Femtosecond vibrational nuclear dynamics in the electronically excited state of the I_2 molecule

O. M. Sarkisov,^{a} F. E. Gostev,^{a} V. V. Lozovoy,^{a*} E. A. Sviridenkov,^{b}
A. A. Titov,^{a} D. G. Tovbin,^{a} and S. Ya. Umansky^a

^{a}*N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,*
4 ul. Kosygina, 117977 Moscow, Russian Federation.
Fax: +7 (095) 938 2156. E-mail: kinet@glas.apc.org
^{b}*P. N. Lebedev Physical Institute, Russian Academy of Sciences,*
53 Leninsky prosp., 117924 Moscow, Russian Federation.
Fax: +7 (095) 938 2251

Dynamics of the nuclear motion in the bound electronic B-state of the I_2 molecule was studied in the real time scale. Experiments were performed by the femtosecond "pump—probe" technique, which measured the dependence of the intensity of fluorescence $P(\Delta t)$ in the highly excited f-state on the time delay between pump and probe pulses. The $P(\Delta t)$ dependence observed has an oscillating character with a period of ~300 fs. The pump pulse was generated by a femtosecond dye laser and amplified in a pulse dye laser amplifier; its spectral width was 5.6 nm, the wavelength in the center of the spectrum was 614 nm, and the duration was 90 fs. The probe pulse was generated in a KDP crystal due to duplication of the light frequency; its spectral width was 1.2 nm, the wavelength in the center of the spectrum was 307 nm, and the duration was 120 fs. The $P(\Delta t)$ dependence on the parameters of the probe and pump pulses was theoretically analyzed in terms of the quantum model based on the known energies of electronic vibrational-rotational states in the X-, B-, and f-terms of the iodine molecule. Experimental and calculated $P(\Delta t)$ plots at time delays of up to 1.5 ps and time resolution of less than 100 fs were compared. Values of potentials in the X-, B-, and f-terms of the iodine molecule, spectra, and durations of pump and probe pulses are sufficient data for quantitative calculation of the experimentally obtained $P(\Delta t)$ plot.

Key words: femtosecond dynamics, experiment, pump—probe, laser induced fluorescence, B $^3\Pi_u^+$-state of molecular iodine, vibrational-rotational wavepacket model.

Recent achievements in laser technique resulted in development of a new field of studies: photochemistry of elementary reactions. The use of the "pump—probe" technique with femtosecond time resolution makes it possible to observe the dynamics of intramolecular motion of atoms in time on potential energy surfaces (PES) of various types. For example, a phenomenon of regeneration of a vibrational wavepacket on the bonding PES was found,[1] and the dynamics of photodissociation for repulsive PES [2] and quasi-crossed PES [3] as well as the dynamics of elementary reactions in van der Waals complexes[4] were studied. These studies provided new experimental grounds for development of the theory of the dynamics of molecular photodissociation and bimolecular reactions.

The "pump—probe" method is the following. A pump light pulse converts a molecule to the state in which the dynamics is studied. A probe pulse converts the state studied to another electronic state, whose fluorescence is registered. The dependence of the fluorescence intensity on the time delay between pulses ($P(\Delta t)$) reflects the dynamics of atoms in the molecule and is determined by the peculiarities of three PES, parameters of light pulses, and distribution over initial states of the molecules. The registered intensity $P(\Delta t)$ depends on the Fourier components of electromagnetic field strengths of light pulses at the frequencies of electronic vibrational-rotational transitions of the molecule.

As a rule, information about parameters of light pulses is limited. Only the spectrum of the pulse power and time correlation second-order functions of the light intensity are usually measured in chemical experiments. Thus, a question arises about quantitative accuracy of description of the dynamics of the vibrational wavepacket motion over PES, if information about light pulses is limited. This work is devoted to elucidation of this question by an example of the dynamics of the bound B-state of I_2 molecule.

The iodine molecule was chosen as the object, because we have previously developed theoretical approaches[5] for calculation of $P(\Delta t)$ in a diatomic system, and the necessary spectroscopic information for this molecule is available. The femtosecond dynamics of the bound state of I_2 was experimentally studied.[6] An at-

tempt to describe theoretically the experiments[6] was made in Ref. 7. The authors of Ref. 7 mentioned the disagreement between the experimental results[6] and their theoretical calculations, but their attempts to explain this disagreement were unsuccessful. The quantum-chemical model developed in Ref. 7 does not take into account rotation of a molecule, which is necessary, in our opinion, for quantitative comparison with experiment. The model taking into account rotations was developed in Ref. 1, but it was used for analysis of regeneration of the vibrational wavepacket at long evolution times.

Experimental

The photochemical scheme of the processes occurring in the experiment is presented in Fig. 1. Before irradiation, I_2 molecules are in stationary vibrational-rotational states v'', j'', and m'' (v, j, and m are the vibrational, rotational, and magnetic quantum numbers, respectively) of the ground electronic state $X\ ^1\Sigma_g^+$ corresponding to thermodynamic equilibrium. A pump pulse with λ_1 wavelength converts them to vibrational-rotational states v, j, and m of the electronic term $B\ ^3\Pi_u^+$. Free vibrations and rotation of the molecule occur in this electronic term. A probe pulse with λ_2 wavelength follows the pump pulse after some time delay Δt and converts molecules to vibrational-rotational states v', j', and m' of the electronic term $f\ 0_g^+$. The intensity of fluorescence $P(\Delta t)$, proportional to the population of the f-state, is measured. The dependence of the fluorescence intensity on the time delay between the probe and pump pulses is studied in the experiment.
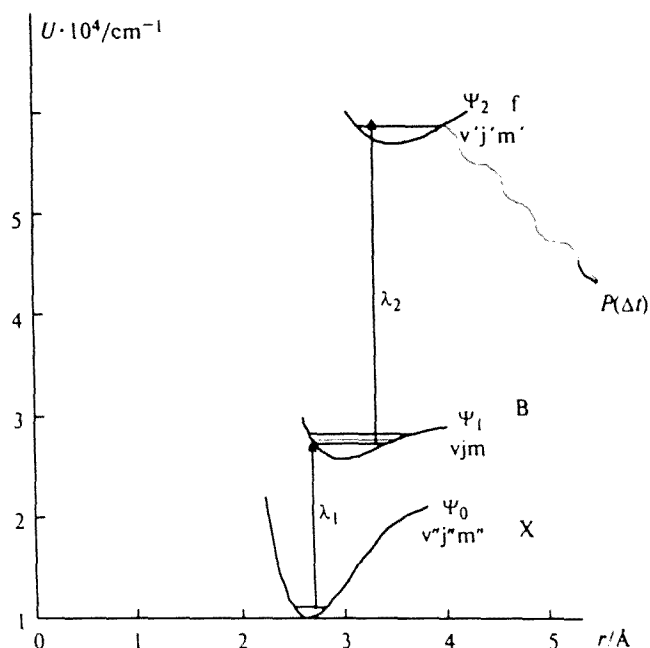
The scheme of the experimental setup is presented in Fig. 2. A continuous argon ion laser (*1*) pumps a femtosecond dye laser (*3*), which generates a series of femtosecond pulses. The energy of femtosecond pulses increases in a laser amplifier (*4*) pumped by an YAG : Nd^{3+} pulse laser (*2*). The amplified femtosecond pulse passes through a dispersion group velocity compensator (*5*). Some fraction of the amplified femtosecond pulse is used as a pump pulse, and a second harmonic pulse, which is generated in a block (*6*), is used as a probe pulse. A time delay is established by an optical delay of the probe pulse (*7*). Time parameters of pulses are measured by an autocorrelator (*8*), and spectral parameters are measured by a polychromator (*9*). Molecules under study are in a cell (*10*), and the fluorescence is registered by a photoelectron amplifier (*11*). The experiment is controlled, and the results are processed on computers (*12*) connected to the setup by the KAMAK system (*13*).

The femtosecond laser (FL) used is a ring dye laser with colliding pulses, passive mode synchronization, and an intracavity prismatic dispersion compensator, and it is similar to that described previously.[8] A jet with a solution of rhodamine 6G in ethylene glycol was used as an amplifier, and dye 5156-U (produced at the Institute of Organic Chemistry of the National Academy of Sciences of the Ukraine, Kiev) was used
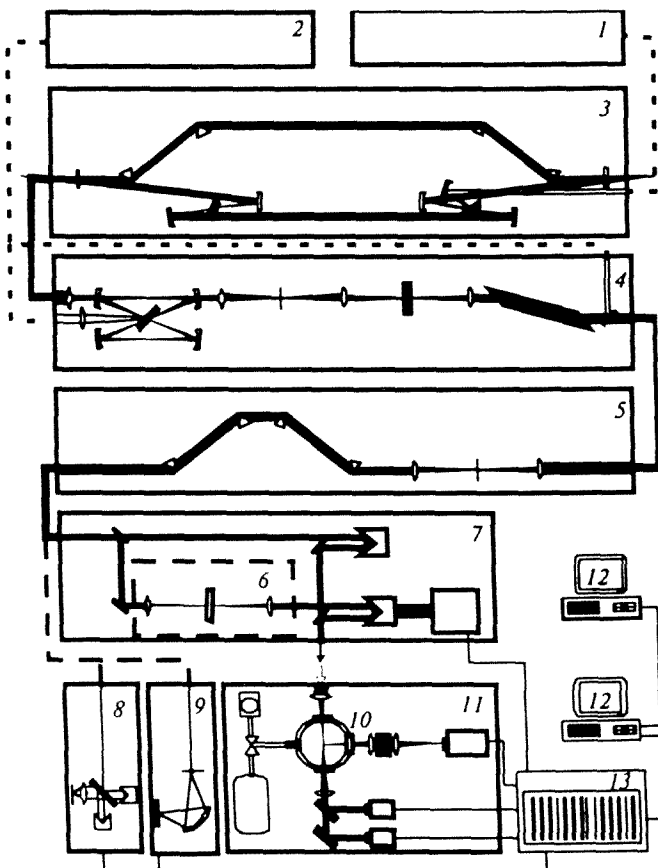

Fig. 1. Photochemical scheme of experimental processes in an I_2 molecule. U is the potential energy; r is the distance between nuclei; Ψ_0, Ψ_1, and Ψ_2 are the nuclear wave functions for electronic X-, B-, and f-states, respectively.

Fig. 2. Scheme of the setup: *1*, argon ion laser; *2*, YAG : Nd^{3+} laser; *3*, femtosecond laser; *4*, laser amplifier; *5*, light dispersion compensator; *6*, block of generation of the second harmonic light pulse; *7*, block of time delay; *8*, autocorrelator; *9*, polychromator; *10*, cell; *11*, registration system; *12*, computers; *13*, KAMAK.
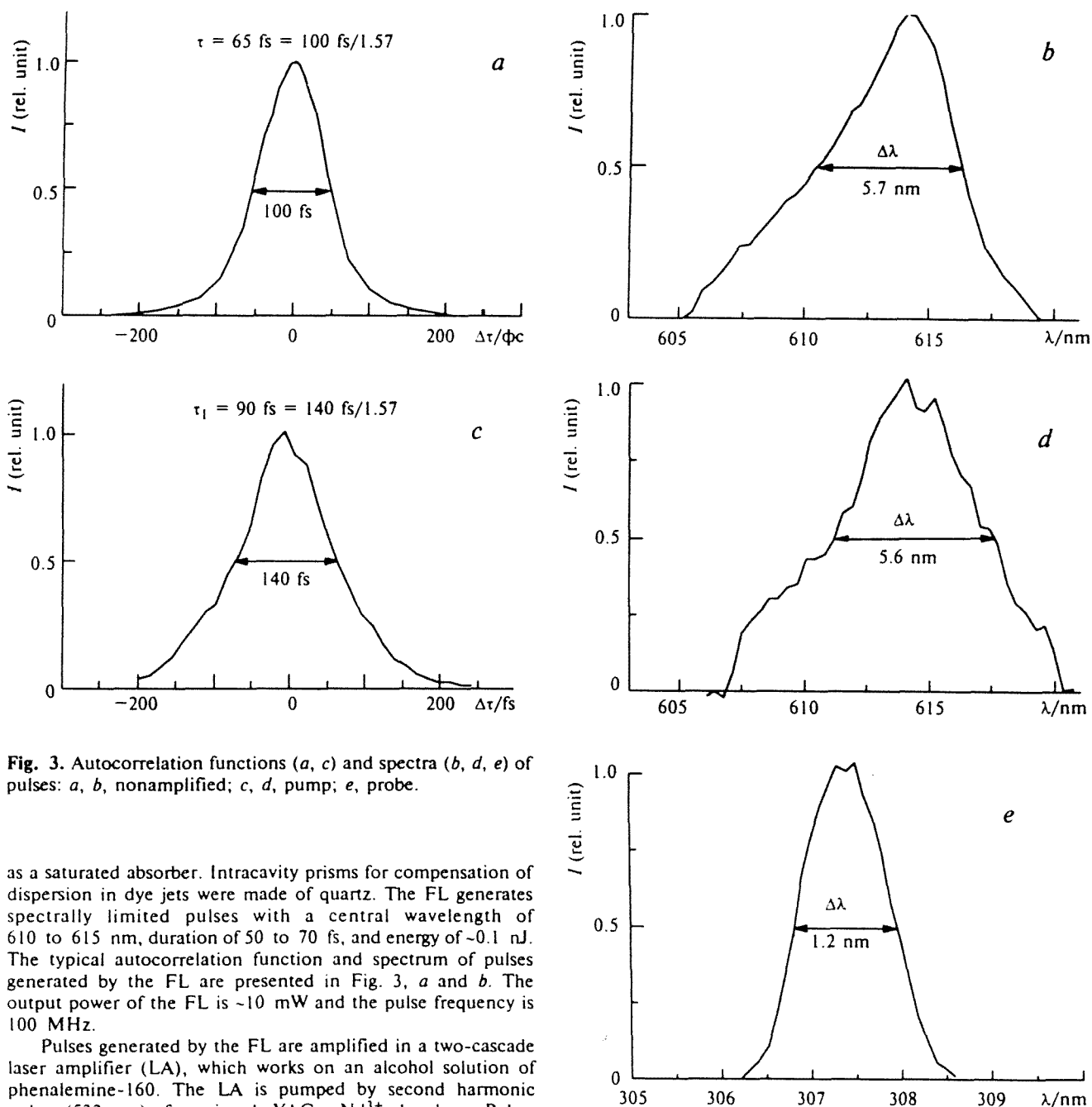
Fig. 3. Autocorrelation functions (a, c) and spectra (b, d, e) of pulses: a, b, nonamplified; c, d, pump; e, probe.

as a saturated absorber. Intracavity prisms for compensation of dispersion in dye jets were made of quartz. The FL generates spectrally limited pulses with a central wavelength of 610 to 615 nm, duration of 50 to 70 fs, and energy of ~0.1 nJ. The typical autocorrelation function and spectrum of pulses generated by the FL are presented in Fig. 3, a and b. The output power of the FL is ~10 mW and the pulse frequency is 100 MHz.

Pulses generated by the FL are amplified in a two-cascade laser amplifier (LA), which works on an alcohol solution of phenalemine-160. The LA is pumped by second harmonic pulses (532 nm) of a unimode YAG : Nd^{3+} glass laser. Pulses of the pump laser have duration of ~8 ns, energy of ~30 mJ, and frequency of 10 Hz. The first amplification cascade is made as a six-pass confocal amplifier (the optical scheme of its prototype was described in Ref. 9). A solution of the dye was passed through a cell 1 mm in width. The energy of a femtosecond pulse after the multi-pass amplifier was ~5 µJ. The second amplifier cascade was made as a cell 10 cm in length and 4 mm in diameter with longtidudinal pumping through a dichroic mirror. The energy of the femtosecond pulse after the second cascade was ~100 µJ. A pin-hole and a cell with an alcohol solution of Malachite Green were placed between the LA cascades. The pin-hole serves as a spatial filter and forms a beam, which clarifies a solution with the saturated absorbent. The solution of the absorbent was passed through a cell 1 mm in width.

The spatial energy distribution over the cross section of the beam worsens when it passes through the LA. To improve this distribution, the beam is focused and passes through a pin-hole of a smaller cross section than that of the beam. The light pulse lengthens to several hundred femtoseconds due to the positive dispersion in lenses and solutions of dyes. A glass TF-5 prismatic compressor, whose scheme is described in Ref. 10, is used for reverse time compression of the light pulse. The autocorrelation function and spectrum of amplified pulses are presented in Fig. 3, c and d.

Half of an amplified light pulse was used as a pump pulse, and a second harmonic light pulse generated in the KDP crystal with an ~10 % efficiency from another half of an amplified pulse was used as a probe pulse. The time delay

between the pump and probe pulses varied to 40 ps with an increment of 1.4 fs in the optical delay line, in which a mirror V-deflector was removed by an stepping-motor controlled by a computer through a controlling module of the stepping-motor (performed in the KAMAK standard).

Pump pulse duration was measured by an autocorrelator based on a noncolinear generation scheme of the second harmonic of the KDP crystal. In the autocorrelator, the pulse measured is divided into two beams, one of which is delayed relative to the other by time $\Delta\tau$. The second harmonic intensity A generated by the superposition of these beams in the nonlinear crystal is measured. The $A(\Delta\tau)$ function is related to the pulse intensity $I(t)$ by the equation

$$A(\Delta\tau) = \int_{-\infty}^{+\infty} I(t)I(t - \Delta\tau)d(t). \tag{1}$$

The form of the experimental $A(\Delta\tau)$ dependence (Fig. 3, *c*) is well described by Eq. (1) under assumption of $I(t) = \text{sech}^2(t)$. In this case, the duration (a width at the half-height of the $I(t)$ function) of the light pulse (τ_I) can be expressed *via* a width at the half-height of the autocorrelation function τ_A by the equation $\tau_I = \tau_A/1.57$. The duration of the pump pulse τ_1 thus measured is equal to 90 fs. No measurements of the probe pulse duration were performed, and its spectrum is presented in Fig. 3, *e*. Assuming spectral boundedness of the pulse and Gaussian form of the envelope intensity, we find that the total duration of the probe pulse at the half-height (τ_2) is equal to 120 fs (this τ_2 value will be discussed in more detail below).

Thus, the pump pulse has a wavelength at the spectral maximum $\lambda_1 = 614$ nm, duration $\tau_1 = 90$ fs, and energy ~20 μJ; the probe pulse has a wavelength at the spectral maximum $\lambda_2 = 307$ nm, duration $\tau_2 = 120$ fs, and energy ~2 μJ.

Molecular iodine under study is in a cell at ~20 °C and ~0.3 Torr. The pump and probe beams 5 and 3 mm in diameter are superposed on the dichroic mirrror and focused to the center of the chamber by a quartz lens with a focal length of 500 mm. The pump pulse energy is measured by a pyroelectric detector, and the energy of the probe pulse is measured by the photomultiply tube (PMT).

Fluorescence that appears upon passing pump and probe pulses is collected at an angle of 90° with a lens condenser and focused to an output gap combined with an image of the pumping and probing beams. The fluorescence that appears upon absorption of the pump and probe pulses is separated by FS-1 and SZS-21 glass optical filters. The fluorescence intensity is recorded by PMT, whose signal is measured by a stroboscopic voltmeter. Signals from the voltmeter are accumulated in the buffer storage of an A/D converter (performed in the KAMAK standard) and transferred to a computer connected to a controlling computer in the local computer network.

Theoretical Model

It is assumed in the theoretical model using the photochemical scheme of the processes (Fig. 1) that light pulses are coherent and have linear polarization; polarizations of pump and probe pulses are perpendicular; an amplitude envelope of the field strength of light pulses has a Gaussian form; and the time delay between pulses is greater than their duration. The interaction

between light and the molecule was assumed to be weak. The method is based on calculation of the probabilities of electronic vibrational-rotational transitions in the molecule under the action of pump and probe pulses. The matrix elements of the B ← X and f ← B transitions are calculated in the Condon approximation in terms of overlap integrals of vibrational wave functions, and these integrals are determined under the assumption that the potential of interaction of the I atoms in the I_2 molecule can be described by Morse functions.

Before the action of the pump pulse, the system can be described by an ensemble of molecules in the thermodynamic equilibrium in the X-state. Each state of the ensemble is described by the wave function:

$$\Psi_0 = \chi_{0v}\phi_{j''m''}, \tag{2}$$

where ϕ is the stationary rotational wave function, χ is the stationary vibrational wave function, and index 0 denotes that the function is related to the X-term.

After the action of the pump pulse, the molecule converts to the B-state, and it can be described by the nonstationary wave function:

$$\Psi_1(t) = \sum_{vjm} \exp(-i2\pi\nu_{vj}t) \cdot b_{vjm} \cdot \chi_{1v}\phi_{jm} , \tag{3}$$

where t is time passed after the pump pulse, ν_{vj} is the frequencies of transitions between vibrational-rotational states in the B- and X-terms, b_{vjm} is the population amplitude of the v,j,m-state in the B-term, and index 1 means that the functions are related to the B-term. Amplitudes b_{vjm} depend on the quantum numbers in the X- and B-states and on the parameters of the pump pulse. In the coordinate representation, the square of the module of wave function $\Psi_1(t)$ forms the vibrational-rotational wavepacket. The nuclear dynamics in the potential of the B-state is described by the time evolution of this wavepacket.

The probe pulse results in the excitation of the molecule from the B-state to the f-state with the wave function:

$$\Psi_2(\Delta t) = \sum_{v'j'm'} c_{v'j'm'}(\Delta t) \cdot \chi_{2v'}\phi_{j'm'} , \tag{4}$$

where Δt is the time delay between the pump and probe pulses, index 2 means that the functions are related to the f-term, and $c_{v'j'm'}$ is the population amplitude of the vibrational-rotational state in the f-term. Amplitudes $c_{v'j'm'}$ depend on Δt, the quantum numbers of the initial and final states, and the parameters of pump and probe pulses.

The population of the f-state is determined by the time delay between pump and probe pulses. This dependence can be described in the semiclassical language in the following way. In the time interval between pump and probe pulses, the wavepacket moves along the potential curve of the B-state. At the moments when a maximum of the wavepacket passes through a point in

the potential curve, which is in resonance with the carrier frequency of the pump light, the probability of absorption of the probe pulse is maximum and depends on the spatial sizes of the wavepacket and its position and rate of movement along the potential curve for each particular time interval Δt.

In the quantum model used in this work, the population amplitude of each final state is an interference of amplitudes of transitions of all vibrational-rotational states in the B-term and can be calculated from the equation

$$c_{v'j'm'}(\Delta t) \propto \sum_{vjm} \exp(-i2\pi v_{vj}\Delta t) \cdot \Gamma'_{jm}\Gamma''_{jm}S'_vS''_vF'_{vj}F''_{vj} \cdot \qquad (5)$$

where coefficients Γ''_{jm} and Γ'_{jm} are determined by the matrix elements of the dipole moment of the I_2 molecule between the B- and X-states and the f- and B-states, respectively; S''_v and S'_v are the overlap integrals between the vibrational functions in the B- and X-states and the f- and B-states, respectively; F''_{vj} are the Fourier components of the field strength of the pump pulse at the frequencies of electronic vibrational-rotational transitions between the B- and X-terms; F'_{vj} are the Fourier components of the field strength of the probe pulse at the frequencies of electronic vibrational-rotational transitions between the B- and f-terms.

Population amplitudes $c_{v'j'm'}(\Delta t)$ determine the dependence of the fluorescence intensity on the time delay, if the fluorescence is detected from one vibrational-rotational f-term. As can be seen from Eq. (5), population amplitude $c_{v'j'm'}(\Delta t)$ is presented by the sum of terms, each of which oscillates with frequencies v_{vj}. If there are several such terms, beats appear in the $c_{v'j'm'}(\Delta t)$ dependence. The frequencies of these beats are equal to the differences between frequencies v_{vj}. Since v_{vj} are determined by the potential, the beat frequencies in the $c_{v'j'm'}(\Delta t)$ dependence are related only to the form of the potential curve of the B-term.

The time behavior of the $c_{v'j'm'}(\Delta t)$ amplitudes is determined by the dependence of the coefficients in the right-hand side of Eq. (5) on the quantum numbers v and j. The coefficients in Eq. (5) can be divided into three pairs. The first pair (F''_{jm}, F'_{jm}) determines the $c_{v'j'm'}(\Delta t)$ dependence on the initial rotational states and pulse polarizations. The second pair (S''_v, S'_v) determines the vibrational states between which efficient optical transitions are possible and, hence, in which frequencies of pump and probe pulses should be present. The third pair (F''_{vj}, F'_{vj}) depends on the spectral intensity of the pump and probe pulses at the frequencies of electronic vibrational-rotational transitions in the molecule. These coefficients mainly determine the $c_{v'j'm'}(\Delta t)$ dependence on the parameters of the f-, X-, and B-terms and both light pulses.

The aforesaid concerns the calculation of the population amplitude of one final vibrational-rotational state in the f-term with account of one initial vibrational-rota-

tional state in the X-term. To calculate the $P(\Delta t)$ intensity, which further will be compared with the experiment, the squares of modules of the $c_{v'j'm'}(\Delta t)$ amplitudes are summated over all final states and averaged over all initial states:

$$P(\Delta t) \propto \sum_{v''j''m''} \frac{e^{-\frac{E_{v''j''}}{kT}}}{Q} \sum_{v'j'm'} \left| c_{v'j'm'}(\Delta t) \right|^2 \cdot \qquad (6)$$

where $E_{v''j''}$ is the energy of the initial state, T is the temperature of the gas, and Q is the statistical sum of vibrational-rotational states of the electronic X-term.

Results and Discussion

The dependence of the fluorescence intensity of the I_2 molecule on the time delay between pump and probe pulses was studied in the experiment. The difficulty was that the energy of the pump pulse and, hence, that of the probe pulse unambiguously determined by the pump pulse varied from pulse to pulse in the experiment. Therefore, the experimental results were processed in the following way. At each time delay, 1000 measurements were performed, in each of which the fluorescence intensity and pump pulse energy were measured. Then the $P(\Delta t)$ dependence was plotted at the fixed (scatter was lower than 5 %) value of energy of pump pulses, and the integral fluorescence intensity (sum of $P(\Delta t)$ over all time delays at the certain energy of the pump pulse) was calculated. The $P(\Delta t)$ dependences thus plotted at various energies of pump pulses were normalized by dividing by the calculated integral fluorescence intensity.

The normalized $P(\Delta t)$ dependences are presented in Fig. 4, *a*. The normalized $P(\Delta t)$ intensities were averaged at each Δt value to enhance the signal/noise ratio. These averaged $P(\Delta t)$ values are shown in Fig. 4, *c*, and the calculation results will be compared with them.

The parameters of pump and probe pulses determined from their autocorrelation function and spectra presented in Fig. 3 were used for calculation of $P(\Delta t)$. As mentioned above, the duration value at the half-height (τ_1) equal to 90 ps was obtained from the analysis of the autocorrelation function of the pump pulse (Fig. 3, *c*). For our problem, the time dependence of the pulse intensity in the form of the Gaussian function with a width at the half-height of 90 fs was used. (The difference between $sech^2(t)$ and $exp(-t^2)$ can be considered insignificant for our problem.) The spectrum of the pump pulse is presented in Fig. 3, *d*, the wavelength at the maximum is ~614 nm, and the width at the half-height ($\Delta\lambda_1$) is equal to 5.6 nm. Since $\Delta v_1 \tau_1 = 0.4$, the pump pulse can be considered spectrally bounded, which was used in the theoretical model.

The spectrum of the probe pulse is presented in Fig. 3, *d*, the wavelength at the maximum is ~307 nm, and the width at the half-height ($\Delta\lambda_2$) is 1.2 nm. The
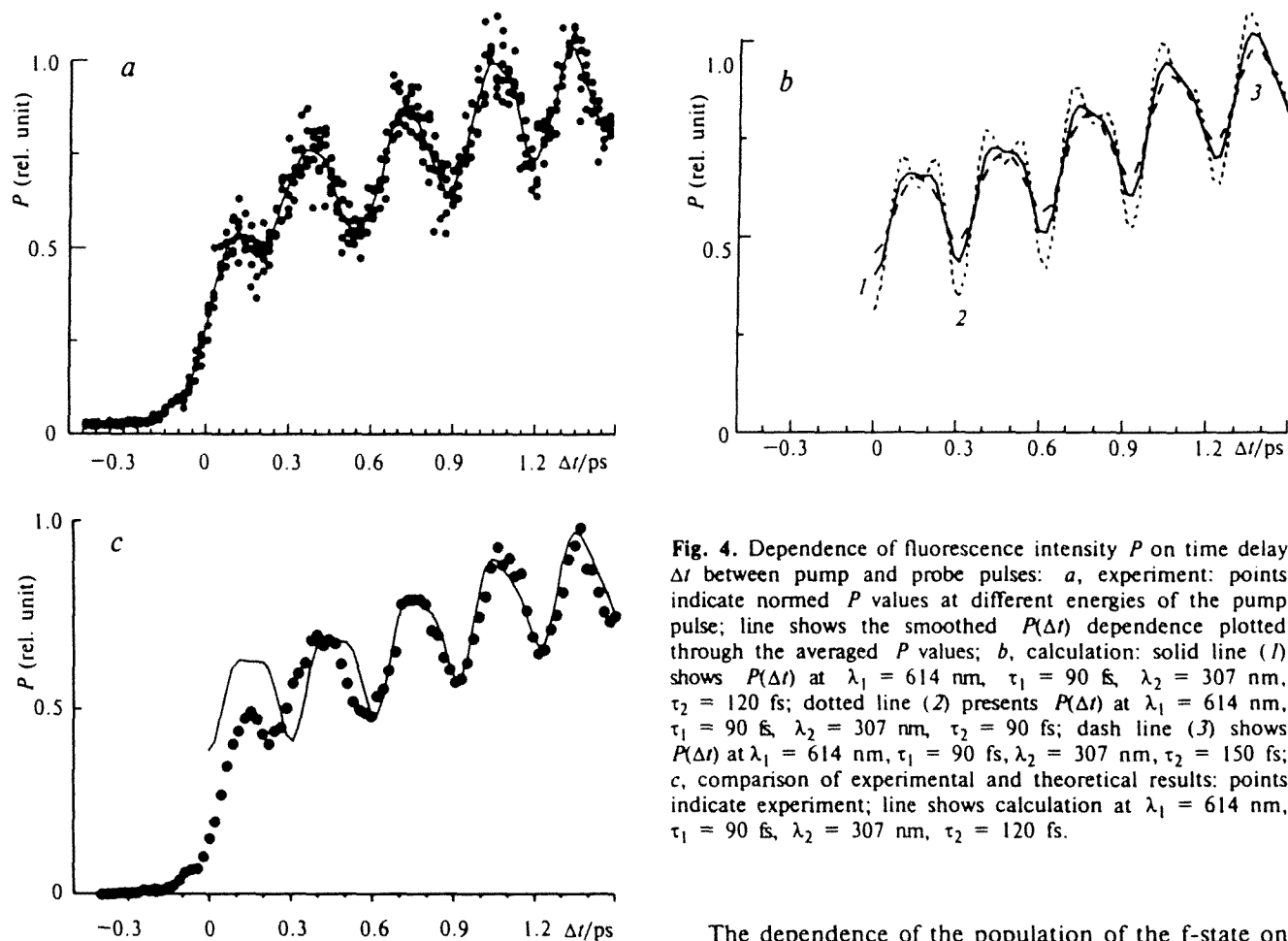
Fig. 4. Dependence of fluorescence intensity P on time delay Δt between pump and probe pulses: *a*, experiment: points indicate normed P values at different energies of the pump pulse; line shows the smoothed $P(\Delta t)$ dependence plotted through the averaged P values; *b*, calculation: solid line (*1*) shows $P(\Delta t)$ at $\lambda_1 = 614$ nm, $\tau_1 = 90$ fs, $\lambda_2 = 307$ nm, $\tau_2 = 120$ fs; dotted line (*2*) presents $P(\Delta t)$ at $\lambda_1 = 614$ nm, $\tau_1 = 90$ fs, $\lambda_2 = 307$ nm, $\tau_2 = 90$ fs; dash line (*3*) shows $P(\Delta t)$ at $\lambda_1 = 614$ nm, $\tau_1 = 90$ fs, $\lambda_2 = 307$ nm, $\tau_2 = 150$ fs; *c*, comparison of experimental and theoretical results: points indicate experiment; line shows calculation at $\lambda_1 = 614$ nm, $\tau_1 = 90$ fs, $\lambda_2 = 307$ nm, $\tau_2 = 120$ fs.

literature data indicate that the spectrally limited pulse generates the spectrally limited second harmonic pulse in the KDP crystal. Therefore, we assumed that the probe pulse is spectrally limited and has the Gaussian form, at which the equality $\Delta v_2 \tau_2 = 0.44$ should be fulfilled. Substituting Δv_2 from the experiment to this equality, one can find that the probe pulse duration (τ_2) is equal to 120 fs. Thus, it is assumed in the calculation that both pulses are spectrally limited and have Gaussian forms with durations at the half-heights of 90 fs (pump pulse) and 120 fs (probe pulse).

The spectroscopic data for description of the vibrational potential and electronic vibrational-rotational energy for the X- and B-states are taken from Ref. 11 and those for the f-state are taken from Ref. 12. The following vibrational states are substantial for an I_2 molecule at room temperature and spectral parameters of the pulses used: from $v'' = 1$ to $v'' = 4$ for the X-term, from $v = 6$ to $v = 13$ for the B-term, and from $v' = 18$ to $v' = 30$ for the f-term. The transitions from rotational states from $j'' = 10$ to $j'' = 200$ should be taken into account for the ground electronic state. The rotational states for the electronic B- and f-terms were determined by the selection rules for rotational transitions.

The dependence of the population of the f-state on the time delay between pump and probe pulses was calculated from Eqs. (5) and (6). The details of the calculation algorithm can be found in Ref. 5. Comparison of the calculated and experimental $P(\Delta t)$ dependences shows that the period of oscillations and the modulation depth of the $P(\Delta t)$ values coincide. Since the experimental and theoretical $P(\Delta t)$ dependences have relative units of measure, they were chosen in such a way that amplitudes of these $P(\Delta t)$ dependences coincided. In the experiment, the point in the time delay scale corresponding to $\Delta t = 0$ is unknown. Therefore, the experimental $P(\Delta t)$ dependence was shifted in such a way that its best coincidence with the calculated $P(\Delta t)$ dependence was obtained.

The experimental and calculated dependences of the fluorescence intensity on the time delay between pump and probe pulses are presented in Fig. 4, c, which illustrates their good coincidence. A deviation of the model from the experiment at short time delays can be explained by overlapping of pump and probe pulses over time. The account of this should result in a decrease in the calculated $P(\Delta t)$ values at short times.

Since the autocorrelation function of the probe pulse was not measured, this forced us to perform calculations with the probe pulse duration (τ_2), which somewhat differs from that determined from the spectral width.

The results of the calculations with τ_2 = 90, 120, and 150 fs are presented in Fig. 4, *b*. At τ_2 = 90 fs, the calculated $P(\Delta t)$ intensity contains doublets that were not observed in the experiment. If τ_2 is assumed to be equal to 150 fs in the calculations, the depth of oscillations of the calculated curve is smaller than in the experiment. Thus, it is shown by the example of the I_2 molecule that the measurements of the spectral width or duration of femtosecond pulses are enough for quantitative description of the intramolecular nuclear motion.

Let us discuss the questions from Ref. 7, where experimental data[6] on studying the dependence of the fluorescence intensity of the I_2 molecule on the time delay between pump and probe pulses were analyzed (a wavelength of the pump pulse was 620 nm and that of the probe pulse was 310 nm). First of all, it was mentioned (see Ref. 7, Fig. 8, *b*) that $P(\Delta t)$ were split to doublets in the calculations, while no doublets were observed in the experiment. In addition, there is the second difference between the calculated and experimental $P(\Delta t)$ dependences. In the experiment at the time delays lower than 2 ps for $P(\Delta t)$, a growth of the mean line, relative to which oscillations take place, was observed. The calculation did not provide such a growth.

We used our model for the analysis of the experimental results[6] and explanation of the differences between them and calculated[7] $P(\Delta t)$ dependences. In our opinion, the second difference is explained by the fact that rotation of a molecule was not taken into account in the theory developed.[7] In fact, the calculation based on our model (with account of rotation) results in a growth of $P(\Delta t)$ at first picoseconds for the case of perpendicular polarizations of pump and probe pulses. However, another disagreement between the experiment and calculation cannot be eliminated by the introduction of rotations to the model. Doublets remain in the calculated $P(\Delta t)$ dependence with the parameters of light pulses

presented in the brief description of the experimental setup[6] (pulse durations are considered to be equal to 50 fs). In the calculated $P(\Delta t)$ dependence doublet disappear, if the duration of the probe pulse is accepted to be equal to ~100 fs.

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