LASER−INDUCED PHOTOFRAGMENTATION OF MOLECULES. A THEORETICAL STUDY OF PHOTOCHEMISTRY AND PHOTOPHYSICS OF ORGANIC MOLECULES

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New method is discussed for detecting nonfluorescent molecules and molecules with overlapping spectra. The approach proposed in this paper is based on different dependences of photodissociation rates at the wavelength of exciting radiation for different molecules. In order to varify the proposed technique a theoretical study and estimation of dissociation of the OH radical from a number of aliphatic alcohols and of the COH formyl radical from some aldehydes were carried out.

Modern laser techniques in experimental studies of gas phase molecules make it possible to detect nonfluorescent molecules or molecules with overlapping spectra. First of all this statement refers to organic molecules with identical chromophore groups.

Most molecules fluoresce very weakly in their gas phase. One of the new methods of detecting the organic molecules is laser induced photofragmentation.[1] Theoretical studies must provide the increasing demand on the accurate data from photophysics and photochemistry of molecules and on computational techniques to describe the dynamics of laser-induced molecular processes.

The method we offer is based on the theory of transitional state and on using photodissociation rate constants from the RRKM theory.[2] Different molecules feature different dependences of their photodissociation rates on excitation energy. Using the data on the vibrational and electronic structure of these molecules we can retrieve the dependences of their photodissociation rates on excitation energy. To investigate the dynamics of the process in more detail it is necessary to study the potential energy surfaces. Modern nonempirical calculations make it possible to identify transition states and other characteristic properties of potential surfaces.

To test this approach we studied theoretically and estimated the rate of disengagement of the OH radical from aliphatic alcohols and of the COH formyl radical from certain aldehydes. Pathways of molecular decomposition of these molecules were also studied. We involved a package of the following quantum-mechanical programs in our calculations: MONSTERGAUSS, MINDO/3, and the programs using the CNDO/S technique. The MONSTERGAUSS program was used to optimize the geometry of alcohols and to calculate the potential surfaces of the first excited state S_1 The geometries of ethanol and propanol are given in Ref. 3, and the geometry of butanol is shown in Fig. 1. We calculated vibrational spectra using programs from Ref. 4; they are given in Tables II−IV.

We used the basic formula from the RRKM theory for the rate of molecules disintegration[1]:

$$K(E) = cL \left[\prod_{i=1}^{s} v_i \bigg/ \prod_{i=1}^{s-1} v_i' \right] \left(\frac{E - E_0}{E} \right)^{s-1} , \qquad (1)$$

where c is the velocity of light; L is the number of disintegration pathways; v_i, v_i' are the vibrational frequencies of the molecule and the activated complex, respectively; E_0 is the dissociation energy. Thus we obtained the dependences of disintegration rates for alcohols in the state S_0 on excitation energy.

TABLE I.

Intermolecular length, Å			Angle, deg			
$N1$	$N2$	R	$N1$	$N2$	$N3$	α
$C1$	$C2$	1.5407	$C3$	$C2$	$C1$	112.3121
$C2$	$C3$	1.544	$C4$	$C3$	$C2$	112.1307
$C3$	$C4$	1.5456	$O5$	$C4$	$C3$	108.3488
$C1$	$H6$	1.0859	$H15$	$O5$	$C4$	103.9669
$C1$	$H7$	1.0859	$H13$	$C4$	$O5$	111.1533
$C1$	$H8$	1.0859	$H11$	$C3$	$C4$	108.8128
$C2$	$H9$	1.0886	$H9$	$C2$	$C3$	109.3007
$C2$	$H10$	1.0886	$H6$	$C1$	$C2$	110.7335
$C3$	$H11$	1.088	$H8$	$C1$	$C2$	110.5586
$C4$	$O5$	1.4352				
$C4$	$H13$	1.0972				
$H6$	$O5$	0.9910				
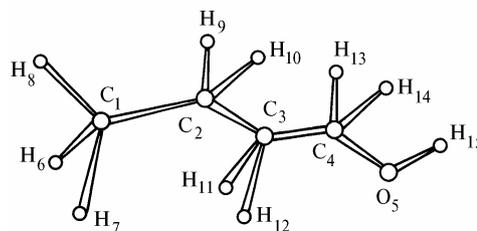
FIG. 1. The geometry of butanol.

TABLE II.

No.	Ethanol	Propanol	Butanol
	ν, cm^{-1}		
1	1320.20	199.13	214.35
2	405.49	171.2	221.31
3	848.49	247.51	249.16
4	907.27	288.93	296.03
5	913.92	723.39	435.08
6	1033.37 Q(CO)	432.56	538.01
7	1144.09	858.57	859.17
8	1186.58	859.21	857.11
9	155.01	1005.66	878.16
10	1394.83	1067.93	1004.17
11	1396.54	1102.29 Q(CO)	1061.02
12	1449.82	995.50	1033.21 Q(CO)
13	1708.46	1199.06	1085.27
14	1543.71	1249.55	995.73
15	2909.12	1272.68	1178.37
16	2938.47	1346.04	1271.63
17	2959.04	1450.21	1283.71
18	2960.36	1487.01	1341.67
19	2996.25	1520.84	1451.22
20	3687.04 Q(OH)	1552.16	1483.16
21	3912,00	1612,58	1521,31
22		2850,22	1553,17
23		2894,10	1558,27
24		2919,48	1612,53
25		2907,98	1711,47
26		2984,97	2851,21
27		2987,10	2893,10
28		2955,21	2911,45
29		1286,53	2985,91
30		3678,42 Q(OH)	2987,10
31			2957,20
32			2918,18
33			2872,13
34			2873,29
35			3675,42 Q(OH)
36			191,13
37			173,15
38			211,15
39			210,47

This dependence is shown in Fig. 2. As can be seen from the plot, disintegration rates tend to be lower for complex molecules. This is clear from the point of view of the RRKM theory, which is based on calculating the probability for finding the energy at least equal to the critical energy E_0, for a single oscillator selected from a set of harmonic oscillators of the total energy E. With increase of the number of oscillators, the probability of concentration of energy at a single bond decreases. However, the statistical theory enjoys a limited applicability only.

For the excited singlet state S_1 of studied alcohols, $C_nH_{2n+1}OH$ ($n = 2 - 4$) their excitation energy is localized on the COH group as alcohols become more complex.[3] While the length of the carbon backbone chain increases, changes basically take place in the COH group. As alcohols become more complex, the probability for OH to break off increases that agrees with experiment.[5] The increase in energy of the verticil transition, as the structure of alcohols gets more and more complicated,

results, for $n > 2$, in the molecule receiving energy which exceeds the critical energy of decay accompanied by the formation of OH(A$^2\Sigma^+$). This agrees with the results cited in Ref. 5: generation of OH(A$^2\Sigma^+$) without collisions is only possible for large molecules. Our *ab initio* calculation of S_1 stale for alcohols yields such a state as fragmentation.[5] The molecule in such a state cannot be treated as a closed stable system, so that its dissociation does not result from thermodynamic fluctuation, as the statistical theory entails. Excessive energy is not distributed over all the degrees of freedom but is localized to the carbonyl group, COH.
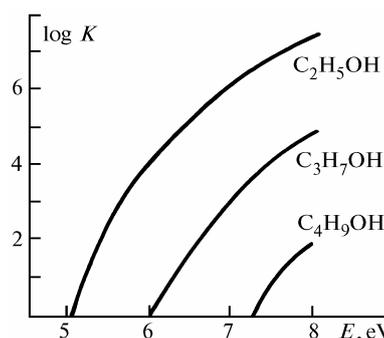
FIG. 2. Dependence of photodissociation rate onstants of $C_nH_{2n+1}OH + h\nu \to C_nH_{2n+1} + OH$ on excitation energy.
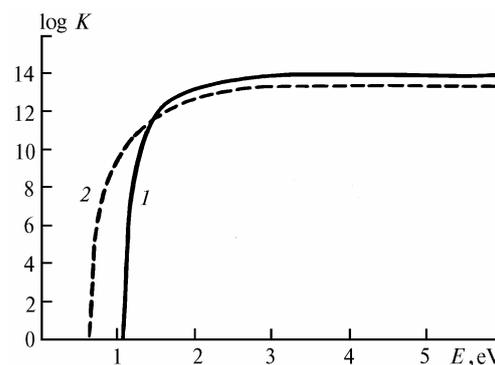
FIG. 3 The dependence of photodissociation rate constants of $RCOH + h\nu \to R + OHC$ on excitation energy. 1) formaldehyde, 2) acetaldehyde.

Our calculations for aldehydes show that in the whole range of energy variations the rate of disintegration of formaldehyde™ the molecular channel exceeds that for acetaldehyde, while the same rate for benzoldehyde remains negligible. Radical reactkn for aldehydes develops from the state S_0 without the formation of an activated complex. Dissociation accompanied by the formation of radicals via activated complex takes place from the state T_1. In this case, the dissociation barrier in Eq. (1) should be counted off from the ground vibrational level of the state T_1. Vibrational frequencies must also be calculated for the state T_1. As for the aldehydes, Eq. (1) may be used to calculate the rate of dissociation from the triplet state T_1. As can be seen from Fig. 3, the rate of disintegration for formaldehyde only partly exceeds the one for acetaldehyde across the energy range. Only

acetaldehyde is broken in the $0.6 < E < 1.07$ eV range. No dependence on the number of degrees of freedom is found in the excited state T_1, in contrast to the state S_0. Judging by changes in bond orders and in the electron density, as calculated after the CNBO/S technique, the states T_1 and S_1 of acetaldehydes are of the $n - \pi$ character (Table III–V). One can assume the state S_1 to have a similar dependence of disintegration rate on excitation energy.

The fact that wavelength dependences of the break–off rate of formyl COH radical for different aldehydes are different, allows one to separate them via photofragments spectroscopy.

TABLE III.

Acetaldehyde			
Bond degrees		Bond degrees variation $\Delta B(1)$	
Atoms	$B(1)$	$S_1\,(n \to \pi^*)$	$T_1\,(n \to \pi^*)$
$(C1, C2)$	0.691	0.002	0.002
$(C1, H4)$	0.676	0.000	0.000
$(C1, H5)$	0.672	−0.002	−0.002
$(C1, H6)$	0.672	−0.002	−0.002
$(C2, O3)$	0.851	−0.056	−0.056
$(C2, H7)$	0.648	−0.003	−0.003

TABLE IV.

Acetaldehyde			
Electron density		Electron density variation	
Atoms	$B(1)$	$S_1\,(n \to \pi^*)$	$T_1\,(n \to \pi^*)$
$C1$	4.035	−0.045	−0.045
$C2$	3.755	0.568	0.568
$O3$	5.456	−0.480	−0.480
$H4$	1.005	−0.001	−0.001
$H5$	1.012	0.011	0.011
$H6$	1.012	0.011	0.011
$H7$	1.023	−0.065	−0.065

TABLE V.

Benzoldehyde			
Bond degrees		Bond degrees variation $\Delta B(1)$	
Atoms	$B(1)$	$S_1\,(n \to \pi^*)$	$T_1\,(n \to \pi^*)$
$(C1, C2)$	0.914	− 0.009	− 0.009
$(C1, C6)$	0.915	− 0.009	− 0.009
$(C1, C7)$	0.715	0.002	0.002
$(C2, C3)$	0.928	0.000	0.000
$(C2, H9)$	0.659	0.000	0.000
$(C3, C4)$	− 0.923	− 0.002	− 0.002
$(C3, H10)$	0.665	0.000	0.000
$(C4, C5)$	0.922	− 0.001	− 0.001
$(C4, H11)$	0.663	0.000	0.000
$(C5, C6)$	0.927	0.001	0.001
$(C5, H12)$	0.661	0.001	0.001
$(C6, H13)$	0.661	− 0.001	− 0.001
$(C7, O8)$	1.032	− 0.065	− 0.065
$(C7, H14)$	0.595	− 0.025	− 0.025

Studying the dynamics of reactions induced by laser radiation is one of fundamental problems of physics and chemistry. Presently, the region of nonequilibrium configurations on the potential energy surface is only experimentally studied for systems with a small number of the degrees of freedom. Theory plays a principal role for a system with a large number of the degrees of freedom. Theoretical calculations yield helpful information to understand the dynamics of natural processes.

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