

Contribution to the theory of the effect of orientation of atoms produced in photodissociation of molecules

O. S. Vasyutinskii

A. F. Ioffe Physicotechnical Institute, USSR Academy of Sciences

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A general theory is developed for the orientation effect of atoms produced in the photodissociation of molecules. The effect is studied qualitatively and quantitatively. Expressions based on the equation for the density matrix of the excited state of a diatomic molecule are obtained and describe the population, orientation, and alignment of the atoms formed upon photodissociation of molecules. Examples are given of obtaining oriented and aligned atoms in various photochemical reactions. The general conditions required for the existence of the effect are determined. Various possibilities of applying the effect are mentioned. Some of the more important are: a) obtaining oriented atoms of various elements (including those which cannot be obtained by ordinary means); b) obtaining qualitatively new information regarding the structure of the ground and excited states of molecules.

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Observation of orientation of atoms in the course of photodissociation of molecules by circularly polarized radiation was recently reported.¹ Oriented cesium atoms in the ground state, produced by photolysis of CsI molecules by ultraviolet radiation in the reaction



were registered.

The gist of the observed physical phenomenon is that the angular momentum introduced by the polarized light into the molecular system is transferred via unstable excited states of the molecules to the atoms produced as a result of the photodissociation.

The present paper is devoted to a theoretical treatment of this phenomenon for the purpose of clarifying the main regularities of the observed effect and of determining the possibility of observing it in other molecules. As a preliminary, model concepts are used for a qualitative analysis of the described phenomenon. The equation of the density matrix of the excited states of a diatomic molecule is used next to obtain general expressions for the population, orientation, and alignment of the atoms produced in the photodecay of the molecule. The conditions needed for the existence of the considered phenomenon are determined. It has turned out that these conditions are quite general, so that the effect should be observed on many types of molecules. The degree of orientation and alignment of the produced atoms is determined by the properties of the exciting radiation and by the structure of the ground and excited states of the molecule.

Examples of the production of oriented atoms corresponding to various types of molecule photodecay are considered, and in a number of cases the degree of orientation can be quite high and close to 100%.

The possible applications of the effect of atom orientation in the course of molecule photodissociation are indicated. In particular, the effect can be used to obtain oriented atoms of hydrogen, alkali metals, halogens, silver, thallium, and others. In addition, it is possible to obtain important information on the structure of the

short-lived excited states of the molecules. These states are presently intensively investigated theoretically and experimentally,²⁻⁷ owing primarily to the possibility of developing photodissociation lasers.⁸ It is shown in the present paper that the registration of the orientation or alignment of atoms produced in photodissociation of molecules makes it possible to measure the relative contributions of various molecular levels in the course of photodissociation for levels of arbitrary symmetry, and also to ascertain certain other properties of excited states, many of which cannot be determined by other known methods.

§ 1. QUALITATIVE TREATMENT OF ATOM ORIENTATION IN THE COURSE OF MOLECULE PHOTODISSOCIATION

Here and elsewhere we consider the photodecay of a diatomic molecule, but it appears that the atom-orientation effect should be observed also in the photodecay of polyatomic molecules.

We consider a diatomic molecule AB (Fig. 1), characterized by a nuclear angular momentum N and an electronic excited-state angular momentum J_{e1} . We consider for the sake of argument the case of strong spin-orbit interaction in the molecule (the case of "c" coupling after Hund,⁹) when J_{e1} should be taken to mean the

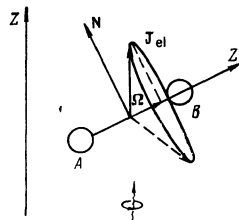


FIG. 1. Schematic representation of a diatomic molecule AB ; N —angular momentum of the rotation of the nuclei; J_{e1} —electron angular momentum of the excited state of the molecule; Ω —projection of the vector J_{e1} on the molecule axis Z' . The exciting light is circularly polarized and propagates in the direction of the laboratory coordinate axis Z .

total electronic angular momentum of the molecule.

Let the light that causes the photodissociation be polarized circularly and direct along the Z axis. Then, as a result of the angular-momentum conservation law, it can be assumed that at the instant when a light photon is absorbed the molecule goes to an excited state with angular momentum J_{e1} directed along the Z axis. Since the electrons move in the molecule in the presence of a strong electric field directed along the molecule axis Z' , the angular momentum begins to precess around the axis joining the nuclei,⁹ as shown in Fig. 1. The result is the averaging of the electron orientation in the excited state of the molecule. However, the averaging is not complete, since the projection of the angular momentum on the Ω axis of the molecule is preserved. An exception is the case $\Omega=0$, when the angular momentum introduced into the excited state of the molecule is completely averaged out. In this case, no orientation of the atoms produced in the photodecay of the molecule should be observed. As will be shown below, this conclusion is confirmed also in a more rigorous analysis of the described phenomenon. If $\Omega \neq 0$, further averaging of the orientation in the excited state of the molecule takes place as a result of rotation of the molecule, and also on account of the coupling of the electron motion with the nuclear motion. If, however, the photodecay proceeds rapidly enough compared with the times that characterized the last two processes (and it is precisely this case which is usually realized⁹), the atoms produced upon decay of the molecule should be predominantly directed along the total electronic angular momenta, and it is this process which is called orientation.¹⁰

§2. EQUATION FOR THE DENSITY MATRIX OF AN EXCITED STATE OF A MOLECULE

Let the quantum numbers J , m , and Ω characterize, respectively, the total angular momentum of the excited state of a diatomic molecule and its projection on the Z axis in the laboratory frame and on the Z' axis that coincides with the molecule axis. The analogous quantum numbers for the ground state of the molecule are designated J_0 , m_0 , and Ω_0 . We confine ourselves to molecules whose ground state is $^1\Sigma$. For this type of molecule $\Omega_0=0$. In the Born-Oppenheimer approximation¹¹ we can write down the total wave function of the molecule in the form

$$\Psi(\mathbf{R}, \mathbf{r}_i) = \sum_{Jm\Omega} a_{Jm\Omega}^n \Psi_{n\Omega}^{AB}(\mathbf{R}, \mathbf{r}_i) \Psi_{Jm\Omega}^{\text{rot}}(\mathbf{R}) + \sum_{J_0 m_0} b_{J_0 m_0} \Psi_0^{AB}(\mathbf{R}, \mathbf{r}_i) \Psi_{J_0 m_0}^{\text{rot}}(\mathbf{R}), \quad (2)$$

where the quantum numbers n and Ω characterize the electron wave function of the molecule AB , and the last factor in each term describes the rotation of the molecule. \mathbf{R} is a vector characterizing the relative arrangement of the nuclei, and \mathbf{r}_i is the aggregate of the coordinates of all the electrons of the molecule.

We obtain now an equation for the density matrix of the excited state:

$$\rho^{AB} = \rho_{Jm\Omega, J'm'\Omega'}^{AB} = a_{Jm\Omega}^n \alpha_{J'm'\Omega'}^n. \quad (3)$$

We make the following assumptions concerning the properties of the electronic state of the molecule and the properties of the light that interacts with the molecular system:

- 1) The width of the excitation spectrum exceeds substantially the frequencies corresponding to the energy intervals between the magnetic sublevels m, m' ; m_0, m'_0 of the excited and ground states.
- 2) The width of the excitation spectrum is less than the value of the rotational quantum of the ground state. This condition is introduced only to make things definite. Failure to satisfy it leads only to a change of the proportionality coefficient in the formulas that are obtained below and does not influence the degree of orientation or alignment of the atoms.
- 3) The reciprocal lifetime of the molecule in the excited state (Γ^{-1}) exceeds substantially the frequencies that characterize the evolution of the density matrix in the excited state of the molecules (for example, the rotation frequency of the molecule).
- 4) Phenomena connected with transitions of the molecule from one potential curve of the excited state to another are not considered; this corresponds to the adiabatic approximation.¹²
- 5) All the magnetic sublevels of the molecular spin state described by the given value J_0 , are equally populated.

We note that not all the conditions 1–5 are necessary for the existence of the physical phenomenon under consideration. The conditions necessary for the existence of the effect will be presented below.

It can be shown that when conditions 1–5 are satisfied, the equation that describes the evolution of the density matrix of the excited state of the molecule takes the form (we use here and elsewhere a system of units in which $\hbar=1$).

$$\frac{d}{dt} \rho_{Jm\Omega, J'm'\Omega'}^{AB} = F_{Jm\Omega, J'm'\Omega'} - \rho_{Jm\Omega, J'm'\Omega'}^{AB} / \Gamma. \quad (4)$$

The first term in the right-hand side of (4) describes the appearance of the molecules in the excited state on account of absorption of the light:

$$F_{Jm\Omega, J'm'\Omega'} = F_0 \sum_{m_0} \langle Jm\Omega | \hat{d}e | J_0 m_0 \rangle \langle J'm'\Omega' | \hat{d}e | J_0 m_0 \rangle^*, \quad (5)$$

where \hat{d} is the operator of the electric dipole moment of the molecule, e is the polarization vector of the exciting light, and the constant F_0 is proportional to the intensity of the exciting light and depends on its spectral composition and on the population of the considered vibrational-rotational sublevel of the ground state.

Expressions (4) and (5) can be obtained by the same method as used in Ref. 13 to obtain the equations for the density matrix of the excited state of an atom.

The second term in the right-hand side of (4) describes the departure of the molecules from the excited state as a result of their decay. On the basis of (4) and (5) we can obtain an expression for the density matrix $\rho^{(A^*B)}$ of the atoms produced in the decay of the mole-

cule. It is necessary beforehand, however, to derive a relation between the density matrices ρ^{AB} and $\rho^{(A+B)}$.

§3. DERIVATION OF A RELATION BETWEEN ρ^{AB} AND $\rho^{(A+B)}$

We consider the expression for the total wave function of the excited state of the molecule:

$$\Psi^{\text{exc}}(\mathbf{R}, \mathbf{r}_i) = \sum_{J_m \Omega} a_{J_m \Omega}^n \Psi_{n \Omega}^{AB}(\mathbf{R}, \mathbf{r}_i) \Psi_{J_m \Omega}^{\text{rot}}(\mathbf{R}). \quad (6)$$

We change in (6) from the molecular to the atomic basis. It is necessary to bear in mind here that the sought relation must be valid only in the limiting case $R \rightarrow \infty$, inasmuch as it is precisely at large R that the molecule decays into atoms. We can therefore write the wave function $\Psi_{n \Omega}^{AB}(\mathbf{R}, \mathbf{r}_i)$ in the form

$$\Psi_{n \Omega}^{AB} = \sum_{J_1 \Omega_1, J_2 \Omega_2} T_{J_1 \Omega_1, J_2 \Omega_2}^n \Psi_{J_1 \Omega_1}^A \Psi_{J_2 \Omega_2}^B.$$

Here $J_1, \Omega_1, J_2, \Omega_2$ are the total angular momenta of the atoms A and B and their projections on the molecule axis, while the elements of the matrix T differ from zero only if $\Omega = \Omega_1 + \Omega_2$.

Expanding $\Psi_{J_1 \Omega_1}^A$ and $\Psi_{J_2 \Omega_2}^B$ in terms of the atomic wave functions referred to the laboratory frame, and expressing the function $\Psi_{J_m \Omega}^{\text{rot}}(\mathbf{R})$ in the form¹⁴

$$\Psi_{J_m \Omega}^{\text{rot}}(\mathbf{R}) = \left(\frac{2J+1}{8\pi^2} \right)^{1/2} D_{\Omega m}^J(\omega),$$

where $D_{\Omega m}^J(\omega)$ is the Wigner D function¹⁵ and ω is the aggregate of the Euler angles that describe the rotations of the molecule in space, we can transform (6) into

$$\Psi^{\text{exc}} = \sum_{n_1, m_1} a_{J_1 m_1}^{(A+B)}(\omega) \Psi_{J_1 m_1}^A \Psi_{J_2 m_2}^B.$$

This leads to the sought relation between the atomic and molecular density matrices:

$$\rho^{(A+B)}(\omega) = a^{(A+B)}(\omega) [\alpha^{(A+B)}(\omega)]^+ = \hat{S}(\omega) \rho^{AB} \hat{S}^+(\omega). \quad (7)$$

Here $\hat{S}(\omega)$ is the transformation matrix:

$$S(\omega; J m \Omega n; J_1 m_1 J_2 m_2) = \frac{\Pi_J}{(8\pi^2)^{1/2}} D_{\Omega m}^J(\omega) \sum_{\Omega_1, \Omega_2} T_{J_1 \Omega_1, J_2 \Omega_2}^n D_{\Omega_1 m_1}^{J_1}(\omega) D_{\Omega_2 m_2}^{J_2}(\omega),$$

where $\Pi_J = (2J+1)^{1/2}$.

§4. DERIVATION AND TRANSFORMATION OF THE EXPRESSION FOR THE ATOMIC DENSITY MATRIX

We shall use hereafter the density matrix ρ^A , which describes the state of the atoms of type A produced in the decay of the molecule. This matrix can be obtained by averaging the total atomic density matrix $\rho^{(A+B)}$ over the states of the atoms of type B :

$$\rho^A = \rho^A(J_1) = \text{Sp}_B \rho^{(A+B)} / \text{Sp}_B \rho^{(A+B)}. \quad (8)$$

Using (4), (5), (7), and (8), averaging over the ensemble of molecules (assuming that the distribution of the directions of the molecule axes in space is isotropic) and summing over m, m', m_0, J , and J' , the expression for the density matrix $\rho(J_1)$ can be written in the form

$$\begin{aligned} \rho_{m_1 m_1'}^{(J_1)} &= \frac{\sqrt{3}(-1)^{m_1}}{N} \sum_{C_1 \Gamma_1'} \frac{(-1)^{q_1 - \Gamma_1'}}{\Pi_C} C_{J_1 - m_1, J_1 m_1'}^{C_1 \Gamma_1'} \\ &\quad \times C_{J_1 - q_1, q_1}^{C_1 \Gamma_1'} C_{J_1 - \Omega_1, J_1 \Omega_1'} \Phi_{C_1 \Gamma_1'}(\mathbf{e}) L^{J_1 J_1'}(x); \\ \Phi_{C_1 \Gamma_1'}(\mathbf{e}) &= \sum_{p_1, p_2} (-1)^{p_1} e_{p_1} e_{p_2} \begin{pmatrix} 1 & 1 & C \\ p_1 & -p_2 & -\Gamma_1' \end{pmatrix} \\ L^{J_1 J_1'}(x) &= T_{J_1 \Omega_1, J_2 \Omega_2}^n T_{J_1 \Omega_1', J_2 \Omega_2'}^{n' \Omega_1'} \langle \Omega | d_{q_1} | 0 \rangle \langle \Omega' | d_{q_1} | 0 \rangle. \end{aligned} \quad (9)$$

Here d_{q_1} and d_{q_2} are cyclic projections of the operator d in a coordinate system that is rigidly fixed in the molecule, the matrix elements depend only on the "internal" quantum numbers n, n', Ω, Ω' and on the form of the potential curves of the ground and excited states, while x is taken to mean the aggregate of the symbols $n, n', \Omega, \Omega', \Omega_1, \Omega_1', \Omega_2, q_1$, and q_2 . The normalization factor N is of the form

$$N = 3^{-1/2} \sum_x L^{J_1 J_1'}(x) \delta_{\Omega_1 \Omega_1'}.$$

It was taken into account in the summation that matrix elements of the type $\langle \Omega | d_{q_1} | 0 \rangle$ satisfy the selection rules $\Omega = q_1$.¹¹

The obtained expression (9) yields the dependence of the change of the matrix $\rho(J_1)$ on the direction and polarization of the exciting light, and also on the structure of the ground and excited states of the molecule. In practice, however, the use of these formulas is not convenient. The equations in (9) can be substantially simplified by changing over to a density matrix in the irreducible-tensor representation. The transition from the atom density matrix in the m_1, m_1' representation to the density matrix in the irreducible κ, Q representation is by means of the formula¹⁶

$$\rho_{\kappa Q}(J_1) = \Pi_{J_1} \sum_{m_1, m_1'} (-1)^{J_1 - m_1} \begin{pmatrix} J_1 & \kappa & J_1 \\ -m_1 & -Q & m_1' \end{pmatrix} \rho_{m_1 m_1'}(J_1).$$

The use of the density matrix $\rho_{\kappa Q}(J_1)$ enables us to employ in the calculation the mean values of the physical quantities observed in the experiment:

$$\rho_{00}^A(J_1) = \text{Sp}_A \rho^A = 1, \quad \rho_{10}^A(J_1) = (-1)^Q \langle \hat{J}_{1Q} \rangle / [J_1(J_1+1)]^{1/2}.$$

The degree of orientation of the atoms is determined in this case from the equation

$$P_A = (-1)^Q \left(\frac{J_1+1}{J_1} \right)^{1/2} \rho_{10}^A(J_1). \quad (10)$$

The expressions obtained on the basis of (9) for the density matrix in the κ, Q representation can be written in the following form:

$$\begin{aligned} \rho_{\kappa Q}(J_1) &= \Phi_{\kappa Q}(\mathbf{e}) M_{\kappa}^{J_1 J_1'}, \\ M_{\kappa}^{J_1 J_1'} &= - \frac{(-1)^{\kappa}}{N} \sum_x C_{J_1 \Omega_1, \kappa(\Omega_1 - \Omega_1')}^{J_1 \Omega_1'} C_{J_1 \Omega_1, \kappa(\Omega_1 - \Omega_1')}^{J_1 \Omega_1'} L^{J_1 J_1'}(x). \end{aligned} \quad (11)$$

We have thus obtained an invariant expression for the density matrix of the atom produced when light interacts with a molecular system.

The right-hand side of (11) consists of two factors, the first of which $\Phi_{\kappa Q}(\mathbf{e})$ is determined completely by the direction and polarization of the exciting light. The second factor $M_{\kappa}^{J_1 J_1'}$ characterizes the properties of the molecular system. We note that the function $\Phi_{\kappa Q}(\mathbf{e})$ coincides with the function $\Phi_{\kappa Q}(\mathbf{e})$ introduced by D'yakonov¹⁶ in his development of a theory of resonant scattering of

light by atoms. This function differs from zero only for the values $\kappa = 0, 1, 2$ corresponding to transfer from the light to the molecule of the zeroth polarization moment (population) and of the first and second polarization moments (orientation and alignment). The values of this function for all characteristics of the excited radiation are given in Refs. 10 and 16.

Expression (11) permits certain general conclusions to be drawn with respect to the connection between the polarization moments of the atoms produced in photolysis, and the types of dipole transitions in the molecule. Thus, from the properties of the Clebsch-Gordan coefficients that enter in (11) it follows that transitions that take place without a change of the quantum number $\Omega = \Omega_1 + \Omega_2$ [these transitions include, for example, $^1\Sigma_0^+ - ^1\Sigma_0^+$ in Cs_2 (Ref. 17) and $^1\Sigma_0^+ - ^3\Pi_0^+$ in Cl_2 (Ref. 9)] cannot lead to orientation of the produced atoms, but can cause them to become aligned.

More detailed information the electronic states of atoms produced in the considered photoprocess can be obtained considering actual particular cases.

§5. USE OF THE DERIVED EXPRESSIONS

In an actual calculation by means of Eqs. (11) it is necessary to determine first the values of the matrices T in these equations. The matrices T , determined by the form of the potential of the interaction between the atoms at large distances, can be obtained in the course of the determination of the eigenfunctions of the Hamiltonian $H = H_{so} + H_{int}$, where H_{so} is the spin-orbit interaction operator, and H_{int} is the operator of the interaction between the atoms under the condition that $H_{so} \gg H_{int}$.

Equation (11) remains valid for any type of interaction between the atoms at large distances,¹¹ but in the present paper we consider for simplicity, only the frequently encountered case when one of the atoms produced in the photodecay is in the $^2S_{1/2}$ state and the other in the $^2P_{1/2}$ or $^2P_{3/2}$ state. The photodissociation of the molecule AB can be described in this case by the following equations of the reactions:



Let us examine certain types of photodecays that follow these schemes.

1. *Photodecay of alkali-halide molecules.* These molecules will hereafter be designated MX , where M is the alkali-metal atom and X is the halogen atom. The structures of the ground and of the first two excited states of molecules of this type are shown in Fig. 2. According to Ref. 18, the excited states of these molecules are characterized by Hund's coupling scheme "c" and the first excited state consists of five sublevels, corresponding to the quantum numbers $\Omega = 2, 1, 1, 0^+, 0^-$, while the second excited state consists of three sublevels with $\Omega = 1, 0^+, 0^-$. The processes of photodecay via the first and second excited states can be described by Eqs. (12) and (13), by carrying out the transformations $A \rightarrow M$, $B \rightarrow X$. The treatment of the matrix elements of the van der Waals interaction in the basis

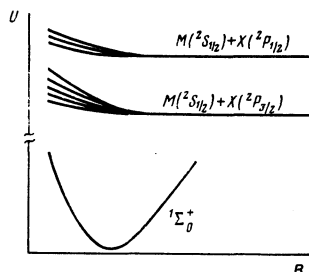


FIG. 2. Potential curves of the ground and of the first two excited states of the molecules MX (Ref. 18); U —potential energy of the interaction; R —distance between the nuclei.

$\Psi_{J_1 \Omega_1}^A, \Psi_{J_2 \Omega_2}^B$ makes it possible to determine the matrix T . The nonzero elements of the matrices T , which correspond to molecular sublevels to which transitions from the ground state are allowed, will be given below. One of the sublevels of the first excited state with $\Omega = 1$ is designated 1, and the second 1'.

First excited state:

$$T_{1/2 \pm 1/2, 1/2 \pm 1/2}^{\pm 1} = 1; T_{1/2 \mp 1/2, 1/2 \pm 1/2}^{\pm 1'} = 1; T_{1/2 \mp 1/2, -1/2}^{0^+} = 1/\sqrt{2}; T_{1/2 - 1/2, 1/2}^{0^+} = -1/\sqrt{2}. \quad (14)$$

Second excited state:

$$T_{1/2 \pm 1/2, 1/2 \pm 1/2}^{\pm 1} = 1; T_{1/2 \mp 1/2, -1/2}^{0^+} = 1/\sqrt{2}; T_{1/2 - 1/2, 1/2}^{0^+} = 1/\sqrt{2}. \quad (15)$$

We note that the sublevels belonging to a given excited state are regarded as overlapping in accordance with condition 3 of §2.

The atomic density matrices corresponding to the photodecay of the MX molecules can be written, using (11), (14), and (15) in the following form.

Photodecay in accordance with the reaction (12)

$$\rho_{1,0^+}^A(^1/2) = \frac{1}{N_1} \Phi_{1,0}(e) [a_1^2 - a_1'^2 - 2 \operatorname{Re}(a_1 b_1^*)], \quad (16a)$$

$$\rho_{1,0^+}^B(^2/2) = \frac{1}{\sqrt{5}N_1} \Phi_{1,0}(e) [3a_1'^2 + a_1^2 + 2 \operatorname{Re}(2a_1 b_1^* - \sqrt{3}a_1' b_1^*)], \quad (16b)$$

$$\rho_{2,0^+}^B(^2/2) = -\frac{\sqrt{3}}{5N_1} \Phi_{2,0}(e) [a_1'^2 + b_1^2 - a_1^2 - 2\sqrt{3} \operatorname{Re}(2a_1' a_1^* + a_1' b_1^*)]. \quad (16c)$$

Photodecay in accordance with the reaction (13):

$$\rho_{1,0^+}^B(^1/2) = \rho_{1,0^+}^A(^1/2) = \sqrt{2} \Phi_{1,0}(e) [a_2^2 + 2 \operatorname{Re}(a_2 b_2^*)] / [2a_2^2 + b_2^2], \quad (16d)$$

$$N_1 = [2a_1^2 + 2a_1'^2 + b_1^2] / \sqrt{2}.$$

We have introduced here the following notation for the matrix element of the electric dipole moment operator \hat{d} .

First excited state:

$$\langle 1|d_1|0\rangle = a_1, \quad \langle 1'|d_1|0\rangle = a_1', \quad \langle 0|d_0|0\rangle = b_1.$$

Second excited state

$$\langle 1|d_1|0\rangle = a_2, \quad \langle 0|d_0|0\rangle = b_2.$$

In the presented expression, Eq. (16a, b, c) describe the orientations of the atoms of the metal and of the halogen, while Eq. (16c) describes the alignment of the halogen atoms.

As seen from (16), an important role in the formation of the orientation and alignment of the atoms is played

by optical transitions that lead to coherence in the excited state of the molecules.

To determine the orientation and the alignment of the atoms produced in photodecay of the molecules MX , we calculated the matrix elements contained in (16). We used two-electron antisymmetrical wave functions, constituting in the general case the sum of the products of wave functions of noninteracting atoms. The two-electron approximation was used many times to calculate the transition probabilities in the diatomic MX molecules.^{2,19} To describe the excited states, orthogonal linear combinations of the atomic wave functions $\Psi_{J_1 \Omega_1}^A$, $\Psi_{J_2 \Omega_2}^B$ were used (accurate to terms of order Φ , where Φ is the overlap integral). The ground-state wave function used in the present paper was of the form

$$\Psi_0^{\text{gnd}} = \Psi_0^{\text{ion}} + \varepsilon_1 \Psi_0^{(1)} + \varepsilon_2 \Psi_0^{(2)}. \quad (17)$$

The subscripts of the wave functions represent the values of the quantum number $\Omega = 0$; $\Psi_0^{(1)}$ and $\Psi_0^{(2)}$ are the wave functions of the first and second excited states; Ψ_0^{ion} is the wave function describing the ion coupling in the ground state.¹⁹

It was assumed in Ref. 19 that $\varepsilon_1 = \varepsilon_2$, but these coefficients can be determined from the conditions for the orthogonality of the functions Ψ_0^{gnd} , $\Psi_0^{(1)}$, and $\Psi_0^{(2)}$. Confining ourselves to terms of order Φ , we obtain

$$\varepsilon_1 = -(\sqrt{2}/3)\Phi, \quad \varepsilon_2 = -2/3\Phi.$$

After calculating the values of the matrix elements and substituting them in (16), expressions were obtained for the matrices $\rho_{\alpha Q}$. It was assumed here that the pumping light is circularly polarized and propagates along the Z axis.

Photodecay in accordance with the reaction (12):

$$\rho_{10}^{\alpha}(\frac{1}{2}) = -\sqrt{5}\rho_{10}^{\alpha}(\frac{1}{2}) = \sqrt{\frac{5}{12}}t, \quad (18)$$

$$\rho_{20}^{\alpha}(\frac{1}{2}) = (3t+2)/10\sqrt{5}.$$

Photodecay in accordance with the reaction (13):

$$\rho_{10}^{\alpha}(\frac{1}{2}) = \rho_{10}^{\alpha}(\frac{1}{2}) = t/\sqrt{3}, \quad t = (A^2 - 2A\Phi R_0)/(2A^2 + \Phi^2 R_0^2).$$

Here $\Phi = \int \varphi_{00}^M \varphi_{10}^X d\mathbf{r}$, $A = \int \varphi_{00}^M r_1 \varphi_{1-1}^X d\mathbf{r}$ is the two-center dipole integral, φ_{00}^M and φ_{LM}^X are the orbital wave functions of the metal and halogen atoms, respectively, and R_0 is the equilibrium distance between the atoms and the molecule. If Slater orbitals² are used as the orbital functions, then the quantity ΦA is negative.

As seen from (18), the orientation and the alignment of the produced atoms depend on one parameter t , and if the photodecay follows the reaction (13), then the orientations of the atoms M and X are equal, while if the photodecay follows the reaction (12) the orientations of the atoms M and X have opposite signs and are unequal.

Recognizing that the interaction between the atoms and the excited states of the MX molecule is weak, we can conclude that in the first excited state of these molecules an "antiparallel" coupling of the angular momenta of the atoms is realized upon photodissociation, when

the angular momentum $\langle \hat{J}_M \rangle$ of the atom M is directed opposite to the angular momentum $\langle \hat{J}_X \rangle$ of the atom X . On the other hand, in the second excited state of the MX molecule there is realized a "parallel" scheme of the coupling of the angular momenta of the atoms M and X , with the average angular momenta having the same direction. An experimental confirmation of the correctness of this conclusion should be oppositely oriented atoms M for photodecay in accordance with reactions (12) and (13). An experiment performed by the author on CsI molecules²⁰ yielded an affirmative result.

We note that the dependence of the quantities $\rho_{\alpha Q}$ in (16) on the different matrix elements makes it possible to determine experimentally the relative contributions of the different energy sublevels of the excited state in the photodissociation process.

According to Refs. 2, 18, and 19, the probabilities of the transverse ($\Delta\Omega = 1$) and longitudinal ($\Delta\Omega = 0$) transitions in the MX molecules are close in value. The degrees of orientation (10) of the atoms M and X should then be close to their maximum values, namely $P_M = P_X = 1.0$ for photodissociation in accordance with reaction (13) and $P_X = 0.83$; $P_M = -0.5$ for photodissociation in accordance with reaction (12).

2. *Photodecay of molecules of the type HI and AgI.* In the contrast of the just-considered case, the excited states of molecules of this type are characterized by a strong interaction between atoms, comparable in magnitude with the spin-orbit interaction in the atoms. The photodecay of the lower excited states of such molecules is described by Eqs. (12) and (13) (Refs. 21 and 22), and the atom B should in this case be identified with the halogen atom (iodine).

Each of the energy levels that characterizes the state of separated atoms is adiabatically coupled to a small number of molecular levels, which can be optically excited from the electronic ground state. Thus, for the HI molecule, the potential curves for which are shown in Fig. 3 (Ref. 21), the level corresponding to decay in accordance with reaction (12) is coupled to two molecular levels ($^3\Pi_1, ^1\Pi_1$), where the level corresponding to decay in accordance with reaction (13) is coupled to only one molecular energy level ($^3\Pi_0$).

It is clear without calculations that the atoms produced in the photodissociation process in accordance

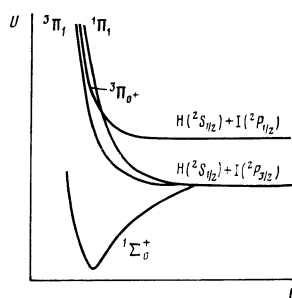


FIG. 3. Potential curves of ground and lower excited states of the HI molecule²¹; U —interaction energy; R —distance between nuclei.

with reaction (13) can have neither orientation nor alignment. The absence of orientation follows from the general rule obtained above, while alignment of atoms characterized by a total angular momentum $J_A = 1/2$ is impossible.¹⁰

We consider now photodissociation in accordance with reaction (12). The expressions that can be obtained in this case for the density matrix are similar to the already presented expressions (16a, b, c), in which it is necessary to drop all the interference terms and put $b_1 = 0$. In this case a_1 and a_1' have the meaning of the matrix elements of the operator \hat{d} for the transition from the ground electronic states into $^3\Pi_1$ and $^1\Pi_1$, respectively.

If, for example, the exciting radiation is right-circularly polarized and directed along the z axis, then the expressions for the orientation of the produced atoms are

$$\rho_{10}^R(^{1/2}) = \frac{1}{2\sqrt{3}} \frac{a_1^2 - a_1'^2}{a_1^2 + a_1'^2}, \quad \rho_{10}^I(^{3/2}) = \frac{1}{2\sqrt{15}} \frac{3a_1'^2 + a_1^2}{a_1^2 + a_1'^2}. \quad (19)$$

As seen from (19), the orientation of the hydrogen atoms and of the halogen depends substantially on the relative contribution of the $^3\Pi_1$ and $^1\Pi_1$ states of the molecules in the photodissociation process. These contributions can be determined experimentally by measuring the degree of orientation of the produced atoms.

3. *Photodecay of dimers of alkali metals M_2 .* In this case it is also possible to use the decay schemes (12) and (13), in which one must put $B=A=M$ (Ref. 23). The difference between this type of photodecay and the ones considered above is that the interaction between the atoms at large distances has here a dipole-dipole character,¹¹ leading to other values of the matrix T . It is known that the photodecays of dimer molecules in accordance with the reaction (12) proceeds via the molecular state $^1\Pi_u$, while the photodecay in accordance with the reaction (13) proceeds via the molecular state $^1\Sigma_u$ (Refs. 6, 17, 23). In analogy with the procedure used above, it can be directly concluded that the atoms produced via reaction (13) should have neither orientation nor alignment. The elements of the matrix T , which characterize the photodecay in accordance with reaction (12), can be determined by using the correlation diagrams²³

$$T_{1/2, 1/2, 1/2}^1 = \left[\frac{\sqrt{7}-2}{2\sqrt{7}} \right]^{1/2}, \quad T_{1/2, -1/2, 1/2}^1 = \left[\frac{\sqrt{7}+2}{2\sqrt{7}} \right]^{1/2}. \quad (20)$$

If, for example, the exciting radiation is linearly polarized, the photodecay results in aligned atoms in the excited state $^2P_{3/2}$. Using (11), (20), and the equation of Refs. 10 and 16, which describes the intensity of the fluorescence light, it is easy to calculate the degree of polarization of the radiation that should be observed in this case. If the exciting radiation is characterized by a polarization vector directed along the Z axis, and linear polarization of the fluorescence light propagating along the x axis is registered, the degree of polarization is $n = 6/(5\sqrt{7} - 2)$.

We note that linear polarization of the fluorescence of excited atoms produced in photodissociation of mole-

cules by anisotropic excitation having alignment symmetry was predicted in Ref. 24. The values of the degree of linear polarization of the fluorescence, given in Ref. 24, can be obtained on the basis of the general formulas (11) and from the formula given in Refs. 10 and 16 for the intensity of the fluorescence light, if spinless atomic states are considered (this is physically justified only for atoms with very weak spin-orbit interaction), and if it is assumed that each energy level that characterizes the state of the separated atoms is connected with only one molecular level.

We note that in the foregoing analysis the presence of nuclear spins was disregarded. The justification for this is the fact that the duration of photodecay act in the typical cases considered above is much shorter than the reciprocal hyperfine splitting. If account must be taken of the hyperfine interaction in the atoms over a time elapsed from the instant of photodecay to the instant of registration, this can be done with the aid of a known procedure.^{25, 26}

§6. CONDITIONS FOR THE EXISTENCE OF THE EFFECTIVE ATOM ORIENTATION IN THE MOLECULE PHOTODISSOCIATION PROCESS

The phenomenon discussed has by now been experimentally registered only in a photoprocess in which CsI molecules take part.¹¹ The results of the present paper offer evidence, however, that orientation and alignment of atoms should be observed in the photolysis of various types of molecules. We can point out the following conditions that are needed for the existence of the effect:

- The exciting radiation should be anisotropic.
- Orientation and alignment of atoms produced in the S state are possible only in the case when the time that characterizes the spin-orbit interaction in the atoms that make up the molecule does not exceed the lifetime of the molecule in the excited state.
- The orientation of the atoms is possible if the decay of the molecule takes place within a time that is short compared with the molecule rotation period¹⁾ and if transverse ($\Delta\Omega = 1$) transitions participate in the photoprocesses.

The foregoing conditions are satisfied for many types of photoprocesses accompanied by molecule decay.⁹

§7. POSSIBLE APPLICATIONS OF THE CONSIDERED PHENOMENON

1. It follows from the foregoing theoretical analysis that photolysis of molecules by circularly polarized radiation makes it possible to obtain oriented atoms of such elements as hydrogen, silver, alkali metals, halogens, and others, many of which cannot be obtained by ordinary methods.²⁶

2. The results of the present study indicate that the magnitudes of the orientation and alignment of the atoms produced in photodecay of the molecules depend significantly on the structure of the excited states of the molecules. Therefore, registration of the orientation or of

the alignment of these atoms can yield important information on the properties of the short-lived excited states of a number of molecules. In particular, the correctness of one model or another of the excited and ground states can be established. One of these models was used in the present paper to calculate the transition probabilities in alkali-halide molecules.

The relative contributions of various excited states to the photodissociation process, including also states of equal symmetry, can be determined for a large class of molecules. The possible nonadiabatic transitions in molecules¹² should lead to different degrees of orientation and alignment of the produced atoms than expected on the basis of the adiabatic approximation. This makes it possible to investigate experimentally non-adiabatic processes in the molecules and to determine the molecule lifetimes in the excited state.

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¹This condition is important only for molecular states whose lifetime exceeds the time that characterizes the coupling of the electron angular momentum with the molecule axis.

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