UDC 533.9.004.14; 621.039.6

V.A. Konstantinov*, V.V. Sagan,
V.P. Revyakin and A.V. Karachevtseva

B. Verkin Institute for Low Temperature Physics and Engineering, 47 Lenin Ave.,
61103 Kharkov, Ukraine
*E-mail:Konstantinov@ilt.kharkov.ua

Pseudo-rotational motion of cyclic molecules and thermal conductivity of tetrahydrofuran

Pseudo-rotation is a large amplitude motion arising from the interaction of two degenerate, or nearly degenerate out-of-plane ring puckering modes in the presence of a small barrier to planarity of the molecule [1]. Pseudo-rotation in tetrahydrofuran (THF), C4H8O, arises from near cancellation of the angular strain forces due to nontetrahedral bond angles in the skeleton ring and torsional forces due to hydrogen-hydrogen repulsion

Key words: amplitude, angular forces cyclic molecules.

В.А. Константинов, В.В. Саган, В.П. Ревякин и А.В. Карачевцева

Псевдо-вращательное движение циклических молекул и теплопроводности в тетрагидрофуране

Псевдо-вращение, движение, при котором амплитуда возникающего при взаимодействии двух вырожденных или почти вырождаться вне плоскости кольца стягивает моды в присутствии небольшого барьера на плоскостности молекулы [1]. Псевдо-вращения в тетрагидрофуране (ТГФ), C4H8O, возникают из вблизи аннулированных угловых сил деформации вследствие валентных углов в скелете кольца и скручивающих нагрузок из-за отталкивания водород - водорода [2-3].

Ключевые слова: амплитуда, угловые силы, циклические молекулы.

В.А. Константинов, В.В. Саган, В.П. Ревякин және А.В. Карачевцева

Тетрагидрофурандағы жылуөткізгіштіктің және молекулалардың циклдік жалған-айналатын қозғалысы

Жалған-айналыс, молекула кеңістігінде үлкен емес кедергі жағдайында пайда болатын қайта қалпына келу әсерлесулері болмаса сақина кеңістігінен тыс қозғалыс болып табылады [1]. Тетрагидрофурандағы (ТГФ) жалған айналыс, C4H8O,сақина қаңқасындағы валентті бұрыштардың бұрыштық күштердің салдарынан деформациялануынан немесе сутегі- сутегі [2-3] арасындағы иірілген күштердің арасындағы тебінулер салдарынан пайда болады.

Түйін сөздер: амплитуда, бұрыштық күштер, циклдік молекулалар.

Pseudo-rotation is a large amplitude motion arising from the interaction of two degenerate, or nearly degenerate out-of-plane ring puckering modes in the presence of a small barrier to planarity of the molecule [1]. Pseudo-rotation in tetrahydrofuran (THF), C_4H_8O, arises from near cancellation of the angular strain forces due to nontetrahedral bond angles in the skeleton ring and torsional forces due to hydrogen-hydrogen repulsion [2-3]. Experimental evidence strongly suggests that in solid THF the pseudo-rotational motion becomes a large-amplitude ring deformation vibration with a fundamental frequency of about 140 cm^{-1}. THF has only one crystallographic modification (monoclinic space group C_2/c with 4 molecules in the unit cell) and melts at 164.9 K with a large entropy change on melting $\Delta Sf/R$=7.07 (R is the gas constant) indicating a high degree of order

in solid [4-5]. The possible influence of pseudo-rotation on the thermal conductivity was not previously studied.

For correct comparison with theory at TD is the Debye temperature) the thermal conductivity must be measured at constant density to exclude the thermal expansion effect. The isochoric thermal conductivity of solid THF was measured on three samples of different densities in the interval from 125 K to the onset of melting. The thermal conductivity was also investigated at saturated vapor pressure on the sample grown under a pressure of several atmospheres. The isochoric thermal conductivity of all three samples decreases with rising temperature by the law much weaker than κ_1/T, has a bend and then decreases more rapidly. The bend can be associated with the onset of the sample melting. The Bridgman coefficient $g=-(d\ln\kappa/d\ln V)T$ calculated from our experimental data is 7.7±0.6 at 160 K.

It is shown that the experimental data can be described in framework of a modified Debye model of thermal conductivity with allowance for heat transfer by both low-frequency phonons and «diffuse» modes. The calculated parameters of the model are close to values observed for orientationally ordered phases of other molecular crystals. No significant contribution of pseudo-rotation on the thermal conductivity has been detected.

References

1 D.O. Harris, G.G. Engerholm, C.A. Tolman, A. Luntz, R.A. Keler, H. Kim and W.D. Gwinn, J. Chem. Phys. 50, 2438 (1969).
2 W.J. Lafferty, D.W. Robbinson and R.W. St. Louis, J. Chem. Phys. 42, 2915 (1965).
3 D.G. Melnik, S. Gopalakrishnan and T.A. Miller, J. Chem. Phys. 118, 3589 (2003).
4 B.V. Lebedev, I.B. Rabinovich, V.I. Milov and V.Ya. Lityagov, J. Chem. Thermodynamics, 10, 321 (1978).
5 P. Luger, J. Buschmann, Angew. Chem. Int. Ed. Engl., 22, 410 (1983).