Formation of oriented metastable thallium atoms by molecule photodissociation

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We report detection and investigation of oriented metastable $6^2P_{3/2}$ thallium atoms produced when TlBr molecules are photodissociated by 266-nm circularly polarized laser emission. The atom orientation was recorded using free-precession supplementary-light signals from a thallium lamp. We have investigated the dependence of the atom orientation on the laser-emission intensity and examined the cause of this dependence. The degree of orientation of the atoms at the instant of their creation is $P_0 = (19 \pm 2)\%$. The measured constant of quenching metastable thallium atoms by TlBr molecules is $\langle \sigma_{qu} v \rangle = (3.1 \pm 0.3) \cdot 10^{-11}$ cm^3/s. The experimental results are interpreted theoretically. A quantum-mechanical theory that takes consistently into account the non-adiabaticity of the interactions in the decaying molecule and the rotation of the molecule axis, is presented. The dynamics is considered of formation of oriented Tl($6^2P_{3/2}$) atoms in photodissociation of TlBr molecules via an excited $C^1\Pi_1$ state. It is established that the degree of orientation of these atoms is the same for the three possible components of the moment $|\Omega| = 1$ of the molecule decay channels and is not sensitive to radial nonadiabatic transitions in the molecule. A theoretical value $P_{\text{th}} = 15.1\%$ is obtained for the degree of atom orientation. It is shown that the excess of the experimental degree of orientation over the theoretical is apparently due to interference effects in the excited states of the dissociating molecules.

1. INTRODUCTION

Oriented atoms are widely used at present in various branches of science and engineering, such as nuclear physics, atomic and molecular spectroscopy, physics of electron and atom collisions, and quantum magnetometry. Investigations of the interaction of oriented atoms with other atoms and molecules, as well as with radiation, yield for atoms, molecules, and atomic nuclei detailed structure information difficult to obtain by other means.

The most widely known methods of obtaining oriented atoms are that of optical orientation, proposed by Kastler[1,2] and based on direct interaction of atoms with polarized radiation, as well as a method using the spin exchange in collisions between optically oriented atoms with other atoms.[2]

At the same time, methods of obtaining oriented atoms on the basis of other physical principles have recently been reported. One of them is based on the atom orientation accompanying photodissociation of molecules.[3–5] Its gist is that the angular momentum acquired by a molecule interacting with a circularly polarized photon is partially conserved during the photodissociation and is transferred to the produced atoms.

Owing to the presence of broad absorption bands in molecules, the method permits the use of high-power UV lasers to obtain oriented atoms, and has very low inertia (all the way to 10^{-12} s). It makes it possible therefore to produce within a short time high densities of polarized atoms of various elements, both in the ground and excited states.

Investigations have shown that study of orientation of atoms produced by photodissociation of molecules can yield important information, frequently unobtainable by other methods, on the dynamics of this process. It is thus possible to investigate the symmetry of unstable excited states of molecules, nonadiabatic interactions in decaying molecules, as well as coherent effects.

We report here observation and investigation of oriented thallium atoms in a metastable $6^2P_{3/2}$ state, produced by photodissociation of TlBr molecules by circularly polarized 266-nm laser emission in the reaction

$$\mathrm{TlBr}(^1\Sigma_0^+) + h\nu \rightarrow \mathrm{TlBr}(C^1\Pi_1) \rightarrow \mathrm{Tl}(^2P) + \mathrm{Br}(^2P). \quad (1)$$

We determined the degree of orientation of the thallium atoms at the instant of their production, and found a theoretical interpretation of the experimental results with allowance for nonadiabatic interactions in the decaying molecules and for their rotation. We measured the quenching-rate constant of metastable atoms of thallium atoms by TlBr molecules.

2. EXPERIMENT

The geometry of the experiment and the experimental setup are shown in Fig. 1. The absorbing cell AC containing TlBr vapor at a pressure $P \approx 10^{-3}$ Torr was irradiated by pulsed circularly polarized laser emission of wavelength 266 nm, propagating perpendicularly to the magnetic field $H_0 \approx 1.2$ Oe. This radiation dissociated the TlBr molecules in the AC in accordance with reaction (1), with 16% of the Tl atoms produced in the $6^2P_{3/2}$ state.[6] It is these atoms which were investigated by us.

The nonequilibrium population of the magnetic sublevels of the produced metastable atoms was macroscopically manifested by the existence of an average magnetic dipole moment (orientation). This moment precessed around the direction of the magnetic field, causing a periodic variation of the dichroism of the atomic vapor for light of frequency close to that of the atomic absorption line.[7]

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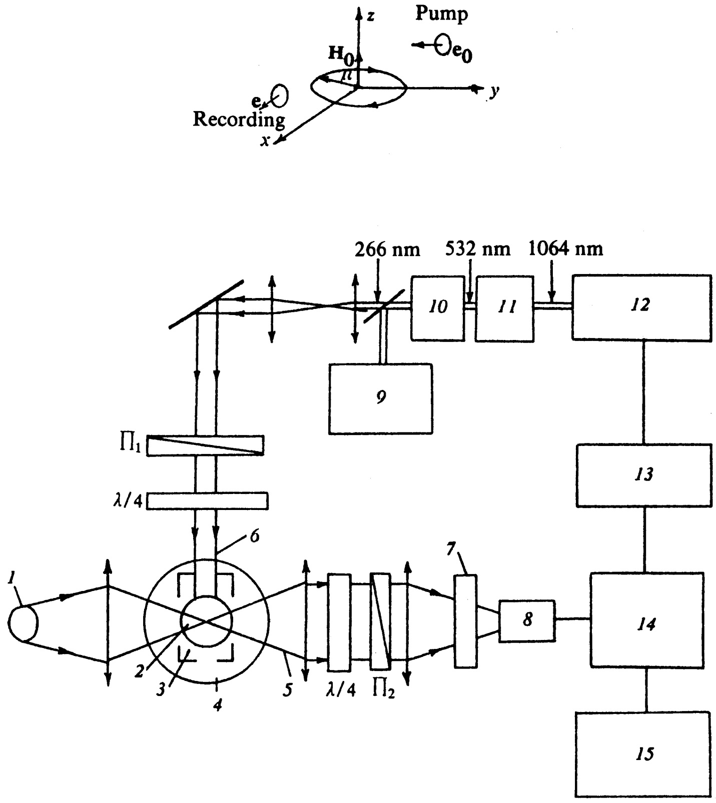

FIG. 1. Geometry of experiment and diagram of experimental setup. *1*—Tl lamp, *2*—AC, *3*—oven, *4*—Helmholtz coils, *5*—test beam, *6*—pump beam, *7*—535 nm filter, *8*—photomultiplier, *9*—IE-6 - energy meter, *10*—KDP, *11*—LiNbO$_3$, *12*—Nd:YAG laser, *13*—square-wave generator G5-56, *14*—S9-16 oscilloscope, *15*—computer.

This dichroism was recorded with the aid of an unpolarized test beam of wavelength 535 nm from a thallium lamp. This beam was perpendicular both to the exciting beam and to the magnetic field H_0, guided by a system of lenses through the absorbing cell of a polarization analyzer consisting of an array consisting of a $\lambda/4$ phase plate, a linear polarizer Π_2, and a 535 nm interference filter, and then focused on the cathode of a photoelectron multiplier (PEM). The signal from the PEM was fed to an S9–16 digital oscillogram connected to a computer, in which the received signals were transformed and stored. A scheme of the employed lower energy levels of the Tl atoms is shown in Fig. 2.

Ultraviolet circularly polarized 266-nm exciting radiation was obtained by successively doubling 1064-nm Nd:YAG laser emission with nonlinear LiNbO$_3$ and KDP crystals, and the residual rays with wavelengths $\lambda = 1064$ and $\lambda = 532$ nm were produced by dichroic mirrors (not shown in Fig. 1). The laser was Q-switched at a repetition frequency $f_{\text{rep}} = 14$ Hz produced radiation pulses of duration $\tau_p = 5$ ns. To decrease the optical thickness of the cell absorbing the recorded radiation, the laser beam was passed through a second multiplying crystal and broadened by a telescope to 10 mm. The beam was next passed through a circular polarizer consisting of a prism-based interference linear polarizer and a $\lambda/4$ crystalline-quartz phase plate, and was incident on the AC. The ultraviolet-pulse energy incident on the AC was $E_i \approx 2$ mJ, and the degree of its circular polarization was 92%.

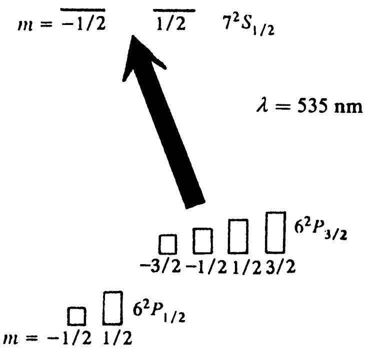

FIG. 2. Three lowest energy levels of thallium atom without allowance for the hyperfine structure. The rectangles indicate the populations of the magnetic sublevels of the metastable state of the thallium atoms. The arrow marks the $6^2P_{3/2} \rightarrow 7^2S_{1/2}\lambda = 535$ nm transition used to observe the orientation of the atoms.

The source of the 535-nm test radiation was a continuously operating electrodeless Tl lamp of 20 mm diameter. A natural thallium isotope mixture was used in the experiment. It is important that for a correct interpretation of the experimental data it was necessary to take into account the intensity ratios of the hyperfine components in the 535-nm line from the lamp. The hyperfine structure of this line, determined with a Fabry-Perot étalon, is shown in Fig. 3.

The absorption cell was a sealed quartz sphere of 50 mm diameter, with a stub containing the TlBr salt. In the course of its production it was evacuated while heated at 800 °C for about 25 hours. The salt was then distilled in the cell by a burner and the cell sealed off from the vacuum system. The residual air pressure in the cell was not higher than 10^{-3} Torr. During the experiment the AC was placed in an oven with quartz windows, and the stub temperature was maintained by an independent heater at a temperature about 150° lower than the bulk of the cell. This made it possible to set

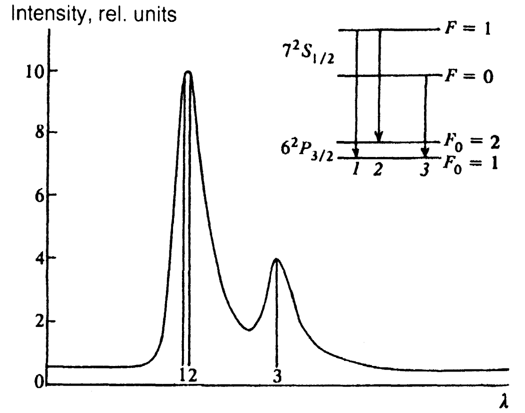

FIG. 3. Hyperfine structure of the $\lambda = 535$ nm resonance line of the transition $7^2S_{1/2} \rightarrow 6^2P_{3/2}$ in the radiation emitted by a thallium lamp. The vertical lines show the theoretical positions of the hyperfine components.

independently the temperature and the vapor density of the TlBr.

The magnetic field H_0 at the location of the AC was produced by three pairs of Helmholtz coils with mutually perpendicular axes.

3. EXPERIMENTAL RESULTS

One of the obtained signals is shown in Fig. 4; Fig. 4a shows the total signal, and Fig. 4b a fragment in magnified time scale. The laser-pulse instants correspond in both cases to the time $t = 0$, and the pulse duration is negligibly small in the scale of the figure.

As seen from Fig. 4a, absorption of the test beam first increases jumpwise when the laser pulse is turned on, owing to the appearance of metastable thallium atoms in the AC, and then decreases exponentially at a quenching rate Γ_{qu} determined by the lifetime of the metastable atoms colliding with the molecules inside the AC and with its walls. We shall call such signals hereafter absorption signals.

Signals of the type shown in Fig. 4a were used to determine the quenching rate constant of the metastable $6^2P_{3/2}$ thallium atoms in the $6^2P_{1/2}$ ground state, due to the collisions with the TlBr molecules. We used in these investigations an AC containing, together with the TlBr salt, also Xe, at 3 Torr pressure, as a buffer. This gas cooled the photodissociated metastable Tl atoms the AC temperature. The dependences of Γ_{qu} on the density of the TlBr molecules in the AC is shown in Fig. 5. To obtain this dependence, the quenching rate was determined at various temperatures of the stub, and the TlBr molecule density in the cell volume was calculated from known equations.[8] The rate constant of the quenching of $6^2P_{3/2}$ Tl atoms by TlBr molecules at $T = 670$ K, determined using the relation shown in Fig. 5, was

$$\langle \sigma_{qu} v \rangle = (3{,}1 \pm 3) \cdot 10^{-11}\ \mathrm{cm}^3/\mathrm{s}. \qquad (2)$$

The signal oscillations shown in Fig. 4b directly past the laser pulse are due to the precession, described above, of the atomic momentum around the direction of the constant magnetic field. The signal shown in Fig. 4b will be called the orientation signal. It follows from the theory of the effect[4] that the atoms produced by photodissociation of molecules by circularly polarized light can be either oriented or aligned; the presence in the $6^2P_{3/2}$ state of thallium atoms of two hyperfine (hf) sublevels with total momenta $F = 1$ and 2 and with different g-factors should lead in the general case to a complex precession signal with four different frequencies.

Thus, under the conditions of the described experiment the expression for the absorption of the recorded radiation by the atomic vapor, an expression derived under the assumption that the atom polarization at the intial instant of time is purely electronic1) takes the form (see the Appendix):

$$\begin{aligned}(I - I_{ab})/I_{ab} = \frac{1}{3k+1}\Big\{ & \frac{3}{8}(k+4)P_e \sin(\omega_1 t) + \frac{27}{8} k P_e \sin(\omega_2 t) \\ & + \frac{4-k}{32} A_e [1 - 3\cos(2\omega_1 t)] \\ & + \frac{7k}{32} A_e [1 - 3\cos(2\omega_2 t)]\Big\} \exp(-\Gamma_d t). \qquad (3)\end{aligned}$$

Here I is the intensity of the 535-nm radiation absorbed on the $6^2P_{3/2} \rightarrow 7^2S_{1/2}$ transition in the presence of a nonequilibrium population of the magnetic sublevels of the atoms; I_{ab} is analogous intensity for the case of equilibrium population of the magnetic sublevels; $P_e = \langle j_z \rangle / j$ is the degree of electron orientation of $6^2{}_{3/2}$ thallium atoms at the instant of their production;

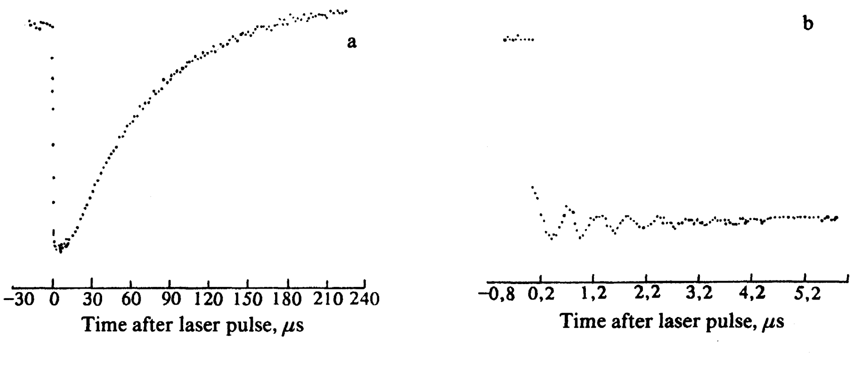

FIG. 4. Characteristic absorption signal of oriented $6^2P_{3/2}$ thallium atoms obtained by photodissociation of TlBr molecules with density $N = 2.53 \times 10^{13}$ cm^{-3}: a—total signal; b—the same signal in enlarged time scale.

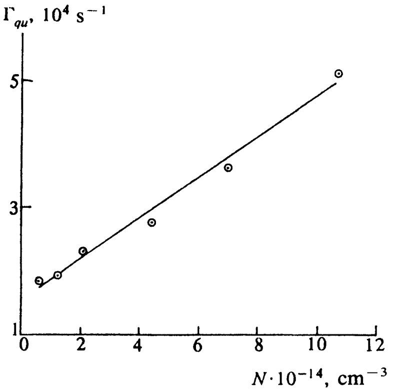

FIG. 5. Dependence of the quenching rate constant of metastable thallium atoms on the density N of TlBr in the absorbing cell.

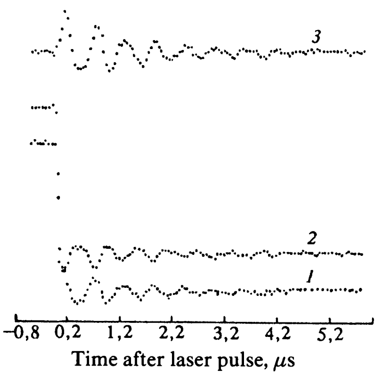

FIG. 6. Reduction of experimental signals. Signals *1* and *2* were obtained by irradiating the AC with left- and right-circularly polarized laser radiation. Signal *3* is the difference of signals *1* and *2*. The signals are displaced vertically for clarity.

$$A_e = \langle 3j_z^2 - \mathbf{j}^2\rangle / j(2j-1)$$

is the degree of alignment of these atoms; $j = 3/2$; $\mathbf{j}$ and j_z are the operators of the total electron momentum of the thallium atom and its component along the z axis in the lab; k is the ratio of the intensities of two hyperfine components in the radiation of the probing-beam source, with values 2–3, depending on the operating regime of the lamp (Fig. 3); ω_F are the Larmor frequencies for the hf sublevels $F = 1$ and 2, whose values for the magnetic field intensity $H_0 = 1.26$ Oe used in the experiments were $\omega_1 = 2\pi f_1 = 16.6\cdot 10^6$ s^{-1}, $\omega_2 = 2\pi f_2 = 10.1\cdot 10^6$ s^{-1}; Γ_d is the rate of atom depolarization in the AC.

The first and second terms in the curly brackets of the right-hand side of (3) describe the contribution made to the orientation signal by both hf sublevels, while the third and fourth terms describe the contribution of the alignment of these sublevels. Expression (3) was derived in an approximation with an optically thin layer in the AC. The ratio of the amplitudes of the orientation signals from the hf sublevels $F = 1$ and 2, which is given by Eq. (3), depends both on the ratio of the populations of these sublevels and on the intensity ratio k of the corresponding hf components in the spectrum of the recorded radiation.

It is seen from Fig. 4b that the main contribution to the experimental signal is made by oscillations of frequency ω_2 corresponding to orientation of metastable thallium atoms on the hf sublevel $F = 2$. The contribution of atoms oriented on the hf sublevel $F = 1$, corresponding to oscillations at the frequency ω_1, was much smaller, and no higher-frequency signals of the alignment of the Tl atoms were observed in the present experiment. These results agree qualitatively with the relative contributions of corresponding-frequency signals, which follow from Eq. (3). The exponential damping of an orientation signal with a characteristic time $\tau \approx 2$–$3\,\mu$s is due to depolarization of the thallium atoms by collisions with the TlBr molecules, the AC walls, and the gas molecules escaping from the walls of the cell during its operation.[9]

The following procedure was used for a more detailed analysis of the obtained orientation signals: Two signals were recorded, corresponding to left- and right-circular polarization of the pump radiation, accomplished by a 90° rotation of the phase place in the circular polarizer Π_1 (Fig. 1); the change of the oscillation-orientation signal was in this case equal to π (Fig. 6, signals 1 and 2). The signals were next subtracted from each other, causing the absorption "step" to vanish and leaving only damped double-frequency oscillations of the orientation signal (Fig. 6, signal 3). The Fourier spectrum of this signal is shown in Fig. 7. It is seen to contain oscillations at frequencies close to ω_1 and ω_2. The amplitude of the oscillations at the frequency ω_2 in our experiments was 3–4 times larger than that at frequency ω_1. The signals obtained in this manner were parametrized in accord with Eq. (3) without allowance for the last two terms describing the alignment of the atoms. The parametrization results for one such signal is shown in Fig. 8. The dots on this figure are the experimental results, and the solid curve shows a fit to the equation

$$F(t) = A + \exp(-\Gamma_d t) \times \left[\frac{27}{28} P_e \sin(2\pi f_2 t + \psi_2) + \frac{9}{28} P_e \sin(2\pi f_1 t + \psi_1)\right] \tag{4}$$

with fit parameters

$$A = 0{,}003,\quad \Gamma_d = 4{,}1\cdot 10^{-4}\,\mathrm{s}^{-1},\quad P_e = 0{,}167,$$
$$f_1 = 2{,}73\ \mathrm{MHz},\quad \psi_1 = 3{,}4\ \mathrm{rad}, \tag{5}$$
$$f_2 = 1{,}7\ \mathrm{MHz},\quad \psi_2 = 3{,}2\ \mathrm{rad}.$$

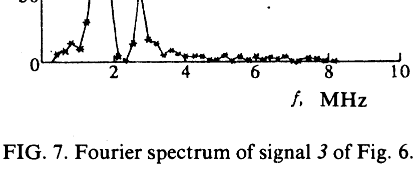

FIG. 7. Fourier spectrum of signal *3* of Fig. 6.

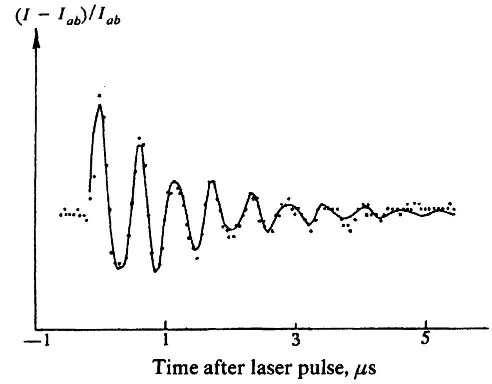

FIG. 8. Parametrization of experimental signal. The dots designate the experimental values, and the solid curve was obtained by parametrization of these values in accordance with Eq. (4) with fit parameters (5).

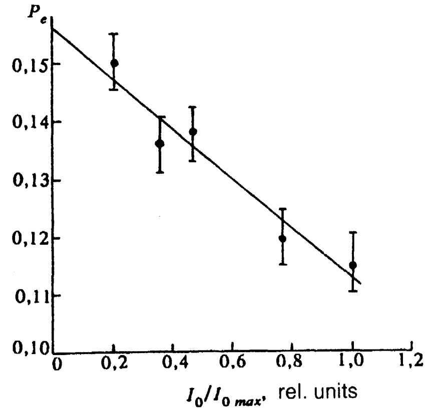

FIG. 9. Degree of orientation of metastable $6^2P_{3/2}$ thallium atoms on the exciting-laser emission intensity.

As seen from Fig. 8, the experimental signal shows beats at the frequencies ω_1 and ω_2.

The signals in question were observed only when the exciting radiation was circularly polarized, in which case the oscillation frequencies varied when the magnetic field H_0 was varied and corresponded to the Larmor frequencies ω_2 and ω_1. The observed signals are thus due to orientation of the hyperfine sublevels $F = 2$ and $F = 1$ of the metastable $6^2P_{3/2}$ of thallium.

We shall show below that the orientation P_e at the atoms at the instant of their creation contains important information on the dynamics of the photodissociation reaction (1). Determination of P_e by the described procedure showed this quantity to depend on the intensity of the exciting laser radiation. The reason was the dependence of the density of the produced atoms and, as a consequence, of the optical thickness of the AC for the recorded radiation, on the intensity of the exciting beam. The value of P_e was therefore measured several times for different intensities I_0 of the exciting radiation, followed by extrapolation to $I_0 \to 0$. One of the corresponding experimental dependences is shown in Fig. 9. As seen from this figure, the dependence obtained can be approximated, within the limits of experimental error, by a straight line. The degree of orientation of the Tl($6^2P_{3/2}$) atoms at the instant of their production, obtained by averaging the values of P_e ($I_0 \to 0$) from six experiments, turned out to be, with allowance for the use of non-ideal polarizers,

$$P_e = (19 \pm 2)\%. \tag{6}$$

In the theoretical interpretation of the experimental result we used the theory of Ref. 5 for atom orientation in photodissociation of molecules. The results of this interpretation are given in the next section.

4. BASIC PREMISES OF THE THEORY OF THE EFFECT

Consider the diatomic-molecule photodecay when we are interested in the polarization state of one photofragment. The cross section of this process should be averaged over the state of the second atom, and a definite type of polarization of the first atom can be separated by using a corresponding polarization operator. Denoting the set of quantum states in the photodecay channel by $|j_1m_1\rangle$ and $|j_2m_2\rangle$ for the first and second channels, where j_i and m_i are the values of the total electron moment and of its projection for the ith atom, we introduce the polarization operators[2]

$$\hat{T}_{K_iQ_i}(j_i j_i) = \sum_{m_i, m_i'} \left(\frac{2K_i + 1}{2j_i + 1}\right)^{1/2} C^{j_i m_i'}_{j_i m_i K_i Q_i} |j_i m_i'\rangle\langle j_i m_i|, \tag{7}$$

where $C^{j_i m_i'}_{j_i m_i K_i Q_i}$ is a Clebsch–Gordan coefficient.

We are interested in the polariztion state of the entire system. It is defined by the operator product

$$\hat{T}_{KQ}(j_1 j_1)\hat{T}_{00}(j_2 j_2),$$

and the corresponding cross section is connected with the photodissociation cross section $\sigma^{j_1 j_2}_{m_1 m_1', m_2 m_2'}$ in the j,m representation by the relation

$$\sigma_{KQ}(j_1) = \sum_{j_2} (2j_2 + 1)^{1/2} \mathrm{Sp}\, \hat{\sigma}\hat{T}_{KQ}(j_1 j_1)\hat{T}_{00}(j_2 j_2), \tag{8}$$

where the operator $\hat{\sigma}$ is of the form

$$\hat{\sigma} = \sum_{m_1, m_1'} \sum_{m_2, m_2'} \sigma^{j_1 j_2}_{m_1 m_1', m_2 m_2'} |j_1 m_1\rangle |j_2 m_2\rangle\langle j_1 m_1'|\langle j_2 m_2'|. \tag{9}$$

The cross sections $\sigma_{KQ}(j_1)$ were calculated in Refs. 5 and 10 under the assumption of a quasiclassical rotational degree of freedom of the molecule. Using these results, we can express the cross section $\sigma_{00}(j_1)$ that determines the population of the photofragment, and the cross section $\sigma_{10}(j_1)$ that determines its orientation in the form

$$\sigma_{00}(j_1) = \frac{1}{[3(2j_1 + 1)]^{1/2} G_g} \sum_{n_e \Omega_e} \sum_{\Omega_g} [\sigma^{\perp}_{\Omega_g; n_e \Omega_e}(\omega) + \sigma^{\parallel}_{\Omega_g; n_e \Omega_e}(\omega)] \Phi_{00}(\mathrm{e}), \tag{10}$$

$$\sigma_{10}(j_1) = \frac{1}{[3(2j_1 + 1)]^{1/2} G_g} \sum_{\Omega_1} \sum_{j_2 \Omega_2} C^{j_1 \Omega_1}_{j_1 \Omega_1 10} \sum_{n\Omega} \sum_{n_e \Omega_e} \left| T^{n\Omega}_{j_1 \Omega_1 j_2 \Omega_2} \right|^2 \times \sum_{\Omega_g} C^{1, \Omega_e - \Omega_g}_{1, \Omega_e - \Omega_g; 1,0} \sigma^{\perp}_{\Omega_g; n_e \Omega_e}(\omega) \langle \cos \xi \rangle \bar{W}_{n_e \Omega_e; n\Omega} \Phi_{10}(\mathrm{e}). \tag{11}$$

Here Ω_g is the component of the angular momentum of the ground state of the molecule along its axis; Ω_e, Ω and n_e, n are the components of the angular momentum and the sets of the remaining quantum numbers indicative of the excited state of the molecule; Ω_1 and Ω_2 are the components of the total electronic elements of the atoms 1 and 2 along the molecule axis, $G_g = 1$, if $\Omega_g = 0$ and $G_g = 2$, if $\Omega_g \neq 0$.

In (10) and (11) we have introduced the irreducible covariant components of the polarization tensor $\Phi_{KQ}(e)$ of the pump radiation; these components are defined by the relation:[2]

$$\Phi_{KQ}(\mathrm{e}) = \sum_{q_1 q_2} (-1)^{1+q_1} C^{KQ}_{1q_2 1q_1} e^*_{-q_1} e_{q_2}, \tag{12}$$

where e_q are the cyclic components of the polarization vector. In the case of right-circular polarized light

$$\Phi_{00}(\mathrm{e}) = 1/\sqrt{3}, \quad \Phi_{10}(\mathrm{e}) = 1/\sqrt{2}. \tag{13}$$

The parameters $\sigma^{\perp}_{\Omega_g; n_e\Omega_e}(\omega)$ and $\sigma^{\parallel}_{\Omega_g; n_e\Omega_e}(\omega)$, are the cross sections, averaged over the equilibrium state of the molecule, for absorption of a photon of frequency ω. These quantities are expressed in expanded form in terms of the matrix elements of the electric dipole moment operator and in terms of the overlap integrals of the radial wave functions of the ground and excited states in the vicinity of the transition point. The summation in expressions (10) and (11) is over all states $n_e\Omega_e$ which lead to formation of the first photofragment in a state with total momentum j_l.

We have separated in (10) and (11) two types of cross section. The cross section $\sigma^{\perp}$ corresponds to transverse optical transitions for which $\Omega_e = \Omega_g \mp 1$. It is easily seen from (11) that it is just this cross section which is responsible for optical orientation. The cross section $\sigma^{\parallel}$ corresponds to longitudinal transitions for which $\Omega_e = \Omega_g$ and determines the total population and the alignment of the photoeffect.

The matrix $T^{n\Omega}_{j_1\Omega_1 j_2\Omega_2}$ in (11) describes the correlation of the adiabatic molecular states $|n\Omega\rangle$ with the states of isolated atoms in the region of large internuclear distances R (Ref. 4):

$$|n\Omega\rangle \rightarrow \sum_{\Omega_1\Omega_2} T^{n\Omega}_{j_1\Omega_1 j_2\Omega_2} |j_1\Omega_1; j_2\Omega_2\rangle. \tag{14}$$

The actual form of the matrix $T^{n\Omega}_{j_1\Omega_1 j_2\Omega_2}$ is determined by the character of the long-range interatomic interaction.

The most important characteristics of photodecay, which influence substantially the degree of orientation of the atoms, is the average angle ξ of molecular-axis rotation in atom-spreading process and the probability $W_{n_e\Omega_e; n\Omega}$ of the adiabatic transition. The latter is determined by the possible nonadiabatic transitions between the states $n_e\Omega_e$ into which the molecules are photoexcited and the states $n\Omega$ that correlate with the states of the free atoms. It is important that the adiabatic states $n_e\Omega_e$ and $n\Omega$ cannot belong to terms that convert to one energy level as $R \rightarrow \infty$. The corresponding nonadiabatic transitions are unobservable in measurements of the photofragment density and can be observed by measuring their polarization.

The degree of orientation of the produced atoms P^{th}_e is determined by the ratio of the cross sections

$$P^{th}_e = \left(\frac{j_1 + 1}{3j_1}\right)^{1/2} \frac{\sigma_{10}(j_1)}{\sigma_{00}(j_1)}. \tag{15}$$

Expressions (10), (11), and (15) describe thus the orientation of the atoms produced in photodissociation of an arbitrary diatomic molecule by circularly polarized light. The derived general expressions will be used in the next section to analyze the experimental results of the present study.

5. DISCUSSION OF EXPERIMENTAL RESULTS

Splitting of molecular terms that correlate with the states $\mathrm{Tl}(^2P_{3/2})$ and $\mathrm{Br}(^2P_{3/2})$ in the region of large internuclear distances R is determined by quadrupole-quadrupole interaction of the atoms. In this case there are two symmetry states 0^+, two 0^-, states $|\Omega| = 1$, two $|\Omega| = 2$, and one $|\Omega| = 3$.

The exact position of the corresponding terms at small R in the optical-transition region is unknown, since the theoretical calculations are quite complicated. However, as shown in Ref. 6 in the case of photoexcitation of the TlBr molecule from the ground state $^1\Sigma^+_{0^+}$ by light of wavelength 266 nm, a transverse optical transition is realized into the state $|\Omega_0| = 1$ in the $C\,^1\Pi_1$ continuum, followed by registration of $\mathrm{Tl}(^2P_{3/2})$ atoms in channel (1). The subsequent evolution of the molecular system is determined by the character of the separation of the atoms and by the ensuing nonadiabatic transitions from the state Ω_e into molecular states that correlate with $\mathrm{Tl}(^2P_{3/2})$ and $\mathrm{Br}(^2P_{3/2})$, two types of such transitions being possible:[11] radial ($\Delta\Omega = 0$) and Coriolis ($\Delta\Omega = \pm 1$). Let us estimate the probabilities of these transitions in the case considered.

It can be stated, on the basis of the theory of nonintersection of terms of like symmetry, and with allowance for the behavior of TlBr molecular terms in the vicinity of the optical-transition point (6), that the state $|\Omega_e| = 1$ correlates adiabatically with the lower energy state of the family $|\Omega| = 1$. Consider the possible nonadiabatic transitions into states $|\Omega| \neq 1$, determined by a Coriolis interaction. Calculation of the molecular terms and of quantum states of a quasimolecule in the asymptotic region shows that in this region the terms 0^σ ($\sigma = \mp$) and $|\Omega| = 2$ are separated from the lower energy state of symmetry $|\Omega| = 1$. Thus, Coriolis nonadiabatic transitions, for which $\Delta\Omega = \pm 1$, can be realized only as transition in possible intersection points of terms of different symmetry. An estimate of the corresponding transition probability can be obtained in the Landau–Zener model, and this probability is determined by the rotation angle $\Delta\xi$ of molecule as it passes through the intersection point. In the case of photodecay in accordance with the reaction (1) and excitation by light of wavelength 266 nm the average molecule-axis rotation angle is $\xi \approx 25°$. Recognizing that $\Delta\xi \ll \xi$, the probability of Coriolis nonadiabatic transitions is insignificant and can be neglected in the calculation.

As to the radial nonadiabatic transitions in states $|\Omega| = 1$, they are possible but, as will be shown below, they do not influence the orientations of produced $\mathrm{Tl}(^2P_{3/2})$ atoms.

We denote the symmetry states $|\Omega| = 1$ which correlate with the $\mathrm{Tl}(^2P_{3/2})$ and $\mathrm{Br}(^2\mathrm{P}_{3/2})$ states, in increasing order of symmetry, by $|1\rangle$, $|1'\rangle$, $|1''\rangle$. The coefficients $T^{n\Omega}_{j_1\Omega_1 j_2\Omega_2}$ defined by Eqs. (16), take for these states in the case of quadrupole interactions between the atoms, the form

$$T^{1}_{\frac{3}{2}\frac{1}{2}\frac{3}{2}\frac{1}{2}} = 1,$$

$$T^{1'}_{\frac{3}{2},\frac{3}{2};\frac{3}{2},-\frac{1}{2}} = 1/\sqrt{2}, \quad T^{1'}_{\frac{3}{2},-\frac{1}{2};\frac{3}{2},\frac{3}{2}} = 1/\sqrt{2}, \tag{16}$$

$$T^{1''}_{\frac{3}{2},\frac{3}{2};\frac{3}{2},-\frac{1}{2}} = 1/\sqrt{2}, \quad T^{1''}_{\frac{3}{2},-\frac{1}{2};\frac{3}{2},\frac{3}{2}} = -1/\sqrt{2}.$$

Substituting these coefficients into (11) and assuming in accordance with the foregoing remarks that only the contribution of the states $|\Omega| = 1$ is significant, we obtain with the aid of relations (15) for the degree of orientation of the $\mathrm{Tl}(^2P_{3/2})$ atoms the expression

$$P_e^{th} = \frac{1}{6}\langle\cos\xi\rangle(W_{\Omega_0;1} + W_{\Omega_0;1'} + W_{\Omega_0;1''}) = \frac{1}{6}\langle\cos\xi\rangle. \quad (17)$$

It is taken into account in the second equation that the total probability of a transition from a state Ω_e to all possible states Ω is equal to unity. As seen from (17), the degree of orientation of the produced atoms depends only on the rotation angle ξ of the molecule axis, but not on the probability of possible nonadiabatic transitions. The physical reason is that for the case of quadrupole-quadrupole interaction between atoms with total angular momenta $j_1 = j_2 = 3/2$ the degree of orientation is the same for all three possible $|\Omega| = 1$ dissociation channels and is equal to 1/6 (disregarding the molecule-axis rotation). We emphasize that this is a feature of only the given type of photodecay and that if alignment is produced in these atoms the influence of the radial nonadiabatic transitions is substantial.

In accordance with the summary expression (17), recognizing that $\xi \approx 25°$, we obtain for the degree of orientation of $\mathrm{Tl}(^2P_{3/2})$ atoms the theoretical value

$$P_e^{th} = 15{,}1\,\%. \quad (18)$$

We compare this quantity with the experimental degree of orientation $P_e = (19 \pm 2)\%$. On the whole the theoretical value (18) agrees with the experimental results, but is somewhat lower. Our investigations have shown that this difference cannot be attributed to experimental error, but is systematic. A possible explanation may be provided by interference effects in the excited states of the decaying molecules, which were not taken into account in the derivation of (11). These effects have been considered in Ref. 12. We are unable here to estimate quantitatively the influence of these effects, for lack of knowledge of the adiabatic terms of the TlBr molecule, but allowance for these effects should, generally speaking, increase the degree of orientation.

6. CONCLUSIONS

Thallium atoms oriented in a metastable $6^2P_{3/2}$ state and produced by photodissociaton of molecules have thus been observed for the first time ever. The photodissociation of TlBr molecules by radiation of wavelength 266 nm was observed. The degree of orientation, $P_0 = (19 \pm 2)\%$, of these atoms at the instant of their production was determined. The photodissociation dynamics of the TlBr molecules via a $\mathrm{C}^1\Pi_1$ excited state with allowance for the symmetry of the excited states of the molecules, for the nonadiabatic transitions between these states, and for the rotation of the molecule axis were considered.

It was shown that radial nonadiabatic transitions cannot influence the orientation of metastable thallium atoms, but can affect their alignment. The calculated theoretical value of the degree of orientation of the thallium atoms agrees with the experimental results.

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APPENDIX

A theory of interaction of polarized radiation with optically oriented atoms was developed in Refs. 7. In the case of an optically dense medium, the corresponding generalizations were carried out in Ref. 13. Using the results of these references one can determine the radiation intensity of weak probing unpolarized radiation of a thallium lamp at the exit of an AC and of a polarization analyzer.

The intensity of thallium-lamp radiation passing through an AC and a right-hand circular polarizer in optical hyperfine transitions $1 \to 2$ and $1 \to 1$ is of the form

$$I_+^{(12+11)} = \frac{1}{2} e^{-A}[\mathrm{ch}\, B + \frac{B_z}{B}\,\mathrm{sh}\, B] I_0^{(12+11)}, \quad (\mathrm{A}1)$$

where $I_0^{(12+11)}$ is the radiation intensity of these transitions on entering the gas cell, and the parameters A, B, and B_z are defined by the relations

$$A = \tau_0\left[\sqrt{5}\rho_{00}(2) + \frac{\sqrt{7}}{2\sqrt{2}}\rho_{20}(2) + \frac{1}{\sqrt{3}}\rho_{00}(1) - \frac{1}{2\sqrt{6}}\rho_{20}(1)\right],$$

$$B_z = \tau_0\left[\frac{3\sqrt{5}}{2\sqrt{2}}\rho_{10}(2) + \frac{1}{2\sqrt{2}}\rho_{10}(1)\right], \quad (\mathrm{A}2)$$

$$B_x - iB_y = \tau_0\left[\frac{\sqrt{21}}{2}\rho_{22}(2) - \frac{1}{2}\rho_{22}(1)\right],$$

$$B = (B_x^2 + B_y^2 + B_z^2)^{1/2},$$

τ_0 is the optical thickness of the gas cell for the $P_{3/2} \to S_{1/2}$ transition and is determined neglecting the hyperfine interaction; $\rho_{\varkappa,q}(F)$ are the polarization moments of the density matrix of the hyperfine sublevel of the Tl atom, characterized by a total angular momentum F,

$$\rho_{\varkappa q}(F) = \mathrm{Sp}\,\hat{\rho}\hat{T}_{\varkappa q}(FF), \quad (\mathrm{A}3)$$

where ρ is the density matrix of the atoms, and the polarization operators $T_{\varkappa q}(FF)$ are defined by relations similar to (7). A coordinate frame with z axis directed along the detecting beam was used in (A2).

The radiation intensity passing from a thallium lamp through the AC and a right-hand circular polarizer on the $0 \to 1$ hyperfine transition is given by

$$I_+^{(01)} = \frac{1}{2} e^{-\alpha}\left[\mathrm{ch}\,\beta + \frac{\beta_z}{\beta}\,\mathrm{sh}\,\beta\right] I_0^{(01)}, \quad (\mathrm{A}4)$$

$I_0^{(01)}$ is the radiation intensity for the corresponding transition on entering the AC,

$$\alpha = \tau_0 \frac{2}{3}\,[\sqrt{3}\rho_{00}(1) + \frac{\sqrt{3}}{\sqrt{2}}\rho_{20}(1)],$$

$$\beta_z = \tau_0\sqrt{2}\rho_{10}(1), \quad (\mathrm{A}5)$$

$$\beta_x - i\beta_y = \tau_0 2\rho_{22}(1),$$

$$\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}.$$

The polarization operators in (A3) can be connected with analogous operators defined for the nuclear $T_{\varkappa_1 q_1}(II)$, I is the nuclear spin) and electron $T_{\varkappa_2 q_2}(jj)$ subsystems:

$$\hat{T}_{\varkappa q}(FF) = \sum_{\varkappa_1\varkappa_2} (2F+1)[(2\varkappa_1+1)(2\varkappa_2+1)]^{1/2} \begin{pmatrix} I & I & \varkappa_1 \\ j & j & \varkappa_2 \\ F & F & \varkappa \end{pmatrix} \times \{\hat{T}_{\varkappa_1}(II) \times \hat{T}_{\varkappa_2}(jj)\}_{\varkappa q},$$

where $\{\ldots\times\ldots\}_{\varkappa q}$ is an irreducible tensor product.

Using relations (A1–A6), assuming the layer to be optically thin, and recognizing that at the atom-creation instant there is no nuclear polarization, so that $\mathrm{Sp}\hat{\rho}\hat{T}_{\varkappa_1 q_1}(II) = 0$, we obtain for the signal (3) an expression corresponding to the experimental conditions.

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[1)] Note that a typical effective duration of photodissociation is always substantially shorter than the period of the hyperfine interaction in the molecule, so that the effect of the onset of polarization of the nuclear spins during the photodecay time can be neglected here.