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Oxygen-assisted enhancement of H atom UV-photogeneration from hydrocarbons in van der Waals complexes RH–O₂

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ABSTRACT

The strong enhancement of H-atom UV-photogeneration is revealed in van der Waals complexes of unsaturated hydrocarbons RH (RH=ethylene C₂H₄, propylene C₃H₆, butadiene C₄H₆, butene-2 C₄H₈) with oxygen RH-O₂ as compared with the 'free' RH molecules. The results obtained indicate enhancement of H atom yield to be due to one-quantum photoprocess ¹RH-³O₂ + hv \rightarrow 3RH* + ³O₂(¹O₂) providing triplet RH molecules with excitation level sufficient for dissociation.

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1. Introduction

The van der Waals molecular complex is an ideal model for the study of the effect of weakly bound molecular environment on the photoinitiated processes in molecules. This effect is known to be very essential for the photophysics and photochemistry of molecular oxygen O₂ where the electronic transitions in the spectral region from IR to UV are spin and/or orbital symmetry forbidden. The drastic enhancement of UV-photochemistry in van der Waals complexes of oxygen X–O₂ has been revealed when oxygen atoms $O({}^{3}P_{1})$ were detected which arise from complex photodissociation [1–5]. In papers [1–4] the observed rise of the yield of O atoms was attributed to the direct excitation of charge-transfer (CT) state of complex. This assignment was based on the results of estimation of the spectral position of CT band. In paper [5] the velocity map imaging of $O({}^{3}P_{1})$ atoms arising from the complexes X–O₂ with different X revealed not only quantitative but also qualitative change in the process of O_2 photodissociation in a complex as compared with the dissociation of the free O₂. Several photodissociation channels differing by the kinetic energy and angular anisotropy of recoil directions for O atoms arising in X-O₂ photodissociation have been revealed [5]. The channel providing the biggest contribution was found to correspond not to the direct excitation to the CT state but to the direct excitation of the covalent state of O₂ molecule leaving X molecule in the ground state. Besides the dissociation of O₂ giving rise to O atoms the photoexcitation of van der Waals complexes $X-O_2$ was found to result in the formation of singlet oxygen in *b* [5] and *a* states [6]. Singlet oxygen in *a* state was also detected to appear due to enhanced UV-absorption by encounter complexes of oxygen O_2-O_2 and N_2-O_2 [7,8] which are short-lived structures similar to van der Waals complexes.

In the presented work the oxygen-assisted enhancement of photogeneration of hydrogen atom H from hydrocarbons RH in van der Waals complexes $RH-O_2$ has been revealed. The results of the experimental investigation are presented and the possible mechanism responsible for this enhancement is discussed.

2. Experimental

The van der Waals complexes RH-O₂ of hydrocarbons RH= C_2H_4 , C_3H_6 , C_4H_6 , C_4H_8 , C_6D_{12} with oxygen have been generated in the pulsed molecular beam apparatus. The supersonic beam has been generated with the home-made electrodynamic valve providing gas jet with pulse duration of 200 µs. Premixed gas with varied content of hydrocarbon RH, oxygen O₂ and helium as a carrier gas was expanded into the chamber through the 0.27 mm nozzle. The mixtures $RH(0.1\% \text{ or } 0.4\%) + O_2(1.7\% \text{ or } 5\%) + He$, RH(0.4%) + He and $O_2(5\%)$ + He have been used. Backing pressure was varied within the interval $0.5 \div 7$ atm. Central part of the gas jet passed through the 2.5 mm skimmer mounted 60 mm downstream and got into the region of homogeneous electric field, created by electrodes of the time-of-flight mass-spectrometer (TOF-MS). Molecular beam was directed perpendicular to the TOF axis. In this region the pulsed laser UV radiation crossed molecular beam at a right angle. This UV radiation (1 mJ in the pulse) has been produced as a second harmonic of a pulsed dye laser pumped by excimer XeCl laser (308 nm, 100 mJ, 15 ns). The light was





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focused by the lens with a focus length of 25 cm. This radiation was used simultaneously for excitation of a complex and for (2 + 1) resonance enhanced multiphoton ionization (REMPI) of hydrogen atoms H (wavelength 243.13 nm) or D (243.09 nm) and oxygen atoms $O({}^{3}P_{2})$ (225.65 nm)). Ions were detected by microchannel plate (MCP) detector.

The arrangement utilized for velocity map imaging (VMI) of H atoms and D atoms was similar to that used in paper [9] with 'off-axis' arrangement of the pulsed valve. Three-electrode electrostatic lens with two open electrodes with the holes of 16 mm in diameter have been used for extracting ions. The F2225-21P Microchannel plate assembly (Hamamatsu) has been used as a two-dimensional detector of ions. The 2D images on the phosphor screen were recorded by CCD camera (Videoscan-285/O-2001) with objective *f* = 2.5 cm and stored in a PC.

3. Details of ab initio calculations

3.1. Structure and binding energy of van der Waals complex $C_2H_4-O_2$.

The structure of van der Waals complex of ethylene with oxygen $C_2H_4-O_2$ has been found with optimization of geometry providing minimum of the sum of total electronic energy $E[C_2H_4-O_2]$ with basis set superposition error BSSE found by counterpoise method [10]. The calculations have been carried out within MP2/ 6-311++G(2d,2p) approach. Several initial configurations differing by distance between ethylene and oxygen molecules and their orientation have been taken as the starting ones for optimization. This allowed us to find nine local minima corresponding to the stationary states of C_{2v} symmetry for complex $C_2H_4-O_2$. The binding energy (E_{bind}) in each stationary point of van der Waals complex $C_2H_4-O_2$ has been then calculated with taking into account of BSSE and zero point energy (ZPE). The planar configuration of the complex with O-O axis being parallel to C-C bond of ethylene ('parallel' configuration) was found to be most stable. The distance between O-O and C-C axis in this configuration was found to be 3.75 Å. In paper [2] the bisected structure of complex $C_2H_4-O_2$ with O-O axis being perpendicular to the plane of ethylene molecule was found to be the most stable one but the authors of Ref. [2] did not consider the 'parallel' structure. The bisected structure was among nine geometries considered in our calculations and the 'parallel' configuration was found to be the most stable one. Then for this configuration the binding energy calculations have been carried out within MP2 approach with basis sets aug-cc-pVnZ (n = 2, 3, 4) of different size. The results allowed us to provide extrapolation to the infinite basis set within the equation $E_{\text{bind}}(n) = E_{\text{bind}}(\infty) + a \cdot (1/n)$ [11]. The binding energy value resulted from this extrapolation was found to be $E_{\text{bind}}(\infty)=206 \text{ cm}^{-1}=0.026 \text{ eV}$.

3.2. Energy gap for vertical $T \leftarrow S$ excitation of cyclohexane

The energy gap for vertical excitation of cyclohexane has been calculated within spin-unrestricted time-dependent DFT approach TD//UB3LYP/6-311++G(2d,2p). Complete optimization of the ground singlet state of cyclohexane in the chair conformation has been carried out. Highest occupied molecular orbital HOMO was found to be provided by the combination of binding sp³ hybrid atomic orbitals (AOs) consisting of C atom 2s- and 2p-orbitals and to have e_g symmetry. The first transition to the triplet state corresponds to the transfer of one electron to the virtual molecular orbital of a_{1g} symmetry being the linear combination of diffuse AOs similar to C atom Rydberg 3s-AO. The energy for vertical transition to the triplet state T₁(³E_g) \leftarrow S₀(¹A_{1g}) was calculated to be of 7.06 eV.

All calculations have been carried out with the use of GAUSSIAN 03 package [12].

4. Results and discussion

4.1. Enhancement of the yield of H atoms

Figure 1 shows REMPI signal of H atoms arising from irradiation of molecular beam generated by expansion of unsaturated hydrocarbons RH in helium with or without premixed oxygen O₂. The spectral dependence of H⁺ signal in presented mass-spectra was found to correspond to REMPI (2 + 1) line of H atoms with the center at 243.13 nm. The presence of oxygen in the expanded mixture provides well pronounced enhancement of H atom yield for all four unsaturated hydrocarbons under study. We attribute this enhancement to the photochemistry of van der Waals (vdW) complexes of hydrocarbons with oxygen RH–O₂. To confirm the formation of van der Waals complexes RH-O₂ in our conditions we have investigated the photogeneration of oxygen O atoms by the complexes and the results are presented in Figure 2. Figure 2(a-c) demonstrate that the well pronounced signal of O⁺ ions is observed only when RH is admixed to O₂-containing expanded mixture. These O^+ ions are provided exclusively by REMPI (2 + 1) of $O({}^{3}P_2)$ atoms with the center of the line at 225.65 nm. This dramatic enhancement of O atoms yield is similar to that observed in papers [1-5] and interpreted to be due to rise of the cross-section of UV-absorption by O₂ in van der Waals complexes RH–O₂ as compared with the free O_2 . In Figure 2(d–f) the pressure dependence of O^+ signal is shown. High values of power in these pressure dependencies within the interval from 3.7 to 2.3 indicate the complex RH-O₂ to be a source of O atoms detected. We expect the backing pressure dependence with the power index value of three for the formation of one-to-one complex RH-O₂ because it appears in the termolecular collisions.

$$\mathbf{RH} + \mathbf{O}_2 + \mathbf{He} \to \mathbf{RH} - \mathbf{O}_2 + \mathbf{He} \tag{1}$$

The results of Figure 3 demonstrate similar pressure dependence with power index close to three for enhanced H atom production. This confirms the upper assumption about van der Waals complexes $RH-O_2$ as a main source of enhanced H atom photogeneration.

We have also revealed one example where formation of van der Waals complex $RH-O_2$ doesn't provide the enhancement of H atom yield. The results presented in Figure 4 demonstrate absence of D atom yield enhancement for deuterated cyclohexane C_6D_{12} . Deuterated sample of this substance was taken because small yield of hydrogen atom for cyclohexane C_6H_{12} with or without oxygen in the expanded mixture was comparable with H atom signal in the background. Background for D atom was negligible.

Effect of binding with oxygen on photogeneration of H atoms has been tested also for two other hydrocarbons RH=benzene C_6H_6 and isoprene C_5H_8 . But these RH molecules absorb in this wavelength region themselves and were found to provide very high yield of H atoms even without oxygen in expanded mixture. So addition of oxygen and formation of complexes RH–O₂ did not affect very high H signal.

Enhancement factor for H atom signal in Figure 1 for RH= C_2H_4 , C_3H_6 , C_4H_6 and C_4H_8 has a value of 10–20 times. But signal observed after irradiation of molecular beam of RH without oxygen corresponds mainly to background signal provided by H atoms arising in photodissociation of hydrocarbon molecules existing in vacuum lines. Oil molecules existing in vacuum lines are a source of these background H atoms. When special efforts have been applied with long-time heating and pumping of parts of setup the background of H atoms reduced. Promptly after this cleaning the



Figure 1. Mass spectra of H atoms arising in photodissociation of hydrocarbons (a)-ethylene, (b)-propylene, (c)-2-butene and (d)-1,3-butadiene with and without oxygen in expanded mixture. Content of hydrocarbon in expanded mixture was 0.4%. Content of O₂ in oxygen containing mixture was 5%. Excitation wavelength was 243.13 nm which corresponds to center of REMPI (2 + 1) line of H atom (m/z = 1). Signal at m/z = 1 on lower traces obtained without oxygen mainly corresponds to H atoms existing in background.

measurements provided values of enhancement factor up to about 90. Besides the contribution of background there is also another factor reducing measured value of enhancement. In our conditions most of RH molecules are not complexed with oxygen. This conclusion can be made because there is no saturation in the backing pressure dependence of H atom yield presented in Figure 3. This factor together with unavoidable background of H atoms allow us to conclude that measured values of enhancement factor even at the level of 90 are only the lower estimates for enhancement of H atom photogeneration cross-section in complex $RH-O_2$

 $(\sigma_{\rm RH-O_2}^{\rm H})$ as compared with a free RH molecule $(\frac{\sigma_{\rm RH-O_2}^{\rm H}}{\sigma_{\rm RH}^{\rm H}})$.

On velocity maps of H atoms appearing due to photoexcitation of van der Waals complexes $RH-O_2$ we saw only isotropic spot corresponding to rather wide unimodal kinetic energy distribution with maximum located at the level of several tenths of eV (0.24 eV at maximum with full width at half maximum of 0.25 eV for the case of $C_2H_4-O_2$ complex).

4.1.1. Mechanism of H atom photogeneration from van der Waals complex RH–O $_2$

Process of the H atom photogeneration from complexes $RH-O_2$ is expected to proceed via scheme shown below for complex of ethylene.

$$C_2H_4 - O_2 + h\nu(5.1 \text{ eV}) \to C_2H_3 + H + O_2 \quad \Delta E \approx 0.3 \text{ eV} \eqno(2)$$

Value of excess energy ΔE to be distributed between degrees of freedom of fragments has been estimated with the use of enthalpy $\Delta H_0^0 = 4.78 \text{ eV}$ of dissociation $C_2H_4 \rightarrow C_2H_3 + H$ estimated with

 D_{298}^0 =111.2 ± 0.8 kcal/mol [13] and with correction of this value for average translational and rotational energy of C₂H₄, C₂H₃ and H at T = 298 K. To the best of our knowledge binding energy for complex C₂H₄-O₂ was not experimentally measured. Our quantum chemical calculation of binding energy described above gives the value of 0.026 eV. For one-quantum excitation of this complex the kinetic energy of fragment H cannot exceed the value of about 0.3 eV. Value of 0.24 eV measured with velocity map imaging doesn't exceed that limit. This result confirms one-quantum excitation scheme (2) as a source of H atom. Enhancement of H atom generation due to binding of RH with O₂ can be explained with taking into account complex-specific absorption analogous to collision-induced absorption of oxygen in UV region. The UV-absorption of oxygen induced by collisions with various X molecules is attributed to enhanced absorption by encounter X-O₂ complexes giving rise to excitation of O_2 molecule in Herzberg III ($A'^3 \Delta_u$) state [14]. To provide enhancement of H atom yield the excitation should be localized on X partner molecule, in our case on RH molecule. We attribute this enhancement to singlet-triplet transition in RH enhanced by presence of nearby O2 molecule in van der Waals complex RH–O₂. The O₂-assisted enhancement of $T_1 \leftarrow S_0$ absorption was first revealed for aromatic hydrocarbons by Evans [15] who observed the appearance of singlet-triplet absorption bands in presence of oxygen at a pressure up to about 100 atm. Similar approach allowed Evans to reveal $T_1 \leftarrow S_0$ absorption for unsaturated hydrocarbons including ethylene and butadiene [16]. Hoijtink attributed this enhancement to exchange interaction between RH and paramagnetic triplet O₂ molecules [17]. Minaev



Figure 2. (a–c) The part of mass spectra containing peak of O atom (m/z = 16) arising in photodissociation of oxygen (5%) with (0.4%) and without hydrocarbon in expanded mixture: (a)-ethylene, (b)-propylene, (c)-1,3-butadiene. (d–f) Pressure dependence of O⁺ ion amplitude provided by REMPI (2 + 1) at 225.65 nm of O(³P₂) atoms arising in experiments with molecular beam provided by expansion of the mixture shown on the graph. Coefficient tg α is the tangent of the angle of slope of the straight line obtained by fitting of the experimental data.

et al. carried out quantum-chemical calculations of this enhancement values for pairs $C_2H_4-O_2$ [18] and $C_6H_6-O_2$ [19]. For our case of van der Waals complexes RH-O₂ this process looks like

$${}^{3}({}^{1}RH - {}^{3}O_{2}) + h\nu \rightarrow {}^{3}({}^{3}RH^{*} - {}^{3}O_{2}) \rightarrow {}^{3}RH^{*} + {}^{3}O_{2}, \tag{3}$$

where ${}^{3}RH^{*}$ is vibrationally excited triplet RH molecule resulted from vertical excitation of ground state RH. Since vertical excitation (3) should leave triplet oxygen vibrationally unexcited the excitation should be localized on the hydrocarbon molecule that results in further dissociation

$${}^{3}\mathrm{RH}^{*} \to \mathrm{R} + \mathrm{H}.$$
 (4)

Similar excitation of triplet state of hydrocarbon can be provided due to transition in van der Waals complex $RH-O_2$ with simultaneous change of spin of partner molecules.

$${}^{3}({}^{1}RH - {}^{3}O_{2}) + h\nu \rightarrow {}^{3}({}^{3}RH^{*} - {}^{1}O_{2}) \rightarrow {}^{3}RH^{*} + {}^{1}O_{2}. \tag{5}$$

This transition is total spin allowed and is governed by near the same Frank–Condon factor for RH molecule excitation. It is only blue-shifted as compared with transition (3) by 0.977 eV due to energy gap for vertical excitation of oxygen into singlet $a^1\Delta_g$ state. In recent paper [6] transition (5) was concluded to be responsible for formation of $O_2(a^1\Delta_g)$ arising in UV-photoexcitation of van der Waals complexes X–O₂. In Table 1 energy gap for vertical excitation is presented for transitions of the types (3) and (5) in com-

plexes of RH molecules where O₂-assisted H atom yield enhancement was investigated. Presented values involve recommended values obtained by *ab initio* calculations [20] and based on experimentally observed spectral location of the maximum of singlet-triplet $T_1 \leftarrow S_0$ absorption band [21] as well as value for cyclohexane calculated *ab initio* in this Letter.

Overlapping of corresponding band with excitation wavelength (243.1 nm) and sufficiency of ³RH^{*} excitation level as compared with RH bond energy govern the role of transitions (3) and (5) in H atom photogeneration from complexes RH–O₂ at our wavelength. In process (3) the sum of electronic and vibrational excitation of RH molecule is equal to exciting quantum energy hv = 5.1 eV = 117.6 kcal/mol. In process (5) this excitation is less by 0.977 eV and equal to 95.1 kcal/mol.

4.1.2. Complex $C_2H_4-O_2$

Excitation energy higher than bond dissociation energy (BDE) for ethylene $D_{298}^0 = 111.2 \pm 0.8$ kcal/mol can be provided by transition (3) and not by (5). Spectra of transitions (3) and (5) in van der Waals complexes X–O₂ should be similar to those in encounter complexes X–O₂ observed in gaseous phase or in liquids containing dissolved oxygen. For RH=C₂H₄ the identified part of transition (3) is located spectrally in region of 270–350 nm [16] and is composed of progression of vibronic subbands with average spacing of 990 cm⁻¹ governed by C–C stretching vibration in T₁ triplet state [22]. Energy gap ΔE_{vert} for singlet-triplet T₁ \leftarrow S₀ vertical excitation



Figure 3. Backing pressure dependence of H^* ion amplitude provided by REMPI (2 + 1) at 243.13 nm of H atoms arising in experiments with molecular beam provided by expansion of mixture RH(0.4%)+O₂(5%)+He shown on the graph. Coefficient tg α is the tangent of the angle of slope of the straight line obtained by fitting of the experimental data.



Figure 4. The part of mass-spectrum of fragments arising in photodissociation of deuterated cyclohexane C_6D_{12} (0.4%) with (5%) and without oxygen in expanded mixture. Excitation wavelength is 243.09 nm which corresponds to maximum of REMPI (2 + 1) line of D atoms (m/z = 2). Signal at m/z = 1 corresponds to H atoms existing in background.

presented in Table 1 indicates the position of maximum for this band to be at about 275 nm (hv = 4.5 eV). Wavelength 243.1 nm (hv = 5.1 eV) used in our Letter is shifted from this maximum by 0.6 eV. In absorption spectrum of $C_2H_4-O_2$ at about 270 nm the red wing of other band starts [22] which has spacing between vibronic subbands similar to that for $T_1 \leftarrow S_0$ band [23] but higher oscillator strength. We attribute this band to transition (5). This band masks the blue wing of transition (3) absorption. But near 1 eV total width (275–350 nm) of red wing of transition (3) allows us to expect similar width for blue wing. So we can expect that transition (3) still contributes to absorption of complex C₂H₄-O₂ at our excitation wavelength and gives rise to processes (3)-(4) providing enhanced generation of H atoms. Excitation of C₂H₄ molecule in the processes (3) or (5) provides triplet ethylene with vibrational excitation of C-C stretching vibration. Further dissociation via the rupture of C-H bond needs preliminary intramolecular vibrational redistribution. So the dissociation of ${}^{3}C_{2}H_{4}^{*}$ is expected to be not prompt. That is why the velocity map image of H atoms has no anisotropic features.

The results from literature on ab initio calculations for pair $C_2H_4-O_2$ allow us to estimate the maximum expected factor of H atom yield enhancement provided by suggested mechanism for the case of complex RH-O₂ as compared with the 'free' RH molecule. Minaev et al. [18] calculated the oscillator strength f for transition (3) in pair C₂H₄-O₂ as a function of intermolecular distance as well as oscillator strength for singlet-triplet transition in the free ethylene molecule ($f = 10^{-9}$). We have calculated equilibrium intermolecular distance in vdW complex $C_2H_4-O_2$ to be equal to 3.75 Å. The calculated oscillator strength for the pair $C_2H_4-O_2$ at the close distance of 3.6 Å is calculated by Minaev et al. to be $f = 4.5 \times 10^{-6}$ [18]. The Frank-Condon factors for singlet-triplet absorption $(T_1 \leftarrow S_0)$ in ethylene molecule when it is free or bound in complex $C_2H_4-O_2$ should have similar spectral profile. So in complex the singlet-triplet absorption cross-section should be enhanced by a factor of about 10⁴ corresponding to the ratio of oscillator strength values. This level of H yield enhancement could be observed with binding in complexes RH-O₂ of all RH molecules in the beam and complete subtraction of background contribution to H atom yield.

4.1.3. Complex $C_3H_6-O_2$

Recommended value of room temperature BDE for weakest C–H bond in propylene ($CH_2=CHCH_2-H$) is given in Handbook [13] to be of 88.2 ± 0.7 kcal/mol. This means that both transitions (3) and (5) at our excitation wavelength can provide excitation of C_3H_6 molecule sufficient for dissociation giving rise to H atoms. As it is seen from Table 1 the center of transitions (3) and (5) in complex of propylene $C_3H_6-O_2$ should be shifted slightly to the red as compared with those for complex of ethylene. We cannot exclude that transition (3) still contributes to H atom photogener-

Molecule RH	$\Delta E_{vert}({}^{3}RH \leftarrow {}^{1}RH)$ (eV) transition (3)	$\begin{array}{l} \Delta E_{vert} \\ ({}^{3}RH \leftarrow {}^{1}RH) \text{+} \ \Delta E_{vert} \ ({}^{1}O_{2} \leftarrow {}^{3}O_{2}) \\ (eV) \ transition \ (5) \end{array}$	H atom yield enhancement detected with $hv = 5.1 \text{ eV}$
C_2H_4	4.5 [20]	5.5	Yes
C ₃ H ₆	≈4.2 [21]	5.2	Yes
E-C ₄ H ₆	3.2 [20];	4.2	Yes
	$5.1(T_2 \leftarrow S_0)$ [20]	6.1	
C ₄ H ₈	≈4.1 [21]	5.1	Yes
C ₆ H ₁₂	7.1 (this Letter)	8.1	No

Table 1 The data on energy gap ΔE_{vert} for vertical transitions (3) and (5) in complexes of RH molecules and detected enhancement of H atom yield from van der Waals complex RH–O₂.

ation. And definitely we can expect contribution of process (5). UVphotodissociation of complex $C_3H_6-O_2$ was studied before with velocity map imaging of arising $O({}^3P_J)$ atoms [5]. According to arguments given in paper [6] the images from [5] indicate formation of singlet oxygen $O_2(a^1\Delta_g)$ after UV-excitation of $C_3H_6-O_2$ complex at 226 nm. This formation of singlet oxygen $O_2(a^1\Delta_g)$ was attributed to cooperative transition (5) in complex X-O₂ [6]. Closeness of that exciting radiation wavelength to that used in current Letter (243.1 nm) allows us to assume process (5) to occur in our excitation conditions as well.

4.1.4. Complex C₄H₆-O₂

Value of room temperature BDE for C-H bonds in butadiene (CH₂=CHCH=CH₂) can be estimated to be close to that for ethylene of about 111 kcal/mol. So only transition (3) and not (5) can provide formation of H atoms from complex $C_4H_6-O_2$. For butadiene absorption at both transitions (3) and (5) with excitation of RH in T₁ state are shifted to the red from exciting wavelength used (see Table 1). But process (3) with direct absorption to T_2 state should be accessible at the wavelength used. We believe also that transition (5) with excitation of RH in T₂ state and of oxygen in $a^1\Delta_{\rm g}$ state covers our excitation wavelength. In recent paper the formation of singlet oxygen in $a^1\Delta_g$ state was detected when van der Waals complex of isoprene with oxygen C₅H₈-O₂ was excited within the wavelength region of 213-260 nm [6]. This formation of singlet oxygen was attributed to channel ${}^{3}({}^{1}X-{}^{3}O_{2}) +$ $h\nu \rightarrow 3({}^{3}X(T_{2})-{}^{1}O_{2}(a {}^{1}\Delta_{g}))$ which corresponds to process (5). Taking into account that singlet-triplet transitions in isoprene and butadiene molecules have similar spectral locations [16] we believe that similar process (5) provides vibrationally excited butadiene ${}^{3}C_{4}H_{6}(T_{2})$ giving rise then to H atoms we observe.

4.1.5. Complex C₄H₈-O₂

As it is seen in Table 1 for 2-butene the center of absorption giving rise to process (5) coincides with excitation wavelength in our experiments. Recommended value of bond dissociation energy (BDE) at 298.15 K for weakest C-H bond in trans-2-butene (CH₃₋ CH=CHCH₂-H) is given in Handbook [13] to be of 85.3 kcal/mol which is less than energy of RH excitation in process (5).

4.1.6. Complex C₆D₁₂-O₂

The BDE value for C–H bonds in cyclohexane of 99.5 kcal/mol [13] is lower than excitation provided by transition (3). But we did not observe any O_2 -assisted enhancement of D atoms yield

and this correlates with very large shift of transition (3) to the blue from excitation wavelength used.

Finally we can attribute formation of hydrogen atoms resulted from excitation of van der Waals complexes $RH-O_2$ to decay of vibrationally excited triplet hydrocarbon ³RH* generated via processes (3) and/or (5) for complexes of unsaturated hydrocarbons under study. We expect that revealed O₂-assisted photoprocesses of hydrocarbons decomposition take place in the encounter complexes of oxygen with hydrocarbons $RH-O_2$ in gas and condensed phases.

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