

THEORETICAL INVESTIGATION OF THE ALDEHYDES PHOTOFRAGMENTATION

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The proposed approach to photodissociation of aldehydes using photofragmentation spectroscopy is based on a different dependence of COH radical dissociation rate for different aldehydes on the exciting wavelength. To establish this dependence, numerical calculations have been made of the lowest electronically excited states of acetaldehyde and benzaldehyde as well as the vibrational structure of these molecules. The data have been used for numerical calculation of the dissociation rate.

Aldehydes are of dramatic importance for photochemical processes in the atmosphere. Thus, formaldehyde HCOH is an intermediate product of the chain of reactions leading to oxidation of methane CH₄ and to production of CO even in the clear atmosphere.¹ In the polluted atmosphere over the industrial regions aldehydes are the products which leads to further photochemical production of CO, radicals, and compounds from original reactants thus playing a dominant role in smog formation.² Moreover, aldehydes are emitted directly into the atmosphere by different enterprises. Therefore, the measurement of aldehydes is now the urgent problem from the viewpoint of choosing a correct way of monitoring the atmospheric pollution.

The results of measurements of formaldehyde using the fluorescence method were discussed in Ref. 3. However, the direct application of this method for the polluted atmosphere makes it possible to measure only total concentrations of aldehydes since the spectra of formaldehyde HCOH⁴ and acetaldehyde CH₃COH⁵ overlap almost completely.⁵

It is possible to distinguish between aldehydes if the methods of photofragmentation spectroscopy are used. The method proposed is based on different dependences of the photodissociation rate of formil radical COH on the exciting wavelength for different aldehydes. To ascertain this dependence the calculations of the lowest electronically excited states of acetaldehyde CH₃COH and benzaldehyde C₆H₆COH were performed employing the computer programs of Timiryazev Agricultural Academy, Moscow (TAA) based on the method of complete neglecting of differential overlap (CNDO). The vibrational structure of the spectra of these molecules was calculated using the computer programs.¹⁰ The vibrational spectra for acetaldehyde have already been calculated,^{11,12} but we wanted to obtain the calculated results in the same approximation for both molecules. Our calculations provide for the larger quantity of data. In addition to vibrational frequencies, we compute the energy distribution over the degrees of freedom of the molecule in per cents.

These data were used for calculating the photodissociation rate K from the formula⁶

$$K(E) = \left(\prod_{i=1}^s v_i \right) / \left(\prod_{i=1}^{s-1} v_i' \right) \left[\frac{E - D_0 + E_0'}{E + E_0'} \right] cM, \quad (1)$$

where M is the number of reaction pathways, s is the number of vibrational degrees of freedom, v_1, v_1' and E_0, E_0' are the vibrational frequencies and the energies of zeroth mode for a molecule and a transitional complex, respectively. D_0 is the dissociation barrier, and c is the speed of light.

1. CALCULATION OF THE ACETALDEHYDE VIBRATIONAL STRUCTURE

The geometry of molecule is to be specified for calculating its vibrational structure. We used the data and notation of Ref. 7 for acetaldehyde. Figure 1 presents the geometry of the acetaldehyde molecule.

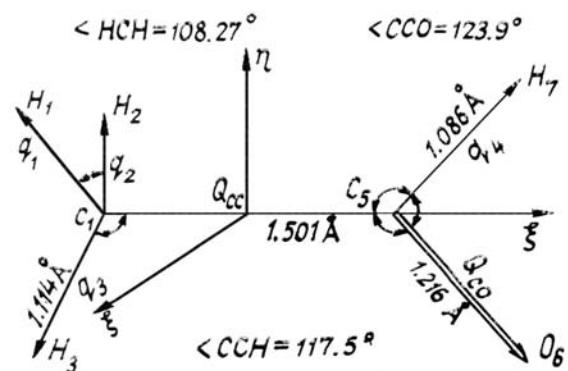


FIG. 1. The geometry of the acetaldehyde of the acetaldehyde molecule.

The electro-optical parameters were taken from Ref. 8. The values of force constants were taken from Ref. 9.

Interpretation of the obtained vibrational spectrum of frequencies is presented in Table I. The absolute intensities are listed in Table II.

We can obtain the following information from the data on the energy distribution over the groups of equivalent internal coordinates: for normal mode at a frequency of $\nu = 2823.66 \text{ cm}^{-1}$ 98.7% of energy is concentrated on the internal coordinate q_{CH} of the COH species; for normal

mode of the C–C bond at $\nu = 936.57 \text{ cm}^{-1}$ 60.4% of energy is concentrated at the internal coordinate Q_{cc} ; for mode of $C=O$ at $\nu = 1760.05 \text{ cm}^{-1}$ 29.2% of energy is at the internal coordinate Q_{cc} , 33.8% is at $\beta(\text{CCH})$, and 27.2% is at $\gamma(\text{CCO})$. That is, the most part of the vibrational energy is concentrated in the carbonyl species of COH. This fact increases the probability of dissociation.

TABLE I. Interpretation of the vibrational spectrum of acetaldehyde (ν, cm^{-1})

Symmetry	Species	ν_{exp} (Ref. 11)	ν_{calc} (Ref. 11)	ν_{calc} (Ref. 11)	ν_{calc} (Ref. 12)
A''	$q''_{\text{CH}_3}(\text{C-H})$	3013	3024	2982.94	3347
A'	$q^-_{\text{CH}_3}(\text{C-H})$	2967	2967	2980.69	3242
A'	$q^+_{\text{CH}_3}(\text{C-H})$		2917	2908.49	—
A'	$q_{\text{OHC}}(\text{C-H})$	2821	2804	2823.66	2822
A'	$q(C=O)$	2715	2736	—	—
A'	$\alpha^-_{\text{CH}_3}(\text{HCH})$	1743	1743	1760.05	1760
A'	$\alpha^-_{\text{CH}_3}(\text{HCH})$	1441	1441	1499.48	1594
A''	$\alpha''_{\text{CH}_3}(\text{HCH})$	—	1441	1408.19	1504
A'	$\beta(\text{OCH})$	1410	1410	1422.31	—
A'	$\alpha^+(\text{HCH})$	1352	1352	1339.99	1504
A'	$\beta(\text{CCH})$	1123	1122	1122.35	—
A''	$\beta''(\text{CCH})$	1103	1104	1143.82	—
A'	$q(\text{C-C})$	919	919	936.57	1121
A''	$\rho = \text{C-H}$	867	880	903.46	1025
A'	$\gamma(\text{CCO})$	509	509	596.14	534
A''	χ_{CH_3}	—	150	146.39	—

TABLE II. Interpretation of the vibrational spectrum of acetaldehyde (ν, cm^{-1})

Symmetry	Species	I_{exp} (Ref. 11)	I (our calculations)
A''	$\rho = \text{CH}$	2.3	4.1
A'	$Q(\text{C-C})$	3.3	
A'	$\gamma(\text{CCO})$	8.3	10.49
A'	$\beta(\text{CCH})$	16.3	9.9
A''	$\beta''(\text{CCH})$	—	20.9
A''	$Q(\text{C=O})$	73	19.2
A'	$\alpha_{\text{CH}_3}(\text{HCH})$	17	14
A''	$\alpha''_{\text{CH}_3}(\text{HCH})$		45
A'	$\beta_{\text{CH}_3}(\text{OCH})$	10	15.8
A'	$\alpha^+_{\text{CH}_3}(\text{HCH})$		5.52
A''	$q''_{\text{CH}_3}(\text{C-H})$	8.8	1.17
A'	$q^-_{\text{CH}_3}(\text{C-H})$		1.97
A'	$q^+_{\text{CH}_3}(\text{C-H})$		7.5
A'	$q_{\text{OHC}}(\text{C-H})$	59	78.3

2. THE NUMERICAL CALCULATION OF THE BENZALDEHYDE VIBRATIONAL STRUCTURE

The geometry of benzaldehyde was optimized employing the computer program based on the MINDO/3 method. Figure 2 represents the numeration of benzaldehyde

atoms. The results of optimization of the geometry are given in Table III. The frequencies and the absolute Intensities are listed in Table IV.

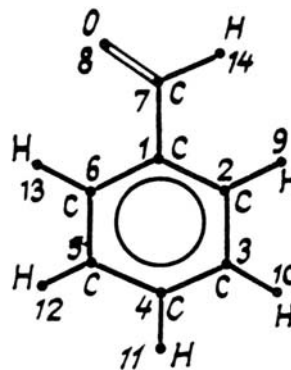


FIG. 2. The numeration of benzaldehyde atoms.

Table III. The optimized geometry of benzaldehyde.

Bond length	$r^*(\text{C}_1\text{C}_7)$	$r(\text{C}_1\text{C}_2)$	$r(\text{C}_1\text{C}_6)$	$r(\text{C=O})$	$r(\text{CH})$
Our calculation	1.492	1.4124	1.4124	1.1956	1.1395
The calculation of Ref. 13	1.518	1.4	1.4	1.223	1.103
Valence angles	HC_6C_1	HC_2C_1	$\text{C}_2\text{C}_1\text{C}_7$	$\text{C}_1\text{C}_7\text{O}$	$\text{C}_1\text{C}_7\text{H}$
Our calculation	120	120	120	128.889	111.312
The calculation of Ref. 13	119.8	119.2	119.8	123.6	114.6

* r is the bond length.

TABLE IV. Absolute intensities and frequencies in the IR spectrum of benzaldehyde.

Symmetry	Species	$\nu (\text{cm}^{-1})$	$I(A \cdot 10^8 \text{ cm}^2 \text{ c}^{-1} \text{ mol}^{-1})$
A'	$\beta(\text{CCH}_r)$	3013	3.47
A'	$\beta(\text{CCH}_r)$	1026.83	4.62
A'	$\gamma(\text{CCH}_r)$	989.13	0.011
A'	$\gamma(\text{CCH}_r)$		
A'	$\beta(\text{CCH}_r)$	1054.82	2.96
A'	$\gamma(\text{CCC}_r)$	1023.66	1.18
A'	$Q(\text{C}_1\text{C}_7)$		
A'	$\beta(\text{CCH}_r)$	1139.39	0.024
A'	$\beta(\text{CCH}_r)$	1285.92	0.0036
A'	$Q(\text{CC}_r)$	1323.81	0.299
A'	$\beta(\text{CCH}_r)$		
A'	$Q(\text{CC}_r)$	849.89	5.17
A'	$\beta(\text{CCH}_r)$		
A'	$\beta(\text{CCH}_r)$	1420.99	7.09
A'	$\gamma(\text{CCC}_r)$		
A'	$\beta(\text{CCH}_r)$	1441.77	53.37
A'	$\beta(\text{HCO})$		
A'	$Q(\text{CO})$	1497.57	6.39
A'	$\beta(\text{CCH}_r)$		
A'	$\beta(\text{HCO})$	632.69	0.622
A'	$\beta(\text{CCH}_r)$		
A'	$\gamma(\text{CCC}_r)$	695.69	2.64
A'	$\beta(\text{CCH}_r)^*$		
A'	$\gamma(\text{CCC}_r)$	391.56	0.1724
A'	$\gamma(\text{CCC}_r)$		

Symmetry	Species	ν (cm ⁻¹)	$I(A \cdot 10^8 \text{ cm}^2 \text{ c}^{-1} \text{ mol}^{-1})$
A'	Q(CC _r)	1618.51	1.78
	β (CCH _r)		
	γ (CCC _r)		
A'	Q(CC _r)	1602.54	1.396
	β (CCH _r)		
	γ (CCC _r)		
A'	β (CCH _r)	79.86	1.446
	γ (CCC _r)		
A'	Q(C=O)	1694.41	2.598
	γ (CCC _r)		
	β (HCO)		
A'	q (CH _r)	3060.75	7.8
A'	q (CH _r)	3057.12	0.0005
A'	q (CH _r)	3056.64	0.024
A'	q (CH _r)	3070.63	2.2019
A'	q (CH-COH)	2842.94	68.29
A''	χ_r	94.95	0.0016
A''	χ_r	65.28	0.0398
A''	χ_r	21.12	0.016
A''	χ_r	173.80	0.027
A''	χ_r	256.40	6.21
A''	χ_r	522.91	11.45
A''	χ_r	573.88	0.1244
A''	χ_r	641.42	1.954
A''	χ_r	718.11	0.13
A''	χ_r	783.68	0.197
A''	χ_r	548.08	24.41
A''	$\rho_{\text{CH}}(\text{COH})$	1096.41	0.986

* The letter "r" denotes the benzene ring.

We have the following information on energy distribution over the groups of equivalent internal coordinates: for normal mode at a frequency of $\nu = 2842.94 \text{ cm}^{-1}$ 98.6% of the energy is concentrated at the internal coordinate q_{CH} of the COH species; at $\nu = 1203.66 \text{ cm}^{-1}$ 32.67% of energy is at the internal coordinate $Q(\text{C}_1\text{C}_7)$, the COH species; at $\nu = 1203.66 \text{ cm}^{-1}$ 32.6% of energy is at the internal coordinate $Q(\text{C}_1\text{C}_7)$, 11.3% is at $Q(\text{C}=\text{O})$, and 15.1% and 10.6% are at $\beta(\text{CCH}_r)$; for normal mode at $\nu = 1694.41 \text{ cm}^{-1}$ 27.6% is concentrated at $Q(\text{C}=\text{C})$, 24.2% is at $\gamma(\text{CCO})$, and 21.2% is at $\beta(\text{HCO})$. Thus, the most part of the vibrational energy is concentrated in the COH species. This facilitates photodissociation.

3. CALCULATION OF THE ENERGY OF THE ACETALDEHYDE AND BENZALDEHYDE ELECTRONIC (E), SINGLET (S), and TRIPLET (T) STATES

State	Acetaldehyde	
	$E_{\text{theor}}(\text{eV})$	$E_{\text{exp}}(\text{eV})$ (Ref. 14)
$S_1(n \rightarrow \pi^*)$	3.778	4.140
$S_2(n \rightarrow \pi^*)$	7.623	6.875
$S_3(n \rightarrow \pi^*)$	7.825	7.750
$T_1(n \rightarrow \pi^*)$	3.777	3.713
$T_2(n \rightarrow \pi^*)$	5.049	—
$T_3(n \rightarrow \pi^*)$	7.622	—
	Benzaldehyde	
$S_1(n \rightarrow \pi^*)$	4.231	3.8
$S_2(n \rightarrow \pi^*)$	4.76	4.46
$S_3(n \rightarrow \pi^*)$	5.053	5.175
$T_1(n \rightarrow \pi^*)$	3.267	—
$T_2(n \rightarrow \pi^*)$	4.179	—

4. CALCULATION OF THE PHOTODISSOCIATION RATE

The data on vibrational and electronic spectra were employed for calculating $K(E)$ from formula (1).

Acetaldehyde

$M = 1$; $\nu = 936.57 \text{ cm}^{-1}$ (breaking of the C—C bond); $E(S_1) = 3.8 \text{ eV}$ (328 nm); $E_0 = 1.49 \text{ eV}$, $E_0 = 1.43 \text{ eV}$; $D_0 = 3.2 \text{ eV}$ (389 nm); $K = 2.8 \cdot 10^{13} \cdot \text{s}^{-1}$; $S = 15$;

$$K(E) = 2.8 \cdot 10^{13} \cdot \left(\frac{E - 1.77}{E + 1.49} \right)^{14}$$

$E = 3.5 \text{ (eV)}$	$K = 1 \cdot 10^7 \text{ (s}^{-1}\text{)}$	$\lg K = 7.00$
$E = 3.68$	$K = 2.48 \cdot 10^7$	$\lg K = 7.39$
$E = 3.8$	$K = 4.9 \cdot 10^7$	$\lg K = 7.69$
$E = 4.02$	$K = 1 \cdot 10^8$	$\lg K = 8.00$
$E = 4.13$	$K = 1.5 \cdot 10^8$	$\lg K = 8.18$
$E = 5.0$	$K = 1.69 \cdot 10^9$	$\lg K = 9.22$
$E = 7.622$	$K = 5.69 \cdot 10^{10}$	$\lg K = 10.76$
$E = 7.825$	$K = 6.7 \cdot 10^{10}$	$\lg K = 10.83$

Benzaldehyde

$M = 1$; $\nu = 1203.66 \text{ cm}^{-1}$; $E(S_1) = 4.231 \text{ eV}$ (294 nm); $E_0 = 2.7 \text{ eV}$, $D_0 = 3.8 \text{ eV}$; $S = 36$; $K = 3.6 \cdot 10^{13} \cdot \text{s}^{-1}$;

$$K(E) = 3.6 \cdot 10^{13} \cdot \left(\frac{E - 1.1}{E + 2.77} \right)^{36}$$

$E = 3.267 \text{ (eV)}$	$K = 1.3 \cdot 10^{-2} \text{ (s}^{-1}\text{)}$	$\lg K = -1.89$
$E = 3.5$	$K = 9.1 \cdot 10^{-2}$	$\lg K = -1.04$
$E = 4.18$	$K = 1.5 \cdot 10$	$\lg K = 1.18$
$E = 4.231$	$K = 2.12 \cdot 10$	$\lg K = 1.326$
$E = 4.76$	$K = 3.9 \cdot 10^2$	$\lg K = 2.59$
$E = 5.0$	$K = 1.2 \cdot 10^3$	$\lg K = 3.08$

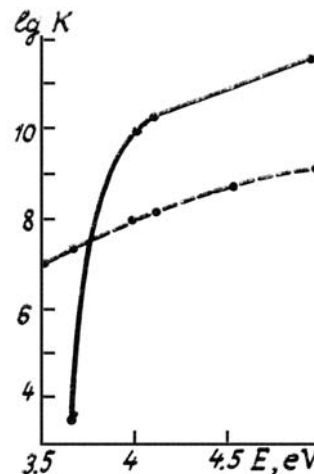


FIG. 3. The rates of the photodissociation of the foimil COH radical as a function of the excitation energy for acetaldehyde (the dashed curve) and foimaldehyde (the solid curve).

For benzaldehyde the rate of photodissociation turns out to be negligible for the entire excitation interval 250–350 nm. The analogous calculations were performed for formaldehyde using the data of Ref. 15. It follows from Fig. 3 that for

excitation of the mixture of two aldehydes due to radiation with $\lambda \leq 308$ nm. ($E \geq 4.02$ eV) the rate of COH photodissociation for formaldehyde is about two orders of magnitude greater than the corresponding rate for acetaldehyde. Different situation occurs for excitation due to the radiation, e.g., with $\lambda = 347$ nm ($E = 3.57$ eV). In this situation the photodissociation of the COH radical of acetaldehyde also occurs at high rate, whereas for formaldehyde such process does not take place.

The subsequent monitoring of the COH radical may be carried out using the method of induced fluorescence.^{16,17} Thus, the COH radical was excited due to the radiation of a dye laser with $\lambda = 614.48$ nm coinciding with that of the transition $XA^1(00^1_0) A^2A''(09^0_0)$. The signals of fluorescence were observed at $\lambda = 658.2$ nm, 708, 722.4, 764, and 781.4 nm.

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