*Quantum Electronics* **36** (10) 984 – 988 (2006)

PACS numbers: 33.15.Mt; 33.55. –b; 42.65.Re
DOI: 10.1070/QE2006v036n10ABEH013226

# Study of the subpicosecond rotational molecular dynamics in liquids

V.G. Nikiforov, V.S. Lobkov

***Abstract*. The parameters of the femtosecond vibration – rotation molecular dynamics of liquid acetonitrile $CH_3CN$, trimethylacetonitrile $(CH_3)_3CCN$, propionitrile $CH_3CH_2CN$, fluoroform $CHF_3$, and chloroform $CHCl_3$ are found by analysing the ultrafast optical Kerr effect. The influence of the molecular structure on the features of rotational (diffusion and libration) motions is studied. It is shown that the distribution of libration frequencies is described by the Maxwell distribution.**

***Keywords***: *vibration – rotation molecular dynamics in liquids, ultrafast optical Kerr effect, intermolecular interactions.*

## 1. Introduction

The nature of chemical reactions in liquids [1] is considerably determined by femtosecond and picosecond intermolecular interactions [2]. For example, in the process of matrix biosynthesis these interactions are extremely complicated and, therefore, the investigations of molecular motions of simple model systems such as acetonitrile [3] or chloroform [4] are of current interest. These studies are required for a better understanding of the more complex vibration – rotation dynamics of biological molecules, which are currently being actively investigated by the methods of ultrafast optical spectroscopy [5 – 7].

Femtosecond molecular motions can be observed by the methods of optical polarisation spectroscopy based on the optical Kerr effect [8, 9] with the use of optical heterodyning [10 – 14]. The Kerr signal appears due to the nonlinear cubic response of a medium [15 – 18], which contains low-frequency vibration – rotation responses of molecules excited by laser pulses of duration 10 – 100 fs. Together with responses of intramolecular vibrations and rotational diffusion, the responses from collective molecular motions are also detected [19 – 23]. These motions occur in local potential wells due to the interaction of molecules with their nearest environment [24]. They represent libration (rotational) vibrations near the equilibrium position and occur for the time $10^{-10} - 10^{-12}$ s between rotational diffusion hops. Coherent librations form a response in the Kerr signal with the relaxation time less than 1 ps [8, 25].

The theoretical interpretation of the Kerr signal is based on the detailed analysis of the optical nonlinear cubic response of a medium. This problem is complicated and the detailed quantum-mechanical description of the molecular dynamics in liquids [16 – 18] is not always possible. Because of this, experimental results are often simulated by using simple phenomenological approaches. The libration response is described, as a rule, by the harmonic oscillator model [25 – 28] assuming fast fluctuations simulated by friction in the system. However, such an approach cannot be used to analyse correctly the libration response. This is explained by the fact that fluctuations produced by the nearest environment cannot occur much faster than intramolecular vibrations with a period of tens or hundreds of femtoseconds, which is comparable with the relaxation time of the libration response. For example, the irreversible relaxation time of liquid carbon disulfide ($CS_2$) obtained from the Kerr signal [25, 27, 29] is an order of magnitude lower than the libration period, which is probably inconsistent with real physical mechanisms of molecular motions.

We described the libration response in the Kerr signal by the method in which relaxation was simulated by the dephasing of coherent librations [30]. Different libration motions appear due to the local inhomogeneity of a liquid and are taken into account by the distribution function of libration frequencies. This allows one to describe the response without using additional irreversible relaxation constants. We use this approach here to analyse Kerr signals in liquid acetonitrile ($CH_3CN$), trimethylacetonitrile [$(CH_3)_3CCN$], and propionitrile ($CH_3CH_2CN$). These molecules were chosen because they have similar atomic groups and at the same time strongly differ in their spatial structure. We also analysed the ultrafast motions of fluoroform ($CHF_3$) and chloroform ($CHCl_3$) molecules, which were studied experimentally in [4]. These molecules and the $(CH_3)_3CCN$ molecule have similar spatial structures but strongly differ in atomic groups. By analysing theoretically the Kerr signal in these liquids, we found the distribution of libration frequencies and determined the influence of the spatial structure of molecules and intermolecular interactions on the type of femtosecond rotational (diffusion and libration) motions.

## 2. The theory

In Kerr experiments [8 – 11], two-pulse excitation of the medium was used. The first, pump pulse $E_p$ induces the transient anisotropic polarisability in a liquid, which is then probed by a weak probe pulse $E_0$ delayed by the time $\tau$. The direction of polarisation of the probe pulse $E_0$ makes an angle 45° with the direction of polarisation of the pump

---

**V.G. Nikiforov, V.S. Lobkov** E.K. Zavoisky Kazan Physical-Technical Institute, Kazan Scientific Center, Russian Academy of Sciences, ul. Sibirskii trakt 10/7, 420029 Kazan, Russia;
e-mail: vgnik@mail.ru, lobkov@kfti.knc.ru

Received 16 May 2006
*Kvantovaya Elektronika* **36** (10) 984 – 988 (2006)
Translated by M.N. Sapozhnikov

field (Fig. 1). The angle $\theta$ in Fig. 1 is the angle between the selected molecular axis (in our case, this is the $y$ axis in the molecular coordinate system) and the direction of polarisation of the pump pulse. The optical frequency $\omega_0$ of both pulses lies within the transparency region of a sample. The useful signal was amplified by using optical heterodyning. For this purpose, the probe pulse field was mixed with the field $E_{\mathrm{loc}}$ of the local oscillator [13, 14], whose polarisation is orthogonal to the polarisation of the probe field $E_0$ and the phase is shifted by 90°. We describe the temporal profile of the amplitude of the light field of pulses of duration $\tau_{\mathrm{las}}$ by a Gaussian $E_{\mathrm{p}}(t) \propto E_0(t) \propto E_{\mathrm{loc}}(t) \propto \exp(-t^2/2\tau_{\mathrm{las}}^2)$. The response of the medium is described by using the polarisability tensor of a molecule in the molecular coordinate system $\alpha_{xx} = \alpha_{zz} = \alpha_{\perp}$, $\alpha_{yy} = \alpha_{\parallel}$; the other components are zero. It is convenient for calculations to represent the degree of anisotropy of the polarisability of a molecule in the form $\alpha_{\parallel}(t) - \alpha_{\perp}(t) \equiv \Delta\alpha + \delta\alpha(t)$, where the term $\delta\alpha(t)$ reflects the influence of nuclear coordinates. In this case, the signal $S(\tau)$ detected in the experiment can be written in the form [30–32]

$$S(\tau) = \frac{1}{T}\lim_{T\to\infty}\int_{-T/2}^{T/2} s(\tau, t)\,\mathrm{d}t, \qquad (1)$$

where $T$ is the observation time interval;

$$s(\tau, t) \propto E_{\mathrm{loc}}(t-\tau)E_0(t-\tau)$$

$$\times \int_0^{\pi}\int_0^{2\pi}[R_{\mathrm{m}}(\theta, t) + R_{\mathrm{el}}(t)]\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi \qquad (2)$$

is the instant value of the detected signal;

$$R_{\mathrm{el}}(t) \propto \gamma I_{\mathrm{p}}(t); \qquad (3)$$

$$R_{\mathrm{m}}(\theta, t) \propto [\Delta\alpha + \delta\alpha(t)]\left(\cos^2\theta - \frac{1}{3}\right); \qquad (4)$$

$I_{\mathrm{p}}(t)$ is the pump-pulse intensity; the function $R_{\mathrm{el}}(t)$ is proportional to the coefficient of the 'instant' electronic cubic hyperpolarisability $\gamma$; and the molecular response function $R_{\mathrm{m}}(\theta, t)$ is proportional to the degree of anisotropy of the polarisability of a molecule.

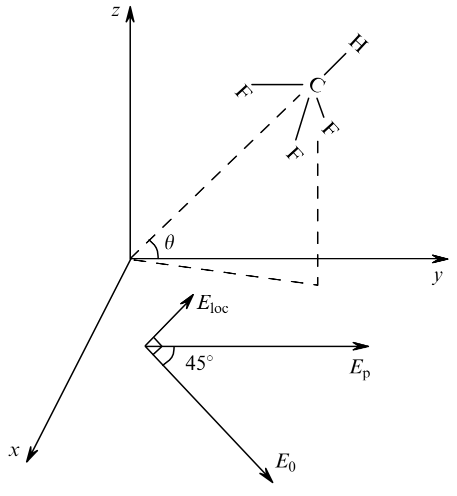

**Figure 1.** Orientation of a molecule and directions of polarisation of the pump pulse $E_{\mathrm{p}}$, probe pulse $E_0$, and local oscillator field $E_{\mathrm{loc}}$.

Molecular motions are usually described by neglecting a weak correlation between rotational and intramolecular vibrations [11]. This makes it possible to assume that the intramolecular response is $R_n(\theta_0, t) = \langle R_{\mathrm{m}}(t)|_{\theta(t)\approx\theta_0}\rangle_{\theta_0}$, where $\theta_0$ is the angle corresponding to the equilibrium position of a molecule in the local potential; the angle brackets $\langle ...\rangle_{\theta_0}$ denote averaging over molecular orientations. The influence of intramolecular vibrations on the nonequilibrium polarisability $\delta\alpha(\theta_0, t)$ is described by the normal vibrational coordinates $q_i(\theta_0, t)$ of a molecule

$$\delta\alpha(\theta_0, t) = \sum_{i=1}^{N}\alpha_i^1 q_i(\theta_0, t), \qquad (5)$$

where $\alpha_i^1$ is the coefficient characterising the degree of polarisability of a molecule for the $i$th vibrational mode and $N$ is the number of vibrational modes. The solution for the vibrational coordinates $q_i(\theta_0, t)$ can be written in the form [33]

$$q_i(\theta_0, t) = \frac{\alpha_i^1}{2m_i}\cos(\theta_0)\Phi_n(\Omega_{ni}, \tau_{ni}, t), \qquad (6)$$

$$\Phi_n(\Omega_n, \tau_n, t) = (\Omega_n^2 - \tau_n^{-2})^{-1/2}$$

$$\times \int_0^{\infty} I_{\mathrm{p}}(t-t')\exp\left(-\frac{t'}{\tau_n}\right)\sin[(\Omega_n^2 - \tau_n^{-2})^{1/2}t']\,\mathrm{d}t', \qquad (7)$$

where $m_i$ is the reduced mass of the $i$th oscillator; $\Omega_n$ and $\tau_n$ are the vibrational frequency and the relaxation time of the $n$th mode. After averaging over the equilibrium angles $\theta_0$, we obtain the total intramolecular response

$$R_n(t) \propto \sum_{i=1}^{N}(\alpha_i^1)^2\Phi_n(\Omega_{ni}, \tau_{ni}, t). \qquad (8)$$

The pump pulse excites most efficiently the Raman-active vibrational modes with period that is larger than or comparable with the pulse duration. For example, low-frequency vibrations of a benzene ring conjugated with groups of the type $-\mathrm{OH}$, $-\mathrm{CH_3}$, $-\mathrm{Cl}$ etc. can be observed for pulse durations ~ 100 fs [19, 31].

Rotational motions are excited when the polarisability of a molecule is anisotropic ($\Delta\alpha \neq 0$). Taking into account a weak correlation between individual molecular motions, we will assume that the diffusion response is

$$R_{\mathrm{d}}(t) = \left\langle R_{\mathrm{m}}(t)\Big|_{|\delta\alpha| \ll |\Delta\alpha|}\right\rangle_{\theta_0} = \Delta\alpha\left\langle\frac{3}{2}\left[\cos^2(\theta_0(t)) - \frac{1}{3}\right]\right\rangle_{\theta_0}.$$

The solution for the diffusion response has the form [12, 31, 34]

$$R_{\mathrm{d}}(t) \propto (\Delta\alpha)^2 D\int_{-\infty}^{t}\eta(t')\exp\left(\frac{t'-t}{\tau_{\mathrm{d}}}\right)\mathrm{d}t', \qquad (9)$$

where $\eta(t) = I_{\mathrm{p}}(t)/kT$; $k$ is the Boltzmann constant; $T$ is temperature; $D = 1/(6\tau_{\mathrm{d}})$ is the diffusion coefficient; and $\tau_{\mathrm{d}}$ is the relaxation time of the diffusion response. The characteristic relaxation times $\tau_{\mathrm{d}}$ vary from several picoseconds for simple molecules of the carbon disulfide type [8] to several tens of picoseconds for molecules of the type of acetophenone and its derivatives [19]. The rotational-diffusion response $R_{\mathrm{d}}(t)$ is a curve exponentially decaying immediately after the end of the pump pulse.

The libration response is described by using the distribution function $\rho(\Omega_{\text{lib}})$ of libration frequencies. By neglecting the role of spectral diffusion and taking into account that the amplitude of libration oscillations is small, the libration response can be written in the form [30]

$$R_{\text{lib}}(t) \propto (\Delta\alpha)^2 \int_0^\infty d\Omega_{\text{lib}} \rho(\Omega_{\text{lib}}) \Phi_{\text{lib}}(\Omega_{\text{lib}}, t), \qquad (10)$$

where

$$\Phi_{\text{lib}}(\Omega_{\text{lib}}, t) = \Omega_{\text{lib}}^{-1} \int_0^\infty I_{\text{p}}(t - t') \sin(\Omega_{\text{lib}} t') dt'. \qquad (11)$$

According to expression (10), the libration response depends on the distribution function $\rho(\Omega_{\text{lib}})$ of libration frequencies, which can be found by solving the inverse problem in the analysis of Kerr signals. Below, we analyse in this way Kerr signals from liquids selected for the study.

## 3. Experiment and simulation of libration motions

Liquid $CH_3CN$, $(CH_3)_3CCN$, and $CH_3CH_2CN$ were studied at room temperature ($298 \pm 1$ K) by using an Avesta Ti : sapphire laser pumped by a 7-W LGN-512 laser. The average energy of a 70–80-fs pulse at 800 nm was $5 \times 10^{-9}$ J. The laser beam was split in a beamsplitter into probe pulses (10 % of power) propagating through an optical delay line and pump pulses (90 % of power). The signal-to-noise ratio was improved by using optical heterodyning; a signal from the local oscillator field and related noise were rejected by means of a lock-in detector with the modulation frequency $\sim 300$ Hz [31]. The experimental data for liquid $CHF_3$ and $CHCl_3$ were taken from paper [4] where the same pump–probe method with 24-fs pulse was used.

The experimental data and the results of their simulation are presented in Fig. 2 and the parameters of simulation of the ultrafast molecular dynamics are presented in Table 1.

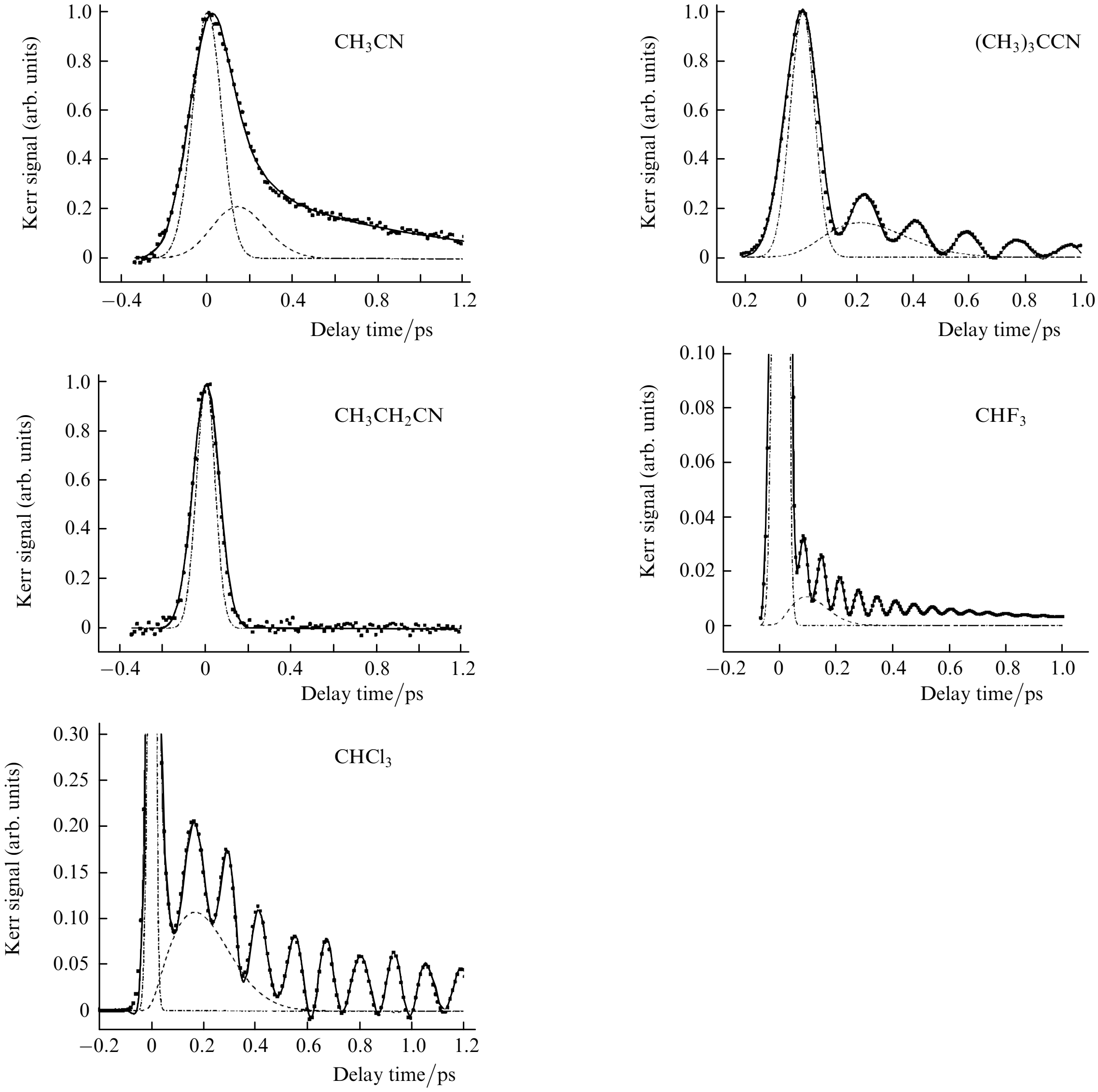

**Figure 2.** Kerr signals for pure liquids: acetonitrile ($CH_3CN$), trimethylacetonitrile [$(CH_3)_3CCN$], propionitrile ($CH_3CH_2CN$), fluoroform ($CHF_3$), and chloroform ($CHCl_3$). Points: Kerr signal; solid curve: Kerr signal simulation; dot-and-dash curve: pump-pulse envelope; dashed curve: libration molecular response.

**Table 1.** Simulation parameters of the ultrafast molecular dynamics.

| Parameters | $CH_3CN$ | $(CH_3)_3CCN$ | $CH_3CH_2CN$ | $CHF_3$ | $CHCl_3$ |
|---|---|---|---|---|---|
| $J_{xx}/\ 10^{-20}$ g mol$^{-1}$ m$^2$ | 55 | 182 | 18 | 48 | 151 |
| $J_{yy}/10^{-20}$ g mol$^{-1}$ m$^2$ | 3 | 109 | 106 | 85 | 291 |
| $J_{zz}/10^{-20}$ g mol$^{-1}$ m$^2$ | 55 | 182 | 118 | 48 | 151 |
| $\Omega_{n1}/\mathrm{cm}^{-1}$ | – | $180.0 \pm 2.5$ | – | $512.0 \pm 2.6$ | $260 \pm 2.8$ |
| $\tau_{n1}/\mathrm{ps}$ | – | $0.65 \pm 0.07$ | – | $0.200 \pm 0.017$ | $1.38 \pm 18$ |
| $\Omega_{n2}/\mathrm{cm}^{-1}$ | – | – | – | – | $365 \pm 5$ |
| $\tau_{n2}/\mathrm{ps}$ | – | – | – | – | $1.1 \pm 0.3$ |
| $\tau_{\mathrm{d}}/\mathrm{ps}$ | $0.75 \pm 0.03$ | $0.52 \pm 0.10$ | – | $0.8 \pm 0.1$ | $1.2 \pm 0.2$ |
| $\Omega_{n\,\mathrm{lib}}/\mathrm{cm}^{-1}$ | $42.4 \pm 1.5$ | $28.1 \pm 2.7$ | – | $58.3 \pm 3.8$ | $31.8 \pm 2.6$ |

Note: components of the inertia moment tensors $J$ (and of polarisability tensors) are presented in the molecular coordinate system.

Our analysis has shown that the Kerr signal in liquid $CH_3CH_2CN$ appears only due to the electronic cubic hyperpolarisability and is the autocorrelation function caused by the term $R_{\mathrm{el}}$ in expression (2). The Kerr signal in liquid $CHF_3$ and $(CH_3)_3CCN$ contains the response of one intramolecular vibrational modes, and in $CHCl_3$ – of two such modes, which were described by using expression (8).

The vibrational molecular frequencies presented in Table 1 are in good agreement with the corresponding Raman frequencies: for $(CH_3)_3CCN$, we obtained $\Omega_{n1} = 183$ cm$^{-1}$; according to [35], the vibrational frequency for $CHF_3$ is $\Omega_{n1} = 508$ cm$^{-1}$, and for $CHCl_3$, $\Omega_{n1} = 266.5$ cm$^{-1}$ and $\Omega_{n2} = 364.8$ cm$^{-1}$. The long exponential decay of the rotational-diffusion response observed in liquid $CH_3CN$, $(CH_3)_3CCN$, $CHF_3$, and $CHCl_3$ can be described by expression (9). The libration response is typical for all liquids except $CH_3CH_2CN$. It has the inertial nature: the signal achieves a maximum within ~ 100 fs after the end of the pump pulse and then decays to zero for ~ 600 fs. The numerical solution of the inverse problem based on (10) gave the distribution function $\rho(\Omega_{\mathrm{lib}})$ of libration frequencies for these liquids. This function is well described by the Maxwell distribution

$$\rho(\Omega_{\mathrm{lib}}) \propto \Omega_{\mathrm{lib}}^2 \exp\left(-\frac{\Omega_{\mathrm{lib}}^2}{2\Omega_{n\,\mathrm{lib}}^2}\right), \qquad (12)$$

where $\Omega_{n\,\mathrm{lib}}$ is the width of the distribution function whose values for each of the liquids are presented in Table 1. It is important to note that the libration response was simulated without using additional irreversible relaxation constants. Thus, our analysis has shown that the libration response rapidly decays due to strong dephasing of molecules caused by a considerable scatter in vibrational frequencies. This suggests that dynamic fluctuations of libration motions at the scale of hundreds of femtoseconds do not affect noticeably the relaxation of the libration response, and can be estimated as $\delta\Omega_{\mathrm{lib}} \ll 1$ cm$^{-1}$.

## 4. Discussion of results

The theoretical analysis of Kerr signals observed in liquid acetonitrile ($CH_3CN$), trimethylacetonitrile [$(CH_3)_3CCN$], propionitrile ($CH_3CH_2CN$), fluoroform ($CHF_3$), and chloroform ($CHCl_3$) leads to the following conclusions about the rotational dynamics of these molecules at room temperature.

Note first of all that the Kerr signal for $CH_3CH_2CN$, unlike $CH_3CN$ and $(CH_3)_3CCN$ compounds of a similar structure, did not contain vibration–rotation responses, which is explained by the absence of low-frequency motions with period more than 50 fs in $CH_3CH_2CN$. We assume that the main reason is that individual fragments in the $CH_3CH_2CN$ structure are more mobile than in $CH_3CN$ and $(CH_3)_3CCN$ molecules. As a result, Raman-active vibration–rotation modes cannot be excited by 70-fs laser pulses.

We emphasise that the distribution functions $\rho(\Omega_{\mathrm{lib}})$ for $CH_3CN$, $(CH_3)_3CCN$, $CHF_3$, and $CHCl_3$ have the same form (12). The features of the libration dynamics are simulated by using the only parameter $\Omega_{n\,\mathrm{lib}}$ determining the width of the distribution function. Our study suggests that this type of the distribution function can be also typical for other liquids whose molecules contain a small number of atoms. Note also that because librations are related to the intermolecular interaction, the distribution function $\rho(\Omega_{\mathrm{lib}})$ should be sensitive to the thermodynamic parameters of a medium. This is confirmed by the recent study of the temperature dependence of the Kerr signal in liquid acetonitrile [3] in which the response of the fast component of the signal decreased by half with increasing temperature from 8 to 75 °C.

The parameters of the vibration–rotation molecular dynamics presented in Table 1 allow us to compare the parameters of local potentials in which molecules are located. We assume that the 'bottom' of local potentials, where librations mainly occur at room temperature, is parabolic: $U(\Delta\theta) = \mu(\Delta\theta)^2$ ($\mu$ is the parameter characterising the width of the potential well, $\Delta\theta$ is the deviation from the equilibrium orientation). The value of $\mu$ can be estimated from the libration frequency $\Omega_{n\,\mathrm{lib}}$ and the inertia moment of molecules $J_\perp = J_{xx} = J_{yy}$: $\mu = \frac{1}{2}(\Omega_{n\,\mathrm{lib}})^2 J_\perp$. The libration amplitude $\Delta\theta_{\max}$ can be found by assuming that $U(\Delta\theta_{\max}) = kT$. The estimates for $\mu$ and $\Delta\theta_{\max}$ for liquids under study are presented in Table 2.

**Table 2.** Estimates of the local potential parameter $\mu$ and libration amplitude $\Delta\theta_{\max}$.

| Parameters | $CH_3CN$ | $(CH_3)_3CCN$ | $CHF_3$ | $CHCl_3$ |
|---|---|---|---|---|
| $\mu/10^{-20}$ J deg$^{-2}$ | 2.9 | 4.3 | 4.8 | 4.5 |
| $\Delta\theta_{\max}/\mathrm{deg}$ | 20 | 17 | 16 | 17 |

One can see from Table 2 that the parameters of local potentials $\mu$ for liquid $(CH_3)_3CCN$, $CHF_3$, and $CHCl_3$ have close values, which differ by a factor of 1.5 from the value of this parameter for acetonitrile. Note here that $(CH_3)_3CCN$, $CHF_3$, and $CHCl_3$ molecules strongly differ in their masses, inertia moments, and atomic compositions (see Table 1). In addition, liquid fluoroform exists at room temperature only at high pressures [4]. However, despite considerable differences, all these compounds have nearly tetrahedral spatial structure. Unlike them, the structure of the $CH_3CN$ molecule is linear. Therefore, the values of $\mu$ in Table 2 indicate that it is the spatial structure that affects predominantly the parameters of local potentials in liquids under study and, hence, the type of molecular librations. Molecular librations are characterised by small deviation angles from the equilibrium position (of the order of 20°), which, as we believe, are determined first of all by the possibility of the mutual spatial orientation of a molecule and its nearest surrounding.

Note in conclusion that the mechanisms of rotational molecular dynamics in liquids require further experimental and theoretical studies, which can include the detection of the fifth-order nonlinear response [16, 18, 36] in the three-dimensional pulsed Kerr experiments. We assume that the excitation of a Raman echo at libration frequencies will provide more detailed information about libration motions in molecular liquids.

***Acknowledgements.*** This work was supported by the Dynasty Foundation and the Foundation for Support of the Russian Science, the Russian Foundation for Basic Research (Grant. No. 06-02-16491) and Grant No. NSh-6213-2006.2 of the President of the Russian Federation for Support of the Leading Scientific Schools.

## References

1. Krasnov K.S. *Fizicheskaya khimiya. Kn. 2. Elektrokhimiya. Khimicheskaya kinetika i kataliz* (Physical Chemistry, Vol. 2: Electrochemistry. Chemical Kinetics and Catalysis) (Moscow: Vysshaya shkola, 1995).
2. Lehn J.M. *Supramolecular Chemistry. Concepts and Perspectives* (New York, Basel, Cambridge, Tokyo: VCH Verlagsgesellschaft mbH Weinheim, 1995) p. 333.
3. Foggi P., Bartolini P., Bellini M., Giorgini M.G., Morresi A., Sassi P., Cataliotti R.S. *Eur. Phys. J. D*, **21**, 143 (2002).
4. Laurent T.F., Henning H., Ernsting N.P., Kovalenko S.A. *Phys. Chem. Chem. Phys.*, **2**, 2691 (2000).
5. Kaden P., Mayer-Enthart E., Trifonov A., Fiebig T., Wagenknecht H.A. *Angew. Chem. Int. Ed.*, **44**, 1636 (2005).
6. Pecourt J.M., Peon J., Kohler B. *Am. Chem. Soc.*, **123**, 10370 (2001).
7. Wang H., Saxena C., Quan D., Sancar A., Zhong D. *J. Phys. Chem. B*, **109**, 1329 (2005).
8. McMorrow D., Lotshaw W.T., Kenney-Wallace G.A. *IEEE J. Quantum Electron.*, **24**, 443 (1988).
9. Righin R. *Science*, **262**, 1389 (1993).
10. Maker P.D., Terhune R.W., Savage C.M. *Phys. Rev. Lett.*, **12**, 507 (1964).
11. Sala K., Richardson M.C. *Phys. Rev. A*, **12**, 1036 (1975).
12. Ho P.P., Lu P.Y., Alfano R.R. *Phys. Rev. A*, **21**, 1730 (1980).
13. Levenson M.D., Eesley G.L. *Appl. Phys.*, **19**, 1 (1979).
14. Eesley G.L., Levenson M.D., Tolles W.T. *IEEE J. Quantum Electron.*, **14**, 45 (1978).
15. Yan Y.J., Mukamel S. *Phys. Rev. A*, **41**, 6485 (1990).
16. Steffen T., Fourkas J.T., Duppen K. *J. Chem. Phys.*, **105**, 7364 (1996).
17. Tanimura Y., Mukamel S. *J. Chem. Phys.*, **99**, 9496 (1993).
18. Tanimura Y., Mukamel S. *Phys. Rev. E.*, **47**, 118 (1993).
19. Wang Y., Ushida K., Tominaga Y., Kira A. *Chem. Phys. Lett.*, **299**, 576 (1999).
20. Smith N.A., Meech S.R. *Faraday Discuss.*, **108**, 35 (1997).
21. Hunt N.T., Turner A.R., Wynne K. *J. Phys. Chem. B*, **109**, 19008 (2005).
22. Ricci M., Bartolini P., Chelli R., Cardini G., Califano S., Righini R. *Phys. Chem. Chem. Phys.*, **3**, 2795 (2001).
23. Idrissi A., Bartolini P., Ricci M., Righini R. *Phys. Chem. Chem. Phys.*, **5**, 4666 (2003).
24. Frenkel Ya.I. *Kineticheskaya teoriya zhidkosti* (Kinetic Theory of Liquids) (Moscow: Izd. Akad. Nauk SSSR, 1945).
25. Kalpouzos C., McMorrow D., Lotshaw W.T., Kenney-Wallace G.A. *Chem. Phys. Lett.*, **150**, 138 (1988).
26. Ruhman S., Kohler B., Joly A.G., Nelson K.A. *IEEE J. Quantum Electron.*, **24**, 470 (1988).
27. Fridman J.S., Lee M.C., She C.Y. *Chem. Phys. Lett.*, **186**, 161 (1991).
28. Barker C.E., Trebino R., Kostenbauder A.G., Siegman A.E. *J. Chem. Phys.*, **92**, 4740 (1993).
29. McMorrow D., Lotshaw W.T. *J. Phys. Chem.*, **95**, 10395 (1991).
30. Nikiforov V.G., Moiseev S.A. arXiv.org:physics/0601195 (2006).
31. Lobkov V.S., Moiseev S.A., Nikiforov V.G., Salikhov K.M., Dunaev D.M. *Laser Phys.*, **13**, 1138 (2003).
32. Moiseev S.A., Nikiforov V.G. *Kvantovaya Elektron.*, **34**, 1077 (2004) [*Quantum Electron.*, **34**, 1077 (2004)].
33. Akhmanov S.A., Koroteev N.I. *Metody nelineinoi optiki v spektroskopii rasseyaniya sveta: aktivnaya spektroskopiya rasseyaniya sveta* (Methods of Nonlinear Optics in Light Scattering Spectroscopy: Active Light Scattering Spectroscopy) (Moscow: Nauka, 1982).
34. Shen Y.R. *The Principles of Nonlinear Optics* (New York: Wiley, 1984; Moscow: Nauka, 1989).
35. Sverdlov L.M., Kovner M.A., Krainov E.P. *Kolebatel'nye spektry mnogoatomnykh molekul* (Vibrational Spectra of Polyatomic Molecules) (Moscow: Nauka, 1970).
36. Loring R.F., Mukamel S. *J. Chem. Phys.*, **83**, 2116 (1985).