



Cite this: *Phys. Chem. Chem. Phys.*,  
2015, 17, 28565

# Singlet oxygen photogeneration from X–O<sub>2</sub> van der Waals complexes: double spin-flip vs. charge-transfer mechanism

Alexey V. Baklanov,<sup>\*ab</sup> Alexandr S. Bogomolov,<sup>a</sup> Alexandra P. Pyryaeva,<sup>ab</sup>  
Georgii A. Bogdanchikov,<sup>ab</sup> Sergei A. Kochubei,<sup>c</sup> Zahid Farooq<sup>d</sup> and  
David H. Parker<sup>d</sup>

The channel of singlet oxygen O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) photogeneration from van der Waals complexes of oxygen X–O<sub>2</sub> has been investigated to discriminate between two possible mechanisms based on charge-transfer (CT) or double spin-flip (DSF) transitions. The results obtained in this work for complexes with X = ethylene C<sub>2</sub>H<sub>4</sub>, 1,3-butadiene C<sub>4</sub>H<sub>6</sub>, deuterated methyl iodide CD<sub>3</sub>I, benzene C<sub>6</sub>H<sub>6</sub> and water H<sub>2</sub>O and for those investigated previously indicate the DSF mechanism as a source of singlet oxygen. The formation of O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) is observed only when the energy of exciting quantum is sufficient for DSF transition. Universally detected low vibrational excitation of O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) arising in the photodissociation of van der Waals complexes X–O<sub>2</sub> indicates the DSF mechanism as its source. For complex of ethylene C<sub>2</sub>H<sub>4</sub>–O<sub>2</sub> *ab initio* calculations of vertical energy ΔE<sub>vert</sub> for DSF and CT transitions have been carried out. The positive results of singlet oxygen formation from C<sub>2</sub>H<sub>4</sub>–O<sub>2</sub> can be explained by the DSF but not by the CT mechanism.

Received 30th May 2015,  
Accepted 5th August 2015

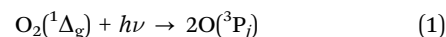
DOI: 10.1039/c5cp03129j

www.rsc.org/pccp

## 1 Introduction

The crucial effect of a weakly bound environment on the UV-photophysics and photochemistry of oxygen has been revealed in a series of studies of van der Waals complexes of oxygen X–O<sub>2</sub>.<sup>1–7</sup> Besides a dramatic increase in oxygen atom photogeneration yield<sup>1–6</sup> new photodissociation channels giving rise to singlet oxygen have been observed.<sup>5,6</sup> These channels have been revealed on the basis of the analysis of the velocity map images of oxygen atoms (<sup>3</sup>P<sub>j</sub>) appearing after UV photo-excitation of complexes X–O<sub>2</sub>. Among the revealed channels differing by kinetic energy and angular anisotropy of O atom recoil directions there was a channel with kinetic energy of O atoms equal to about 0.7 eV observed for complexes with partner molecules X = C<sub>3</sub>H<sub>6</sub>, CH<sub>3</sub>I and numbered as C5.<sup>5</sup> Formerly this channel was attributed to the photodissociation of a superoxide anion O<sub>2</sub><sup>–</sup> + hν → O(<sup>3</sup>P<sub>j</sub>) + O<sup>–</sup>, which was supposed to appear *via* excitation of a complex into a charge-transfer (CT) state X<sup>+</sup>–O<sub>2</sub><sup>–</sup> with further photodecomposition of CT by the same pulse X<sup>+</sup>–O<sub>2</sub><sup>–</sup> + hν → X<sup>+</sup> + O<sub>2</sub><sup>–</sup>.<sup>5</sup> Oxygen atoms with a similar image

have been later observed to appear after photodissociation of the complex of isoprene with oxygen C<sub>5</sub>H<sub>8</sub>–O<sub>2</sub>.<sup>6</sup> Two-laser arrangement of experiment in this case allowed us to testify the earlier assumption about the formation of ionic intermediates of O atoms in this C5 channel. This test definitely indicated the non-ionic character of the species being the precursor of O atoms with this kinetic energy. This conclusion allowed us to assume the singlet oxygen O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) to be this precursor. Its photodissociation at the used wavelength of 226 nm (Chamberlain continuum) proceeding *via* the process



should give oxygen atoms with energy coinciding with the measured values within experimental uncertainty. A similar image observed earlier for complexes X–O<sub>2</sub> with X = C<sub>3</sub>H<sub>6</sub>, CH<sub>3</sub>I in ref. 5 was also reinterpreted to be due to photodissociation of singlet oxygen *via* process (1).<sup>6</sup> This assignment is confirmed by the results recently published by Farooq *et al.*<sup>8</sup> who studied photodissociation of singlet oxygen with velocity map imaging. In that work singlet oxygen O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) was generated in a pulsed discharge. The images of the photofragment O atoms were found to be similar to those observed earlier<sup>5,6</sup> in photodissociation of complexes X–O<sub>2</sub>. Revealing process (1) indicates the formation of singlet oxygen O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) after UV-excitation of complexes X–O<sub>2</sub>. The fact that singlet oxygen in these three systems appears vibrationally cold was interpreted within a mechanism involving one-quantum supramolecular excitation

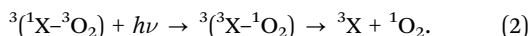
<sup>a</sup> Institute of Chemical Kinetics and Combustion, Institutskaya Str. 3, Novosibirsk 630090, Russia. E-mail: baklanov@kinetics.nsc.ru

<sup>b</sup> Novosibirsk State University, Pirogova Str. 2, Novosibirsk 630090, Russia

<sup>c</sup> Institute of Semiconductor Physics, ac. Lavrent'ev Ave., 13, Novosibirsk 630090, Russia

<sup>d</sup> Institute for Molecules and Materials, Radboud University Nijmegen, Toernooiveld 1, Heyendaalseweg 135, 6525 ED Nijmegen, The Netherlands

of the complex with a simultaneous change in spin states of partner molecules<sup>6</sup>



Here we define this process as a double spin-flip (DSF) transition. The van der Waals complex X-O<sub>2</sub> is a model of “oxygen in a molecular environment”. The latter can be an encounter complex in the gas phase or a “contact complex” in the condensed phase. We can expect the same mechanism of singlet oxygen photogeneration to take place universally in gas or condensed phases containing oxygen.

After the work by Evans<sup>9</sup> it is known that in the spectra of various solvents containing dissolved oxygen new absorption bands appear which were not observed in individual oxygen or solvent under study. For aromatic molecules<sup>10</sup> and unsaturated hydrocarbons<sup>11</sup> containing oxygen two new bands are observed with one of these identified to be a singlet-triplet transition T ← S in solvent molecules enhanced by interaction with oxygen. A more intense band shifted to the blue was assigned by Tsubomura and Mulliken to be due to transitions into a charge-transfer (CT) state of a “contact complex” X-O<sub>2</sub>.<sup>12</sup> Ogilby and coauthors revealed that photogeneration of singlet oxygen resulted from the excitation of solvents containing oxygen within these CT bands.<sup>13–16</sup> Based on the assignment of these bands the charge-transfer state X<sup>+</sup>-O<sub>2</sub><sup>-</sup> of the contact complex has been concluded by these authors to be a source of singlet oxygen. These CT and DSF mechanisms should provide different photo-physics and photochemistry of singlet oxygen photogeneration.

In the current paper we have analyzed the data on singlet oxygen photogeneration in van der Waals complexes of oxygen X-O<sub>2</sub> to discriminate between these two mechanisms. Below the experimental data for several van der Waals complexes X-O<sub>2</sub> (X = ethylene C<sub>2</sub>H<sub>4</sub>, butadiene C<sub>4</sub>H<sub>6</sub>, benzene C<sub>6</sub>H<sub>6</sub>, deuterated methyl iodide CD<sub>3</sub>I, and water H<sub>2</sub>O) are presented. Then all new and earlier studied cases with positive and negative results of singlet oxygen observation are analyzed from the point of view of correspondence of the data to one of these mechanisms. For the complex of ethylene with oxygen the results of quantum chemical calculations for electronic excited states are also exploited for making a choice between these two mechanisms.

## Experiment

Two velocity map imaging setups have been used. The setup used in Nijmegen is similar to that one invented by Eppink and Parker.<sup>17</sup> The vacuum chamber was equipped with the pulsed solenoid valve (general valve) providing the generation of the molecular beam. The molecular beam passes through a 2 mm skimmer mounted 20 mm downstream from the nozzle and propagates further in the direction of the time-of-flight axis (on-axis arrangement). About 100 mm downstream from the nozzle the molecular beam passes through the hole in the repeller electrode and enters the region between the repeller and extractor electrodes, where photoexcitation takes place.

The frequency doubled radiation of a dye laser (Coumarin 47) pumped by the third harmonic of a Nd-YAG laser has been used for the generation of UV radiation with a pulse energy of about 1 mJ and a pulse duration of 5 ns. The radiation was focused using a lens with a focal distance of 20 cm. This radiation at 226.223 nm (hereafter λ<sub>vac</sub>) has been used simultaneously for excitation of the complex and for REMPI (2 + 1) of appearing O(<sup>3</sup>P<sub>0</sub>) atoms. This state was used for detection because the results obtained previously<sup>5,6</sup> definitely indicate a higher yield of it as compared with <sup>3</sup>P<sub>1</sub> and <sup>3</sup>P<sub>2</sub> states of O atoms arising in photodissociation of singlet oxygen. The second setup used in Novosibirsk is described elsewhere.<sup>18</sup> It differs by the use of off-axis arrangement where a molecular beam is directed perpendicular to the TOF axis. The supersonic beam has been generated using the home-made electrodynamic valve providing gas jet with a pulse duration of 200 μs. Premixed gas was expanded into the chamber through the 0.27 mm nozzle. Backing pressure was varied within the interval of 0.5–7 atm. The central part of the gas jet passed through the 2.5 mm skimmer mounted 60 mm downstream and got into the region of extracting electric field. In this region the pulsed laser UV radiation crossed the molecular beam at a right angle. This UV radiation (0.5 mJ in the pulse) has been produced as a second harmonic of a pulsed dye laser pumped by an excimer XeCl laser (308 nm, 100 mJ, 15 ns). Light was focused using a lens with a focus length of 25 cm. Again this radiation was used simultaneously for excitation of a complex and for (2 + 1) REMPI of O(<sup>3</sup>P<sub>0</sub>) (226.233 nm) atoms. The F2225-21P Micro-channel plate assembly (Hamamatsu) has been used as a two-dimensional detector of ions. The 2D images on the phosphor screen were recorded using a CCD camera with objective f = 2.5 cm and stored in a PC.

Van der Waals (vdW) complexes X-O<sub>2</sub> of substances X = ethylene C<sub>2</sub>H<sub>4</sub>, butadiene C<sub>4</sub>H<sub>6</sub>, deuterated methyl iodide CD<sub>3</sub>I, benzene C<sub>6</sub>H<sub>6</sub> and water H<sub>2</sub>O with oxygen have been generated *via* the expansion of a premixed gas mixture. The mixtures C<sub>6</sub>H<sub>6</sub> (0.1%) + O<sub>2</sub> (5%) + He at the backing pressure P = 2 bar, CD<sub>3</sub>I (0.26%) + O<sub>2</sub> (5%) + He at P = 1.5 bar, C<sub>4</sub>H<sub>6</sub> (0.9%) + O<sub>2</sub> (5%) + He at P = 1.2 bar, C<sub>2</sub>H<sub>4</sub> (1%) + O<sub>2</sub> (5%) + He at P up to 6 bar and H<sub>2</sub>O (0.15%) + O<sub>2</sub> (5%) + He at P = 2 bar were used.

## Details of *ab initio* calculations

Vertical energy (ΔE<sub>vert</sub>) necessary for double spin-flip (DSF) and charge-transfer transitions in the van der Waals complex C<sub>2</sub>H<sub>4</sub>-O<sub>2</sub> have been calculated *ab initio* for the most stable configuration of the complex. The planar configuration of C<sub>2v</sub> symmetry with both C<sub>2</sub>H<sub>4</sub> and O<sub>2</sub> molecules being in one plane and an O-O axis being parallel to a C-C bond of ethylene (“parallel” configuration) was found earlier with *ab initio* calculations to be most stable for complex C<sub>2</sub>H<sub>4</sub>-O<sub>2</sub>.<sup>7</sup> The distance between O-O and C-C axes in this configuration was found to be 3.75 Å. This geometry has been used for calculations of a vertical energy gap between the electronic ground and first CT states. The vertical energy of the charge-transfer transition in the van der Waals

complex  $C_2H_4-O_2$  has been calculated within the method of Complete Active Space involving 12 electrons and 10 molecular orbitals MP2 CAS(12,10)/CAS(12,10)/6-311++G(2d,2p) approach. Ten molecular orbitals include six orbitals of oxygen and four orbitals of ethylene. Orbitals of oxygen are the pair of bonding and antibonding  $\sigma$ -orbitals as well as two pairs of bonding and antibonding  $\pi$ -orbitals. Involved orbitals of ethylene are the pair of bonding and antibonding  $\sigma$ -orbitals as well as the pair of bonding and antibonding  $\pi$ -orbitals. The same approach has been applied for the calculation of energy necessary for the vertical double spin-flip transition in the complex. This approach has been tested with calculations of energetic characteristics for free partner molecules  $C_2H_4$  and  $O_2$ . Calculations have been carried out for transitions in free partner molecules, which are relevant to the supramolecular transitions in the complex  $C_2H_4-O_2$  under study. The results are presented in Table 3 together with the experimental data from literature. Good agreement of our calculated results with experimental data for neutral and ionic states of molecules involved indicates adequacy of the approach applied.

Then this approach has been applied for calculations of energy for excited states of the van der Waals complex  $C_2H_4-O_2$  responsible for supramolecular CT and DSF transitions to the states shown in two bottom rows in Table 1. The energy value of 7.7 eV for the CT transition corresponds to excitation to the lowest charge-transfer state. This state has a dipole moment of 16.6 Debye.

All calculations have been carried out with the use of a Gaussian 03 package.<sup>24</sup>

## Results and discussion

In Fig. 1 the images of  $O(^3P_0)$  atoms appearing after photoexcitation of van der Waals complexes of oxygen  $X-O_2$  ( $X = C_2H_4, CD_3I, C_4H_6, C_6H_6, H_2O$ ) and of free  $O_2$  molecules are presented. A one-to-one complex  $X-O_2$  is supposed to be a source of O atoms providing all images observed for complexes. For  $X = CD_3I$  and  $C_4H_6$  cases expansion conditions are similar to those used in experiments with  $CH_3I$ <sup>5</sup> and  $C_5H_8$ ,<sup>6</sup> respectively, where conclusions on a simple complex as a source of O atoms were made.

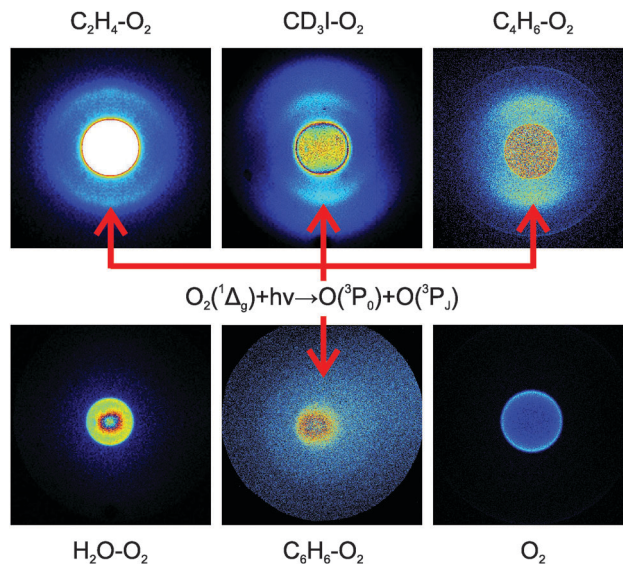


Fig. 1 Velocity map images of  $O(^3P_0)$  atoms appearing after photoexcitation of van der Waals complexes  $X-O_2$  at a wavelength of 226.233 nm. Arrows indicate the image of  $O(^3P_0)$  atoms arising in photodissociation of singlet oxygen  $O_2(^1\Delta_g)$  by the same laser pulse.

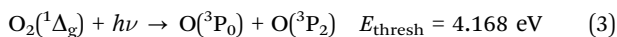
These earlier conclusions were based on the data for O atom signal dependence on stagnation-pressure and expanded mixture composition. Experiments with water and benzene complexes have been carried out under similar conditions but with even a smaller content of  $H_2O$  and  $C_6H_6$  in the expanded mixture. Reduction of oxygen content also did not affect the shape of these images. This allows us to think that the one-to-one complex is a source of O atoms in these cases as well. The same conclusion was made for the ethylene case in ref. 7. Dependence of the O atom signal on stagnation-pressure and expanded mixture composition allowed the authors to infer a simple complex  $C_2H_4-O_2$  to be a source of oxygen-enhanced photochemistry under the conditions similar to those used in the current work.<sup>7</sup> The images of complexes contain contributions of several dissociation channels with the kinetic energy of O atoms lower than the value of 0.19 eV for the dissociation of free  $O_2$ . These channels are similar to those observed earlier.<sup>5,6</sup>

Table 1 Results of *ab initio* calculations of energy for excited electronic states of the van der Waals complex  $C_2H_4-O_2$  as well as for relevant states of  $C_2H_4$  and  $O_2$  molecules and their ions

Molecule (symmetry)	State (symmetry)	$T_e$ , eV		$\Delta E_{vert}$ , eV	
		Calculated, this work	Experiment	Calculated, this work	Experiment
$O_2$ ( $D_{\infty h}$ )	$X^3\Sigma_g^-$	0	—	0	—
	$a^1\Delta_g$	0.98	0.982 (ref. 19)	0.98	—
	$b^1\Sigma_g^+$	1.64	1.636	1.73	—
	$2^1\Pi_g$	—0.45	—0.448 (ref. 20)	0.06	—
$O_2^-$	$2^1\Pi_g$	—	12.070 (ref. 21)	12.31	12.30 (ref. 22)
$O_2^+$	$2^1\Pi_g$	12.04	—	—	—
$C_2H_4$ ( $D_{2h}$ )	$S_0$ ( $^1A_g$ )	0	—	0	—
	$T_1$ ( $^3B_{1u}$ )	3.15 ( $D_{2d}$ ) <sup>a</sup>	—	4.45	4.6 (ref. 23)
	$S_0^+$ ( $^2B_{3u}$ )	10.64	10.51 (ref. 21, 22)	10.74	—
	$C_2H_4$ ( $S_0$ )- $O_2$ ( $^3\Sigma_g^-$ ) ( $^3B_1$ )	0	—	0	—
$C_2H_4-O_2$ ( $C_{2v}$ )	$C_2H_4$ ( $T_1$ )- $O_2$ ( $^1\Delta_g$ ) ( $^3A_2$ )	—	—	5.4	—
	$C_2H_4^+-O_2^-$ ( $^3A_2$ )	—	—	7.7	—
	$C_2H_4^+-O_2^-$ ( $^3A_2$ )	—	—	—	—

<sup>a</sup> Equilibrium geometry in the triplet state of ethylene corresponds to the  $D_{2d}$  symmetry point group.

A sharp highest energy channel with a kinetic energy of  $O(^3P_0)$  atoms equal to 1.93 eV observed in Fig. 1 for complexes  $C_4H_6-O_2$  is provided by the dissociation of molecular oxygen excited *via* the two-quantum process into a Schumann-Runge state:  $O_2 + 2h\nu \rightarrow O(^1D) + O(^3P)$ . This rather weak image takes place in oxygen itself.<sup>25</sup> Its contribution depends on the intensity of pumping radiation. It was seen better in experiments where the intensity was high enough due to higher laser pulse energy or harder focusing conditions. The smeared highest energy ring in  $CD_3I-O_2$  is supposed also to belong to this two-quantum excitation of  $O_2$  in complex. Its higher intensity in complex may be due to strong enhancement of this transition by intermolecular interaction in a complex. Enhancement of one-quantum transition in oxygen bound in complex with methyl iodide is very strong.<sup>5</sup> This enhancement can effect two-quantum excitation as well. In the current paper we are interested in one particular channel, which corresponds to photogeneration of singlet oxygen with its further photodissociation by the same pulse giving rise to  $O(^3P_0)$  atoms. The image of this channel is indicated by arrows in Fig. 1. It is changed in intensity for different complexes but it is definitely observed for complexes  $X-O_2$  with  $X = C_2H_4$ ,  $CD_3I$ ,  $C_4H_6$  and  $C_6H_6$ , but not for  $X = H_2O$ . Similar to the previous cases<sup>5,6</sup> the biggest relative contribution of this channel was observed when O atoms in the  $^3P_0$  state were detected. For all other channels the signal of O atoms dropped in the order  $^3P_2 > ^3P_1 > ^3P_0$ .<sup>5</sup> This indicates the similar nature of this channel for all cases where it was detected. In Fig. 2 kinetic energy distribution of  $O(^3P_0)$  atoms arising in this channel is shown. Measured average kinetic energy release (KER) values for  $O(^3P_0)$  atoms differ slightly for four complexes. The threshold energy value  $E_{\text{thresh}} = 4.168$  eV for photodissociation (3) giving rise to  $O(^3P_0)$  atoms



has been calculated with the use of a bond energy value for the  $O_2$  ground state of  $D_0(O-O) = 41268.6 \text{ cm}^{-1}$  (5.117 eV),<sup>26</sup> the value of the energy gap of  $7882.39 \text{ cm}^{-1}$  (0.977 eV) between  $\nu = 0$  levels of the ground state and the  $a^1\Delta_g$  state of  $O_2$ ,<sup>19</sup> and the energy of  $226.977 \text{ cm}^{-1}$  (0.028 eV) for the  $J = 0$  level of an O atom.<sup>27</sup> For our used excitation quantum energy  $h\nu = 5.480$  eV vibrationally unexcited singlet oxygen  $O_2(^1\Delta_g, \nu = 0)$  should give rise to  $O(^3P_0)$  atoms with a total kinetic energy release (TKER) equal to  $TKER_{\nu=0} = 1.312$  eV. This corresponds to  $KER = 0.656$  eV for an  $O(^3P_0)$  atom arising in process (3). Values of KER extracted from inverted velocity map images are given in the inserts in Fig. 2 and in Table 2. The level of vibrational excitation of  $O_2(^1\Delta_g)$  is calculated as an average number of vibrational quanta  $\nu_{O_2} = \frac{TKER - TKER_{\nu=0}}{\omega_e}$ , where TKER is equal to the doubled KER value given in Table 2. Vibrational wavenumber for  $O_2(^1\Delta_g)$  is equal to  $\omega_e = 1483.5 \text{ cm}^{-1}$  (0.181 eV).<sup>19</sup> The numbers obtained for four complexes under study are given in Table 2. There are also the numbers for the excitation level of singlet oxygen detected to appear from the complex of isoprene  $C_5H_8-O_2$  with  $KER = 0.74$  eV measured for channel C5 in the paper.<sup>6</sup> There are also the numbers for similar channels observed

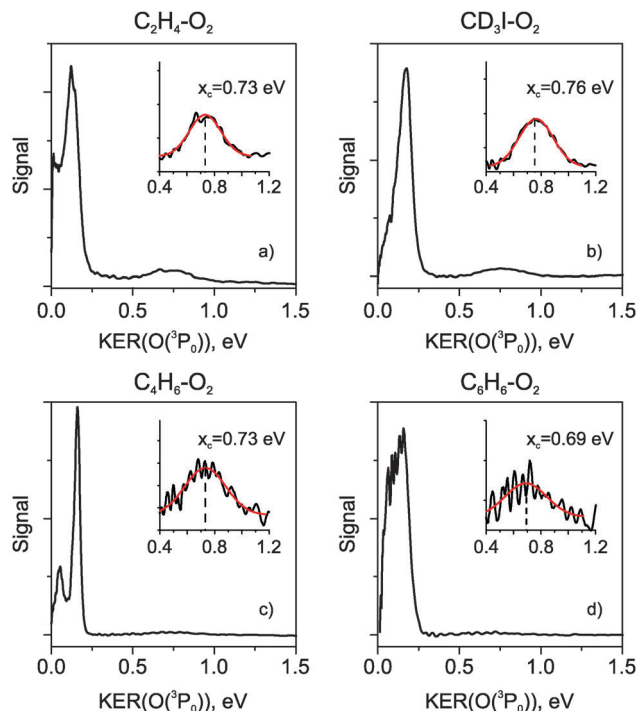
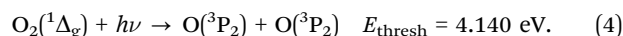


Fig. 2 Results of Abel inversion of images presented in Fig. 1. In the insets there are the values of average kinetic energy release (KER) for  $O(^3P_0)$  atoms arising in photodissociation of singlet oxygen  $O_2(^1\Delta_g)$ .

Table 2 Experimentally measured kinetic energy release (KER) values for  $O(^3P_j)$  atoms and calculated corresponding vibrational excitation of singlet oxygen  $O_2(^1\Delta_g)$  appearing after photoexcitation of van der Waals complexes  $X-O_2$

$X-O_2$	KER of $O(^3P_j)$ atoms, eV	$\nu_{O_2}$
$C_2H_4-O_2$	0.73 $\{O(^3P_0)\}$	$\leq 0.8$
$CD_3I-O_2$	0.76 $\{O(^3P_0)\}$	$\leq 1.1$
$C_4H_6-O_2$	0.73 $\{O(^3P_0)\}$	$\leq 0.8$
$C_6H_6-O_2$	0.69 $\{O(^3P_0)\}$	$\leq 0.3$
$CH_3I-O_2$	$0.69 \pm 0.02 \{O(^3P_2)\}$ (ref. 5)	$\leq 0.1 \pm 0.2$
$C_3H_6-O_2$	0.69 $\{O(^3P_2)\}$ (ref. 5)	$\leq 0.1$
$C_5H_8-O_2$	0.74 $\{O(^3P_0)\}$ (ref. 6)	$\leq 0.9$

for complexes of methyl iodide  $CH_3I-O_2$  and propene  $C_3H_6-O_2$  where these measurements were carried out for an O atom in the  $^3P_2$  state probed by (2 + 1) REMPI at 225.65 nm ( $h\nu = 5.495$  eV).<sup>5</sup> The channel of  $O(^3P_2)$  atom formation with  $KER = 0.69$  eV measured earlier<sup>5</sup> corresponds to a process analogous to (3)

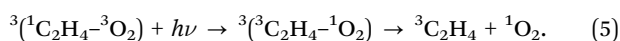


With this exciting quantum energy  $h\nu = 5.495$  eV KER values for  $O(^3P_2)$  atoms appearing in channel C5<sup>5</sup> correspond to  $\nu_{O_2} \approx 0.1$ . These numbers are also given in Table 2. The uncertainties given in this table correspond to the scattering of measured KER data in the series of experiments carried out under similar conditions. The sign less than or equal to ( $\leq$ ) in the results is used because there is a reason to expect that real vibrational excitation is even less than the measured value. There is some effect of Coulomb repulsion, which expands the image to some extent and so makes the measured KER values somewhat bigger



than the real ones. Laser radiation provides not only detected  $O^+$  ions seen in the images in Fig. 1 but some other ions as well. These extra ions can be due to an ionic background provided by photoionization of molecules existing in the chamber. For example isoprene  $C_5H_8$  and butadiene  $C_4H_6$  absorb in this wavelength region and produce parent and fragment ions  $C_nH_m^+$ , which are seen in the mass-spectrum of photoions. These ions contribute to Coulomb repulsion, which expands the image to some extent. When we increased the pulse energy fluence by harder focusing of laser radiation or increased concentration of molecules in the beam we observed an extension of the image size and an increase in extracted KER values. We have tried to reduce this effect with the reduction of exciting pulse energy but we cannot exclude that the excess of  $\nu_1O_2$  values over 0 are due to this Coulomb repulsion contribution. Anyway the results of O atom KER measurements presented in Table 1 allow us to conclude that singlet oxygen  $O_2(^1\Delta_g)$  is formed with small, if any, vibrational excitation.

This small excitation of singlet oxygen is in accordance with the double spin-flip (DSF) transition (2) as a source of singlet oxygen photogeneration from complexes  $X-O_2$ . In Fig. 3 the potential curves of the electronic states involved in the DSF transition for the complex  $C_2H_4-O_2$



are presented. In this transition excitation of both complex partners takes place. In the van der Waals complex the remote molecules X and  $O_2$  interact only weakly in the ground and in the excited states. Therefore the potential of  $O_2$  in complex should not differ essentially from that in free molecules. So the probability of the DSF transition to the state of complex with the resulting  $O_2(^1\Delta_g, \nu)$  state should correlate with the Franck-Condon (FC) factor of corresponding transition in a free  $O_2$  molecule. In Fig. 3 potential curves of the ground  ${}^3\Sigma_g^-$  and excited  ${}^1\Delta_g$  states of oxygen are shown and values of the FC factor for transitions to different vibrational levels of the  $O_2(^1\Delta_g)$  state calculated in ref. 28 are given. These numbers allow us to expect vibrationally unexcited  $O_2(^1\Delta_g)$  as a product of DSF process (5). If we do not neglect weak influence of the neighbor triplet molecule  $X(T_1)$  on the shape of the potential curve of  $O_2$  in the excited  ${}^1\Delta_g$  state, then some small vibrational

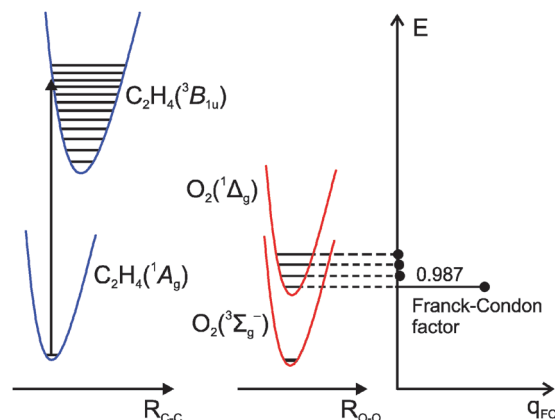


Fig. 3 Scheme of potential energy curves for the ground and excited electronic states of molecules  $C_2H_4$  and  $O_2$  participating in the double spin-flip (DSF) transition in the complex  $C_2H_4-O_2$  (see text). Arrows indicate “vertical” transitions. Coordinates  $R_{CC}$  and  $R_{OO}$  are “accepting” modes for shown transitions. On the right side the calculated values of the Franck-Condon factor ( $q_{FC}$ ) for transitions into different vibrational states of the singlet  ${}^1\Delta_g$  electronic state in a free  $O_2$  molecule are given.

excitation of  $O_2(^1\Delta_g)$  could be expected. The same conclusion can be extrapolated to DSF transitions in any complexes  $X-O_2$ . Experimental data given in Table 2 correspond to this expectation.

The list of van der Waals complexes where we detected the formation of singlet oxygen should be compared with the expectations based on the DSF mechanism of  $O_2(^1\Delta_g)$  production. First we should consider the excitation energy necessary to provide the DSF transition. The spectral maximum of the absorption band corresponding to DSF transition in the complex  $X-O_2$  should correspond to quantum energy  $h\nu_{max}$  approximately equal to the sum of energy gaps for “vertical” transitions  ${}^3X \leftarrow {}^1X$  and  ${}^1O_2 \leftarrow {}^3O_2$  in free X and  $O_2$  molecules ( $\Delta E_{vert}({}^3X \leftarrow {}^1X)$  and  $\Delta E_{vert}({}^1O_2 \leftarrow {}^3O_2)$ ). In Table 3 so calculated positions of DSF absorption maxima are given for all studied complexes. “Vertical” excitation energy  $\Delta E_{vert}({}^1O_2 \leftarrow {}^3O_2)$  for transition in oxygen  ${}^1\Delta_g \leftarrow X^3\Sigma_g^-$  is equal to an energy gap of 0.977 eV between  $\nu = 0$  levels of the ground state and the excited ( ${}^1\Delta_g$ ) state of  $O_2$ .<sup>19</sup> For values of “vertical” energy gap  $\Delta E_{vert}({}^3X \leftarrow {}^1X)$  the literature data obtained from spectroscopy or

Table 3 The estimated position of absorption maxima ( $h\nu_{max}$ ) for double spin-flip (DSF) transitions (2) in van der Waals complexes  $X-O_2$  under study and the results of singlet oxygen  $O_2$  ( ${}^1\Delta_g$ ) detection

Complex $X-O_2$	$\Delta E_{vert}({}^3X \leftarrow {}^1X)$ , eV	$h\nu_{max} \approx \Delta E_{vert}({}^3X \leftarrow {}^1X) + \Delta E_{vert}({}^1O_2 \leftarrow {}^3O_2)$ , eV	Detection of $O_2(^1\Delta_g)$ with exciting quantum energy $h\nu \approx 5.5$ eV
$C_2H_4-O_2$	4.5 (ref. 29)	5.5	YES
$C_3H_6-O_2$	$\approx 4.2$ (ref. 30)	5.2	YES
$C_4H_6-O_2$	3.2 (ref. 29); 5.1 ( $T_2 \leftarrow S_0$ ) (ref. 29)	4.2; 6.1	YES
$C_5H_8-O_2$	3.2; 5.1 ( $T_2 \leftarrow S_0$ ) <sup>a</sup>	4.2; 6.1	YES
$C_6H_6-O_2$	4.15 (ref. 29)	5.1	YES
$CH_3I-O_2$	4.4 (ref. 31)	5.4	YES
$CD_3I-O_2$	4.4 <sup>b</sup>	5.4	YES
$H_2O-O_2$	7.0 (ref. 32)	8.0	NO
$C_6H_{12}-O_2$	7.1 (ref. 7)	8.1	NO
$Xe-O_2$	8.4 $\{6s[3/2]_1\}$ (ref. 33)	9.4	NO

<sup>a</sup> Data for isoprene are taken to be the same as for butadiene  $C_4H_6$  from ref. 29. <sup>b</sup> Data for  $CD_3I$  are taken to be the same as for  $CH_3I$  from ref. 31.

calculated with methods of quantum chemistry have been used. In Table 3 experimental results of singlet oxygen detection are also presented. Comparison of these results with estimated values of  $h\nu_{\max}$  shows that singlet oxygen is observed only when excitation ( $h\nu \approx 5.5$  eV) takes place close to the spectral maximum ( $h\nu_{\max}$ ) expected for DSF absorption in van der Waals complexes X-O<sub>2</sub> under study. So we can conclude that the results obtained correspond to the expected ones for DSF transition (2) as a source of singlet oxygen.

For the complex of ethylene with oxygen C<sub>2</sub>H<sub>4</sub>-O<sub>2</sub> we have carried out quantum-chemical calculations of energy necessary to excite this complex into a lowest charge-transfer (CT) state C<sub>2</sub>H<sub>4</sub><sup>+</sup>-O<sub>2</sub><sup>-</sup>. The results of these calculations are given in Table 1. Calculated energy gaps for vertical CT and DSF transitions have been found to be equal to 7.7 eV and 5.4 eV, respectively. Earlier DeBoer *et al.* calculated the vertical energy for CT absorption in the complex C<sub>2</sub>H<sub>4</sub>-O<sub>2</sub> with the use of a (4,3)-CASSCF approach to be  $E_{\text{CT}} = 5.31$  eV.<sup>2</sup> Essential extension of active space together with MP2 correction in the method MP2 CAS(12,10) we used provides much more adequate approach and results in the increase in the  $E_{\text{CT}}$  value by about 2.4 eV. Our calculated *ab initio* value  $E_{\text{CT}} = 7.7$  eV has been used then to build the potential energy profiles for excited DSF and CT states of complex which are shown in Fig. 4. For the CT state the calculated value  $\Delta E_{\text{vert}} = 7.7$  eV was taken as a starting point corresponding to  $R_{\text{O-O}} = 1.2075$  Å which is equal to the equilibrium distance value for the O<sub>2</sub> ground state. The relative change in the potential along the  $R_{\text{O-O}}$  coordinate in C<sub>2</sub>H<sub>4</sub><sup>+</sup>-O<sub>2</sub><sup>-</sup> was taken to be corresponding to the potential curve for a free anion O<sub>2</sub><sup>-</sup> in its ground X<sup>2</sup>Π<sub>g</sub> state. The effect of a cation C<sub>2</sub>H<sub>4</sub><sup>+</sup> on this profile was neglected. The Morse curve presented for this state was built to be corresponding to the literature data for bond energy, geometry, and vibrational energy for O<sub>2</sub><sup>-</sup>(X<sup>2</sup>Π<sub>g</sub>).<sup>34</sup> For the DSF state the *ab initio* calculated value  $\Delta E_{\text{vert}} = 5.4$  eV has been used as a starting point. Then the relative change in

potential along the  $R_{\text{O-O}}$  coordinate in a <sup>3</sup>C<sub>2</sub>H<sub>4</sub>-<sup>1</sup>O<sub>2</sub> state was taken as a Morse curve for singlet oxygen corresponding to literature data for the O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) state.<sup>33</sup> Potential energy profiles in Fig. 4 definitely indicate that one-quantum excitation by radiation used ( $h\nu \approx 5.5$  eV) can provide the double spin-flip transition but not charge-transfer transition in the complex C<sub>2</sub>H<sub>4</sub>-O<sub>2</sub>.

Here we should repeat that the earlier assignment of the CT state of the X-O<sub>2</sub> complex to be a source of singlet oxygen formation was based on the CT assignment of corresponding absorption bands. We should mention here that in literature there was also an alternative idea of these band assignment. Dijkgraaf and Hoijtink considered this absorption in oxygen-saturated naphthalene to be due to “simultaneous” cooperative transition in the complex naphthalene-O<sub>2</sub> with simultaneous change in spin states of partner molecules.<sup>35</sup> This assignment was based on the value of separation of this band from the T ← S transition band. This separation was found to be equal to the energy of O<sub>2</sub> excitation (<sup>1</sup>Δ<sub>g</sub> ← <sup>3</sup>Σ<sub>g</sub><sup>-</sup>) into the singlet state. This “simultaneous” transition is just the double spin-flip transition in our notation (the first step of process (2)). Khalil and Kasha made a similar assignment of absorption bands for the complex C<sub>6</sub>H<sub>6</sub>-O<sub>2</sub> in solution by detecting excitation of phosphorescence of triplet benzene.<sup>36</sup> Minaev and coauthors calculated transition dipole moments for these “simultaneous” cooperative transitions in collisional complexes of C<sub>2</sub>H<sub>4</sub>-O<sub>2</sub><sup>37</sup> and C<sub>6</sub>H<sub>6</sub>-O<sub>2</sub>.<sup>38</sup> This assignment is in agreement with the DSF mechanism of singlet oxygen photo-generation from van der Waals complexes we conclude.

To estimate the strength of the DSF transition we do not have all necessary data. We can estimate the fraction of O atoms due to the DSF channel in the integral yield of O(<sup>3</sup>P<sub>j</sub>) atoms. This estimate gives from 0.1 to 1% for different complexes. To estimate the relative contribution of the DSF channel it is necessary to know the ratio of the yield of O(<sup>3</sup>P<sub>j</sub>) atoms appearing due to one-quantum absorption by “free” singlet oxygen (Chamberlain continuum) to the total yield of O atoms due to photoexcitation of the van der Waals complex X-O<sub>2</sub> under consideration. Absorption of singlet oxygen at 226 nm is concluded to be much stronger than absorption of the “free” ground state oxygen O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>).<sup>8</sup> And absorption at this wavelength in van der Waals complexes X-O<sub>2</sub> is much stronger than that in “free” O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>).<sup>1-7</sup> Both these last estimates are not quantitative.

Minaev *et al.* carried out *ab initio* CI calculations of transition-dipole-moment as a function of intermolecular distance for different transitions in the collisional complex C<sub>2</sub>H<sub>4</sub>-O<sub>2</sub>.<sup>36</sup> According to the results presented in Fig. 4 of that paper the cross-section of transition which we assign to be DSF is estimated to be less than the cross-section of other transition C<sub>2</sub>H<sub>4</sub>(S<sub>0</sub>)-O<sub>2</sub>(<sup>3</sup>Δ<sub>u</sub>) ← C<sub>2</sub>H<sub>4</sub>(S<sub>0</sub>)-O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) by about 10–20 times. The latter transition is the most intense one among transitions providing excitation of O<sub>2</sub> in complexes X-O<sub>2</sub> at 226 nm.<sup>5</sup> So it is possible to consider this result as an estimate of the relative contribution of DSF transition in the van der Waals complex C<sub>2</sub>H<sub>4</sub>-O<sub>2</sub>. We should mention that calculations in ref. 37 were

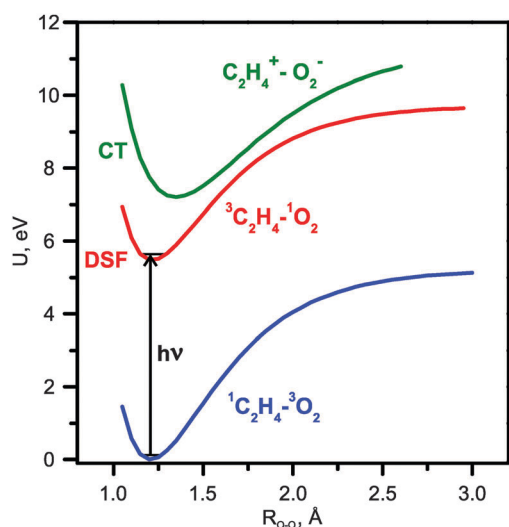
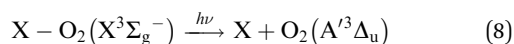


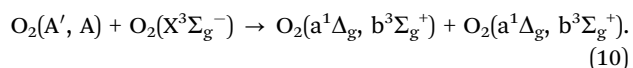
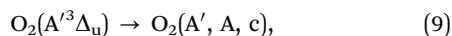
Fig. 4 Potential energy profiles of the electronic states excited via double spin-flip and charge-transfer transitions in a van der Waals complex of ethylene with oxygen C<sub>2</sub>H<sub>4</sub>-O<sub>2</sub> (see text).

carried out for intermolecular orientation in a  $C_2H_4-O_2$  pair different from configuration we have found most stable with calculations described in our manuscript. Minaev *et al.* carried out similar calculations for the collisional complex of benzene with oxygen as well.<sup>38</sup> Numbers taken from these calculations provide the estimate of contribution of the DSF transition to be at a level of 1% of oscillator strength of the strongest oxygen enhanced transition  $C_6H_4(S_0)-O_2(^3\Delta_u) \leftarrow C_6H_6(S_0)-O_2(^3\Sigma_g^-)$ . An interesting point is that in this paper the energy of CT states has been also calculated within the same approach. At the intermolecular distance value of 3.6 Å which is reasonable for van der Waals complexes the energy of the lowest CT state was found to be of 7.2 eV, that is much higher than the energy of 5 eV for the state responsible for DSF transition. So these results also indicate that the DSF process is not a result of direct excitation into the CT state of complex. Here we should mention that our experimental results have been obtained with an exciting quantum energy of 5.5 eV.

Not all earlier considered cases assigned to be due to CT excitation can be explained by the DSF transition. Scurlock and Ogilby observed the formation of  $O_2(^1\Delta_g)$  in oxygenated cyclohexane at 266 nm ( $h\nu = 4.66$  eV).<sup>14</sup> But for the van der Waals complex of cyclohexane with oxygen  $C_6H_{12}-O_2$  the formation of singlet oxygen was not detected at 226 nm and according to the energetic reasons the contribution of the DSF mechanism for this complex is impossible in the UV region (see Table 3). We can explain the photogeneration of singlet oxygen in oxygenated cyclohexane by the mechanism recently concluded to take place in the gas phase with the participation of the encounter complexes of oxygen  $X-O_2$  ( $X = O_2, N_2, C_5H_8$ ).<sup>39-41</sup> This mechanism involves enhanced UV-absorption within Herzberg bands of  $O_2$ . Enhanced absorption into the Herzberg III state of oxygen in complexes  $X-O_2$



is followed by collisional formation of singlet oxygen *via* processes



Eqn (9) describes fast collisional equilibration between nearby lying Herzberg states ( $A^3\Sigma_g^+$ , ( $c^1\Sigma_g^-$ ) and ( $A'^3\Delta_u$ ). Spectral profiles of enhanced absorption in  $O_2$  within Herzberg bands look similar to absorption in “free” oxygen molecules but enhanced absorption in complex  $X-O_2$  (an encounter complex in the gas phase or a “contact” complex in the condensed phase) is more intense by several orders of magnitude.<sup>42-44</sup> A characteristic feature of the latter mechanism is a similarity of an enhanced absorption spectrum to that of “free” oxygen with the location of the red-side limit of absorption at about 290 nm which is characteristic for Herzberg absorption in oxygen. This is the case for absorption in oxygen-saturated cyclohexane.<sup>14</sup> In van der Waals complexes  $X-O_2$  enhanced Herzberg absorption is observed for all studied complexes including the case of

$C_6H_{12}-O_2$ .<sup>5</sup> But under the conditions of molecular beam experiment the secondary process (10) is impossible. That is why mechanisms (8)–(10) do not work in a molecular beam. Molecules of oxygen excited into the Herzberg state *via* process (8) in the solvent can then collide with the dissolved ground state  $O_2$  molecules giving rise to singlet oxygen in a process (10) discussed by Trushina *et al.*<sup>40</sup> for the gas phase. This should universally take place in the gas or condensed phase in the spectral region of Herzberg absorption at wavelengths below 290 nm. This mechanism can be responsible for singlet oxygen photogeneration in aliphatic hydrocarbons saturated with oxygen<sup>14</sup> and for the photodegradation of nanocrystal quantum dots in hexane in real-world technologies.<sup>45</sup>

## Conclusions

The results of the detection of singlet oxygen  $O_2(a^1\Delta_g)$  arising from photodissociation of van der Waals complexes of oxygen  $X-O_2$  have been used to discriminate between two earlier suggested mechanisms of its formation. One of them involves supramolecular excitation of the complex with simultaneous change in spin states of partner molecules. We name this excitation here as a double spin-flip (DSF) transition. Another mechanism suggested earlier in literature involves excitation of the complex into a charge-transfer (CT) state  $X^+-O_2^-$  with its further decay resulting in  $O_2(a^1\Delta_g)$  formation. The list of cases where singlet oxygen appearance was detected ( $X =$  ethylene  $C_2H_4$ , propylene  $C_3H_6$ , butadiene  $C_4H_6$ , isoprene  $C_5H_8$ , benzene  $C_6H_6$ , methyl iodide  $CH_3I$  and its deuterated analogue  $CD_3I$ ) and where it was not detected ( $X =$  cyclohexane  $C_6H_{12}$ , water  $H_2O$  and xenon  $Xe$ ) strongly correlates with that expected for the DSF mechanism.

The fact that singlet oxygen detected is always vibrationally cold corresponds directly to that expected for DSF transitions in complexes  $X-O_2$ .

For the complex of ethylene  $C_2H_4-O_2$  *ab initio* calculations of vertical energy  $\Delta E_{\text{vert}}$  for DSF and CT transitions have been carried out. The calculated values of  $\Delta E_{\text{vert}}$  allow us to make direct choice between two mechanisms in favor of DSF transition as a source of singlet oxygen appearance from the van der Waals complex  $C_2H_4-O_2$ .

Explanation is also given for the illusory contradiction between the absence of singlet oxygen UV-photogeneration from van der Waals complexes of cyclohexane  $C_6H_{12}-O_2$  in molecular beam and the presence of  $O_2(a^1\Delta_g)$  UV-photogeneration in liquid cyclohexane saturated with oxygen described in literature. The energy of exciting quantum is not sufficient to provide the DSF transition in this complex. The appearance of singlet oxygen in liquid is provided by other mechanism suggested recently to explain singlet oxygen photogeneration observed in experiments at the elevated pressure of oxygen. It involves collision-induced absorption by oxygen with transition into the Herzberg III state  $O_2(A'^3\Delta_u)$  followed by triplet–triplet annihilation in collision with the ground state oxygen  $O_2(X^3\Sigma_g^-)$  giving rise to singlet oxygen. In experiments with van der Waals complexes  $X-O_2$  in molecular

beam enhanced absorption into the Herzberg state also takes place but the secondary collisional processes are excluded. This two-step mechanism should universally contribute to the generation of singlet oxygen when oxygen-containing medium is irradiated within the spectral range of Herzberg absorption below 290 nm.

The universal applicability of the DSF mechanism as a source of singlet oxygen photogeneration in van der Waals complexes of oxygen X-O<sub>2</sub> allows us to make general conclusion about singlet oxygen photogeneration in oxygen-containing media. We can conclude that the double spin-flip mechanism is usually responsible for UV-photogeneration of singlet oxygen in earlier studied systems where the charge-transfer mechanism was postulated. With excitation below 290 nm the mechanism based on collision-enhanced excitation into the Herzberg state of oxygen can also contribute.

## Acknowledgements

The financial support of this work by Russian Foundation for Basic Research (Grant No 12-03-00170-a) and NWO Russia-Netherlands Cooperative Research Grant 047.009.001 is gratefully acknowledged.

## References

- 1 G. DeBoer and M. A. Young, *J. Chem. Phys.*, 1997, **106**, 5468–5477.
- 2 G. DeBoer, A. Preszler Prince and M. A. Young, *J. Chem. Phys.*, 2001, **115**, 3112–3120.
- 3 A. Giardini Guidoni, A. Paladini, M. Veneziani, R. Naaman and T. M. Di Palma, *Appl. Surf. Sci.*, 2000, **154**, 186–191.
- 4 B. F. Parsons and D. W. Chandler, *J. Phys. Chem. A*, 2003, **107**, 10544–10553.
- 5 A. V. Baklanov, G. A. Bogdanchikov, K. V. Vidma, D. A. Chestakov and D. H. Parker, *J. Chem. Phys.*, 2007, **126**, 124316.
- 6 K. V. Vidma, P. W. J. M. Frederix, D. H. Parker and A. V. Baklanov, *J. Chem. Phys.*, 2012, **137**, 054305.
- 7 A. V. Baklanov, A. S. Bogomolov, L. M. Chikishev, G. A. Bogdanchikov and S. A. Kochubei, *Chem. Phys. Lett.*, 2013, **558**, 25–30.
- 8 Z. Farooq, D. A. Chestakov, B. Yan, G. C. Groenenboom, W. J. van der Zande and D. H. Parker, *Phys. Chem. Chem. Phys.*, 2014, **16**, 3305–3316.
- 9 D. F. Evans, *J. Chem. Soc.*, 1953, 345–347.
- 10 D. F. Evans, *J. Chem. Soc.*, 1957, 1351–1357.
- 11 D. F. Evans, *J. Chem. Soc.*, 1960, 1735–1745.
- 12 H. Tsubomura and R. S. Mulliken, *J. Am. Chem. Soc.*, 1960, **82**, 5966–5974.
- 13 R. D. Scurlock and P. R. Ogilby, *J. Am. Chem. Soc.*, 1988, **110**, 640–641.
- 14 R. D. Scurlock and P. R. Ogilby, *J. Phys. Chem.*, 1989, **93**, 5493–5500.
- 15 M. Kristiansen, R. D. Scurlock, K.-K. Iu and P. R. Ogilby, *J. Phys. Chem.*, 1991, **95**, 5190–5197.
- 16 P.-G. Jensen, J. Arnbjerg, L. P. Tolbod, R. Toftegaard and P. R. Ogilby, *J. Phys. Chem. A*, 2009, **113**, 9965–9973.
- 17 A. T. J. B. Eppink and D. H. Parker, *Rev. Sci. Instrum.*, 1997, **68**, 3477–3484.
- 18 A. S. Bogomolov, B. Grüner, S. A. Kochubei, M. Mudrich and A. V. Baklanov, *J. Chem. Phys.*, 2014, **140**, 124311.
- 19 K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (data prepared by J. W. Gallagher and R. D. Johnson, III) in *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, ed. P. J. Linstrom and W. G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, <http://webbook.nist.gov>, retrieved September 19, 2014.
- 20 J. E. Bartmess, Negative Ion Energetics Data, in *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, ed. P. J. Linstrom and W. G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, <http://webbook.nist.gov>, retrieved September 19, 2014.
- 21 S. G. Lias, Ionization Energy Evaluation, in *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, ed. P. J. Linstrom and W. G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, <http://webbook.nist.gov>, retrieved September 19, 2014.
- 22 K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki and S. Iwata, Ionization energies, ab initio assignments, and valence electronic structure for 200 molecules, *Handbook of HeI Photoelectron Spectra of Fundamental Organic Compounds*, Japan Scientific Soc. Press, Tokyo, 1981.
- 23 A. J. Merer and R. S. Mulliken, *Chem. Rev.*, 1969, **69**, 639–656.
- 24 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03 (Revision C.02)*, Gaussian Inc., Wallingford, CT, 2004.
- 25 B. Buijsse, W. J. van der Zande, A. T. J. B. Eppink, D. H. Parker, B. R. Lewis and S. T. Gibson, *J. Chem. Phys.*, 1998, **108**, 7229–7243.



- 26 P. C. Cosby and D. L. Huestis, *J. Chem. Phys.*, 1992, **97**, 6108–6112.
- 27 Kramida, A., Ralchenko, Yu., Reader, J., and NIST ASD Team (2014), *NIST Atomic Spectra Database (ver. 5.2)*, National Institute of Standards and Technology, Gaithersburg, MD, <http://physics.nist.gov/asd>, accessed February 2015.
- 28 R. W. Nicholls, *J. Res. Natl. Bur. Stand., Sect. A*, 1965, **69A**, 369–373.
- 29 M. Schreiber, M. R. Silva, S. P. A. Sauer and W. Thiel, *J. Chem. Phys.*, 2008, **128**, 134110.
- 30 M. Itoh and R. S. Mulliken, *J. Phys. Chem.*, 1969, **73**, 4332–4334.
- 31 A. B. Alekseyev, H. P. Liebermann, R. J. Buenker and S. N. Yurchenko, *J. Chem. Phys.*, 2007, **126**, 234102.
- 32 G. A. Garcia, L. Nahon and I. Powis, *Rev. Sci. Instrum.*, 2004, **75**, 4989–4996.
- 33 A. A. Radzig and B. M. Smirnov, *Reference Data on Atoms, Molecules, and Ions*. Springer Series in Chemical Physics, Springer, Berlin, 1985, vol. 31.
- 34 K. M. Ervin, I. Anusiewicz, P. Skurski, J. Simons and W. C. Lineberger, *J. Phys. Chem. A*, 2003, **107**, 8521–8529.
- 35 C. Dijkgraaf and G. J. Hoijtink, *Tetrahedron*, 1963, **19**(Suppl. 2), 179–187.
- 36 G. D. Khalil and M. Kasha, *Photochem. Photobiol.*, 1978, **28**, 435–441.
- 37 B. F. Minaev, V. V. Kukueva and H. Ågren, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 1479–1486.
- 38 B. F. Minaev, K. V. Mikkelsen and H. Ågren, *Chem. Phys.*, 1997, **220**, 79–94.
- 39 A. P. Trushina, V. G. Goldort, S. A. Kochubei and A. V. Baklanov, *Chem. Phys. Lett.*, 2010, **485**, 11–15.
- 40 A. P. Trushina, V. G. Goldort, S. A. Kochubei and A. V. Baklanov, *J. Phys. Chem. A*, 2012, **116**, 6621–6629.
- 41 A. P. Pyryaeva, V. G. Goldort, S. A. Kochubei and A. V. Baklanov, *Chem. Phys. Lett.*, 2014, **610**, 8–13.
- 42 Y. Oshima, Y. Okamoto and S. Koda, *J. Phys. Chem.*, 1995, **99**, 11830–11833.
- 43 G. Y. Zelikina, V. V. Bertsev, A. P. Burtsev and M. B. Kiseleva, *Opt. Spectrosc.*, 1996, **81**, 751–756.
- 44 G. Y. Zelikina, M. B. Kiseleva, A. P. Burtsev and V. V. Bertsev, *Opt. Spectrosc.*, 1998, **85**, 520–524.
- 45 V. W. Manner, A. Y. Kuposov, P. Szymanski, V. I. Klimov and M. Sykora, *ACS Nano*, 2012, **6**, 2371–2377.