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ДИНАМИКА ФОТОДИССОЦИАЦИИ ПРОСТРАНСТВЕННО ОРИЕНТИРОВАННЫХ МОЛЕКУЛ ПО ДАННЫМ МЕТОДА ДИФРАКЦИИ ЭЛЕКТРОНОВ С ВРЕМЕННЫМ РАЗРЕШЕНИЕМ

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Анизотропные ансамбли лазерно-возбужденных молекул могут быть образованы, например, под действием фемтосекундных импульсов поляризованного лазерного излучения. Теоретически предсказано, что дифракционные картины, полученные для пространственно ориентированных молекул в газовой фазе, позволяют определять не только межъядерные расстояния, но и валентные углы – 3D структуру молекулы. В настоящей статье предложены основные элементы теории, которые могут быть использованы для анализа экспериментальных данных метода дифракции электронов с временным разрешением, полученных для пространственно ориентированных/выровненных лазерно-возбужденных молекул. Этот формализм применим для исследования процессов диссоциации и ядерной динамики процессов фотодиссоциации. Теория иллюстрируется моделированием интенсивностей рассеяния для фотоиндуцированной диссоциации молекул ICN. Рассчитаны зависящие от времени интенсивности молекулярного рассеяния и соответствующие функции радиального распределения межъядерных расстояний в процессах фотодиссоциации ICN. На основе модельных расчетов, представленных в этой статье, возможно сделать заключение о том, что метод дифракции электронов с временным разрешением даёт принципиальную возможность изучения когерентной динамики фотодиссоциации в реальном масштабе времени, значительно меньшем, чем длительность зондирующего электронного импульса 300 фс, что достигается в настоящее время в ряде экспериментов, выполненных методом дифракции электронов с временным разрешением. Полученные результаты сопоставлены с данными предыдущих модельных исследований неупорядоченных, а также ориентированных ансамблей двухатомных молекул.

Ключевые слова: дифракция электронов с временным разрешением, когерентная структурная динамика, процесс фотодиссоциации, ориентированные молекулы, определение 3D-структуры молекул в газовой фазе

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PHOTODISSOCIATION DYNAMICS OF SPATIALLY ALIGNED MOLECULES BY TIME-RESOLVED ELECTRON DIFFRACTION

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The anisotropic ensembles of laser-excited molecules can be formed, for example, under the action of fs pulses of polarized laser radiation. It was theoretically predicted that the electron diffraction pattern from aligned molecules in the gas phase allows determining not only internuclear distances but also valence angles that is 3D molecular structure. In the current article, we propose the basic elements of the theory that can be employed for analyze of time-resolved electron diffraction (TRED) data obtained from oriented/aligned laser-excited molecules. This formalism is applicable to dissociative processes and to nuclear dynamics studies of photo dissociation studies. The theory is illustrated by modeling the diffraction intensities of photo generated dissociation of ICN molecules. The time-dependent intensities of the molecular scattering and the corresponding radial distribution functions of the internuclear distances at the processes of the photo dissociation of ICN were calculated. Based on model calculations presented in this article we conclude that TRED method provides the principal possibility of study of coherent dissociation dynamics for real scale of time which is essentially less than the electron pulse duration of 300 fs, which is achieved at present in a number of TRED experiments. The results obtained were compared with our previous modeling studies of randomly oriented and diatomic aligned molecular ensembles.

Key words: time resolved electron diffraction, coherent structural dynamics, photodissociation process, aligned molecules, 3D structure determination in the gas phase

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INTRODUCTION

The application of femtosecond laser pulses made it possible to observe for the first time the real-time dynamics of fast elementary molecular processes and to obtain snapshots of molecules at different stages of chemical reactions. The new discipline, femtochemistry [1-4] or coherent chemistry [5], emerged. The temporal resolution provided by femtosecond laser pulses proved sufficient for investigations into the nuclear dynamics in the molecule.

Because of the chaotic orientation of molecules in the gas phase, unlike X-ray diffraction by a crystal, the electron diffraction technique in the absence of additional information (e.g., about equilibrium configuration symmetry of the study system, equivalence of certain chemical bonds, character of vibrational energy distribution) permits determining only a one-dimensional molecular structure or a set of internuclear distances. It restricts applications of the electron diffraction method for studying the structure and dynamics of complex polyatomic molecules. The solution of a structure-related problem even in the case of relatively small molecules implies the involvement of results obtained by other experimental methods, such as vibrational spectroscopy and/or quantum-chemical computation.

X-ray crystallography is believed to be the most adequate tool for the elucidation of the structure of complex polyatomic molecules. However, this method can be applied only for the study of crystalline objects. Moreover, the local environment of a molecule distorts its structure and makes it difficult to study the nuclear dynamics.

A new approach to structural research based on isolated molecule irradiation by a large number of photons contained in a single X-ray laser pulse was proposed in Ref. [6]. The use of rather short laser pulses enabled the researchers to obtain diffraction patterns before the study system was destroyed. Diffraction patterns for micro- and nanometer objects were taken with femtosecond pulses of soft X-ray radiation [7-10]. However, this method is currently employed only in studies of fairly large objects, such as nano-sized particles.

An alternative approach takes advantage of the time-resolved electron diffraction (TRED) method as applied to anisotropic ensembles ('oriented' molecules whose dipole transitions are oriented in the direction of polarization of the laser radiation) in the gas phase. The anisotropic environment of laser-excited molecules can be formed, for example, under the effect of fs pulses of polarized laser radiation. It was theoretically predicted in Refs. [11-17] that the electron diffraction pattern from `oriented' molecules in the gas phase furnishes an opportunity of determining not only internuclear distances but also valence angles.

The theory was first confirmed experimentally in Refs. [18, 19] for adiabatically oriented CS_2 molecules using the TRED method with a resolution of 10 ns. To elucidate the structure of organic molecules, such as low-molecular weight proteins scarcely amenable to crystallization, the authors of Ref. [20] used a jet of liquid gel droplets and a continuous electron beam producing a diffraction pattern. Organic molecules, e.g., small proteins, in a droplet or inside a glassy ice shell can be spatially oriented under the effect of polarized radiation of a powerful continuous wave laser. Iterative methods for solving the phase problem have been proposed.

In the current article we propose the basic elements of the theory that can be employed in analyses of TRED data recorded from oriented/aligned laser-excited molecules. The formalism is applicable to dissociative processes and to nuclear dynamics studies of dissociation phenomena. The theory will be illustrated by modeling the diffraction intensities of photogenerated dissociation of ICN molecules. The results will be compared with our previous modeling studies of randomly oriented [21] and diatomic aligned molecular ensembles [13].

1. THEORY: BASIC ASSUMPTIONS AND APPROXIMATIONS

The interaction of ultrashort pulses of polarized laser radiation on an isotropic medium of randomly oriented molecules leads to photoexcitation of the molecules which dipole momentums are oriented in the direction of the laser radiation polarization. Thus, the spatial anisotropy of coherently excited molecules is created, generating different types of spatial order of the ensemble. The electron scattering theory for spatially oriented ensembles of molecules require substantial modification of the electron diffraction theory for randomly oriented molecules in the gas phase [11-17]. Assuming single scattering processes for fast electrons (>10 keV) with short (attosecond) coherence time, the electrons encounter molecules that are essentially "frozen" in their rotational and vibrational states. Thus, the latter can be accounted for by using probability density functions (p.d.f.) that characterize the ensemble under investigation. If the molecular systems investigated are not at equilibrium, as is the case in studies of laser-excited molecules, a time-dependent p.d.f. must be used to describe the structural evolution of the system. In addition, rotational and vibrational motions can be separated adiabatically, since the latter involves much faster processes.

The equation for the time-dependent molecular scattering intensity can be written as follows (please, see, e.g. Ref. [13]):

$$I_{mol}(s,t)=\langle\langle I_{mol}(s)\rangle_{vib}\rangle_{sp}=(I_0/R_2)\sum\sum_{i\neq j=1,N}|f_i(s)||f_j(s)|\mathrm{Re}\{\exp[i\Delta\eta_{ij}(s)]\times$$
$$\times\langle\langle\exp(\boldsymbol{i}\mathbf{sr}_{ij})\rangle_{vib}\rangle_{sp}\}=(I_0/R^2)\sum\sum_{i\neq j=1,N}|f_i(s)||f_j(s)|\cos(\Delta\eta_{ij}(s))\times$$
$$\int_{0,\infty}P_{vib}(r_{ij},t)[\int_{0,\infty}\int_{0,2\pi}P_{sp}(\alpha_{ij},\beta_{ij},t)\exp(\boldsymbol{i}\mathbf{sr}_{ij})\sin\alpha_{ij}d\beta_{ij}d\alpha_{ij}]dr_{ij} \qquad (1)$$

In Eq. (1) ⟨ ... ⟩ correspond to vibrational and spatial (orientational) averaging over the scattering ensemble. $P_{vib}(r_{ij},t)$ and $P_{sp}(\alpha_{ij},\beta_{ij},t)$ – vibrational and orientational probability density functions (PDFs), respectively; $\alpha_{ij}$and β_{ij} – angles in the spherical polar coordinate system (Fig. 1), which defines the orientation of the internuclear distance vector $\mathbf{r}_{ij}$.

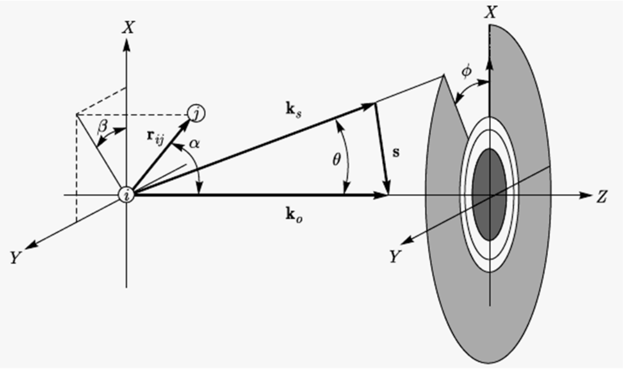

Fig. 1. Definition of scattering coordinates used for the development of intensity equations in electron diffraction. Θ is the scattering angle and φ the azimuthal angle in the detector plane; $\mathbf{k}_0$ and $\mathbf{k}_s$ are the wave vectors of the incident and scattered electrons, respectively; s is the momentum transfer vector; $\mathbf{r}_{ij}$ is the internuclear distance vector between the nuclei of atoms i and j, which are positioned at $\mathbf{r}_i$ and $\mathbf{r}_j$, respectively; and α_{ij} and β_{ij} give the orientation of the molecular framework with respect to the XYZ laboratory frame

Рис. 1. Система координат, используемая при выводе уравнений, описывающих интенсивность рассеяния электронов. Θ – угол рассеяния, φ – азимутальный угол в плоскости детектора; $\mathbf{k}_0$ и $\mathbf{k}_s$ – волновые векторы падающего и рассеянного электронов, соответственно; s – вектор передачи импульса; $\mathbf{r}_{ij}$ - вектор межъядерного расстояния; α_{ij} и β_{ij} – углы в сферической системе координат, которая определяет ориентацию вектора межъядерного расстояния в координатах рассеяния

For spatially isotropic ensemble of randomly oriented molecules $P_{sp}(\alpha_{ij},\beta_{ij}) = 1/4\pi$. The equation (1) becomes:

$$I_{mol}(s,t) = (I_0/R^2)\sum\sum_{i\neq j=1,N}|f_i(s)||f_j(s)|\cos(\Delta\eta_{ij}(s))\times$$
$$\times\int P_{vib}(r_{ij},t)[\sin(sr_{ij})/sr_{ij}]dr_{ij} \qquad (2)$$

Time-dependent functions $P_{sp}(\alpha_{ij},\beta_{ij},t)$ and $P_{vib}(r_{ij},t)$ in Eq. (1) determine the molecular scattering intensity at time t. The first function determines the evolution of the spatial distribution. Vibrational probability density function describes the structural dynamics in the ensemble of laser-excited particles. Orientational probability density function for an ensemble of laser-excited molecules is described in several publications [22-24]. A systematic study was carried out by Zare [23]. In this study there were obtained equations in classical and quantum mechanical approximations. For spatial anisotropy produced via plane-polarized laser beam, both approximations yield similar results.

While Eq. (1) is general enough for description of polyatomic molecules we first consider the case of linear polyatomic molecules. For electron scattering on oriented linear molecules we need to consider two main cases: scattering from molecules oriented parallel to the primary electron beam, which will be called the *parallel scattering* and scattering from molecules oriented perpendicular to the incident electron beam, which we call *perpendicular scattering*. In the first case, $P_{sp}(\alpha,\beta;t)$ depends only on angle α (Fig. 1), since the polarization of the laser beam is collinear to axis Z. Laser radiation at the initial time t=0 separates the excited and unexcited molecules ensembles. In this case, the PDF can be written as [22, 23]:

$$\|P_{sp}^{ex}(\alpha) = (3/4\pi)\cos^2\alpha \qquad (3)$$
$$\|P_{sp}^{unex}(\alpha) = (3/8\pi)\sin^2\alpha, \qquad (4)$$

where $\|P_{sp}^{ex}$ and $\|P_{sp}^{unex}$ refer to the excited and unexcited ensembles, respectively.

For perpendicular scattering, the polarization vector of the laser beam is perpendicular to the Z axis and the PDF is dependent on the angle α, and the angle β:

$$^{\perp}P_{sp}^{ex}(\alpha,\beta) = (3/4\pi)\ \sin^2\alpha\cos^2\beta \qquad (5)$$
$$^{\perp}P_{sp}^{unex}(\alpha,\beta) = (3/8\pi)\ [1 - \sin^2\alpha\cos^2\beta] \qquad (6)$$

The scalar product $(\mathbf{sr}_{ij})$ in Equation (1) can be written in terms of trigonometric functions of angles α and β, which determine the orientation of the vector $\mathbf{r}_{ij}$ in coordinates of scattering angles θ and ϕ, which describe electron scattering:

$$(sr_{ij}) = [-\cos\phi\cos(\theta/2)\sin\alpha\cos\beta-\sin\phi\cos(\theta/2)\sin\alpha\sin\phi+$$
$$+\sin(\theta/2)\cos\alpha]srij \qquad (7)$$

Using the Eq. (1) and PDF (Eq. 3-6), after integration by α and β [25, 26] we obtain the intensities for parallel molecular scattering of electrons:

$$\|I_{mol}^{ex}(s,t)=(I_0/R^2)\sum\sum_{i\neq j=1,N}|f_i(s)||f_j(s)|\cos(\Delta\eta_{ij}(s))\times$$
$$\times\int P_{vib}(r_{ij},t)\{[\sin(sr_{ij})/sr_{ij}][(1/s^2r_{ij}^2)(1-3s^2/4k_0^2)+s^2/4k_0^2]-$$
$$-[\cos(sr_{ij})/s^2r_{ij}^2](1-3s^2/4k_0^2)\}dr_{ij} \qquad (8)$$
$$\|I_{mol}^{unex}(s,t)=(I_0/R^2)\sum\sum_{i\neq j=1,N}|f_i(s)||f_j(s)|\cos(\Delta\eta_{ij}(s))\times$$
$$\times\int P_{vib}(r_{ij},t)\{[\sin(sr_{ij})/sr_{ij}]\times(1-s^2/4k_0^2)-[\cos(sr_{ij})-$$
$$-\sin(sr_{ij})/sr_{ij}](1/s^2r_{ij}^2)(1-3s^2/4k_0^2)\}dr_{ij} \qquad (9)$$

As can be seen from Eq. (8, 9), the dependence on the wavelength of electrons ($k_0 = 2\pi/\lambda$) is weak for electrons with energies greater than 10 keV in the whole range of typical values of s. Moreover, just as in the case of isotropically oriented molecules, scattering intensity is axially symmetric and depends only on the scattering angle θ.

In contrast to this result, the intensity of perpendicular molecular scattering is not axially symmetric and explicitly depends on the azimuthal angle ϕ:

$$^{\perp}I_{mol}^{ex}(s,\phi,t)=(I_0/R^2)\sum\sum_{i\neq j=1,N}|f_i(s)||f_j(s)|\cos(\Delta\eta_{ij}(s))\times$$
$$\times\int P_{vib}(r_{ij},t)\{[\sin(sr_{ij})/(sr_{ij})-\cos(sr_{ij})](1/sr_{ij})^2-(1-s^2/4k_0^2)\times$$
$$\times[(3/s^3r_{ij}^3-1/sr_{ij})\sin(sr_{ij})-(3/s^2r_{ij}^2)\cos(sr_{ij})]\cos^2\phi\}dr_{ij} \quad (10)$$

$$^{\perp}I_{mol}^{unex}(s,\phi,t)=(I_0/R^2)\sum\sum_{i\neq j=1,N}|f_i(s)||f_j(s)|\cos(\Delta\eta_{ij}(s))\times$$
$$\times\int P_{vib}(r_{ij},t)\{[\sin(sr_{ij})/(sr_{ij})][1-(1-s^2/4k_0^2)\cos^2\phi]+$$
$$+[\cos(sr_{ij})-\sin(sr_{ij})/(sr_{ij})](1/sr_{ij})^2[1-(1-$$
$$-s^2/4k_0^2)3\cos^2\phi]\}dr_{ij} \quad (11)$$

For derivation of those equations, each PDR (Eq. 3-6) was normalized. Therefore, $I_{mol}(s,t)$ represented by Eq. (8-11) are also normilized. In the ensemble of excited and unexcited particles there must be introduced corresponding relative weights of these states [13]. The Eq. (8-11) require explicit equations for $P_{vib}(r_{ij},t)$, which can be represented by, for example, on the basis of the stochastic approach proposed in the paper [13].

For accounting for quantum effects in the diffraction intensitys it is required to define time-dependent PDFs, $P(r,t) = |\psi(r,t)|^2$ by solving corresponding time-dependent Schrödinger equation. Various approaches for solving this problem were suggested [27-29]. In an article of [13] suggested utilizing FGH (Fourier Grid Hamiltonian) method [29-32].

2. MODELING THE COHERENT DISSOCIATION DYNAMICS OF LASER-ALIGNED ICN MOLECULAR ENSEMBLES

The schematic experimental layout for TRED study of aligned molecules is presented in Fig. 2. A linearly polarized laser pulse (ε) excites molecules in the gas phase and the sample is diagnosed by an electron pulse generated with a given delay time. The laser and electron beams intersect at 90°. The electron pulse scattered from the sample is a bunch of electrons; its longitudinal extent is vΔt, where v is the electron velocity, and Δt is the pulse length.

The pulse (electron bunch) leaving the scattering volume makes up the central core of unscattered electrons surrounded by the expanding cloud of scattered electrons of varying intensity, shown in the figure in the form of rings. The electron diffraction pattern is taken far from the scattering center in a relatively small region of scattering angles on a flat detector, the center of which coincides with the incident beam axis. Each point on the detector is characterized by scattering angle θ and azimuthal angle ϕ, corresponding to the wave vector **k** and the momentum variation vector **s**. The ra-

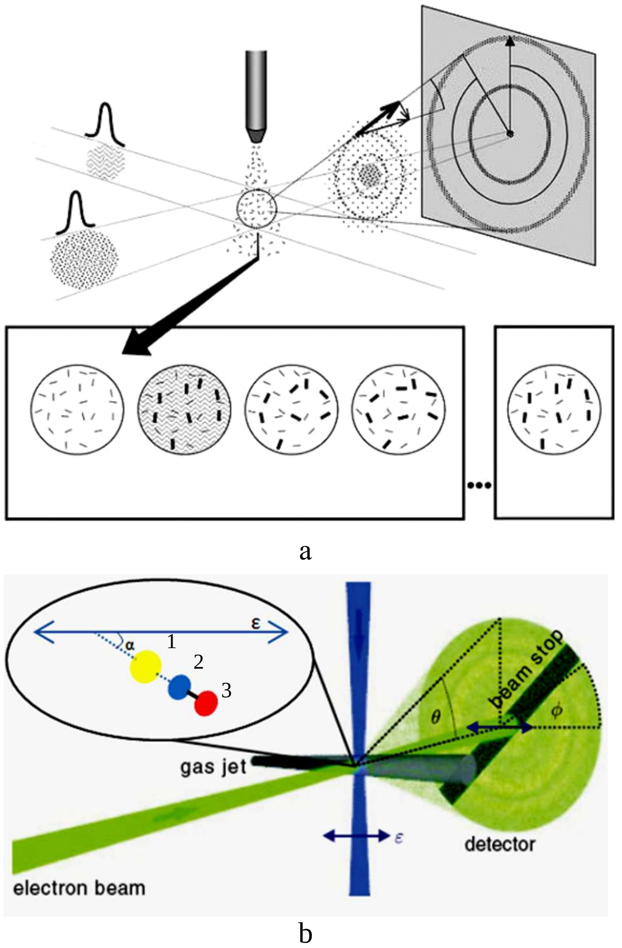

Fig. 2. (a) Schematic layout of the TRED experiment designed to study anisotropic ensembles of laser-excited molecules. The inset schematically presents the temporal sequence of dipole transitions in sample molecules in the TRED scattering volume. At t = 0, a vertically polarized laser pulse traverses the volume and creates a population of excited states composed of molecules with dipole transitions oriented largely in the vertical direction (dark lines). (b) Schematic diagram of the experimental setup: electron beam, laser and molecular beam are orthogonal to each other. θ - scattering angle and φ - azimuthal angle in the plane of the detector relative to the polarization of the laser radiation. ε - the polarization vector of the laser light (blue arrow); α - the angle between the bond C-I (dissociation axis) and the polarization of the laser radiation. The atoms in a molecule ICN: I-1, C- 2, N – 3

Рис. 2. (а) Схема TRED-эксперимента для исследования анизотропных ансамблей лазеро-возбужденных молекул. Показано схематичное представление временного ряда дипольных переходов молекул образца в рассеивающем объеме установки TRED. При t = 0 импульс лазера, имеющий вертикальную поляризацию, пересекает объем, создавая определенную заселенность возбужденных состояний, состоящую из молекул, имеющих дипольные переходы, преимущественно ориентированные в вертикальном направлении (темные линии). (в) Геометрия эксперимента: электронный пучок, лазерное излучение и молекулярный пучок ортогональны. θ – угол рассеяния, φ – азимутальный угол в плоскости детектора относительно поляризации лазерного излучения. ε – вектор поляризации лазерного излучения (голубая стрелка); α – угол между направлением связи C-I (ось диссоциации) и поляризации лазерного излучения. Атомы в молекуле ICN: I – 1, C – 2, N – 3 dial distance between the registration point and the center of the unscattered beam denoted by s' is presented in the figure as the expression through quantities **s** and **k**; the camera distance between the scattering point and the center of the diffraction pattern on the detector is denoted by L.

Rotation of excited and unexcited molecules with different angular velocities causes dephasing of oriented molecules and the loss of the initial order. The order can be restored on significantly longer time intervals for the wave packet rotational revival.

To illustrate the basic effects arising in the scattering time-dependent intensities and their corresponding Fourier transforms (the radial distribution functions of the inter-atomic distances), we will focus on the linear triatomic molecules (A-B-C), in which the action of a laser pulse breaks the bond A-B. In many cases, the potential function for such systems can be expressed as [33]:

$$V(R, r) = V_0 \exp[-(R - \gamma r)/\rho], \qquad (12)$$

where R – the distance between the nucleus A and the center of mass of the fragment B-C in the molecule A-B-C; $r = r_0(BC) - r_e(BC)$; $\gamma = m_C/(m_B + m_C)$; $r_0(BC)$ and $r_e(BC)$ – internuclear distance in the ground vibrational state and the equilibrium internuclear distance of the fragment B-C, respectively; ρ – a so-called range parameter [33, 34]. The reactions and APES of this kind are well known for a number of the systems [33-35]. In the first stage of the analysis, it has been shown the manifestation of the nuclear dynamics in the scattering of the ultrashort pulses of the fast electrons by the systems that dissociate in accordance with the adiabatic potential functions.

The ground state of the ICN molecule is approximated by a Morse function with the parameters: $a_M = 190$ pm^{-1}, R_e(iodine to center-of mass distance) = 261.7 pm, D_e = 26340 cm^{-1}. The dissociative state is selected from several that are possible, and obeys Eqn. (12), with the parameters V_0 = 242720 cm^{-1}, R_0 = 262.2 pm and ρ = 80 pm, as given in refs. [35, 36].

The photodissotiation of ICN has been studied extensively both by experimental and theoretical methods, including femtosecond transient state spectroscopy (please, see ref. [37] and references therein).

The dissociation of ICN (210 < λ< 350 nm) proceeds via two channels [37, 38]:

$$ICN \rightarrow I(^2P_{3/2}) + CN(X^2\Sigma^1) \qquad (13)$$

$$ICN \rightarrow I(^2P_{1/2}) + CN(X^2\Sigma^1), \qquad (14)$$

producing the CN radicals predominantly in the ground electronic state $X^2\ \Sigma^1$, and the iodine atoms in the $^2P_{3/2}$ and $^2P_{1/2}$ states. The vibrational distribution of the CN fragment of the ICN molecule was measured [39] and at 266 nm it was found that vibrational population ratios, $n(v = 1)/n(v = 0) = 0.012$; $n(v = 2)/n(v = 0) = 6\cdot10^{-4}$; $n(v = 3)/n(v = 0) = 1\cdot10^{-4}$.

In the 266 nm photolysis, the experiment [39] determined rotational distribution of the radicals can be presented as a sum of three B_0 main distributions centered at the rotational temperatures T_1 = 37(3) K, T_2 = =489(12) K and T_3 = 6134(250) K, with approximately equal in grated fractional populations.

Rotational excitation of the CN fragments requires an additional term in the potential function, Eqn. (12), and can be approximated in diffraction intensities by including the centrifugal distortion Δr of the r(CN) internuclear distance in a relatively long time range. However, considering time scale of the dissociation, the evolution of the angular momentum can be neglected.

In a series of studies (please, see, e.g., ref. [37] and references cited therein) it was shown that, at the wavelength of 306 nm, the dissociation channel leading to the iodine excited state $I(^2P_{1/2})$ is effectively closed. Thus, based on the experimental studies described in ref. [37], in our model calculations the dissociation of the ICN was assumed to proceed via a stretching reaction coordinate, and the parameters of ref. [37] for the dissociative potential leading to $I(^2P_{3/2})$ were used (Eq. 13). The molecular electron diffraction intensities, sM(s), for the molecule in their ground state were calculated with the parameters of refs. [13] and [36] using standard computational procedures [40].

One approach that can be used to describe the dynamics of the excited molecules is an approximation of the wave packet [41-44]. The wave packet carries the information on the relative positions and nuclear momenta, as well as their components at different APES, corresponding to different electron states [42, 43]. For the wave function with minimal uncertainty Gaussian function can be used as the basis for the creation of the wave functions of the system, as it was proposed in refs. [43-45]; please, see also [42]). Considering the classical trajectory in the phase space, where the Hamiltonian in the vicinity of the moving point $\{p(t); R(t)\}$ can be expressed in terms of the degrees of $(p - \langle p(t)\rangle)$ and $(R - \langle R(t)\rangle)$ up to the second order, the wave function is defined as follows [43]:

$$\psi(r,t) = \exp\{(2\pi i/h)[\alpha(t)(R-\langle R(t)\rangle)^2 + \\ + \langle p(t)\rangle(R-\langle R(t)\rangle) + \gamma(t)]\}, \qquad (15)$$

where $\alpha(t)$ gives the spreading of the wave packet, $\gamma(t)$ – its complex phase, and $\langle ...\rangle$ – is the expected value. Using the time-dependent Schrödinger equation, we can obtain the differential equations for the position and the momentum:

$$\partial\langle R(t)\rangle/\partial t = \langle p(t)\rangle/m \text{ and } \partial\langle p(t)\rangle/\partial t = -\langle\partial V(R)/\partial R\rangle, \quad (16)$$

where $V(R)$ – the potential in the Born-Oppenheimer approximation. The Eq. (16) describe the trajectory of the wave packet. For large temporal delays after the excitation of the studied molecules and the use of longer probing electron pulses it should be considered the increase of the width (the spreading) of the wave packet, which manifests in the diffraction pattern. In this case, the probability density of the inter-atomic distances in the ensemble of the dissociated molecules can be represented as follows:

$$P(R, t) = [2\pi\sigma^2(t)]^{-1/2}\exp\{-[R-R(t)]^2/2\sigma^2(t)\}, \quad (17)$$

where $\sigma(t = 0)$ – the dispersion of the wave packet at the initial time of the laser excitation, and $R(t)$ – the classical trajectory of the center of gravity of the wave packet. Consequently, the dispersion of the propagating wave packet can be expressed as a linear function of time during its free motion:

$$\sigma(t) = \sigma(0)[1 + h^2t^2/16\pi^2m^2\sigma^4(0)]^{1/2}. \quad (18)$$

If the pulse laser pump has a form of δ-function at $t = 0$, the temporal dependence of the molecular intensity will be:

$$sM(s, t) = g(s) \int(\sin (sR)/R)P(R, t)dR. \quad (19)$$

When the form of the probing electron pulse is approximated by the Gaussian function with the central point $t = t_0$ and corresponding duration of τ, the averaged molecular intensities can be written as:

$$\langle sM(s,t)\rangle_\tau = (2\pi\tau^2)^{-½}\int\exp[-(t-t_o)^2/2\tau^2]sM(s,t)dt \quad (20)$$

Using the above theory, it were calculated the time-dependent intensities of the molecular scattering and the corresponding radial distributions of the internuclear distances during the processes of the photodissociation of ICN, Fig. 3 (please, see ref. [45] for comparison of the results).

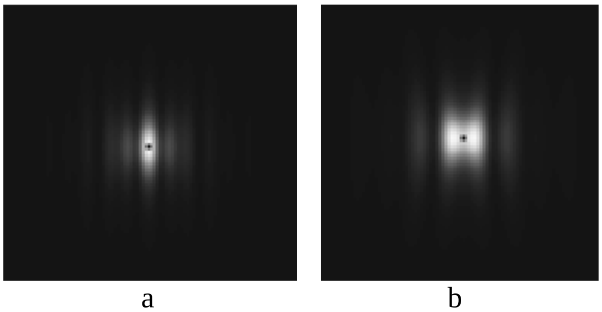

Fig.3. Molecular scattering intensities sM(s,ϕ) of isotropic (···ISO) and anisotropic vibrationally excited non-equilibrium molecular ensembles of ICN molecules for angles ϕ= 0 (a), and 45° (b). Linear polarization of laser radiation is directed along the axis X (perpendicular scattering). The figures were obtained using the algorithm described in [46]

Рис. 3. Молекулярные интенсивности рассеяния sM(s,ϕ) изотропного (···ISO) и анизотропного колебательно возбужденных молекулярных ансамблей ICN для углов ϕ= 0 (a), and 45° (b). Линейная поляризация лазерного излучения направлена вдоль оси X (перпендикулярное рассеяние). Рисунки получены с использованием алгоритма, описанного в работе [46]

Comparison of the diffraction intensities for parallel and perpendicular scattering (Eq. (8) and (10)) shows differences (Fig. 3) in the angular dependence of the molecular intensities. The intensity pattern of the latter is no longer axially symmetric, the essential features can still be recorded with a linear detector system, such as CCD camera. This is because all angular effects at the detector can be measured by rotating the plane of polarization of the laser light. The vibrational p.d.f. is rather flexible for use in studies of different types of vibrational distributions in laser-excited molecules [11, 13]. It can be used in analyses of TRED data by refining the parameters that define $P_{vib}(r, t)$, directly from the experimental data. However, it cannot be applied to dissociative processes, because the cumulant expansion does not converge in such cases.

Correlations between wave packet dynamics and the modes of laser excitation are important for spectroscopic investigations, but not for electron scattering. Thus, they were not taken into account in the current modeling calculations. Some representative results for ICN obtained in this way are given in Fig. 4.

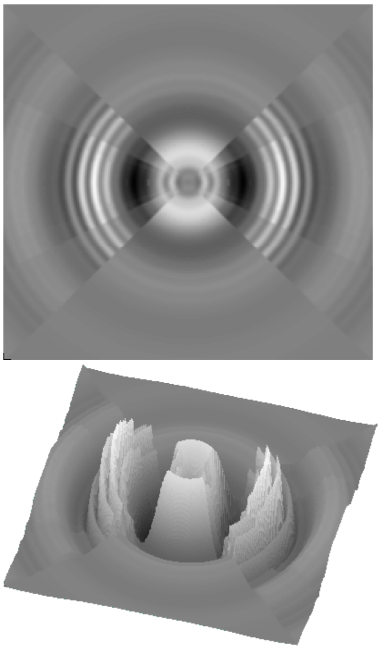

Fig. 4. Diffraction pattern simulated according to Eq. (11). The following experimental parameters were used: the distance between the nozzle and the recording material is l = 478 mm, probe time is t = 200 fs and the probe pulse duration is τ = 25 fs

Рис. 4. Электронограмма, смоделированная по уравнению (11). Параметры эксперимента: Расстояние сопло-регистрирующий материал l=478 мм, t=200 фс и время импульса электронного пучка τ=25 фс

The speed of propagation of the ICN wave packet is faster in the current calculations than in those reported previously [11]. This is so because the speed of propagation of the center of gravity of the wave packet in the calculations of ref. [11] depends on the asymptotic group velocity $v = (2E/m)^{1/2}$, which in turn depends on the available energy E. The present calculations refer to slightly higher available energy values.

The good agreement between the two sets of results – those based on quantum dynamical calculations and those based on the Gaussian wave packet approximation [11, 13] is an important finding because the latter represent a more straightforward and convenient method for analysing TRED data in terms of a limited number of adjustable parameters which can be refined more readily from the experimental data.

CONCLUSIONS

By providing intensity expressions for spatially anisotropic ensembles, the current study is a continuation of our efforts [11, 13, 21] to create a theoretical base for analysing TRED data. The time-dependent molecular intensity equations for spatially anisotropic ensembles have been derived to study the coherent nuclear dynamics of laser excited species.

The study also shows that TRED intensities can be readily calculated for dissociative processes, provided the APES is known. Because of this correlation, if the TRED intensities are expressed directly in terms of the APES, solution of the inverse problem seems feasible, which provide information on coherent structural dynamics of the transient state of the chemical reaction from TRED data.

Based on model calculations presented in this article we conclude that, by TRED method, time-dependent coherent dissociation dynamics can in principle be resolved at a realistic time scale that significantly shorter than the electron pulse duration of 300 fs, which is achieved at present in a number of TRED experiments.

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