

SELECTIVE PREDISSOCIATION OF ORTHO-I₂ MOLECULES BY LASER RADIATION

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We produced selective predissociation of ortho-I₂ molecules with argon-laser radiation. A relatively rapid conversion of para-I₂ into ortho-I₂ was observed. The rate constants of the elementary process that may be responsible for the conversion were estimated, together with the quantum yield of predissociation from the I₂-molecule excited state B³Σ_{0+u} with v = 43

One of the most important applications of laser radiation is selective action on matter. Several schemes of selective action (excitation, ionization, dissociation, etc.) have been proposed and realized by now. These schemes make possible the separation of various isotopes, nuclear isomers, ortho- and para-molecules, molecular stereoisomers, etc. (see the review [1]). The simplest and most effective scheme for selective action is to excite the molecules in a narrow spectral line; this excitation causes the molecule to dissociate via the predissociation effect.¹⁾ We report here the first realization of selective predissociation of I₂ molecules with odd nuclear spin (ortho-molecules).

The experimental setup is illustrated in Fig. 1. The iodine is exposed to radiation from a cw argon laser (λ = 5145.3 Å); this radiation is at resonance with the P(13) and R(15) lines of the 43 - 0 electronic transition B³Σ_{0+u} ← X¹Σ_g⁺ [4], and therefore excites only the ortho-I₂ molecules with odd rotational quantum numbers. The length of the sealed cell with iodine vapor was 6 cm, the volume 20 cm³, and the I₂ pressure in the cell 0.25 Torr.

To investigate the kinetics of the transformation of the ortho-I₂ molecules into para-I₂ molecules, we have registered the resonance-fluorescence signal, which is proportional to the density of the ortho-I₂ molecules. The fluorescence has been observed to fall off within about 10 - 20 minutes after the laser is turned on and flatten out thereafter. The fall-off time and the

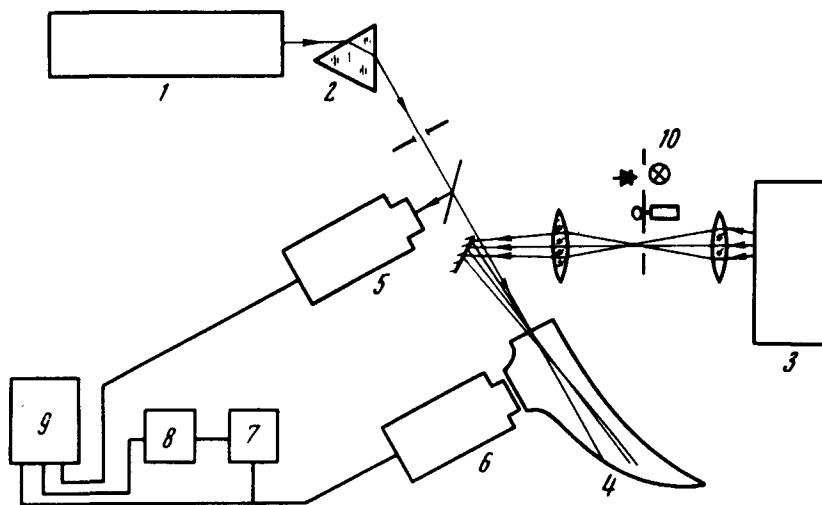


Fig. 1. Schematic diagram of setup: 1 - cw Ar II laser, 2 - dispersion prism, 3 - mercury lamp, 4 - cell with iodine, 5, 6 - photomultipliers, 7 - narrow-band amplifier, 8 - synchronous detector, 9 - automatic recorder, 10 - modulator.

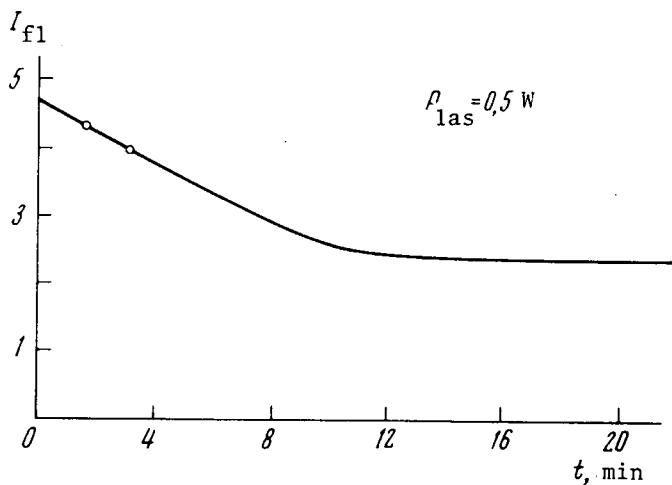


Fig. 2. Characteristic time dependence of the resonance fluorescence of I₂, excited by the λ = 5145.3 Å line of an Ar II laser at a power 0.5 W.

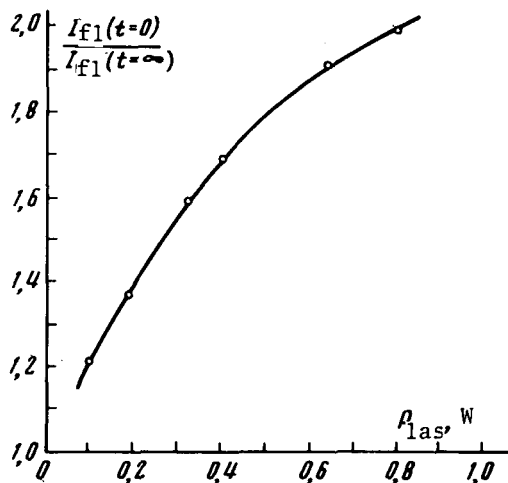


Fig. 3. Dependence of the depth of fluorescence fall-off on the laser radiation power.

ratio of the initial and final signals depend on the laser radiation power. The time variation of the fluorescence is illustrated in Fig. 2. The dependence of the ratio of the initial fluorescence signal to the signal at the plateau on the laser power is shown in Fig. 3. The degree of fall-off increased with power (but not proportionally). We monitored simultaneously the total number of iodine atoms by means of a weak test signal of fluorescence excited by the broad green line of a high-pressure mercury lamp (the width of the $\lambda = 5461 \text{ \AA}$ line is of the order of 4 cm^{-1}). Within the limits of measurement accuracy, no change in the fluorescence from the mercury lamp was observed. We measured independently the absorption coefficient of iodine at the $\lambda = 5145.3 \text{ \AA}$ wavelength of the argon laser, and obtained $\kappa = (2.7 \pm 0.3) \times 10^{-2} \text{ cm}^{-1} \text{ Torr}^{-1}$.

It can be concluded from the experimental results that interaction with the laser radiation transforms the ortho- I_2 molecules into para- I_2 molecules. The effect can be interpreted as selective predissociation [5] of the ortho- I_2 molecules followed by recombination of a fraction of the produced iodine atoms into para- I_2 molecules. The fact, however, that only partial conversion

takes place indicates that an important role is played by conversion processes, i.e., by the reconversion of the para- I_2 molecules into ortho- I_2 molecules. Conversion of the two modifications can occur in collisions, but the rates of such processes are exceedingly small even for collisions with paramagnetic particles [6, 7]. It is most probable that the conversion is due to the presence of atomic iodine in the mixture during the course of the irradiation process, and is effected either by the bimolecular double-exchange reaction



or via production of an intermediate complex I_3 in accordance with the scheme²⁾



The formal description of the conversion is the same for both possibilities. The conversion rate is characterized by a quantity k_{conv} equal to $k_{\text{conv}} = k_1 I$ for the bimolecular-exchange reaction, or to $k_{\text{conv}} = k_2 [I_2]$ for reaction with formation of the complex I_3 ,

An analysis of the kinetics of the processes of predissociation, recombination, and conversion shows that the fluorescence fall-off characteristic time t_{char} and the depth $I_{f1}(t=9)/I_{f1}(t=\infty)$ are independent combinations of the dissociation rate W_{diss} of the ortho- I_2 molecules, the recombination rate constants k_r , and the conversion rate k_{conv} :

$$t_{\text{char}} = \frac{12p}{5W_{\text{diss}}} \left(\frac{p^2}{4} + 1 \right)^{-1/2}, \quad \frac{I_{f1}(t=0)}{I_{f1}(t=\infty)} = \left[1 + \frac{p^2}{2} - p \left(\frac{p^2}{4} + 1 \right)^{1/2} \right]^{-1}, \quad (1)$$

where $p = (5/2\sqrt{21})(W_{\text{diss}}k_r)^{1/2}/k_{\text{conv}}$. Knowing that $k_r \approx 10^{13} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$ [9], we can estimate from (1) the rate constants of the alternative conversion processes (I) and (II) as well as the value of W_{diss} . Such an estimate was obtained for the curve corresponding to a laser power 0.4 W, namely $k_1 \approx 4.9 \times 10^7 \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$, $k_2 \approx 3.3 \times 10^{15} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$, and $W_{\text{diss}} \approx 2.4 \times 10^{-3} \text{ sec}^{-1}$. The obtained values of k_1 and k_2 are typical of the corresponding processes. The question of the conversion mechanism therefore remains open.

The dissociation rate is connected with the laser-radiation power, with the cross section σ_{ortho} of absorption calculated for all the ortho- I_2 molecules, the predissociation quantum yield γ , and with the length and volume L_c and V_c of the cell by the relation

$$W_{\text{diss}} = \frac{\gamma \sigma_{\text{ortho}} P}{\hbar \omega} \frac{L_{\text{cell}}}{V_{\text{cell}}} \quad (2)$$

From the obtained value of W_{diss} and the measured value of the absorption coefficient follows an estimate of the quantum yield of predissociation from the excited state $B^3\Pi_{0+u}$ with $v = 43$, namely $\gamma \approx 0.5 \times 10^{-2}$.

We note in conclusion that our experiment uncovers a possibility of investigating the predissociation of molecules and the conversion of ortho- and para-modifications of molecules, and of separating the radioactive iodine isotopes.

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1) This method of realizing selective chemical reactions was proposed in [2] and used in [3] to separate the hydrogen isotopes in H_2CO , a process likewise considered in [2].

2) The formation of I_3 , accompanied by the reaction $I + I_3 \rightarrow 2I_2$, was used in [8] to explain the anomalously large value of the rate constant of recombination of iodine atoms in the presence of I_2 molecules.

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SATURATION EFFECTS IN STIMULATED RAMAN SCATTERING AND RESONANT ABSORPTION (AMPLIFICATION) OF A STRONG NONMONOCHROMATIC FIELD

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1. We consider in this article stimulated Raman scattering (SRS) in the field of strong optical noise, with saturation effects taken into account. We discuss a new regime of strong energy transfer from broadband exciting radiation to a harmonic Stokes signal.

To analyze the nonlinear effects produced when incoherent light interacts with quantum systems, we propose to use an approach analogous to the Dyson-equations technique in the theory of waves in turbulent media [1], generalized to include nonlinear problems [2, 3].

2. Let \hat{L} and \hat{N} be a nonlinear and a linear operator. We seek the mean value \bar{x} of a quantity x satisfying the equation $\hat{L}x = \hat{N}(x)$, in which N or the initial (boundary) conditions for x contain a random function ξ with known characteristics. In our case $\xi(t)$ is the complex amplitude of a nonmonochromatic field incident on the medium and having a line shape $G(\omega)$, an average intensity $I_0 = \int_{-\infty}^{\infty} G(\omega) d\omega$, and a spectral width $\Delta\omega$. Putting $x = \bar{x} + \tilde{x}$ (\tilde{x} is the fluctuation), we obtain two equations: (a) $\hat{L}\bar{x} = \langle \hat{N} \rangle$ and (b) $\hat{L}\tilde{x} = \hat{N} - \langle \hat{N} \rangle$. By determining \tilde{x} from the second equation in the form of a series in ξ (in which case \bar{x} is regarded as a variable parameter of Eq. (b) and is assumed independent of ξ) and substituting the result in (a), we obtain for \bar{x} the equation

$$\hat{L}\bar{x} = \sum_{n=0}^{\infty} N^{(2n)}(\bar{x}),$$