ATOMS AND MOLECULES

L.M. BABKOV,[1] J. BARAN,[2] N.A. DAVYDOVA,[3] I.V. IVLIEVA,[1] E.A. PONEZHA,[4]
V.YA REZNICHENKO [3]

[1] Faculty of Physics, Saratov State University
  (83, Astrakhanskaya Str., Saratov 410026, Russia)
[2] Institute of Low Temperature and Structure Research, PAS
  (2, Okolna Str., Wroclaw 50-950, Poland)
[3] Institute of Physics, Nat. Acad. of Sci. of Ukraine
  (46, Prosp. Nauky, Kyiv 03028, Ukraine; e-mail: davydova@iop.kiev.ua)
[4] Bogolyubov Institute for Theoretical Physics, Nat. Acad. of Sci. of Ukraine
  (14b, Metrologichna Str., Kyiv 03680, Ukraine)

INFRARED SPECTRA OF TRIPHENYL PHOSPHITE AND THEIR INTERPRETATION ON THE BASIS OF QUANTUM CHEMISTRY CALCULATION

In situ IR spectroscopic investigation of the structural changes during the glaciation and crystallization processes in triphenyl phosphite (TPP) is performed in the 400–4000 cm^{-1} spectral range. The 6-31G(d) basis set at the B3LYP level of the density functional theory has been applied to the calculation of the energies, dipole moments, geometric parameters, harmonic vibrational frequencies, and infrared intensities for different conformers of TPP. It is shown that at least five conformers differed by the bond lengths P–O and C–O and by angles in O–P–O, C–O–P, and P–O–C–C can be realized. The conclusion about probable conformational structures of different phases of TPP is drawn.

K e y w o r d s: infrared spectroscopy, conformers, glaciation, nucleation, triphenyl phosphite, simulation, density functional theory.

1. Introduction

Triphenyl phosphite (TPP) is well known to exhibit the intriguing transformation of a supercooled liquid [1]. If TPP is cooled rapidly enough, it enters firstly into a supercooled liquid state below the melting point ($T_{\rm m} \sim 299$ K) as usual liquids and then into a glass state at the glass-transition temperature ($T_{\rm g} \sim 208$ K). On the other hand, if TPP is quenched to a certain temperature between 212 and 225 K (above $T_{\rm g}$) and then annealed at that temperature, a new apparently amorphous phase named the

"glacial" phase emerges in a supercooled liquid and grows with time. The transformation to the glacial phase was called a glaciation [1].

The existence of the glacial phase in TPP stimulated the intensive experimental researches of this unusual phenomenon, and many different and controversial explanations were proposed for it. Among others, the glacial phase is considered as the second type of supercooled liquid (liquid with very anomalous molecular reorientation) [2–4], as a highly correlated second liquid (liquid phase possessing a more developed structural correlation than the ordinary liquid) [5–7], as a poorly crystallized defect-ordered phase with large unit cell and small crystallites, which could result from the structural frustra-
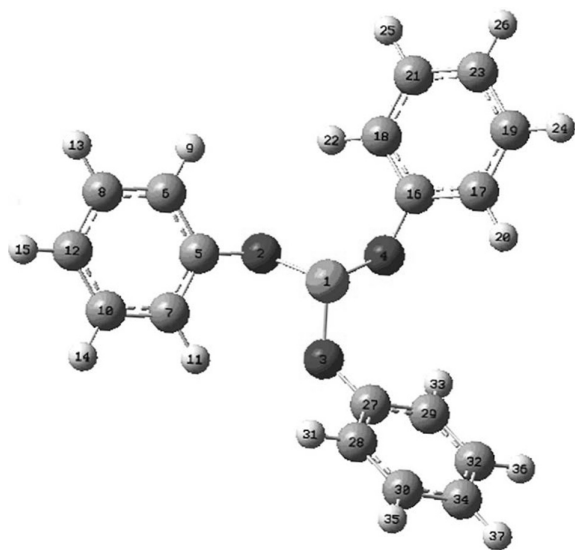
Fig. 1. Structure and the numbering scheme of atoms of a TPP molecule

tion [8–10] predicted by the "frustration-limited domain theory" [11], as a liquid crystal or plastic (orientationally disordered) crystal [12, 13], and as the mixture of a non-transformed supercooled liquid and micro(nano)crystals with structural properties of the ordinary crystal [14–22]. Mosses et al. [23], by using the technique of fluorescence lifetime imaging, interpreted the liquid-liquid transition as a phase transition associated with frustrated molecular clusters.

As can be seen to date, there is no clear understanding of the origin of the glacial phase. This was the motivation of the present work to study this unusual phase. For this purpose, we used the method of infrared spectroscopy. The IR spectroscopy gives us an opportunity to analyze the structural evolution of TPP during different phase transitions in real time. So far, this method has not been used for the study of the phase transitions in TPP.

To get information on changing the structure of TPP from the IR spectra during the phase transitions, it is necessary to interpret IR spectra. For this quantum chemical calculations of the IR spectra by means of the density functional theory, the method (B3LYP/6-31G (d)) with the use of the GAUSSIAN'03 software package has been applied.

2. Experimental Details

TPP [$P(OC_6H_5)_3$] of 99% purity was purchased from Aldrich and used without further purification. The

molecular and crystal structures of TPP have been studied in [18]. The molecule is highly flexible, insofar as six torsion angles can be identified. The P atom is tricoordinate. The crystals have a needle-like shape and crystallize in the structure with hexagonal space group $R3$. The crystal structure is formed by means of intermolecular CH$\cdots\pi$ interactions. The molecular geometry of TPP displays roughly Cs symmetry [18].

Infrared measurements were done with a Fourier-transform infrared (FTIR) spectrometer (Bruker model IFS-88) at a resolution of 2 cm^{-1}, and 32 scans were typically co-added for an individual spectrum. The data processing was performed with the OPUS software. For the IR measurements, a liquid sample was sandwiched between two CsI windows at room temperature. The thickness of such a cell was approximately a few micrometers. Such a sample was then fixed in a closed-cycle Oxford cryostat providing for a temperature variation in the range 330–11 K.

The computer simulation of the optimized geometry and IR spectra of TPP has been performed with the Gaussian03 software package [24] at the B3LYP level of the density functional theory with the 6-31G(d) basis set [25, 26].

3. Results and Discussion

3.1. Computer simulation

In the computer simulation, the full optimization of the geometry and the energy of an isolated molecule of TPP has been performed followed by the calculation of a dipole moment, normal vibration frequencies in the harmonic approximation, and infrared intensities. The results of calculations of the structure of an isolated TPP molecule have shown that at least five stable conformers differed by the bond lengths P–O and C–O, values of the angles in O–P–O, P–O–C, and P–O–C–C (dihedral angle), which corresponds to the rotation of the phenyl group around an axis constituted by O–C bond, are realized (denoted as conformers I, II, III, IV, and V). The structure and the numbering scheme of atoms of a TPP molecule are presented in Fig. 1.

The energies of conformers I–V were found to be –1261.991493 (I), –1262.007903 (II), –1262.005736 (III), –1262.004931 (IV), and –1262.000501 (V) Hartree. The difference between the values of energy between the conformers does not exceed 0.006410

Hartree. The closeness of the energy parameters suggests an equal probability of the conformers. The dipole moments for conformers I–V were found to be 1.14 (I), 2.03 (II), 1.15 (III), 1.99 D (IV and V). The difference between them does not exceed 0.89 D. The calculated bond lengths and the angle values for conformers I-V are listed in Table.

It should be noted that the density functional theory study of TPP has been performed previously [22]. However, only three conformers (I–III) were found there, and the IR spectra for them were not calculated. The geometrical parameters of the conformers I–III defined in [22] are slightly different from ours, but this can be related to the different functional method and basis set, namely MPW1PW91/6-31G* used in [22].

The significant frequency changes in the calculated IR spectra are observed, when going from one conformer to another one in the 700–800 cm^{-1} spectral region, where the in-plane stretching and in-plane bending vibrations of a PO$_3$ group and in-plane wagging vibrations of a benzene ring appear (Fig. 2, *a*); and in the 840–900 cm^{-1} spectral region, where the in-plane stretching of P–O and C–O, in-plane bending of a benzene ring, and wagging vibrations appear (Fig. 2, *b*).

Calculated bond lengths and angle values for conformers I-V of a TPP molecule from the B3LYP/6-31 G(d) model

Bond (Å) angle (grad)	Geometric parameters				
	I	II	III	IV	V
P$_1$–O$_2$	1.629	1.651	1.654	1.668	1.668
P$_1$–O$_3$	1.650	1.651	1.647	1.669	1.667
P$_1$–O$_4$	1.673	1.651	1.654	1.666	1.668
O$_2$–C$_5$	1.382	1.390	1.392	1.390	1.392
O$_4$–C$_{16}$	1.391	1.390	1.392	1.392	1.392
O$_3$–C$_{27}$	1.389	1.390	1.393	1.393	1.392
O$_2$–P$_1$–O$_3$	107	96	102	97	97
O$_2$–P$_1$–O$_4$	97	96	91	97	97
O$_3$–P$_1$–O$_4$	109	96	102	96	97
P$_1$–O$_2$–C$_5$	132	122	122	120	119
P$_1$–O$_3$–C$_{27}$	122	122	126	119	119
P$_1$–O$_4$–C$_{16}$	121	122	122	120	119
P$_1$–O$_2$–C$_5$–C$_6$	143	108	43	121	106
P$_1$–O$_3$–C$_{27}$–C$_{28}$	105	117	156	91	102
P$_1$–O$_4$–C$_{16}$–C$_{17}$	107	96	102	97	97

3.2. Infrared spectra

We have studied the evolution of the IR spectra during the glaciation and crystallization processes in TPP in the wide spectral range 400–4000 cm^{-1}. However, based on the computer simulation results, we will focus on the 700–900 cm^{-1} spectral region, where the spectra of different conformers differ most strongly from one another. It should be noted that we did not present here the 3300–3600 cm^{-1} spectral range, where the intermolecular C–H···O hydrogen bonds manifest themselves because of their unusually weak intensity.
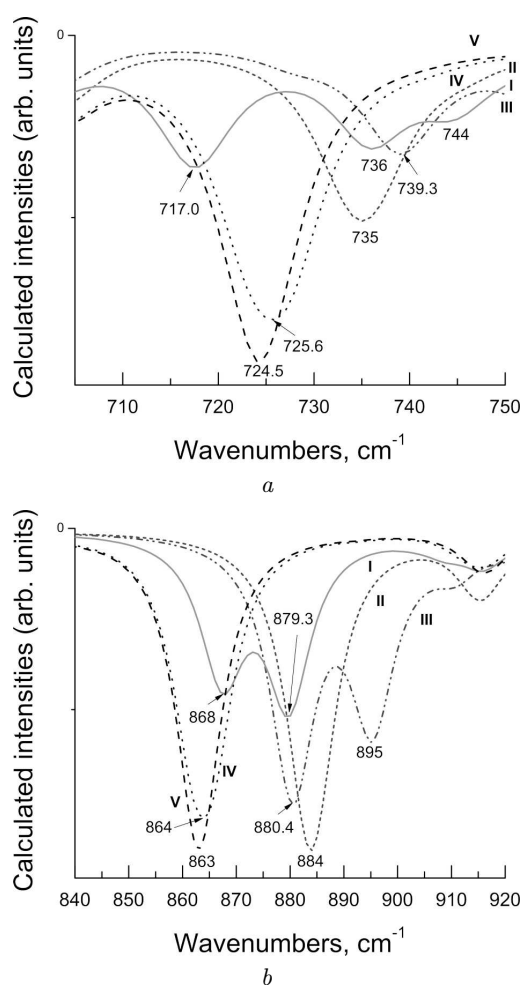

Fig. 2. Calculated IR spectra for conformers I–V of a TPP molecule from B3LYP/6-31 G(d) in the 700–750 cm^{-1} spectral region. The scaling factor is 0.99 (*a*). Calculated IR spectra for conformers I–V of a TPP molecule from B3LYP/6-31 G(d) in the 840–920 cm^{-1} spectral region (*b*)
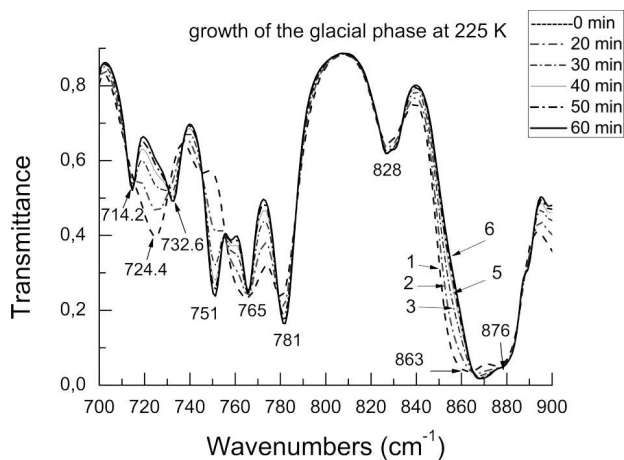
Fig. 3. Evolution of the IR transmittance spectra of TPP during the glaciation at 225 K in the 700–900 cm⁻¹ spectral region. *1* – the spectrum of the supercooled liquid recorded after the melting of the glass state and then heated to 225 K temperature; curves *2, 3, 4, 5,* and *6* (solid) were recorded in 20, 30 40, 50, and 60 min after the recording of the spectrum (*1*)
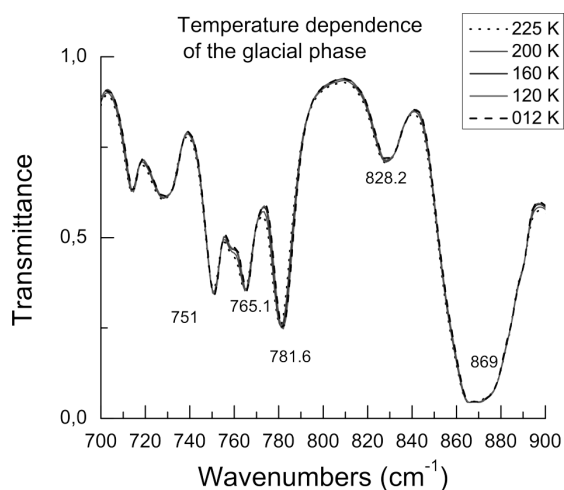

Fig. 4. Temperature dependence of the IR spectra of the glacial phase prepared at 225 K in the 700–900 cm⁻¹ spectral region. Temperatures are: 225 (dotted) 200, 160, 120, and 12 K (dashed)

For the preparation of the glacial phase, the sample was heated starting from below the glass transition temperature to an aging temperature $T_a = 225$ K and was kept at this temperature. At T_a, the glaciation process was analyzed by continuously measuring the IR spectra during the isothermal aging (Fig. 3). The dashed curve *1* shows the IR spec-

trum of TPP recorded immediately after reaching 225 K. The next curves (*2–6*) were recorded in 20, 30, 40, 50, and 60 min (solid curve) after recording the spectrum (*1*). A significant change of the IR spectrum during the glaciation process can be easily observed. The band at 724.4 cm⁻¹ in the IR spectrum of the initial supercooled liquid phase (Fig. 3, curve *1*) transforms into two new bands at 714.2 and 732.6 cm⁻¹, and the new band at 751 cm⁻¹ is starting to emerge (Fig. 3, curve *6*). The broad band in the region 840–890 cm⁻¹ consists of two overlapping bands at 863 and 876 cm⁻¹ (Fig. 3, curve *1*) in the supercooled liquid state spectrum. During the transformation, the band at 863 cm⁻¹ shifts toward the high frequency side to 868 cm⁻¹, and a small shoulder at 889 cm⁻¹ appears on the high-frequency side of the band at 876 cm⁻¹ at the end of the transformation (Fig. 3, curve *6*). After 60 min, the spectra practically coincide and are not changed with time. This means that the process of glaciation at 225 K is completed within 60 min.

This glacial phase was then cooled down to 12 K in order to obtain its temperature-dependent IR spectra in the range of 225–12 K (Fig. 4). It is seen that no major evolution of the IR spectra is observed in this temperature range.

The crystallization of TPP can be easily achieved by raising the temperature from the glacial phase up to 240 K. The sample was kept at 240 K, and the process of crystallization was analyzed, by continuously measuring the IR spectra during the crystallization (Fig. 5). We may say that, during the crystallization, almost all of the bands in the IR spectra become narrower and more intense. Especially, this concerns the bands at 732 and 765 cm⁻¹ and the broad band in the 860–880 cm⁻¹ region. The crystallization is accompanied by the appearance of the band at 889 cm⁻¹ (Fig. 5, curve *4*). Within 70 min, the crystallization process at 240 K is completed.

To obtain the temperature dependence of the IR spectra of the crystalline TPP, the crystal was cooled from 240 K down to 12 K, and its temperature-dependent IR spectra were recorded on heating in the range 12–295 K (Fig. 6). It is seen that, as the temperature increases, the IR spectra of TPP crystal are essentially unchanged.

Figure 7 allows us to compare the IR spectra of TPP in three phases: glass, glacial, and crystal ones at 12 K. It is seen that, instead of the band at
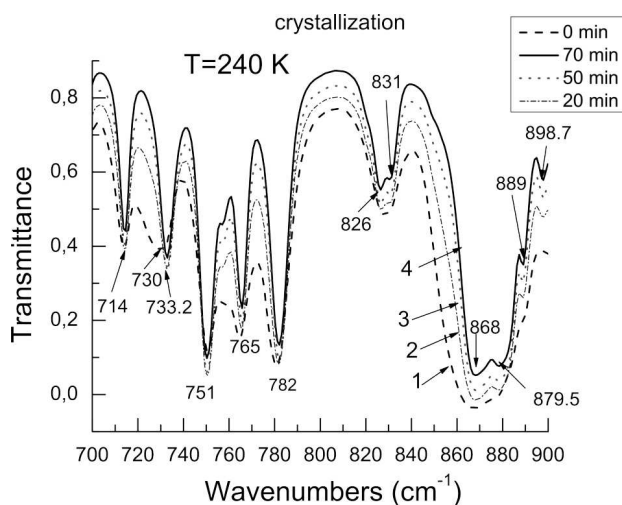
Fig. 5. Evolution of the IR transmittance spectra of TPP at 240 K during the crystallization from the glacial phase in the 700–900 cm^{-1} spectral region. *1* – spectrum of the supercooled liquid phase at 240 K after melting the glass phase; curves *2–4* were recorded in 20, 50, and 70 min after recording the spectrum (*1*)

724.5 cm^{-1} in the glass phase (curve *1*), two bands at 715.3 cm^{-1} and 728.7 cm^{-1} appear in the spectrum of the glacial phase (curve *2*). In the crystal spectrum (curve *3*), these two bands are transformed into narrow intense bands at 715.3 and 733.3 cm^{-1}. The band at 863 cm^{-1} in the spectrum of the glass phase becomes narrower due to the shift of the low-frequency side of the band toward the high frequency going to the glacial phase (curve *2*) and then to the crystal phase (curve *3*). The shoulder at 889 cm^{-1} in the spectrum of the glacial phase (curve *2*) develops into a band in the crystal, which is absent in the spectrum of the glass phase (curve *1*). It is seen that the spectrum of the glacial phase corresponds to the crystal spectrum envelope.

3.3. Discussion

The experimental results allow us to agree with the interpretation proposed by Hedoux and co-workers [14–22] that the glacial phase consists of crystalline nuclei. However, an open question remains whether the glacial phase consists of nuclei in the matrix of a non-transformed supercooled liquid, or the supercooled liquid also transforms during the glaciation process. Some information regarding the structure of the glacial phase can be obtained by analyzing the calculated and experimental spectra.
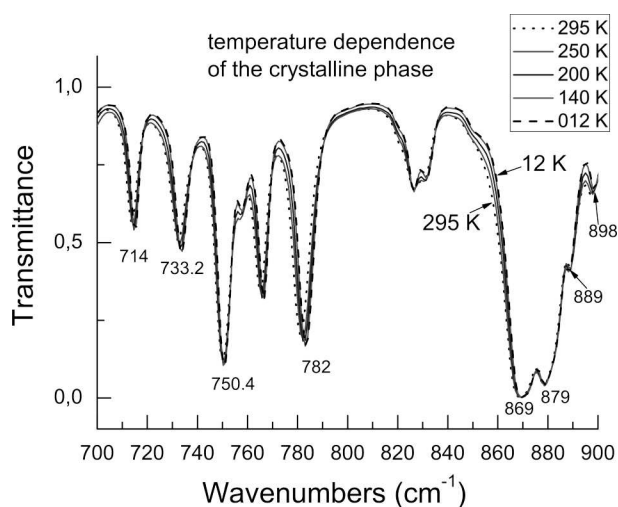
Fig. 6. Temperature-dependent IR spectra of the crystalline phase of TPP recorded on heating in the 700–900 cm^{-1} spectral region. Temperatures are (top to bottom): 12 (dashed) 140, 200, 250, and 295 K (dotted)
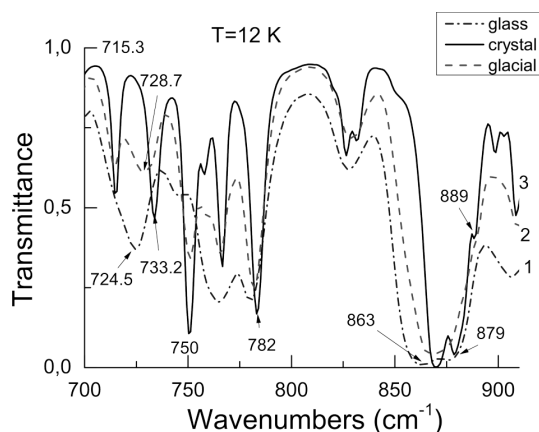

Fig. 7. Comparison of the IR spectra of the glass, glacial, and crystal phases of TPP in the 700–900 cm^{-1} spectral region, respectively: glass *1*; glacial phase *2*; crystalline phase *3*

At first, it should be noted that the differences should be expected in the frequencies of the calculated and experimental spectra due to the fact that the calculations were made for an isolated molecule. In the spectral region of the in-plane stretching and in-plane bending vibrations of a PO$_3$ group, two bands at 724.5 and 725.6 cm^{-1} are seen in the spectra of conformers V and IV (Fig. 2, *a*). In the experimental spectrum of the glass phase, the broad band at 724.5 cm^{-1} is present (Fig. 7, curve *1*). So, it can be concluded that, in the glass phase, conformers IV

and V, which are responsible for the broad band at 724.5 cm^{-1} in the experimental spectrum, are most likely realized. In the IR spectrum of the crystal, this band (724.5 cm^{-1}) is absent, so we may conclude that conformers IV and V are not present in the crystalline phase structure. In the calculated spectrum of conformer I, the bands at 717.0 and 736 cm^{-1} are seen (Fig. 2, *a*). The same bands at 715.3 and 733.2 cm^{-1} also present in the experimental spectrum of the crystal (Fig. 7, curve *3*). So, it can be concluded that conformer I is realized most likely in the crystal phase structure. Conformers II and III may also be present in the crystal structure, by giving contribution to the band at 733.2 cm^{-1} in the spectrum (Fig. 7, curve *3*).

Analyzing the experimental spectrum of the glacial phase (Fig. 7, curve *2*), we can say that, due to the fact that this spectrum corresponds to the envelope of the spectrum of the crystal, the same conformers as in the crystal must be present in the glacial phase. Conformers IV and V, which are absent in the crystal phase, will also be absent in the glacial phase structure.

In the spectral region of 840–910 cm^{-1}, where the in-plane stretching (PO) and (CO) vibrations give the largest contribution to the calculated IR spectra, two bands at 863 and 864 cm^{-1} are seen in the spectra of conformers V and IV (Fig. 2, *b*). These bands also present in the glass phase spectrum (Fig. 7, curve *1*). So, it can be concluded that conformers IV and V are realized most likely in the glass structure, which gives the broad band in the experimental spectrum.

In the experimental spectra of the glacial and crystalline phases (Fig. 7, curves *2* and *3*), the bands at 863 and 864 cm^{-1} are absent, but the other four bands at 868, 879, 889, and 897 cm^{-1} are seen. In the spectrum of conformer I, there are two bands at 868 and 879.3 cm^{-1} (Fig. 2, *b*), so it can be concluded that, in the glacial and crystalline phases, conformer I most likely forms the structure, but conformers IV and V are not present either in the glacial phase or in the crystalline phase structure. In the spectrum of conformer III, there are bands at 880.5 and 895 cm^{-1} (Fig. 2, *b*). These bands may be responsible for the bands at 879 and 897 cm^{-1} in the experimental spectra of the glacial and crystalline phases (Fig. 7, curves *2* and *3*). So, it can be concluded that, in the glacial and crystalline phase structures, except for conformer I, conformer III may also be realized.

Conformer II is characterized by a single band at 884 cm^{-1}, which is absent in the experimental spectra of glass, glacial, and crystal phases. However, as was shown in our recent paper [27], TPP can be crystallized in a metastable polymorphic phase. It was found that there is a strong band at 884.5 cm^{-1} in the IR spectrum of the metastable phase, which is absent in the spectrum of the stable crystalline phase. The fact that the band at 884 cm^{-1} is present in the spectrum of conformer II (Fig. 2, *b*) allows us to conclude that, in the metastable crystalline phase, conformer II is realized with high probability.

The comparative analysis of the experimental and calculated spectra of TPP leads to the conclusion that the glacial phase consists of conformers that are also present in the crystal; however, the conformers present in the glass phase are absent in the glacial phase. Thus, we can give a positive answer to the question whether the glacial phase consists of nuclei in the matrix of a non-transformed supercooled liquid, or the supercooled liquid is also transformed during the glaciation process. The glacial phase consists of nuclei in the matrix of a transformed supercooled liquid. In the case where the glacial phase is consisted of nuclei in the matrix of a non-transformed supercooled liquid, conformers IV and V of TPP would be presented in its structure.

4. Conclusion

Based on the B3LYP level of the density functional theory with the 6-31G(d) basis set, it is shown that, due to the huge conformational flexibility of a TPP molecule, its five stable conformers differed by the bond lengths P–O and C–O, and values of the angles in O–P–O, P–O–C, and P–O–C–C can be realized.

The comparative analysis of the experimental and calculated spectra has shown that the TPP glass phase consists of conformers IV and V. The glacial and crystal phases consist mainly of conformers I and, in a smaller amount, conformers II. Conformers IV and V are absent in the glacial phase, which means that the TPP glacial phase consists of crystalline nuclei in the matrix of a highly transformed supercooled liquid.

1. A. Ha, I. Cohen, X. Zhao, M. Lee, and D. Kivelson, J. Phys. Chem. **100**, 1 (1996).
2. R. Kurita, Y. Shinohara, Y. Amemiya, and H. Tanaka, J. Phys.: Condens. Matter **19**, 152101 (2007).

3. R. Kurita and H. Tanaka, Phys. Rev. B **73**, 104202 (2006).

4. H. Tanaka, R. Kurita, and H. Mataki, Phys. Rev. Lett. **92**, 25701 (2004).

5. S. Dvinskikh, G. Benini, J. Senker, M. Vogel, J. Wiedersich, A. Kudlik, and E. Rossler, J. Phys. Chem. **103**, 1727 (1999).

6. J. Senker and E. Rossler, Chem. Geol. **174**, 143 (2001).

7. M. Mizukami, K. Kobashi, M. Hanaya, and M. Oguni, J. Phys. Chem. B **103**, 4078 (1999).

8. Ch. Alba-Simionesco and G. Tarjus, Europhys. Lett. **52**, 297 (2000).

9. G. Tarjus, Ch. Alba-Simionesco, M. Grousson, P. Viot, and D. Kivelson, J. Phys.: Condens. Matter. **15**, S1077 (2003).

10. D. Kivelson and G. Tarjus, J. Non-Cryst. Solids **307–310**, 630 (2002).

11. S.A. Kivelson, X. Zhao, D. Kivelson, T.M. Fischer, and C.M. Knobler, J. Chem. Phys. **101**, 2391 (1994).

12. G.P. Johari and C. Ferrari, J. Phys. Chem. B **101**, 10191 (1997).

13. B. Demirjian, G. Dosseh, A. Chauty, M.-L. Ferrer, D. Morineau, C. Lawrence, K. Takeda, D. Kivelson, and S. Brown, J. Phys. Chem. B **105**, 2107 (2001).

14. A. Hedoux, Y. Guinet, and M. Descamps, Phys. Rev. B **58**, 31 (1998).

15. A. Hedoux, O. Hernandez, J. Lefebvre, Y. Guinet, and M. Descamps, Phys. Rev. B **60**, 9390 (1999).

16. A. Hedoux, Y. Guinet, M. Descamps, and A. Benabou, J. Phys. Chem. **104**, 11774 (2000).

17. A. Hedoux, Y. Guinet, and M. Descamps, J. Raman Spectrosc. **32**, 677 (2001).

18. O. Hernandez, A. Hedoux, J. Lefebvre, Y. Guinet, M. Descamps, R. Papoular, and O. Masson, J. Appl. Cryst. **35**, 212 (2002).

19. A. Hedoux, Y. Guinet, M. Foulon, and M. Descamps, J. Chem. Phys. **116**, 9374 (2002).

20. A. Hedoux, Y. Guinet, P. Derollez, O. Hernandez, R. Lefort, and M. Descamps, Phys. Chem. Chem. Phys. **6**, 3192 (2004).

21. P. Derollez, A. Hedoux, Y. Guinet, J. Lefebvre, M. Descamps, and O. Hernandez, Z. Kristallogr. Suppl. **23**, 557 (2006).

22. O. Hernandez, A. Boucekkine, and A. Hedoux, J. Phys. Chem. A **111**, 6952 (2007).

23. J. Mosses, C.D. Syme, and K.W. Wynne, J. Phys. Chem. Lett. **6**, 38 (2015).

24. J. Frisch, G.W. Trucks, and H.B. Schlegel, *Gaussian03, Revision B.03* (Gaussian, Pittsburg, PA, 2003), 302 p.

25. W. Kohn, Usp. Fiz. Nauk **172**, 336 (2002).

26. J.A. Pople, Usp. Fiz. Nauk **172**, 349 (2002).

27. J. Baran, N.A. Davydova, and M. Drozd, J. Chem. Phys. **140**, 104512 (2014).

Л.М. Бабков, Я. Баран, Н.О. Давидова,
І.В. Івлієва, О.О. Понежа, В.Я. Резніченко

ІНФРАЧЕРВОНІ СПЕКТРИ ТРИФЕНІЛ
ФОСФІТУ ТА ЇХ ІНТЕРПРЕТАЦІЯ НА ОСНОВІ
КВАНТОВО-ХІМІЧНИХ РОЗРАХУНКІВ

Р е з ю м е

Структурні зміни в ТРР у процесах гласіації та кристалізації досліджувалися методом інфрачервоної спектроскопії в спектральній області 400–4000 см$^{-1}$. Методом теорії функціонала густини (B3LYP/6-31G(d)) розраховано енергії, дипольні моменти, геометричні параметри, частоти коливань у гармонійному наближенні та інтенсивності в ІЧ спектрах різних конформерів ТРР молекули. Показано, що можливе існування принаймні 5 конформерів, що різняться довжинами зв'язків P–O, C–O й кутами O–P–O, C–O–P і P–O–C–C. Зроблено висновки щодо можливої конформаційної структури різних фаз у ТРР.