Ab initio study of isomers of neutral and ionized van der Waals dimer (CH$_3$I)$_2$

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Abstract

Ab initio calculations at the MP2 level have been carried out for two most stable neutral isomers of van der Waals dimer (CH$_3$I)$_2$ and for their ionized forms. It was found within MP4(SDTQ)//MP2 approach that neutral head-to-tail HT isomer (dimerization energy -778 cm^{-1}) is more stable than head-to-head HH form (dimerization energy -699 cm^{-1}). Comparison of calculated ionization potentials and earlier experimentally observed appearance potential of dimer ion allowed us to conclude that ionization of the more stable neutral HT form is followed by conversion into the ionic HH$^+$ form which is more stable than HT$^+$ by 0.97 eV.
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1. Introduction

The van der Waals (vdW) molecular complex is a next step of complexity on the way from isolated molecule to the molecule in condensed medium. The vdW complex is thus the simplest model which allows one to study the role of surrounding in the chemical and physical processes taking place in condensed medium. The structure, binding energy, spectroscopy and photoprocesses in van der Waals complexes are the subjects of the large body of literature devoted to this field of the research. Here we can refer to the recent special issue of Chemical Reviews [1] devoted to the theoretical and experimental studies of van der Waals complexes. Among the molecular clusters high attention has been paid during the last 15 years to the clusters of methyl iodide (CH$_3$I)$_n$ and the simplest member of this series the van der Waals dimer (CH$_3$I)$_2$ [2–22]. The interest into these clusters is due to the new routes in the photochemistry of those as compared with the isolated CH$_3$I molecule revealed firstly by Sapers et al. [2] and then studied by several groups [2–15,19]. The spectroscopy studies have been also carried out for these clusters [15–17,20,21]. Wang et al. [15] studied

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resonance Raman scattering spectra and Vaida et al. performed UV absorption studies of $(CH_3I)_n$ clusters [16,17]. The IR absorption spectra of matrix-isolated CH_3I clusters were obtained by Momose et al. [20] and Ito et al. [21]. The photo-ionization by electron impact [19] as well as one-quantum vacuum ultraviolet (VUV) photo-ionization [12] have been studied as well. In the last Letter Chen et al. [12] measured the appearance potentials of cluster parent ions as well as ionized fragments. The structure of the dimers $(CH_3I)_2$ and dimerization energy have been also studied with quantum chemical calculations. Wang et al. [15] have calculated the geometry of the dimers at the semi-empirical AM1 level. Recently Ito et al. [21] carried out ab initio calculation of the $(CH_3I)_2$ dimer structure and vibrational wavenumbers as well as the dimerization energy at the MP2 level. The dimerization energy in $(CH_3I)_2$ complex was estimated in the papers of Vaida and coworkers [16,18]. In the paper [16] the binding energy of two CH_3I molecules in dimer was estimated on the basis of the blue shift value in the absorption spectrum of dimer as compared with that one of isolated molecule. In the paper [18] the enthalpy of dimer formation has been calculated on the basis of temperature dependent changes in the UV-absorption spectrum of CH_3I vapor attributed to the contribution of dimer absorption.

In this paper the results of ab initio calculations of the structure and dimerization energy of CH_3I molecules in the neutral van der Waals dimer $(CH_3I)_2$ are presented as well as the ionization potentials and the structure of dimer ions. The results of calculations are compared with the existing experimental data.

2. Calculations

For evaluation of intermolecular interaction in the van der Waals complex the expanded basis set with the addition of polarization and diffuse functions has been used. For carbon and hydrogen atoms the aug-cc-pVTZ basis functions suggested by Dunning [23] have been used. For iodine atoms SDB-aug-cc-pVTZ basis functions elaborated by Martin and Sunderman [24] have been applied.

These last functions in conjunction with a relativistic core polarization potential RECP suggested by Bergner et al. [25] have been taken from the online version [26].

For CH_3I monomer the geometry was optimized and vibrational wavenumbers were calculated at the MP2 level. The calculated wavenumbers have been obtained with the use of scaling factor determined via the method of least squares to fit the experimentally determined values. This geometry of monomer has been used then to reveal the most stable relative configurations of CH_3I molecules in the dimer $(CH_3I)_2$. Two most stable configurations have been then fully optimized at the MP2 level. The vibrational wavenumbers have been calculated for isomers of dimer with the use of scaling factor determined for monomer.

The dimerization energy (E_{dim}) has been calculated at MP4(SDTQ)//MP2 level. In our calculations E_{dim} was corrected with taking into account basis set superposition error (BSSE) by the counterpoise method [27] and zero-point energy (ZPE), calculated within MP2 approach for optimized molecular structures.

The adiabatic and vertical ionization potentials (IP_{ad} and IP_{vert}) have been calculated at the MP2//MP2 level without ZPE corrections.

All the calculations have been carried out with GAUSSIAN package 98 [28] on the SGI Origin 3800 1024 node system of SARA Computing and Networking Services in Amsterdam.

3. Results and discussion

The results of calculations of CH_3I monomer geometry and vibrational wavenumbers are given in Table 1. The calculated wavenumbers given in Table 1 have been obtained with the use of scaling factor 0.95058. As it is seen from Table 1 the calculated and experimentally determined geometry as well as vibrational wavenumbers are in a good agreement.

The geometry of two most stable isomers $(CH_3I)_2$ with C_{2h} (head-to-tail, HT) and C_s (head-to-head, HH) symmetry found in calculations is shown in Fig. 1. The calculated geometry and vibrational wavenumbers of these dimers are

Table 1
The results of MP2 calculations for CH$_3$I molecule

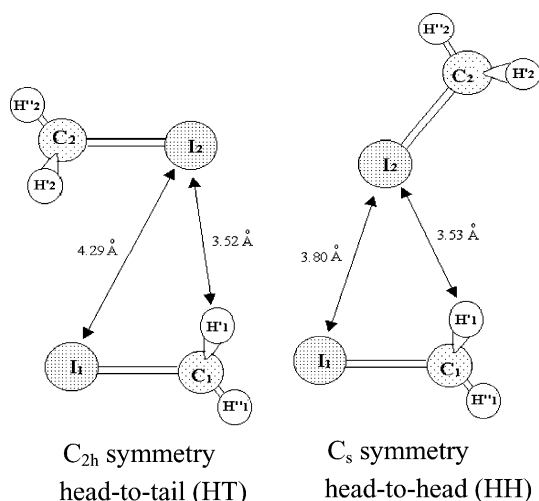| Molecule, symmetry, experimental geometry [29]	Calculated geometry	Symmetry and assingment of vibrations [30]	Vibrational wavenumbers (cm^{-1})	
			Experiment [30]	Calculations (scaling factor 0.95058)
CH$_3$I, C$_{3v}$				
$\angle HCH = 111.2°$	$\angle HCH = 111.0°$	v_1-A$_1$ symmetric CH$_3$ stretching	2933	2959
$r_{C-H} = 1.084$ Å	$r_{C-H} = 1.084$ Å	v_2-A$_1$ symmetric CH$_3$ deformation	1252	1238
$r_{C-I} = 2.132$ Å	$r_{C-I} = 2.116$ Å	v_3-A$_1$ C–I stretching	533	548
		v_4-E degenerate C–H stretching	3060	3072
		v_5-E degenerate CH$_3$ deformation	1436	1417
		v_6-E degenerate CH$_3$ rocking	882	868

Fig. 1. Optimized structure for two stable isomers of (CH$_3$I)$_2$. Plane of symmetry coincides with the plane of the sheet. The third H atom in CH$_3$ groups is not seen due to screening by H′ atom.

presented in Table 2. Recently Ito et al. [21] carried out similar calculations for (CH$_3$I)$_2$ dimers at the MP2 level but with the use of double zeta basis functions: for carbon and hydrogen atoms the D5++(d,p) basis set suggested by Dunning and Hay [31] was used; for iodine atoms the similar basis set modified by Glukhovtsev et al. [32] plus the effective core potential by Wadt and Hay [33] were applied. Our data and results of Ito et al. have been obtained by the same method but with the use of different basis sets. The data of Ito et al. for distances $r_{I_1-I_2} = 4.43$ Å, $r_{I_2-H'_1} = 3.64$ Å for HT-(CH$_3$I)$_2$ and $r_{I_1-I_2} = 3.96$ Å and $r_{I_2-H'_1} = 3.64$ Å for HH-(CH$_3$I)$_2$ can be compared with our results $r_{I_1-I_2} = 4.288$ Å, $r_{I_2-H'_1} = 3.515$ Å for HT-(CH$_3$I)$_2$ and $r_{I_1-I_2} = 3.802$ Å, $r_{I_2-H'_1} = r_{I_2-H'_1} = 3.526$ Å for HH-(CH$_3$I)$_2$ (see Fig. 1 and Table 2). The use of triple zeta basis set in our calculation gives more compact structure of dimer as compared with the data of Ito et al. obtained with double zeta functions. This more compact structure is in better agreement with the experimental data on the structure of crystal solid CH$_3$I studied by Kawaguchi et al. [34] who found $r_{I_1-I_2} = 4.25$ Å for HT-(CH$_3$I)$_2$ and $r_{I_1-I_2} = 3.895$ Å for HH-(CH$_3$I)$_2$. This last agreement gives us an indication to the correct inclusion of the dispersion interaction in our SDB-aug-cc-pV + RECP approach. Earlier, the geometry of dimer (CH$_3$I)$_2$ has been calculated also by Wang et al. at the semi-empirical AM1 level [15]. They found HH-configuration to be most stable. The calculated I–I distance was equal to 3.0 Å that is much shorter than the values obtained in our calculations as well as in the work by Ito et al. [21]. The semi-empirical level seems to be too simple to provide the appropriate accuracy in the evaluation of the intermolecular interaction, probably due to underestimation of exchange repulsion.

We, as well as Ito et al. [21], have calculated dimerization energy for HT-(CH$_3$I)$_2$ and HH-(CH$_3$I)$_2$. In our calculations $E_{dim} = \Delta E + BSSE + \Delta ZPE$, where $\Delta E = E[(CH_3I)_2] - 2E[CH_3I]$ and $\Delta ZPE = ZPE[(CH_3I)_2] - 2ZPE[CH_3I]$. Calculated

Table 2
The results of MP2 calculations for neutral dimers $(CH_3I)_2$: HT-$(CH_3I)_2$ and HH-$(CH_3I)_2$

HT-$(CH_3I)_2$, symmetry C_{2h}				HH-$(CH_3I)_2$, symmetry C_s			
Geometry[a]	Symmetry, wavenumber (cm^{-1}) and correspondence to the vibrational mode in CH_3I molecule[b]			Geometry[a]	Symmetry, wavenumber (cm^{-1}) and correspondence to the vibrational mode in CH_3I molecule[b]		
$\angle H'_1C_1H'_1 = 110.7°$	B_u	2957	v_1	$\angle H'_1C_1H'_1 = 110.8°$	A'	2956	v_1
$\angle H'_2C_2H'_2 = 110.7°$	A_g	2957	v_1	$\angle H'_2C_2H'_2 = 110.9°$	A'	2956	v_1
$\angle H'_1C_1H''_1 = 111.6°$	A_g	1235	v_2	$\angle H'_1C_1H''_1 = 111.5°$	A'	1233	v_2
$\angle H'_2C_2H''_2 = 111.6°$	B_u	1238	v_2	$\angle H'_2C_2H''_2 = 110.9°$	A'	1237	v_2
$\angle I_1C_1H'_1 = 107.5°$	B_u	547	v_3	$\angle I_1C_1H'_1 = 107.6°$	A'	545	v_3
$\angle I_2C_2H'_2 = 107.5°$	A_g	549	v_3	$\angle I_2C_2H'_2 = 108.1°$	A'	548	v_3
$\angle I_1C_1H''_1 = 107.7°$	A_g	3072	v_4	$\angle I_1C_1H''_1 = 107.8°$	A'	3068	v_4
$\angle I_2C_2H''_2 = 107.7°$	B_u	3072	v_4	$\angle I_2C_2H''_2 = 107.9°$	A''	3068	v_4
$\angle C_1I_1I_2 = 64.5°$	B_g	3074	v_4	$\angle C_1I_1I_2 = 73.6°$	A'	3070	v_4
$\angle C_2I_2I_1 = 64.5°$	A_u	3075	v_4	$\angle C_2I_2I_1 = 168.9°$	A''	3071	v_4
$\angle I_1C_1I_2 = 86.0°$	A_g	1408	v_5	$\angle I_1C_1I_2 = 74.1°$	A'	1410	v_5
$\angle I_2C_2I_1 = 86.0°$	B_u	1409	v_5	$\angle I_2C_2I_1 = 7.2°$	A''	1412	v_5
$r_{C_1-H'_1} = 1.084$ Å	B_g	1410	v_5	$r_{C_1-H'_1} = 1.084$ Å	A'	1417	v_5
$r_{C_1-H''_1} = 1.084$ Å	A_u	1411	v_5	$r_{C_1-H''_1} = 1.084$ Å	A''	1417	v_5
$r_{C_2-H'_2} = 1.084$ Å	A_g	870	v_6	$r_{C_2-H''_2} = 1.084$ Å	A''	863	v_6
$r_{C_2-H''_2} = 1.084$ Å	B_u	870	v_6	$r_{C_2-H''_2} = 1.084$ Å	A'	863	v_6
$r_{C_1-I_1} = 2.117$ Å	A_u	871	v_6	$r_{C_1-I_1} = 2.117$ Å	A'	869	v_6
$r_{C_2-I_2} = 2.117$ Å	B_g	872	v_6	$r_{C_2-I_2} = 2.120$ Å	A''	871	v_6
$r_{I_1-I_2} = 4.288$ Å	A_g	82		$r_{I_1-I_2} = 3.802$ Å	A'	73	
$r_{C_1-C_2} = 4.564$ Å	B_u	76		$r_{C_1-C_2} = 5.525$ Å	A''	45	
$r_{I_1-C_2} = 3.879$ Å	A_u	45		$r_{I_1-C_2} = 5.896$ Å	A'	43	
$r_{I_2-C_1} = 3.879$ Å	B_g	35		$r_{I_2-C_1} = 3.792$ Å	A'	37	
$r_{I_1-H'_2} = 3.515$ Å	A_g	28		$r_{I_1-H'_2} = 6.254$ Å	A''	26	
$r_{I_2-H'_1} = 3.515$ Å	A_u	18		$r_{I_2-H'_1} = 3.526$ Å	A''	6	

[a] Designation of atoms corresponds to Fig. 1.
[b] The wavenumbers have been calculated with the use of scaling factor 0.95058.

E_{dim} values are presented in Table 3. The dimerization energy values found are equal to $E_{dim} = -778$ and -699 cm^{-1} for HT- and HH-complex correspondingly. So the HT-complex is more stable than HH one by 79 cm^{-1}. Ito et al. [21] did not take into account ΔZPE correction ($E_{dim} \approx \Delta E + BSSE$) and calculated $E_{dim} = -636$ and -451 cm^{-1} correspondingly. To compare our results we subtract ΔZPE correction from our E_{dim} and obtain values -909 and -789 cm^{-1} for HT-$(CH_3I)_2$ and HH-$(CH_3I)_2$. That means that the basis set used by Ito et al. [21] results in the underestimation of the binding energy and overestimation of the difference in the stability of two isomers. Earlier Donaldson et al. [16] estimated the binding energy to be within the interval 500–1000 cm^{-1} on the basis of the blue shift value in the absorption

spectrum of dimer relative to the monomer. Waschewsky et al. [18] have experimentally determined the enthalpy of dimerization of CH_3I in the temperature interval 200–298 K and found $\Delta H_{dimer} = -993 \pm 127$ cm^{-1}. The calculated value should be compared with dimerization enthalpy value at 0 K (ΔH_0^0). This value can be extracted from ΔH_{dimer} determined by Waschewsky et al. with taking into account the average thermal energy of dimer ($\langle E \rangle_{dim}$) and monomer ($\langle E \rangle_{mon}$, including all the degrees of freedom: $\Delta H_0^0 = \Delta H_{dimer}(\bar{T}) - \langle E \rangle_{dim} + \langle E \rangle_{mon}$, where $\bar{T} = 250$ K is average temperature in the experiments of Waschewsky et al. The average thermal energy of the internal vibrational degrees of freedom of CH_3I moieties is very small and approximately equal in monomer and dimer as follows from the calculated

Table 3
Calculated dimerization energy E_{dim} of CH_3I molecules in van der Waals neutral complex $(CH_3I)_2$: $E_{dim} = \Delta E + BSSE + \Delta ZPE$

Complex	ΔE	BSSE	ΔZPE	E_{dim}
	MP4(SDTQ)//MP2	MP4(SDTQ)//MP2	MP2//MP2	
HT-$(CH_3I)_2$	−1162	253	131	−778
HH-$(CH_3I)_2$	−995	206	90	−699

All the values are given in cm^{-1}.

wavenumbers shown in Table 2. The smallest six wavenumbers from Table 2 corresponding to the relative motion of CH_3I moieties in dimer are less or much less than $k\bar{T} = 173$ cm^{-1} and probably most of them correspond to the hindered or even free internal rotations. In this limiting case $\Delta H_0^0 = \Delta H_{dimer}(\bar{T}) = -993 \pm 127$ cm^{-1}. Our calculated value of dimerization energy (-778 cm^{-1}) for the more stable HT-dimer is close to this value. In the less probable limiting case of all these six degrees of freedom to be the harmonic oscillators the result would be $\Delta H_0^0 = -1377 \pm 127$ cm^{-1}.

For the two dimers described above, the adiabatic and vertical ionization potentials (IP_{ad} and IP_{vert}) have been also calculated. A test of the approach used has been made on the example of monomer CH_3I where the experimental value of IP is well known. The calculation of IP for A species has been carried out via formula $IP(A) = \Delta E(A^+, A) + \Delta ZPE(A^+, A)$, where $\Delta E(A^+, A) = E(A^+) - E(A) = 9.71$ eV was calculated at MP4(SDTQ)//MP2 level and $\Delta ZPE(A^+, A) = ZPE(A^+) - ZPE(A) = -0.05$ eV with MP2//MP2 approach. The resulting value $IP_{ad}(A) = 9.66$ eV is slightly higher than the experimental value 9.54 ± 0.02 eV [30]. With the calculation of $\Delta E(A^+, A)$ value at a lower MP2//MP2 level the resulting value $IP_{ad}(A) = 9.67$ eV is very close to the upper value obtained with MP4(SDTQ)//MP2 approach. This allowed us to use the lower level calculations at MP2 level for determination of IP characteristics of ionic species under study. The estimations of ZPE corrections for ionic species, which are open shell systems, are very expensive from the point of computer time and we excluded these corrections from our further calculations for ions. This approach gives for CH_3I monomer $IP_{vert} = 9.74$ eV and $IP_{ad} = 9.72$ eV. In both cases

of vertical and adiabatic ionization the unpaired electron density is mainly located on iodine with $\rho_I \sim 1.07$. The small difference of 0.02 eV between IP_{vert} and IP_{ad} is due to minor change in the equilibrium geometry of ion as compared with the neutral molecule: elongation of C–H bonds by about 0.01 Å and shortening of C–I bond by about 0.01 Å.

The fully optimized geometry of two cation radicals of the dimer $(CH_3I)_2$ is shown in Fig. 2. It is worth mentioning that the symmetry C_{2h} does not change after ionization in the case of HT-$(CH_3I)_2$ and changes from C_s to C_2 symmetry in the HH-$(CH_3I)_2$ case. For the dimers both ionization potentials IP_{ad} and IP_{vert} are close to or less than to those for monomer. They are equal to $IP_{vert} = 9.74$ and 9.51 eV, $IP_{ad} = 9.42$ and 8.44 eV for HT-$(CH_3I)_2$ and HH-$(CH_3I)_2$ correspondingly. In the case of HT-$(CH_3I)_2$ vertical ionization the electron is detached from iodine atoms and spin density is equally distributed over both I atoms with $\rho_{I_1} = \rho_{I_2} \sim 0.53$ (see Fig. 1). Then the geometry of ion relaxes to the equilibrium geometry for HT-$(CH_3I)_2^+$ (see Fig. 2) with the similar distribution of spin density on I atoms $\rho_{I_1} = \rho_{I_2} \sim 0.53$. The energy release resulting from this relaxation is equal to 0.32 eV and is higher than that in monomer (0.02 eV, see upper text). In the case of HH-$(CH_3I)_2$ vertical ionization the electron is detached from iodine atom I_1 with $\rho_{I_1} = 1.07$ ($\rho_{I_2} = -0.04$). Then full optimization applied gives the structure relaxation with substantial change of the ion geometry and equalization of spin densities on both iodine atoms $\rho_{I_1} = \rho_{I_2} = 0.55$. This relaxation is followed by substantial energy release of 1.07 eV which is much higher than that in the cases of HT-$(CH_3I)_2^+$ and CH_3I^+. On the contrary in the case of neutral dimers where the HT-configuration is more stable, the ground state of

C$_{2h}$ symmetry
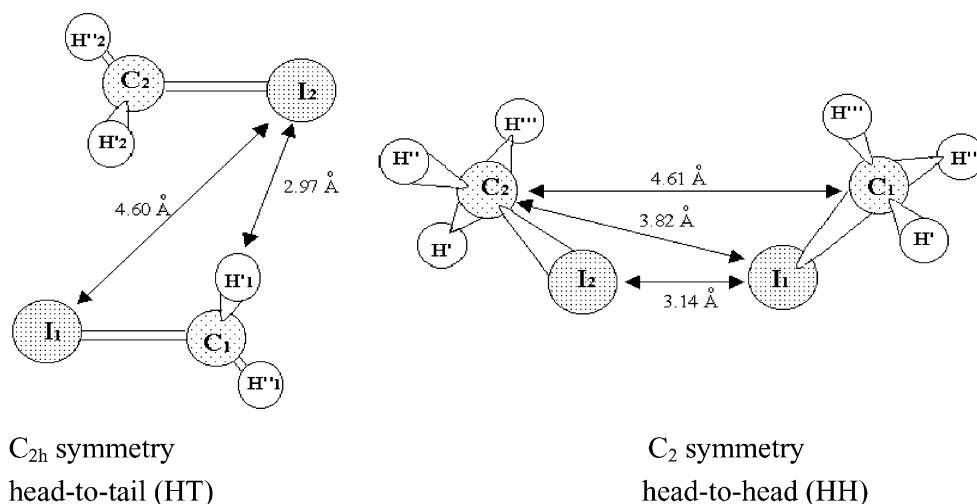head-to-tail (HT)

C$_2$ symmetry
head-to-head (HH)

Fig. 2. Optimized structure for two isomers HH$^+$ and HT$^+$ of cation radical (CH$_3$I)$_2^+$. In the left part of the figure the plane of symmetry coincides with the plane of the sheet and the third H atom in CH$_3$ groups is not seen due to screening by H' atom.

HH-configuration is more stable by 0.97 eV in the case of ion. The stability of HH-dimer in ion case is mainly due to the formation of I–I bond in this configuration.

Recently, Chen et al. [12] have experimentally measured appearance potentials of ions (CH$_3$I)$_2^+$ (AP = 9.19 ± 0.05 eV) in one-quantum photoionization of neutral dimers. The appearance potential value should lie in between the values of IP$_{ad}$ and IP$_{vert}$. The HT-isomer is more stable for the neutral dimer. We thus consider its level as zero. Its IP$_{vert}$ is equal to 9.74 eV and IP$_{ad}$ = 9.42 eV which both are higher than AP observed in the Letter of Chen et al. [12]. If we suppose that the ionization of HT-isomer is followed by conversion to the much more stable configuration of HH-ion (IP$_{ad}$ = 8.45 eV) then the experimentally determined value AP = 9.19 ± 0.05 eV [12] lies just in between the calculated values 9.74 and 8.45 eV. This conversion can be responsible for the delayed formation of ions in the experiments of Poth et al. [10] on the femtosecond (fs) photoexcitation of clusters of CH$_3$I. Poth et al. studied the appearance of ionic photofragments as a function of the time delay between pumping and probing fs pulses. They observed two modes in the formation of all the ions corresponding to the prompt (pumping

and probing pulses coincide in time) and delayed formation of ionic fragments. The authors [10] interpreted the second (delayed by about 1 ps) mode as due to the delayed formation of the ions precursor in clusters. Poth et al. supposed that this precursor corresponds to the electronically excited CH$_3$I molecule resulting from the delayed recombination of highly excited iodine atoms in the 6s ^{4}P$_{5/2,3/2}$ states (arising in the multiphoton dissociation of CH$_3$I molecule) with CH$_3$ radical. We can consider one more explanation of this phenomenon based on the upper discussed HT$^+$ → HH$^+$ conversion. The conversion of HT isomer to HH one involves the rotation of one CH$_3$I fragment around the axis perpendicular to C–I bond (see Fig. 2). The rotation half period of CH$_3$I molecule around this axis is estimated (rotational constant $B \approx 0.25$ cm^{-1}) to be about 1 ps at 300 K. The internal energy of the dimer after photoionization in the experiments of Poth et al. [10] is not known but the rotational period depends on the energy of the corresponding degree of freedom as a square root, i.e., rather smoothly. This coincidence of the estimated period of CH$_3$I rotation and appearance time of the second precursor of ions in experiments of Poth et al. allows us to suppose that this precursor is HH form of ionized cluster which

appears in the upper conversion of HT isomer after ionization. In the experiments of Poth et al. this delayed formation was characteristic not only for ions arising from ionized dimer but also from higher clusters. We suppose that conversion similar to $HT^+ \rightarrow HH^+$ in dimer can take place in higher clusters too.

4. Conclusions

Ab initio calculations at the MP2 level have been carried out for neutral isomers of van der Waals dimer $(CH_3I)_2$ as well as for their ionized forms. In agreement with earlier data from literature two most stable forms head-to-tail (HT) and head-to-head (HH) have been established. As it was found within MP4(SDTQ)//MP2 approach the HT (dimerization energy -778 cm^{-1}) isomer is more stable than HH (dimerization energy -699 cm^{-1}) for the neutral dimer which are close to the experimentally determined value. The ionization potentials (IP_{ad} and IP_{vert}) for HH and HT isomers as well as the structure of the corresponding ions have been also studied. Comparison of calculated IP and earlier experimentally observed appearance potential (AP) of dimer ion allowed us to conclude that ionization of the most stable neutral HT form is followed by conversion into the ionic HH^+ form which is more stable than HT^+ by 0.97 eV.

Acknowledgements

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