HeI Photoelectron and Ab Initio Study of Retinal Derivatives

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The HeI photoelectron spectra of all-*trans*-retinal, 13-*cis*-retinal and 9-*cis*-retinal have been observed in the gas phase by using an infrared heating device, which was developed in this laboratory. The first four ionization energies (I_{obs}) of all-*trans*-retinal have been determined to be 7.55, 8.40, 9.21, and 10.03 eV, and the ionization energies for the other two derivatives were also equal to them within the experimental error. Ab initio calculations were performed to study the optimized structures of neutral and cationic ground states of retinals and to elucidate the valence electronic structures associated with the observed ionization energies. The structural change from the neutral to the cation was considered, and the bond lengths and dihedral angles between the planes of the β-ionone ring and the polyene chain in each of retinals have been determined.

Vitamin A (all-*trans*-retinol) and its derivatives, such as retinoic acids and retinals, are sensitive to air, light, heat, etc., because of their polyene skeleton, octatetraene. They are essential compounds for the maintenance of health in an organism. Their structures are very similar and only differ at the polar end. However, their physiological functions are markedly different. Vitamin A, apart from being a metabolic precursor of 11-*cis*-retinal, which is involved in the mechanism of vision in animals, is essential for reproduction, while retinoic acid is active in the promotion of growth.[1] It is well-known that two distinct light-transducing proteins, rhodopsin and bacteriorhodopsin, consist of an isomer of retinal as a chromophore. Very recently, the light-induced structural changes of 11-*cis*-retinal to all-*trans*-retinal within rhodopsin have been reported in detail.[2] Some groups have also simultaneously reported on the detailed molecular mechanisms of proton translocation associated with a light-induced structural change of all-*trans*-retinal to 13-*cis*-retinal within bacteriorhodopsin.[3–5]

We have recently presented the HeI photoelectron and an ab initio study for vitamin A and the all-*trans*- and 13-*cis*-retinoic acids.[6] From our ab initio calculations for vitamin A and the retinoic acids, the dihedral angles between the $C_5{=}C_6$ in cyclohexene ring and $C_7{=}C_8$ of polyene chain were found to be $\sim 60°$ in the neutral ground states and $\sim 20°$ in the cationic ground states. By ionization, the double bonds become longer by 0.075 Å for $C_9{=}C_{10}$ at the maximum, while the single bonds become shorter by 0.078 Å for C_6–C_7 at the maximum. HeI (58.4 nm) photoelectron spectroscopy is a powerful method to study the molecular valence electronic structure.[7–9] It is attractive to study their electronic structures and the geometrical changes of retinal derivatives related to isomerization in rhodopsin and bacteriorhodopsin by the HeI photoelectron spectroscopy and ab initio calculations.

Experimental

Measurements of the photoelectron spectra were carried out in the gas phase by using a HeI (58.4 nm) photoelectron spectrometer with an infrared heating system. The apparatus used has been described in detail elsewhere.[6–8] Briefly, a hemi-spherical electrostatic analyzer (10 cm in diameter) was used in the photoelectron spectrometer, and the heating system consisted of an infrared heating furnace and a temperature controller. A Pyrex glass tube containing a solid sample was placed in a Swagelok stainless-steel tube fitting connected with a copper pipe. The tube fitting and the copper pipe were placed in a quartz tube that was fitted to a furnace, and the sample was heated by infrared radiation. The other end of the copper pipe was inserted into an ionization chamber, but not touching, so that the ionization chamber was kept at room temperature during infrared heating of the sample.

In this work, the temperature of the copper pipe was maintained at about 99, 117, and 103 °C in measurements of the all-*trans*, 13-*cis* and 9-*cis*-retinals, respectively. Calibrations of the ionization energy scale were carried out with the first ionization energies of Ar and H_2O. The energy resolution in this work was ΔE (fwhm) $= 62$ meV for the Ar $(3p)^{-1}$ peak at an analyzer voltage of ± 1.0 V at room temperature.

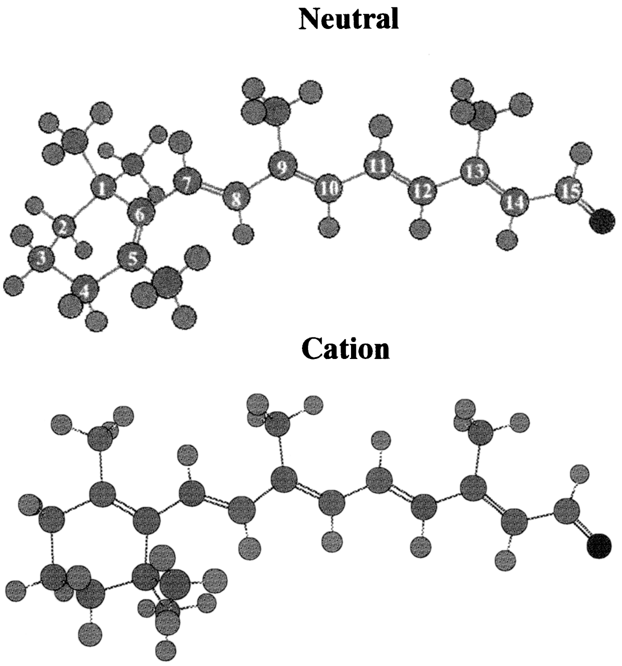
The compounds studied in the present work were all-*trans*-retinal, 13-*cis*-retinal, and 9-*cis*-retinal, which were purchased from SIGMA and Aldrich Chem. Co., respectively, and used without further purification.

Ab Initio Calculations

Ab initio self-consistent-field molecular orbital (SCF MO) calculations were carried out with the Gaussian 98W program,[10] by use of the 6-311G basis set. This program was interfaced with the software of CS Chem3D and GaussView under Windows.[11] Full geometry optimization was performed by the energy gradient method. Therefore, ab initio RHF/6-311G and UHF/6-311G calculations were carried out to determine the optimized geometries of both the neutral and cation ground states of the retinal derivatives studied in this work, respectively. The MO energies of the retinal derivatives were calculated by using their optimized geometries. Theoretical ionization energies $I_{\text{calc}}(i)$ based on Koopmans' theorem were compared with the observed vertical ionization energies, $I_{\text{obs}}(i)$. The optimized geometries and MO drawings were obtained with CS Chem3D and GaussView.

Results and Discussion

Calculated Geometrical Parameters. Ab initio calculations using various molecular conformations were performed to investigate the most stable geometries for the neutral and cationic retinals and retinoic acids. Figure 1 shows the optimized geometries of the neutral and cationic ground states of all-*trans*-retinal, in which there is a chain of five $\pi_{C=C}$ conjugated double bonds; namely, four in the polyene chain and one in the cyclohexene ring (β-ionone ring). The neutral state and the cationic state of the all-*trans*-retinal have a 6-*s-cis* and a 6-*s-trans* configuration, respectively, with respect to the dihedral angle between the planes of the ring ($C_5{=}C_6{-}C_7$) and the chain ($C_6{-}C_7{=}C_8$). The prefix s before cis or trans indicates that a single bond (C_6–C_7) is referred to. The optimized lengths of the bond lengths of all-*trans*-retinal are listed together with the experimental data and those of all-*trans*-retinoic acid in Table 1. In the present work, the most stable conformations of the neutral and cationic all-*trans* retinoic acids were recalculated and were different from what were reported previously,[6] that is, the bond lengths are almost the same, but the dihedral angles are different. The total energies are more stable by 185 cm^{-1} for neutral and 430 cm^{-1} for cation, respectively, than those in a previous study. The calculated results of the geometrical structures of vitamin A derivatives including 11-*cis*-retinals will be given in elsewhere.


Neutral

Cation

Fig. 1. Optimized geometries of the neutral and the cationic ground state of all-*trans*-retinal, showing the numbering system. The conformations of the neutral and the cation consist of 6-*s-cis* and 6-*s-trans* configurations, respectively. The dihedral angles between the planes of the ring ($C_5{=}C_6{-}C_7$) and the chain ($C_6{-}C_7{=}C_8$) are 57.5° and −172.5° from exact *s-cis*, for the neutral and cation, respectively.

From Table 1, our optimized parameters of all-*trans*-retinal calculated with 6-311G basis set are in excellent agreement with the experimental ones[12] with a deviation of less than 0.013 Å. Our calculated geometry for the neutral ground state is in good agreement with the geometry obtained by Car-Parrinello ab initio molecular dynamics.[13] The geometry parameters of the neutral form of all-*trans*-retinal are exactly equal to those of the all-*trans*-retinoic acid (Table 1). This is also the case for the cation forms (Table 1). The parameters of 13-*cis*- and 9-*cis*-retinals studied in this work are also very similar to those of all-*trans*-retinal.

The cationic ground states of the retinals are induced upon ionization from HOMO (the highest occupied molecular orbital). By ionization of all-*trans*-retinal (all-*trans*-retinoic acid), the $C_9{=}C_{10}$ and $C_7{=}C_8$ double bonds become longer by 0.073(0.077) and 0.065(0.064) Å, while the C_6–C_7 and C_8–C_9 single bonds become shorter by 0.078(0.079) and 0.068(0.072) Å, respectively. Structural changes caused by ionization are quite similar to those in carbon skeleton displacements of all-*trans*-retinal and all-*trans*-retinoic acid. It is noticeable, however, that though geometrical changes of the CHO group in the retinal are considerably large, those of the COOH group in all-*trans*-retinoic acid are very small.

From the present ab initio calculations of the neutral ground states, the dihedral angles between $C_5{=}C_6$ and $C_7{=}C_8$ have been found to be +57.5°, +57.5°, +57.9°, and −60.4° in all-*trans*-, 13-*cis*-, 9-*cis*-retinals, and all-*trans*-retinoic acid, respectively. The plus and minus mean that the $C_5{=}C_6$ segment as the β-ionone ring plane rotates anticlockwise and clockwise with respect to the $C_7{=}C_8$ as polyene chain plane, respectively. In conclusion, the neutral states of retinals have the 6-*s-cis* configuration, as shown in Fig. 1, while the rotational angle (−60.4°) of the β-ionone ring in the retinoic acid is different from those (+57.5°) of other retinals. Hamanaka et al.[12] reported that the dihedral angle between the planes of the ring and the chain is 62° in the crystal structure of all-*trans*-retinal. On the other hand, the dihedral angles in the optimized geometries of the cations have been found to be −172.5°, −172.5°, −172.5° and −172.4° in all-*trans*-, 13-*cis*-, and 9-*cis*-retinals, and all-*trans*-retinoic acid, respectively. Conformations of all the cations have the 6-*s-trans* configuration as shown in Fig. 1. These conformations may be mainly induced by a strong steric hindrance between the hydrogen of C_8–H and a hydrogen of a methyl group attached to C_5, because the single bond of C_6–C_7 is shorten by ionization. Therefore, the $\pi_{C=C}$ orbitals of the polyene chain in the neutral ground states of retinals are not considered to be completely conjugated with the $\pi_{C=C}$ of the cyclohexene ring, while the cations may be almost planar molecules and the $\pi_{C=C}$ orbitals are conjugated effectively. The change in the dihedral angle from neutral to the cation is 130.0° in all-*trans*-retinal, being equal to that in 13-*cis*- and to that in 9-*cis*-retinal, while the change in the all-*trans*-retinoic acid is 112.0°.

Photoelectron Spectra. The HeI photoelectron spectra observed for (a) all-*trans*-retinal, (b) 13-*cis*-retinal, and (c) 9-*cis*-retinal are shown together with (d) all-*trans*-retinoic acid[6] in Fig. 2. Our HeI photoelectron spectrum of all-*trans*-retinal agrees well with the spectrum measured in the gaseous phase

Table 1. The Optimized Geometrical Parameters of All-*trans*-Retinal and All-*trans*-Retinoic Acid at the Neutral Ground State as Well as the Cationic Ground State, Obtained by RHF and UHF/6-311G Calculations

Values in parentheses are displacements in bond lengths between the cation and the neutral.

Bond length	All-*trans*-retinal[a)]		All-*trans*-retinoic acid[a)]	
	Neutral[b)]	Cation	Neutral	Cation
C1–C2	1.543	1.549 (0.006)	1.543	1.549 (0.006)
C2–C3	1.523	1.520 (−0.003)	1.523	1.520 (−0.003)
C3–C4	1.524	1.520 (−0.004)	1.523	1.520 (−0.003)
C4–C5	1.517	1.501 (−0.016)	1.515	1.501 (−0.014)
C5=C6	1.338 [1.329]	1.406 (0.068)	1.337	1.404 (0.067)
C1–C6	1.546	1.548 (0.002)	1.545	1.549 (0.004)
C6–C7	1.487 [1.483]	1.409 (−0.078)	1.488	1.409 (−0.079)
C7=C8	1.330 [1.317]	1.395 (0.065)	1.331	1.395 (0.064)
C8–C9	1.472 [1.469]	1.404 (−0.068)	1.473	1.401 (−0.072)
C9=C10	1.342 [1.346]	1.415 (0.073)	1.342	1.419 (0.077)
C10–C11	1.455 [1.444]	1.402 (−0.053)	1.455	1.401 (−0.054)
C11=C12	1.336 [1.339]	1.402 (0.066)	1.336	1.401 (0.065)
C12–C13	1.468 [1.455]	1.420 (−0.048)	1.469	1.427 (−0.042)
C13=C14	1.343 [1.346]	1.404 (0.061)	1.343	1.392 (0.049)
C14–C15	1.457 [1.458]	1.421 (−0.036)	1.455	1.451 (−0.004)
C15=O	1.220 [1.200]	1.271 (0.051)	1.218	1.220 (0.002)
C15–OH			1.355	1.351 (−0.004)

a) Dihedral angle of C5=C6–C7=C8 in the neutral and cation ground states are +57.5° and −172.5° for all-*trans*-retinal, and −60.4° and −172.4° for all-*trans*-retinoic acid, respectively.

b) The values in brackets are the experimental data taken from Ref. 12.

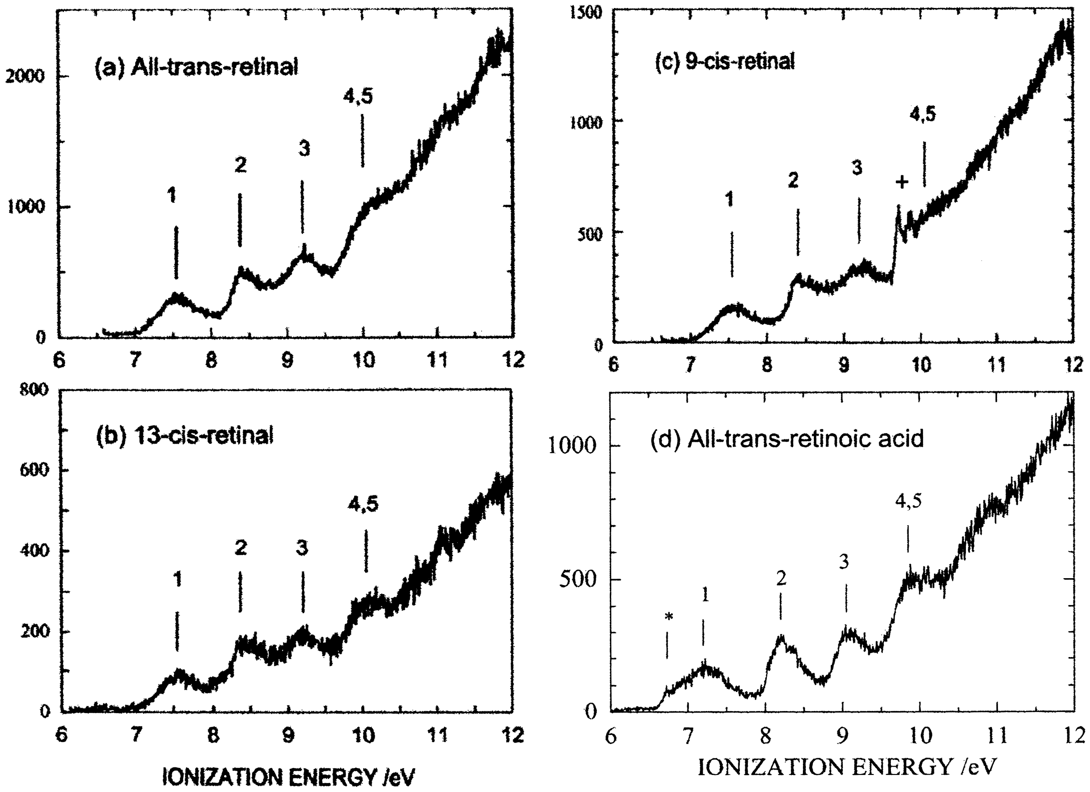


Fig. 2. HeI photoelectron spectra of (a) all-*trans*-retinal, (b) 13-*cis*-retinal, and (c) 9-*cis*-retinal measured in the present work, and (d) all-*trans*-retinoic acid taken from Ref. 6. The + in (c) and * in (d) mean an impurity band and an adiabatic band, respectively.

by Jericevic et al.[14] The first four bands in spectra (a) and (b) are clearly observed in the region below 10.5 eV, whereas the fourth band in spectrum (c) are somewhat noisy because of the overlap of an impurity band (+ mark) due to a decomposed species of an impurity on heating. This impurity band became gradually weaker even if the bands of 9-*cis*-retinal became stronger. All of the four photoelectron bands have been assigned by comparisons with the ab initio MO energies on the basis of Koopmans' theorem.

As can be seen in Fig. 2, the first three vertical ionization energies I_{obs} (i = 1–3) for each of three retinals have been found to be 7.55, 8.40, and 9.20 eV in common within the experimental error of ±0.05 eV. These values may be interestingly close to I_{obs} (i = 1–3), that is, 7.20, 8.20, and 9.05 eV for all-*trans*-retinoic acid. The band shapes of retinoic acid are also very similar to those of the retinals, except for the first band. With regard to the first bands of the retinals, the bands assignable to the adiabatic ionization energies could not be detected, while a weak peak on the left side of the first broad band of the retinoic acid was assigned to an adiabatic ionization energy (6.73 eV) corresponding to the $v = 0$ vibrational level of the cation.[6] The difference between the first band shapes in the spectra of the retinals and retinoic acid may be attributed to the difference in the Franck–Condon transition caused by the structural change of the neutral and cationic states, as mentioned below.

Interpretation of the Photoelectron Spectra. The four vertical ionization energies I_{obs} (i = 1–4) obtained from the photoelectron spectra of the three compounds are summarized in Table 2. The assignments were performed by Koopmans' theorem, $I_{\mathrm{calc}} = -E$, using MO energies (E) obtained from the present ab initio calculations. In each spectrum, the first three bands (1, 2, 3) correspond to the first three highest occupied MO's (HOMO, HOMO-1 and HOMO-2), respectively. The intensified fourth band must be taken as an overlap of two bands, and they may be assigned to the next two occupied MO's. A Plot of the vertical ionization energy against the MO energy indicates a good linear relationship for each of the three retinals.

GaussView drawings of the four highest occupied MO's in all-*trans*-retinal are shown in Fig. 3, in behalf of understanding electronic structures related to the ionization energies. The first highest occupied MO (HOMO) has four nodal planes in the chain of the five $\pi_{\mathrm{C=C}}$ bonds, as expected from the quantum theory of a one-electron model in a one-dimension box. The MO characteristics in Table 2 are represented in terms of "chn-$\pi_{\mathrm{C=C}}$" (N = 0, 1, 2, 3, 4), "n(O)", and σ(CH–CHO), where chn-$\pi_{\mathrm{C=C}}$(N) means the chain of the five $\pi_{\mathrm{C=C}}$ bonds with the number (N) of nodal planes, and n(O) and σ(CH–CHO) mean the oxygen nonbonding orbital of the CHO group and the σ orbitals forming the CH–CHO group, respectively. The character of the highest occupied MO (HOMO) is represented as chn-$\pi_{\mathrm{C=C}}$(4) with the four nodal planes, indicating that all of the five $\pi_{\mathrm{C=C}}$ bonds are bonding and four C–C bonds corresponding to four nodal planes are antibonding. Therefore, in the cation induced upon ionization from HOMO, the geometry displacements may become longer for the C=C bonds and shorter for the C–C bonds, as shown in Table 1. The second and third

Table 2. Comparison of Experimental I_{obs}'s with $-E$'s, and MO Characters for Retinals

Band	Exptl.	Ab initio SCF MO [6-311G]		
	I_{obs}/eV	$-E$/eV	MO	Character[c]
All-*trans*-retinal[a]		[Total energy = −23083.408 eV]		
1	7.55	7.59	(HOMO, 78)[b]	chn-$\pi_{\mathrm{C=C}}$(4)
2	8.40	9.02	(HOMO-1)	chn-$\pi_{\mathrm{C=C}}$(3)
3	9.21	10.11	(HOMO-2)	chn-$\pi_{\mathrm{C=C}}$(2)
4	10.02	11.32	(HOMO-3)	chn-$\pi_{\mathrm{C=C}}$(1)
5	10.02	11.38	(HOMO-4)	n(O), σ(CH–CHO)
13-*cis*-retinal		[Total energy = −23083.391 eV]		
1	7.54	7.65	(HOMO, 78)	chn-$\pi_{\mathrm{C=C}}$(4)
2	8.38	9.05	(HOMO-1)	chn-$\pi_{\mathrm{C=C}}$(3)
3	9.21	10.12	(HOMO-2)	chn-$\pi_{\mathrm{C=C}}$(2)
4	10.06	11.31	(HOMO-3)	n(O), σ(CH–CHO)
5	10.06	11.34	(HOMO-4)	chn-$\pi_{\mathrm{C=C}}$(1)
9-*cis*-retinal		[Total energy = −23083.386 eV]		
1	7.55	7.65	(HOMO, 78)	chn-$\pi_{\mathrm{C=C}}$(4)
2	8.40	9.06	(HOMO-1)	chn-$\pi_{\mathrm{C=C}}$(3)
3	9.20	10.12	(HOMO-2)	chn-$\pi_{\mathrm{C=C}}$(2)
4	10.05	11.34	(HOMO-3)	chn-$\pi_{\mathrm{C=C}}$(1)
5	10.05	11.36	(HOMO-4)	n(O), σ(CH–CHO)

The error of vertical ionization energies is within ±0.05 eV. a) In Ref. 14, the first four ionization energies are 7.43, 8.28, 9.17, and 9.82 eV. b) The number expresses the order of MO. c) "chn-$\pi_{\mathrm{C=C}}$" means a chain of the five $\pi_{\mathrm{C=C}}$ bonds, where the number of the nodes is given in parentheses. CH–CHO means the aldehyde group. n(O) means the nonbonding orbitals of the oxygen atoms in the C=O bond.

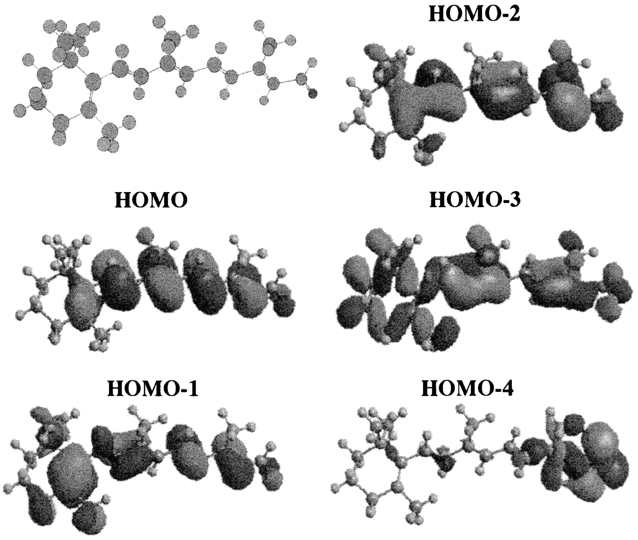


Fig. 3. Chem3D and Gauss View drawings of the molecular structure and the first four highest occupied MO's of all-*trans*-retinal.

highest MO's (HOMO-1, and HOMO-2) depict three and two nodal planes in the $\pi_{C=C}$ chain, respectively. The fourth and fifth MO energies are almost the same. The fifth highest occupied MO (HOMO-4) may be interpreted as a mixture of n(O) with σ(CH–CHO), as shown in Fig. 3. The characteristics of the first five MO's of 9-*cis*-retinal are essentially the same as those of all-*trans*-retinal. The character of the fourth and fifth MO's of 13-*cis*-retinal reverses the order of the corresponding MO's of all-*trans*-retinal. The calculated total energies in Table 1 give us the stabilized order of three retinal isomers. Furthermore, 11-*cis*-retinal has been found to be the most unstabilized isomer in the retinals studied in this work, because of the calculated total energy of -23083.173 eV.

The first band of all-*trans*-retinoic acid shown in Fig. 2 exhibits the adiabatic ionization band, which is very broad compared with the first bands of the retinals. Takeshita[15] reported for the first time on a theoretical study of the vibrational structures of the photoelectron spectra of dichloroethylenes using the calculated Franck–Condon factor. He calculated the magnitude of the geometrical change by ionization and the classical half-amplitudes of the zero-point vibrational level for each vibrational mode. The effect of each vibrational mode on the intensity in connection with the change in the geometry by ionization has been discussed. If the magnitudes of the geometric changes in a few bonds or angles are larger than the classical half-amplitudes of the vibrational modes related to the changes, the 0–0 transition weakens. In all-*trans*-retinal and the retinoic acid, the geometrical changes in the cations induced by ionization are considerably large for all of the bond lengths of the polyene-carbon-skeleton and for the dihedral angles of the $C_5{=}C_6{-}C_7{=}C_8$ segment, as listed in Table 1. Therefore, the fact that an adiabatic band could not be detected in the first bands of the retinals is reasonable, but the appearance of an adiabatic band in the first band of retinoic acid cannot be explained. The assignment of the adiabatic band of retinoic acid should be reexamined both experimentally and theoretically.

Conclusions

The geometrical and electronic structures of the all-*trans*-, 13-*cis*-, and 9-*cis*-retinals have been studied by means of HeI photoelectron spectroscopy and ab initio calculations. By optimized geometry calculations of the cations caused on ionization, the large structural changes between the neutral and cation ground states were confirmed in this work, especially in the dihedral angles between the planes of the β-ionone ring and the polyene chain. The most stable conformations of the neutral and the cationic ground states of the retinals have the 6-*s-cis* and the 6-*s-trans* configurations, respectively.

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