

The Stability of the Pheromones of Xylophagous Insects to Environmental Factors: An Evaluation by Quantum Chemical Analysis

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Abstract—The ground and excited states of the pheromone molecules produced by xylophagous insects (the bark beetle *Ips typographus* L., the black fir sawyer beetle *Monochamus urussovi* Fisch., and the black pine sawyer *M. galloprovincialis* Oliv.) were modeled using a quantum chemical method utilizing DFT (density functional theory) with the B3LYP functional. The absorption wavelengths (energies) and dipole moments were calculated; the transitions of electrons from occupied to empty molecular orbitals were considered. The computed data were used to assess the stability of pheromone molecules exposed to environmental factors, such as solar radiation and humidity.

Keywords: insects, xylophages, pheromones, molecules, chemical properties, environment, impact, information, research, effectiveness

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Xylophagous insects, which live under tree bark and damage tree trunk, branch, and root phloem and xylem, are a widespread and economically significant group of forest insects. The lifecycle of xylophages consists of the search for trees that are suitable for larvae to grow, attraction of individuals of the opposite sex, mating, and egg laying under the tree bark by females. Males search for trees suitable for living; once the habitat is found, the male produces a specific pheromone, thereby attracting both females and other males for a cooperative attack on the tree [1, 2].

The system of pheromone communication comprises the stages of pheromone synthesis and release by the source individual; pheromone spreading in the air; perception of a pheromone signal by other individuals; and decision making on the selection of the direction of movement by these individuals. The main directions in the research on pheromone communication are identification of chemical compositions of pheromone mixtures and the ratio of the components [3–5]; elaboration of methods for synthesis of pheromones [6]; design and improvement of pheromone traps [7, 8]; development of models that simulate

insect behavior [9–11], and studies of the structure of insect receptors and description of the mechanisms that underlie their interaction with pheromone molecules [12, 13]. The chemical composition of pheromones has been determined so far for a large number of insect species [14]. However, the details of the mechanism that insects use when searching for the source of pheromone signal are still rather vague. Pheromone molecules can spread with air flows for several kilometers from the source insect to the signal recipient [15]. In the process, pheromones interact with some substances in the air, are exposed to environmental factors (solar radiation and temperature), and can be absorbed on various surfaces.

The effectiveness of pheromone communication is determined by how the recipient individual perceives the corresponding molecules [16–18]. For the pheromone molecule to be trapped at a relatively long distance from the source individual, the lifespan of such molecules should be rather long. On the one hand, if the molecules are too stable they can change the direction of their movement several times while migrating with turbulent air flows. In this case, the recipient

individual will not get adequate information about the location of the source individual. Thus, an excessively stable molecule will generate noise in the receptors of the recipient.

Presumably, evolutionary development has led to the situation that the pheromone molecules of the existing insect species have specific physicochemical properties that allow the minimization of both the fading of the pheromone signal associated with degradation of pheromone molecules and the information noise, as finally determined by the resistance of these molecules to environmental factors [19–21].

However, the instrumental physicochemical analysis of pheromone molecules is a technically complex and organizationally unfeasible problem; thus, quantum chemical methods were used in this study to obtain the main characteristics of pheromone molecules. Many factors act on the pheromone molecules, including wind, temperature, humidity, and solar radiation. Analysis of the calculated physicochemical properties of molecules will make it possible to determine which particular factors can lead to deactivation of pheromones because of the changes in their atomic structure.

The effect of solar radiation on pheromone molecules is that molecules can pass to an excited state, where the atomic structure can be changed via complete degradation. The possibility of interaction between pheromone molecules and water in the air is determined by the value and direction of the dipole moment of the pheromone molecules. Quantum chemical computations make it possible to analyze the effects of these factors without using complex experimental methods.

RESEARCH OBJECTS

Pheromones of three xylophagous insects, that is, bark beetle *Ips typographus* L., black fir sawyer beetle *Monochamus urussovi* Fisch., and black pine sawyer *Monochamus galloprovincialis* Oliv., were selected as the objects for his study. The bark beetle is one of the most serious spruce pests and is ubiquitous in Western and Eastern Europe [22–24]. The black fir sawyer beetle is spread over the entire forest area of temperate latitudes from Finland and Belarus to Mongolia, China, Japan, and Magadan oblast. In European Russia, this species is highly abundant in the northern forest zone and comparatively low abundant in the south of the country. The foci of black fir sawyer beetle mass reproduction have been recorded only in Siberia and only on the Siberian fir [25]. The bark beetle larvae, which damages the phloem and wood, are the most harmful phase. In the foci of mass reproduction, the black fir sawyer beetle can affect viable trees [26–29]. The black pine sawyer lives in the coniferous forests of North America, Asia, and Europe mainly on trees that

have been already damaged by phylophagous insects, for example, the bordered white moth [30].

The larger part of the pheromone molecules produced by xylophagous species are terpenes [31, 32]. The pheromone of the bark beetle *I. typographus* L. consists of six components that belong to the class of alcohols, namely, 2-methyl-3-buten-2-ol, *cis*-verbenol, *trans*-verbenol, 2-phenylethanol, myrtenol, and *trans*-myrtenol [33, 34]. The pheromone of the black fir sawyer beetle consists of five substances (none of them contain oxygen): 1S- α -pinene, 1R- α -pinene, S-3-carene, R-limonene, and α -terpinolene [25]. The black pine sawyer pheromone consists of three major components, namely, ipsenol, α -pinene, and 2-methyl-3-buten-1-ol [35–37]. The structures of the corresponding molecules for xylophagous insects are shown in Fig. 1.

MATERIALS AND METHODS

The structures and properties of pheromone molecules were computed by the quantum chemical method utilizing the density functional theory (DFT), namely, the B3LYP functional [38–40] with the cc-pVDZ basis set of GAMESS [41]. Time-dependent (TD) DFT were used to compute the excited molecules [42, 43]. B3LYP is one of the most popular functionals; it provides high convergence of the computed parameters for organic compounds to the experimental data [44–46]. The correlation-consistent cc-pVDZ basis set makes it possible to adequately describe the bond lengths, bond angles, dipole moment, electron-density distribution, and other structural and spectral characteristics of organic molecules [47, 48]. The choice of the basis is determined by the studied objects, size of the system, nature of the substance, and computational capabilities. Note that the bases with a sufficient number of functions give similar results [49].

Since pheromones are spread in the air medium, the computations are performed for molecules in a gas phase. At the first stage, conformers of molecules that insignificantly differ in the mutual arrangement of atoms were simulated from the known pheromone chemical compositions of xylophagous insects [14]. The geometry was optimized for all conformers using B3LYP/cc-pVDZ; the absolute energy and dipole moment of molecules were computed and their atomic structures were assessed. The energy difference between the conformers did not exceed 5 kJ/mol; further computations were performed for the structures with a minimum energy. Absorption spectra were computed for the selected molecules by the TD-DFT method. The wavelength values that corresponded to the most intensive electron transitions, i.e., the largest oscillator strength, were selected from the spectra to analyze the properties of the studied molecules and their comparison to the specific behavioral features of insects. The resulting wavelengths and absorption energies can be regarded as sufficient for tran-

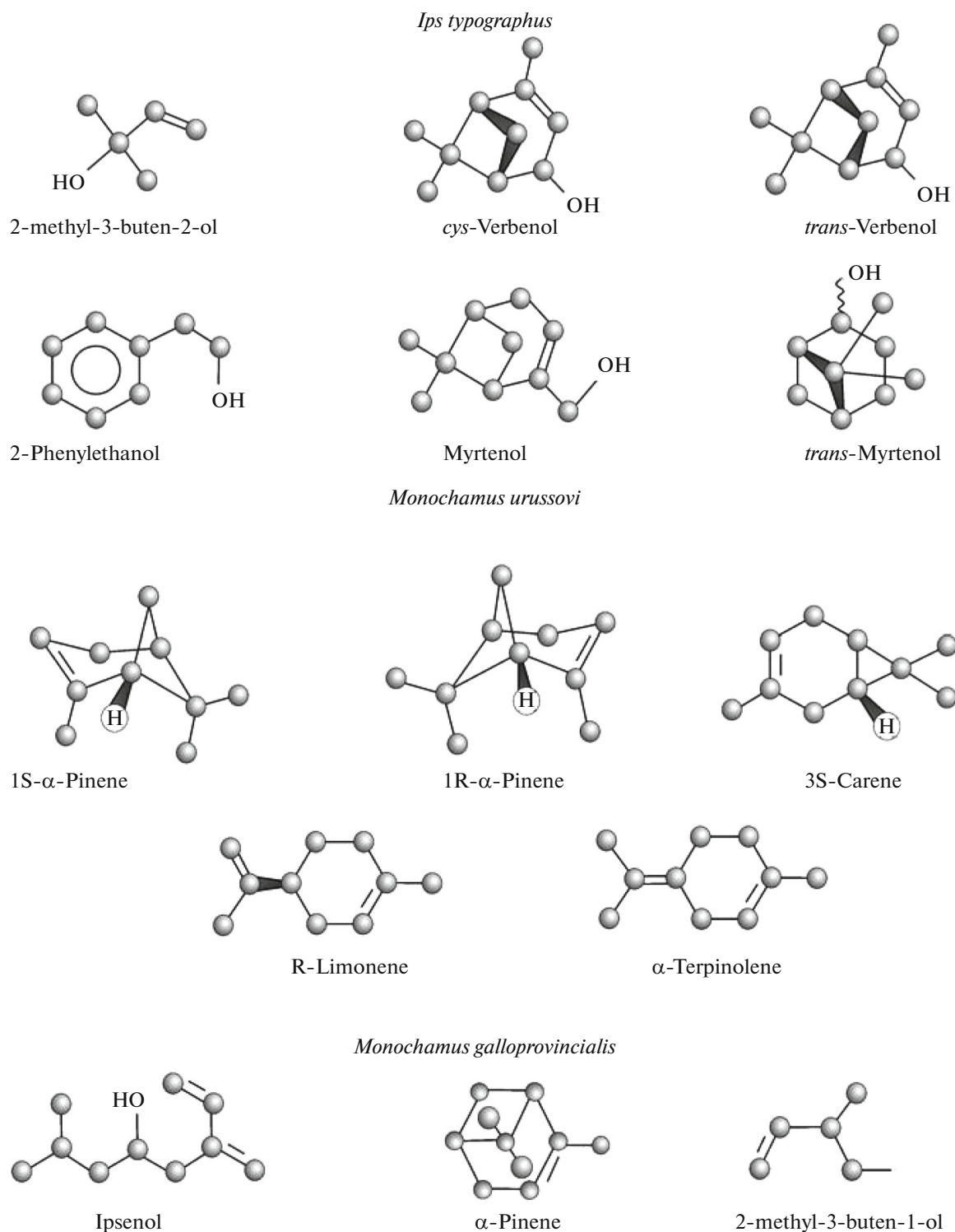


Fig. 1. The structural formulas of the pheromone molecules produced by the bark beetle *Ips typographus* L., black fir sawyer beetle *Monochamus urusovi* Fish., and black pine sawyer *M. galloprovincialis* Oliv.

sition of the molecules from a ground to an excited state. In order to assess how the energy absorption influences the structure of pheromones, the geometry in an excited state was optimized. Thus, the types and structural characteristics of the excited molecules were obtained.

RESULTS AND DISCUSSION

The values of the dipole moment for a pheromone molecule containing an oxygen atom fall into the range of 1.28–1.71 D (Table 1). The pheromones that

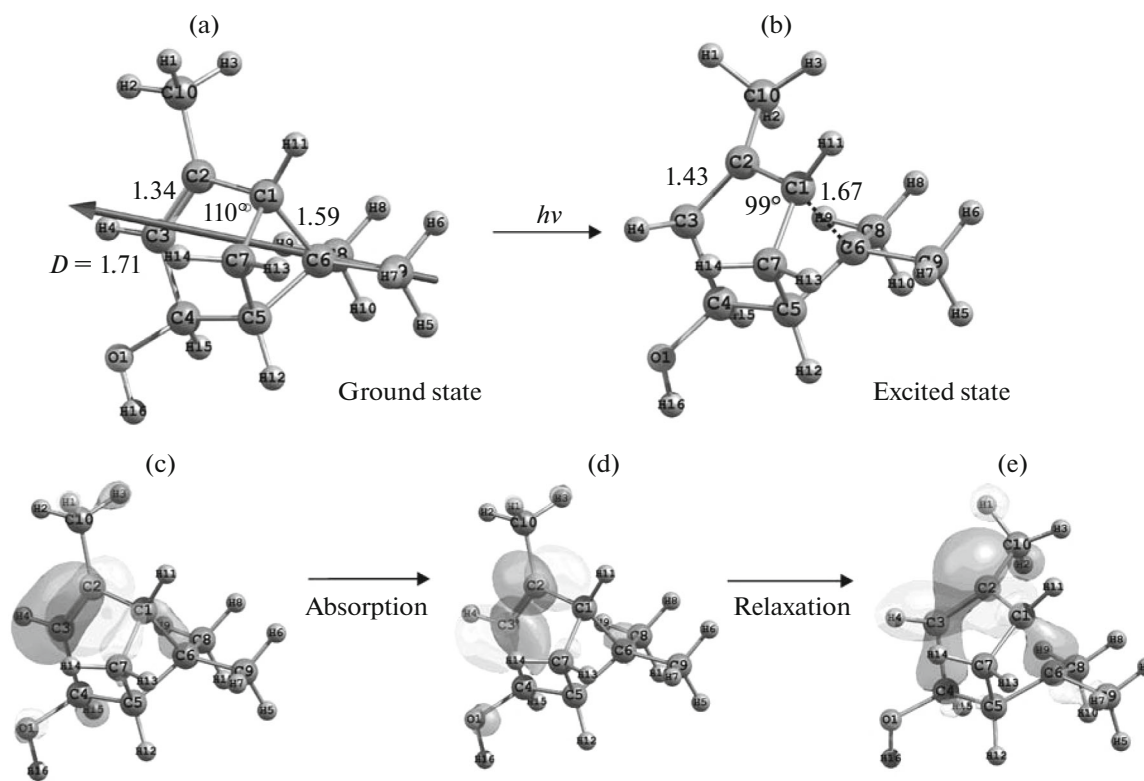


Fig. 2. The atomic structure of the *trans*-verbenol molecule in its (a) ground and (b) excited states; (c) the electronic structure of the upper occupied molecular orbital in the *trans*-verbenol molecule in its ground state; (d) electronic structure of the lower vacant molecular orbital in the *trans*-verbenol molecule; and (e) electronic structure of this molecule in its excited state.

carry a partial positive and a partial negative charge in different parts of the molecule mutually orient themselves in space so that other polar molecules, that is, air components, for example, water molecules (1.85 D), would be nearby. The resulting Coulomb interaction between the polar fragments of the molecules can create favorable conditions for chemical reactions [50]. Thus, the value and direction of the dipole moment (Fig. 2a) in a pheromone molecule make it possible to assess their predisposition to chemical interaction with polar molecules present in the air. The pheromone molecules that lack an oxygen atom have a dipole moment of 0.16 to 0.70 D. The interaction with polar molecules for them is unlikely; correspondingly, factors such as air humidity would hardly have a significant effect on their stability.

The absorption wavelengths for all of the considered molecules fall into the range of 156–223 nm (Table 1), which corresponds to the ultraviolet part of the spectrum. The energy necessary for the transition of molecules from a basic to an excited state is 5.6 to 7.9 eV, respectively. In the event of energy absorption, an electron passes from the molecular orbital it occupies to a vacant orbital, thereby changing the electronic structure of the molecule. Computation of the absorption spectrum by the TD-DFT method also gives the type of molecular orbitals involved in the

electron transitions along with the values of energy and wavelengths. As an example, Fig. 2 shows a component of the bark beetle pheromone, *trans*-verbenol molecule.

Figure 2c shows the upper occupied molecular orbital that corresponds to a ground state of the molecule. The electron density mainly concentrates at the C₂ and C₃ atoms in the six-membered ring and at C₇–C₁–C₆ atoms in the small ring. The angle between C₂–C₁–C₆ atoms is 110°; this arrangement provides an efficient overlapping of *p* orbitals with formation of σ_{p-p} bonds. The electron transition from the upper occupied molecular orbital to the lower vacant one in a *p*–*p* absorption is the most intensive. The electronic structure of the *trans*-verbenol molecule when an electron occupies this orbital is shown in Fig. 2d. The molecular orbitals between C₂ and C₃ atoms in the large ring and between C₇–C₁–C₆ atoms in the smaller ring were looser after absorption.

As a rule, a change in the electronic structure influences the geometry of a molecule. Figure 2 shows the atomic structure of *trans*-verbenol computed by geometry optimization in a ground (Fig. 2a) and an excited (Fig. 2b) state. The molecule in a ground state (Fig. 2a) comprises two rings: the six-membered ring C₁–C₂–C₃–C₄–C₅–C₆ and the four-membered ring

Table 1. The parameters of the pheromone molecules produced by the bark beetle *Ips typographus* L., black fir sawyer beetle *Monochamus urussovi* Fisch., and black pine sawyer *M. galloprovincialis* Oliv. computed using B3LYP/cc-pVDZ

| Pheromone | Electric dipole moment, D | λ , nm | E , eV | Oscillator strength, relative units |
|---|---------------------------|----------------|----------|-------------------------------------|
| <i>Ips typographus</i> | | | | |
| 2-Methyl-3-buten-2-ol | 1.63 | 161 | 7.7 | 0.41 |
| * <i>cis</i> -Verbenol | 1.33 | 209 | 5.9 | 0.08 |
| ** <i>cis</i> -4,6,6,-Trimethylbicyclo[3.1.1]hept-3-en-2-ol | | | | |
| <i>trans</i> -Verbenol | 1.49 | 193 | 6.4 | 0.11 |
| <i>trans</i> -4,6,6,-Trimethylbicyclo[3.1.1]hept-3-en-2-ol | | | | |
| 2-Phenylethanol | 1.71 | 179 | 6.9 | 0.56 |
| Myrtenol | 1.49 | 203 | 6.1 | 0.11 |
| (6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)methanol | | | | |
| <i>trans</i> -Myrtenol | 1.33 | 156 | 7.9 | 0.03 |
| (1S,5R)-6,6-Dimethylbicyclo[3.1.1]heptan-2-ol | | | | |
| <i>Monochamus urussovi</i> | | | | |
| 1S- α -pinene | 0.17 | 194 | 6.4 | 0.16 |
| (1S)-2,6,6,-Trimethylbicyclo[3.1.1]hept-2-en | | | | |
| 1R- α -pinene | 0.17 | 190 | 6.5 | 0.16 |
| (1R,5R)-2,6,6-Trimethylbicyclo[3.1.1]hept-2-en | | | | |
| S-3-Carene | 0.20 | 184 | 6.7 | 0.12 |
| (1S)-3,7,7-Trimethylbicyclo[4.1.0]hept-3-en | | | | |
| R-Limonene | 0.70 | 170 | 7.3 | 0.31 |
| (R)-1-Methyl-4-(1-methylethenyl)-cyclohexane | | | | |
| α -Terpinolene | 0.23 | 191 | 6.5 | 0.31 |
| 1-Methyl-4-(1-methylethylidene)-cyclohexane | | | | |
| <i>Monochamus galloprovincialis</i> | | | | |
| Ipsenol | 1.28 | 223 | 5.6 | 0.18 |
| 2-Methyl-6-methylene-7-octen-4-ol | | | | |
| α -Pinene | 0.16 | 194 | 6.4 | 0.16 |
| 2,6,6-Trimethylbicyclo[3.1.1]hept-2-en | | | | |
| 2-Methyl-3-buten-1-ol | 1.45 | 167 | 7.4 | 0.24 |

Dipole moment of water molecule is 1.85 D; * trivial name and ** chemical name.

$C_1-C_7-C_5-C_6$. The larger ring contains a double bond between the C_2 and C_3 atoms (1.34 Å). For the smaller ring, the bonds between carbon atoms are single and strained, which is characteristic of bicyclic terpenes; the longest bond in the ring is between the C_1 and C_6 atoms at 1.59 Å. The angle between the $C_2-C_1-C_6$ atoms is 110°. The transition to an excited state leads to the following changes in the geometry of the molecule (Fig. 2b): the bond between C_2 and C_3 in the large ring increases to 1.43 Å, which corresponds to the transition of a double into a sesqui bond, and the distance between the C_1 and C_6 atoms increases to 1.67 Å, suggesting a weak σ_{p-p} bond, which potentially can lead to further destruction and opening of the rings, since the C_1-C_6 is present in both rings. The angle between $C_2-C_1-C_6$ changes from 110 to 99°.

Thus, a new six-membered ring, $C_1-C_2-C_3-C_4-C_5-C_7$, is formed.

The excited state is unstable; the molecule passes to the ground state losing energy by radiation, oscillation, or collision with other molecules. Figure 2d shows the distribution of the electron density in *trans*-verbenol after electronic relaxation. Arrangement of $C_2-C_1-C_6$ atoms at an angle of 99° is less effective for overlap of the p -orbitals of the C_1 and C_6 carbon atoms compared with the initial structure, thereby weakening the C_1-C_6 bond. The length of the C_1-C_6 bond in the ground state (Fig. 2a) is 1.59 Å; thus, after excitation it is reasonable that the molecule will pass to a more stable structure lacking strained bonds. Analogous changes take place in all pheromone molecules of xylophagous insects that contain two strained rings.

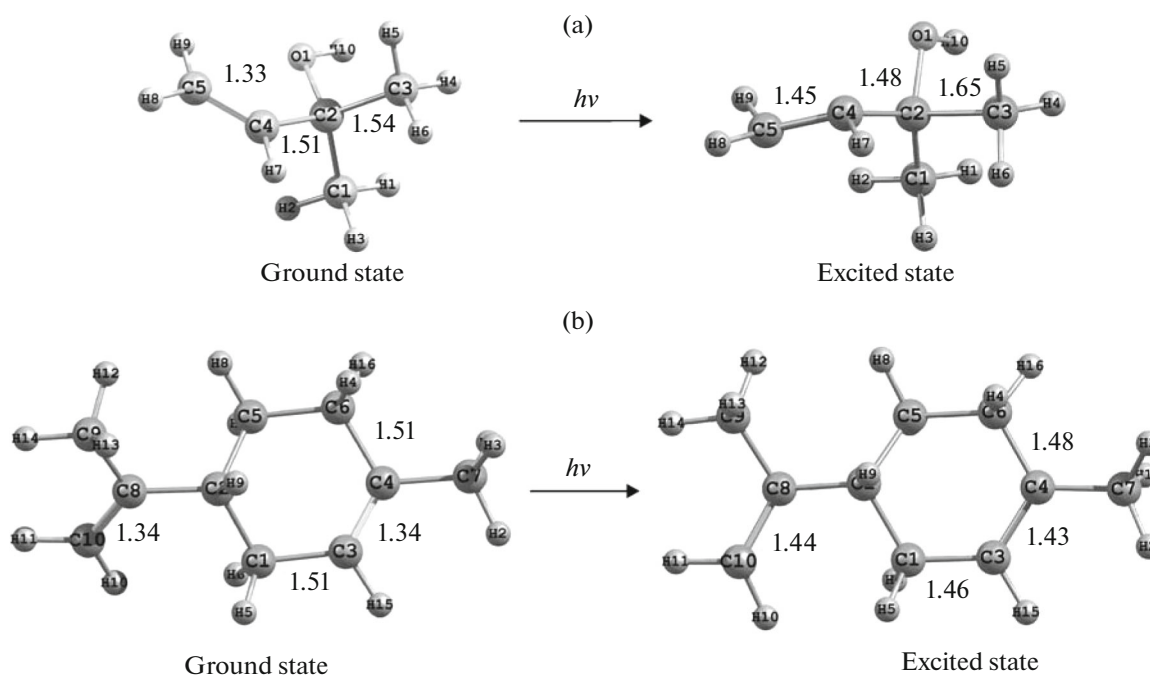


Fig. 3. The geometry of the (a) 2-methyl-3-buten-2-ol and (b) R-limonene molecules in the ground and excited states.

Along with bicyclic terpenes, xylophage pheromones contain noncyclic and monocyclic molecules. Figure 3 shows the structures of 2-methyl-3-buten-2-ol and R-limonene molecules in the ground and excited states.

The C₃-C₄ and C₈-C₁₀ double bonds in R-limonene molecule and C₄-C₅ in 2-methyl-3-buten-2-ol increase on the average by 0.1 Å after transition from a ground to an excited state (Fig. 3). Changes in the length of interatomic bonds suggest an increase in the reactivity after molecules absorb electromagnetic radiation. Unlike bicyclic terpenes, the initial structures of these molecules do not contain strained bonds; correspondingly, their destruction without a chemical reaction is unlikely. The pheromones of xylophages migrate in the air of the forest zone, where trees evolve reactive oxygen during photosynthesis. Thus, the air is saturated with negatively charged ions (for example, OH⁻), which readily react with organic compounds [50]. Thus, even if it does not directly lead to destruction excitation of molecules decreases the stability of the molecules by enhancing chemical reactions.

CONCLUSIONS

This theoretical analysis demonstrated that pheromone molecules can obtain energy from solar electromagnetic radiation that is sufficient for their excitation. This can change interatomic distances and bond angles in pheromone molecules, leading to their activation. Knowing the changes that take place in the structure of molecules, it is possible to assume that

pheromone molecules lose their information transfer effectiveness after radiation. This may explain certain diurnal and seasonal regular patterns in insect behavior.

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