\sigma}$) is the electron creation (annihilation) operator at a localized orbital m (n) with spin σ . t_{mn} is the one-electron integral or hopping matrix element between the localized orbital m and n . V_{mn} is the electron–electron Coulomb interaction between two electrons separately at the local orbitals m and n . Therefore, H_e is the one-electron part of the Hamiltonian which describes the dynamics of a single π electron in the absence of other π electrons. H_{ee} is the two-electron part of the Hamiltonian which represents the effective Coulomb interaction among electrons. Zero differential overlap (ZDO) approximation [26] is employed here. Nuclear charge for every site is +1.

Effective Coulomb interaction V_{mn} is usually unknown. However, its functional form may be derived from many-body theory or determined empirically. It has been demonstrated that the Onhn formula [27] describes well the effective interaction among the π electrons in conjugated polymers. The interaction may be expressed as follows:

$$V_{mn} = \frac{U_{AB}}{\sqrt{1 + (r_{mn}/a_0)^2}} \quad (1)$$

where r_{mn} is the distance between the orbitals m and n . $U_{AB} \equiv U_{AB}^0/\epsilon$ determines the overall amplitude of interaction between two electrons on A and B with A (B) representing the type of atom at m (n). U_{AB}^0 is the unscreened repulsion. ϵ is the static dielectric constant representing the screening by σ electrons, and is set to 1.5 in our calculations. In Refs. [24] and [25], it has been determined that U_{CC}^0 , U_{NN}^0 , and U_{NC}^0 are 9.93, 7.08 and 8.39 eV respectively. a_0 is of the same magnitude as the bond length, and is set to be 1.0 Å.

Table 1
The bond lengths of *all-trans* non-protonated **1a** and protonated **1b** Schiff bases of retinal

	1a	1b
$r_{1,2}$	1.326	1.331
$r_{2,3}$	1.502	1.494
$r_{3,4}$	1.326	1.336
$r_{4,5}$	1.492	1.471
$r_{5,6}$	1.331	1.358
$r_{6,7}$	1.479	1.435
$r_{7,8}$	1.325	1.367
$r_{8,9}$	1.492	1.425
$r_{9,10}$	1.329	1.403
$r_{10,11}$	1.486	1.385
$r_{11,12}$	1.284	1.345

All data are in units of Å.

Denote the ab initio Hartree–Fock ground-state reduced density matrix ρ_0 . Consider the effective Hamiltonian H and its Hartree–Fock ground-state reduced single-electron density matrix ρ , we construct a quantity S which measures the difference between ρ and ρ_0 [24]:

$$S = \sum_{i,j} W_{ij} [\rho(i,j) - \rho_0(i,j)]^2 + \mathcal{F}, \quad (2)$$

where W_{ij} is positive weighting coefficient, and $\rho(i,j)$ and $\rho_0(i,j)$ are respectively the matrix elements of ρ and ρ_0 with the row index i and the column index j ; \mathcal{F} represents the variational constraint which sets constraints on the relative energies of atomic orbitals (t_{ii}) and relation among the hopping matrix elements (t_{ij} , $i \neq j$) [24,25]. In this work we set $W_{ij} = 1.0$ for all (i,j) , and $W_1 = W_2 = 0.1$. Like that in Ref. [25], an annealing Monte Carlo procedure is employed to find a set of $\{t_{ij}\}$ that minimizes \mathcal{F} . An artificial simulation temperature T is introduced, and five different values are used for

the temperature T : $T = 1.0$, 1.0×10^{-1} , 1.0×10^{-2} , 1.0×10^{-3} , and 1.0×10^{-4} . At each temperature T M different sets of $\{t_{ij}\}$ are tried. $M = 200$, 500, 2500, 500, and 400 for the above five temperatures respectively.

We may determine the effective Hamiltonians of Schiff bases of retinal. Employing the Gaussian 94 program, we obtain the Hartree–Fock ground states for molecules **1a**, **1b**, **2**, **3**, **4**, **5a**, **5b**, **6**, **7**, **8**, and **9**. Geometry optimization is carried for each molecule. The minimal basis set STO-3G is used in the calculation. Our ab initio calculations indicate that for protonated Schiff bases of retinal **1b** is the most stable isomer, and this is consistent with Morokuma's calculation [9]. Using these calculations we evaluate the ground-state reduced single-electron density matrices ρ_0^{ab} of these molecules. The ρ_0^{ab} is in the nature atomic orbital (NAO) basis set [28]. The π orbitals in polyacetylene have zero overlap with other occupied orbitals, and therefore the π electrons may be separated explicitly from the rest of electrons. However, this is not the case for the retinal and its derivatives. The π orbitals in these systems do have overlaps with other occupied atomic orbitals of different types. The total electron occupation number in the localized π orbitals for a Schiff base of retinal is not equal to N , where $N = 12$ is the number of $2p\pi$ orbitals in the system. Therefore, the resulting ab initio Hartree–Fock ground-state density matrices ρ_0^{ab} need to be renormalized as follows:

$$\rho_0(i,j) = N \rho_0^{ab}(i,j) / \sum_i^N \rho_0^{ab}(i,i). \quad (3)$$

The renormalized reduced density matrix ρ_0 is employed as the input to calculate the effective Hamiltonian for each molecule via the above density ma-

Table 2
Reduced density matrix elements $\rho(i,i)$ and $\rho(i,i+1)$ for **1a** and **1b**

i	1	2	3	4	5	6	7	8	9	10	11	12
$\rho(i,i)$	0.979	1.025	0.994	1.012	0.968	1.027	0.989	1.008	0.952	1.030	0.945	1.070
$\rho(i,i+1)$	0.922	0.277	0.915	0.292	0.896	0.307	0.909	0.291	0.903	0.283	0.953	
$\rho(i,i)$	0.905	1.057	0.871	1.081	0.783	1.118	0.764	1.132	0.681	1.197	0.736	1.678
$\rho(i,i+1)$	0.902	0.311	0.872	0.368	0.793	0.469	0.741	0.540	0.617	0.657	0.612	

The upper two data lines are for **1a**; the lower two lines are for **1b**.

Table 3
Optical properties of Schiff bases of retinal

	$\alpha_z(0)^a$	$\beta_{zz}(0)^a$	$\gamma_{zz}(0)^a$	BOA	$E_g(\text{th})^a$	$E_g(\text{exp})^b$
1a	49.5	4.59	22.8	0.6215	3.51	
1b	86.5	72.0	70.3	0.4819	2.67	
2	81.4	-26.9	33.9	0.4861	2.71	2.18 ^d
3	60.8	-22.9	16.4	0.4767	2.67	
4	82.7	-18.2	26.7	0.4058	2.33	
5a	43.8	1.26	15.7	0.6219	3.53	3.40 ^c
5b	76.8	43.8	43.1	0.4849	2.77	2.79 ^c
6	62.8	-8.6	14.5	0.4918	2.75	
7	47.2	-16.2	10.1	0.4835	2.76	
8	70.9	-28.6	27.0	0.4871	2.71	
9	55.0	-22.0	14.9	0.4991	2.52	

^a Our calculation results.

^b Experimental results.

^c Ref. [10].

^d Ref. [2]. $\alpha_z(0)$, $\beta_{zz}(0)$ and $\gamma_{zz}(0)$ are in units of 10^{-24} , 10^{-30} and 10^{-35} esu respectively. E_g is in units of eV.

trix variation approach. We concentrate our discussion on **1a** and **1b**. The bond lengths of **1a** and **1b** are indicated in Table 1. The average bond length alternations (BLAs) of **1a** and **1b** are 0.170 and 0.085 Å, respectively. Note that the average BLA of **1b** is much less than that of **1a**. Their ground-state reduced density matrix elements $\rho_0^{ab}(i, i)$ and $\rho_0^{ab}(i, i + 1)$ with $i = 1$ to 12 for the π electrons are listed in Table 2. The bond order alternation (BOA) of each molecule is listed in Table 3. The reduced density matrix of **1a** is similar to that of a polyacetylene oligomer with 12 carbon atoms, and its average BOA is 0.62. The reduced density matrix of **1b** is quite different. The positive charge at NH_2^+ induces large change of the chemical structure. The density of electrons is not uniform among carbon atoms on the backbone. The bond orders for the bonds close to NH_2^+ are approximately equal, which leads a much less average BOA (0.48). This correlates with the geometric structure near NH_2^+ . For instance, the bond length between the sites 9 and 10 is approximately the same as that between the sites 10 and 11 for **1b**. The effective Hamiltonians for **1a** and **1b** are tabulated in Table 4. The parameters in the effective Hamiltonians correlate well with the structures of **1a** and **1b**. **1a** has larger BLA than **1b** (see Table 1), and thus has larger t_{ij} difference between the double and single bonds. For instance, double bond lengths of **1a** and **1b** between the sites 3 and 4 are 1.326 and 1.336 Å, respectively; and the corresponding values

of $t_{4,3}$ are respectively -2.51 and -2.28 eV. The single bond lengths between the sites 4 and 5 are 1.492 and 1.471 Å respectively for **1a** and **1b** with the two corresponding values of $t_{5,4}$ being -1.77 and -1.85 eV.

Table 4
The values of t_{ij} for **1a** and **1b**^a

	1a	1b
$t_{2,1}$	-2.51	-2.20
$t_{2,2}$	-0.15	-0.22
$t_{3,2}$	-1.71	-1.59
$t_{3,3}$	-0.56	-0.52
$t_{4,3}$	-2.51	-2.28
$t_{4,4}$	-0.56	-0.65
$t_{5,4}$	-1.77	-1.85
$t_{5,5}$	-0.21	-0.07
$t_{6,5}$	-2.59	-2.55
$t_{6,6}$	-0.43	-0.62
$t_{7,6}$	-1.90	-2.19
$t_{7,7}$	-0.37	-0.37
$t_{8,7}$	-2.70	-2.59
$t_{8,8}$	-0.34	-0.68
$t_{9,8}$	-1.88	-2.26
$t_{9,9}$	0.04	-0.03
$t_{10,9}$	-2.81	-2.34
$t_{10,10}$	-0.21	-0.85
$t_{11,10}$	-2.02	-2.37
$t_{11,11}$	-0.56	-0.68
$t_{12,11}$	-3.38	-2.61
$t_{12,12}$	-2.00	-3.94

^a All data are in units of eV.

3. Optical properties

To investigate the structure dependence of the optical properties, we calculate the absorption, SHG and THG spectra of the Schiff bases of retinal in Figs. 1 and 2. The external electric field $E(t)$ is polarized along the z axis, as shown in Figs. 1 and 2. In Fig. 3, we plot the absorption spectra of **1a**, **1b**, **2**, **3** and **4**. Like that of polyacetylene [29], the oscillator strength of each molecule concentrates on the first absorption peak. Only **4** has a modest second absorption peak at the frequency $\omega = 3.62$ eV. The absorption spectra of **2** and **3** have not only similar structures but also similar energetics. For instance, their optical gaps are both about 2.7 eV, and near 4.9 eV both have another absorption peak. **1a** has the largest optical gap among the five isomers, and **1b** has the smallest gap. In Table 3 we list the values of the optical gaps (E_g) for all molecules in Figs. 1 and 2. Among **5a**, **5b**, **6**, **7** and **8**, the optical gap of **5a** is the largest. Thus the non-protonated Schiff bases of retinal have much larger optical gaps than their protonated counterparts, which is consistent with the experimental results [10]. The experimental values of

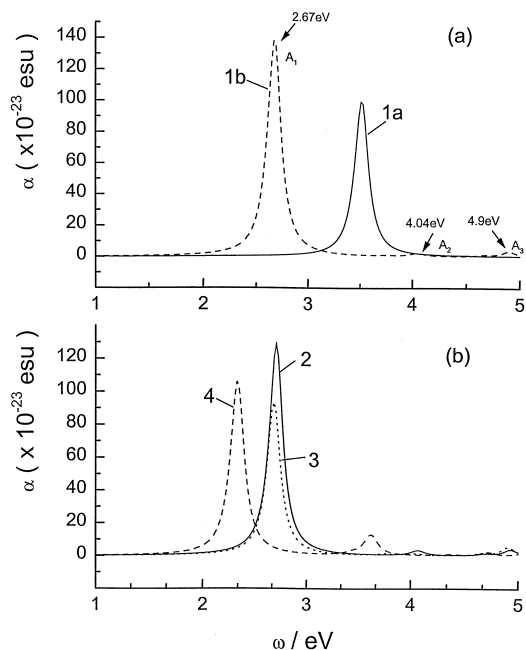


Fig. 3. Absorption spectra for (a) **1a** and **1b**; and (b) **2**, **3** and **4**.

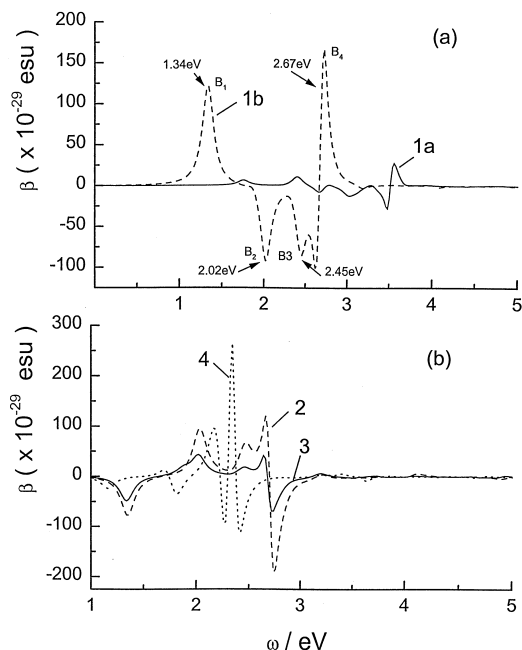


Fig. 4. Second harmonic generation spectra for (a) **1a** and **1b**; and (b) **2**, **3** and **4**.

E_g for **2**, **5a** and **5b** are respectively 2.18, 3.40 and 2.79 eV, while the calculated values are 2.71, 3.53 and 2.77 eV respectively.

Since all these Schiff bases of retinal are asymmetric, they have non-zero SHG signals. We plot the SHG spectra of **1a**, **1b**, **2**, **3** and **4** in Fig. 4. **1a** has the smallest amplitude, because among the five molecules **1a** has a chemical structure closest to that of polyacetylene. Polyacetylene has zero second order induced dipole moment since it is centro-symmetric. **2** and **3** have similar SHG structure; see Fig. 4b. In Fig. 4a, the energies of the two positive peaks B_1 and B_4 for **1b** are respectively 2.34 and 2.67 eV, and thus correspond to A_1 in Fig. 3a. B_1 is the SHG peak of A_1 . The other peaks B_2 and B_3 are respectively at $\omega = 2.02$ and 2.45 eV. Thus they correspond with the peaks A_2 (4.04 eV) and A_3 (4.90 eV). Obviously, B_2 and B_3 are more prominent than A_2 and A_3 in their respective spectra, and thus can be more easily measured and characterized. Similarly, the SHG spectra of **1a**, **2**, **3** and **4** provide richer information of the systems than their linear absorption counterparts. The calculated THG spectra

of **1a**, **1b**, **2**, **3** and **4** are plotted in Fig. 5. Clearly, the THG spectra provide much more information about the systems than the absorption spectra. For instance, C_1 and C_8 correspond to A_1 , while other peaks of **1b**'s THG spectrum reveal the properties of its other electronic excited states. In this paragraph we select **1b** and focus more of the description on its spectra. Moreover, we indicate in Figs. 3a, 4a and 5a the energies of various peaks for **1b** to clarify the relationship among its absorption, SHG and THG spectra.

We calculate the static polarizability $\alpha_z(0)$, first hyperpolarizability $\beta_{zz}(0)$ and second hyperpolarizability $\gamma_{zzz}(0)$ of all the Schiff bases of retinal depicted in Figs. 1 and 2. The results are listed in Table 3, and are consistent with the calculated data for the donor–acceptor substituted polyene oligomer of the same length [30]. Brédas et al. calculated the static first hyperpolarizability of a structure very similar to **5b**, except that an H at NH_2^+ is replaced by Bu. They employed the INDO/SOS method and summed over 40 states. Their calculated value (2.1×10^{-28} esu) is somewhat larger than ours (4.3×10^{-29} esu).

4. Discussion and conclusion

The effective valence shell Hamiltonian (H^v) theory has been employed to determine the effective Hamiltonians for the π electrons in a series of protonated Schiff bases of retinal [13–15]. The resulting values for t_{ij} ($i \neq j$) and U are larger than our calculated data. It is known that the TDHF method leads usually to larger optical gaps of π conjugated systems. Since we adjusted our TDHF optical gaps to the experimental values in Refs. [24] and [25], it is expected that our values for t_{ij} and U may be slightly smaller.

Both ab initio and semiempirical methods have been used to calculate the excited states of the 6-*cis* retinal [11,10]. Merchán and González-Luque used the CASSCF and CASPT2 methods to calculate the ground and excited states of the 6-*cis* retinal. They found that the optical gap was 6.82 eV (CASSCF) or 5.78 eV (CASPT2). Full geometry optimization was carried out at the Hartree–Fock (HF) level using the 3-21G basis set in their calculation [11]. Brédas et al. calculated the optical gap and the static first hyperpolarizability of 6-*cis* retinal using the semiempirical intermediate neglect of differential overlap/configuration interaction/sum-over-states (INDO/CI/SOS) method. Their calculated values of the optical gap and the first hyperpolarizability are 3.50 eV and 41.5×10^{-30} esu respectively. The experimental value for the optical gap of 6-*cis*-retinal is 3.26 eV [10], which is of the same magnitude of our calculated value for **5a**.

The level ordering of the low-lying excited states of retinals has been investigated extensively [31,32]. It is believed that the lowest excited states of the Schiff bases are 1Ag or 1Ag-like states, while the protonated Schiff bases have the lowest-lying Bu-like states. Our results are consistent with this conclusion [31,32]. For instance, let us examine the absorption and SHG spectra of **1a** and **1b**. The lowest Bu-like excited states of **1a** and **1b** lie at 3.51 and 2.67 (A_1) eV above their ground states, respectively (Fig. 3a). No other dipole-allowed transition has been observed between 1 and 5 eV for **1a**. Since **1b** is of low symmetry, it has two additional weak absorption peaks at 4.04 (A_2) and 4.90 (A_3) eV; see Fig. 3a. In Fig. 4a, the lowest energy peak (B_1) corresponds to A_1 in Fig. 3a while B_2 , B_3 and B_4 correspond to

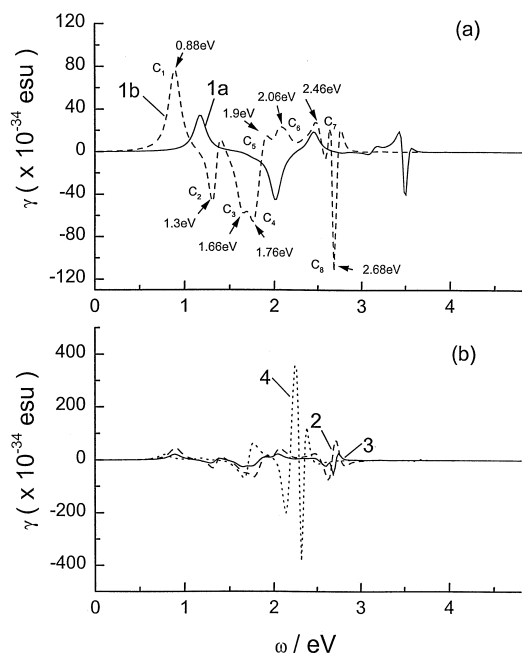


Fig. 5. Third harmonic generation spectra for (a) **1a** and **1b**; and (b) **2**, **3** and **4**.

A_2 , A_3 and A_1 respectively. Therefore, we conclude that the lowest-lying excited state of **1b** is a Bu-like state. However, **1a** has a SHG resonance at 2.5 eV (see Fig. 4a) which is absent in its absorption spectrum (Fig. 3a). This resonance is thus induced by a Ag-like excited state which is below the Bu state (which is 3.51 eV above the ground state).

To summarize, starting from their *ab initio* Hartree–Fock ground state reduced single-electron density matrices, we determine the effective Hamiltonians of π electrons in several *all-trans* and *cis* Schiff bases of retinal. Moreover we calculate the linear and non-linear spectra of these isomers. This work demonstrates a procedure to calculate the excited-state properties from the ground-state density matrix. Since the effective Hamiltonian is only for the reduced system, for instance, π electrons in conjugated molecules, this procedure provides a practical way to calculate the excited-state properties of very large electronic systems.

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