Formation of the photoionization mass spectrum of polyatomic molecules by ultraviolet laser radiation

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We investigate the formation of the photoionization mass spectrum of polyatomic molecules (benzene and benzaldehyde) by ultraviolet radiation from a KrF laser in the intensity range 5×10^4–5×10^9 W/cm^2. It is found that an important role in the formation of the mass spectrum of benzaldehyde is played by the dissociation of the molecule in the intermediate electronically excited state. Regrouping dissociation of the benzaldehyde into benzene and CO molecules is observed. An anomalously high kinetic energy of the fragmentation ion $C_6H_5CO^+$ of the benzaldehyde molecule is noted. The mechanism of formation of the photoionization mass spectrum of the molecules by intense UV radiation is discussed.

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1. INTRODUCTION

The possibility of using two-step IR-VUV laser photoionization of molecules in a mass spectrometer to increase its sensitivity and selectivity was noted in 1972.[1] The possibility of developing on this basis a two-dimensional mass-optical spectrometer as a new highly selective method of detecting tract amounts of complex molecules was discussed many times.[2] Selective two-step photoionization was first realized for this purpose in Ref. 3, with the formaldehyde molecule in the gas phase as the example. The use of two lasers, one IR and the other VUV, with controllable delay between the lasing pulses, made it possible to investigate the decay kinetics of the intermediate electronic state. Further experiments on multistep ionization (MSI) by laser radiation in the molecular jet of a mass spectrometer[4] have demonstrated the high sensitivity of registration of the optical absorption spectra of polyatomic molecules. It turned out that the mass spectra of MSI of polyatomic molecules are quite sensitive to intramolecular processes in intermediate vibronic states.

Work on multiphoton ionization (MPI) of molecules has developed in parallel since 1975. The first MPI investigations[5] were performed in a gas and the total ion signal was recorded in a parallel-plate capacitor. Later studies[6] were devoted to MPI and to fragmentation of very simple diatomic molecules in a mass spectrometer. The investigation of the MPI spectra yielded valuable information on the Rydberg states as well as on states forbidden to single-photon transitions.[7] It was shown,[8] with the benzene molecule as the example, that at intensities 10^{10} W/cm^2 the MPI is accompanied by rather effective fragmentation of the molecules, way down to C^+ fragments. It turned out to be impossible, however, to investigate the character of the fragmentation as a function of the radiation intensity, since the limiting stage with respect to the ion yield was two-photon absorption from the ground state, and the succeeding transitions were close to saturation.

An attempt was made in Ref. 9 to investigate the fragmentation of the benzene molecule by radiation from an excimer KrF laser through real molecular levels. The experiment revealed an intense molecular benzene ion, but the high level of background ionization of the residual gas in the mass spectrometer made it impossible to register the mass spectrum of the fragmentary ions. In investigation[10] of stepwise photoionization of benzene the radiation intensity was too low to observe the formation of fragmentary ions.

We report here an investigation, for the first time ever, of the formation of the mass spectrum in photoionization of benzaldehyde and benzene molecules by the radiation from an excimer laser with $\lambda=249$ nm in a wide intensity band $5.10^4 - 5.10^9$ W/cm. The first laser photon excited the benzaldehyde molecule to high vibrational states of the second electronic singlet S_2 and partially into state S_3, and the benzene molecule into the state S_1. It was of interest to track the change in the photoion mass spectra on going from the "soft regime" of two-step photoionization through real quantum states at low laser intensity to photoionization in fields of the order of several GW/cm when multiphoton ionization already proceeds effectively.

The results of the experiment have shown that fragmentation ions appear at a radiation intensity as low as 1 MW/cm^2. The mechanism of their production mechanisms are different for the benzaldehyde and benzene molecules. At relatively low radiation intensities, the largest mass is possessed by the ions produced by two-stage ionization. These are molecular benzene and benzaldehyde ions and the fragmentation ion $m/e=78$ produced in photoionization of benzaldehyde and corresponding to the benzene ion. It was shown that the appearance of the benzene ion in the photoionization mass spectrum of benzaldehyde is evidence of regrouping dissociation of benzaldehyde in the electronically excited state into the benzene and CO molecules.

With increasing radiation intensity, ever lighter ions appear in the photoionization mass spectrum, down to C^+, and may be produced by multiphoton ionization.

2. EXPERIMENTAL SETUP

Collimated radiation of an excimer KrF laser of wavelength 249 nm, pulse duration 20 nsec, and maximum lasing energy 20 mJ was directed through atten-

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uators to the ion source of a time-of-flight mass spectrometer specially developed for laser-photoionization experiments.[1] The dimensions of the photoionization volume was $0.5\times1\times4$ mm^3 when working in the intensity range $5.10^4 - 10^7$ W/cm and $0.075\times0.4\times4$ mm^3 when working in the range $10^7 - 5.10^9$ W/cm^2.

The ions produced in the photoionization volume were accelerated and mass-separated in the field-free region, after which they were incident on *a* the cathode of a VÉU-2B "venetian blind" secondary-electron multiplier with a gain 10^7. The photoion registration efficiency was 50%. The signal from the multiplier was measured on a 50 Ω load with an S8-12 memory oscilloscope. The mass-spectrometer resolution at the 0.5 level was 200.

Oil-free vacuum pumping of the mass-spectrometer volume was effected with an NORD-100 magnetodischarge pump after preliminary pumping with a zeolite adsorption pump. The effective rate of evacuation of the ionization chamber was 3 liter/sec. To reduce the background ionization of the residual gas the volume of the mass spectrometer was pumped out prior to the experiment for a day at a pressure 10^{-8} Torr. Benzaldehyde or benzene vapor was fed to the ion source through a needle leak valve. The working pressure of the medium during the experiment was maintained at 2×10^{-6} Torr with continuous gas flow. The gas pressure was measured with a *VI*-14 ionization vacuum meter and was monitored against the discharge current of the NORD-100 magnetodischarge pump. Prior to admission to the mass spectrometer, the benzaldehyde was purified by passing through sodium bisulfite,[12] followed by distillation in a helium atmosphere and analysis with a chromatograph. The impurity content did not exceed 0.1%. Chromatographically pure benzene was used in the experiments.

3. FORMATION OF PHOTOION MASS SPECTRUM

A. Experimental results

Figure 1 shows the photoionization mass spectra of benzaldehyde at two intensities of the laser radiation, 2 MW/cm^2 and 1 GW/cm^2. To determine the relative intensities of the mass-spectrum components we compared the time integrals of the corresponding signal pulses from the secondary electron multiplier. At high intensities the photoionization mass spectrum reveals a most intense fragmentation of the molecule, down to C^+ ions. From a comparison with the mass spectrum of benzaldehyde under electron impact,[13] shown in the same figure, it is seen that the observed fragmentary photoions are practically the same as obtained by electron impact. The relative intensities of the light ions are, however, much higher. Even at relatively low radiation intensity 2 MW/cm^2 the fraction of the molecular ion $C_6H_5CHO^+$ in the spectrum is small.

The picture is qualitatively different in photoionization of the benzene molecule (Fig. 2a). Here the molecular ion dominates in the photoionization mass spectrum at the 2 MW/cm^2 intensity and the entire mass spectrum is more similar to the electron-impact mass spectrum (Fig. 2b). The molecular ion of benzene remains maximal in the mass spectrum also at higher intensities, at least up to 20 MW/cm^2.

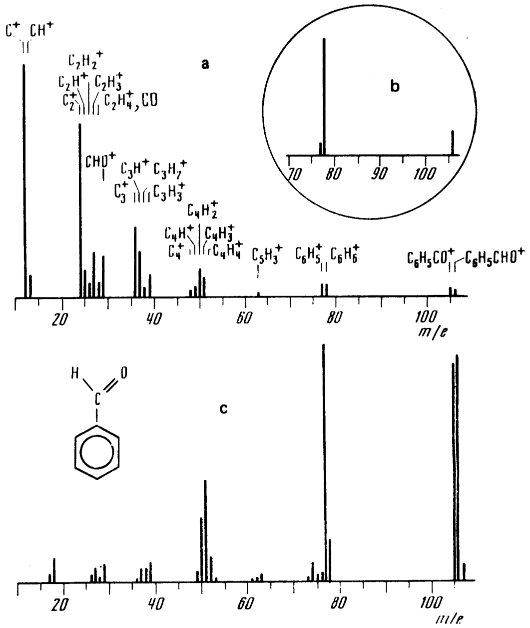

FIG. 1. Mass spectra of benzaldehyde molecule: a—photoionization mass spectrum at laser radiation intensity I= 1 GW/cm^2, b—photoionization mass spectrum at I= 2 MW/cm^2, c—mass spectrum in ionization by electron impact.

The dependences of the intensities of the most characteristic mass peaks of the photoionization mass spectra of benzaldehyde and benzene on the emission intensity are shown in Fig. 3. The registered ion signal was normalized to unit volume.

Attention is called to the fact that the effectiveness of benzene photoionization exceeds that of benzaldehyde by more than two orders of magnitude. The maximum registered signal of an individual ion component amounted to 10^4 ion/pulse and was limited by the region

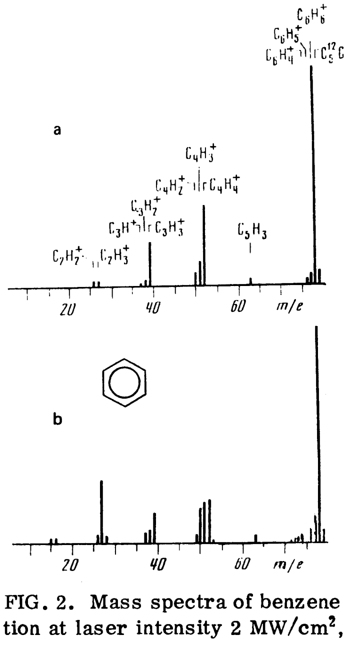

FIG. 2. Mass spectra of benzene molecule: a—photoionization at laser intensity 2 MW/cm^2, b—by electron impact.

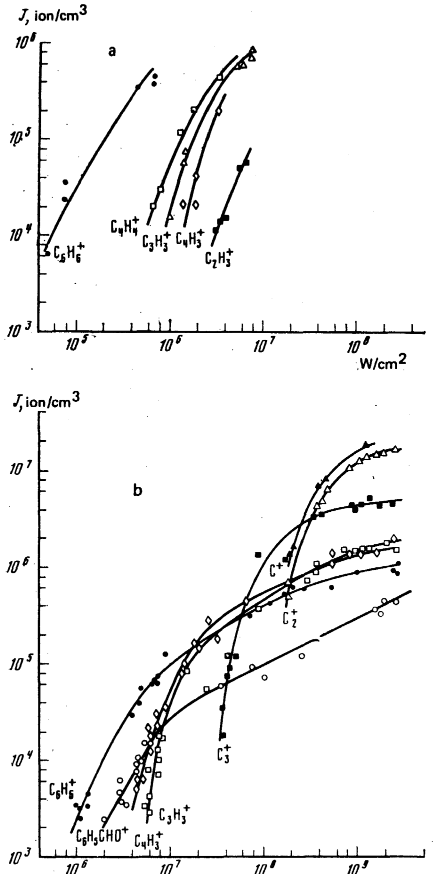

FIG. 3. Intensities J of individual components of the mass spectrum vs the intensity of the laser radiation: a—benzene, b—benzaldehyde.

of linearity of the secondary electron multiplier. The mass spectrum of benzene was therefore measured at radiation intensities not exceeding 10 MW/cm². The photoionization mass spectrum of benzaldehyde was investigated in a wide range of radiation intensities, from 5×10^4 to 5×19^5 W/cm². Absorption saturation in the first stage took place in this case at a radiation intensity $I_{\text{sat}} = \hbar\omega/\tau_{\text{pul}}\sigma_{\text{abs}} = 6\times10^7$ W/cm². For the benzene molecule no absorption saturation was reached at the first stage, $I < I_{\text{sat}} = 1.3\times10^2$ W/cm².

To calculate the saturation of the benzaldehyde and benzene we used the measured absorption cross sections σ_{abs} at the UV laser wavelength; these were equal to 6.2×10^{-19} and 3×10^{-19} cm², respectively. In the case of the benzene molecule the laser wavelength agrees well with the oscillations in the first electronic singlet S_1. Benzaldehyde has in this wavelength region a structureless absorption spectrum.[14] The absorption corresponds to the start of the strong absorption band in S_3, as well as to some fraction of the highly excited vibrational states in S_2.

The general tendency of the transformation of the photoionization mass spectrum with increasing laser radiation intensity consists in the appearance of ever more lighter ions and a simultaneous saturation of the yield of the heavier ions. At maximum radiation intensities 2—5 GW/cm² practically all the ion peaks reach saturation. It is typical that the yields of all the ion components increases monotonically with intensity.

In the region of the lowest intensities, 0.05—2 MW/cm², the predominant ions in the spectrum are those having a quadratic dependence of the yield on the intensity. These are the molecular and fragmentary ion $m/e = 78$ in the case of benzaldehyde and one molecular ion in the case of benzene. The quadratic dependences point to a two-step photoionization process. This agrees in both cases with the energetics of the ionization: the energy of the two laser emission photons $2\hbar\omega \approx 10$ eV exceeds the ionization potentials 9.51 and 9.25 eV of the benzaldehyde and benzene molecules, respectively.[15] The question of the appearance of the fragmentary ion $m/e = 78$ in benzaldehyde will be considered in Sec. 4.

B. Discussion of experimental results

The mechanism of formation of the mass spectrum when the molecule is ionized by electron impact differs from molecule photoionization by intense UV laser radiation. In the former case the molecule acquires immediately the entire energy, which exceeds greatly the ionization potential, and this is followed by ionization of the molecule and subsequent cascade decay of the overexcited ion into fragments.[16] When the molecule is ionized by laser radiation, two channels of fragmentary-ion formation are possible. In the first (Fig. 4a) the ions are produced during the time of the laser pulse via successive processes of radiation absorption, dissociation, and subsequent ionization of the fragments. The second channel (Fig. 4b) corresponds to successive dissociation of the produced ions, starting with the molecular ion in the laser-radiation field. Nonetheless, the photoionization mass spectra and the electron-impact mass spectra are qualitatively similar, all the peaks in the photoionization mass spectrum are present also in the mass spectrum of the molecule in the case of electron impact. Moreover, at low radiation intensities the yield of the fragmentation ions reflects qualitatively the potential at which they appear.[11] The ions with the larger yield are those with the smaller appearance potentials. This is evidence that an important role in the formation of the mass spectrum is played by the energetics of the bonds in the molecule regardless of how it is excited.

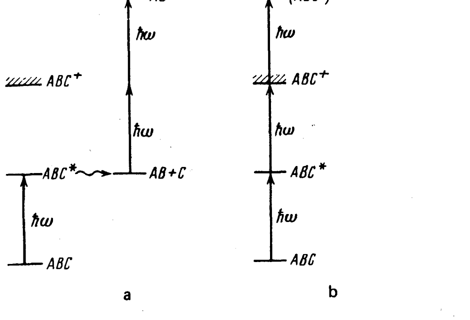

FIG. 4. Scheme of possible channels of photoion production: a—photoionization of neutral fragments of the molecule, b—dissociation of molecular ion by laser radiation.

However, not all the fragmentary ions have an intensity corresponding to the appearance potential. For example, in the case of benzene the fragmentary ion with the smallest appearance potential is $C_6H_5^+$, but its yield is nevertheless quite small. In principle this is not surprising if it is recognized that during each stage of the absorption process the character of the photophysical processes depends essentially on the radiation wavelength and on the structure of the electron-excited states. The fact that all the characteristic mass peaks are preserved in the photoionization mass spectrum, as well as that at radiation intensities ~1 GW/cm^2 the mass spectrum depends little on the intensity, uncovers a possibility of using the ionization of the molecules by an intensive UV laser for the purposes of mass-spectral analysis.

In the general case the photoionization mass spectrum of the molecules is apparently produced simultaneously via both channels. However, the second mechanism seems to predominate in the case of the benzene molecule. Inasmuch as upon excitation by radiation of wavelength $\lambda = 249$ nm the benzene molecules does not dissociate within the pulse time,[17] the molecule is effectively ionized by the second photon. This explains the high yield of the molecular benzene ion. Further formation of fragmentary ions is more probable when the molecular ion is dissociated by radiation than when the radicals are ionized, since the latter are produced only after the molecule has absorbed the second radiation photon.

The photofragmentation of the benzaldehyde molecule is mainly via the first channel. The low yield of the molecular ion and the predominance of the fragmentary ions in the mass spectrum even at relatively low radiation intensity point to effective dissociation of the molecule during the first stage. The constant growth of the molecular-ion yield up to a maximum intensity 5 GW/cm^2 is the result of the competition between the rates of dissociation and ionization of the molecule from the electron-excited state.

It should be noted that the benzaldehyde molecule is ionized from the electronic states with a large reserve of vibrational energy. The sum of the two laser-radiation photons exceeds by only 0.5 eV the molecule ionization threshold. This should lead on principle to small Franck-Condon factors for the absorption of the second radiation photon with ionization, and to an increase of the fraction of the dissociating molecules. The mass spectrum of benzaldehyde is thus formed mainly by ionization of neutral fragments of the molecules. This leads on the whole to a rather low photon yield. The total number of ions registered at a radiation intensity 5 GW/cm^2, corresponding to saturation of the mass spectrum, amounts to approximately 0.1% of the number of molecules in the photoionization volume. Assuming that the general character of the dependences of the yield of the benzene photoions at high intensities is similar to the curves for benzaldehyde, we can expect the total yield of the benzene ions at the same intensity to be about 10%.

The formation of molecular ions of benzene and benzaldehyde follows the scheme of two-step photoionization through an electron-excited intermediate state. An estimate of the cross section of photoionization of the benzene molecule from the excited electronic S_1 state yields a value 2×10^{-18} cm^2. The light fragmentary ions, especially in the case of the benzaldehyde, can be produced at high radiation intensities via multiphoton ionization of the molecule dissociation products. The effectiveness of multiphoton ionization of molecules at radiation intensities 10^{10} W/cm^2 was demonstrated in a number of studies.[8,9]

4. REGROUPING DISSOCIATION OF BENZALDEHYDE INTO BENZENE MOLECULES AND CO

A characteristic feature of the photoionization mass spectrum of the benzaldehyde molecule is the presence of the component $m/e = 78$, corresponding to the molecular benzene ion $C_6H_6^+$, and at low radiation intensities this peak is the highest in the spectrum and has a quadratic dependence on the radiation intensity. It is obvious that simple removal of arbitrary parts of the benzaldehyde molecule cannot lead to production of benzene. This calls for detachment of the aldehyde group CHO with transfer of a hydrogen atom from the aldehyde group to the benzene ring.

There are three channels through which a benzene ion can be produced at all:

1) Ionization of the benzaldehyde molecule from an excited state by a second radiation photon with formation of a regrouped benzene ion together with a molecular benzaldehyde ion. It is known[16] that in the case of electron impact and ordinary single-photon photoionization the mass spectra of the molecules frequently contain components corresponding to regrouping ions. In the case of benzaldehyde and single-photon photoionization, however,[18] no such ion was observed even when the photon energy exceeded the ionization threshold by more than 3 eV. It is therefore most unlikely that in two-stage photoionization with total photon energy 10 eV this process will predominate over the yield of a molecular ion.

2) The formation of a benzene ion in the case of regrouping dissociation of a molecular benzaldehyde ion under the influence of laser radiation. This channel does not account for the quite larger yield of the benzene ion compared with the molecular benzaldehyde ion, nor the quadratic dependence on the radiation intensity.

3) Regrouping dissociation of benzaldehyde into benzene by ionization of the benzene by the second photon. Simple thermochemical calculations show that this dissociation is an exothermic reaction in which an energy 0.1 eV is released. This means that the benzaldehyde molecule is metastable with respect to decay into benzene and CO, but the high potential barrier makes this molecule stable in the electronic ground state.

The experimental data on the benzene-ion yield agree well with the last mechanism. The potential barrier in the electron-excited state of benzaldehyde is apparently significantly lowered and the molecule dissociated into

CO and electron-excited benzene, which is ionized by the second radiation photon (Fig. 5). It was established in Ref. 10 that when benzaldehyde is excited into an electron-excited state the molecule dissociates into benzene and CO, with a high quantum yield. The data of that reference, however, pertain to the case when the collisions between the molecules in the gas play an important role. In the present paper we have established that regrouping dissociation of the benzaldehyde molecule takes place in the collisionless case.

We note that stepwise laser photoionization of molecules in a mass spectrometer can be systematically used to investigate collisionless photodissociation of molecules. Particular interest attaches in this connection to the use of two time-synchronized pulsed lasers.[3,4]

5. FORMATION OF THE FRAGMENTARY BENZALDEHYDE ION $C_6H_5CO^+$ WITH ANOMALOUSLY HIGH KINETIC ENERGY

When the laser radiation intensity exceeds 0.5 GW/cm^2, the ionic component $m/e = 105$ of the photoionization mass spectrum of benzaldehyde is strongly broadened (Fig. 6). This indicates that $C_6H_5CO^+$ ions produced in the photoionization volume of the time-of-flight mass spectrometer have an anomalously large kinetic energy, estimated at 0.08 – 0.1 eV. The mechanism of formation of a $C_6H_5CO^+$ ion with so high a kinetic energy is not yet clear. If it is assumed that the fragment C_6H_5CO is produced by detachment of a hydrogen atom from the benzaldehyde molecule, the required kinetic energy of the hydrogen atom is 8 – 10 eV, an unlikely figure.

6. CONCLUSION

Experiments on the photoionization of benzene and benzaldehyde molecules via an intermediate electron-excited state have shown that irradiation by a UV laser of intensity $I > 5$ MW/cm^2 results in intense fragmentation of the molecules. A characteristic feature of the change of the mass spectrum of the molecules when the radiation intensity is increased is the appearance of ever lighter ions with saturation of the yield of the heavy ions. The fact that practically all the ionic component of the photoionization mass spectrum are present also in the mass spectrum obtained by electron impact, and that their intensities correspond to the appearance potentials, is evidence that the energetics of the bonds in the molecule influences substantially the direction of the fragmentation, regardless of the molecule-excitation method.

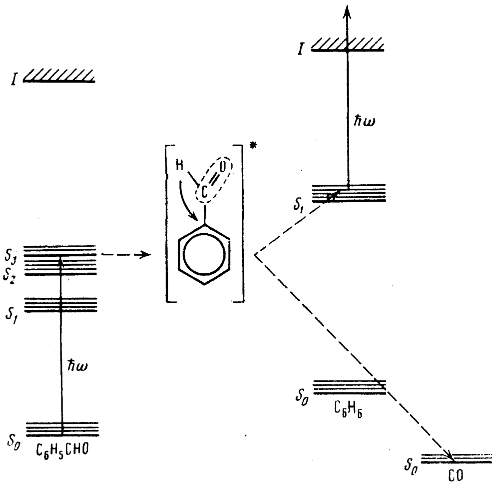

FIG. 5. Scheme of formation of benzene ion in photoionization of benzaldehyde.

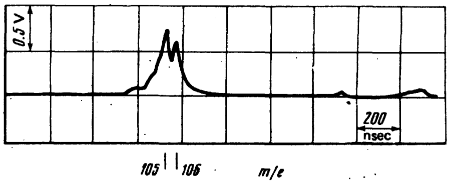

FIG. 6. Oscillogram of section of the photoionization mass spectrum of benzaldehyde in the region $m/e = 105$.

Owing to the presence of intermediate resonant levels, the ionization of the benzene and benzaldehyde molecules proceeds via a two-stage photoionization with a large photon yield. The molecule fragments can become ionized at a laser radiation intensity $I > 100$ MW/cm^2 via multiphoton ionization.

The data on the photoion yield in benzaldehyde attest to the important role of the dissociation in the intermediate electron-excited state of the molecule in the formation of the photoionization mass spectrum. It was observed that at moderate intensities the dominant role in the photoionization mass spectrum of benzaldehyde is played by the component $m/e = 78$, which corresponds to the benzene ion. It was shown that the formation of the benzene ion is due to regrouping dissociation of the benzaldehyde from the electron-excited state into benzene and CO molecules, followed by ionization of the benzene by the second laser-radiation photon. At a radiation intensity higher than 0.5 GW/cm^2, an anomalously high kinetic energy of the fragmentary ion $C_6H_5CO^+$ of the benzaldehyde was observed.

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Asymmetry of breakup of optically active molecules by longitudinally polarized relativistic electrons

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We estimate the optical asymmetry produced in a racemic mixture of dextro- and levorotatory molecules under the influence of longitudinally polarized electrons. We show how this effect is connected with the known asymmetry of the photochemical action of circularly polarized light. The expected asymmetry of the order of 10^{-6} is in agreement with not all the experiments on the chemical action of polarized electrons that are naturally obtained in β decay.

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1. INTRODUCTION

The predominance of certain optically active molecules over their antipodes in living matter is a puzzle long troubling the physicists, chemists, and biologists. The discovery of parity nonconservation in weak interaction has raised hopes that the dextro- and levorotatory asymmetry in living matter can be connected with weak interaction (see Refs. 1 and 2).

In principle the situation may involve the energy contribution of weak interaction, particularly on account of neutral currents,[3-6] which shifts the thermodynamic equilibrium. Another variant is connected with the longitudinal polarization of the electrons produced in the β decay of radioactive elements. It is known that the degree of their polarization, of the order of $p/E = (E^2 - m^2c^4)^{1/2}/E$, approaches unity for relativistic electrons. The chemical reactions caused by such electrons can have a somewhat different probability for dextro- and levomolecules, and this can lead to the appearance of optical activity in an initially racemic mixture. A general review of the problem, including specific biological enhancement mechanisms, can be found in Ref. 7. The first to suggest the role of polarization of β particles was Ulbricht (see Refs. 1 and 2).

Experiment[8-11] yields contradictory results, from zero to several percent. In view of the difficulty of the experiments and the various possible experimental errors, an independent theoretical estimate of the possible effect is highly desirable. It must be kept in mind here that in the case of photochemical action of cir-